Materials Science and Technology

Catania, December 12 - 16, 2016

Conference Chairs

Corrado Spinella (DSFTM - CNR)

Luigi Ambrosio (DSCTM - CNR)

BOOK OF ABSTRACTS

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Plenary sessions

Monday, December 12

11:30-12:30	**Maurizio Prato**	University of Trieste, (IT) “Novel Functional Carbon Bio-Interfaces”
14:00-15:00	**Matteo Santin**	University of Brighton (UK) “Synthetic Extracellular Matrix Analogues as Surface Functionalisation Moieties of Medical Devices and Tissue Engineering Products”

Tuesday, December 13

09:00-10:00	**Guglielmo Lanzani**	Politecnico di Milano / IIT (IT) “Elementary excitation dynamics in Hybrid Lead-Halide Perovskites”
16:30-17:30	**Giorgio Rossi**	University of Milan / IOM - CNR (IR) “The ESFRI Roadmap 2018 and the Landscape of Analytical Research Infrastructures”

Wednesday, December 14

09:00-10:00	**Francesco Sette**	European Synchrotron Radiation Facility (FR) “Science at synchrotrons and the ESRF EBS”

Thursday, December 15

09:00-10:00	**Philip Kim**	University of Harvard (USA) “Materials in 2-dimension and beyond: platform for novel electronics and optoelectronics”

Novel Functional Carbon Bio-Interfaces

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Connecting nanostructured materials to biological compartments is a crucial step in prosthetic applications, where the interfacing surfaces should provide minimal undesired perturbation to the target tissue. Ultimately, the (nano)material of choice has to be biocompatible and promote cellular growth and adhesion with minimal cytotoxicity or dis-regulation of, for example, cellular activity and proliferation.

In this context, carbon nanomaterials, including nanotubes and graphene, are particularly well suited for the design and construction of functional interfaces. This is mainly due to the extraordinary properties of these novel materials, which combine mechanical strength, thermal and electrical conductivity.

Our group has been involved in the organic functionalization of various types of nanocarbons, including carbon nanotubes, fullerenes and, more recently, graphene. The organic functionalization offers the great advantage of producing soluble and easy-to-handle materials. As a consequence, since biocompatibility is expected to improve upon functionalization, many modified carbon nanomaterials may be useful in the field of nanomedicine.

In particular, we have recently shown that carbon nanotubes and graphene can act as active substrates for neuronal growth, a field that has given so far very exciting results. Nanotubes and graphene are compatible with neurons, but, especially, they play a very interesting role in interneuronal communication. Improved synaptic communication is just one example.

During this talk, we will show the latest and most exciting results obtained in our laboratories in these fast developing fields.

Matteo Santin

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Synthetic Extracellular Matrix Analogues as Surface Functionalisation Moieties of Medical Devices and Tissue Engineering Products

Abstract

Traumatic and pathological conditions leading to the disruption of tissue integrity require clinical intervention through either an implantology or a regenerative medicine approach. The integration of medical devices within the surrounding tissues as well as tissue regeneration by tissue engineering constructs depend on the ability of the implanted biomaterials to control the activity of cells. In any natural tissue, this activity is influenced by extracellular matrix (ECM) macromolecules like proteins and polysaccharides that present in a spatially-ordered manner specific bioligands to the cell receptors. This nanometric control determines the ability of the cell to migrate, proliferate and ultimately regenerate the tissue. Hence, the design and development of novel biomaterials able to resemble the physicochemical and biological properties of the ECM macromolecules have been widely advocated for the surface functionalisation of both medical implants and tissue engineering products.

The lecture will present a novel class of synthetic hyperbranched macromolecules and their grafting to conventional biomaterials to provide implants and 3D scaffolds with new biological properties.

Examples of these synthetic macromolecules and their applications in a range of clinical applications will be illustrated and critically discussed in the light of the elicited *in vitro* and *in vivo* biological responses as well as in the light of their industrial sustainability.

Elementary excitation dynamics in Hybrid Lead-Halide Perovskites

Guglielmo Lanzani

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After a brief introduction on renewable energy sources and the opportunity of printed organic photovoltaics I will turn to the emergent hybrid perovskites field. Perovskites have the potential to overcome the performance limits of current technologies and achieving low cost and high integrability. Hybrid halide perovskite, e.g. CH3NH3PbX3 [X = Cl, Br, or I], are usually deposited as polycrystalline thin-films with variable mesoscale morphology depending on the growth conditions. I will demonstrate that the electron-hole interaction is sensitive to the microstructure of the material. By controlling the material processing during fabrication both free carrier and Wannier excitonic regimes are accessible, with strong implications for applications in optoelectronic. The simple solution processability at room temperature exposes lead halide perovskite semiconductors to a non-negligible level of unintentional structural and chemical defects. I will report on the use of excitation correlation photoluminescence (ECPL) spectroscopy to investigate the recombination dynamics of the photo-generated carriers in lead bromide perovskites. This experiments allows to identify the energetics of the defects. In fact, in the case of polycrystalline films, depending on the synthetic route, we demonstrate the presence of both deep and shallow carrier traps. The shallow defects, which are situated at about 20meV below the conduction band, dope the semiconductor leading to a substantial enhancement of the photoluminescence quantum yield in spite of carrier trapping. At excitation densities relevant for lasing we observe breakdown of the rate-equation model indicating a build-up of a highly correlated regime of the photo-carrier population that suppresses the non-radiative Auger recombination.

Giorgio Rossi

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The ESFRI Roadmap 2018 and the Landscape of Analytical Research Infrastructures

The European Strategy Forum for Research Infrastructure is mandated, by the Council for Competitiveness, to identify the elements of a strategy-led policy to shape and strengthen the European Research Infrastructure system. ESFRI elaborates a Roadmap that contains selected Projects with pan-European relevance and support, as well as Landmarks that are implemented projects leading the science production in their field. A key part of the Roadmap is the Landscape Analysis that, in each domain of research, recognizes the existing and operational infrastructures that are accessible by the European scientists as well as the gaps of competitiveness that could be filled by novel infrastructure projects. A portfolio of analytical facilities is identified that represents a key asset for Europe’s competitiveness in physics of matter and materials science.

Science at synchrotrons and the ESRF EBS

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Synchrotron science is increasingly in demand to support research in many fields. Improvements in source reliability and properties open new science reach, and impressive instrumentation achievements in the data acquisition open new opportunities in frontier research at synchrotrons for both traditional users' communities and for applied and industrial research.
Non-disruptive 3D-imaging with *nanometer* space resolution is particularly impressive when coupled with X-ray scattering and spectroscopy methodologies, as it can provide images with single atom chemical, bonding, magnetic, etc. information. Progress in synchrotron science is paralleled by important advances in other techniques and methods as the development of X-ray science at XFELs, and progress in optical and electron microscopies. It is important, therefore to consider advances in synchrotron science in the broader context.

This presentation reviews frontier science using synchrotron radiation from present and future storage rings, and refers to the ongoing Upgrade Programme (UP) of the ESRF. Launched in 2009, it aims to develop X-ray science in the study of the structure and dynamics of condensed and living matter down to *nanometer* space resolution, and time-scales down to the *nanosecond*. The UP objectives and science case were presented in 2007 in the ESRF Purple Book (http://www.esrf.fr/Apache_files/Upgrade/ESRF-SciTechProg2008-2017.pdf), and its first phase was successfully concluded in 2015 with the delivery of 19 new instruments and beamlines, and the conception of a new storage ring. This new hybrid multiple bend achromat storage ring lattice design efficiently enables the delivery of diffraction limited hard X-rays by drastically reducing the electron beam horizontal emittance; its adaptation to the existing ESRF storage ring tunnel will improve today's performances by 100 in terms of brightness and transverse coherence. This exciting project, following the footsteps of the MAX-IV multiple bend storage ring implemented in Lund, is under construction at the ESRF since almost two years and will be operational in 2020. This ESRF Extremely Brilliant Source (EBS) programme has attracted worldwide attention, triggering similar conceptual studies in almost all existing and future synchrotron laboratories on the planet. The ESRF Orange Book (http://www.esrf.eu/Apache_files/Upgrade/ESRF-orange-book.pdf) describes the whole ESRF EBS programme including an update of the science case. The ESRF-EBS will deliver a new and first-of-a-kind storage ring, new adapted beamlines, and an ambitious instrumentation programme centred on X-ray detector developments and data handling strategies.

Philip Kim

Harvard University

Materials in 2-dimension and beyond: platform for novel electronics and optoelectronics

Heterogeneous interfaces between two dissimilar materials are an essential building block for modern semiconductor devices. The 2-dimensional (2D) van der Waals (vdW) materials and their heterostructures provide a new opportunity to realize atomically sharp interfaces in the ultimate quantum limit for the electronic and optoelectronic processes. By assembling atomic layers of vdW materials, such as hexa boronitride, transition metal chalcogenide and graphene, we can construct atomically thin novel quantum structures. Unlike conventional semiconductor heterostructures, charge transport in of the devices is found to critically depend on the interlayer charge transport, electron-hole recombination process mediated by tunneling across the interface. We demonstrate the enhanced electronic optoelectronic performances in the vdW heterostructures, tuned by applying gate voltages, suggesting that these a few atom thick interfaces may provide a fundamental platform to realize novel physical phenomena. In this presentation, we will discuss several recent development of electronic and optoelectronic properties discovered in the van der Waals heterostructures, including hydrodynamic charge flows, cross-Andreev reflection across the quantum Hall edges states, and interlayer exciton formation and manipulations.

Parallel sessions

12 Dec – PM1

Stimuli responsive materials

Composites, Light weight materials and sustainability

Materials and methods for Conservation of Cultural Heritage

2D materials for energy applications

Materials and processes for environmental protection and sustainability

12 Dec – PM2

Solid state lighting and LEDs

Biomimetic materials triggering cell phenotype and tissues regeneration

Oxide and nanomaterials for non-volatile memories

Mechanical properties of 2D materials composites

Materials and processes for environmental protection and sustainability

13 Dec - AM

Stimuli responsive: bio-organic materials

Biomimetic materials triggering cell phenotype and tissues regeneration

Oxide and nanomaterials for non-volatile memories

Energy storage and water splitting

Materials and processes for environmental protection and sustainability

13 Dec – PM1

Stimuli responsive: organic-inorganic materials

Printed electronics

Wide band gap semiconductors for power electronics and sensor applications

Energy storage and water splitting

Smart surfaces and functionalization

13 Dec – PM2

Materials and processes for environmental protection and sustainability

Nanobiocomposites for in-vitro diagnostics and targeted drug

Wide band gap semiconductors for power electronics and sensor applications

Growth and synthesis of 2D materials

Smart surfaces and functionalization

14 Dec - AM

Photovoltaics

Nanobiocomposites for in-vitro diagnostics and targeted drug

Wide band gap semiconductors for power electronics and sensor applications

Growth and synthesis of 2D materials

Smart surfaces and functionalization

14Dec – PM1

Photovoltaics

Nanobiocomposites for in-vitro diagnostics and targeted drug

Electronic/optical/magnetic/quantum properties of 2D materials

Materials under extreme conditions and ultra-fast transitions

Printed electronics

15 Dec - AM

Magnetic materials for medicine

Biological applications of 2D materials

Electronic/optical/magnetic/quantum properties of 2D materials

3D printing materials in biomedical research

Organic electronics

15 Dec – PM1

Photovoltaics

Chemistry and functionalization of 2D materials

Magnetism and spintronics

Materials under extreme conditions and ultra-fast transitions

Organic electronics

15 Dec – PM2

Photovoltaics

Chemistry and functionalization of 2D materials

Magnetism and spintronics

Materials under extreme conditions and ultra-fast transitions

Thermoelectrics

16 Dec - AM

Magnetic materials for medicine

Novel 2D materials based devices

Fuel cells

Optical fiber materials and devices

Active packaging materials

Monday December 12

Session title	**Chairman**
Stimuli responsive materials	**Veronica Ambrogi**
Composites, Light weight materials and sustainability	**Toni Recca**
Materials and methods for Conservation of Cultural Heritage	**Domenico Acierno**
2D materials for energy applications	**Vincenzo Palermo**
Materials and processes for environmental protection and sustainability	**Adriano Cola**
Solid state lighting and LEDs	**Giuseppe Gigli**
Biomimetic materials triggering cell phenotype and tissues regeneration	**Simone Sprio**
Oxide and nanomaterials for non-volatile memories	**Massimo Longo**
Mechanical properties of 2D materials composites	**Valentina Tozzini**
Materials and processes for environmental protection and sustainability	**Natalie Stingelin**

#001 - Smart Polymeric Materials for Microencapsulation

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Microcapsules are small particles which contain an active agent or core material surrounded by a coating or shell. The encapsulation of materials for protection and phase separation has evolved into a major interdisciplinary research focus.[1] The utility of microcapsules for efficient cargo storage and targeted release is of considerable importance in self-healing materials, nutrient preservation, agricultural applications, fragrance release, and drug delivery.[2] One of the most challenging tasks and the ultimate purposeof developing delivery systems is to modulate the release of encapsulated cargo substances. Strategies such as heat treatment, ionic strength, magnetic fieldsand light-induced morphology change have been used to alter the shell density and integrity, and then to influence capsule permeability.[3] As one of the most interesting parts of stimuli-responsive capsules, photo-stimuli responsive capsules are capable of affecting their micro-/nano-structures in the form of remote control triggered by external light e.g., sun light, without requirement of direct contact or interactions. Moreover, triggering the release of microcapsules by light has a number of advantages over other external stimuli: (i) photons do not contaminate the reaction systems and they have very low or negligible toxicity in contrast to chemicals; (ii) the excitation wavelength can be controlled through the design of the photo-responsive molecule, (iii) it is easy to control the time and/or local excitation.[4] The development of such highly light sensitive vesicles is of great importance, especially in the fields of surface sciences and environmental applications, where sometimes light would be the only available stimulus to drive the systems. In this presentation, some examples of light-sensitive polymeric microcapsules will be described, that also show how the wavelength of the triggering light can be moved from the UV to the visible region, depending on the desired final application.

References

1. Zhang et al. (2012) Science 335, 690-694

2. Esser-Kahn, et al. (2011) Macromolecules 44, 5539.

3. Abbaspourradet al. (2013) J. Am. Chem. Soc 135(20), 7744–7750

4. Asanuma et al. (2007) Nature protocols 2(1), 203-212

#002 - Light-responsive scaffolds made of wool keratin for triggered antimicrobial applications.

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Antimicrobial photodynamic therapy (APDT) is a very promising alternative to conventional antibiotics for the efficient inactivation of pathogenic microorganisms. The mode of action employs light combined to a photosensitizer (PS) and oxygen to produce phototoxic species such as reactive oxygen species (ROS) including superoxide, hydroxyl radicals, and excited state singlet oxygen. Immobilizing PSs on a scaffold surface represents a strategy to prevent the attachment of bacteria, avoiding colonization (biofilm) and subsequent deterioration. In the present work, porous 3D scaffolds made of wool keratin functionalized with PSs are proposed as systems with triggered antimicrobial properties. Keratin is the most abundant protein in the epidermis of vertebrates and its appendages such as feathers, hair, wool, nails, horns and claws. Keratin was selected as biopolymer because it is a non-food protein largely employed in biomedical and regenerative medicine applications, due to the presence of cell binding motifs (Arg-Gly-Asp and Leu-Asp-Val) in its primary structure, capable of supporting cellular attachment and proliferation. Moreover, recycling keratin for biomedical applications helps reduce the environmental problems caused by the accumulation of keratin wastes from stock farming, butchery and textile industries. The freeze-drying process of aqueous keratin solutions is herein proposed as a green and simple method to produce porous sponges with the desired chemicol-physical properties. In particular, mean pore size and he porosity can be reduced by increasing the keratin concentration; on the other hand, increasing the freezing rate allows the design of sponges with stacked leaflet structures and oriented pores. Two different PSs belonging to the classes of porphyrin and phenothiazinium compounds, were used for the photo-functionalization of the keratin sponges. It was found that the photo-activity, and thereby the antimicrobial effects, can be fine-tuned by properly selecting the PSs nature and amount, as well as the irradiation time. Finally, all the prepared sponges support human fibroblast growth, while no significant impairment of cell viability is observed upon light irradiation. Our data support the premise that this type of materials, combining the properties of 3D-scaffolds made of a bioactive polymer with the antimicrobial properties of ROS-producing compounds, could be useful in a wide range of areas where sterility needs to be maintained or enforced, including wound-healing, surgery implants and tissue engineering.

#003 - Light-triggered release of essential oils from polymer nanocapsules

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Nanocapsules are known as very effective and reliable release systems in many application fields, and successful loading of active agents has been vastly reported in literature [1].

In this work we report the preparation and the release behavior of UV-responsive polymeric nanocapsules containing essential oils as an active core, synthesized by miniemulsion interfacial polymerization [2]. The obtained capsules were able to release the antimicrobial oil under continuous UV irradiation (360 nm) due to the presence of azobenzene moieties in the main chain of the polymer. At this specific whavelength, *E-Z* photoisomerization of azobenzene is triggered [3], resulting in a massive rearrangement of the polymer shell, from a "closed" conformation to a more "open" one.

Essential oils were succesfully employed both as active agent and solvent for monomers involved in the interfacial polymerization. Therefore they represent a good alterntive to the toxic organic solvent traditionally used, resulting in a more sustainable functional system.

Nano-sized capsules mean size was measured via Dynamic Light Scattering (DLS) . Shape and morphology were analyzed through Scanning Electron (SEM) and Transmission Electron Microscopy (TEM). UV-Vis spectroscopy was used to evaluate the release kinetics of the encapsulated essential oils. In absence of irradiation, in fact, the absorbance intensity appeared to be constant over time, while it increased progressively when the sample was irradiated with 360 nm UV light, proving the release of the encapsulated material. The possibility of releasing multiple active agents was also tested, by introducing a fluorescent probe molecule in the core. The effectiveness of this multiple release system was demonstrated by the observed buildup of fluorescence upon UV light irradiation, in accordance with the increase of the probe molecule concentration in the release medium.

[1] P. Couvreur, et al. Crit. Rev. Ther. Drug Carrier Syst. 19i2,10 (2002).

[2] V. Marturano et al, Polymer 70, 222 (2015).

[3] B. Tylkowski et al, Eur. Polym. J. 45, 1420 (2009).

#004 - Multifunctional electrically controllable/hygromorphic conductive polymer actuators for soft robotics

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Responsive polymer-based actuators are attracting increasing attention in recent years because of their potential applications in several fields, including soft robotics, environmentally activated sensors, programmable origami, and energy generators [1]. These kinds of actuators exhibit reversible shape changes (e. g., bend, fold, curl, and rotate) in response to a given stimulus, such as heat, moisture, light, or electric voltage. In this framework, the cooperation between the electrical conductivity and the hygroscopic nature of conductive polymers such as PPy and PEDOT:PSS has recently led to the development of a new class of CP actuators working in ambient air [2]. The actuation principle lies in the reversible volume expansion/contraction of the material in air resulting from the spontaneous sorption/desorption of environmental moisture. Furthermore a reversible contraction can be induced through the application of an electric current, ascribed to desorption of water vapor as a result of Joule heating.

Here we present a class of double-layered, anisotropic humidity-driven actuators based on a passive layer of a soft silicone elastomer (PDMS) and an ultrathin active layer of PEDOT:PSS [3, 4]. The proposed actuators simultaneously combine electric- and humidity-driven active/passive actuation capabilities along with touch- and humidity-sensing properties within a single composite material.

Thanks to the reduced complexity and high tailorability of the proposed processing strategy, which consists of a few steps of spin coating deposition, direct laser cutting and patterning, it is easy to change the design of the actuators to meet the requirements of the target application. Several examples are reported, including site specific actuation (hand with individually addressable fingers), plants inspired structures (leaves, flowers), touch sensitive structure inspired by Mimosa pudica, and others. In addition to bending movement, more complex behavior such as twisting can be imparted to the bilayer by an appropriate asymmetric pattern design on the active surface.

The electro-thermo-mechanical and hygromorphic responses were evaluated on millimeter-scale beam-shaped structures, confirming the high reproducibility and reliability of the actuators.

The proposed smart material structures, whit intrinsic sensing and actuation capabilities, permit to envision a series of interesting applications as active bioinspired elements in soft device/robots, soft grippers, manipulators, or millimeter-scale walking robots.

[1] M. A. Cohen Stuart, et al., Nat. Mater. 2010, 9, 101.

[2] H. Okuzaki, et al., Adv. Funct. Mater. 2013, 23, 4400.

[3] S. Taccola, et al., ACS Appl. Mater. Interfaces 2013 , 5 , 6324.

[4] S. Taccola, et al., Adv. Mater. 2015, 27, 1668.

#005 - SELF-PROPELLING CATALYTIC SYSTEMS: A MICROFLUIDIC APPLICATION

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Control on the movement of fluids and an efficient mixing are basic steps to perform a number of chemical and biological microfluidic processes. The progress in microfluidic technologies has made possible complicated manipulations of solutions at the microscale [1], but many devices rely on external instruments such as microsyringe pumps or power sources. Moreover, liquid flow in microchannels is completely laminar and uniaxial, with a very low Reynolds number regime [2]. To increase fluid mixing, complex three-dimensional networks inducing chaotic advection have to be designed. Alternatively, turbulence in the liquid can be generated by active mixing methods or by adding small quantities of viscoelastic polymers to the working liquid [3]. We have used polyelectrolyte multilayer capsules (PMCs) embodying a catalytic polyoxometalate complex, Ru_4POM [4] to propel fluids inside microchannels and to create elastic turbulence. These chemical systems are functional actuators, that is, materials systems that respond to reagents/stimuli at the molecular level (input) and produce a mechanical effect (output) at the macroscale level. The overall effect is enhanced and controlled by feeding the polyoxometalate-modified capsules through hydrogen peroxide, H_2O_2, thus triggering an on-demand propulsion due to oxygen evolution resulting from H_2O_2 decomposition [5].

In this frame, the capillary dynamics of the aqueous mixtures with different H_2O_2 concentrations flowing across microchannels have been analyzed to quantify key dynamic parameters such as speed, pressure, viscosity, as well as, Reynolds and Weissenberg numbers. Increase in fluid speed together with the capsule-induced turbulence effects have been found to be proportional to the H_2O_2 [6]. The catalytic system has been also studied in hydrodynamic pumping conditions: pressure and volumetric flow rate have been monitored by means of microfluidic sensors. Moreover, the effects of the catalytic reaction on a polydimethylsiloxane (PDMS) membrane bulge have been evaluated and then we have demonstrated the membrane can be used as chemically actuated diaphragm to move fluids within microfludic systems. Finally, a decreasing of mixing time between fluid lamellae has been demonstrated in a serpentine microreactor in presence of such self-propelling systems.

Compared to other materials, our chemical system is expected to be more convenient due to (i) a controlled oxygen production *in situ*, (ii) minimized interference in chemical and biochemical processes, and (iii) fuel-dependent elastic properties of our materials.

1. L. Restrepo – Perez, et al, Lab Chip, 14 (2014), 1515

2. A. D. Stroock, et al, Science, 295 (2002), 647

3. A. Groisman et al, Nature, 410 (2001), 905

4. A. Sartorel, et al, J. Am. Chem. Soc., 130 (2008), 5006

5. L. L. del Mercato, et al, Chem. – Eur. J., 20 (2014), 10910

6. A. Zizzari et al, Lab Chip, 14 (2014), 4391

#006 - Different MWCNT Contents Affect On Shape Memory Effect of Lightly Cross-Linked Elastomers

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Shape memory materials (SMM) belong to the class of smart materials. Their main characteristic consists in the ability to recover their original shape after they underwent a deformation, thanks to the application of an external stimulus. This effect is known as shape memory effect (SME). [1]

Among SMM, shape memory polymers (SMP) represent an important part of this class of materials. In this study the synthesis of an epoxy liquid crystalline elastomer (LCE) is presented. SME in LCEs is thermally triggered, exploiting the phase transition from anisotropic to isotropic phase. [2, 3]

What we have aimed was the realization of lightly cross-linked liquid crystalline elastomer films filled with multi-walled carbon nanotubes (MWCNT), in order to obtain nanocomposites at different content of nanofillers (0,75%, 1,50%, 3,00%). In order to obtain a homogeneous incorporation of MWCNT within the polymer matrix, a compatibilization strategy of nanofillers through the grafting of epoxy monomers, on their surface was performed.

Thanks to this procedure an enhancement of thermoactuation properties of the nanocomposites with respect to the neat resin was achieved. Moreover, the nanocomposites presented an increase in the sensitivity to the applied thermomechanical stress.

These effect of nanotubes on the shape memory features of the prepared systems was related to their microstructure, defined through morphological, thermal and mechanical analysis.

Thanks to these properties, LCEs have the potential to be used in different fields, ranging from the biomedical, aerospace to the electronic engineering.

[1] A. Lendlein, S. Kelch, *Angew. Chem. Int*., 41, 2034 (2002)

[2] H.Qin, P.T. Mather, *Macromolecules*, 42, 273 (2009)

[3] Z. Pei, Y. Yang, Q. Chen, E.M. Terentjev, Y. Wei, Y. Ji, *Nat.Mater*., 13, 36 (2014)

#007 - Active micromotors: efficient Marangoni-driven microgears and self-assemblying Janus micromachines

Claudio Maggi - NANOTEC-CNR, Institute of Nanotechnology, Soft and Living Matter Laboratory

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In the first part of the talk I will present a new type of light-activated motors with unprecedented efficiency[1] (see movie at https://www.youtube.com/watch?time_continue=4&v=-NX-vNCWWS0). These consist in asymetric microfabricated gears covered by an absobing coating that converts the energy of wide-field illumination into rotational motion. These micromotors are suspended at an air-liquid interface and produce a non-homogenous heating of the fluid that, in turn, causes a surface tension-driven torque spinning the rotor up to 300 rpm. It is shown that these microdevices have an efficiency orders of magnitude higher than rotors relying on direct optical momentum transfer or on thermophoresis. In the second part of the talk I will show how we were able to design self-assemblying micromotors from catalytic (Janus) self-propelling particles and passive microgears[2] (see movies at http://onlinelibrary.wiley.com/wol1/doi/10.1002/smll.201502391/full). This combination leads to the fully autonomous construction and propulsion of rotors via the almost perfect alignment of Janus particles with the gear's edge. It will be discussed how the performaces of these motors are affected by hydrodynamics and competition for fuel.

[1] C. Maggi, F. Saglimbeni, R. Di Leonardo et al. Nature Communications 6, 7855 (2015)
[2] C. Maggi, F. Saglimbeni, R. Di Leonardo et al. Small, 12 446 (2016)

#008 - The Diels-Alder reaction applied to polymers from renewable resources: thermal reversibility and recyclability

Alessandro Gandini (I) - Grenoble Polytechnic, France and São Carlos Chemistry Institute, University of São Paulo, Brazil

The Diels-Alder (DA) reaction applied to monomers incorporating furan and maleimide moieties is discussed in terms of the synthesis of different macromolecular structures based on renewable resources, including linear, branched and crosslinked architectures of homo- and co-polymers.

Emphasis is placed, on the one hand, on the interest associated with this strategy regarding the thermal reversibility of these DA materials, which allows their mendability and recyclability to be readily attained, and, on the other hand, on the specific application of these features to monomers or polymers from renewable resources, such as plant oils, starch, cellulose and natural rubber, quite apart from the ubiquitous presence of the furan heterocycle in all the systems described.

#009 - Eco-friendly thermoplastic composite laminates: mechanical properties and morphological issues

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In the last decades, the increasingly widespread use of plastics with enhanced functional and structural peculiarities for industrial applications and the simultaneous growing awareness of the environmental issues associated with their disposal have driven the interest of both academic and industrial research toward the development of new eco-friendly materials. These latter, best known as biocomposites or green composites, are based on polymer matrices intrinsically biodegradable as poly(lactic acid) resins (PLAs) or from renewable raw materials as polyhydroxy alkanoates (PHAs) or from plastic wastes and natural fibers (e.g. jute, flax, cotton, kenaf, sisal, coconut, bamboo).

Poly(lactic acid) resins (PLAs), among biodegradable resins, are widely used because of their good mechanical properties similar to those of polystyrene, its degradability in relatively short period of time in contrast to conventional plastics and high productivity compared with other biodegradable resins.

About the recycling of plastic waste streams, taking into account that polyolefins like polyethylene and polypropylene resins, given their outstanding physical, mechanical, thermal and chemical properties, are largely involved in plastic products for packaging and automotive applications, special attention has been paid to the mechanical recycling of these fractions in designing and manufacturing of items for civil and building applications.

Finally, regarding the reinforcement, the use of natural fibers, eventually pre-treated to improve the interfacial adhesion with the reference hosting matrix, in place of synthetic ones as glass fibers or carbon fibers, even so far mainly dedicated to the reinforcement of petrochemical based resins, have been reviewed by several authors. Among them, jute has been largely considered due to its low cost, large amount of production and high specific strength.

In the frame of the above considerations, activities were focused on the development of various environmentally friendly composite laminates prepared by conventional techniques as the film stacking and compression molding and mainly validated in terms of mechanical performances. Specifically, laminated plates based on PLA and recycled polyolefin wastes reinforced with commercial plain wave fabrics of jute or glass fibers were evaluated under static and dynamic flexural loadings as well as by low-velocity impact tests. Mechanical results were also interpreted by visual inspections and morphological analysis (scanning electron microscopy) of damaged areas.

#010 - Particle Stabilized Liquid Foams as Precursors for Porous Materials

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Particle stabilized liquid foams can be used as templates to obtain porous materials with open cell structure, high specific area and hierarchical porosity. The preparation method here presented relies on gel casting to strengthen the structure of the liquid foams, followed by high temperature treatment, or sintering, to eliminate organic components and obtain solid foams with adequate consistence and mechanical resistance.

This method has been applied to different ceramic and carbonaceous materials [1-3] using, as foam stabilizers, micro/nanosized solid particles of different chemical nature. Some key results are here reported, as examples, where porous materials are produced from aqueous dispersion of titanium dioxide, TiO_2, nanoparticles and commercial Activated Carbon powders.

The peculiarity of this method is that the analysis of the physicochemical interfacial and bulk properties of the initial dispersions is a fundamental tool to establish the structural and mechanical properties of the final solid materials. A key aspect, in fact, is the association of specific surfactants to the colloidal particles to improve their capability as liquid foam stabilizers. This is evidenced by the analysis of the micro-structure and textural properties of the final solid foams, performed by SEM and gas adsorption methods.

1. D. Zabiegaj et al, J. Nanoscience and Nanotechnology, 15 (2015) 3618-3625

2. D. Zabiegaj et al, Colloids & Surfaces A, 438 (2013) 132-140

3. D. Zabiegaj et al, Colloids & Surfaces A, 473 (2015) 24-31

#011 - ELECTRODEPOSITION OF ALUMINIUM/CERAMIC METAL MATRIX COMPOSITE COATINGS FROM IONIC LIQUIDS

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Metal Matrix Composites (MMCs) have evoked a keen interest in recent years for the very large number of potential application field. They range from aerospace and automotive industries to energy production and tools for everyday life. In particular, the interest on these materials is related to their superior strength-to-weight ratio and high corrosion and tribocorrosion resistance. However, in some cases, the widespread adoption of MMC for engineering applications has been hindered by the high production cost or the toxicity of the metal matrix. In order to save energy and row materials, the use of MMC coatings would be preferred upon bulk MMC materials. Electrodeposition is the more commonly used technique to obtain MMC coatings and its application can be traced back to 1928 when copper/graphite composite was realized for self-lubricating surface for automotive purpose. Since that several MMC have been produced especially with nickel or copper matrix. That raise concerns about toxicity (nickel) and scarcity (nickel and copper) limiting their use in niche applications. Alternative metal matrix have been proposed and, on the ground of its low weight, high corrosion resistance, abundance and low toxicity, aluminium resulted among the most promising metal matrix. However, aluminium-based MMCs are much more complex to be produced since aluminium can not be electrodeposited from aqueous media. Ionic Liquids (ILs) can be used to overcome this issue. It is well known that technically thick aluminium coatings can be electrodeposited from chloroaluminate ILs and industrialization of this process is currently under development for the realization of high-tech engineered metallic materials for automotive and aeronautic sectors.

In this contribution preliminary results of a running study aiming to the production of aluminium matrix MMC composite coatings will be presented. The coatings were obtained via codeposition, at room temperature, of metallic aluminium and ceramic microparticles dispersed in a chloroaluminate IL. The morphology and microstructures of the MMC coatings as well as the amount of embedded ceramic particles were evaluated by means of SEM-EDS on the deposit surface and cross-section. The results were related to the electroplating bath composition (nature and amount of dispersed particles) and the electrodeposition parameters (current density and deposition potential) in the attempt to determine the optimal conditions for the deposition of aluminium-based MMC coatings.

#012 - Atomistic study of semiconducting polymers in solvents via Flory-Huggins theory

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Conjugated semiconducting polymers are easy to process and relatively cheap: they can be easily synthesized from solution and deposited by standard inkjet printing techniques on different substrates. The polymer solubility accordingly plays a crucial role in determining their performances.

For example, in solution processed poly(3-hexylthiophene) (P3HT) transistors the field effect mobility depends on the polymer miscibility in solvents. Another important solubility-related property is the ability to blend with other components dispersed in the solvent: rr-oligo(3-alkylthiophenes) (rr-P3ATs) have demonstrated to be able to selectively wrap semiconducting carbon nanotubes depending upon the polymer solubility.

Another example is represented by the n-type polymer P(NDI2OD-T2), which has been observed to have a tendency to preaggregate in specific organic solvents. Preaggregation in the liquid phase has an impact on the thin film morphology at different length scales: for example, organic solar cells obtained from nonaggregated chains have shown highly increased power conversion efficiency with respect to those built from preaggregated ones.

The Flory-Huggins theory is the appropriate tool for studying the solubility of macromolecules: it describes the solvent - solute interaction through an effective parameter called the Flory−Huggins interaction parameter χFH, which can be calculated by atomistic simulations.

Here we report a model potential molecular dynamics study of p- and n-type polymers in different solvent by using the FH theory. In particular, we first study the solubility of a series of rr-P3ATs in THF as a function of the length of their alkyl chains. Furthermore, we investigate the solubility of P(NDI2OD-T2) in two different solvents, namely toluene and chloronaphthalene, which have shown to give opposite effects in terms of polymer preaggregation in the liquid phase.

Our results are in agreement with the available experimental observations, both for the rr-P3ATs and for P(NDI2OD-T2). We find that the oligothiophenes with side chains made of up to four carbon atoms are not soluble in THF. We also confirm the experimental observation of a better solubility of P(NDI2OD-T2) in chloronaphthalene, and we observe that (i) the chain is able to explore a higher number of configurations in toluene due to a higher diffusivity in this solvent and (ii) that the chain backbone is more planar in chloronaphthalene due to the larger aromatic core of this solvent with respect to toluene. These two characteristics are likely to have an impact on long chain aggregation, suggesting a higher probability of folding in toluene.

References:

C. Caddeo, D. Fazzi, M. Caironi and A. Mattoni; J. Phys. Chem. B 118, 12556-12565 (2014)

C. Caddeo, A. Mattoni; Macromolecules 46 (19), 8003-8008 (2013)

C. Caddeo, C. Melis, L. Colombo, A. Mattoni; J. Phys. Chem. C 114, 21109-21113(2010)

#013 - Thermal and morphological characterizations of drug loaded chitosan nanocomposites using TGA/FTIR and AFM techniques.

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Over the last years many different biopolymeric nanocomposites have been developed for biomedical applications and many studies are reported about the properties and their uses as carriers for drug delivery. The performance of these carriers and their release properties strongly depend on their morphological, thermal, and dynamical properties that, therefore, should be controlled carefully while using them with desired properties.

Environmental changes encountering stored pharmaceuticals may lead to some modifications in the material structure, morphology and biological properties. Consequently, stability testing data are required to understand how the quality of pharmaceuticals changes with time under the influence of various environmental factors. In particular, the recent development of the controlled release technology requires a detailed knowledge about the influence of the matrices used as drug carriers on the pharmaceuticals stability. Among biopolymeric carrier, chitosan is widely used for controlled drug release because of its low toxicity and biodegradability. However, chitosan based composites suffer from the drawbacks of low thermal/chemical stability and of low drug-loading capacity. An interesting strategy to overcome this limit is the addition of clay minerals into the biopolymeric matrix.

The main goal of this work was to investigate the decomposition processes of chitosan/clay matrices loaded with acetaminophen. Despite its various therapeutic uses, acetaminophen exhibits low solubility in water. This reduces its bioavailability in the human body. A modified form of delivery system is then required for the enhancement of the pharmaceutical properties of such drug. Developing new pharmaceutical formulations requires as a preliminary stage the knowledge of the thermal stability of these systems.

In this frame, the present work aims to characterize chitosan/clay nanocomposites loaded with acetaminophen for which systems a literature survey revealed just a few investigations regarding their thermal and morphological properties. Here, different chitosan/montmorillonite matrices were prepared by varying the clay content and the effects of the confinement of acetaminophen inside the different matrices were investigated by means of thermogravimetric analysis (TGA), thermogravimetric analysis coupled to IR spectroscopy (TGA-FTIR), and tapping mode atomic force microscopy (AFM). It was found that the presence of the clay enhances the thermal stability of these nanocomposites. FTIR analysis of the evolved products from their thermal degradation showed the release of water, aldehydes, carboxylic acids and CO_2. The different amount of MMT affected also the morphologies of these systems. The amount of MMT affected also their surface properties. Thus, it has an effect on the adsorption of acetaminophen in the CS-MMT carriers.

#014 - PREFABRICATED CONSTRUCTION SYSTEM MADE UP OF CARDBOARD

Dario Luigi Distefano - University of Catania / DICAR

Other Authors: Antonio Gagliano (DIEEI), Vincenzo Sapienza (DICAR)

New forms of contemporary inhabiting are sons of social categories in continuously evolution which bring with them new needs, from comfort to sustainability, to functional flexibility. Young workers, students and researchers offside, low-income families, disasters victim, migrant or refugee are only a few examples. In this front, new materials and technologies, centred on fast and low cost applications, play an important role. Hence the idea of developing Archicart, a prefabrication system whose base element consist in an alveolar corrugated cardboard panel, able to reduce transport and installation costs and usable in case of self-construction. In the proposal paper, after a description of Archicart system, the authors will show a possible application to realize an emergency village for Civil Protection, in one of the strategical area of Catania. The type module is a terraced unit of two floors made up of structural members filled with cellulose fiber to increase thermic performances. Furthermore, they will be presented the results of an experimentation conducted to compare the performances of base component in some alternative fillings.

#015 - Materials and methods for the conservation of Cultural Heritage

Piero Baglioni (I) - UNIVERSITY OF FLORENCE

Colloid and surface Science has always been central disciplines in many applicative areas, and fundamental knowledge from colloids has been applied across a range of industries as pharmaceutical, detergency, paint, and food industries. A precise control on structure and dynamics of colloids is required to transfer a laboratory-scale know how to field applications. This will be even truer in the near future, with the development of sophisticated hierarchically organized systems, where single components combine in a synergistic or orthogonal way to provide enhanced performances for the intended end-applications.

The Florence group has pioneered the application of soft matter and materials science to several fields, one of the most exotic is the conservation of cultural heritage that was pioneered by us. In this field, the same tenets as for the above-mentioned applicative areas hold. Art Conservation poses a formidable and exciting challenge to Colloid and Interface Scientists in two respects. First of all, the majority of the most performing and environmentally-safe cleaning and consolidation agents for artworks are soft matter systems. Secondly, the interaction of these agents with the artifact involves an exceptionally complicated range of interfacial interactions.

In this lecture I will review the most meaningful achievements of my group in this field, focusing on the application of colloidal dispersions of increasing complexity, from nanoparticles to o/w microemulsions to semi-interpenetrating hydrogels containing o/w microemulsions. These systems have been used on artifacts of the most diverse origins, from Renaissance frescoes to Picasso and Pollock. I will show how chemical and colloidal design can be implemented to meet the requirements of the end-users and how precise knowledge of structure, dynamics and interfacial interactions can contribute to overcome the traditional serendipitous approach used by conservators. Finally, I will try to summarize the main perspectives that this field can disclose for the colloid community.

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#016 - Virtual unrolling and deciphering of Herculaneum papyri by X-ray phase-contrast tomography

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After Antonio Piaggio’s mechanical unrolling of Herculaneum papyri and the more recent ‘Norwegian’ chemical system, the last frontier of (Herculaneum) papyrology is to read virtually the text written inside unopened papyrus rolls without damaging them at all. This fundamental objective appears to be a hopeless task with conventional imaging techniques. X-Ray Phase-Contrast Tomography, a pioneering technique developed at the European Synchrotron Radiation Facility (Grenoble), has eventually made this goal achievable, paving the way for the future edition and interpretation of the unknown texts contained in hundreds of still unopened Herculaneum papyri. Thanks to the exceptional properties of Synchrotron Radiation and the development of dedicated algorithms for the virtual unrolling and flattening of rolled-up papyri, it was possible to read for the first time, with unprecedented resolution and contrast,full expressions, textual portions and a marginal sign inside *PHerc*. 375 and *PHerc.* 495, two Herculaneum papyrus rolls owned by the National Library of Naples. Our study enabled an accurate investigation of the internal structure, the handwriting and the Greek text hidden inside each roll, providing precious information about their probable author and the work contained in *PHerc.* 495. The study revealed also unexpected events historically experienced by this latter.

#017 - Nanostructured polymeric coatings for the active protection of copper-based works of art

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Degradation processes occurring in copper-based artifacts represents a critical issue since can irreversibly compromise the conservation status of valuable works of art and modify the object surface appearance leading to the formation of alteration products and reactive compounds, such as chlorides, hydroxy-chlorides and sulfates. In particular, the presence of chloride species is extremely harmful since is responsible for the “bronze disease” that is based on the cyclic copper corrosion.

At present, concerns related to degradation phenomena are still relevant in both ancient and modern copper-based artifacts and innovative approaches for a safe and reliable protection are demanding.

To overcome the drawbacks due to the use of conventional corrosion inhibitors and large amounts of organic solvents, we have focused our attention on the development of polymeric nanostructured coatings able to provide an active protection of copper-based works of art by using safer procedures. This work is carried out within the ongoing NANORESTART “Nanomaterials for the restoration of Works of Art” project, recently founded by the European Commission,in order to develop innovative, safe and long-lasting strategies for the protection of modern copper-based works of art.

To this aim, we are working on the development of active protective systems based on the use of low toxic of corrosion inhibitors and environmentally friendly polymers obtained from renewable sources: chitosan (CHIT) and amorphous poly(vinyl alcohol) (HAVOH).

The obtained results suggest that the coatings, which are optically transparent and easily removable, effectively preserve the surface characteristics of bronze substrates during accelerated corrosion tests, and thus represent a promising solution for the protection of Cu-based alloy artworks stored or exhibited in indoor environment. In particular, a synergic effect has been observed between the chemical protection provided by the inhibitors and the physical one provided by the polymer matrix. Indeed, the addition of low amounts of inhibitor to the coatings significantly improves their appearance and protective efficacy, and contextually the inhibitor-loaded coatings have shown superior performances with respect to the pure inhibitors.

Moreover, the use of nanocarriers guarantee the storage of the inhibitors which will be released under external stimuli related to the beginning of corrosion processes. The controlled release of corrosion inhibitors allows to hinder degradation phenomena and to develop long-lasting protective coatings.

#018 - Micro-Raman innovative methodology to identify tarnishing corrosion products on Ag based archaeological artefacts

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Silver is a well known ductile and malleable metal exhibiting brilliant metallic lustre with the highest electrical and thermal conductivity among metals, which is proved stable in oxygen and pure water. In fact, thanks to its characteristics, in the past it has been usually employed for jewellery, tableware, coins and medals.

Silver and high-Ag-content alloys are sensitive to exposure to atmospheric agents: the presence in the environment of aggressive agents, such as H_2S, carbonyl sulphide (COS) and SO_2, even in small quantities, combined with the presence of high relative humidity (RH), can quickly cause an alteration from a shining surface to a dark adherent coating known as *tarnishing*.

This study has unveiled microscopic details of the *tarnishing* process, furnishing an innovative, cheap and non-destructive methodology based on µ-Raman spectroscopy to identify the species and composition of Ag-Cu sulphides in tarnished production, according to the equilibrium conditions shown in the Ag_2S-Cu_2S pseudo-binary system. To this purpose both Roman and Punic coins and mixed Cu-Ag alloys with different compositions subjected to an accelerated sulphidation process have been analyzed in order to apply this methodology on archaeological samples and identify the Ag-Cu sulphides species present on the surface patina. This permits to study the best strategy to prevent the formation of the tarnishing patina and to develop *ad hoc* solutions for the treatment of Ag-Cu artefacts. Furthermore a direct correspondence between the Ag percent in the alloy and the Raman band features of the surface sulphides has been revealed.

#019 - Distinguishing different molecular species adsorbed on a flat gold surface with 20 nm resolution by Tip enhanced Raman Spectroscopy in ambient conditions

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Tip Enhanced Raman Spectroscopy (TERS) offers new possibilities to perform few molecules detection through the plasmonic amplification of the vibrational Raman fingerprint of molecules. Near field enhancement of the electric field is provided by the close proximity of metallic tip with a nanometric radius of curvature [1-3]. Coupling this technique with a scanning probe microscopy it is possible to distinguish with very high spatial resolution different molecular species adsorbed on a flat surface, even if they are very similar from a structural point of view [4]. This way it is possible to understand if the two species form large molecular patches of the same specie or they are distributed homogeneously on the whole surface. Furthermore analysis of TERS spectra can give useful information about the orientation of the molecules with respect to the surface on which molecules are adsorbed. In this work we investigate the spatial distribution of Rhodamine 6G (R6G) 100 µM and Crystal Violet (CV) 6 µM molecules simultaneously absorbed on a surface of monocrystalline Au(111). TERS mapping is carried out in gap mode using a Horiba NanoRaman setup with homemade gold tips [5] working in ambient conditions. Samples are excited via a 100X objective (NA=0.7) at 638nm in a side-illumination configuration, with polarization parallel to the tip axis [6]. TERS maps show the spatial distribution of the two molecular compounds, indicating they interact in a similar way with gold surface. It is possible to observe, with a resolution of 20 nm, TERS spectra highlighting areas characterized by R6G spectrum and few little spots containing CV. This points out the possibility to detect few molecules even if they are dissolved in solutions with other molecular species more concentrated. Applications to local spectroscopy and mapping of azobenzene and single wall carbon nanotubes are also shown. References [1] R.M. Stöckle et al., Chem. Phys. Lett. 318, 131–136 (2000). [2] G. Sharma et al. / Advanced Drug Delivery Reviews 89, 42–56 (2015). [3] Mauser, N. and Hartschuh, Chem. Soc. Rev. 43, 1248–1262 (2014). [4] Jiang et al., Nature Nanotech. 10, 865-869 (2015). [5] Lopes et al. Rev. Sci Instrum. 84, 073702 (2013). [6] Gucciardi et al. Nanotechnol. 19, 215702 (2008)

#020 - STATUS OF THE STAR PROJECT

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We report on the work in progress for the realization of the Southern Europe Thomson back-scattering source for Applied Research – STAR – currently under construction at the University of Calabria (Italy). The source is designed to deliver monochromatic, polarized and tunable hard X-ray beams (40 ÷140 KeV) whose temporal structure provides pulses in the ps range with a 10 ms repetition rate. The source main components are installed (RF photo-injector, the accelerating section, laser systems for collision and photo-cathode, RF Power Source and magnets) and their first tests are running. The design of laser lines has been optimized to provide a tunable experimental setup. The RF power network is close to be tested, it's based on a 55MW (2.5us pulse) S-band Klystron driven by a 500kV Pulse Forming Network based modulator and a Low Level RF system, running at 100 Hz. The STAR Control System, developed in the EPICS environment, manage each machine parameter as well as the conditioning system and the access control. We expect to start commissioning the machine by the end of 2016 and obtain the first collisions within the first part of 2017. The µTomo beamline, aimed to microtomographic studies in various fields, is also under commissioning.

#021 - SERS study on organic pigments: comparison between DFT calculations and experimental data

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Identification and characterization of organic pigments used in works of art and cultural heritage play a fundamental role in order to detect a precise geographic area and a specific historic moment.[1,2]

Unfortunately, pigments and dyes commonly employed in artistic production are often extremely fluorescent, making detection through Raman spectroscopy difficult or impossible. Conventional Raman spectra are generally affected by the intense luminescence of several pigments showing weak Raman activity beside a strong fluorescence that inhibits their identification. [3, 4, 5]

This study presents an innovative SERS (Surface enhanced raman spectroscopy) technique is able to quench fluorescence, to enhance strongly the weak Raman scattering effect, and to require small amount of material and minimal sample handling.

More specifically, we tested new substrates by using sandpaper as template. This material is very cheap, flexible, durable and widely available featuring an intrinsic roughness at µm scale. The substrate is based on common sandpaper on which silver nanoparticles were deposited by means of Pulsed Laser Deposition (PLD). In this work, alizarin, purpurin and carminic acid have been studied using SERS by Ag substrates deposited by PLD technique. Finally, we compared the experimental and theoretical spectra, obtained with DFT calculation, to study bands involved into interactions between pigment and substrate.

[1] A. Claro, M.J. Melo, S. Schafer, J.S. de Melo, F. Pina, K.J. van den Berg and A. Burnstock, Talanta 74 (2008) 922.

[2] C. Clementi, C. Miliani, A. Romani, U. Santamaria, F. Morresi, K. Mlynarska and G. Favaro, Spectrochim. Acta Part A 71 (2009) 2057.

[3] F. Pozzi, S. Zaleski, F. Casadio and R. P. Van Duyne, J. Phys. Chem. C, 120 (2016) 21017.

[4] L.H. Oakley, S.A. Dinehart, S.A. Svoboda and K.L. Wustholz, Anal. Chem. 83 (2011) 3986.

[5] E. Fazio, S. Trusso and R.C. Ponterio, Applied Surface Science 272 (2013) 36.

#022 - Morphing graphene for energy applications

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In spite of its exceptional properties, for many applications bare graphene is not optimal. Its null density of states at the Fermi level limits the exploitation of its conducting properties [1]; it is weakly interacting, which limits its potentialities as medium for gas storage in spite of its exceptional surface to mass ratio. In addition, storage applications requires building 3D graphene based frameworks [2]. Therefore morphing and functionalization of graphene in controlled way are the current challenges in the field of graphene-based technologies.

Here, combined simulation-experimental studies on the relationship between graphene morphology and its electronic and chemical properties are reported. Structural deformation and rippling, defects (structural or substitutional), chemical decoration and functionalization are evaluated and the relationships between each other are shown. For instance, the presence of defects or corrugation enhances reactivity, which in turn favors the chemical functionalization [3-5]. On one side, this can directly favor both chemical adhesion and physical interaction of hydrogen with graphene[3,6-9]. On the other hand, it allows controlling the concentration and location of spacer molecules for designing of 3D pillared multilayers structures[10,11]. These studies additionally returned side-results on the relationship between structural and electronic properties, exploitable for graphene based-nanoelectronics [3,10].

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[1] V Tozzini, V Pellegrini JPCC, **115** 25523 (2011)

[2] V Tozzini, V Pellegrini Phys Chem Chem Phys, **15** 80 (2013)

[3] T Mashoff, V Tozzini, et al APL **106** 083901 (2015)

[4] S Goler, V Tozzini, et. al. JPCC **117** 11506 (2013)

[5] A Rossi, S Piccinin, V Pellegrini, S de Gironcoli, V Tozzini JPCC **119** 7900 (2015)

[6] K Kakhiani, V Tozzini, in preparation.

[7] V D Camiola, T Cavallucci, A Rossi, V Pellegrini, V Tozzini FM, **2** 00003 (2015)

[8] V D Camiola, R Farchioni, V Pellegrini, V Tozzini 2DM **2** 014009 (2015)

[9] T Cavallucci, V Tozzini, JPC C **120**, 7670 (2016)

[10]T Cavallucci, , MsD Thesis, Supervisor: V Tozzini (2014)

[11] Y Murata, et al APL **105** (2015), 221604

#023 - Self-assembly synthesis of layered, vertically aligned 2D molybdenum trioxide functional scaffolds for host-guest photo-electrochemistry in hybrid organic/inorganic hydrogen evolution devices.

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Photoelectrochemical H_2 production through hybrid organic/inorganic interfaces exploits the capability of polymeric absorbers to drive photo-induced electron transfer to an electrocatalyst in water environment. A working photocathode was recently demonstrated exhibiting substantial performances[1,2] and research in organic photo-electrochemistry is now moving its first steps.

Hybrid photocathode's design poses the need to manage simultaneously charge injection, selective contacts, bands engineering together with orthogonalization of light absorption and photogenerated carrier collection. These multiple requirements naturally drive the development of multi-layer architectures based on structured absorbers.

This work reports on the synthesis and characterization of host-guest organic photocathodes based on vertically aligned 2D MoO_3 layered-structures. Scaffolds are synthetized using a pulsed laser deposition ballistic approach exploiting gas dynamic of the nanoclusters-inseminated supersonic jet flow field. Control over nanoclusters' kinetic energy allows versatile synthesis of nanostructured, layered films. Resulting morphologies range from densely packed layered films to spatially separated, vertically aligned layered 2D nano-walls. Scaffolds are conformally coated with 30 nm thick P3HT:PCBM polymers blend, a TiO_2 selective contact and a Pt electrocatalyst. The resulting architecture allows for the design of a new generation of 3D nanostructured electrodes combining optimized opto-electrical properties and structural/morphological features resulting in an hybrid photocathode showing a photocurrent density of 2 mA/cm^2 at +0.2 V_{RHE} and an onset potential of +0.65V_{RHE}. Light absorption and photon/electron conversion efficiency dominate device performances especially in the case of short exciton diffusion length and thin film, absorbers like rr-P3HT in flat stacked architectures often trades-off charge transport for increasing light harvesting. ns-MoO_3 scaffolds covered with 20 nm P3HT:PCBM (plus TiO_2/Pt overlayer) guest layer allows for comparable H_2 evolution performances with flat devices covered with 200 nm thick flat P3HT:PCBM (plus TiO_2/Pt overlayer). Photons trapping enhancement originating by internal multi reflection/refraction of the incident light owing to the nanostructured 2D nano-walls morphology was investigated by means of femtosecond-laser spectroscopy. More importantly, nanostructured photocathodes demonstrated a performance improvement with respect to flat systems suggesting that out-of-plane films structuration may disclose potential for effective devices architectures beyond the stacked layers approach.

[1] F. Fumagalli, *J. Mat. Chem. A* **2016**, 4, 2178-2187.

[2] H. Comas-Rojas, *En. Envir. Sci.* **2016** 10.1039/C6EE01655C advance article.

#024 - Direct synthesis and characterization of colloidal WS2 nanoplatelets

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The tailored fabrication and advanced characterization of two-dimensional nanostructures of transition-metal dichalcogenides (2D-TMCs), such as MoS_2, WS_2, $MoSe_2$, and WSe_2 made of a single to few stacked atomic layers, represent hot research topics of extreme significance to the broad (nano)materials science community as these nanomaterials stand out as the inorganic analogues of graphene. 2D-TMCs exhibit unique thickness-dependent anisotropic photophysical, structural and mechanical properties that make them considerably attractive for several applications, such as photovoltaic devices, lithium-ion batteries, hydrogen-evolving photocatalysts, transistors, and memory devices. However, the production of individually addressable, easily-processable 2D-TMCs with controllable and uniform thickness and lateral dimensions is very challenging. The currently available repertory of 2D-TMCs mostly comprises sheet-like nanostructures with irregular micrometer-scale extended edges derived by liquid-phase exfoliation of corresponding bulk materials or by vapour-phase deposition on solid substrates, which inherently suffer from low chemical and mechanical stability against folding, wrinkling and uncontrolled aggregation when post-synthesis manipulated for device integration. Recently, wet-chemical synthetic approaches have emerged a powerful alternative routes to achieve morphologically and structurally controlled 2D-TMDs in the form of robust freestanding nanostructures with finely adjusted geometric parameters, stabilized by organic ligands bound to their surface and, hence, sufficiently stable in the liquid phase to be safely manipulated and transferred to applications.

In this contribution, we describe an effective liquid-phase synthetic protocol for the synthesis of colloidal 2D-WS_2 nanocrystals with tunable platelet- or sheet-like habits via a direct surfactant-assisted pyrolytic route. By adjusting synthetic parameters, such as the concentrations of the tungsten and sulphur precursors, type and concentration of surfactants, and reaction temperature, the lateral edge sizes and morphology of the nanocrystals can be varied within the sub-50 nm regime. We have monitored the reaction progress by the combination of different techniques of structural-morphological investigation (XRD, SEM, TEM) and spectroscopic measurements.We demonstrate that the developed soft organic-template approach leads to soluble and stable 2D-WS_2 nanostructureswith high structural and optical quality.

#025 - Development of 3D graphene structures and their promising energy applications

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3D graphene materials have attracted a lot of interest due to their ability to transfer many of the unique properties of 2D graphene to a macroscale, with high surface area, high electrical conductivity, and good structural integrity. Good quality graphene may be grown on templates of virtually any shape by Chemical Vapour Deposition (CVD), and in this way free-standing macrostructures called graphene foams (GF) were first produced from nickel foam templates in 2011. Since then there have been many investigations into their use either alone or in composites with other materials in applications such as electrodes for supercapacitors and batteries, gas sensors and adsorbents. We present our investigations into the synthesis of graphene foams and expand their potential even further by significantly reducing the pore size from the 200-400 µm range to which they are limited when using commercially available metal foam templates. To achieve this, we have developed a new technique to reach a pore size range of 1-10 µm using networks of nanoparticles as the templates for graphene growth, significantly increasing the graphene surface area available in a given volume. In addition, we present the promising preliminary results of two different applications that we are exploring for 3D graphene structures. In the first, we demonstrate their potential as electrodes in Li-ion batteries, and show that by using an electrochemical method to completely cover the surface of the graphene with flower-like iron (III) oxide nanocrystals, we can further enhance the properties. In the second application, graphene foams are successfully colonised with microorganisms and proposed as electrode materials for microbial fuel cells, which have the potential to directly harvest chemical energy from several classes of environmental and waste waters.

#026 - Interface engineering of Perovskite Solar Cells: The role of graphene and related materials

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In the broad context of graphene applications [1], new generation photovoltaic underwent beneficial effects in terms of efficiency, stability and costs by exploiting graphene-based materials in the devices structure [2,3]. In particular, the dramatic development exhibited in the last few years by perovskite solar cells (PSC) technology has triggered the scientific community efforts in findings more efficient and stable PSC structures [4]. In this exciting scenario, our work presents a new interface engineering strategy by using graphene and related 2D materials (GRM), [5,6] with the aim to both increase power conversion efficiency (PCE) and stability of PSCs.

By doping the mesoporous TiO_2 layer with graphene flakes ($mTiO_2$+G), produced by liquid phase exfoliation of pristine graphite,[7,8] and by inserting graphene oxide (GO) as interlayer between perovskite and Spiro-OMeTAD layers, we demonstrate a PCE of 18.2% with the two-step deposition procedure, carried out in air. The obtained PCE value is due mainly to improved charge carriers injection/collection processes with respect to conventional PSCs. Although the addition of GRMs does not influence the shelf-life, it is instead beneficial for the stability of PSC under several aging conditions. In particular, $mTiO_2$+G PSCs retain more than 88% of the initial PCE after 16 hours of prolonged 1 SUN illumination at maximum power point. Moreover, when subjected to prolonged heating at 60°C, the GO based structures show enhanced stability with respect to the $mTiO_2$+G one, which shows thermal induced modification at $mTiO_2$+G/perovskite interface.

The as-proposed interface engineering strategy based on GRM has been exploited for the fabrication of state-of-the-art large area perovskite modules. We indeed demonstrated a PCE of 12.6% on a monolithic module with an active area exceeding 50 cm^2. The use of GRM is beneficial to increase the PCE by more than 10% with respect to “conventional” modules, i.e. without GRM interfaces.

References

[1] A. C. Ferrari et al., Nanoscale, 7, 4587, (2015).

[2] F. Bonaccorso, et al, Science, 347, 1246501, (2015).

[3] E. Singh, H. Singh Nalwa, Journal of Nanoscience and Nanotechnology, 15, 6237, (2015).

[4] N.-G. Park, Materials Today, 18, 65, (2015).

[5] A. Agresti et al., Advanced Functional Materials, 26, 2686 (2016).

[6] A. Agresti et al. ChemSusChem (2016) DOI: 10.1002/cssc.201600942

[7] A. Capasso, et al. Solid State Commun. 224, 53 (2015).

[8] F. Bonaccorso et al. Adv. Mater., 28, 6136 (2016).

#027 - Cooperative Effect of GO and Glucose on PEDOT:PSS for High VOC and Hysteresis-Free Solution Processed Perovskite Solar Cells

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Hybrid organic–inorganic halide perovskites have emerged at the forefront of solution-processable photovoltaic devices. Being the perovskite precursor mixture a complex equilibrium of species, it is very difficult to predict/control their interactions with different substrates, thus the final film properties and device performances. Here the wettability of CH3NH3PbI3 (MAPbI3) onto poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) hole transporting layer is improved by exploiting the cooperative effect of graphene oxide (GO) and glucose inclusion. The glucose, in addition, triggers the reduction of GO, enhancing the conductivity of the PEDOT:PSS+GO+glucose based nanocomposite. The relevance of this approach toward photovoltaic applications is demonstrated by fabricating a hysteresis-free MAPbI3 solar cells displaying a 37% improvement in power conversion efficiency if compared to a device grown onto pristine PEDOT:PSS. Most importantly, VOC reaches values over 1.05 V that are among the highest ever reported for PEDOT:PSS p-i-n device architecture, suggesting minimal recombination losses, high hole-selectivity, and reduced trap density at the PEDOT:PSS along with optimized MAPbI3 coverage.

#028 - Self-standing graphene-enriched anodes for lightweight lithium ion batteries

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Lithium-ion batteries (LIBs) currently represent the dominant power source for portable electronic devices. Common anode materials (such as Co_3O_4, Fe_2O_3 andother transition metal oxides) exhibit poor transport properties and low electronic conductivity. Thus, conductive additives, such as carbon black (CB), and polymeric binders are usually included in the battery for electrical conduction and better physical contacts between active materials and current collector, with consequent significant LIB weight increase [1]. Moreover, the pulverization of the anode material, caused by the large volume changes during the lithiation/delithiation cycles, and the consequent loss of electrical contact strongly limit the battery life cycle.

Encapsulating oxide nanoparticles within a self-standing carbon network can help in overcoming the mentioned drawbacks, reducing weight of the LIB, improving its performances and lengthening its life cycle. This can be accomplished by the use of electro-spinning (ES), a very commercially competitive technique for the growth of 1-dimensional materials [2].

This contribution deals with the synthesis by ES of self-standing and flexible fibrous graphene-enriched C/Co_3O_4-based membranes ($G/C/Co_3O_4$) and their testing as binder-free anodes in LIBs.

Electrochemical performancesof the membranes are compared with those of the reference electro-spun Co_3O_4 powders. Half-cell tests are carried out using a lithium foil, 1M $LiPF_6$ in EC+PC+DMC 1:1:1 v/vand glass fibres as the counter electrode,the electrolyte and the separator, respectively.The working electrode is prepared by adding no chemicals to the G/C/Co_3O_4 mats and CB+PVDFto the powders. Powders exhibit higher initial specific capacity (1580 mA h/g), but very poor stability (91%reduction after 10 cycles). On the contrary, in spite of the lower initial capacity, after 75 cycles the mats retain a capacity (453 mA h/g)higher than that of graphite with ~100% Coulombic efficiency.

Lightweight (areal density < 1.2 mg/cm^2) and flexibility of the G/C/Co_3O_4-based anodes might be exploited for the fabrication of LIBs addressed to flexible and/or wearable electronic devices, and aerospace applications, as well.

[1] D.H. Ha, M.A. Islam, R.D. Robinson, *Nano Lett.*, 12(2012) 5122.

[2] G. Faggio, V. Modafferi, G. Panzera, D. Alfieri, S. Santangelo, *J. Raman Spectr.* 43 (2012) 761

#029 - Interface engineering in organic photovoltaic blends: Gaining insights in charge generation processes and Voc

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In the past decade, significant progress has been made in the fabrication of organic photovoltaic devices (OPVs), predominantly due to important improvements of existing materials and the creation of a wealth of novel compounds. Many challenges, however, still exist. Real understanding of what structural and electronic features determine, for instance, the short-circuit current (Jsc), open-circuit voltage (Voc) and fill factor are still lacking; and the role of charge transfer states and which charge transfer states are critical for efficient charge generation are still debated. Here we attempt to obtain further insight of relevant structure/processing/performance interrelations using classical polymer processing 'tools'. We present a survey on the principles of structure development of this material family and how it can be manipulated, with focus on how to control the phase morphology and important interfaces (molecular and between different phase regions). Goal is to tailor and tune the final 'morphology' towards establishing correlations with relevant device characteristics. We will discuss interrelations of the presence of intermixed phases with charge transfer absorption, how we can manipulate the charge transfer energy and what structural features seem to influence Voc.

#030 - INNOVATIVE POLYMERIC MATERIALS FOR WATER TREATMENT

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In this work we present two different approaches for the treatment of wastewater. The first method consists in using TiO_2 based polymeric nanocomposites as valid photocatalytic materials for the degradation of organic pollutants and removal of bacteria. Such nanocomposites were synthesized in a freestanding form by sonication and solution casting method, using poly (methyl methacrylate) as polymer matrix. The combination of titanium dioxide with electron scavengers has been the strategy used to increase the photocatalytic efficiency of these nanocomposites under UV light. Whereas, in order to synthesize operative materials under visible light the adopted strategy consisted in the functionalization of TiO_2 surface with a porphyrin. The photocatalytic activity of the obtained nanocomposites has been evaluated by the degradation of dyes and phenol in an aqueous medium. The antibacterial activity has been instead tested through CFU count using *Escherichia coli* as a model organism. These PMMA based materials are stable, harmless and cheap and they overcome many of the current issues that prevent the real application of the nanomaterials for water treatments, such as their dispersion in water and the consequent related toxicology aspects. [1]

The second approach relies on the use of molecularly imprinted polymers (MIPs) for the selective removal from water of non-steroidal anti-inflammatory drugs, considered "emerging contaminants" in aquatic environments. MIPs are synthesized by copolymerization of cross-linking and functional monomers in the presence of a target analyte, which acts as a molecular template. Following the polymerization, the template is removed to leave cavities with selectivity for the analyte, allowing the polymer to rebind the analyte with a very high specificity. In this work, molecularly imprinted co-polymers have been prepared using as template a non-steroidal anti-inflammatory drug, such as the diclofenac. The difference in the recognition properties of imprinted and non-imprinted polymers were studied using a quartz crystal microbalance or by UV-Vis spectrophotometry. The results demonstrate that MIP materials provide an effective solution for the selective removal of these drugs from wastewater.

[1] M. Cantarella, R. Sanz, M. A. Buccheri, F. Ruffino, G. Rappazzo, S. Scalese, G. Impellizzeri, L. Romano, V. Privitera; *Journal of Photochemistry and Photobiology A: Chemistry,* 321, 1-11 (2016)

#031 - Towards eco-friendly water-processable organic solar cells via low band-gap rod-coil block copolymers

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Even if organic solar cells (OSCs) could have many advantages with respect to silicon devices, their industrial implementation is still limited by some relevant drawbacks. Besides reduced stability and efficiency, the commonly used techniques in laboratory are not suitable for application on industrial scale. To improve efficiency of the devices, morphology control during the active layer deposition results a key point for achieving high efficiency in OSCs. Optimized interpenetrating networks of donor and acceptor materials, nanoscale phase separation, and vertical percolation pathways are essential for effective separation, transport, and collection of the charges. Usually this control is obtained through the use of mixed organic solvents for the active layer deposition (chlorinated and/or aromatic solvents), the use of additives or post-fabrication treatments, as thermal or solvent annealing.1 The preparation of water-processable nanoparticle (NP) dispersions of semiconducting polymers recently emerged as an elegant technique to control morphology at nanoscale. At the same time, it allows lowering chlorinated solvents waste, thus reducing the environmental payback of energy obtained from OPVs and paving the way for the industrial application. The NPs dispersion can be obtained through the miniemulsion method that requires use of a great amount of surfactant agents to ensure NPs stability, the excess of surfactant has to be removed at the end of the process through dialysis.2 Rod-coil block copolymers (BCPs) can be powerful tools to achieve ideal morphologies because of their self-assembly capability that is strictly connected to the length of the two blocks and to their physical-chemical properties.3 We report on the PV application of rod-coil BCPs, PCPDTBT-b-P4VP, constituted by a low band-gap copolymer, PCPDTBT as the rigid segment, studied as donor material in hybrid and organic devices,4 and tailored segments of poly-4-vinylpyridine (P4VP) able to interact with acceptor materials commonly used in OPVs,5 as fullerene derivatives. Taking advantage of hydrophilic behavior of their flexible moiety, these amphiphilic rod-coil BCPs were used for preparing NPs in blend with PCBM, through miniemulsion method in aqueous medium without use of surfactants, thus avoiding dialysis purification. The NPs were fully morphologically and electrically characterized, showing suitable properties for PV application. The PCBM:BCP blend NPs dispersed in aqueous medium were used for the preparation of efficient eco-friendly OSCs, reaching a power conversion efficiency over 2%, near the best result reported for the same system studied in chlorinated solvents.6 1. Polymers 2014, 6, 2832 2. Nature Mat 2003, 2, 408 3. Mater Sci Eng R 2008, 62, 37 4. ACS Nano 2013, 7, 4846; Chem Commun 2013, 49, 8602 5. Eur Pol J 2014, 60, 222 6. Adv Mater 2010, 22, 367

#032 - NaH, a green initiator for renewable polymers: ROP of glycolide and lactide, and characterization of the obtained PLGAs.

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While our society is becoming more and more aware of the importance of sustainable development, green chemistry and renewability, poly(glycolide) (PGA), poly(lactide) (PLA) and their copolymers have already proven to be a valid, renewable alternative to the petrobased plastics in a wide range of applications,[1] The most efficient way to obtain these polymers is via ring-opening polymerization (ROP) of their cyclic esters, and the most common initiator is tin octoate. [2] Although it is FDA approved, its cytotoxicity raises several issues, along with the need of a more benign initiator.

We have already reported the polymerization of ε-caprolactone promoted by sodium hydride (NaH) [3]. We now report on the use of NaH as initiator in the ROP of L-lactide, glycolide and in their copolymerization for the synthesis of poly[glycolide-*co*-(L-lactide)]s (PLGAs). NaH is not only a commercially available, cheap and easy-to-handle compound, but also a non-toxic initiator. Polymerization runs have been performed in bulk, without solvents, and random copolymers were obtained in the case of PLGAs. Their microstructure was characterized by nuclear magnetic resonance (^{1}H and ^{13}C NMR) and matrix assisted laser desorption time of flight mass spectrometry (MALDI MS). Thermal properties were studied via thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Transport properties to water vapour were also evaluated and correlated to the copolymer composition.

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References

[1] V. Nagarajan, A. K. Mohanty, M. Misra, *ACS Sustainable Chem. Eng.* **2016**, *4*, 2899-2916.

[2] Handbook of Ring-Opening Polymerization; Dubois, P., Coulembier, O., Raquez, J. M., Eds.; Wiley-VCH Verlagh GmbH & Co.: KGaA: Weinheim, Germany, 2009.

[3] G. Gorrasi, D. Pappalardo, C. Pellecchia, *React. Funct. Polym.* **2012**, *72*, 752-756.

#033 - Constrained Amorphous Interphase and Mechanical Properties of Bio-Based Polyesters: Polyhydroxyalkanoates

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Polyhydroxyalkanoates (PHAs) are a group of biocompatibleand completely biodegradable polyesters, synthesized by many bacteria as intracellular carbon and energy reserve. Owing to their biodegradability, they can be utilized to make a variety of useful products, in particular for application in packaging and agriculture. The homopolymer poly[(*R*)-3-hydroxybutyrate] (PHB) is the most widespread, lowest-cost and best characterized member of the polyhydroxyalkanoate family. But also some its copolymers, as poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate), (PHBV) are of great interest,because of their improved mechanical properties with respect to plain PHB.

Both PHB and PHBV are semi-crystalline materials, therefore their physical properties must be explained by taking into account the contribution of both the crystalline and the amorphous phases. The classical description of semi-crystalline polymers, which considers only two distinct phases, has been replaced in recent years by a more complete one, which takes into account also the constrained amorphous nano-phase present at the amorphous/crystal interface. A detailed description of the micro- and nano-phase structure is decisive for a full understanding of the physical properties of the semi-crystalline polymers. Indeed, it has been recently proved that many macroscopic properties, as for example mechanical and barrier properties, are defined not only by the degree of crystallinity, but also by the percentage of constrained amorphous interphase. The quantification of this nano-phase is therefore a crucial step in the characterization of a polymeric material, since different processing conditions affect in different ways the evolution of the crystalline and amorphous fractions. The subject of the presentation will be the evolution, during solidification, of the constrained amorphous interphase in PHB and some PHBV copolymers. In addition, the effect of the physical ageing on the mechanical properties of these materials will be presented and discussed in the light of both the crystalline and the rigid amorphous nano-phase percentages.

#034 - Constrained Amorphous Interphase and Mechanical Properties of Bio-Based Polyesters: Polyhydroxyalkanoates

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#035 - Use of geopolymers as innovative materials for wicking

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Wicking is the transport of a fluid through a porous medium due to capillary suction at liquid-gas interfaces at the surface or within the porous medium. Porous wick structures are integral part of fluid capacitance and transport in many systems, such as heat pipes.

A heat pipe is a heat transfer device widely used in space applications. It can exchange large quantities of heat by means of evaporation and condensation of a working fluid. The evaporator is the heart of the device and it contains capillary-porous structures generally based on metals or organic polymers. Both plastic and metals have some drawbacks such as low capillarity (organics) and high diffusivity, thermal expansion and high cost (metals).

A possibility to increase the capacity of thermal exchange is through the replacement of conventional materials with ceramic like materials, such as geopolymers, thanks to their fine interconnected porosity, high thermal and chemical inertia and low thermal conductivity. Geopolymers are alkali bonded ceramics produced at low temperature (< 100 °C) by reacting an aluminosilicate powder with an aqueous alkali hydroxide and/or alkali silicate solution. The microstructure of the geopolymer matrix consists of nanoprecipitates and mesopores. Moreover, geopolymerization allows the tailoring of the porosity by direct and indirect foaming methods. It follows that geopolymers can be used to develop porous near-net-shape components in the pore size range from nanometres to millimetres and total porosity from 30% up to 90%.

This study is based on the prototyping of the evaporator of a loop heat pipe device (LHP), where conventional wicks are replaced by innovative geopolymer wicks.

In detail, two concentric wicks were realized by optimizing the compositions and the shaping process conditions. The external (primary) wick, with fine and uniform porosity for the development of an high capillary pressure, was achieved through the casting in situ, while the macroporous secondary wick was produced by direct foaming.

Preliminary tests with acetone as working fluid, in the range -35°C ÷ +60°C, revealed as the tailored porosity of the wicks allowed the operation of the LHP, furthermore, the use of geopolymer materials combined with the production process at low temperature and with simple process techniques allowed to lower the production costs of the wicks.

#036 - A new synthetic way to hyper-crosslinked polymers and nanocomposites.

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Hyper-crosslinked (HCL) styrene resins have attracted scientific attention for their high specific surface area (SSA) and adsorption capacity. In particular, among microporous materials, they stand out for their low density, high chemical and thermal stability, and for the possibility of tailoring their structure, porosity and functionality. They find primary application in liquid and gas purification processes, gas storage and catalysis. HCL resins are typically prepared through a two-step procedure, based on the suspension polymerization of the precursor resin and the following hyper-crosslinking through Friedel-Crafts reaction (1).

In this work, a new synthetic method is described, based on the bulk polymerization of the precursor resin. HCL resins based on vinylbenzyl chloride (VBC), styrene (ST) and divinylbenzene (DVB) have been prepared, and the effect of the monomer composition on the SSA, porosity and adsorption properties has been evaluated.

Moreover, through the proposed bulk prepolymerization method, it is also possible to effectively embed carbon nanofillers within the hosting matrix. Then, HCL nanocomposites have been prepared, adding to the precursor resin properly surface modified multiwalled carbon nanotubes and graphene oxide. In particular, an effective surface modification strategy of the nanofillers has been set up (2), to promote their dispersion in the polymer matrix and their participation to the HCL step. Volumetric gas adsorption tests have been performed to evaluate SSA, porosity, and selective CO_2/N_2 adsorption ability of the realized materials. Moreover, phenol uptake capacity has been evaluated through solid phase extraction.

Bulk prepolimerized HCL resins and nanocomposites are characterized by adsorption properties comparable or even better than those shown by the resins prepared by suspension polymerization. As concerning the HCL nanocomposites, a very homogeneous distribution of the modified nanofiller within the matrix has been obtained, as well as tunable porosity and adsorption properties.

(1) Fontanals, N., Marcé, R.M., Borrull, F., Cormack, P.A.G., 2015. Hypercrosslinked materials: preparation, characterisation and applications. Polym. Chem. 6, 7231-7244.

(2) Chen, X., Zhou, M., Hou, Q., Tu, X., Wu, X., 2013. Active poly(4-chloromethyl styrene)-functionalized multiwalled carbon nanotubes. 214, 1829-1835.

#037 - Near-Infrared Fluorescent Organic-Light Emitting Diodes

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Near-infrared (NIR) emitters are attracting interest in relation to a variety of applications spanning from photodynamic therapy, to security, defence, as well as so-called "light fidelity" (Li-Fi) all-optical networking systems, which offer a valuable alternative to "wi-fi" radio communications, especially for the "last meter" (or two) of integrated systems, that already suffer from band-crowding problems. In addition to photodynamic therapy, the transparency of biological tissue to wavelengths in the 700-1000 nm range holds significant potential within the biomedical sector. For such a potential to be realised however, it is important that bio-compatibility is preserved. In turn, this means favouring metal-free, fluorescent materials over phosphorescent ones that achieve relatively high-efficiency only thanks to the exploitation of heavy/toxic metals.

In recognition of the issues above, in the last few years we have studied in our group different families of NIR emitters, accessed through collaboration with various synthetic groups, and incorporated them in sandwich-type LEDs with different structures and architectures. Through our combined efforts we have been trying to address and overcome two major hurdles: the intrinsically low-efficiency of organic NIR emitters (due to the so-called "Energy-Gap law"), and management of intermolecular interactions that may become detrimental in certain circumstances (e.g. with formation of H-aggregates).

In my talk I will describe different families of NIR materials, and report on our recent results, which to the best of our knowledge represent the state-of-the-art in terms of efficiency values for non-phosphorescent, metal-free active materials.

#038 - Broadband amplified spontaneous emission and random lasing from wurtzite CdSe/CdS “giant-shell” nanocrystals

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Colloidal nanocrystals (NCs) are attractive materials for light-emitting applications thanks to their flexible synthesis, size-dependent properties and bright emission.In particular, CdSeCdS core-shell nanocrystals show extremely bright luminescence, demonstrate low-threshold optical gain and even lasing from self-assembled coffee rings [1-4].Yet, colloidal NCs still present a narrow gain band (full-width-half maximum around 10 nm) which limits their application to single-color lasers. Widening of the gain band by specifically engineered NCs can further improve the prospect of this class of materials toward the fabrication of solution-processed white-emitting or color-tunable lasers. In this talk I will report broadband amplified spontaneous emission (ASE) from wurtzite CdSe/CdS “giant-shell” nanocrystals (g-NCs) with unprecedented large core up to 7.5 nm in diameter that were synthesized through a continuous injection route. The combination of large core and shell enable ASE from different CdSe optical transitions as well as from the CdS. Importantly, thin films of g-NCs with large CdSe core (7.5 and 5.1 nm in diameter) show ASE at different colors with a similar threshold, indicating that light emission amplification can be achieved from different optical transitions simultaneously. Tuning of the core diameter allows to obtain ASE in a wide spectral range, and blending of g-NCs with different core sizes gives rise to a continuous amplified spontaneous emission band from green to red (510 to 650 nm). Drop-cast films of CdSe/CdS g-NCs demonstrate simultaneous dual-color random lasing under ns-pulsed excitation.

References:

1. Margherita Zavelani-Rossi, Maria Grazia Lupo, Roman Krahne, Liberato Manna, Guglielmo Lanzani, Lasing in self assembled microcavities of colloidal core/shell CdSe/CdS quantum rods, Nanoscale 2, 931 (2010)

2. Roman Krahne, Margherita Zavelani-Rossi, Maria Grazia Lupo, Liberato Manna, Guglielmo Lanzani, Amplified Stimulated Emission from Core and Shell Transitions in CdSe/CdS Nanorods fabricated by Seeded Growth, Applied Physics Letters 98, 063105 (2011)

3. Margherita Zavelani Rossi, Roman Krahne, Giuseppe Della Valle, Stefano Longhi, Isabella R. Franchini, Salvatore Girardo, Francesco Scotognella, Dario Pisignano, Liberato Manna, Guglielmo Lanzani and Francesco Tassone, Self-assembled CdSe/CdS nanorod micro-lasers fabricated from solution by capillary jet deposition, Laser & Photonics Reviews 6, 678 (2012)

4. Francesco Di Stasio, Joel Q. Grim, Vladimir Lesnyak, Prachi Rastogi, Liberato Manna, Iwan Moreels, and Roman Krahne, Single-mode lasing from colloidal water-soluble CdSe/CdS quantum dot-in-rods, Small 1328 (2015)

#039 - Optical Properties of Colloidal CdSe/CdS Dot-in-Rods

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In recent years, a growing concern toward environmental sustainability has favored light sources that ensure lower energy consumption. Light emitting diodes (LEDs) have attracted strong interest because of their high efficiency and long lifetime. In addition, new materials with high color purity are strongly favored for future LED-based display technologies. Colloidal semiconductor nanocrystals (NCs) are ideal candidates for solid-state lighting, as they can be used as color-converting phosphors or as active layers in LEDs for display and lighting applications. They are well-suited for solution-based processing, and their optical properties can be tailored by controlling size and shape, yielding a narrow emission over a wide spectral range. A near-unity quantum efficiency (QE)[1] can be achieved when core surface states are passivated by the growth of a shell of a second semiconductor; as a result CdSe-based NCs are already used to fabricate efficient LEDs and as solution-processed phosphor in SSL.[2,3]

To steer these materials from research to practical processing and devices, fast and reliable characterization methods of the NC suspensions and a further control over the fluorescence, e.g. in terms of emission lifetime, are essential. In this work, we provide this by a study of the optical properties of CdSe/CdS NCs by absorption and time-resolved fluorescence spectroscopy. We used CdSe/CdS NCs with a CdSe core embedded in an isotropic (dot-in-dot, DiD) and an anisotropic (dot-in-rod, DiR) CdS shell.

Working at energies far above the NC band gap, where quantum confinement effects are weak, we calculated the intrinsic absorption coefficient. This yields the NC concentration directly from the absorption spectrum, avoiding a more cumbersome elemental analysis.[4] Then, knowledge on the intrinsic absorption allowed us to correlate the band-edge absorption and emission. Due to the peculiar band alignment of CdSe and CdS, the electron can delocalize into the shell while the hole is confined to the core, this leading to a potentially reduced overlap of the electron and hole wave functions with lower recombination rates. In CdSe/CdS DiDs with a thick CdS shell this yields photoluminescence lifetimes up to 700 ns.[5] In DiRs however the wave function overlap is mainly determined by the overall DiR diameter and unaffected by the shell length. Lifetimes remain overall below 50 ns, making CdSe/CdS DiRs interesting candidates for SSL as the large absorption can be combined with high brightness and short lifetime.

References

[1] Chen et al., Nature Materials 12, 445–451 (2013).

[2] Castelli et al., Nano Lett. 15, 5455-5464 (2015).

[3] Jang et al., Adv. Mater. 22, 3076-3080 (2010).

[4] Angeloni et al., ACS Photonics 3, 58–67 (2016).

[5] Christodoulou et al., J. Mater. Chem. C 2, 3439 (2014).

#040 - Hybrid LEDs with thermally evaporated MAPbBr3 emitting layer

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Organic-inorganic metal-halide perovskites have been exploited above all for the fabrication of solar cells, till now, due to their large carrier mobility and diffusion lengths, showing astonishing performances improvements in a short lapse of time.[1,2]

However, perovskite also revealed very high emission quantum yields and can be easily spectrally tuned due to the possibility of exchanging each of the perovskite components. For these reasons perovskite have attracted much attention as suitable materials for efficient light sources, like light-emitting diodes (LED).[3,4]

Like organic semiconductors, high quality perovskites films are deposited using facile solution processes or evaporation methods.[5,6]

Recently perovskite-based LED with emission in the visible range have been fabricated exploiting solution-based deposition techniques.[7] However, to increase the possibility of high power light source fabrication, the introduction of hetero-structures could be a key factor to improve the efficiency of the device. This kind of architecture is more easily implemented through solvent-free thermal evaporation.[8]

We fabricated for the first time a hetero-structured LED usig $MAPbBr_3$ as emitting layer, deposited by dual source thermal evaporation. We show, through X-Ray diffraction spectra and scanning electron microscope images, that, starting from the evaporated precursors, a soft thermal treatment is a fast way to accelerate crystal growth, improving the photoluminescence quantum yield of $MAPbBr_3$ film by several orders of magnitude. Moreover, since perovskite formation is hardly influenced by the underlayers, proper carrier transport materials have to be used to obtain a pure and uniform perovskite film; experimental details about this effect will be illustrated, showing the first electro-optical results obtained using different hole injection layers under the perovskite film, which allowed to obtain a promising uniform light emission.

[1] M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, H. J. Snaith, *Science* **338**, 643 (2012).

[2] W. S. Yang, J. H. Noh, N. J. Jeon, Y. C. Kim, S. Ryu, J. Seo, S. I. Seok, *Science* **348**, 1234 (2015).

[3] G. Li, Z.-K. Tan, D. Di, M. L. Lai, L. Jiang, J. H.-W. Lim, R. H. Friend, N. C. Greenham, *Nano Lett.* **15**, 2640 (2015).

[4] R. L. Z. Hoye, M. R. Chua, K. P. Musselman, G. Li, M. L. Lai, Z.-K. Tan, N. C. Greenham, J. L. MacManus-Driscoll, R. H. Friend, D. Credgington, *Adv. Mater.* **27**, 1414 (2015).

[5] Z. Fan, K. Sun and J. Wang, *J. Mater. Chem. A* **3**, 18809 (2015).

[6] M. Liu, M. B. Johnston and H. J. Snaith, Nature **501**, 395 (2013).

[7] H. Cho, S.-H. Jeong, M.-H. Park, Y.-H. Kim, C. Wolf, C.-L. Lee, J. H. Heo, A. Sadhanala, N. S. Myoung, S. Yoo, S. H. Im, R. H. Friend, T.-W. Lee, *Science* **350**, 1222 (2015).

[8] A. Genco, F. Mariano, S. Carallo, V. L. P. Guerra, S. Gambino, D. Simeone, A. Listorti, S. Colella,

G. Gigli, M. Mazzeo, *Adv. Electron. Mater.* **2**, 1500325 (2016).

#041 - Silicon Nanowires: Synthesis, structural properties and photonic applications

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Semiconductor nanowires (NW) are currently attracting the interest of a wide scientific community for cutting-edge applications in photonics, sensing and photovoltaics. Using percolative Au layers that exhibit a fractal arrangement as the catalyst of a metal-assisted wet etching process, we achieved a 2D random fractal array of vertically aligned Si NW, realized without any lithographic process. By designing different fractal textures through the optimization of NW size and spatial arrangement, we were able to control and tune the optical properties of the system. NW achieved by this technique exhibited a very bright room temperature PL, tunable with NW size in agreement with the occurrence of quantum confinement effects. Light emitting devices based on Si NW, showing an efficient room temperature EL at low voltage, were also reported. We fabricated a low-cost multiwavelength light source working at room temperature, achieved combining Si NWs and carbon nanotubes (CNT). The NW/CNT hybrid system exhibits a tunable emission both in the visible range, due to Si NWs, and in the IR range from CNT, and the conditions leading to the prevalence of the visible or the IR signal have been identified.

#042 - Bismuth doping of silicon compatible materials for efficient visible light emitting devices

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In the last decades, rare earths containing materials have been proposed as active media in Si compatible light sources for a wide number of applications, such as lighting for vehicles and flat displays, lab-on-chip sensors for bio-applications, telecommunications.

However, REs transitions, forbidden by the parity selection rules, become partially permitted only in presence of a crystalline field. Otherwise heavy metals with ns^2 electronic configuration can exploit permitted transitions characterized by more intense emission. Among them, bismuth has been recently proposed as a visible emitter whose emission band can be shifted by controlling the crystalline field felt by Bi ions and the stabilized valence state (from 0 to +5). The emission is then strongly influenced by the host, the chemical environments and the synthesis conditions. However Bi incorporation in Si based materials is subject of unwanted issues, such as the precipitation in metallic nanoparticles after high temperature treatments. In order to solve this limit, we have proposed the Bi introduction in Si compatible thin films, such as yttrium oxide and yttrium silicate. These compounds permit to dissolve high content of optically active Bi ions, since they occupy substitutional Y positions in the crystalline lattice. We have synthetized Bi doped yttrium compounds on Si wafers by ULSI compatible processes, such as ion implantation and magnetron co-sputtering. The structural properties of the films have been studied by X-ray diffraction, transmission electron microscopy, energy dispersive X-ray analyses and will be widely discussed. Moreover the optical properties will be analyzed in details by photoluminescence and decay times measurements at room temperature. In particular the possibility to tune the visible Bi emission from the blue to the orange will be highlighted by the stabilization of different Bi oxidation states or the proper host and the excitation conditions under both optical and electrical pumping. These results are straightforward and make Bi-doped Si-based compounds suitable light emitting devices totally integrable in Si platform.

#043 - Degradation mechanism in blue phosphorescent OLEDs based on FIrpic emitter: evidences from combined theoretical and experimental studies on working devices

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One of the main issue in organic light emitting diode technology (OLED) is related to the stability of the emissive organic materials. OLED degradation occurs because of the accumulation of non-radiative recombination centers and luminescence quenchers at morphological and chemical defects. In this contest, the study of degradation pathways, ultimately leading to OLED failure, is essential to meet the device lifetime and efficiency requirements.[1]

FIrpic [bis(difluorophenylpyridinate)Ir(picolinate)] is one of the most used blue emitter used in OLEDs. Its degradation, involving the loss of fluorine and/or the loss of picolinate ligand, have been observed, while yet unclear.[2,3] In our study we designed and realized a model, fully vacuum processed, OLED where FIrpic is used as neat emitting material and BPhen both as the electron transport one and probe for evidencing FIrpic degradation . First, we investigated the FIrpic reactivity towards thermal ligand metathesis with BPhen. The chemical evidence of the picolinate instability in FIrpic is proved through combined photoluminescence and mass spectroscopy experiments, trapping the coordinative-unsaturated chromophore with BPhen to yield $Ir(F_2ppy)_2(BPhen)^+$. Second, we performed DFT ab-initio molecular dynamics and TDDFT calculations to elucidate the microscopic mechanisms of the degradation of FIrpic and its derivatives. Finally, we realized and aged an OLED with the structure $ITO/NPD/Ir(ppz)_3/neatFirpic/Bphen/LiF/Al$, and studied the degradation occurring at the interface FIrpic/BPhen. Upon aging of the device, the bluish electroluminescence spectrum evolves into the green and red one clearly indicating the formation of low energy emissive species compatible with the emission of the $Ir(F_2ppy)_2(BPhen)^+$.

1) Scholz S., Kondakov D., Lüssem B., Leo K., Chem. Rev. 115 (2015) 8449−8503. 2) de Moraes I. R., Scholz S., Lüssem B., Leo K., Org. Electron. 12 (2011)341−347. 3) Sivasubramaniam V., Brodkorb F., Hanning S., Loebl H. P., van Elsbergen V., Boerner H., Scherf U., Kreyenschmidt M., J. Fluorine Chem. 130 (2009)640−649.

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#044 - From molecular zinc complexes to metallopolymers with enhanced solid state photoluminescence

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Complexation of zinc(II) with aroylhydrazone based conjugated ligands and pyridine produced efficient luminescent materials in the solid state. These complexes revealed a wide possibility of tuning their photophysical properties by easy functionalization of the central coordination core with electron acceptor/donor substituents and/or by adding sterically hindered moieties, which can affect nuclearity of metal complexes, intermolecular packing effects and luminescence efficiency. Crystalline molecular complexes showed high photoluminescence quantum yield and a considerable dependence of the emitted wavelengths on the *push-pull* system. Modulation of the emitted color across the entire visible spectrum was achieved by varying the electron acceptor strength of terminal substituents on the conjugated ligand. The introduction of a pyridinic moiety in the main ligands led to crystal structures with mononuclear, dinuclear and 1-D polymeric arrangements, depending on the position of the pyridyl nitrogen. A general enhancement of PLQY was observed for crystalline metallopolymers with respect to mono- and dinuclear complexes, suggesting that the assembling of crystals into packed polymeric structures could provide an enhancement of PL emission.Computational studies allowed to ascribe this higher PLQY to the continuous rather than discrete structure in the solid state and to the tight crystal structure that permits an efficient electron hopping. The outstanding photoluminescence performances of crystalline complexes were also successfully transferred into amorphous metallopolymers by grafting the Zn-ligand fragments onto preformed poly-(4-vinylpyridine). The wide color tuning of the emission was effectively reproduced. Broader emission bands were evidenced with respect to the small molecular complexes, extending in some cases to the NIR region beyond 700 nm. The PL quantum yields of molecular complexes were strongly enhanced in most of 10 wt% grafted polymeric materials. Analogous complexes and polymers with cadmium(II) were also synthesized and characterized, showing average lower luminescence performances.

#045 - Investigations of ultra-thin Silicon Nanowires synthesized by Inductively Coupled Plasma

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The interest in nanomaterials, such as thin-films, quantum dots and nanowires has rapidly increased in the recent past decades from both theoretical and technological points of view. In particular, silicon nanowires (SiNWs) have received a great attention from the scientific community since electrons and holes occupy discrete energy levels, demonstrating remarkable electrical and optical properties in this laterally quantum-confined structures that have not been observed in the corresponding bulky materials. Moreover, as Si is the leading material in microelectronics, the perspective to exploit its already well-established technology makes the interest toward SiNWs crucial for technological applications. In this work we present the Inductively Coupled Plasma (ICP) as an innovative and high throughput technique suitable for the synthesis of ultra-thin SiNWs (as thin as 2 nm) at the industrial level. The investigation of their structure, conducted by Transmission Electron Microscopy (TEM) based techniques, allowed us to elucidate that their growth was induced by two competitive mechanisms: Oxide Assisted Growth (OAG) and Vapor-Liquid-Solid (VLS). Some OAG synthesized SiNWs were found to present an intriguing internal nanostructure, made of "chapelet-like" Si nanocrystals (ranging between 3 and 6 nm), eventually connected by an extremely thin SiNW (~2 nm) and embedded into an otherwise continuous silica nanocylinder. This structure is demonstrated to result from Rayleigh instability due to rapid post-synthesis heating of the SiNWs before their cooling down in the final part of the ICP reactor. Finally, we studied the effect of post-thermal annealing on the nanostructural changes of SiNWs. In this way, we were able to reach the Rayleigh instability conditions and structurally transform the SiNWs into a spherical Si nanocrystal (SiNC) chain embedded in a silica wire. Such Si nanostructures provide a new kind of nanocomposite, where quantum confinement effects are expected. Indeed, our photoluminescence studies confirmed the occurrence light emission in over all the 620-950 nm spectral range. These results prove the ICP as a genuinely bulk process, which can be advantageously exploited for large scale production of ultra-thin SiNWs needed to integrate Si into attractive large-area optoelectronic devices and flexible electronics.

#046 - Collagen-based scaffold micro patterning to induces morphogenetic pathways regulation in adult nerve regeneration

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Peripheral nervous system injury is a frequent traumatic event, affecting a growing field of population, according to the change in lifestyle. Nerve autograph is still the golden standard, however it is invasive and limited in terms of amount and dimension of the available source. Various alternative therapeutic approaches have been proposed and results have been, so far, inconsistent, in terms of both quality and extent of nerve regeneration and re-innervation. Here, a novel technique is presented able to produce tubular collagen-based scaffolds, characterized by a radially/axially patterned microporosity (MPCS). The process has been modelled by means of the Lamm differential equation, according to appropriate scaling laws. In the present investigation, we tested *in vivo* the clinico-pathological impact of this MPCS over a 10-mm critical size defects in the adult rat sciatic nerve. Rats with transection of the sciatic nerve and implanted with either commercial collagen or silicon conduits were used as controls. MPCS-implanted rats showed significantly improved nerve regeneration at both neurophysiological and neuropathological levels, as compared to control rats. Our data demonstrate that this specific tubular scaffold micro-patterning orchestrates physiological regeneration in the adult rat sciatic nerve over a 10-mm critical size defect. Indeed, whole genome gene expression analyses confirm that the MPCS induces selective gene expression patterns and enhanced cells proliferation, motility and myelination, with a remarkable cell-instructing behavior. The development of morphogenesis phenomena during nerve regeneration process opens new perspectives towards the clinical application of MPCS in this field, owing to its ease of production, cost-effectiveness, favorable degradation rate and remarkable cell-instructing behavior.

#047 - Wool fibrils micro- and macroporous scaffold for bone tissue engineering

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Among the natural polymers proposed for biomedical applications, seeking for biocompatibility, biodegradability and, enhanced cellular adhesion, keratin-based materials have emerged as promisingly candidates.

Keratin, found in hair, wool, horn, hooves and nails, shows the highest amount of the amino acid cystine in comparison with other proteins. Wool shows a complex histological structure: the external envelop (cuticle) is made of overlapping cuticle cells arranged like roof tiles which wrap the cortex and the cell membrane complex.

The cortex is the bulk made of elongated spindle shaped “cortical cells” (fibrils), while the cell membrane complex, sticks the cortical and cuticle cells together. Keratin fibrils sponges have been produced by disruption of the histological structure of the wool fibres through mild alkali treatment, followed by ultrasonication, casting and salt-leaching.

The sponges showed highly interconnected porosity (93 %) and a microscopic structure which mimics the Extracellular Bone Matrix (ECM). The alcali treatment converts intermolecular disulphide cystine bonds into shorter monosulphide lanthionine bonds resulting in an improvement of the thermal and water stability. The sponges show a volume swelling in water up to 38 %, however, sponges were stable in water without structural changes and showed excellent resilience to repeated compression stresses.

The sponges showed cell adhesion and proliferation for the SAOS-2 cell line, according to in vitro biocompatibility-cell viability assays, due to the excellent biocompatibility of wool keratin and the unique structure of the cortical cells network, with controlled-size macroporosity for cell guesting, in addition to structural interconnected micro-porosity suitable for nutrient feeding.

#048 - Semiconductor polymers are light nanotransducers in eyeless animal

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The latest designs of optoelectronic devices powered research on fundamental properties of light and how it interacts with matter. In the context of a living cell, this interaction is hampered by the complexity of the living matter, making technological advancement key aspect of this research. Nanotechnologies may provide unique tools to finely tune biological functions, through development of biocompatible light nanotransducers. Here we exploit the possibility to modulate cell function by photostimulation of polymer nanoparticles based on poly(3-hexylthiophene) (NP-P3HT), a conjugated polymer widely used in photovoltaic application. By using a freshwater polyp as model organism, presenting photic behaviour despite the absence of proper eyes, we show that NP-P3HT internalized into animal tissue enhances animal photosensitivity. The possibility to artificially enhance light sensitivity in eyeless animals put forward the potential of this approach toward the control of physiological functions in living organisms.

#049 - Magnesium incorporation into 3D mineralized recombinant collagen scaffolds enhances osteogenic differentiation in vitro

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The demand of bone substitutes is increasing worldwide and will maintain to do so as the continually rising average life span of human [1]. Current strategies focus on mimicking biophysical and biochemical cues from bone extracellular matrix (ECM) in order to formulate favorable binding sites to actively regulate and control cell behavior while interacting with host cells. We propose the design of spongy bone-like scaffolds by biomimetic mineralization of a recombinant collagen type I derived protein (RCP) enriched in RGD sequences (Cellnest^{TM} by FUJIFILM Europe B.V.). RCP mineralization was carried out in the absence (Ap/RCP) and in the presence of magnesium (MgAp/RCP). The effect of mineral phase on porosity, pore size, degradation and mechanical properties were evaluated. Then, mouse mesenchymal stem cells (mMSCs) were cultured on 3 different scaffold compositions (RCP, Ap/RCP and MgAp/RCP) and cell adhesion, viability, cell colonization and osteogenic differentiation were evaluated.

Isotropic scaffolds with heterogeneous pore size distribution ranging from 100-300 µm were obtained as indicated by scanning electron microscopy observations. The presence of mineral phase slightly reduced the scaffold porosity. *In vitro* degradation studies showed a faster ion release (Ca and Mg) from MgAp/RCP scaffolds mainly composed of amorphous calcium phosphate.mMSCs proliferated over the time without significant differences between 3 scaffold compositions. Nonetheless, a more prominent cell colonization was observed on MgAp/RCP scaffolds after 14 days of cell culture. Besides, cells cultured on MgAp/RCP showed an up-regulation of the osteogenic related markers indicating the important biological impact of that biomaterial.This effect could be associated to the Mg incorporation during RCP biomineralization imposing both biophysical (i.e. topography) and biochemical (i.e. composition) cues [2].

Summarizing,we synthesized spongy-like bone scaffolds through biomimetic mineralization of recombinant collagen protein enriched in RGD sequences and the further freeze-drying. *In vitro* studies showed that mMSCs attached and proliferated without significant differences between 3 scaffold compositions whereas a better cell colonization and up-regulation of osteogenic markers pointed to MgAp/RCP scaffolds as the best option for bone tissue regeneration.

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[1] Wu S, Liu X, Yeung KW, Liu C, Yang X. Biomimetic porous scaffolds for bone tissue engineering. Mater Sci Eng R. 2014;80:1-36.

[2] Ramírez-Rodríguez GB, Delgado-López JM, Iafisco M, Montesi M, Sandri M, Sprio S, et al. Biomimetic mineralization of recombinant collagen type I derived protein to obtain hybrid matrices for bone regeneration. J Struct Biol. 2016.

#050 - Imaging collagen packing dynamics during mineralization of engineered bone tissue

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Bone is a complex hierarchical structure, where the interplay of organic and inorganic mineral phases at different length scale (from micron to atomic scale) affects its functionality and health. Thus, the understanding of bone tissue regeneration requires to image its spatial-temporal evolution (i) with high spatial resolution and (ii) at different length scale. In particular, the structure and organization of the Type I collagen microfibrils during mineral nanoparticle formation appear as the key factors for a deeper understanding of the biomineralization mechanism.

In this work we investigate the dynamics of collagen packing during mineralization of porous hydroxyapatite implant scaffolds seeded with Bone Marrow Stromal Cells (BMSC) and implanted in-vivo in mice. Our experimental approach combines synchrotron high resolution X-ray phase contrast micro-tomography (XPCT) and synchrotron scanning X-ray micro-diffraction (sXRmD). While XPCT provides the direct 3D image of the collagen fibers network organization with micrometer spatial resolution, sXRmD allows to probe the structural statistical fluctuations of the collagen fibrils at nanoscale. In particular we apply basics space statistics to the mapped structural fluctuations of (i) size of the mineral nanoparticles along the longitudinal and transverse directions; (ii) lateral spacing and orientation of the interposed collagen molecules. Spatial correlations and distribution of these structural fluctuations are interpreted as being due to temporal changes' comprehensive information: first, the early mineral particle nucleation fills the collagen gaps producing an isotropic-lyotropic transition of collagen; second, after having filled the gaps, nanocrystals thicken and shorten recalling a needle-platelets like shape transition.

This work throws light on the bone regeneration multiscale process. Moreover this approach can provide important information in the characterization of tissue in health, aging and degeneration conditions and it could open novel routes for the early detection of different degenerative conditions of tissue.

Cedola, Alessia; Campi, Gaetano; Pelliccia, Daniele; et al., *Three dimensional visualization ofengineeredbone andsofttissuebycombinedx-raymicro-diffractionandphasecontrasttomography,* PHYSICSINMEDICINEANDBIOLOGYVolume:59Issue:1Pages:189-201Published:JAN62014.

G.Campi,M.Fratini,I.Bukreeva,G.Ciasca,M.Burghammer,F.Brun,G.Tromba, M.Mastrogiacomo, andA.Cedola,*Imagingcollagenpackingdynamicsduringmineralizationof engineeredbonetissue* ACTA BIOMATERIALIA Volume: 23 Pages: 309-316 Published: SEP 1 2015.

#051 - Status of Ferroelectric HfO2 based 1T FeFET

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Based on the physical mechanism, ferroelectrics are ideally suited as the active material in nonvolatile memories, since during switching only the minimum current required to move the charges of the dipole is flowing and hence ferroelectricity promises both low power writing and nonvolatility [1]. Therefore, already in the 1950 the possibility to use ferroelectrics in nonvolatile memories has been exploited [2]. When the effect was combined with the then established semiconductor technology in the late 1980s, first products were realized [3]. However, traditionally the ferroelectric effect is observed in perovskites or layered perovskites like lead zirconium titanate (PZT) or strontium bismuth tantalate (SBT). These materials have a complex structure and are extremely difficult to integrate into a semiconductor process [4]. As a result, ferroelectric memories are scaling much slower than their floating gate or charge trapping based counter parts and are therefore limited to niche applications. In 2011 it was first reported that ferroelectricity can be observed in hafnium oxide based materials which are already established as gate dielectrics in modern CMOS transistors [5]. This discovery solves the CMOS compatibility issue. Due to the much lower permittivity and the higher coercive field in this materials, they also enable 1T ferroelectric field effect transistors [6] that were extremely difficult to realize based on PZT or SBT materials [7]. In the last five years significant research efforts were undertaken to clarify the physical origin of the ferroelectricity in hafnium oxide and on the other side exploit its practical application in 1T ferroelectric FET based memories. This paper will first summarize the fingerprint of the ferroelectric effect in hafnium oxide. The second part will give insight into the current understanding of its physical basis. Finally the status of its implementation in 1T ferroelectric FET memories will be discussed and an outlook to the possible implementation negative capacitance FETs will be goiven.

References

[1] J. F. Scott, Ferroelectric Memories, Springer-Verlag, Berlin (2000)

[2] D.A. Buck, master thesis, MIT Digital Computer Laboratory (1952)

[3] D. Bondurant, Ferroelectrics 112, 273-282 (1990)

[4] C.-U. Pinnow, T. Mikolajick, J. Electrochem. Soc. 151, K13-K19 (2004)

[5] T. S. Böscke et al., *Appl. Phys. Lett.*, 99, 112904 (2011)

[6] J. Müller qt al., IEEE Electron Device Lett. 33, 185-187 (2012)

[7] T.P. Ma and J.-P. Han, IEEE Electron Device Lett. 23, 386-388 (2002)

#052 - HfO2 - RRAM for neural networks

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Memristive systems represent today a disruptive technology for the semiconductor industry with high potential for a wide range of applications ranging from non-volatile memories, to analog circuits, neuromorphic computing paradigms, and development of intelligent and adaptive systems towards the ‘Internet of Things’ concept. Among the various proposed approaches, we focus on those memristive technologies based on the formation and dissolution of nanoscaled filamentary paths in ionic conductive oxide, also known as resistive random access memories (RRAM) [1]. These devices are based on a two terminal metal/oxide/metal structure and exhibit a reversible non-volatile change in their resistance upon electrical stimuli, with low power consumption, sub-nanoseconds switching times, and high scalability [2]. While RRAMs have already demonstrated their great potential for non-volatile memory applications, an increasing interest is currently devoted to their use as synaptic elements in neural networks, i.e. devices that can emulate the potentiation and depression of the communication strength of biological synapses (synaptic plasticity).

The investigated devices in this work rely on the TiN/HfO_2/Pt and TiN/HfO_2/Ti/TiN structures, with HfO_2 films deposited by atomic layer deposition. The switching properties are analyzed in micro- to nanoscale devices. In particular, we studied the device switching dynamics and the possibility to tune, upon application of electrical stimuli, the device conductance in an analog way, which is requested for robust learning systems [3-5]. Moreover, pulse shapes have been optimized in such a way that the memristor conductance can be increased or reduced depending on the temporal order of the pulses arrival at the two terminals of the devices. Such operation corresponds to a translation of the so called synaptic Spike-Timing-Dependent-Plasticity (STDP), which is acknowledged as a fundamental learning rule at the base of the cognitive functions of the brain. The demonstration of STDP in artificial synaptic devices allowed the simulation of a simple fully connected Spiking Neural Network based on the experimental results that is able to autonomously learn and recognize five different patterns [4].

[1] S. Brivio, G. Tallarida, E. Cianci and S. Spiga Nanotechnology 25, 385705 (2014).

[2] J. Frascaroli , S. Brivio, F. F. Lupi , G. Seguini, L. Boarino, M. Perego, and S. Spiga, ACS Nano 9, 2518 (2015).

[3] E. Covi, S. Brivio, M. Fanciulli, S. Spiga, Microelectronic Engin. 147 41 (2015);.

[4]E. Covi, S. Brivio, A. Serb, T. Prodromakis, M. Fanciulli, and S. Spiga, Proceedings of IEEE International Symposium on Circuits and Systems (ISCAS) 2016, pp. 393

[5] S. Brivio, E. Covi, A. Serb, T. Prodromakis, M. Fanciulli and S. Spiga, Appl. Phys. Lett. 2016, (in press)

#053 - Ab-initio modeling of the organization of oxygen vacancies in HfO2 based RRAM

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Metal-Oxide Resistive random access memories RRAM based on 'filamentary switching' represent a very promising candidate for the future market of memory devices in which the extreme device downscaling still remains compatible with excellent attainable performances and good industrial compatibility.

Notwithstanding the theoretical and experimental efforts, the physico-chemical changes occurring in the Insulating Metal Transition have not been fully identified. Although the presence of a less resistive filament has been observed by Transmission Electron Microscopy (TEM) and Conductive Atomic Force Microscopy (C-AFM), it is still unclear how shape, growth and local composition of the filament evolves during the electrical operation leading to the switching. Furthermore a debate exists regarding the mechanisms of charge transport (coherent tunnelling, or trapped assisted by phonons) in the LRS, and regarding the electronic defect configuration that assists the electronic transport.

Via in-silico modelling, we provide key information on the physico-chemical mechanisms governing the HfO_2-RRAM operations, like forming and switching. In particular, we describe the atomistic structure of the material corresponding to conductive filament conditions which can assist a charge transport. The evolution of the filament shape and composition due to the re-organization of the oxygen vacancies after heating and under the effect of an external electric field during the switching operation are further investigated. Our study is meant to unravel the role of the temperature and external electric fields in modulating the electrical properties, endurance and data retention of sub-stoichiometric HfO_2 based RRAM

#054 - The Role Of Ag and Sb Ions In The Resistive Switching Mechanism Of Conductive Bridging Random Access Memories

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Conductive Bridging Random Access Memories (CBRAM), are considered a promising technology for next generation of non-volatile memories. These resistive memories, which utilize the reversible switching of a dielectric between two distinct conductive states for data storage, are based on the electrochemical growth or dissolution of a conductive filament of metal ions in a solid electrolyte.
One of the most interesting CBRAM system consists in an Ag-GeSx glass sandwiched between an Ag electrochemically active anode (providing the ions to form the filament) and an inert cathode [1]. The addition of Sb to the alloy resulted in improved retention of the low resistance and conductive state [2]. However, the exact switching mechanism and the ways to stabilize the conductive state remains not fully understood. We report here on the characterization of CBRAM devices by depth selective X-ray Absorption Spectroscopy at the Ag-K and Sb-K edges before and after electrical cycles of SET and RESET. The experiment was carried out at the LISA beamline at the ESRF. In particular the structure just below the Ag electrode and in the deep bulk of the electrolyte have been compared. The study has evidenced that Ag is present in a sulphide form (inside the electrolyte) or in metallif form. The surface contains a higher amount of Ag meaning that the conducting whiskers grow from the active electrode and that the switching

process lead to the increase of the fraction of metallic Ag. The addition of Sb was shown to hamper the Ag sulphidation creating stable bonds with S [4].

References
[1] F. Longnos, et al., Solid State Electronics, 2013, 84, 155.
[2] E. Vianello, et al., Proceedings of the International Electron Devices Meeting 2012, 741.
[3] E. Souchier, et al. Phys. Chem. Chem. Phys., 2015,17, 23931
[4] F. d'Acapito, et al., Phys. Status Solidi A 213, 311 (2016).

#055 - Switching features of Al-doped HfO2 RRAM: role of oxide non homogeneities

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Resistive switching memories (RRAMs, recently named also memristors) are encountering a widespread interest not only for memory technology, but also for futuristic computational schemes as well as for sensor applications. RRAMs are two terminal metal/insulator/metal devices that undergo commutation between two stable resistance states (high resistance and low resistance states) in response to electric stimulation. Devices based on HfO_2 have been acknowledged by several research groups as one of the most performing given their fast switching, low power operation, scalability and possible 3D integration. On the other hand, issues related to switching uniformity and retention still require material development.

With this contribution, we will present a wide spectrum of experimental characterization, as well as, modelling results that have led us to a comprehensive picture of the role in the switching of local non homogeneities of the functional oxide layer of RRAMs and the route for its engineering through Al doping.

Indeed, resistance switching occurs through formation and dissolution of localized chains of oxygen vacancies (conducive filaments, CF) that migrate through the oxide as a result of voltage application and temperature raised by Joule heating. The local nature of the switching mechanism reflects the initial non homogeneous conduction properties of the oxide layer in the out of plane direction, which is one of the causes of variability, one of the most severe RRAM issues. The initial weak conductive spots already present also in amorphous oxide films act as percolative paths for oxygen vacancy migration. Formation and subsequent dissolution of single conductive filaments has been demonstrated through conductive atomic force microscopy (AFM) measurements. [1] The results demonstrate that the switching operation is filamentary and by nature inherently subjected to variability.

Ion doping of the oxide matrix has been proven as a way for artificially introducing defects to localize the CFs and thus reducing the switching variability. On the other hand, the presence of dopants causes additional unwanted effects, which we have characterized in devices constituted by HfO_2 films with different concentration of Al doping and Pt and TiN electrode. We show a degradation of the retention characteristic and a modification of the random telegraph noise features of the high resistance state of the devices. [2] With the help of a phenomenological filamentary model that describes the switching operation, we are able to provide a qualitative comprehensive description of the effect of doping on the switching characteristic and performances of HfO_2-based RRAMs.

[1] S. Brivio, G. Tallarida, E. Cianci and S. Spiga, Nanotechnology 25 385705 (2014);

[2] J. Frascaroli, F. G. Volpe, S. Brivio, S. Spiga, Microelectron. Eng. 104 147 (2015).

#056 - Perovskites: "inorganic chameleon" compounds and not only

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Inorganic perovskites have always been key materials for many technologies going from high-Tc superconductors, to high-k dielectrics, from piezoelectric to colossal magnetoresistance materials, from conducting ionics to multiferroics.

In the last decade, this class of materials has attracted a huge interest, since the novel discovered hybrid perovskites may find applications in photovoltaics, light emitting diodes,etc.

Perovskites are compounds with ABX_3 formula where the anion X form together with A a cubic compact packing, thus A is twelve coordinated, while B, occupying the octahedral holes, has a six-coordination. The countless potentialities of perovskites arise from the possibility to dope both the A and B sites giving rise to a great variety of compositions and properties.

In this presentation, a simple synthetic strategy based on metal organic chemical vapor deposition (MOCVD) for the fabrication of inorganic perovskite thin films will be presented. Some case studies will be reported with particular attention to the ferromagnetic $Pr_{0.7}Ca_{0.3}MnO_3$ and the multiferroic $BiFeO_3$.

The film depositions are carried out using β-dichetonate compounds of the type $M(hfa)_n$•polyether [Hhfa=1,1,1,5,5,5-hexafluoro-2,4-pentanedione; polyether = bis(2-methoxyethyl)ether or 2,5,8,11,14-pentaoxapentadecane) on various substrates. The effects of the deposition conditions on the structural and morphological properties will be scrutinised.

The functional properties of the $Pr_{0.7}Ca_{0.3}MnO_3$ will be discussed based on measurements of magnetization obtained in zero-field-cooling (ZFC) and in field-cooling (FC) modes and through transport measurements, which allowed to establish dependences of conduction properties of the films on temperature and applied magnetic fields.

The ferroelectric/piezoelectric properties of the $BiFeO_3$ films have been investigated at the nanoscale level by Piezoresponce Force Microscopy (PFM) and Single-point Piezoresponce Force Spectroscopy (PFS) measurements.

The used approach offers all the potential advantages of a greatly reliable and reproducible method for the fast production of epitaxial perovskite films with a highly uniform thickness and composition over large areas.

#057 - Resistive Switching and Nanoscale Electronic Transport in Au/Nb:SrTiO3 Schottky Junctions

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Whenever a Schottky barrier is formed at the junction between large work function metals and electron-doped $SrTiO_3$ (STO), the macroscopic rectifying transport is accompanied by a resistance switching (RS) behaviour. Metal/Nb-doped STO (NSTO) junctions represent a model system for the elucidation of the mechanisms driving RS. Here we report on the fabrication and electrical characterization of Au/NSTO single-crystal junctions with nanometer thick electrodes. Unexpectedly, we observe the coexistence within the same device of highly rectifying properties - under laboratory air - and bipolar RS - under reducing vacuum conditions [1]. Furthermore, we use Scanning Tunnelling Microscopy - Ballistic Electron Emission Microscopy to provide direct experimental evidence for the inhomogeneous character of the Au/NSTO interface at the nanoscale [2]. We suggest that the voltage-dependent variation of the low barrier nanometric patches could explain RS effects in transition-metal oxide cells.

[1] R. Buzio, A. Gerbi, *et al.* Appl. Phys. Lett. 101, 243505 (2012)

[2] A. Gerbi, R. Buzio, *et al.* Adv. Mater. Interfaces 1, 1300057 (2014)

#058 - Chemistry and electro-chemistry of graphene and graphene oxide, for applications in energy storage and composites

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At the beginning of its exciting life, graphene was mostly a game for physicists. Then, chemists have learned how to "play" with this unique material by enhancing its processability and versatility. Today it is possible, using covalent or supramolecular chemistry, to tailor graphene into a wide variety of forms ranging from simple, soluble sheets to hierarchical architectures where 2-dimensional (2D) graphene sheets are assembled into three-dimensional (3D) composite materials or foams for applications in electronics, mechanics, energy storage or catalysis.

In particular, we have recently exploited electrochemical approaches to produce, process and functionalize graphene oxide. By using suitable electrolyte and intercalant molecules, bulk amounts of graphite shall be exfoliated in few minutes, yielding stable solutions of electrochemically exfoliated graphene oxide (EGO) featuring large size –and high concentration of monolayers. This material shall be processed in thin layers or foams to be used, as example, as electrodes for energy storage, or coating for packaging applications. It can be functionalized with thin oxides for lithium storage or used as a nano-additive to strengthen bulk polymer composites.

Electrochemistry offers a promising method to exfoliate with high speed and low cost bulk amounts of graphite, and an industrial pilot plant using these electrochemical techniques for the large-scale production of graphene featuring good processability and good quality has been recently implemented.

Using these different approaches there is practically no limit to the number of possible 2D structures inspired to graphene that shall be created.

1. *Graphene-based coatings on polymer films for gas barrier applications.***Carbon**, (2016) **96**, 503.

2. *Synergic Exfoliation of Graphene with Organic Molecules and Inorganic Ions for the Electrochemical Production of Flexible Electrodes.***Chempluschem**, (2014) **79**, 439.

3. *The Exfoliation of Graphene in Liquids by Electrochemical, Chemical, and Sonication-Assisted Techniques: A Nanoscale Study.***Advanced Functional Materials**, (2013) **23**, 4684.

4. *Electrochemically exfoliated graphene oxide/iron oxide composite foams for lithium storage, produced by simultaneous graphene reduction and Fe(OH)(3) condensation.***Carbon**, (2015) **84**, 254.

5. *Nanoscale Mechanics of Graphene and Graphene Oxide in Composites: A Scientific and Technological Perspective.***Advanced Materials**, (2016) **28**, 6232.

#059 - Graphene-based multifunctional nanocomposites through a tailored control of graphene spatial distribution

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Due to its promising properties, graphene and its derivatives has been widely proposed in the preparation of multifunctional polymer-based composites exhibiting enhanced electrical, thermal, barrier and mechanical properties. Despite the intrinsic advantages of graphene and its derivatives, the ultimate properties of these materials mainly depend both on the quality of graphene and its derivatives (i.e the presence of defects and/or the aspect ratio) and the spatial distribution of graphene nanofiller: homogeneous dispersion, 2D-layer seemly to a continuous graphene layer or alternatively 3D-graphene network. This talk will review our activities focused on the tailoring of filler spatial distribution for the design of advanced polymer-graphene composites as well as the increasing of the aspect ratio of the filler by suitable chemical approaches able to promote crosslinking between graphene platelets and graphene/polymers. In details the following materials will be presented:

A) Layer-by-layer (LBL) assembly technique has been adopted for fabricating alternating multilayered coatings of reduced graphene oxide (rGO) and high amorphous vinyl alcohol (HAVOH) deposited on PET substrate. The coating with 30 layers of HAVOH/rGO (~200nm) leads to a decrease of oxygen permeability of about one order of magnitude compared to the bare PET substrate.

B) An innovative approach, based on latex mixing and co-coagulation process, has been developed to prepare natural rubber/rGO and bromobutyl rubber/rGO nanocomposites with a 3D-graphene segregated networkChemical characterization highlighted that during rubber vulcanization by using sulfur (S_8) the graphene platelets significantly affected the crosslinking of rubbers and produced an effective rubber-2D filler interfaces. The segregated morphology reduces significantly the gases permeability compared to pristine rubber matrix. In addition, the increase of the equivalent aspect ratio brought about an exceptionally low value of the electrical percolation threshold, which is more than one order of magnitude lower than in the case of uniform filler dispersion.

C) Two different forms of piezoresistive materials were designed and fabricated, namely, foams for wearable sensors and aerogel for ultra-light force sensing. The obtained graphene-coated polyurethane foams are conductive. Carbon nanotubes have also been added to the formulation to increase the conductivity, due to the enhancement of graphene nanosheets connection. Conductive carbon nanotubes/chitosan aerogel have been also produced. Morphological analysis has shown the presence of an unidirectionally aligned micro-tubular porous structure.

#060 - Effect of Graphene Nano-platelet Morphology on the Young Modulus of Soft and Hard Biopolymers

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Two bio-polyesters having diverse elastic (Young's) moduli (soft and hard) were reinforced (0.1-5 wt.%) with various types of expanded graphite nanoplatelets (GnP flakes) [1]. Free standing biocomposites were fabricated by solvent casting and hot-pressing. Detailed mechanical measurements were conducted in order to investigate the effect of GnP thickness and lateral size on the elastic modulus of both polymers[2]. For comparison purposes other 2D and 3D nanoscale fillers were also used such as organoclay, MoS_2, carbon black, Iron dioxide and silica nanoparticles (see Figure). Under solvent casting conditions, GnPs did not perform better compared to other model fillers in increasing the elastic modulus of the soft bio-polyester. On the other hand, GnPs increased the elastic moduli of the hard bio-polyester biocomposites more than other fillers. Due to hot-pressing induced alignment of the 2D flakes with the polymer matrices, large (~ 1µm) many layer GnPs (≥8) induced better elastic moduli enhancement performance compared to other GnPs and 2D and 3D fillers at 3 wt.% concertation levels. Large many layer GnPs also suppressed elastic modulus decline of the soft bio-polyester due to heating near its melting point.

References

[1] Jang et al., Journal of Material Science, **43** (2008) 5092.

[2]Cataldi et al., Carbon, **109** (2016) 331–339.

#061 - Nanotribology of inkjet printed graphene flakes

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Layered materials such as graphite and MoS_2 have long been recognized as effective surface lubricants and they have been used to control friction and wear in a number of applications [1]. In fact, their use reduces friction because they offer interlayer sliding interfaces with low interfacial shear strength. The ability to isolate single atomic layers and few-layer sheets has recently promoted research into the frictional properties of two-dimensional lubricant materials [2]. In this context, graphene is rapidly evolving from a material with fascinating properties [3-5] to one with practical tribological application [6]. Nowadays, the majority of the fundamental studies on graphene friction have been carried out in single-asperity regime by Atomic Force Microscopy (AFM), using almost exclusively the micrometric flakes prepared by micromechanical cleavage of pristine graphite [6,7].

Here, we exploit AFM to address the friction response of few-layer graphene nanoflakes obtained from the liquid phase exfoliation of graphite [8,9,10]. To this purpose we print state-of-the-art graphene inks [11] on bare and hexamethyldisilazane-terminated SiO_2. We characterize the printed stripes by optical microscopy, electron microscopy, AFM imaging and lateral force microscopy/spectroscopy. We find that large, atomically-flat portions of the printed features show friction response comparable with that typically reported for bulk graphite. Local friction excess is observed at the surface roughness originated by the flakes self-assembling process. Overall, our work demonstrates that printable inks are suitable for exploring and quantifying graphene and few-layer graphene nanoflakes friction by means of AFM.

References

[1] A. Erdemir in *Handbook of Modern Tribology*, (Ed. B. Bhushan) CRC Press 2001, 787-818.

[2] J. C. Spear, B. W. Ewers and J. D. Batteas, *Nano Today*, 2015, **10**, 301–314.

[3] A. C. Ferrari et al., *Nanoscale* 2015, **7**, 4598-4810.

[4] G. Fiori et al., *Nature Nanotech*. 2014, **9**, 768-779.

[5] F. Bonaccorso et al., *Science* 2015, **347**, 1246501.

[6] D. Berman, A. Erdemir and A. V. Sumant, *Mater. Today*, 2014, **17**, 31–42.

[7] J. C. Spear, J. P. Custer, J. D. Batteas, *Nanoscale* 2015, **7**, 10021.

[8] O. M. Maragò, et al. ACS Nano 2010, **4**, 7515-7523.

[9] T. Hasan, et al. *Phys. Status Solidi*, 2010, **247**, 2953–2957.

[10] A. C. Capasso, et al. Solid State Comm. 2015, **224**, 53-63.

[11] F. Bonaccorso et al., Adv. Mater. 2016, **28**, 6136-6166.

#062 - Ab initio investigation of atomistic mechanisms in solid and boundary lubrication

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Tribologically-induced chemical modifications of surfaces interacting with lubricant additives or other molecules present in the environment surrounding the sliding media can substantially change the adhesion and friction of materials in contact. Therefore, is highly desirable to understand how they take place. However, tribochemical reactions are difficult to monitor in real-time by experiments, which leaves a gap in the atomistic understanding required for their control.

We apply *ab initio* molecular dynamics to monitor chemical reactions involving common solid lubricants, namely molybdenum disulfide, graphene/graphite and diamond like carbon, interacting with water molecules in the presence of mechanical stresses. Our simulations elucidate atomistic mechanisms relevant for understanding the effects of humidity on the lubricating properties of these materials.[1,2]

As second issue, we investigate the tribochemistry of sulfur, phosphorus and graphene on iron and discuss the role of metal passivation in reducing the interfacial adhesion and shear strength. We generalize the result by establishing a connection between the tribological and the electronic properties of interfaces. This adds a new piece of information for the ultimate understanding of the fundamental nature of frictional forces. [3,4]

[1] P. Restuccia, G. Levita and M. C. Righi *Graphene and MoS2 interacting with water: a comparison by ab initio calculations* Carbon 107, 878 (2016).

[2] S. Kajita and M. C. Righi *A fundamental mechanism for carbon-film lubricity identified by means of ab initio molecular dynamics,* Carbon 103, 193 (2016).

[3] M. C. Righi, S. Loehlé, M. I. De Barros Bouchet, S. Mambingo-Doumbeand J. M. Martin*A comparative study on the functionality of S- and P-based lubricant additives by combined first principles and experimental analysis* RSC Advances, 6, 47753 (2016).

[4] P. Restuccia and M. C. Righi *Tribochemistry of graphene on iron and its possible role in lubrication of steel* Carbon 106, 118 (2016).

#063 - Designing carbon nanotruss networks with nonlinear auxetic and anisotropic mechanical properties

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Graphene has attracted much attention due to its 2D nature and to unsurpassed electronic, optical and mechanical characteristics. In particular, from a mechanical point of view, the high performances presented at nano-scale have to be transferred effectively from nano- to macro-scale and, desirably, to the third dimension. Successfull use of graphene in this regard depends critically on three factors: first, the design of proper architectures that preserve graphene's intrinsic mechanical properties, e.g. the largest ultimate strength ever found and the ability to retain its initial size after strain; second, a better understanding of the properties of 3D carbon-based materials upon compressive and tensile loads; third, the possibility of synthesising these materials by scalable and cost effective practices. In this contribution we present a computational investigation of the mechanical properties of novel graphene-based 3D architectures from atomistic simulations. In particular, we suggest a specific set of mechanically stable nanotruss networks using graphene sheets connected by nanotubular pillars forming nanoporous structures with octet-truss geometry. To investigate these issues and help our understanding of the critical factors affecting the production of high-performance carbon-based foams, such as behavior under tension and compression as a function of nanotube/sphere diameters' ratio, anisotropy of samples, and lattice defects, we perform computational simulations with reactive potential on realistic carbon-based nanotruss structures. The major achievements of this study are three: first, we devise a new way to design novel graphene-based architectures with different intrinsic features; second, we calculate a number of mechanical observables of these nano-foams, such as stress-strain curves, Young modulus, Poisson ratio, density scaling relation, instabilities under compression load and energy absorption characteristics upon impact; third, we show how the mechanical properties of these foams are propagated from nano- to macro-scale. While the mechanical properties turned out to be almost isotropic under tensile load, under compressive regimes the emergence of a response that depends on the orientation of load is observed together with a peculiar local instability. Due to this instability, some of these nanotruss networks present a negative Poisson ratio in compression, like re-entrant foams. The performance of these nanotruss networks is analyzed with regards to their use as impact energy absorbers, finding properties outperforming materials traditionally used in these applications. Finally, the study of instability, touched upon in contribution, has a very high importance in the field of mechanical metamaterials.

#064 - Double-Wall Nanotubes and Graphene Nanoplatelets for Hybrid Conductive Adhesives with Enhanced Thermal and Electrical Conductivity

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Improving the electrical and thermal properties of conductive adhesives is essential for the fabrication of compact microelectronic and optoelectronic power devices. Here we report on the addition of a commercially available conductive resin with double-wall carbon nanotubes and graphene nanoplatelets that yields simultaneously improved thermal and electrical conductivity. Using isopropanol as a common solvent for the debundling of nanotubes, exfoliation of graphene, and dispersion of the carbon nanostructure in the epoxy resin, we obtain a nanostructured conducting adhesive with thermal conductivity of ~12 W/mK and resistivity down to 30 μΩ cm at very small loadings (1% w/w for nanotubes and 0.01% w/w for graphene). The low filler

content allows one to keep almost unchanged the glass-transition temperature, the viscosity, and the curing parameters. Die shear measurements show that the nanostructure resins fulfill the MIL-STD-883 requirements when bonding gold-metalized SMD components, even after repeated thermal cycling. The same procedure has been validated on a high-conductivity resin characterized by a higher viscosity, on which we have doubled the thermal conductivity and quadrupled the electrical conductivity. Graphene yields better performances with respect to nanotubes in terms of conductivity and filler quantity needed to improve the resin. We have finally applied the nanostructured resins to bond GaN-based high- electron-mobility transistors in power-amplifier circuits. We observe a decrease of the GaN peak and average temperatures of, respectively, ~30 °C and ~10 °C, with respect to the pristine resin. The obtained results are important for the fabrication of advanced packaging materials in power electronic and microwave applications and fit the technological roadmap for CNTs, graphene, and hybrid systems.

#065 - Covalent functionalization of high-quality, CVD graphene with self-assembling molecules, using electrochemistry

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We describe a fast and versatile method to functionalize high-quality graphene with organic molecules by exploiting the synergistic effect of supramolecular and covalent chemistry. With this goal, we designed and synthesized molecules comprising a long aliphatic chain and an aryl diazonium salt. Thanks to the long chain these molecules physisorb from solution onto CVD graphene or bulk graphite, self-assembling in an ordered monolayer. The sample is successively transferred into an aqueous electrolyte, to block any reorganization or desorption of the monolayer. An electrochemical impulse is used to transform the diazonium group into a radical capable of grafting covalently to the substrate and transforming the physisorption into a covalent chemisorption. During covalent grafting in water the molecules retain the ordered packing formed upon self-assembly. Our two-step approach is characterized by the independent control over the processes of immobilization of molecules on the substrate and their covalent tethering, enabling fast (*t<10 sec*)covalent functionalization of graphene. This strategy is highly versatile and works with many carbon-based materials including graphene deposited on silicon, plastic and quartz, as well as highly oriented pyrolytic graphite.

BIBLIOGRAPHY

1. *Electrochemical Functionalization of Graphene at the Nanoscale with Self-Assembling Diazonium Salts.* **ACS Nano**, (2016) DOI: 10.1021/acsnano.6b03278

2. *Nanoscale Mechanics of Graphene and Graphene Oxide in Composites: A Scientific and Technological Perspective.* **Advanced Materials**, (2016) DOI: 10.1002/adma.201505469

3. *Supramolecular self-assembly of graphene oxide and metal nanoparticles into stacked multilayers by means of a multitasking protein ring.* **Nanoscale**, (2016) **8**, 6739.

4. *Electrochemically exfoliated graphene oxide/iron oxide composite foams for lithium storage, produced by simultaneous graphene reduction and Fe(OH)(3) condensation.* **Carbon**, (2015) **84**, 254.

5. *Synergic Exfoliation of Graphene with Organic Molecules and Inorganic Ions for the Electrochemical Production of Flexible Electrodes.* **ChemPlusChem**, (2014) **79**, 439.

6. *The Exfoliation of Graphene in Liquids by Electrochemical, Chemical, and Sonication-Assisted Techniques: A Nanoscale Study,* **Advanced Functional Materials**, (2013) **23**, 4684.

#066 - Development of thin film composite membranes based on a polymer of intrinsic microporosity for gas separation

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This work presents the development of composite polymer membranes for potential use in gas separation [1]. The selective layer of the membranes is based on a novel polymer of intrinsic microporosity (PIM) [2], referred to as PIM-(H2)EA-TB, combining the ethanoanthracene unit (EA) with the Tröger's base (TB). This material represents a simple modification of the shape-persistent ladder polymer PIM-EA-TB in which the rigidity of the bicyclic TB and EA units results in a very high permeability and improved gas selectivity due to an enhanced molecular sieve behavior [3]. The preparation conditions and the solvent used for casting membranes from highly permeable glassy polymers affect the final microstructure and the available free volume for permeation. A study on the effect of the solvent used in membrane preparation (chloroform or dichloromethane) showed the lower amount of retained solvent when using dichloromethane. Accordingly, more permeable films were obtained with dichloromethane. This solvent was used for the coating of flat sheet and hollow fiber porous supports. PAN porous hollow fibers were spun ad-hoc by the dry-jet wet process. A morphological analysis evidenced adhesion issues in the case of the HFs and the presence of micropores on the membrane surface, which can be due to condensation of humidity onto the air/polymer solution interface. PAN-based HFs were treated with aqueous NaOH solutions to partially convert the cyano groups to the carboxylic acid, improving the interaction with the ternary amines of the TB unit. Single gas permeation tests confirmed the presence of a dense and selective layer of PIM-(H2)EA-TB on COOH-PAN HFs obtained after hydrolysis in mild conditions and coated in controlled temperature and humidity conditions. Acknowledgements. Financial support was received from the EU's FP7, project "M4CO2", grant FP7-Energy-2013-1-608490. References [1] P. Bernardo, E. Drioli, G. Golemme, Membrane gas separation: a review/state of the art, Industrial & Engineering Chemistry Research 48 (10) (2009) 4638. [2] P.M. Budd, N.B. McKeown, Highly permeable polymers for gas separation membranes, Polym. Chem. 1 (2010) 63. [3] M. Carta, R. Malpass-Evans, M. Croad, Y. Rogan, J.C. Jansen, P. Bernardo, F. Bazzarelli, N.B. McKeown, An Efficient Polymer-based molecular sieve membranes for membrane gas separations, Science 339 (2013) 303.

#067 - Comparative molecular characterization of antibacterial activity of TiO2 nanostructures and CuO/TiO2 composites

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One of the biggest challenges of the 21st century is to provide clean and affordable water to meet human needs. There is a significant need for novel advanced water technologies, in particular to ensure a high quality of drinking water and to augment water supply through safe use of unconventional water sources [1].

Advanced Oxidation Processes (AOPs) represent an interesting alternative as innovative water treatment technologies. Among these, heterogeneous photocatalysis employing semiconductor catalysts has demonstrated its efficiency in degrading a wide range of organic pollutants into readily biodegradable compounds as well as antimicrobial properties. Among the semiconductor catalysts, titanium dioxide (TiO_2) has received the greatest interest in photocatalysis technology [2]. We realized several titania nanomaterials ranging from nanoparticles produced by Pulsed Laser Ablation in Liquids (PLAL), to nanofilms built by ALD, to nanoplumes and CuO/Ti nanostructures.

In order to investigate possible applications of these novel nanomaterials in the process of water purification, their antibacterial activity has been analyzed and characterized using *Escherichia coli* as a model organism. *E. coli* is a well-known Gram-negative species and it is considered to be an indicator of fecal contamination in drinking water. The antibacterial activity was firstly evaluated by Colony Forming Unit (CFU) counts. MTT Assay (based on the use of 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide, i.e. MTT) confirmed the results obtained by CFU counts, showing that the tested nanomaterials effectively reduce bacterial vitality. Besides, surviving colonies show phenotypic signals of stress, as different colonies' morphology.

The *rpoS* factor is usually activated under stress conditions, triggering a stress response [3]. Thus, in order to further characterize the stress induced by our nanomaterials, the relative levels of mRNA expression of *rpoS* and *rpoD* factors were investigated through Real Time PCR.

Elucidating bacterial stress response may lead to a deeper comprehension of the mechanisms behind nanomaterials antibacterial activity. This, in turn, may suggest further improvements in the materials design and may lead to shape better conditions for nanomaterials successful application.

[1] Qu X., Alvarez P.J.J., Li Q., Applications of nanotechnology in water and wastewater treatment, Water Res. 2013 Aug 1;47(12):3931-46

[2] Chong M.N., Jin B., Chow C.W.K., Saint C., Recent developments in photocatalytic water treatment technology: A review, Water Res. 2010 May;44(10):2997-3027.

[3]Battesti A., Majdalani N., Gottesman S., The RpoS-mediated general stress response in *Escherichia coli*., Annu Rev Microbiol. 2011;65:189-213.

#068 - Marine microplastics pollution from synthetic clothes: quantitative analysis and mitigation measures

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The environmental impact of plastic pollution on marine ecosystems has become an urgent problem in the last years. Marine waste consists of 60-80% of plastics and most of the debris is less than 5 mm in size. Such fragments are defined microplastics and are particularly crucial for the marine environment. They remain unaltered and, ingested by aquatic fauna, can eventually enter in the trophic chain inducing serious damages to marine fauna and human population. Recently, an unexpected source of microplastics has been discovered in washing processes of synthetic clothes like polyester, polyamide, polyacrylic and polypropylene. Due to the lack of quantitative information on this topic, this work aims to assess the role of domestic and industrial washing processes of synthetic garments on the release of microfibres. For this purpose, lab simulations of domestic and industrial washings were carried out on standard synthetic fabrics, changing washing conditions (such as temperature, time, etc.) and using different types of detergents (i.e. liquid, powder, etc.). The washing liquor was filtered and the filters were analysed by scanning electron microscopy (SEM), in order to identify and quantify micro and nanofibers detached from synthetic textiles. The obtained results allowed the identification of the parameters that mostly influence the release of microfibers and the washing conditions that are less aggressive on the fabrics. Moreover, in order to mitigate the environmental impact of the microplastics released during textile washing processes new textile finishing treatments were studied. Several textile auxiliaries were selected and applied by padding at laboratory scale, optimizing the process parameters necessary to obtain homogeneous and reproducible films on the surface of the fabrics. The effectiveness of the finishing treatments was tested through morphological and washing resistance analyses.

#069 - Biofunctional particles development by membrane emulsification

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Advances in micro-nanofabrication methods are required to design new ecofriendly functional particles with target properties in terms of size, size distribution and functional activity by maximizing mass and energy utilization and minimizing resources utilization and waste production. The use of microporous architectures like membranes permits to meet these demanding requirements. Membrane emulsification (ME) is a dispersion process to produce monodispersed droplets with controlled size in mild shear conditions. The low local shear stress applied and the precisely controlled particle size and size distribution obtained make the membrane emulsification technique one of the most promising alternative technology for the sustainable production of emulsions and solidified particles.

This work will describe the development of ME for bioactive compounds encapsulation in micro-nanoparticles. The distinguishing aspects of membrane emulsification can meet the ever-increasing performance, safety and environmental demands of sustainable processes in industrial production.

Hydrophilic shirasu porous glass (SPG) membrane with nominal pore size of 3.1 µm has been used to produce a water-in-oil (W/O) emulsion. d-Limonene and PVA have been used as a direct substitute for toxic organic solvents and as biocompatible polymeric material, respectively. Biophenols, recovered and concentrated by advanced membrane process from olive mill wastewaters (OMWWs) coming from olive oil production, have been used as functional ingredients. Pulsed back-and-forward ME has been selected as low shear encapsulation method because is particularly attractive for the production of fragile particulate products, such as W/O microemulsions containing shear sensitive ingredients [1, 2]. The best operative conditions (transmembrane pressure, wall shear stress) to control particle size and particle size distribution and obtain high productivity (dispersed phase flux) have been investigated. W/O emulsions with droplets size approximately 2.3 times the membrane pore diameter, span of the distribution of 0.33 and high encapsulation efficiency (92% ± 3%), were produced [3]. Results demonstrate that the method has a potential to be applied in the production of emulsion based products containing biophenols for applications in food, pharmaceutical or cosmetic field.

1] L. Giorno, E. Piacentini, E. Drioli, Single Pass Pulsed Membrane Emulsification, WO2014020631 A1, Priority Data: 02.08.2012

2] E. Piacentini, E. Drioli, L. Giorno, Pulsed back-and-forward cross-flow batch membrane emulsification with high productivity to obtain highly uniform and concentrate emulsions, Journal of Membrane Science 453 (2014) 119–125

3] E. Piacentini E., Poerio, F. Bazzarelli, L. Giorno, Microencapsulation by membrane emulsification of biophenols recovered from olive mill wastewaters, Membranes, 2016, 6 (2)

#070 - Hydrogenated TiO2 nanoplumes: innovative material for photocatalytic applications

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In the last years, the synthesis of a wide range of advanced inorganic materials (nanocomposite thin films, patterned surfaces and nanostructures) was extensively studied. In particular, the semiconducting oxide TiO_2 has attracted remarkable interest, for its outstanding applications: from solar cells to self-cleaning and water purification. However, the TiO_2 photocatalytic efficiency is limited by its wide band-gap energy (~3 eV), which limits the spectrum of photons able to create electron–hole pairs to the ultraviolet (UV) light [1]. One method to enhance the photocatalytic properties of a semiconductor consists in the band-gap narrowing

Recently, black hydrogenated TiO_2 has received extensive interest, due to its extremely-enhanced absorption in the visible (VIS) and infrared (IR) region. The hydrogenation is always carried out in a tube furnace, with a temperature in the range of 200–550 °C, in a high-pressure H_2 atmosphere (up to 20 bar), and for a time from 3 hours to 5 days [2].

In this work, we investigated the synthesis and properties of hydrogenated TiO_2 nanoplumes for photocatalytic applications. The original material was synthesized by chemical etch, in peroxide solution, of a Ti film deposited by sputtering. The system was morphologically, structurally and optically characterized [3]

Nanoplumes show a lower band-gap energy than TiO_2 film, with an energy gap of 2.2 eV against 3.2 eV, making the material sensitive to visible light. The synthesized materials revealed a remarkable photocatalytic activity under UV-VIS light, correlated to the physical-chemical structures of the sample. In particular, we interpreted the R and T measurements in terms of Fresnel formulae regardless the effects of depolarization due to the roughness and not uniformity of the surface. The model used shows that the nanoplumes layer acts as an antireflective coating, where scattering effects improve the light adsorption by nanoplumes, increasing the electron-hole pairs generation and therefore the photocatalytic properties.

[1] Bendavid A.; Martin P. J.; Jamting A.; Takikawa H.; Thin Solid Films 1999, 355, 6–11.

[2] Chen X.; Liu L.; Yu P. Y.; Mao S. S. Science 2011, 331, 746–750.

[3] Scuderi V.; Impellizzeri G.; Zimbone M.; Sanz R.; Di Mauro A.; Buccheri M. A.; Miritello M.; Terrasi A.; Rappazzo G.; Nicotra G.; Privitera V. Appl. Catal. B: Envir. 2016, 183, 328–334

#071 - Modeling of Gas Phase Nanoparticle Synthesis

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From an atomistic perspective a nanoparticle can be considered as a cluster of bonded atoms or molecules of different species. The ability to simulate reactions, interactions and characterize dynamically, at the atomic level, the various phases that regulate the formation of nanomaterial aggregates can be used in the definition of a computational model at the mesoscale level where bigger systems and their dynamics are investigated in detail.

Quantum, static and dynamics, calculations can provide an accurate description of atomic aggregates but their computational cost limits both the system size and the simulation time. This problem can be overcome by resorting to classical methods based on reactive force fields parametrized on quantum chemistry (QC) calculations of representative models. These approaches are much faster and their use to describe nucleation phenomena, where reactivity of the various species is very often a key element, is useful for sampling very large portions of the configurational space in order to design mesoscale simulation models.

In our project (NanoDome, funded from the European Union's Horizon 2020 Research and Innovation Programme, under Grant Agreement n. 646121, http://www.nanodome.eu/) we adopted ReaxFF(1) to model the early stages of the plasma assisted growth of Si based nanostructures. Our interest is in the simulation of the processes of nucleation and growth of Si clusters in the environment present in a low temperature plasma, with the ambition to model aggregates with dimensions of hundreds of atoms, and not only to determine their optimized structure, but above all to study their dynamics.

A specific parametrization of the reactive force-field has been developed for a good description of the nanoparticle surface. Indeed, that region exposes under-coordinated atoms that drive dynamic interactions with the surrounding atoms by local bond relaxation, charge redistribution, adsorption, etching, sintering, etc.. The model systems and the quantum methods used for the determination of their properties to use as a benchmark (so-called "training set"), the different protocols employed for the optimization of the force field parameters and, finally, the procedure used to validate the force field by simulations of optimized structures and molecular dynamics will be described in detail.

References

van Duin A.C.T. et al. ReaxFF: A Reactive Force Field for Hydrocarbons *J. Phys. Chem. A* **2016**, *105,* 9396-9409

#072 - Pre-resonant enhancement of Amide Raman bands in model peptides as revealed by tunable UV Raman scattering experiments

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The Raman spectra of peptides and proteins are usually rather complicated, due to the presence of a large number of vibration modes associated to the backbone and to the specific chemical groups of amino acids that compose the molecules. In particular, the peptide bonds exhibit a number of so-called amide bands that can be Raman and/or IR active and that are found between 1500 and 1700 cm^{-1} in the vibrational spectra. The Raman Amide bands are widely investigated in scientific literature because these modes are directly related to the secondary structure of peptides and proteins. Therefore, the Amide bands in the Raman spectra constitute a good spectroscopic probe of possible structural rearrangements occurring in proteins during many phenomena of biological interest, including folding, misfolding and aggregation. Here we report an UV Resonant Raman scattering investigation of the behavior of the Amide bands in model peptides N-acethyl-glycine-methylamide (NAGMA) and N-acethyl-leucine-methylamide (NALMA) by changing the excitation energy. The spectra show how the Amide bands are still enhanced at 270 nm, in pre-resonance conditions. In particular, the spectra show how, passing from 270 to 230 nm, the band enhancement is more pronounced for the Amide II band rather than the Amide I, as evidenced by the intensity ratio between these two bands. It can be explained on the basis of the simulation carried out on NAGMA on the electronic transitions which can be occurred on the system. The simulated NAGMA UV Vis spectra show an asymmetric behavior due to the presence of electronic transitions near 230 nm, occurring within molecular orbitals diffused both on Amide bonds and carbonyl groups. Differently, the electronic transitions near 200 nm appear to involve molecular orbitals more closed to the carbonyl groups. The Amide II enhancement occurring above 230 nm on NAGMA and NALMA is replied also in lysozyme, hemoglobin and albumin buffered aqueous solutions, suggesting that the specific considerations carried out for a simple model as NAGMA and NALMA can be extended to more complexes peptides systems.

Tuesday December 12

Session title	**Chairman**
Stimuli responsive: bio-organic materials	**Giuseppe Mensitieri**
Biomimetic materials triggering cell phenotype and tissues regeneration	**Matteo Santin**
Oxide and nanomaterials for non-volatile memories	**Thomas Mikolajick**
Energy storage and water splitting	**Fabio Di Fonzo**
Materials and processes for environmental protection and sustainability	**Manuela Melucci**
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Stimuli responsive: organic-inorganic materials	**Concetto Puglisi**
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Wide band gap semiconductors for power electronics and sensor applications	**Antonino La Magna**
Energy storage and water splitting	**Paolo Bondavalli**
Smart surfaces and functionalization	**Monica Sandri**
Materials and processes for environmental protection and sustainability	**Giuseppe Ciccarella**
Nanobiocomposites for in–vitro diagnostics and targeted drug	**Alessandro Sannino**
Wide band gap semiconductors for power electronics and sensor applications	**Roberta Nipoti**
Growth and synthesis of 2D materials	**Stefan Heun**
Smart surfaces and functionalization	**Alessio Adamiano**

#073 - Eumelanin-Based Biocompatible Coatings: Interfacing in Bioelectronics

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Eumelanins, the black insoluble pigments of human skin, eyes and substantianigra (neuromelanin), stand today as a unique source of inspiration for the design and implementation of soft biocompatible multifunctional materials for bio-optoelectronic devices. Interest in eumelanins stems from bioavailability, biocompatibility and a peculiar set of physicochemical properties , i.e. broadband absorption in the UV-visible range, intrinsic free radical character, water-dependent hybrid ionic–electronic conductor behaviour, supporting optimistic feelings about a possible rise of eumelanin-mimics as innovative bioinspired solutions for organic bioelectronics.

To date, a number of conceptual and technological gaps still hinder rapid progress of melanin-based organic electronics and bioelectronics, including in particular the limited contribution of electronic conductivity and current decay with time under biasing. Herein, we provide a concise overview of the structural and optoelectronic properties of melanins with a view to bringing to focus main issues and challenges en route to bioelectronic applications. Basic structure-property function relationships, fundamental tailoring strategies, processing and the balance of ionic-electronic processes will be addressed along with representative examples of eumelanin-based hybrids to orient ongoing efforts toward efficient and competitive eumelanin-based technology.

#074 - Nano and mesoscopic structures through supramolecular assembly of porphyrins

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The remarkable recent progress in nanotechnology is mainly due to the ability to synthesize, investigate, and exploit materials with structural modulation on the nanometer scale. Porphyrins are well suited building blocks since they i) are relatively easy to synthesize; ii) show interesting and peculiar photophysical properties that can be tuned through careful choice of peripheral substituents and inserted metal ions and iii) are able to self-assemble spontaneously into dimers or higher aggregates through non-covalent interactions. Taking advantage of the self-correcting nature of the supramolecular interactions, defect-free porphyrin structures whose shape, size and photophysical properties are high sensitivity to external stimuli, can be achieved. Porphyrin structuring features can be controlled in order to introduce and tune, in the self-assembled material, functional properties for a wide range of application spanning from catalysis, to sensor, optoelectronic or drug delivery. In particular, water soluble porphyrins are very interesting since their aggregation can be conveniently controlled by screening the charge repulsion through changes in the ionic strength and pH. In this framework, the water soluble tetrakis(4-sulfonatophenyl)porphyrin ($TPPS_4$) provide an iconic example of such behavior, since its diacid form, in particular experimental conditions, is able to self-arrange in well defined J-aggregates supramolecular structures. Our investigations are manly focused on $TPPS_4$ self-aggregation phenomena, supramolecular organization on biological matrices and in confined enviroments.[1] The data reported on this system have allowed gaining important information in the field of supramolecular architectures, highlighting the importance of the role of experimental parameters such as concentration and/or mixing order of the reagents. Recently, we reported on a detailed kinetic investigations to demonstrate the fundamental role of kinetic parameters in assemblies sizing and in expression and transmission of chirality at nano and mesoscopic scale.[2] Despite many reports on this subject, the onset of chirality in J-aggregates of $TPPS_4$ is still an open and intriguing question. Being hydrogen bonding in aqueous solution a key factor in the stabilization of the final aggregates, we focused our attention on the important role of isotopic substitution as well on the hydrogen bonding network of the solvent in presence of chaotropic or kosmotropic ions on both the rates and extent of J-aggregate formation, and the final observed chirality.

1. Castriciano, M. A.; Romeo, A.; De Luca, G.; Villari, V.; Scolaro, L. M.; Micali, N. *J. Am. Chem. Soc.* **2011,** *133*, 765

2. Romeo, A.; Castriciano, M. A.; Occhiuto, I.; Zagami, R.; Pasternack, R. F.; Scolaro, L. M. *J. Am. Chem. Soc.* **2014,** *136*, 40

#075 - Dynamic Cell Instructive Materials for Cell Culture

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A major effort in biomaterials science, related to the field of tissue engineering, is focused on the development of new “smart” cell-instructive materials (CIMs). Biomaterials that can stimulate and guide cells by modulating the cell-material crosstalk. One of the greatest challenges is engineering such type of biomaterials in a well-controlled manner in order to dynamically modulate their physical and chemical properties during cell culture to regulate their interplay with cells.[1] So far, the use of non-reversible strategies to induce changes in biomaterial surface properties has been widely explored,[2] but this approach has the limitation of producing a "static" interaction between cells and the substrate itself, hampering the use of such biomaterials to properly mimic *in vitro* the continuous remodeling of the extracellular matrix (ECM) that normally occurs *in vivo*. Importantly, the use of stimuli-responsive materials enables to overcome the limit of a static presentation of different relevant cues available at the material surface.[3] In particular, with the introduction of molecular photoswitches in the field of biomaterials, a dynamic and reversible control of cell-material interaction, elicited by light, has become a real possibility.[4]

In our work we aim to develop a next generation of CIMs, named as "dynamic CIMs", which are based on biocompatible polymeric matters (2D interfaces[4,5,6,7] or 3D scaffolds[8,9]), which can be chemically modified with azobenzenes for achieving a fine spatio-temporal control over the exhibition of relevant topographic/mechanical/biochemical cues[4,5,6,7] to cells exploiting a dynamic and reversible mechanism triggered by light.

Such type of biomaterials can be useful to engineer cell fate applying a sort of "chronoprogramme" in order to respond to important issues/fundamental quests relevant to the field of tissue engineering.

References

1. M. Ventre, P. A. Netti. *ACS Appl. Mater. Interfaces*, **2015**, *8*, 14896.

2. N. M. Alves, I. Pashkuleva, R. L. Reis, J. F. Mano. *Small*, **2010**, *18*, 2208.

3. J. A. Burdick, W. L. Murphy. *Nat. Commun*. **2012**, *3*, 1269.

4. C. Rianna, L. Rossano, R. H. Kollarigowda, F. Formiggini, S. Cavalli, M. Ventre, P. A. Netti. *Adv. Funct. Mater.*, **2016**.

   DOI: 10.1002/adfm.201602577.

5. C. Rianna, A. Calabuig, M. Ventre, S. Cavalli, V. Pagliarulo, S. Grilli, P. Ferraro, P. A. Netti. *ACS Appl. Mater. Interfaces*, **2015**, *7*, 16984.

6. C. Rianna, M. Ventre, S. Cavalli, M. Radmacher, P. A. Netti. *ACS Appl. Mater. Interfaces*, **2015**, *7*, 21503.

7. E. Vaselli, C. Fedele, S. Cavalli, P. A. Netti. *ChemPlusChem*, **2015**, *80*, 1547.

8. T. J. White, D. J. Broer. *Nat. Mater.* **2015**, *14*, 1087.

9. S.-k. Ahn, T. H. Ware, K. M. Lee, V. P. Tondiglia, T. J. White. *Adv. Funct. Mater.* **2016**. DOI: 10.1002/adfm.201601090

#076 - pH-responsive antimicrobial and antitumoral peptide anchored on surface: a conformational study

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Materials that change properties in response to different local stimuli are increasingly being studied in the context of several application.

Peptides are ideally suited for this purpose because of the range of distinct physical properties available from the amino acids This diversity allows several non-covalent interactions including electrostatic (acidic and basic amino acids), hydrophobic, p-stacking (aromatic amino acids), hydrogen bonding (polar amino acids) as well as covalent (disulfide) bonds and steric contributions (strand directing amino acids). Crucially, each of these interactions depend in different ways such as ionic strength, pH and temperature.

In this work we study the properties of a particular peptide able to respond to specific external stimuli by adopting one of two well-defined conformations.

The Trichogin GA IV here used, belongs to the family of peptaibiotics, antimicrobial peptides rich in the helix-inducer α-aminoisobutyric acid (Aib) residue. One of its analogs, in which four Lysines positive charged residues have been introduced, is able to reversibly switch its conformation between two, well-defined, different helical conformations in response to pH variations.

In this contribution, we describe our latest results obtained from the study of gold surfaces decorated with trichogin GA IV and its positively-charged analog. The peptides were anchored to the gold surfaces through a N-terminal lipoic acid moiety. The loading and the conformational properties of the surface-bound peptides were investigated by means of several techniques, such as Quartz Crystal Microbalance with Dissipation monitoring and Localized Surface Plasmon Resonance.

This peptide which can contract and stretch in response to pH, may find use in the emerging field of the bio-inspired nanotechnology.

#077 - Self-assembled bio-nanostructures from Janus dimers

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In the last years, a considerable attention has been paid to investigate physical properties of Janus particles, i.e. colloids whose surface can be divided in two regions of different chemical composition. Due to their ability in self-assembling into a large variety of bio-nanostructures, including micelles, vesicles and lamellae, such colloids have been extensively investigated by means of both experimental techniques [1] and simulation approaches [2]. Very recently, a “molecular” generalization of these particles, the so-called Janus dimers [3], is capturing an increasing interest, due to the possibility to properly tune their interaction potential [4], as well as their molecular geometry [5], to obtain the desired self-assembled structures. Here we present a detailed investigation of such super-structures by means of Monte Carlo simulations. In our approach, Janus dimers are constituted by two tangent hard spheres of variable sizes, rigidly connected. In addition, one of the spheres is surrounded by an attractive interaction. Upon varying temperature and density, we document the presence of spherical micelles of variable size if the attractive sphere is smaller than the repulsive one. A lamellar phase is observed when the two spheres have comparable size. In this case, also a gas-liquid phase separation begins to take place, giving rise to a very rich and fascinating phase scenario including the presence of other peculiar super-structures at low temperature, like tubes, vesicles and “cavity” liquids. Our results enlighten the role played by the size asymmetry and the interaction range in controlling the onset of these structures of biological interest and the competition between their formation and the gas–liquid condensation. [1] L. Hong, A. Cacciuto, E. Luijten and S. Granick, Nano Letters, 2006, 6, 2510. [2] F. Sciortino, A. Giacometti and G. Pastore, Phys. Rev. Lett., 2009, 103, 237801. [3] G. Munaò, D. Costa, A. Giacometti, C. Caccamo and F. Sciortino, Phys. Chem. Chem. Phys., 2013, 15, 20590. [4] G. Munaò, P. O’Toole, T. S. Hudson, D. Costa, C. Caccamo, A. Giacometti and F. Sciortino, Soft Matter, 2014, 10, 5269. [5] G. Munaò, P. O. Toole, T. S. Hudson, D. Costa, C. Caccamo, F. Sciortino and A. Giacometti, J. Phys.: Condens. Matter, 2015, 37, 234101.

#078 - EUMELANIN MICROTUBES AS BIOISPIRED AND BIOCOMPATIBLE SUBSTRATE FOR NEURON CELLS GROWTH AND CONTROL

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Eumelanin-film-coated materials can find applications in different fields, including biomedicine and organic (bio)electronics thanks to both their physicochemical properties as well as structural features [1]. However, the applicability of eumelanin thin films is strongly restricted by its highly intractable nature. Many attempts have been done finalized to get eumelanin 2D thin–film fabrication [2, 3], but any effort has failed to obtain 3D or 1D eumelanin architecture assembly.

This communication deals with the design and fabrication of eumelanin-based microtubular structures and their potential use as tissue engineering scaffolds for neuronal cells growth and control. Tissue engineered scaffolds must provide both mechanical support for growing cells and biological signals to direct the axonal growth cone to the distal stump. To achieve a microtubular architecture, a proper protocol combining electrospinning, spin coating, solid-state polymerization and TUFT (TUbes by Fiber Templates) process was established [4]. For biological analysis, a human derived cell linefrom neuroblastoma was used and cellular differentiation was induced by retinoic acid (RA). Cells were seeded on eumelanin microtubular structure with a spatial organization both aligned and random, in presence or in absence of RA loaded in the eumelanin wall. GAP-43 expression, as marker of differentiating neurons, by using confocal analysis was assayed; furthermore, cell morphology by using SEM analysis was tested.Results showed that eumelanin microtubes significantly reduced cell proliferation thus promoting differentiation processes. For this reason eumelanin microtubes might be worthy of consideration for future evaluations of new therapeutic strategies for neurodegenerative diseases.

References

1. Meredith, P.; Bettinger, C. J.; Irimia-Vladu, M.; Mostert, A. B.;Schwenn, P. E.Rep. Prog. Phys. 2013, 76, 034501.

2. Wünsche, J.; Deng, Y.; Kumar, P.; Di Mauro, E.; Josberger, E.; Sayago, J.; Pezzella, A.; Soavi, F.; Cicoira, F.; Rolandi, M.; Santato, C.Chem. Mater. 2015, 27, 436−442.

3. Ambrico, M.; Ambrico, P. F.; Cardone, A.; Ligonzo, T.; Cicco, S. R.; Di Mundo, R.; Augelli, V.; Farinola, G. M.Adv. Mater. 2011, 23, 3332.

4. I. Bonadies, F. Cimino, C. Carfagna, A. Pezzella. Biomacromolecules 2015;16:1667−1670.

#079 - Biomorphic transformations: a revolution in development of bioceramics for load-bearing applications

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Effective regeneration of critical size bone defects requires the use of porous scaffolds exhibiting bone-like composition and structure permitting extensive colonization by new bone and vascularization. In addition, when diseased bone is addressed to withstand severe loading, the biomimetic features of the scaffold should also include high mechanical strength and, possibly, ability of bio-resorption by cell-mediated metabolic processes.

Calcium phosphates, particularly hydroxyapatite (HA), are considered as the elective materials for bone regeneration, as their composition closely resembles the inorganic part of bone. However the fine compositional cues of biologic apatite, i.e. ionic substitutions in the calcium and phosphate site, in association with its nanosize and low crystallinity, are all features of pivotal relevance to adequately direct and sustain the regenerative cascade, but they are irredeemably destroyed by the sintering process, which is a fundamental step to consolidate ceramic bodies.

Therefore, there is a lack of biomaterials with effective regenerative ability, particularly when addressed to the treatment of load bearing bone segments. Indeed, sintered HA scaffolds addressed to critical size bone defects can induce good cell adhesion and proliferation, but often the bone penetration is limited to few millimeters due to impervious porosity, which also hampers the development of an appropriate vascular network.

In the present talk, a radically new approach for synthesis of HA scaffolds is presented, basing on a sequence of heterogeneous reactions at the interface between a solid template and a reactive gas. Such a multi-step approach permits the transformation of natural woods presenting channel-like porosity thus resembling the osteon structure of the long bones. In particular, the process includes pyrolysis of the starting wood and a sequence of reactions transforming the resulting porous carbon template into calcium carbide, calcium oxide, calcium carbonate and finally hydroxyapatite. The final step of the process is carried out at low temperature, aiming to induce a dissolution/reprecipitation process transforming the calcium carbonate porous template into hydroxyapatite, whereas retaining carbonate ions into its lattice (B position) and exhibiting nanosize HA particles. Both these features provide outstanding bioactivity and ability to be progressively resorbed during the process of bone remodeling. Besides, the hierarchical organization of the starting wood was successfully translated to the final HA scaffold that was thus endowed with superior mechanical strength. The high bioactivity of the new HA scaffold was demonstrated by cell tests reporting high proliferation with spread morphology and outstanding expression of genes relevant for bone regeneration.

#080 - Bioactivated chitosan-based scaffolds as potential strategies for promoting bone regeneration and preventing inflammatory bone loss

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As life expectancy increases, musculoskeletal diseases such as osteoporosis are becoming an important social problem. Fractures caused by bone inflammatory loss associated with osteoporosis are a major cause of long-term disability in the elderly and determine significant economic burden [1]. Consequently, the clinical goal of osteoporosis treatment is prevention of fractures by regenerating bone mass. The main challenge in tissue engineering is to introduce biomaterial-based scaffold which stimulate the restoration of pathologically altered tissue architecture. Recent findings showed that chitosan, a natural polymer, is useful to achieve scaffold for clinical applications in order to regenerate bone tissue [2]. In this study we aimed to develop a biomimetic chitosan-based scaffold using two different approaches based on the combination of inorganic and organic components. Interesting properties such as an antinflammatory activity of chitosan was also investigated in order to compare potential antioxidant effects with bone tissue growth. For this purpose several marker of inflammation such as intracellular reactive oxygen species (ROS) on hMSC cells were measured. The physicochemical, morphological and mechanical properties of materials, before and after treatments, have been evaluated. Furthermore, biological analysis to analyze the effect of the two different biomimetic approaches on osteogenic differentiation of hMSC were performed.The results showed that bioactivated chitosan-based scaffolds are able to inhibit synthesis of inflammatory mediators thus preventing inflammatory bone loss caused by osteoporosis. Moreover, the presence of bioactive signals on the scaffold surface allows obtaining an osteoinductive effect on hMSC in a basal medium, making the modified chitosan scaffolds a promising candidate for bone tissue regeneration.

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References

[1] S.M. Dyer, M. Crotty, N. Fairhall, J. Magaziner, L.A. Beaupre, I.D. Cameron, C.Sherrington, “A critical review of the long-term disability outcomes following hip fracture”, *BMC Geriatr.,* 2016; 16:158 DOI 10.1186/s12877-016-0332-0

[2] R. Jayakumar, N. Nwe, S.Tokura, H. Tamura, "Sulfated chitin and chitosan as novel biomaterials", *International Journal of Biological Macromolecules*, 2007; 40:175-181

#081 - Membrane Systems and Mesenchymal Stem Cells for the Creation of Human Skin Substitutes

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The development of a suitable support, able to facilitate the several biological processes needed for skin reconstruction is a major issue to restore functional and esthetical integrity in burn patients and to develop in vitro skin models for toxicological tests.

Bioengineered skin substitutes were created by using biodegradable membranes of chitosan (CHT), polycaprolactone (PCL) and a biosynthetic blend of CHT-PCL, prepared by phase inversion process, and MSCs isolated from human dermis, the human Skin-derived Stem Cells (SSCs). Being skin tissue-biased stem cells committed to their specific final dermal and/or epidermal cell differentiation, SSCs are more suitable for skin tissue engineering than other adult MSCs with a different origin, representing a useful autologous cell source for the realization of skin substitutes. Dermal, epidermal and dermal/epidermal membrane systems by using human SSCs and keratinocytes in homotypic and in co-culture systems were created. Biodegradability, morphological, mechanical and physico-chemical membrane properties were characterized and correlated to the different cell adhesion, proliferation, morphological behaviour, and differentiation.

Specific membrane properties were able to modulate the interactions of human keratinocytes and SSCs inducing their terminal differentiation. In particular, PCL membrane influenced keratinocytes differentiation towards a complete proliferative bioartificial epidermal substitute, CHT and CHT-PCL membranes towards specific and distinct epidermal strata, such as the corneum and granulosum, respectively. Both CHT–PCL and PCL membranes induced epidermal and dermal differentiation of SSCs. Furthermore, in the dermal-epidermal membrane systems, a more suitable microenvironment for SSCs differentiation was promoted thanks to the interactions and the mutual interplay with keratinocytes.

These bioengineered constructs provide an interesting approach for manipulating in vitro skin tissue reconstruction providing a valid tool for therapeutic and drug screening applications.

#082 - Biomineralized magnetic hybrid nanocomposite supporting cell proliferation and tuning regenerative process

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In the last decade bioinspired design and manufacture of scaffolds for tissue engineering have received increasing interests to provide the microenvironment similar to the natural extracellular matrix for regenerative cells and tissues. The present work illustrates how bio-mineralization, an amazing natural process with which nature has realized and optimized a profuse collection of living organisms endowed with astonishing abilities can be used to guide efforts for developing biomaterials for bone. In particular it will be illustrated how the reproduction of biomimetic conditions of bone synthesis allows to obtain hybrid constructs where the physicochemical and ultrastructural constraints exerted by the collagen matrix force the apatitic phase to heterogeneous nucleation at specific sites and controlled crystal growth and orientation. These unique features are the source of the bioactivity of the ceramic phase, i.e. the active dialogue between cells and the hybrid composite that enable the cascade of events at the basis of the bone remodeling and repair. In addition, to improve the healing in aged patients and/or in presence of degenerative diseases, it is mandatory to boost the regenerative potential of the innovative designed scaffolds. In this view to increase the osteogenic and angiogenic capacity of biologically inspired scaffolds a new approach has been proposed to avoid the use of biologics and their inherent drawbacks, consisting in the use of superparamagnetism induced by remote activation. A new superparamagnetic, bioactive and bioresorbable apatite nanophase (Fe-HA) was developed through controlled substitution of Ca2+ ions with Fe2+ and Fe3+ ions. Integration of the new magnetic bio-resorbable nano-phase was proposed in different typology of biomimetic scaffolds. XRD analyses in combination with computer simulations on structural models give the clear indication that both Fe species are in Ca-substitutional positions and not in interstitial positions into the HA lattice was obtained. The mineralization process has been applied and tailored to yield fibrous constructs with different extent of apatitic phase components and high mimicry with various mineralized and non-mineralized tissues, to be used as scaffolds for regeneration of multifunctional tissues such as osteochondral and periodontal regions. Hybrid magnetic nanocomposites with different compositions and functionalities have been validated in silico and in vivo and finally cases applied to regenerative medicine will be presented. Thanks to the presented results and preliminary proofs of concept it can be envisaged that the development of new materials inspired by nature can open new horizons for developing innovative bio-devices representing a breakthrough in the wide field of nanomedicine.

#083 - Electrospun Membranes Loading Osteogenic-Bioactive Molecules for Guided Bone Regeneration After Dental Implantation

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Guided bone regeneration (GBR) is a surgical procedure that uses barrier membranes to allow new hard tissue growth on an alveolar ridge permitting stable placement of dental implants. GBR osseous regeneration depends on the migration of pluripotent and osteogenic cells to the bone defect site and on the exclusion of cells impeding bone formation (e.g. epithelial cells and fibroblasts). To accomplish the regeneration of a bone defect, the rate of osteogenesis extending inward from the adjacent boney margins must exceed the rate of fibrogenesis growing in from the surrounding soft tissue. Additional benefits to the use of barrier membranes are the protection of the wound from mechanical disruption and salivary contamination. Nowadays, membrane-based technologies are developed to deliver bioactive molecules with osteogenic, anti-inflammatory, and/or antibacterial properties. Resveratrol is a naturally occurring polyphenolic compound in red wine and numerous plants that could enhance osteogenesis and inhibit adipogenesis in bone marrow–derived mesenchymal stem cells (MSCs). Here we investigate the capacity of new electrospun membranes to release resveratrol for MSCs differentiation. Fibrousmembranesofpoly(-caprolactone) [PCL],poly(lacticacid) [PLA]andtheirblendswerepreparedbyelectrospinningusing optimized parameters to obtain uniform defect-free fibers and successfully encapsulate layereddoublehydroxidenanoparticles(LDH)loadingresveratrol. Synthetizedmembraneswerecharacterizedin termsofmorphologyand*in vitro*release.The scanning electron microscope (SEM) and X-ray analyses suggest that LDH/Resveratrol is well dispersed into membrane, resulting in electrospun nanofibers with average diameter around 0.8-1.2 micron. Resveratrol release was obtained in a controlled and tunable manner. Electrospun membranes, combined with LDH/Resveratrol, upregulated in MSCs the gene expression of osteogenic markers such as runt-relatedtranscriptionfactor2 (RUNX2), osterix(OSX),osteocalcin(OCN),osteonectin(ONN),osteopontin (OPN), and bone sialoprotein (BSP). Moreover, synthetized membranes showed higher alkaline phosphatase activity and alizarin red staining, suggesting increased differentiation and mineralization of MSCs cells. In conclusion, our results provide evidence that the encapsulation of LDH/Resveratrol into electrospun fibers generates bioactive membranes able to promote the osteogenic differentiation of mesenchymal stem cells useful to improve GBR surgical procedure.

#084 - Investigation on 3D hierarchically organized bone substitute from wood: do hydrothermal conditions affect its chemical-physical characteristics?

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The development of scaffolds reproducing the hierarchically organized morphology of bones, join to high mechanical performance, is a challenge. In this viewpoint, the new trends in materials science research are looking at the incomparable characteristics and properties of natural structures as new sources of inspiration to obtain innovative and smart biomorphic devices.

An early new generation of bone substitute deriving from wood, with hierarchic structures and smart anisotropic performances (figs.1-2), was performed through a sequence of chemical and physical transformations of natural wood[1-2].

These final structures are highly organized from the molecular to nano, micro and macro-scales, with extremely functional architectures able to constantly adapt to ever changing mechanical and bio-functional needs.

In the present work, in-depth study was carried out on the final *hydrothermal phosphation* step of the biomorphic process, able to convert calcium carbonate into hydroxyapatitic 3D scaffold.

Infact, following to incomplete phase transformation, calcite residual could cause some drawbacks after implantation of the scaffold, i.e. structural failure due to uncontrolled reabsorption kinetic or inflammatory issues related to carbon dioxide evolution and undesirable secondary-phase formation. For this reason the phosphation reaction was checked very closely, and the kinetics investigated in several range of phosphating solution concentration and reaction temperatures.

Once the parameters influencing the transformation process from carbonate to hydroxyapatite phase were established, optimized phosphation cycles were set up, focusing on its complete phase conversion with desired stoichiometry (i.e. Ca/P molar ratio) and structural defects free (e.g. deformations, cracks, fractures).

References.

[1] S.Sprio, A.Ruffini, A.Tampieri, 2011, In: Recent Advances in Nanostructured Materials: Synthesis, Characterization and Applications, Apple Academic Press Inc, Oakville, Canada.

[2] A.Tampieri et al., *Journal of Materials Chemistry*, 2009, 19, 4973-4980

#085 - In-Sb-Te nanowires for high performing scaled phase change memories

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Ultimate programming energy reduction and fast switching in the emerging phase change memories (PCM) for electronic data storage are expected to come with the programming material volume reduction and other favorable size effects. One viable route is the use of self-assembly processes by chemical deposition methods, to produce low-dimensional phase change nanowires as memory cells, since their growth can be controlled, along with their diameter, composition and crystallinity [1]. In this work, PCM cells based on nanowires (NWs) of In-Sb-Te were realized with diameters down to ~20 nm, in order to investigate on their thermal stability or switching speed with respect to the conventionally employed Ge-Sb-Te alloys. The NWs were grown by metal organic chemical vapor deposition (MOCVD, featured by high process control and large area deposition), coupled to the VLS self-assembly mechanism [2]. Following a morphological (SEM), structural (XRD, TEM) and compositional characterization (EDX, XRF), the electrically contacted NWs, acting as self-heating resistors, exhibited memory switching cycling with very low RESET voltage, current and power consumption, resulting to be promising for the realization of ultra-scaled PCMs with improved performances.

References:

[1] M. Longo, Chpts. 6-7 of “Advances in Non-volatile Memory and Storage Technology”, Woodhead Publishing, edited by: Y. Nishi, ISBN9780857098030, June 2014, p. 200-261.

[2] S. Selmo, S.Cecchi, R. Cecchini, C. Wiemer, M. Fanciulli, E. Rotunno, L. Lazzarini, M. Longo, Phys. Stat. Sol. a, 213 (2016) 335-338.

#086 - Thermal resistance characterization of In3Sb1Te2 nanowires

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$In_3Sb_1Te_2$ has been recently proposed as promising material for Phase Change Memory (PCM) devices, with better electrical and thermal performances than the alloys of the Ge-Te-Sb system. Further advantages in terms of, e.g., consumed power are expected from the use of nanowires-based PCMs with respect to film-based architectures, because of a reduction of the size of the active material and the self-heating mechanism [1]. Heat conduction is clearly a critical aspect in determining the efficiency of the phase change process in such ultra-scaled systems. In particular, the measurement of the thermal resistance is an important parameter for the electro-thermal simulation of heat confinement and Joule heating driven phase transitions. In this work the thermal resistance along the thickness of crystalline $In_3Sb_1Te_2$ nanowires was measured using Scanning Thermal Microscopy (SThM) in 3ω mode. This technique does not require connecting the nanowires, neither handle them in a specific way. The nanowires were grown by Metal Organic Chemical Vapor deposition (MOCVD) and transferred on a SiO_2/Si substrate for the measurements. Two nanowires with different thicknesses (13 nm and 23 nm) were investigated; the obtained results are discussed in terms of the mean free path of phonons in the nanowires with respect to bulk $In_3Sb_1Te_2$.

[1] M. Boniardi et al. 2014 IEEE International, International Electron Devices Meeting, IEDM 2014, 7047131 (2015) 29.1.1-29.1.4

[2] S. Selmo et al. Physica Status Solidi (A), 213 (2016) 335–338.

#087 - Fine tuning of the composition in epitaxial Sb2+xTe3 films

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Antimony telluride (Sb_2Te_3) is a layered chalcogenide material formed by quintuple layers (QLs) bonded to each other by van der Waals (vdW) forces. It has been studied for its topological insulating (TI) surface states [1] and used as building block in phase change and thermoelectric superlattice (SL) structures. [2], [3] Several Sb-rich phases ($Sb_{2n}Te_3$) exist, in which Sb_{2n} blocks are inserted between the QLs. [4] Molecular beam epitaxy (MBE) potentially allows to finely control the excess of Sb, tuning the number of vdW gaps per unit length.

Here we present the structural characterization of $Sb_{2+x}Te_3$ films grown by MBE on Sb-passivated ((√3x√3)R30°-Sb) Si (111) substrates. Starting from stoichiometric Sb_2Te_3, the composition of $Sb_{2+x}Te_3$ was controlled by increasing the atomic flux of Sb while keeping fixed the other growth parameters. The evolution of the composition from Sb_2Te_3 to $Sb_{2+x}Te_3$ can be effectively studied by X-ray diffraction (XRD) radial scans. The appearance and evolution of characteristic features in the curves of $Sb_{2+x}Te_3$ films will be discussed. XRD simulation is necessary to determine the exact composition of the films and will be implemented. Interestingly, X-ray reflectivity and atomic force microscopy data show a reduction of the film surface roughness as a function of the excess of Sb, which might be promising for the optimization of SLs as well as for the study of TI properties. Raman spectroscopy data will also be presented, showing a corresponding evolution of the spectra as the Sb increases in the films.

The present results pave the way for the engineering of a new class of phase change SL structures.

[1] Y. Takagaki, A. Giussani, K. Perumal, R. Calarco, and K.-J. Friedland, “Robust topological surface states in Sb2Te3 layers as seen from the weak antilocalization effect,” *Phys. Rev. B*, vol. 86, no. 12, p. 125137, Sep. 2012.

[2] R. E. Simpson, P. Fons, A. V. Kolobov, T. Fukaya, M. Krbal, T. Yagi, and J. Tominaga, “Interfacial phase-change memory.,” *Nat. Nanotechnol.*, vol. 6, no. 8, pp. 501–505, Aug. 2011.

[3] R. Venkatasubramanian, E. Siivola, T. Colpitts, and B. O’Quinn, “Thin-film thermoelectric devices with high room-temperature figures of merit.,” *Nature*, vol. 413, no. 6856, pp. 597–602, 2001.

[4] K. Kifune, Y. Kubota, T. Matsunaga, and N. Yamada, “Extremely long period-stacking structure in the Sb-Te binary system.,” *Acta Crystallogr. B.*, vol. 61, no. Pt 5, pp. 492–7, Oct. 2005.

#088 - Mechanical and electrical characterization of CVD-grown graphene transferred on chalcogenide Ge2Sb2Te5 layers.

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Non volatile memories based on Phase Change Materials, e. g. $Ge_2Sb_2Te_5$ are considered possible candidates in the present market scenario. The Extreme Ultraviolet Lithography (EUVL) technology, actually, allows to scale the memory device structures in the node of 18-20 nm. The capability of increasing the bits in the storage devices is one of the most important requests of the market for Non-Volatile Memory that remains one of key product segment for the mass production. The scaling possibilities of PCM must be coupled to the need of increasing the device characteristics also in the terms of power performances. The reduction in power consumption for each bit transcription implies also a reduction of the power losses. In the present work we investigate the physical properties of the mechanically transferred CVD-grown graphene layer on 50 nm thick $Ge_2Sb_2Te_5$ and the possible utilization of graphene as scaled contact. Different authors [1-2] showed that carbon nanotubes and carbon nanoribbons can be used as electric contacts in a planar PCM with a relevant reduction in Joule losses. Moreover, it was shown [3] that the interposition of a graphene layer between the PCM active material and the metallic via increases the thermal confinement, due to the weak van der Waals interactions at the interface [4-5], thus reducing the programming current. Here we reported the mechanical and electrical characterization of CVD-grown graphene transferred on Chalcogenide $Ge_2Sb_2Te_5$. The graphene layer was synthesized by C-CVD technique using a Cu foil as catalyst and it was then transferred on the GST layer by standard Cu foil wet-etching and subsequent release of the polymer-supported graphene layer. The physical characterizations show a multi domain nature of the graphene grown and transferred on chalcogenide layer. The bonding forces between the graphene and GST layer in a complete multilayer stack, namely Ni/Au layer - CVD graphene – GST layer, were characterized using the Nano-scratch Tester (CSM instruments). Every sample was tested with the CSM equipment setting a progressive linear scratch using an initial load of 0.05 mN and ending with a load of 11 mN. The indentation and the scratches was performed using a diamond spherical tip with a radius 1 µm. The electrical contact resistance of the same type of complete multilayers was investigated using the Circular Transmission Line Method (CTLM).The preliminary physical and electrical characterizations indicate the possible advantages of graphene utilization as contacts.

[1] F. Xiong, A. Liao, D. Estrada, Eric Pop *Science* 29, Vol. 332, Issue 6029, pp. 568-570, 2011.

[2] A. Behanm, et *al.Appl. Phys. Lett.* 2015, 107, 123508.

[3]C. Ahn et *al. Nano Lett.*15, 6809-6814, 2015.

[4] P. A. V. Guzman, et *al. IEEE Intersociety Conference on thermal and Termomechanical Phenomena in Electronic System*2014, 1385-1389.

[5]Mak, K. F. et *al. Appl. Phys. Lett.* 2010, 97, 221904.

#089 - Phase transitions in phase change materials induced by ion irradiations

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The success of phase change materials as storage media for non volatile memories and the further improvement towards memory devices with lower consumption or multibit storage requires a complete understanding of the basic properties of the phases involved in the transition. Theoretical and experimental studies on the crystalline structures have shown that the rearrangement of vacancies at the nanometric scale is a possible mechanism to explain the modulation of the electrical properties of phase change materials with composition GeSbTe (GST). It is therefore of interest to study the evolution of the crystalline structures as a function of disorder. In this work we use ion irradiation to introduce disorder, in a well controlled way, into polycrystalline GST thin films. Polycrystalline films with different stoichiometires, either in the trigonal stable phase or in the metastable rocksalt structure have been irradiated with 150 keV Ar+ ions. The effects of disorder are studied by electrical, optical, structural measurements and density functional theory (DFT) simulations. In the metastable structure the main effect of ion irradiation is a progressive amorphization, with an optical threshold at a fluence of 3×10^{13} cm^{-2}. For the trigonal structure, a metal-insulator transition and a crystalline transition to rock-salt structure occur prior to amorphization, which requires higher fluence than for the rocksalt phase, and depends on the composition. The bonds of Te atoms close to the van der Waals gaps, present in the trigonal phase and identified by Raman spectroscopy, change as a function of the disorder induced by the irradiation. Comparison with DFT simulations shows that ion irradiation leads to the gradual filling of the van der Waals gaps with displaced Ge and Sb lattice atoms, giving rise first to a metal-insulator transition (9% of displaced atoms) correlated to the modification of the Te bonds, and then induces a structural transition to the metastable rocksalt phase (15% of displaced atoms). The data not only show the possibility to tune the degree of order, and therefore the electrical properties and the structure of phase change materials, by ion irradiation, but also underline the importance of the van der Waals gaps in determining the transport mechanisms and the stability of the crystalline structure.

#090 - Colossal magnetoelectric responses in Ni3TeO6

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The manipulation of magnetic ordering with applied electric fields is of pressing interest for new spintronic and information storage applications. Recently, such magnetoelectric control was realized in multiferroics [1]. However, their magnetoelectric switching is often accompanied by significant hysteresis, resulting from a large barrier, separating different ferroic states. Hysteresis prevents robust switching, unless the applied field overcomes a certain value (coercive field). I will discuss the role of a switching barrier on magnetoelectric control, in particular, in a collinear antiferromagnetic and pyroelectric Ni_3TeO_6 [2,3]. The barrier between two magnetic states in the vicinity of a spin-flop transition is almost flat, and thus small changes in external electric/magnetic fields allow to switch the ferroic state through an intermediate state in a continuous manner, resulting in a colossal magnetoelectric response. This colossal magnetoelectric effect resembles the large piezoelectric effect at the morphotropic phase boundary in ferroelectrics.

[1] T. Kimura, T. Goto, H. Shintani et al., Nature 426, 5 (2003)

[2] Y.-S. Oh, S. Artyukhin J. J. Yang et al., Nature Communications 5, 3201 (2014)

[3] J. W. Kim, S. Artyukhin, E. D. Mun et al., Phys. Rev. Lett. 115, 137201 (2015)

#091 - Memory Effects in Freestanding Manganite Microbridges

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Manganites of general formula $RE_{1-x}M_xMnO_3$ (RE = rare earth, M = Ca, Sr, Ba, Pb) have remarkable structural, magnetic and transport properties due to the mixed valence (3+/4+) of the Mn ions. The phase diagrams of manganites are determined by cations substitution or oxygen stoichiometry (*i.e.* oxygen vacancy concentration). In particular, $(La,Sr)MnO_3$ (LSMO) may present a ferromagnetic and resistive phase transition whose critical temperature varies from 140K up to 360K, depending on the La/Sr ratio. By exploiting the different etching selectivity of Transition Metal Oxides (TMO) to acid solutions, freestanding microbridges made from LSMO thin films can be prepared and applied for studying memory effects. Free-standing microbridges are characterized by low thermal coupling and thus they can be efficiently heated by exploiting Joule self-heating. For instance, Joule self-heating is able to determine electronic phase switching of LSMO microbridges at local scale. We will focus on two aspects related to memory effects in LSMO free-standing microbridges:

1) Electro-thermal bistability: This is a classical electro-thermal phenomenon that in LSMO can be observed due to its non-linear resistance *vs* temperature characteristics. Two different resistance states of a microbridge under current biasing are allowed, depending on the temperature and thermal coupling conditions with the thermostat (substrate) [1].

2) Control of oxygen vacancies: Joule heating can locally increase temperature at the center of the microbridge up to several hundreds of Celsius degrees, with the consequent activation of oxygen diffusion within LSMO and oxygen exchange with the atmosphere. Oxygen vacancies can be thus created in LSMO microbridges by lowering the external O_2 partial pressure under electric biasing conditions. This determines a change of the overall transport characteristics of the device. Reversible control of oxygen vacancies concentration and their distribution is thus achieved by pure electrical biasing under controlled atmosphere [2].

[1] "*Electro-thermal bistability in* $(La_{0.7}Sr_{0.3})MnO_3$ *suspended microbridges: Thermal characterization and transient analysis*" V. Ceriale et al. J. Appl. Phys. 115, 054511 (2014).

[2] "*Reversible oxygen vacancies doping in* $(La_{0.7},Sr_{0.3})MnO_3$ *microbridges by combined self-heating and electromigration*" N. Manca et al. Appl. Phys. Lett. 106, 203502 (2015).

#092 - Graphene based supercapacitors

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Supercapacitors are electrochemical energy storage devices that combine the high energy-storage-capability of conventional batteries with the high power-delivery-capability of conventional capacitors. In this contribution we will show the results of our group recently obtained on supercapacitors with electrodes obtained using mixtures of carbonaceous nanomaterials (carbon nanotubes (CNTs), graphite, graphene, oxidised graphene). The electrode fabrication has been performed using a new dynamic spray-gun based deposition process set-up at Thales Research and Technology (patented).First, we systematically studied the effect of the relative concentrations of Multi-Walled Carbon Nanotubes (MWCNTs) and graphite on the energy and power density. We obtained a power increase of a factor 2.5 compared to barely MWCNTs based electrodes for a mixture composed by 75% of graphite. This effect is related with the improvement of the mesoporous distribution of the composites and to the increase of the conductance as pointes out by Coleman et al. After these results, we decided to test water as a solvent in order to reduce the heating temperature and to obtain a green type process without toxic solvents. To achieve stable suspensions we oxidised the graphene and the CNTs before putting them in water. We observed that changing the Graphene Oxide concentrations we obtained different value of capacitance and energy. The best results were obtained with 90% of GO and 10% of CNTs. We obtained 120F/g and a power of 30kW/Kg. The importance of these results is that it is the first time that these performances have been obtained for graphene related materials using an industrial fabrication suitable technique that can be implemented in roll-to-roll production. In this way we were able to fabricate stable suspensions in less than one hour compared to three days using NMP. All these results demonstrate the strong potential to obtaining high performance devices using an industrially suitable fabrication technique. Finally, new results using mixtures of Carbon nanofibers and graphene will be shown. These new composite allow to use ionic liquid as electrolytes and so to increase dramatically the energy stored in the device without reducing the power.

#093 - Nanoparticles Jet Deposition of amorphous silicon nanopowder for high capacity lithium ion battery anodes.

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In the field of energy storage lithium-ion batteries are widely considered the most mature technology, though still insufficient to fulfil application requirements. [1] Public and private research heavily invested in the development of new high capacity anode materials in order to boost performances. Silicon with its low cost, earth abundancy and high theoretical capacity (4200 mAh/g) [2] represents the most appealing alternative to the commercial graphite anodes (372 mAh/g). The use of amorphous silicon nanostructures combined with carbon-based coatings have been proven to be a suitable strategies to obtain superior cyclability and storage capacity.[3] In fact, from one side amorphous silicon nanostructures, composed by aggregates below the critical size for crack propagation (100 nm) and structured with an optimized system of voids, allows to withstand the volume change upon lithiation (up to 300%), while from the other side, carbon coating increases the stability of the solid electrolyte interface (SEI) Currently, slurry based synthesis of composite anodes with high volumetric capacity is studied as an industrial-compatible fabrication approach. The production of these anode structures usually relies on complex multistep and low yield (45 mg/h) chemical techniques. Moreover, the required range of particle size for anode applications is not currently obtainable with the industrial commercial production methods [4, 5]. In the present work, a novel large area (100 cm^2), high-yield (up to 300 mg/h) plasma-based deposition technique – Nanoparticles Jet Deposition (NANO JeD) – is used for slurry-based fabrication of composite silicon-carbon materials. The fabrication technique relies on a two stages non-conventional ballistic approach: (i) a non-thermal dusty plasma environment allowing low temperature narrow size synthesis of amorphous nanoparticles and (ii) an impaction stage, where aerosol gas dynamic is controlled via nanoparticles-inseminated supersonic jet flow field, enabling efficient collection of the produced powder.Slurry-based anodes are produced by mixing the amorphous silicon nanopowder (10 nm), a suitable polymer binder (PAA) and carbonaceous material (carbon black/graphene). The slurry is drop casted on a copper collector and annealed at 750°C in a nitrogen atmosphere in order to carbonize the polymer, creating a porous conductive matrix decorated with silicon nanoparticles. Electrochemical measurements, carried out in half cells configuration, of the as-prepared anode highlighted a high storage capacity of ~1200 mAh/g and cyclability (above 200 cycles).

1 V. Etacheri, Energy Environmental Science 4, 2011, 3243 (2011)

2 N. Li et al, Nano Energy 5, 105-115 (2014)

3 N. Liu et al, Nature Nanotechnology, DOI: 10.1038/NNANO.2014.6 (2014)

4 C. K. Chan et al, ACS Nano 4, 1443-50 (2010)

5 F. Shi et al, Nature Communications, DOI: 10.1038/ncomms11886 (2016)

#094 - Development of carbon xerogel and sulfonated PEEK materials for redox solid-state supercapacitors

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Recently, solid polymer electrolytes are intensely investigated as suitable materials to be used in the development of flexible, compact and safer solid-state supercapacitors. Here, we report a study supercapacitors composed of electrodes based on a carbon xerogel of high surface area (e.g. 3000 m^2g^{-1}) and a solid polymer electrolyte based on sulfonated polyether ether ketone (sPEEK). The carbon xerogel is a pre-commercial carbon kindly furnished from CSIC-INCAR of Oviedo (Spain); whereas the sulfonated PEEK and the membrane electrolyte were prepared in our lab by a well-experienced process using H_2SO_4 as the sulfonating agent of the bare PEEK polymer. A series of solid-state flexible supercapacitors were realized by contacting face-to-face the SPEEK membrane/electrolyte or a porous paper separator and the two 2 cm^2 electrodes. The electrochemical characteristics of supercapacitors were investigated in a specific designed titanium cell in which a neutral aqueous electrolyte solution of Na_2SO_4/kI is used. The KI solution was here used to impregnate the positive electrode while the Na_2SO_4 was employed to make the Na-SPEEK electrolyte membrane. The latter in these supercapacitors acted as ionic conductor and electronic insulator between two composite electrodes. The KI salt added to aqueous electrolyte (1M Na_2SO_4) is confined to the positive side of supercapacitor supplying additional capacitance through the redox reaction I^-/I_3^-, while a hydrogen electro-sorption occurs in the negative electrode of the carbon–carbon capacitor. These developed redox supercapacitors were electrochemical investigated by cyclic voltammetry (CV), DC galvanostatic charge/discharge and AC electrochemical impedance spectroscopy (EIS). As results, it were found that the solid-state supercapacitor with Na-SPEEK membrane and Na_2SO_4-KI solution in positive electrode exhibited higher specific capacitance (123 Fg^{-1}) compared to that with the reference porous separator in 1M Na_2SO_4 (103 Fg^{-1}), while the specific capacitance obtained with Na-SPEEK electrolyte reached 83 Fg^{-1}. The EIS analysis highlighted that the solid-state supercapacitors based on Na-SPEEK and Na_2SO_4-KI showed very stable resistance and full capacitance retention during the cycling life test (20000 cycles at 2 Ag^{-1}), while the reference aqueous capacitors exhibited a slight increases of ionic resistance with cycling life. Because the remarkable electrochemical performance and excellent cycle life displayed from the investigated supercapacitor in solid-state configuration, these materials may be considered promising for the development of next-generation low cost, high-performance, solid-state and flexible energy storage devices.

#095 - Reduction of antisite defects in the hydrothermal synthesis of LiFePO4 for Li-ion batteries

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$LiFePO_4$ has attracted interest as a cathode material for Li-ion batteries for its superior safety, high theoretical capacity (~170 mAh/g), high stability, and suitable operating voltage (~3.4 V). $LiFePO_4$ has the olivine structure (Pnma), in which Li-ions (at M1 sites) are forming straight column along the [010] direction, and are surrounded by FeO_6 octahedra (Fe at M2 sites) end PO_4 tetrahedra. Several synthetic routes have been developed aiming to overcome the limitation of LifePO4 in electrical and ionic conductivity, even comprising the colloidal synthesis. However, the hydrothermal synthesis remains the cheapest technique for high scale production. Unfortunately, one the main reason of limited conductivity in the obtained crystals is the presence of Fe atoms at the M1 sites (antisite defects) blocking Li-ion transport. In this contribution, we explore the results achievable by nanosizing the obtained crystal in the direction of the Li channels, and improving the ionic conductivity. This is achievable by a synthetic process that start from Vivianite, and further transforming it into Olivine. In the process, an amorphous thin layer (rich in Li) is initially formed, which is used as a reservoir for Li atoms in the final structure. These atoms will gradually replace the Fe antisites atoms at the Li positions present in the initial formation (8-10%). Finally, a $LiFePO_4$ structure with less than 2% antisites defects is obtained [1]. The reduction of Fe antisites has been proven by neutron diffraction (NPD) and confirmed by directly imaging with aberration corrected high angle annular dark field scanning transmission electron microscopy (HAADF-STEM). Moreover, the hydrothermal synthesis time can be dramatically reduced from 5h to 30 min or less by using Ca^{2+} ions [2], which promotes the Li substitution at the Fe antisites at higher rate. The resulted cathodes demonstrate higher capacity when cycled in the battery with respect to pure $LiFePO_4$ counterparts.

[1] Paolella A., Bertoni G., Hovington .P, Feng Z.M., Flacau R., Prato M., Colombo M., Marras S., Manna L., Turner S., Van Tendeloo G., Guerfi A., Demopoulos G.P., Zaghib K. Nano Energy 16 (2015) 256-267 doi: 10.1016/j.nanoen.2015.06.005

[2] Paolella A., Turner S., Bertoni G., Hovington P., Flacau .R, Boyer C., Feng Z.M., Colombo M., Marras S., Prato M., Manna L., Guerfi A., Demopoulos G.P., Armand M., Zaghib K. Nano Letters 16 (2016) 2692-2697 doi: 10.1021/acs.nanolett.6b00334

#096 - Magnesium diboride for Cryogen Free Superconducting Magnetic Energy Storage; the DRYSMES4GRID project.

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The Magnesium Diboride (MgB2) is a relatively young superconductor (discovered in 2001) which can now be produced in long length at competitive costs. It is a superconductor with characteristics intermediate between those of conventional superconductors (LTS) and of high temperature superconductors (HTS). The critical temperature is much higher than that of LTS but the fabrication technology, however, is similar to that of the LTS and does not present the difficult problems of HTS cables realization. Technology of these superconducting wires has been developed at CNR-SPIN and industrialized by Columbus Superconductors. The MgB2 operating temperature allows a cooling technology which does not use liquids (cryogen free) thus avoiding the related issues of supply, safety and costs. In this work the salient properties of this material will be reviewed, as well as developed, even in comparison with other competing materials and we will describe the project (DRYSMES4GRID) to demonstrate the feasibility of SMES (Superconducting Magnetic Energy Storage) in the short/medium term at competitive cost based on Magnesium Diboride recently selected for financial support by MISE. SMES technology offers complementary characteristics with respect to other storage technology: high charge and discharge power, fast response, high number of cycles, high round trip efficiency. Its introduction enables the feasibility of cost effective hybrid energy storage systems (Energy Intensive + Power Intensive), able to meet all the needs both the customer and at the grid level, so as to guarantee high power quality, in particular for network with high DG penetration (existing or planned). In some cases (e.g. sensitive and/or disconnectable customers, distorting and/or impulsive loads, stabilization of microgrids and/or vulnerable subnetworks) the SMES can act as an active filter (thus compensating flickers, harmonic, reactive power, current unbalance, load fluctuation) and can supply loads in island operation condition compensating network disturbances as voltage dips and interruption. We proposed to MISE a cryogen free manufacturing and testing of a SMES demonstrator with 300 kJ/50 kW rating.

#097 - Performance gain of VRFB via carbon nanoparticles treatment

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Development of efficient and cost-effective energy storage systems is nowadays crucial considering the huge amount of electrical energy supplied by the intermittent renewable energy sources and its related issues, such as grid instabilities and volatility in power prices in liberalized electricity markets [1]. Among the energy storage technology, one of the most promising is Vanadium Redox Flow Battery (VRFB) due to the peculiarities to separate power and energy, high efficiency and extremely long charge/discharge cycle life. However the commercialization of VRFB is still hindered by some technological issues, among which low power density is one of the most important. Recently Aaron et al. [2] increased the peak power density of a VRFB system utilizing a serpentine flow field, coupled with a commercial non-wetproofed carbon paper electrodes, Sigracet® SGL 10 AA.

This work presents the results of a novel method for treating commercial carbon electrodes with carbon nanostructures, in order to increase the specific active area. Treated samples are firstly analyzed with ex-situ techniques in order to evaluate and understand material nanostructure. Raman spectroscopy, X-Ray diffraction, Scanning Electron Microscope (SEM) and BET surface area measurement are performed.

Afterwards, polarization curves, cyclic voltammetries and electrochemical impedance spectroscopies are performed in a 25 cm2 modified cell architecture [3], where the negative electrode is a commercial GDE fed with hydrogen, acting as a reference electrode. This hardware permits to characterize the treated materials as VRFB positive electrode, fed with VO2+/VO2+ liquid electrolyte, eliminating V2+/V3+ cross contamination effects. The experimental setup is provided with two tanks, keeping constant the state of charge during the measurements. Stability of carbon nanoparticles to charge/discharge cycles is also verified.

Preliminary results from cyclic voltammetries on a carbon electrode show that this method permit to increase electrode performance, as also confirmed by polarization curves.

References:

[1] B. Zakeri, S. Syri, Electrical energy storage systems: a comparative life cycle cost analysis, Renewable and Sustainable Energy Reviews 42 (2015) 569-596.

[2] D.S. Aaron, Q. Liu, Z. Tang, G.M. Grim, A.B. Papandrew, A. Turhan, T.A. Zawodzinski, M.M. Mench, Dramatic performance gains in vanadium redox flow batteries through modified cell architecture, Journal of Power Sources 206 (2012) 450-453.

[3] V. Yufit, B. Hale, M. Matian, P. Mazur, N. P. Brandon, Development of a regenerative hydrogen-vanadium fuel cell for energy storage applications, Journal of The Electrochemical Society 160 (2013) A856-A861

#098 - A new method to probe atom – specific charge transfer processes with x-ray spectroscopy: application to V-doped TiO2

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An understanding of charge transfer processes at the atomic level is a pre-requisite for knowledge – based materials design and engineering. Recently, some of us have developed a new x-ray spectroscopy method to probe such processes with atomic sensitivity (Angewandte Chemie International, DOI: 10.1002/anie.201412030), the approach is based on High Energy Resolution Fluorescence Detected X-ray Absorption Spectroscopy (HERFD-XAS) under differential (dark/light) visible light illumination. Titanium dioxide is a well-known photo-catalyst for applications such as water splitting for hydrogen production and pollutant degradation. To improve the efficiency of TiO_2 based devices by increasing the absorption of visible light it is necessary to find ways to lower the band gap without introducing detrimental defects. Among the various tested techniques, doping with transition metals, such as Vanadium, is most promising. Using XAFS on different samples (thin films and nanoparticles) we have demonstrated that V substitutes Ti in TiO_2 without significant distortions of the matrix, independently of the overall structure of the sample (anatase or rutile) (Journal of Physical Chemistry C, DOI:10.1021/acs.jpcc.5b12045). Using the mentioned newly developed HERFD-XAS method on the ID26 beamline of ESRF, we have been able to obtain a clear signature of a charge transfer from V to Ti atoms upon illumination with 532 nm light. This signal is stronger in nanoparticle samples than in nanostructured thin films, a finding which is related to the higher density of surface or defective sites.

#099 - Time-Resolved Photoluminescence for the Characterisation of Fluorine-Doped TiO2 Photocatalytic Materials

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Titanium dioxide represents the most active and suitable semiconductor oxide for heterogeneous photocatalysis. However, this material presents two main limitations: i) due to its relatively high energy band gap (i.e. 3.2 eV), only a small fraction (5%) of the sunlight can be exploited for photocatalytic processes; ii) the quite rapid electron-hole pairs recombination may compete with an efficient transfer of charge carriers to substrate molecules adsorbed on the photocatalyst surface.

Different strategies have been exploited to activate TiO_2 under visible light, including anion doping with *p*-block elements. A systematic investigation was performed on an extended series of singly doped or co-doped TiO_2 photocatalysts prepared by the sol-gel method starting from different amounts of N and F dopants. Their photocatalytic behavior was investigated in both thermodynamically down-hill reactions, such as formic and acetic acid degradation, and up-hill reactions for solar fuels production, such as hydrogen production from methanol-water vapor mixtures.

In the present work TiO_2-based doped photocatalytic materials were characterized by time resolved photoluminescence (PL) spectroscopy with UV light excitation, either in the picosecond or nanosecond regimes, aiming at obtaining a better, direct insight on the effects of doping on the dynamics of the charge carriers generated upon band gap excitation.

The PL experiments were performed under different conditions, including vacuum and low temperature (at 77 K). The relaxation dynamics of the UV induced luminescence was separated in different lifetime components.

Interestingly, both the PL spectral shapes and lifetimes were found to be strongly affected by the presence of dopants. In particular, a clear correlation can be outlined between the long-lasting PL decay component and the photocatalytic performance of fluorine doped TiO_2-based materials [1]. This suggests that PL provides valuable insight to investigate the fate of photoproduced trap states originating the long-lasting PL component.These states are relevant for electron transfer paths originating the photocatalytic activity of TiO_2. The effects induced on the PL response by combining fluorine doping with noble metals (Au or Pt) nanoparticles, deposited on TiO_2 will also be discussed.

[1] M.V. Dozzi, C. D’Andrea, B. Ohtani, G. Valentini, E. Selli. *Journal of Physical Chemistry C*, 2013, 117, 25586

#100 - Hybrid protein-gold nanoparticles for heavy metal ions trace monitoring

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Abstract

Water sources pollution by arsenic ions is a serious environmental problem all around the world. Arsenate reductase enzyme (*TtArsC*) from *Thermus thermophilus* extremophile bacterium, naturally binds arsenic ions, As (V) and As (III), in aqueous solutions. In this research, *TtArsC* enzyme adsorption onto hybrid polyethylene glycol-stabilized gold nanoparticles (AuNPs) was studied at different pH values as an innovative nanobiosystem for metal concentration monitoring. Characterizations were performed by UV/Vis and Circular Dichroism spectroscopies, TEM images and in terms of surface charge changes. The molecular interaction between arsenic ions and the *TtArsC*-AuNPs nanobiosystem was also monitored at all pH values considered by UV/Vis spectroscopy. Tests performed revealed high sensitivities and limits of detection equal to 10 ± 3 M^{-12} and 7.7 ± 0.3 M^{-12} for As (III) and As (V), respectively.

#101 - Effect of platinum on the photocatalytic activity of black-TiOx

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TiO_2 is one of the most studied materials together with silicon. It has been used in a huge amount of applications, spanning from third generation solar cells to self-cleaning surfaces coating. This material is particularly promising in the field of sustainable water treatment, inasmuch, due to high photocatalytical activity, it is able to mineralize pollutants in wastewater. Unfortunately, TiO_2 adsorbs only UV light (due to a wide band gap of ~ 3 eV) and this makes it inefficient under solar illumination. Recently, our group developed a titanium oxide based material called “black-TiO_x” that shows high absorption in the full visible range. It has been demonstrated that the laser synthesis methodology is scalable and it was proposed as candidate to overcome the TiO_2 limitation in the water remediation strategies.

The photoactivity of black TiO_x is a complex interface phenomena where electron and holes, created by visible radiation, are transferred to the pollutants adhered on the surface of the catalyst. Holes have a high oxidation power and are responsible for the degradation of the pollutants whereas electrons, having a low reducing power, contribute to the charge neutrality of the solution. An increase of the transfer rate of the electrons to the solution can effectively benefit the holes transfer and can improve the photoactivity. Electron scavenging is a key parameter for achieving a high activity in pollutants degradation.

In this work, we studied the effect, on the photocatalytical activity of black TiO_x, of the scavenging of electrons operated by a platinum layer contacted with the TiO_x. The synthesis of the TiO_x film was performed by irradiating a titanium metal foil immersed in water with a 1064 nm pulsed laser. A layered structure composed by TiO_x film and a Ti substrate is obtained. Then platinum film was deposited according to three sample geometries: in the first, a continuous platinum layer of 10 nm was deposited by sputtering on the front side of the sample realizing a stacked layered structure Pt/TiO_x/Ti; in the second sample, the continuous platinum layer was deposited on the rear side of the sample realizing a stacked layered structure TiO_x/Ti/Pt. In the third, a platinum nanoparticles (PtNps) layer was deposited by drop casting methods in the rear side of the sample realizing the layered structure TiO_x/Ti/PtNps.

The resulting photoactivity increases from the first to the third sample. This effect was discussed in terms efficiency of transferring the electrons (and holes) into the solution. In particular, we discussed the efficiency of transfer electrons from the surface of Pt to solution, the role of the metallic substrate, the covering and shadowing effects of the platinum film on the TiO_x surface, the amount of exposed surface to water environment.

#102 - Preparation of metal and conductive oxide materials of high porosity by electrodeposition in a regime of vigorous gas evolution. Applications of these materials as efficient electrodes.

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Porous electrodes are attracting much interest due to their promising characteristics in numerous applications like reactors, fuel cells, batteries, sensors. An established electrochemical preparation method is based on slow metal electrodeposition through solid templates and final removal of the latter, typically by etching. This method offers excellent control of the deposit properties but is ordinarily costly, time consuming and difficult to scale up. An alternative, simplified approach, is the so-called dynamic hydrogen bubble template (DHBT) electrodeposition, that exploits the actions of confinement and stirring provided by gas evolution during cathodic polarisation with a large current flow [1]. The method has been used for the deposition of porous layers of various common metals including Cu, Sn, Ni, Co, Pb, and of several alloys [1]. The obtained deposits are robust and show large area, hierarchical porosity and increased transport, all properties favourable to the use as electrodes.

We present here the preparation with the DHBT method of: i) porous Cu alloys like Cu-Ni [2] and Cu-Zn, used as cathodes for the reduction of nitrate in alkaline solutions for environmental remediation; ii) porous Ag electrodes [3], proposed for the sensitive electrochemical detection of H_2O_2. Moreover, with a process rather symmetric to the cathodic electrodeposition mentioned above, we have deposited under anodic polarization a conductive porous oxide like PbO_2, by oxidizing Pb^{2+} ions at high current densities involving fast evolution of oxygen bubbles [4]. The charges measured during cycling of porous and compact PbO_2 layers in H_2SO_4 were used to characterise the evolution of surface roughness. The porous lead oxide material may warrant faster charging and higher capacity to the positive element of the lead-acid batteries.

References [1] B.J. Plowman, L.A. Jones, S.K. Bhargava, Chem. Commun. 51 (2015) 4331; [2] L. Mattarozzi, S. Cattarin, N. Comisso, A. Gambirasi, P. Guerriero, M. Musiani, L. Vázquez- Gómez, E. Verlato, Electrochim. Acta 140 (2014) 337; [3] L. Mattarozzi, S. Cattarin, N. Comisso, P. Guerriero, M. Musiani, E. Verlato, Electrochim. Acta 198 (2016) 296; [4] N. Comisso, S. Cattarin, P. Guerriero, L. Mattarozzi, M. Musiani, E. Verlato, Electrochem. Commun. 60 (2015) 144.

#103 - BaCe0.65Zr0.2Y0.15O3-δ-based membranes for hydrogen separation

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Ceramic hydrogen separation membranes are promising devices for separating pure hydrogen in a wide range of processes including power generation with pre-combustion, water-gas shift, methane reforming, etc. Among the different materials, the ones belonging to the Y-doped $BaCe_xZr_{1-x}O_{3-d}$ system are considered the best candidates for these applications thanks to their good compromise between high conductivity at medium temperatures (600 - 800°C) and stability in CO_2 and H_2O rich ambient.

In this study, asymmetrical porous-dense membranes consisting of $BaCe_{0.65}Zr_{0.2}Y_{0.15}O_{3-d}$ (BCZY)-based materials were successfully produced for the first time. A chemical compatibility study between the proton conductive system and different electron conductive ceramic phases was considered. The different critical issues linked to the ceramic process to obtain planar and defect free BCZY-based membranes with the suitable porous-dense microstructure were considered as well.

#104 - A Vapochromic and Chemoresistive Molecular Material for Sensing Volatile Amines

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Volatile organic compounds (VOCs) are chemical species which can be produced naturally or from anthropogenic activities. Among them, volatile amines and nitrogen compounds, better known as total volatile bases (TVBs), are the most common because their formation is an indicator of microbial degradations of food.[1] Despite the relatively low toxicity of VOCs, they can cause long-term health effects and their detection is difficult because of the concentration of these species is in general quite low. For these reasons, the development of a sensor having fast response, high sensitivity and selectivity for VOCs is highly desirable in environment pollution and food safety fields.[2]

Zn^{II} Schiff-base complexes are Lewis acidic species which form aggregates in absence of Lewis bases and monomeric adducts in presence of Lewis bases. The switching from the aggregate to the adduct involves dramatic variations of spectroscopic optical properties, both in solution and in solid state.[3] Thus, these species behave as vapochromic materials when interact with strong Lewis base, such as volatile amines, implying reversible color and structural changes.[4] The formation of adduct should involve the change of resistivity of complexes. These properties are suitable for the design and development of an optical and electrical sensor for specific VOC species, such as volatile amines.

Here, we present the first example of vapochromic, chemiresistor molecular material based on a Zn^{II} complex **1** for the detection of volatile amines.

SEM and AFM investigations spin coated films of **1** show the formation of a 2D network having many holes. These films possess vapochromic and chemiresistor properties. In particular, after exposure to saturated vapors of isopropylamine, used as prototype volatile amine, a naked-eye color change from brown-red to orange-red, accompanied by a dramatic variation of the optical absorption spectrum and resistivity, is observed.[4] By heating the exposed films, both the optical absorption spectra and resistivity are restored after desorption of the isopropylamine. This reversible process is observed even after several adsorption/desorption cycles. Overall features are useful for the development of electrical transducer devices for sensing TVBs for various applications, such as monitoring of fish spoilage.

[1] Al Bulushi, I.; Poole, S.; Deeth, H. C.; Dykes, G. A. *Critical Reviews in Food Science and Nutrition* **2009**, *49*, 369-377.

[2] Potyrailo, R. A.; Surman, C.; Nagraj, N.; Burns *Chem. Rev.* **2011**, *111*, 7315–7354.

[3] Consiglio, G.; Failla, S.; Finocchiaro, P.; Oliveri, I. P.; Purrello, R.; Di Bella, S. *Inorg. Chem.* **2010**, *49*, 5134−5142.

[4] Oliveri, I. P.; Malandrino, G.; Di Bella, S. *Inorg. Chem.* **2014**, *53*, 9771-9777.

#105 - Nanofibre filters for air and water purification by multi-jet electrospinning

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Air pollution and water contamination are serious environmental issues. Small aerosol particles and volatile organic compounds (VOCs) in air adversely affect human health. The discharge of wastewater containing dyes and heavy metals harms the aquatic life and limits water resources.

New filtration systems based on electrospun nanofibres have been proposed. Nanofibre filters showed an enhance filtration efficiency to remove ultrafine particulate from air stream due to small pore size. Nanofibres composed by polymers with functional groups (i.e. keratin) allow the depuration of water from pollutant compounds such as metal ions and dyes, or air purification from VOCs (e.g. formaldehyde) with improved performances thanks to the high specific surface.

Academic and industrial interest for electrospinning raised in the 1990s, but up-scaling of the process have to reach in order to fulfil industrial production requirements. Large-scale electrospinning systems should be designed to increase productivity, allowing continuous nanofibre production and deposition. One approach is the use of multi-nozzle electrospinning plant.

In this work, an electrospinning pilot plant equipped with 62 nozzles was designed and developed. Electrospun nanofibres were continuously deposited on textile substrates, moved during electrospinning by a roll-to-roll system for filter production. The shifting speed of the substrate influenced thickness, porosity and density of the deposited nanofibre layers.

Performances of keratin-based filters in terms of filtration efficiency and air permeability were evaluated, as well as the adsorption of formaldehyde. Moreover, removal of metals ions (copper, nichel, cobalt) and methylene blue were measured by dynamic adsorption tests.

#106 - Real-time structural and morphological study of ceria films during growth, reduction and oxidation

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Oxides are of primary importance for the needs of modern society. Because of their peculiar properties, they find application in several fields like catalysis, energy, memories and biomedicine. When combined with noble metal nanoparticles, oxide catalysts typically increase their reactivity and selectivity.

In this framework, cerium oxide plays a significant role because of its ability to store, release and transport oxygen, due to the ease with which Ce ions can reversibly change their oxidation state, passing from 4+ to 3+, depending on the ambient condition.

Inverse model catalysts of tunable size, specifically ceria (CeO_2) epitaxial ultrathin films on Pt(111), were previously studied, showing that reduction, induced by high temperature heat treatment in UHV, leads to structural modifications, which give origin to additional structures in the LEED pattern, especially for very low coverage. Successive oxidation by annealing in oxygen rich atmosphere restores the original CeO_2 stoichiometry and atomic structure, while the film morphology undergoes irreversible modifications (1). Low energy electron microscopy (LEEM) and microprobe low energy electron diffraction (μ-LEED) are powerful full-field techniques that merge information from the reciprocal space and from the real-space, providing a structural and morphological description of the evolution of the system during different kinds of treatments (2).

In this work, we present the results of an in-depth dynamic investigation by LEEM: we followed in real-time the growth, reduction and oxidation of cerium oxide ultrathin films on Pt(111). In particular, we focused our attention on the effects on morphology and structure of different deposition temperatures (3). Depositing ceria on the Pt substrate at 770°C, we obtained good epitaxial quality ceria islands hundreds of nanometers wide that show epitaxial domains slightly rotated with respect to the Pt surface lattice. On the contrary, growing at lower T, the substrate surface is fully covered by ceria nanostructures of size below LEEM resolution. We used dynamic intensity-voltage LEEM as a tool to identify different growth regimes.

Inducing reduction on these films, we observed a dynamical modification in the LEED patterns, reversibly evolving into a complex superposition of different structures. Real-space LEEM imaging during reduction allows to identify a new phase that extends on the uncovered substrate surface. By oxidation, this phase is transformed into fully oxidized ceria. This suggests that the Ce-Pt alloy could appear during reduction, highlighting the strong interaction between ceria and Pt.

(1) P. Luches, F. Pagliuca, S. Valeri, *Phys Chem Chem Phys* 16, 18848 (2014)
(2) B. Kaemena, S.D. Senanayake, A. Meyer, J.T. Sadowski, J. Falta, J.I. Flege, *J Phys Chem C* 117, 221 (2013)
(3) M. Sauerbrey, G. Gasperi, P. Luches, J. Falta, S. Valeri, J.I. Flege, *Top Catal* (2016), in press

#107 - Oil removal from water-oil emulsions using magnetic nanocomposite fibrous mats

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Oily wastewaters produced by several industries are currently a persistent and common problem, presenting potential environmental and health risks. Oil can appear in wastewater as free oil, soluble oil, or emulsified oil. Each kind of oily wastewater requires specific separation techniques, being in general the emulsified oil the most difficult to separate, due to its high stability in the water, especially in the presence of emulsifiers / stabilizers. In the last years, new materials presenting enhanced selectivity to oil or water absorption have arisen as potential solutions for the removal of oil from water-oil emulsions. In this work, we report the facile fabrication of hydrophobic and oleophilic poly(methyl methacrylate)-based nanocomposite fibers with magnetic properties, as an effective solution for oil removal from stable water-oil emulsions. These fibers were obtained by electrospinning, a well-known and effective technique for the production of fibers of a wide range of polymers with diameters ranging from micrometers to nanometers. It was found that the incorporation of ferromagnetic nanoparticles to the polymer fibers increases the oil removal performance of the fibers, as well as attributes magnetic actuation properties to the material. Following this approach, functional nanocomposite fibrous mats were obtained and tested on stable water-oil emulsions, reaching oil absorption efficiencies up to 90%, independently from the oil content in water which ranges from 5 to 30 v.%. Therefore, the good performance achieved makes the proposed material a promising new candidate for water-oil emulsions separation.

#108 - Mechanochemical transformations by ball milling: From processing parameters to chemical kinetics

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Mechanochemistry is a branch of Chemistry that studies the effects of non-hydrostatic stresses and plastic strain on the chemical reactivity of molecules, crystals, and, most in general, other aggregates of matter[1]. In the presence of unbalanced mechanical stresses, Mechanochemistry is non-equilibrium Chemistry, and mechanochemical transformations exhibit a typical local character. Mass transport processes different from thermally activated ones occur, which can result in unusual physical and chemical behaviors. Although the directional character of mechanical stresses has been recently shown to enable the selective activation of covalent systems, for centuries mechanochemists focused their work on solid materials[2, 3]. The present contribution aims at providing a short overview of the experimental and theoretical attempts performed to deepen the insight into the fundamental mechanisms governing the mechanical activation of solids. We discuss a few experimental cases in which the characterization of the milling dynamics, the related evaluation of the frequency and energy of impacts, and the development of a suitable kinetic model allow estimating the amount of reactants involved in physical and chemical processes during individual impacts. Furthermore, the potential of Mechanochemistry applied to inorganic and organic chemical reactions, tipically conducted under conventional conditions, and some of the related challenges, will be also also discussed[4].

Reference:

1. Peter Balaz et al., **Chem. Soc. Rev.**, 2013,**42**, 7571.

2. Giorgio Cocco, Francesco Delogu, L. Schiffini, **Journal of Materials Synthesis and Processing**, 2000, 8, 167.

3. Samuel A. Humphry-Baker, Sebastiano Garroni, Francesco Delogu & Christopher A. Schuh, **Nature Materials**, pubblished online, August 2016.

4. Rita Mocci, Lidia De Luca, Francesco Delogu, and Andrea Porcheddu**, Adv. Synth. Catal.** 2016, 358, 3135.

#109 - Investigation of mechanical performances of NiFeGa melt spun ribbon for Elastocaloric effect applications

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Melt spinning process is a useful route to prepare thin ribbons like a ready material for smart mechanical applications. Moreover in the elastocaloric effect (eCE) investigation, the melt spun ribbons represents an interesting solution to avoid some complication related to different SMA systems due to their brittleness. Furthermore the thin ribbons show a good relationship between volume and surface to maximize the release and absorption of heat during the eCE. In this work we studied the mechanical properties of Ni55Fe16Ga29 (at%) melt spun ribbons with the perspective of application in eCE devices. Particularly termo-mechanical process are developed to obtain better pseudo-elastic response of the material and to calibrate the residual internal stress due to the preparation process. The thermal treatment under stress seems the best procedure to optimize the mechanical performance of these particular samples.

#110 - Synthesis of gold nanoprisms and nanorods as photothermal agents: comparison of their heating ability for bioapplications

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Hyperthermia (HT) is currently used as a non-invasive technique for cancer therapy, whereby biological tissues are exposed to higher than normal temperatures for selective ablation of tumoral cells. Heating treatments can be applied using external heating sources such as ultrasounds; however, heating only malignant cells is difficult to attain. Recently, there has been a growing interest in the use of gold nanoparticles (AuNPs) to selectively generate heat in a spatiotemporal fashion, which is known as photothermal therapy (PTT). AuNPs can be synthetized as stimuli-responsive systems, which are able to absorb incident light coming from a laser outside the body and generate heat only in the tissues where AuNPs are allocated. In fact, they can be finely tuned to absorb light in the near-infrared (NIR) spectral range, known as the “biological window”, where body tissues are mainly transparent. Although PTT has entered clinical trials, the molecular mechanisms underlying the *in vivo* cellular responses to heat stress remain unclear to date.

Here,in line withEuropean strategies aimed to reduce vertebrate experimentation, we propose an invertebrate animal, the small freshwater polyp *Hydra vulgaris* (Cnidaria, Hydrozoa) to study the response of different AuNPs to PTT. This organism, more complex than cells, exhibit however functional conservation of main physiological pathways, such as the heat response.

To this end, gold nanoprisms (NPr) and nanorods (NR) absorbing in the NIR range have been synthetized, functionalized and characterized. Their heating efficiency upon irradiation with a NIR-laser (1064 nm) *in vitro* has been evaluated, demonstrating that both types of nanoparticles can be effectively used to kill cells. Also, their toxicity, internalization rate and gene profiling after laser irradiation in *Hydra* will be presented. The obtained results demonstrate that AuNPrs serve as an excellent photothermal agent, and that *Hydra* could be considered a good modelto scan the heating properties of AuNPs.

#111 - Ion implantation in polymers for strain gauge applications

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The implantation of ions in inert polymers is an alternative technique to promote the formation of dispersed metal nanoparticles or continuous thin films near the polymer surface. These structures can be easily incorporated in more complex electronic devices for different technological applications, such as strain gauge devices.

Here, different thermoplastic polymers were irradiated at room temperature using high-dose implantation (Pd^+ ions) ranging between 10^{15} and 10^{17} cm^{-2} and optimized ion energy of 90keV. The ion implantation process was simulated by TRIM calculations for a better understanding of the implanted depth profile and surface damage. Morphological, microstructural, compositional and electrical characterizations were intensively performed by Helium ion microscopy (HeIM) and scanning electron microscopy (FESEM) observations, glancing-incidence X-ray diffraction, spectroscopic analyses (FTIR, XPS, SIMS) and electrical resistivity and Hall mobility measurements. Furthermore, the functional properties of the produced metal/polymer nanocomposites were investigated by measuring the electrical resistivity as a function of the mechanical load (bending, deformation) showing a linear response of the electrical resistivity as a function of the mechanical deformation. These findings demonstrate that the nanocomposite materials are suitable and promising for the fabrication of deformation sensor devices.

#112 - Shearing colloidal gels

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Soft matter systems have the intriguing property to be able to form a variety of different arrested states, encompassing (among others) repulsive, attractive glasses and gels. In this work, we numerically study a gel-forming colloidal system[1,2], modeled as a modified Lennard-Jones potential complemented with a repulsive Yukawa tail, under the effect of shear. Starting from an off-equilibrium arrested state at low temperature, we have sheared the system using Lee-Edwards boundary conditions at different shear rates. We find that at high shear rates the energy of the system increases, reaching a non-equilibrium steady state. We thus identify a mapping between shear rate and temperature which enable us to connect sheared gels to equilibrium states: for each shear rate we consider the equilibrium system having the same potential energy and we compare the structure of the two states. We find that shear does not significantly alter the local scales but has a profound effect at large length scale, inducing the system closer to a phase separation. For low shear rates, instead the sheared gel is actually able to visit lower energy states with respect to equilibrium simulations, reaching a crystal state. We then consider a polydisperse version of the model, in order to avoid crystallization and to examine the gel rearrangements at low shear rates.

[1] Campbell, Anderson, Van Duijneveldt, Barlett, *Phys. Rev. Lett.* 94, (2005) 208301.

[2] F. Sciortino, P. Tartaglia, E. Zaccarelli, *J. Phys. Chem. B*, 109, (2005) 21942.

#113 - Thermo-activated solvation mechanism in stimuli-responsive cyclodextrin-based hydrogels

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Hydrogels are a class of materials which are particularly useful in many biological and biomedical applications. These systems are more similar to natural soft tissue than any other type of biomaterial for their high water content and biocompatibility. The possibility to vary the chemical composition and the molecular structure of polymer network of hydrogels allows us to extend the use of these systems to tissue engineering, controlled drug delivery and bio-nanotechnology. Environmentally sensitive hydrogels can change their structure and chemical-physical properties in response to external stimuli, such as pH or temperature variations. In this contest cyclodextrin nanosponges (CDNS) represent a new delivery system which allow a tuning of the therapeutic demands of the pathology, with the presence of both hydrogen-bond donor/acceptor groups in the polymeric backbone of the hydrogel matrix. They offer interesting possibilities to encapsulate both hydrophobic and hydrophilic active ingredients. In particular, the formation of CDNS hydrogels is possible by swelling the polymer in an aqueous solution of a given bioactive compound of interest. In this framework, we approached the study of the thermosensitive behaviour exhibited by pH-responsive cyclodextrin-based hydrogels by the joint use of UV Raman scattering and Brillouin spectroscopy to monitor the phase changes in polysaccharide hydrogel materials and their influence on the localized and collective vibrational dynamics of the system. We combined the information that can be extracted by exploiting the use of UV Raman spectroscopy to investigate how macroscopic properties, like the gelling behaviour of CDNS hydrogels. This mechanism is well described by the so-called activation temperature T* that is defined as the characteristic temperature at which we observe a significant decreasing of the dephasing time tdeph associated to the vibrational modes of specific chemical moieties present in the CDNS polymer structure. This activation temperature T* has been observed to be strongly dependent on the pH conditions of hydration of polymers. In a complementary way, Brillouin scattering is used to probe the collective dynamics of the system, by measuring the propagation velocity and the attenuation of longitudinal acoustic modes at different conditions of temperature and pH. In particular, we observed a decrease of Brillouin peak frequency upon increasing of temperature; as main result, we found that the phase transition temperature strictly depends on pH value, covalent cross-linking degree and hydrophobicity/hydrophilicity balance in CDNS. All the results presented here corroborate the importance of the joint use of different vibrational techniques in order to have a complete comprehension of the molecular structure and behavior of complex system like CDNS hydrogels.

#114 - High frequency printed and direct-written polymer transistors

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Printed organic field-effect transitors (OFETs) have been considered for many novel applications towards large area and flexible electronics [1], since they can enable pervasive integration of electronic functionalities in all sorts of appliances, their portability and wearability. Applications are countless: from personal devices (e.g. wearable health monitoring devices) to large-area sensors (e.g. electronic skin, bio-medical devices), and smart tagging of products with radio-frequency identification tags. It is no doubt that a huge driving force comes from flexible and/or rollable displays deployable on demand, to be integrated with portable and wearable devices. However, printed OFETs fabricated with scalable tools fail to achieve the minimum speed required for example to drive high-resolution displays or to read the signal from a real-time imager, where a transition frequency (f_T), i.e. the highest device operative frequency, above 10 MHz is required. In this contribution I will present different strategies to increase f_T in polymer and polymer-hybrids based devices by combining only printing and laser-based direct-writing techniques. [2] In particular, I will demonstrate the possibility to achieve MHz operation in all-organic transistors on plastic foils, where short channels are ablated by a fs-laser. Moreover, we show that fs-laser sintering is another very promising approach for fast direct-written devices, with the possibility of achieving 10 - 20 MHz regime already with an OFET mobility in the range of 1 cm^2/Vs thanks to the drastically reduced capacitive parasitism. Further improvements towards even faster wearable polymer and hybrid electronics, suited to build wireless body area networks, will be discussed.

References

[1] M. Caironi and Y.-Y. Noh (eds.), Flexible and Large Area Electronics, Wiley, 2015, ISBN: 978-3-527-33639-5

[2] S.G. Bucella, M. Caironi et al., Nature Communications 2015, 6, 8394

#115 - Fully printed Organic Thin Film Transistors: materials and process optimization

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Organic materials offer several advantages for low-cost flexible electronics. Thanks to their solubility, elasticity and low thermal budget they are suitable as inks for several printing techniques. Among these, inkjet has been widely used to realize organic devices and circuits, for the fast prototyping and the high resolution achievable. Some inkjet drawbacks, as the lack of uniformity of the semiconductor layer or the slow printing speed, draw the attention to R2R systems, such as gravure printing, to achieve high throughput, high resolution and uniform thin layers.

In this work we will show the optimization of the fabrication process of fully printed OTFTs and circuits, obtained by using both inkjet and gravure printing techniques, and their electrical characterization. In particular, we have used an inkjet printer (DIMATIX DMP-2831) for depositing with an Ag nanoparticles ink the layers for source/drain and gate electrodes, while the semiconductor and the dielectric layers have been deposited by a modified inverse direct gravure printer (NSM-Labratester) with home-made glass masters. The glass printing plate overcomes some of the limits of the traditional metallic one, allowing to achieve smoother edges, better cells profiles and an easier and effective cleaning procedure to prevent clogging and contamination issues. Furthermore, we combine the glass plates with the use of plastic blades to improve ink transfer and to avoid metallic particles contamination due to wear.

Using our so modified gravure printer we have assessed several formulations of PEDOT:PSS (conductive polymer used for transistor electrodes) and commercial polymeric dielectrics inks. To optimize the ink formulations numerical fluid dynamic, rheological and surface tension analysis have been performed, validating the results through run of printing tests. Afterwards, using the results of these studies, fully printed multi-fingered OTFTs with staggered top-gate configuration have been fabricated on flexible polyethylene-naphtalate substrates 100 µm thick. Source and drain have been also obtained with evaporated Au, defined with lithography, or PEDOT:PSS deposited by gravure printing. The p-type polymeric semiconductor layer thickness is about 50 nm, while the dielectric fluoropolymer is 400 nm thick. Device channel lengths and widths are in the range of 30÷400 µm and 100÷900 µm, respectively. The electrical characteristics of the printed OTFTs show high mobility, low threshold voltage and low contact resistance. Gate leakage current is quite low, thanks to the high quality of the dielectric layer that also provides an effective encapsulation. Fully printed unipolar inverters with enhancement load have been successfully realized by these OTFTs. First results show a gain of about three and a noise margin of about 1 V, however a better match of the load and driver transistors can improve these performances.

#116 - Ultraconformable Temporary Tattoo Multielectrode Array for Skin-Contact Bioelectronics Applications

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The emergent field of **conformable electronics** can enable the development of **unperceivable personal monitoring systems** to be used in healthcare and sport, especially in **skin contact** applications. In this framework ultra-thin polymeric films are envisioned as ideal substrate materials [1] thanks to their intrinsic ultra-conformability: an intimate contact between such films and surfaces with arbitrary topography. While reducing the thickness of polymer substrates is foreseen as the key factor for attaining ultra-conformable devices, the challenge is to not compromise structural integrity and function of electrodes (e.g. for physiological signals recording) and other on-board electronic components. [2] Together with restrictions and difficulties in suitable processing techniques, as a matter of fact main challenges are related to the release, manipulation and transfer on the skin of such ultrathin and conformable devices. We recently reported about a robust, low cost and safe strategy to face these challenges for producing **disposable ultraconformable electrodes for skin-contact electrophysiology applications**, by using **temporary tattoo paper as an unconventional substrate**. Tattoo nanosheet electrodes were fabricated by ink-jet printing of PEDOT:PSS and transferred on skin as temporary transfer tattoos. We demonstrated their successful performances as stable, dry electrodes for surface electromyography (sEMG) for recording muscle activity, permitting the myographic control of a robotic hand.[4] We report here our recent advancements in this technology by presenting **tattoo multielectrode arrays** based on **ink-jet printed PEDOT:PSS** multichannel electrode pads. A full integration of interconnections and of the necessary external connections on top of temporary tattoo paper was provided by means of an optimized fabrication and multi-layer assembly process. As many as 6 different recording channels were fabricated on top of each tattoo which permitted high density sEMG and skin impedance recording with stable adhesion and operation. Long-term recording (up to 3 days) in dry conditions was assessed which favourably compares with pregelled Ag/AgCl electrodes (commonly used in clinical practice) wich suffer from drying of gel after 8-10 hours. Thanks to the use of versatile fabrication techniques (ink-jet printing, laser cutting, lamination) several different configurations of arrays could be customizable for different applications. These achievements permitted to expand the recording capabilities of tattoo electrodes and to envision other on-skin applications, such as electroencephalography (EEG) or electrocardiography (ECG) which were preliminary tested.

References

1. M. Kaltenbrunner *et al.*, *Nature* **499**, 458 (2013).

2. D. H. Kim *et al.*, *Science* **333**, 838 (2011).

3. J.-W. Jeong *et al.*, *Adv. Mater.* **25**, 6839 (2013).

4. A. Zucca *et al.*, *Adv. Healthc. Mater.* **4**, 983 (2015).

#117 - Fully Solution-Processed Conductive Films Based on Colloidal Copper Selenide Nanosheets for Flexible Electronics

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Flexible electronics is a rapidly growing field, which promises the development of a variety of novel commercial products as displays, solar cells and biomedical sensors that can be embedded in clothes and other everyday items.[1] We developed a novel colloidal synthesis of klockmannite copper selenide nanosheets (NSs)[2], with lateral dimensions of up to 3 micron and thickness around 5 nm, for the fabrication of flexible conductive films. These films were prepared via simple drop-casting of CuSe NS dispersions without any additional treatment. The electrical performance of these coatings (with exhibited conductivities of up to 645 $S\cdot m^{-1}$) was benchmarked against copper selenide spherical nanocrystals (SNCs)[3] in order to demonstrate the advantage of 2D morphology of the NSs for flexible electronics. In this contest $Cu_{2-x}Se$ SNC films exhibited higher conductivity but lower reproducibility due to the crack formation leading to discontinuous films. Furthermore, we studied electrical properties of the films deposited on different flexible substrates following their bending, stretching and folding. In these experiments, CuSe NS films restored their conductivity values after releasing the mechanical stress, whereas the conductivity of $Cu_{2-x}Se$ SNC-based films irreversibly dropped after releasing the stress applied to flexible substrates. Moreover, a comparison of $Cu_{2-x}Se$ SNC and CuSe NS films revealed an increased stability of the NS-films under atmospheric conditions. These features make the CuSe nanosheets suitable candidates for printable electronics on flexible substrates (e.g. in medical implantation devices) or for a possible use in stress sensors.[4]

References:

1- Liu, Z.; Xu, J.; Chen, D.; Shen, G. *Chem. Soc. Rev.* **2015,** 44, 161-192.

2 - Liu, Y.-Q.; Wang, F.-X.; Xiao, Y.; Peng, H.-D.; Zhong, H.-J.; Liu, Z.-H.; Pan, G.-B. *Sci. Rep.* **2014,** 4, 5998.

3 - Lesnyak, V.; Brescia, R.; Messina, G. C.; Manna, L. *J. Am. Chem. Soc.* **2015,**137, (29), 9315-9323.

4- Vikulov S, Di Stasio F., Caseracciu L., Saldanha P., Scarpellini A., Dang Z., Khrane R., Manna L. Lesnyak V.; Adv. Funct. Mater. 2016, 26, 3670–3677

#118 - High-performance electrolyte-gated organic field-effect transistors

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Organic electronics has grown impressively in the last 20 years and a plethora of different applications has gained the attention of the scientific community. To date, the best performing devices are based on single crystal organic semiconductors (OSCs) but, several drawbacks limit their practical use. Regarding polycrystalline semiconductors, different insoluble and soluble OSCs have been successfully employed and processed through ultra-high vacuum sublimation along with spin-coating deposition. However, these deposition techniques still remain quite far from a real industrial upscaling.

We propose a strategy that differs from conventional approaches because it exploits the combination of blended materials together with bar-assisted meniscus shearing (BAMS) technique[1,2]. Our active material is prepared by blending an insulating polymer (e.g. polystyrene) with an organic semiconductor (e.g. TIPS-pentacene, DB-TTF, diF-TES-ADT, etc.) yielding thin-films (≈ 30 nm) that display the following advantages: i) high-crystalline domains, ii) a smooth and compact surface and iii) a self-encapsulation layer that makes the polycrystalline semiconductor more stable towards adventitious agents.

The electrical performances of our devices were tested by using conventional OFET architecture (i.e. bottom gate/bottom contact or bottom gate/top contact) and as Electrolyte-Gated Field-Effect Transistors (EGOFETs) where a water droplet acts as gate dielectric. In this configuration a platinum wire, which is the gate electrode, is immersed in the aqueous solution on top of the channel area. The EGOFET is able to work at low operational voltages (<1 V) thanks to the higher capacitance (i.e. tens of $\mu F/cm^2$) with respect to standard gate dielectrics (i.e. tens of nF/cm^2). Our EGOFETs reach excellent performances in terms of mobility as well as subthreshold slope and additionally, show an outstanding stability, which makes them suitable candidates for addressing actual challenges in (bio-)electronics.[3]

References

1. F.G. del Pozo et al., Adv. Funct. Mater., 2016, 26, 2379-2386.

2. I. Temiño et al., Adv. Mater. Tech.,2016, DOI: 10.1002/admt.201600090.

3. F. Leonardi et al., Adv. Mater. (Accepted).

#119 - Current trends in wide band gap semiconductors processing for power devices

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Since decades, silicon (Si) dominates microelectronics industry. However, the future power electronics devices will have to operate at higher power levels, frequencies and temperatures, and with an improved energy efficiency with respect to Si devices. Hence, the introduction of new semiconductors technologies has become mandatory.

Due to their excellent properties, silicon carbide (4H-SiC) and gallium nitride (GaN) are the best candidates to fulfill these requirements, as they allow a reduction of the on-state resistance and an increased breakdown with respect to Si, leading to a reduction of the power losses. In this context, while impressive progresses have been already achieved in many SiC and GaN technologies (Schottky diodes, MOSFETs, HEMTs, etc.), several hurdles must be still overcome to fully exploit the properties of these materials, reaching the desired devices performances [1].

This talk will give an overview of the current trends in wide band gap semiconductor processing reported by the international community, focusing on specific interface issues (oxide/semiconductor, metal/semiconductors, etc.) in practical devices.

First, a key issue in SiC technology is the optimization of the MOSFET mobility. This aspect will be discussed considering the electrical properties of SiO_2/SiC interfaces and the effects of nitrogen- or phosphorous-based post deposition annealing of the gate oxides (“counter doping”) [1]. In spite of the improved mobility after annealing, threshold voltage instabilities can occur, due to the presence of near-interface-traps [2]. Hence, novel processes under investigation to further optimize 4H-SiC MOSFET mobility and reliability (interface doping, alkali earth passivation, new dielectrics, etc.) will be mentioned.

Also Ohmic contacts are important in SiC and GaN devices. Recent investigations on Ti/Al-based metallizations will be reviewed, whose results are applicable both on p-type SiC for JBS diodes [3] or for “Au-free” contacts in GaN HEMTs [4].

Concerning GaN, the development of a reliable normally-off HEMT technology is the most critical issue. The viable routes to obtain normally-off HEMTs will be reviewed (recessed gate, fluorine incorporation, etc.), highlighting the use of the p-GaN gate approach. The effect of annealing conditions on metal/pGaN gate electrodes in normally-off p-GaN HEMTs will be discussed [5].

Finally, the future perspectives of vertical SiC and GaN devices will be presented.

[1]F. Roccaforte, et al., Physica Status Solidi a **211**, 2063 (2014); Appl. Surf. Sci. **301**, 9 (2014)

[2] P. Fiorenza, et al., Appl. Phys. Lett. **105**, 142108 (2014); Appl. Phys. Lett. **109**, 012102 (2016)

[3] M. Vivona, G. Greco, R. Lo Nigro, C. Bongiorno, F. Roccaforte, J. Appl. Phys. **118**, 035705 (2015)

[4] G. Greco, F. Iucolano, F. Roccaforte, Appl. Surf. Sci. **383,** 324 (2016)

[5] G. Greco, et al., IEEE Transaction on Electron Devices **63**, 2735 (2016)

#120 - High growth rate 3C-SiC growth: from hetero-epitaxy to homo-epitaxy

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Cubic Silicon Carbide (3C-SiC) is regarded as a most promising candidate for high power and high frequency device applications since 3C-SiC displays the highest speed of electron transport within the crystal of all of the SiC polytypes. The growth of thick 3C-SiC layers can be extremely interesting for the realization of power devices below a breakdown voltage of 800 V where DC-DC converters and DC-AC inverters are needed for electric vehicles or hybrid cars. To overcome this limitation, silicon power devices are typically used for this important application but it is necessary to use very heavy and expensive heat sinks to reduce the device temperature (due to the high currents) because of the low band gap and low thermal conductivity of the silicon substrate. For these applications, 3C-SiC is the ideal material because it has high channel mobility with almost the same characteristics of the hexagonal polytypes.

Furthermore, one important property of 3C–SiC is that it can be grown on large diameter Si (silicon) substrates. This property is very attractive since the homo-epitaxial growth of SiC is influenced by the limited diameter of commercially available SiC substrates, with the present availability of a maximum of 6 inch diameter 4H– and 6H–SiC substrates. However, the growth of 3C–

SiC on Si substrates is affected by intrinsic problems of the hetero-epitaxial growth such as the mismatch in the lattice parameters and/or the thermal expansion coefficients between two dissimilar materials. The large lattice mismatch, which is about 20% (a_{SiC}=0.436 nm, a_{Si}=0.543 nm), is one of the most serious causes in the generation of stacking faults and/or cracks.

3C-SiC devices are hampered by a high crystal defect density due to the hetero-epitaxial growth of these films, which results in the presence of stacking faults (SF). In this paper high growth rate CVD processes have been used to try to reduce the SF density in 3C-SiC films. In a first step a high growth rate (30 mm/h) has been used to grow 50 mm thick 3C-SiC layer on (100) Si. Then the silicon substrate was removed via etching and a further 3C-SiC growth was performed with a higher growth rate (90 mm/h) at a higher temperature (1600 °C) to obtain a final thickness of 150 mm. The SF presence and density were evaluated by TEM analysis performed on as-grown samples and SEM analysis on KOH etched samples with various thicknesses. A decrease of SF density was observed with an increase of 3C-SiC film thickness, with the best results (500/cm) obtained for the thickest sample. The 3C-SiC film quality and orientation was evaluated by XRD are correlated with film thickness and SF density.

#121 - Structural and funztional characterization of Al+ implanted 4H-SiC

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Now a days, in spite of the fact that 4H-SiC electronic components have gained a significant position in the power electronic market among the low-loss, high-power and high-frequency devices for harsh environments, several issues related to the SiC poly-types growth and the SiC material processing still need final solutions. This presentation is on SiC material processing related issues. The *p*-type doping of 4H-SiC by selected area Al^+ ion implantation is a largely used technology for the fabrication of junction termination extensions around mesa SiC *p-i-n* diodes, p-wells for MOSFETs devices, and ohmic regions; each application with its own optimal Al acceptor concentration. A post implantation annealing process, for the contemporaneous recovery of the damaged SiC lattice and the electrical activation of the implanted Al, is part of the technology itself. A consolidated knowledge about the dependence of the p-type conductivity on the implanted Al concentration in the range $5x10^{18}$-$5x10^{20}$ cm^{-3} and the post implantation annealing temperature in the range 1600-2100 °C has been reached. Now a days, major efforts are dedicated to study the role of the annealing time and the condition of formation and growth of extended and of point defects in implanted and not implanted SiC regions. This presentation contains the results of structural and electrical investigation of Al^+ implanted 4H-SiC showing that on increasing the implanted Al concentration different type of extended defects form and grow in the implanted SiC lattice, while a strong anisotropic hole transport occurs when the Al implanted layer contains stacking faults and its interface with the unimplanted region is featured by a very high density of staking faults, much higher than in the implanted layer itself. This presentation contains also current-voltage characterization in the temperature range 30-563 K of Al^+ implanted 4H-SiC diodes that have been processed in house with different post implantation annealing temperature of 1600-1650 °C and 1950 °C. From the activation energies of the Arrhenius plots of forward and reverse saturation currents the hypothesis of generation-recombination currents due to carbon vacancies (V_C) defects with concentrations dependent on the post implantation annealing temperature has been performed. As V_C is a carrier lifetime killer, such hypothesis has been tested by measuring the ambipolar carrier lifetime on the same diodes by the open circuit voltage decay (OCVD) technique.

#122 - Threshold voltage instability in SiC and GaN transistors employing SiO2 as gate dielectric

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The comprehension of trapping phenomena at insulator/semiconductor interfaces is fundamental for the development of reliable insulated-gate transistors based on wide band gap (WBG) materials, SiC and GaN.

Silicon oxide (SiO_2) is the most widely used dielectric for 4H-SiC and GaN MOS-transistors, owing to the large band gap (~9eV), the large conduction band discontinuity (~3eV) and the high critical electric field (~15MV/cm).

Nevertheless, there are some technological concerns in the control of the SiO_2/WBG semiconductor interface in the gate region. In fact, the density of interface traps (D_{it}) near the conduction band edge at SiO_2/SiC and SiO_2/GaN interfaces is much higher with respect to that at SiO_2/Si interface, thus limiting the channel mobility of the transistors. In addition, WBG devices also suffer of threshold voltage instability phenomena under positive/negative gate bias stress, which are often associated to the presence of electrically active defects (near interface traps, NITs) within the SiO_2 layer.

This work reports on the trapping phenomena at SiO_2/4H-SiC and SiO_2/GaN interfaces in MOS-based devices, with a specific emphasis on the threshold voltage instability effect observed in the transistors. The analyses of MOS capacitors and transistors allowed to discriminate between the contributions of interface states D_{it} and near interface traps (NITs) inside the insulator. In particular, it will be shown that, although appropriate post-deposition-annealing can reduce the interface states in both systems (down to the 10^{11}-10^{12}cm^{-2}eV^{-1} range), the presence of NITs is responsible both for an anomalous behavior of the current conduction and for threshold voltage instabilities [1]. Time-resolved transient current and conductance measurements, performed in appropriate bias ranges, allowed to correlate the presence of slow trapping states to NITs inside SiO_2. From the characteristic trapping time, the location of NITs inside the insulator was estimated to be 1-1.5 nm from the semiconductor interface [2].

Moreover, a methodology to quantify the NITs (~10^{11}cm^{-2}), based on temperature dependent gate-current transient measurements will be presented. In this method, a semi-empirical modified Fowler Nordheim model is used to consider the Coulombic effect of the NITs and to fit the experimental transient current measurements in 4H-SiC MOSFETs [3].

The impact of the observed trapping phenomena on the SiO_2/SiC(GaN) transistor operation will be briefly discussed.

[1] P. Fiorenza, A. Frazzetto, A. Guarnera, M. Saggio, F. Roccaforte, Appl. Phys. Lett. **105**, (2014) 142108.

[2] P. Fiorenza, G. Greco, F. Iucolano, A. Patti, F. Roccaforte, Appl. Phys. Lett. **106** (2015) 142903.

[3] P. Fiorenza, A. La Magna, M. Vivona, F. Roccaforte, Appl. Phys. Lett. **109**, (2016) 012102.

#123 - Temperature dependence of the I-V characteristics of Ni/Au Schottky contacts to AlGaN/GaN heterostructures grown on Si substrates

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AlGaN/GaN heterostructures are intriguing systems, combining excellent properties, like a wide band gap and a high critical field, with the presence of the two-dimensional electron gas (2DEG). These unique features allow the fabrication of high electron mobility transistors (HEMTs) operating at high power and high frequency. Besides the formation of good source-drain Ohmic contacts [1], the comprehension of the transport mechanisms at Schottky interfaces (gate) is required to control the HEMTs behavior. However, while Schottky contacts have been widely investigated on GaN, they are still under debate on AlGaN/GaN heterostructures, since the presence of the 2DEG can influence the barrier properties and must be properly considered.

In this work, the forward I-V characteristics of Ni/Au Schottky contacts on AlGaN/GaN heterostructures have been investigated at different temperatures, in the range 25-150 °C.

While the thermionic emission model led to high values of the ideality factor, a more exhaustive description of current transport was obtained by properly adapting to our AlGaN/GaN system a "two diode model", originally introduced for Schottky interfaces with other heterostructures (e.g., AlGaAs/GaAs) [2]. This approach considers a first diode (D1) at the metal/AlGaN interface and a second one (D2) related to the presence of the 2DEG at the AlGaN/GaN junction [3]. The barrier height Φ_{B2}, related to the diode D2, is an important physical parameter that depends on the heterostructure properties (e.g., band discontinuity, 2DEG carrier density, etc.). Using this model, and a combination of I-V and C-V measurements to experimentally determine Φ_{B2}, allowed to correctly extract the barrier height Φ_{B1} of the metal/AlGaN interface, both at the "zero bias" condition and at "zero electric field", i.e., in flat band condition. The electric value Φ_{B1} at zero bias resulted much lower (0.5-0.8 eV) than the Schottky-Mott predictions ($\Phi_B = \Phi_m^{Ni} - \chi^{AlGaN} = 1.44$ eV) and lower than the typical photoemission measurement values. In addition, it exhibited a dependence on the temperature, indicative of a non-ideal behaviour. On the other hand, the extracted flat band barrier height Φ_{BF} exhibited a higher value (1.37 eV), which was also consistent with the theoretical one expected for the Al-concentration (x=0.24) in our AlGaN layer. In addition, it resulted almost independent of temperature and consistent with literature photoemission results obtained in similar systems [4,5].

The proposed approach can have practical implications to predict and optimize the electrical behavior of Schottky gated GaN-based devices.

[1] G. Greco et al., Appl. Surf. Sci. **383,** 324 (2016).

[2] H-S. Chen et al., IEEE Trans. On Electr. Dev. **35**, 570 (1988)

[3] Y. Lv, et al., Journ. of Appl. Phys. **109**, 074512 (2011)

[4] D. Qiao et al., Journ. of Appl. Phys. **87**, 2 (2000)

[5] L.S. Yu et al. Appl. Phys. Lett. **73**, 3917 (1998)

#124 - Effects of surface preparation and thermal annealings on Al2O3 films deposited by ALD on AlGaN/GaN heterostructures

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In recent years, GaN-based high electron mobility transistors (HEMTs) have shown enormous progresses, in terms of high frequency and high power operation. Nevertheless, the choice of an appropriate gate insulator remains one of the crucial issues to be addressed. Moreover, since the frequency performances depend on the geometric aspect ratio between gate length and barrier thickness, also a precise control of the insulator thickness is required.

Atomic layer deposition (ALD) is a key enabling technique for GaN HEMTs, being a surface controlled layer-by-layer process for thin film deposition with atomic layer accuracy. In this context, since GaN-based substrates do not form a pristine interface with most oxides, studying the pre-deposition surface treatments is very important, due to the potential impact on the nucleation of the oxide layer and, hence, on its dielectric quality.

In this work, the effects of several AlGaN/GaN surface pretreatments before ALD growth have been studied by monitoring the structural and electrical characteristics of the Al_2O_3 films.Al_2O_3 thin films were deposited byPlasma Enhanced-ALD) from trimethylaluminium precursor and oxygen plasma at 250°C [1]. Before deposition, the substrate surfaces were treated for 10 min with the following solutions: A) H_2O_2:H_2SO_4 (piranha), B) HF+HCl and C) piranha+HF. TEM analysis revealed adherent and uniform films with thicknesses of 27-28 nm. However, a different structural evolution has been observed under electron beam effect during TEM. In particular, the formation of polycrystalline grains was observed on sample A, while epitaxial layers were formed for samples B and C. This is an indication that in case of HF-based treatments, the PEALD deposition occurred on very clean AlGaN surface, which can act as seed layer for the formation of epitaxial films when some energy is provided. The surface morphology, monitored by AFM, was smoother for Al_2O_3 films grown on HF-treated surfaces [2]. On the basis of these results, an insight into the initial growth stages has been performed. In particular, 3 nm Al_2O_3 layers have been deposited and investigated by further AFM investigation which demonstrated that the smallest three-dimensional grain nucleation resulted in deposition on HF-HCl treated surfaces [3]. The effect of post-deposition annealings in different atmospheres (such as oxygen or nitrogen) on the electrical characteristics have been also preliminarily discussed, providing useful guidelines for the definition of a fabrication flow for AlGaN/GaN HEMTs using Al_2O_3 films as gate insulator.

[1] E. Schilirò, G. Greco, P. Fiorenza, C. Tudisco, G. G. Condorelli, S. Di Franco, F. Roccaforte R. Lo Nigro, Phys. Status Solidi C **12**, (2015) 980.

[2] R. Lo Nigro, E. Schilirò, G. Greco, P. Fiorenza, F. Roccaforte, Thin Solid Films, in press.

[3] R. Lo Nigro, G. Greco, P. Fiorenza, F. Roccaforte, E. Schilirò, J. Vac. Sci.&Tech, A, submitted.

#125 - Structural and electrical properties of Al2O3 films grown by Atomic Layer Deposition onto thermally oxidized 4H-SiC

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Silicon dioxide (SiO_2) is the gate dielectric typically used for 4H-SiC MOSFETs. However, owing to the permittivity vales of SiO_2 and 4H-SiC (3.9 and 9.7), the electric field in the SiO_2 is 2.5 times higher than in the 4H-SiC drift layer. Hence, to fully exploit the electric field strength of 4H-SiC (3MV/cm), the field in the SiO_2 gate need to approach its breakdown value, which in tun can seriously compromise the device reliability. A possible solution to this problem is the replacement of the SiO_2 with a high permittivity (high-κ) dielectric, to reduce the electric field in the gate oxide during high-voltage operation. Among the high-κ materials, aluminum oxide (Al_2O_3) has been widely investigated, owing to its high permittivity (κ~8.4), relatively large band-gap (~ 9 eV) and high critical electric field (10 MV/cm). However, several physical issues still limit the electrical performance of Al_2O_3 layers on SiC, such as the low band offset with SiC, a high leakage current and significant charge trapping phenomena occurring during MOS devices operation.

In this work, the Al_2O_3 films have been grown by Plasma Enhanced-Atomic Layer Deposition (PE-ALD) onto a thermally oxidized SiO_2 interlayer on4H-SiC substrates.The morphological and structural properties of the insulator have been evaluated by Atomic Force Microscopy (AFM)and Transmission Electron Microscopy (TEM), respectively. Smooth, adherent and amorphous Al_2O_3 films with an uniform thickness of 30 nm, were found.

The electrical behaviour of the Al_2O_3/SiO_2 system has been studied by capacitance-voltage (C-V) and current-voltage (I-V) measurements, on metal-insulator--semiconductor (MIS) capacitors. Films with a permittivity close to the ideal Al_2O_3 value (ε~8.4), low leakage current and high breakdown field (9.2 MV/cm), were found. However, significant electron trapping inside the Al_2O_3 (1×10^{12} cm^{-2}) was observed at positive bias stress (>10V). To explain the origin of this phenomenon, C-V measurements at different temperatures were acquired. Thesemeasurements provide the activation energy related to the trapping process (0.1 eV) [1], which can be associated to points defects in the Al_2O_3 (oxygen vacancies, carbon contaminations). These results represent a step forward in the comprehension of the trapping phenomena in Al_2O_3 films for 4H-SiC devices and, consequently, pave the way to define a strategy to improve its electrical properties.

[1] E. Schilirò, R. Lo Nigro, P. Fiorenza, F. Roccaforte, AIP Advances **6**, (2016) 075201.

#126 - Enhanced H2 production over multilayer WO3 photoanodes prepared by RF-magnetron sputtering

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The photocatalytic cleavage of water is a fascinating topic in the field of solar energy conversion and storage, to provide clean and renewable H_2.

Photocatalytic activity depends on the electronic structure of photoactive materials, determined by their crystal structure and surface morphology. Tungsten oxide is highly interesting as a semiconductor photocatalyst (E_g = 2.6-2.8 eV), enabling efficient light absorption and activity under visible sunlight at $\lambda < 500$ nm.

Nano-structured WO_3 photolectrodes can be much more active than bulk WO_3. Apart from possessing a high surface-to-volume ratio, fundamental for photocatalysis, nano-WO_3exhibits structures and morphologies with unique properties –optical, charge transport and electronic band structure –not existing in the bulk.

In this work, evolution of pure $H_2$and $O_2$by water photosplitting was attained in a two compartment photoelectrocatalytic (PEC) cell [1] employing nanostructured WO_3 photocathodes. WO_3 films were depositedon tungsten foil substrates (purity 99%, 4 cm^2) by reactive RF (13.56 MHz) Magnetron Sputtering [2], starting from a 3-inch W target (purity 99.99%) in O_2/Ar mixtures at different O_2 content (10÷40 %, purity 99.99%) and at various total growth pressure (1.7–3 Pa).Background vacuum level in chamber was less than $1x10^{-6}$ mbar.Multilayered WO_3 coatings were also obtained (2 and 4 layers) by changing the total gas pressure during the deposition. The deposition time was adjusted in order to keep the overall film thickness around 1 mm. After deposition, the coatings were calcined in air at 600°C.

The photoanodes were characterized by XRD, SEM and UV-vis-NIR diffuse reflectance spectroscopy. Their photocatalytic activity was evaluated by Incident Photon-to-Current Efficiency (IPCE) and photocatalytic water splitting measurements in a 3 electrode PEC cell (0.5 M Na_2SO_4 electrolyte solution at 1 V *vs* SCE).

Because of equivalent film thickness and post calcination treatment, all coatings show similar monoclinic crystal structure and optical band gap (around 2.8 eV).Growth conditions, including type of substrate, temperature and pressure, critically affect the final morphology of nano-WO_3. In our case, both the percent O_2 content and total gas pressure in the deposition chamber affect the photocatalytic performance of the films. In particular, the H_2 production rate increases with increasing both the O_2 content and the total pressure during deposition, *i.e.* by decreasing the oxygen vacancies and film density of the WO_3 films. The most relevant photocatalytic performance was attained with the multilayered films, the H_2 production rate increasing from 20.4 mmol h^{-1} cm^{-2}, in the monolayer film, up to 35.6 mmol h^{-1} cm^{-2}, attained with the four layered film.

[1] G.L. Chiarello, C. Tealdi, P. Mustarelli, E. Selli, *Materials*, 9 (2016) 279

[2] M. Pedroni, et al, *Thin Solid Films*, in press, DOI: 10.1016/j.tsf.2016.08.010

#127 - Energy storage by hydrogen adsorption on commercial activated carbons

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Hydrogen is one of the most promising candidate as alternative energy carrier because of it's high gravimetric energy density (39,4 kWh/Kg), three times higher than the normal fossil fuels; unfortunately it has a very low volumetric energy density (1 bar and 25°C: 0,003 kWh/L) compared to the other common fuels (~10 kWh/L).

The hydrogen energy density is increased at 1,5 kWh/L by compression at high pressures (~700 bar) or at 3,3 kWh/L by liquefaction at -240 °C. Nevertheless, both technologies have some issues that are limiting their use for mobile application.

A possible alternative method is represented by storage in solid via physisorption. Since this process is limited by the solid surface, the higher the available surface the higher the amount of hydrogen stored. For this reason, in the past years, materials exhibiting high specific surface areas (SSA) has been studied for hydrogen storage. Among the investigated materials activated carbons (aC) shows a great potential considering their chemical stability, lightness, pore size tunability, thermal conductivity and their easy and inexpensive production from a wide range of organic raw materials.

In this work, different standard techniques were performed to characterize the hydrogen adsorption on commercial aC correlating their structural parameters to the storage performances. Three different samples are chosen by their pore size distribution (PSD) representative of three families of pores: small pores (pore size < 7Å), useful pores (pore size 7÷13 Å) and wide pores (pore size >13 Å).

Hydrogen adsorption/desorption isotherms were performed up to 20 bar in the range of 77÷117 K by using a volumetric apparatus and absolute and net hydrogen storage are determined. Further analysis as nitrogen adsorption, thermal desorption spectroscopy (TDS), enthalpy evaluation, scanning electron microscopy (SEM), and x-ray diffraction (XRD) analysis complete the samples characterization.

Particularly, this work focuses on the usable capacity, i.e. the amount of hydrogen really deliverable, and the determination of best operational temperature. In this regard, we verified that the presence of small pores is a decisive structural parameter because they increase the enthalpy of adsorption and in some situation cause an interesting phenomenon of hydrogen trapping, which may allow a higher operational temperature.

#128 - Performance and durability of advanced materials for water splitting in a PEM electrolyser in the HPEM2GAS project

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Performance and durability of advanced materials for water splitting in a PEM electrolyser in the HPEM2GAS project

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Hydrogen produced from water electrolysis can play a significant role as energy storage. Electrolysis can support the electricity grid in terms of power quality, frequency and voltage control, peak shaving, load shifting and demand response. The overall objective of the HPEM2GAS project is to develop, validate and demonstrate robust, flexible and rapid-response self-pressurising PEM electrolyser technology based on advanced cost-effective components and using novel solutions for interfacing to the grid.

Membrane-electrode assemblies (MEAs) designed for polymer electrolyte membrane (PEM) water electrolysis, based on a novel short-side chain (SSC) perfluorosulfonic acid (PFSA) membrane, Aquivion®, with various cathode and anode noble metal loadings, were investigated in terms of both performance and durability. Utilizing a nanosized $Ir_{0.7}Ru_{0.3}Ox$ solid solution anode catalyst and a supported Pt/C cathode catalyst, in combination with the Aquivion® membrane, gave excellent electrolysis performances exceeding 3.2 $A\cdot cm^{-2}$ at 1.8 V terminal cell voltage (~80 % efficiency) at 90 °C in the presence of a total catalyst loading of 1.6 $mg\cdot cm^{-2}$. A very small loss of efficiency, corresponding to 30 mV voltage increase, was recorded at 3 $A\cdot cm^{-2}$ using a total noble metal catalyst loading of less than 0.5 $mg\cdot cm^{-2}$ (compared to the industry standard of 2 $mg\cdot cm^{-2}$). Steady-state durability tests, carried out for 1000 h at 1 A·cm^{-2}, showed excellent stability for the MEA with total noble metal catalyst loading of 1.6 mg·cm^{-2} (cell voltage increase ~5 µV/h).

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#129 - Composite material based on Mn oxide anchored on a polymeric matrix for hydrogen storage application

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One of the great drawback to the widespread use of hydrogen as a non-polluting fuel for automotive is the lack of a safe and efficient system for on-board storage. The most investigated approaches include hydrogen storage as a liquid at low temperatures, as a gaseous H2 at high pressures or as an atomic hydrogen in a metal hydride. Each of these methods presents a high potentiality even if different engineering problems have been reported. Actually, the interest has been addressed towards the use of the microporous material able to work under moderate pressure and cryogenic temperature. Some of them such as activated carbons and zeolites as well as the more recently developed metal-organic frameworks (MOFs) have been investigated for this application. The organic materials, such as polymers, may offer a significant advantage due to their composition based on light elements. However, only very recently the polymers have been evaluated as materials for H2 storage. In this work, a Poly(ether ether ketone) (PEEK) was chosen as a base polymeric matrix with the aim of producing a low cost and weight hydrogen storage material. The polymer acts as a support for the insertion/anchoring of a manganese oxide, through a substitution in situ reaction between the chloride of the chlorine-sulphonic group of the PEEK and potassium permanganate used to produce the above mentioned oxide [1-2]. A deep characterization of the prepared materials was carried out. Different MnO2 loadings were selected for this investigation in order to understand the relation between the oxide content, chemical-physical characteristic and the H2 sorption properties. In particular, the prepared materials were studied in terms of morphological, structural and H2 sorption/desorption properties. In order to understand the H2 sorption capability, a volumetric analysis (Sievert apparatus) was carried out on each sample at different temperatures and pressures. From these measurements, the sample containing a low oxide content has revealed a very low H2 sorption capability, on the contrary, the sample with highest oxide content shows a very promising H2 sorption. On the latter sample, H2 sorption/desorption cycles were performed demonstrating the reproducibility and reversibility of cycles.

Acknowledgments

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References

[1] R. Pedicini, A. Saccà, A. Carbone, E. Passalacqua, Int J Hydrogen Energy 36, 2011, 9062-9068.

[2] R. Pedicini, B. Schiavo, P. Rispoli, A. Saccà, A. Carbone, I. Gatto, Energy 64, 2014, 607-614.

#130 - Magnesium-based compacted systems for hydrogen and heat storage

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Hydrogen-based economy development requires some technical aspects to be overcome and in particular hydrogen storage. In this field magnesium hydride is a promising material, in particular for stationary applications, due to the reversibility of the reaction of magnesium with hydrogen. Moreover magnesium is widespread on the earth and environmentally compatible. 7.6 wt% of hydrogen, which is one of the highest values among reversible hydrides, could be theoretically stored in MgH_2. About 75 kJ/mol H_2 is the heat evolved during an absorption reaction and for this reason MgH_2 is taken into consideration for heat storage. For these applications one of the main problem is related to the heat management in the reactors. The use of loose powders inside reactors demonstrated to be detrimental for the performances of these systems with cycling due to powder sintering, gas hydraulic losses and particle entrainment in the gas flow. The preparation of compacted powders in the form of pellet demonstrated to be a suitable route for improved reactors. In fact by adding suitable agents it is possible to enhance thermal conductivity of the bed of hydrides, in particular along radial direction, and mechanical stability of the pellets to cycling. Carbon based materials have been tested and demonstrated to be suitable for these purposes. For these reasons pellets have been prepared by pressing ball milled powders of MgH_2 with niobium oxide (Nb_2O_5) and expanded natural graphite (ENG). Ball milling allows to increase the hydrogen mobility within the metal matrix by refining particles' dimension and by creating defects. Moreover a catalyst could be inserted in the particles obtaining improved kinetics. During cycling the pellets tend to swell and this causes the rupture of the pellet with the tendency to become powder again. In order to contrast the swelling with cycling a procedure has been developed which consists in coating the pellets with a metal on its surface. The metal has been coated by sputtering or by evaporation in a vacuum chamber. The quantity of metal deposited is lower than 0.1 wt%. The behavior of these compacted systems has been studied both in terms of kinetics and total hydrogen capacity, but also in terms of microstructure. The compacted systems prepared with this procedure demonstrate higher mechanical stability after 50 cycle respect to the uncoated pellets. The kinetics and the total hydrogen capacity remained unchanged.

#131 - Laser processing of TiO2 colloids for an enhanced photocatalytic water splitting activity

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In the last years, photocatalysis with TiO_2 was applied successfully to several processes, including hydrogen production via water splitting and decomposition of organic pollutants in water. Many investigations have demonstrated that Ti^{3+}-containing (blue) TiO_2nanoparticles, possessing oxygen vacancies, exhibit significant photocatalytic activity in the visible and UV regions. Thermal annealings (under vacuum or using reducing agents) or treatment by hydrogen plasmas were reported to produce reduced TiO_2 containing surface Ti^{3+}, but these methods inevitably involve severe barriers for a practical implementation. TiO_2 sub-micrometer spheres were formed with an 'in situ' joining process by laser irradiation process using UV and/or Visible nanosecond pulsed laser beams.

The photocatalytic water splitting activity of these laser modified titania colloids have been measured, comparing the obtained increased activity with their initial crystalline phase and with the morphological and chemical modifications induced by the laser process. Photocatalysis has been tested using UV and visible light. We have found that laser irradiation increases the hydrogen production efficiency up to a factor of three for anatase, rutile and P25. A hydrogen production rate as high as 30 mmol g^{-1} h^{-1}has been obtained with good stability, tested by repeated runs. The chemical and morphological properties of the nanoparticles have been studied by electron microscopy, X-ray photoelectron spectroscopy and Raman spectroscopy, showing that laser irradiation promotes the formation of disordered surface state and lattice distortion which could be responsible for the observed enhanced photocatalytic activity. The as-developed strategy may open up a new avenue for designing and functionalizing TiO_2 materials in order to enhance visible light absorption, to get band gap narrowing, and improve photocatalytic activity.

#132 - Theoretical study of hydrogen storage in modified carbon-based nanostructured materials

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The hydrogen storage problem is one of the major challenges on the way to hydrogen based energetics. When using hydrogen as a fuel, one needs a safe and capacious fuel tank to store it on board in a sufficient amount. Among the methods of storage which are currently under study and development, the physical adsorption (physisorption) of molecular hydrogen on the large surface of nanostructured materials has certain advantage. It may operate at moderate temperature and moderate pressure range, and provides high charging/discharging rates. The problem here is to provide the sufficient gravimetric storage capacity (at least 6%). The carbon nanostructured materials (activated carbon, carbon nanotubes, etc.) have been intensively studied recently as candidates for the hydrogen storage medium. They have large surface area and rigid structure, but the binding energy to the molecular hydrogen is relatively small. This gives small values of the gravimetric storage capacity of pure carbon materials (~0.5% at 300K and 1-2% at 77K).

We suggest and discuss [1-2] a strategy of modification (doping) of carbon based structures in order to improve the molecular hydrogen binding energy while remaining stable rigid nanostructures possible. Modeling of the adsorption isotherms shows that both the gravimetric and the volumetric hydrogen storage capacity of the new materials would fit the target values stated by the US Department of Energy.

[1] A.V. Avdeenkov, I.V. Bodrenko, D.G. Bessarabov, A.V. Bibikov, A.V. Nikolaev, M.D. Taran, A. Tokarev, E.V. Tkalya, “Thermodynamical model for hydrogen storage capacity in carbon nanostructures”// International journal of hydrogen energy 40, 4184 (2015)
[2] I.V. Bodrenko, A.V. Avdeenkov, D.G. Bessarabov, A.V. Bibikov, A.V. Nikolaev, M.D. Taran, and E.V. Tkalya, “Hydrogen storage in aromatic carbon ring based molecular materials decorated with alkali or alkali-earth metals“// Journal of Physical Chemistry C, 116, 25286 (2012)

#133 - Hybrid Organic-Inorganic Photoelectrochemical Systems: a new class of devices for the Sustainable Conversion of Solar Energy to Fuel

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The direct conversion of solar energy into fuels, H2 in particular, is still a challenge. Recently, organic and hybrid organic-inorganic photoelectrochemical systems emerged as an alternative to the usual transition metal oxides or more costly III-V semiconductors. Here we present different suitable architectures for hybrid organic-inorganic photoelectrochemical devices for the conversion of solar energy to H2. Starting from a prototypical P3HT:PCBM blend as photoactive element, we focused our attention on different interfacial layers and their influence on the photocathode performances. The photoelectrocatalityic activity and stability of a catalysed bulk heterojunction is proven and the effect on hydrogen generation performances of properly engineered selective contacts is investigated. Introduction of an electron selective layer is found to increase the photocurrent response, while a hole blocking layer shifts the onset potential towards positive voltages allowing operation in a electrical region compatible with a tandem photoanode and/or a PV cell. The relevance of our findings can be summarized in few key points: (i) high performances with a maximum photocurrent of 8 mA/cm2 at 0 V vs RHE and 50% IPCE; (ii) 100% faradaic efficiency along the whole electrode’s lifetime; (iii) excellent energetics with onset potential as high as +0.7 V vs RHE; (iv) promising operational activity of several tens of hours and (vi) by-design compatibility for implementation in a tandem architecture [Fumagalli et al. JMCA (2016), Comas et al. EES (2016)]. Moreover, we investigated the influence of photocathode nanostructuration, developing a 3D multi-layered system based on a nanostructured hole selective scaffold, in host/guest architecture. This allowed us to demonstrate efficient devices with an active layer thickness as low as 20 nm, thanks to the orthogonalization of light absorption and carrier collection. Finally, we demonstrate the realization of an efficient and cost-competitive “all-solution processed” photocathode with and without a non-precious catalyst. Such a system exhibits 4mA/cm2 at 0 V vs RHE, an onset potential of 0.4 V at RHE and stability of over 1hr. Collectively, this set of features establish the hybrid architecture we developed well ahead of existing reports on organic photoelectrochemical systems and suggest the potential of the hybrid organic-inorganic photoelectrochemical (HOPEC) concept as real contender to the traditional inorganic counterpart. This work opens up the way to the exploration of the rich library of organic semiconductors developed for OPVs in photoelectrochemistry and to the realization of a new generation of large area, solution processed tandem water splitting devices for renewable and low cost direct conversion of solar energy into hydrogen.

#134 - GLYCOSYLATED BIOMATERIALS: CHALLENGES AND OPPORTUNITIES

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Biomaterial surfaces play an extremely important role in the response of artificial medical devices to the surrounding biological environment. The functionalization of biomaterials with biomolecules, to promote a specific biological response, is a smart strategy to increase the chances of local regeneration. Different classes of biomolecules have been used to produce cell-responsive biomaterials, but until now glycans have been neglected despite it is now well established that they are involved in a plethora of molecular recognition bioprocesses. Glycan interactions with their receptors play a fundamental role in various critical intra- and intercellular events, encoding information that regulates interactions between cells and the extracellular matrix (ECM). On the basis of these premises, the use of saccharidic motifs has undoubted attractiveness for the functionalization of synthetic or natural materials to generate innovative and smart scaffolds with the capability to interact with the biological environment. The surface modification of materials with bioactive carbohydrates is an easy way to fabricate smart materials.

Different strategies for the surface modification of several materials with carbohydrates useful for regenerative medicine will be outlined, including polypropylene [1], PCL [2], collagen [3], hydroxyapatite [4, 5]. Biological behaviour of the functionalised materials with different cell lines will also be presented.

References

[1] L. Russo, S. Zanini, C. Riccardi, F. Nicotra, L. Cipolla, Materials Today, **2011**, *14*, 164-169.

[2] L. Russo, T. Russo, C. Battocchio, F Taraballi, A. Gloria, U. D'Amora, R. De Santis, G. Polzonetti, F. Nicotra, L. Ambrosio, L. Cipolla, *Carbohydr. Res*. **2015**, *405*, 39.

[3] L. Russo, A. Sgambato, M. Lecchi, V. Pastori, M. Raspanti, A. Natalello, S. M. Doglia, F. Nicotra, L. Cipolla, *ACS Chem Neurosci*. **2014**, *5*, 261.

[4] L. Russo, E. Landi, A. Tampieri, A. Natalello, S. M. Doglia, L. Gabrielli, L. Cipolla, F. Nicotra *Carbohydr. Res*. **2011**, *346*, 1564.

[5] L. Russo, F. Taraballi, C. Lupo, J. Jiménez-Barbero, M. Sandri, A. Tampieri, F. Nicotra, L. Cipolla, *RSC Interface Focus* **2014**, *4*, 20130040

#135 - Plasma deposited free-standing Nanofilms with bio-functionality

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Free-standing nanofilms (NFs) are new class of polymeric nanomaterials with thickness in the order of few tens – hundreds of nanometers,characterized by peculiar features as ultra-conformability, and the possibility of being through a syringe without losing integrity. [1] NFs have been used in many applications ranging from nanopatches for closing incisions in surgery [2], to platforms for tailored cell-substrate interaction [3]. In this work we present a new and versatile method to obtain self-supported free-standing plasma-deposited coatings NFs using atmospheric (AP) and low pressure (LP) plasma assisted deposition (PE-CVD) processes.

NFs can be fabricated by single step spin-assisted deposition in in combination with a sacrificial layer and/or a supporting layer [4,5]. PolyVinyl Alcohol (PVA) has been spin-coated on SiO_2 substrates and used as a sacrificial layer. A LP deposition/sputtering process [6] fed with vapors of DiEthylene Glycol DiMethylEther (DEGDME) and argon was performed directly on PVA-coated substrates to fabricate polyethylene-oxide (PEO)-like coatings with (Ag/PEO-like) or without silver nanoclusters embedded [7,8]. In the atmospheric plasma process, a layer of polylactic acid (PLA) was deposited onto the PVA layer. PVA/PLA silica substrates were then coated with a nano/biocomposite PE-CVD coating composed of a hydrocarbon matrix embedding vancomycin molecules.

Plasma deposited free standing NFs with thickness in the range 50-400 nm has been asily obtained after dissolution of the PVA layer in water. PEO-like NFs retained their non fouling properties; Ag/PEO-like and PLA/C_2H_4/vancomycin NFs shown antibacterial properties.

This work is one of the few examples that demonstrate the possibility to deposit free-standing NFs by plasma assisted technology and opens the way to the use of plasma-deposited NFs in several biomedical applications ranging from drug delivery to tissue engineering.

References

[1] T. Fujie et al. Adv. Mat. 19, 3549, 2007.

[2] Y. Okamura et al. Adv. Mat. 21, 4388, 2009.

[3] T. Fujie et al. Langmuir, 27, 13173, 2011.

[4] Y. Okamura et al. Coll. & Surf. a, 318, 184¸ 2008.

[5] Pignatelli et all. Plasma Polym. and Process. 2016. (accepted)

[5] Patent WO2013021409-A1: E. Sardella, P. Favia et al. 2013.

[6] R. d'Agostino, P. Favia, F. Fracassi, E. Sardella, C. Costagliola, A. Mangone, patent WO 2013021409 A8.

[7] M. G. Katsikogianni et al. J. of Biomat. and Nanobiotec., 2013, 4, 30-40

#136 - Functionalized Nanoparticles Inhibiting β2m Fibrillogenesis

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The interaction between proteins and nanoparticles (NPs) is becoming more and more central to several nanotechnological applications [1]. We have recently addressed the behavior of gold nanoparticles stabilized by a shell of citrate surfactants (Cit-AuNPs) with the amyloidogenic protein β_2-microglobulin (β2m) [2]. β2m is responsible for dialysis related amyloidosis (DRA) affecting long-term hemodialysed individuals [3]. Contrary to expectations, no clear aggregation promotion was detected in the presence of Cit-AuNPs, by NMR evidence showing that β2m globular structure is stable and that there is a protein domains preferentially involved in the interaction with the NP surface [2]. In this paper we report the influence of NPs on the fibrillation process of β2m, using a naturally occurring mutant, namely D76N β2m with asparagine substitution for aspartate at position 76. This mutanthas been shown to readily form amyloid fibrils *in vitro* under physiological extracellular conditionsand to be responsible for an aggressive systemic amyloidosis. Its interaction with Cit-AuNPs was characterized by a comprehensive investigation including *multi-scale* modeling (classical atomistic molecular dynamics and rigid-body protein-surface docking), NMR and the fibril formation was analyzed by three different methods: thioflavin T fluorescence, native agarose gel electrophoresis and transmission electron miscroscopy. Our results indicate that AuNPs are able to inhibit D76N β2m fibrillogenesis through the formation of long-life complexes that competes with the binding to other proteins [4].

References.

[1] M. Assfalg *et al*. *Biochimica et Biophysica Acta*, **1864**, 102-114 (201)

[2] G. Brancolini *et al*. *ACS Nano*, **9**, 2600-2613 (2015)

[3] (i) Mangione, P. P. *et al.*, *J. BIOL. CHEM.,* **2013**, *288*, 30917-30930 (ii) G. Esposito *et al. SUBCELL BIOCHEM.*, **2012**, *65*, 165-83.

[4] G. Brancolini *et al*. (2016) *in preparation*

#137 - REAL TIME MONITORING OF BIOMATERIALS AND BIOINTERFACES BY QUARTZ CRYSTAL MICROBALANCE

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Biomaterials research require a particular attention on the analysis of biological interactions with different surfaces. To evaluate biomolecular interactions relevant to human health such as antigen-antibody, cancer cell- cytoskeleton inhibitors, biomaterial surface- adsorbed proteins or aptamers- toxins a sensitive and specific method is requested. Quartz crystal microbalance (QCM) is a useful label free and real-time tool to monitor bio-interactions with high sensitivity and with a number of diverse surface chemistries.

In this field, we have developed specific protocols for detecting pancreatic ductal adenocarcinoma (PDAC) markers with QCM optimizing surfaces less sensitive to non-specific interactions with the final target of studying the interactions between synthetic phosphorylated and un-phosphorylated α-enolase peptides, immobilized on the gold surface of the QCM sensor, with sera of healthy and PDAC patients [1].

Another specific protocol was developed for studying with QCM the impact of small molecule inhibitors on the dynamics of the cytoskeleton of the malignant cell lines MCF-7 adhered to the surface of the QCM sensor: effects of cytochalasin D, Y-27632 and taxol were detected by analyzing changes in the resonance frequency and dissipation factors. The different viscoelastic fluctuations have been correlated with the inhibition mechanism of each drug [2].

In the contact lenses research we have also produced and characterized new fluoropolymer thin films, called P(S3-b-Sz)10 and P(S3-b-Sz)20 (P20) using atomic force microscopy and dynamic contact angle. QCM was used to investigate adsorption of the major proteins in tear fluid. The solutions of polymers were deposited on the QCM sensor and the protein adsorption was evaluated using an artificial solution of tear fluid. [3].

In a recent work, we used QCM to perform a screening of four thiolated ssDNA aptamers monolayers to find the most efficient one in the binding with ochratoxin A (OTA), a toxic fungal metabolite frequently occurring in a variety of foodstuffs [4]. The protocol developed allowed to establish the aptamer with higher affinity for OTA and to calculate the mass of OTA molecules that bind the surface, without the contribution of the Ca^{2+} ions mass of the buffer chelated to the aptamers.

References

[1] M. Bianco, et al. Biosens. Bioelectron 42, 646 (2013)

[2] Xi J Chen et al. J Biochip Tissue chip S5: 001 (2013)

[3] M. Bianco et al. Sci. Adv. Mater. 7, 1387 (2015)

[4] M. Bianco et al. submitted to Sens Actuators B Chem, Major revisions (August 2016)

#138 - Cavity optomechanics using a functionalized silicon nitride membrane: cooling and non-linear dynamics

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Optomechanics is a rapidly expanding field focused on the interaction between light and mechanical motion of a resonator. Optical back-action effects associated with photo-induced forces in an optical cavity are used to decrease the mechanical energy of the mode, showing promise for both applications and fundamental investigation.

Applying the cavity cooling method to optically active semiconductors offers additional interesting prospects, because of their internal electronic degrees of freedom. Engineered semiconductor devices enable strongly enhanced light-matter interactions, while organic materials offer a much broader dynamical range of parameters and are easier to process compared with inorganic semiconductors.

We investigate the optomechanical properties of a cavity containing, as a mirror, a multilayer membrane composed by the molecular organic semiconductor tris(8-hydroxyquinoline) aluminum (Alq_3), silver and silicon nitride, for a total thickness of 130 nm. Excitation is examined at two laser wavelengths: 405 nm, in the absorption spectrum of the Alq_3 and 780nm. We study the photothermal cooling of the first oscillatory modes of the membrane, through the measure of its Brownian motion by using an external probe light and a beam deflection method. Cooling is observed for blue detuning, showing the dominance of photermal effects over radiation pressure. The results are compared with those obtained for a bi-layer membrane, composed of silver and silicon nitride.

We ananlyze the multiple scale dynamics induced by phototermal effects and radiation pressure. Multi-stable regions are observed; instabilities arise depending on the laser power and detuning from resonance. We study the stability of the system using an analytical model in which the response of the photo-thermal force to changes in the cavity field is described by a delay function. We find that the Hopf bifurcation points lie in the range of detuning values for which the mechanical modes are heated.

#139 - Low cost and reproducible strategies for the fabrication of gold nanostructures on large area

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Plasmonic nanostructures provide new ways of manipulating light at nanoscale, moreover thay exhibit optical properties never before seen in the macro-world. The strong absorption and scattering properties they show are due to the excitation of Localised Surface Plasmon Resonance (LSPR) upon interaction with light in a proper wavelength range. Such properties are very sensitive to changes in the refractive index of the surrounding medium. Any modification of the nanoparticles surface can be detected in a label-free manner, exploiting the red-shifts in the LSPR spectral position. This principle is exploited for the realization of label free optical sensors for the detection of chemical and biological species. Several strategies can be used to this purpose, such as the advanced structural design and optimization of the metal transducers using computer simulation, the employment of innovative nanofabrication techniques, the development of sensitive plasmonic detection systems and finally the accurate functionalization of the sensing surface. The most used fabrication methods for metallic nanostructured systems, such as EBL and FIB, are less accessible choices for scientists and industrial applications due to their critical drawbacks, like low speed and high-cost. In this work, different chemical and physical strategies for the deposition of plasmonic transducers on planar substrates are proposed in order to investigate their sensing performances and reproducibility. These fabrication methods are particularly suited for the growth of large-areas and low-cost plasmonic nanostructures with tailored optical functionalities, providing an interesting alternative to sequential and very expensive manufacture techniques. The ultimate goal is the improvement of the sensor performances, including the sensitivity, accuracy, precision, repeatability, and lowest detection limit. These high-throughput methods, developed by the optical sensor group of CNR-IMM of Lecce, enable the fabrication of nanostructured plasmonic materials with possible applications as opto-chemical and biological sensors. In order to achieve sharp LSPR resonances in the visible range, the geometry of the fabricated transducers have been analyzed through numerical modeling, correlating their optical, morphological and functional properties. The models give an explanation to experimental data and allows predicting the optical properties of different nanoparticles systems. Finally, the possible application of the investigated materials as LSPR sensors have been demonstrated, presenting several strategies for the enhancement of their sensing performances.

#140 - Smart Diamond Like Carbon-cotton textiles: flexible and versatile systems for innovative applications

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Diamond-like Carbon (DLC) is an amorphous carbon based material, well known in the industrial field due to its properties (high hardness, low friction, high wear resistance, chemical inertness, high electrical resistivity), depending on the amount of sp^2 and sp^3 electronic configurations and on the hydrogen content.

Cellulose textiles have been functionalised through the deposition of a homogeneous layer of DLCby plasma enhanced chemical vapour deposition (PECVD) techniquefor the development of smart super-Hydrophobic/super-Oleophilic cotton systems.

Changing from hydrophilic to hydrophobic through the deposition of a DLC coating and the introducing a dual-macroscopic and nanoscopic scale structure on the cellulose textile without introducing any harmful chemicals, permits to obtain selective "oil-removing" membranes, showing an high effective oil-water separationbehaviour, while completely repelling water. In addition, it is possible to further modulate the hydrophobic character, by simply undergoing the cotton textile to an opportune plasma pre-treatment before the DLC deposition.

These smart DLC-cotton systems showed high oil-water separation selectivity, absorption capacity and recyclability. These low-cost easily recyclable smart systems present also enhanced stability towards corrosive liquids, resistance to oil fouling and self-cleaning properties. Moreover, the choice of the deposition conditions could allow the precise tailoring of the surface properties of the plasma-treated textile to maximize the flammability resistance and the thermal stability.

These smart super-hydrophobic/super-oleophilic DLC systems could find several innovative applications in textile fields as self-cleaning fibers, in water purification fields as water/oil separation membrane, in safety fields as potential flame retardant materials.

#141 - Platinum nanoclusters on graphene/Ir(111):Insights from ab-initio calculations and experiments

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Fabrication of ordered arrays of metallic nanoclusters (NCs) for catalysis applications is the goal of many efforts. The moire' pattern of graphene/Ir(111) works as an efficient template to this purpose, in particular for the growth of Pt and Ir based NCs, as predicted by ab-initio calculations and observed for different metal loadings. Using DFT calculations and STM measurments we were able to understand the behavior of Platinum NCs on graphene/Ir(111). The chemical and the morphological behavior of those NCs upon interaction with small molecules of enviromental importance such as carbon monoxide is investigated with atomic-level detail from ultra-high vacuum to near ambient pressure by both spectroscopy and microscopy approaches

#142 - Antimicrobial Activity of TiO2 Coatings by Direct Thermophoretic Deposition of Flame-Made Nanoparticles

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This work reports the development of a one-step method for the production of antimicrobial protective coatings for aluminum surfaces with titania nanoparticles. An aerosol flame synthesis system was used to produce monodisperse, ultra-fine TiO_2 nanoparticles, which were directly deposited by thermophoresis onto plates of aluminum alloy by means of a rotating disc. Fuel-lean reactor conditions were used to synthesize pure anatase nanoparticles of 3.5 nm in diameter. Particle and coating characterization was performed by means of Differential Mobility Analysis, Raman and X-Ray Diffraction spectroscopy. Substrates were mounted onto the rotating disc that repetitively passes through the flame. Convection due to the rotational motion cooled the substrates, on which particles were deposited as films by thermophoresis. Such a system allowed to obtain submicron coatings of different thickness and porosity, by varying the total time of deposition (t_{des}=10 s, 30 s and 60 s).

The antimicrobial activity of TiO_2 coatings was tested against the dimorphic fungus *Candida* albicans (ATCC SC5314), the Gram positive bacteria Staphylococcus aureus (ATCC 6538), and the Gram negative bacteria Salmonella Typhimurium. To determine the inhibition of biofilms formation, microbes were plated on TiO_2 coatings and a semi-quantitative colorimetric assay was performed using crystal violet. The tests showed that the TiO_2 coating obtained with t_{des}=10 s completely inhibits Candida biofilm formation, and inhibits up to 70-80% Staphylococcus aureus biofilm formation. The inhibition of biofilms formation was confirmed by means of Scanning Electron Microscopy observation. The results of the present work are promising for using titania films as protective coatings for applications where an antimicrobial activity is required, such as self-cleaning materials able to reduce microbial infections.

#143 - Black-Diamond High-Temperature Cells for Solar Concentrating Systems

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High-temperature solar cells are possible by exploiting the Photon-enhanced Thermionic Emission (PETE) concept, which represents a novel and very attractive mechanism for the exploitation of solar radiation, especially if concentrated, and characterized by promisingly high conversion efficiency (>50%). PETE converters rely on the concept that engineered semiconductor photocathodes can provide an electron emission, induced by hot-electrons produced by photons with sufficient energy, combined to a thermionic emission, sustained by the high temperatures induced by every other thermalization process.

Surface nanotexturing combined to surface-hydrogenation, aimed at achieving negative electron affinity conditions and a work function as low as 1.7 eV with an emitting-layer nitrogen-doping, are here proposed as a radically new and efficient PETE cathode completely based on chemical-vapour-deposited (CVD) diamond, able to operate up to temperatures of 800 °C. CVD diamond is transparent to solar radiation due to its wide bandgap, consequently advanced and novel techniques are needed for implementing a defect-engineering strategy and thus processing diamond to become an efficient sunlight absorbing material: the black diamond

[1, 2]. Surface texturing by fs-laser, boron-implantation, buried and distributed graphitic structures allow for the fabrication of an innovative defect engineered black diamond cathode, to be efficiently exploited for the conversion of concentrated solar radiation.

The final results of the recently concluded European FET project ProME^{3}THE^{2}US^2 (www.prometheus-energy.eu, GA 308975) will be discussed to support the feasibility of the proof-of-concept.

[1] P. Calvani, A. Bellucci, M. Girolami, S. Orlando, V. Valentini, R. Polini, and D. M. Trucchi, “Black Diamond for Solar Energy Conversion”, Carbon 105 (2016) 401-407.

[2] A. Bellucci, P. Calvani, M. Girolami, S. Orlando, R. Polini, and D. M. Trucchi, “Optimization of Black Diamond Films for Solar Energy Conversion”, Applied Surface Science 380 (2016) 8-11.

#144 - Effect of Eu concentration on the photocatalytic activity of Eu doped TiO2 Nanoparticles

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Uniform, spherical shaped europium-doped titanium dioxide nanoparticles (Eu-doped TiO_2 NPs) with different Eu/Ti ratios have been prepared using a low temperature, single-step wet chemical synthesis in the presence of acid oleic as capping agent. The as-prepared NPs were characterized by wide-angle X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), High resolution transmission electron microscopy (HRTEM), Raman spectroscopy, ultraviolet visible light spectroscopy (UV–vis), respectively.

The photodecomposition experiments have been carried out using methylene blue (MB) as probing molecule. The influence of the lighting conditions (UV and visible-light exposure) was also taken into account for evaluating the photocatalytic activity. Finally, all the Eu–doped TiO_2 NPs exhibited a strong red photoluminescence emission being dominated by the $^5D_0$-^7F_j transitions of Eu^{3+} ions, and are expected to be useful in many other applications.

#145 - Tailored polysulfone-graphene oxide composites for water remediation

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The continuous daily use of an increasing amount of organic contaminants is leading to the increased occurrence of a vast array of organic contaminants in urban wastewater system. Most of these substances, known as Emerging Organic Contaminants (EOCs), are not yet regulated and are recalcitrant/not completely removed during conventional wastewater treatments. Consequently, they are able to enter ground and even drinking water and due to their potential adverse effect of EOCs even at low concentration new treatments are highly desirable to minimize their impact on ecosystem. Here, we report the preparation of a new adsorbant for EOCs consisting of a composite of two different materials with synergic properties, i.e. polysulfone (PS), -hydrophobic and processable into highly porous 2D/3D membranes- and graphene oxide (GO), with strong affinity for organic compounds. GO-doped PS membranes (PS-GO) have been exploited to remove seven selected EOCs, including pharmaceuticals and personal care products, in their mixture, from tap water. An adsorption efficiency enhancement respect to PS only membranes, between 300-600 % and 300-800% depending on the pH, was found for carbamazepine and diclofenac respectively, i.e. two widely used pharmaceuticals that are most frequently found in ground water. The mechanism of adsorption in relation to the molecular structure and physical-chemical properties of the target contaminants is rationalized.

#146 - Novel synthesis of ZnO/PMMA composites for photocatalytic applications

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Water is essential for life, but for centuries it was taken for granted, until increasing pollution and reduction of potable water supplies delineated a need to protect our water reserve and develop new technologies to purify water for consumption. An innovative purification method involves the combined use of nanostructures and photocatalysis. Among the semiconductor photocatalysts, ZnO has received a great interest in the field of photocatalytic technology, due to its high photocatalytic activity under UV light irradiation (band-gap energy ~3.3 eV at 300 K), easy growth, low cost, and low environmental impact. Here we present an original, easy, and industrial scalable method to synthesize ZnO-polymer composites. Commercial poly (methyl methacrylate) (PMMA) powders were firstly coated with a thin layer of ZnO (80 nm thick) by ALD, and then the method of sonication and solution casting was applied to produce the ZnO/PMMA composites. The incorporation of nanostructured photocatalysts in polymers is a strategic way to obtain novel water purification systems, with the great advantage of avoiding the recovery of nano-particles dissolved in water after the treatment. The evolution of the materials, from the form of powders to the form of composites was deeply morphologically and structurally investigated, by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD) analyses. In addition, the photocatalytic performance in degrading methylene blue dye and phenol in water was tested under UV light irradiation, showing significant efficiency. The reported results demonstrate that the incorporation of active ZnO nano-material in a polymeric matrix is a powerful tool to overcome the post-recovery of catalyst particles after the water treatment, opening the route for the commercialization of nanostructured photocatalyst-based technology for efficient water treatment and purification.

#147 - Boiler Tube Failure Due to Flow Accelerated Corrosion in Kazeroon Power plant

Soha Mohajeri - Mapna

The failure of Drum & Economizer tubes of a boiler in Kazeroon Power plant occurred in 2015. An analysis of the failure was made by chemical and metallographic examinations and SEM studies.According to inspections, there were numerous small pits in fractured sections and inside surfaces of the failed tubes resembled orange peel which is a representative of Flow Accelerated Corrosion (FAC). The water chemistry of the boiler was examined and investigations revealed that water treatment was performed bytheAll Volatile Treatment method in which dissolved oxygen had been removed by the addition of hydrazine as an oxygen scavenger, and the pH of feedwater was maintained between 9~10 with the addition of ammonia, leading to the formation of a magnetite layer. It was concluded that inappropriatefeed water chemistry was the main cause of tubes failure, and the water chemistry regime must be changed by the Combined Water Treatment method.Thus, an oxidizing fluid was utilized and oxygen was maintained at a level of 150 to 300 ppb to stimulate the formation of a protective layer of hematite on top of the magnetite and prevent the occurrence of single-phase FAC. Simultaneously, the pH was adjusted in the range of 8.0 ~ 9.0 so that two phase-FAC could be avoided.

#148 - Advances Membrane Operations in CO2 Capture

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Membrane-based gas separation systems are today widely accepted and, in many cases, used as a unit operation for generation, separation and purification of gases in gas, chemical, petroleum and allied industries. There are several fields of application of membrane gas separation and several membrane materials and membrane modules solutions available today for the various fields of interest.

CO_2 separation from flue gas coming out from a power plant or a cement industry, as well as CO_2 from biogas and natural gas is one of these fields. Polymeric membranes, thermally rearranged polymer membranes, mixed matrix membranes (CNT loaded), etc. are some examples of membranes investigated c/o the ITM-CNR for separating CO_2 and CH_4 of interest in many industrial cycles. The mass transport properties of these membranes were also analysed feeding gas streams, with different content of water vapour and other aggressive components; these being one of the crucial assets for moving towards to real applications. Other aspects, such as aging owing to water vapour, physical compaction, thermal cycles and contaminants were and are currently under investigation, also with over a period of time (long term characterization). To this purpose, together with material science membrane engineering covers a fundamental role in the development of this technology and its scale-up. Modelling assists experimental analysis for a unified approach to evaluation and development of membrane unit operations. In this logic, a tool was developed in terms of performance maps suitable for analysing also membrane-integrated systems identifying proper operating conditions and proposing possible process schemes for achieving the desired targets for the various streams of interest.

Among the main results achieved, there are the mass transport characterization of membranes, membrane properties restoring after long-time operation, modelling of the membrane gas separation as unit operation and its inclusion in more complex production cycles.

Brunetti A.; Cersosimo M.; Kim J.S.; Dong G.; Fontananova E.; Lee Y.M.; Drioli E.; Barbieri G. “Thermally rearranged mixed matrix membranes incorporating oxidized carbon nanotubes for CO_2 separation”, ACS Applied Materials and Interfaces, 2016, *submitted*

Brunetti A.; Cersosimo M.; Dong G.; Woo K.T.; Lee J.; Kim J.S.; Lee Y.M.; Drioli E.; **Barbieri G.** “In situ restoring of aged thermally rearranged gas separation membranes”, *J. Membr. Sci.,* 2016, 520,671-678,DOI: 10.1016/j.memsci.2016.07.030

#149 - Building functional 3D human tissue in vitro: role of the materials and processes

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In designing scaffolds for tissue engineering, the principal objective is to recreate the extracellular matrix (ECM) function in a temporally coordinated and spatially organized structure. Therefore, future generation of biomaterials with extended functionality and bioactivity requires an increased integration with cell and molecular biology, to identify novel design parameters and novel bio-inspired design approaches. Mastering the interaction between cells and extracellular environment is a fundamental prerequisite in order to engineer functional biomaterial interfaces able to instruct cells with specific commands. Such advanced biomaterials might find relevant application in prosthesis design, tissue engineering, diagnostics and stem cell biology. Because of the highly complex, dynamic, and multifaceted context, a thorough understanding of the cell-material crosstalk has not been achieved yet; however, a variety of material features including biological cues, topography, and mechanical properties have been proved to impact the strength and the nature of the cell-material interaction, eventually affecting cell fate and functions. Although the nature of these three signals may appear very different, they are equated by their participation in the same material-cytoskeleton crosstalk pathway as they regulate cell adhesion events. Attempts to guide and control biological tissues growth in vitro pursued by applying these novel concepts of material design have proved that the enhancement of control in biological signals presentation is favourable for complex tissue morphogenesis. By tightly controlling the presentation of relevant matricellular cues and by tuning their spatial distribution is possible to control cell function, differentiation, and morphogenesis. In this lecture I will present recent and relevant findings on the material-induced cell responses, with a particular emphasis on how the presentation of biochemical/biophysical signals modulates cell behavior. Emphasis will be given to the experimental assessment of the optimal signal presentation via robust and reliable models and their role in unraveling the biochemical mechanisms that underlie morphogenetic potency. Finally, a strategy based on a bottom up approach that aims at integrating this important basic information in the design and manufacturing of a complex human tissue in vitro will be presented. The approach enables the production of viable even heterotypic biological tissue in vitro to be used in tissue-on-chip applications.

#150 - Amphiphilic Block Copolymer Nanoparticles for Drug Delivery: Synthesis and Self-Assembly

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Block copolymer (BCP) amphiphiles' ability to spontaneously segregate (self-assembly) in distinct phases due to opposed interactions with a selective solvent is a powerful tool for the fabrication of polymeric nanoparticles in solution. Polymeric nanoparticles (NPs) are considered very promising carriers for intravenous drug delivery, thanks to their stability and tunability of particle morphology and size. As an example, poly(ethylene oxide)-*block*-poly(lactic acid) (PEO-*b*-PLA) amphiphilic system has already reached the clinical test stage and offers significant advantages, notably PLA degradation by hydrolysis within a few days preventing accumulation and PEO opsonisation resistance effect. The final particle morphology can be predicted to some extent from structural (hydrophilic volume fraction f, overall molecular weight, interaction parameter χ) or solution parameters by thermodynamic considerations, but the picture is further enriched by kinetic effects rising from the macromolecular nature of the amphiphiles. However, comprehensive studies on the self-assembly of amphiphilic BPC are limited to very few systems.

In this contribution, I report on two possible methodologies for the synthesis of amphiphilic BCP, a controlled radical polymerization, RAFT (Reversible Addition-Fragmentation chain-Transfer) and a living ring opening polymerization (ROP). Both methods allows the synthesis of block copolymers with strong control on ratio between the two blocks, the molecular weight and molecular weight distribution. RAFT is a robust and reliable technique that can be used with a large variety of vinyl monomers (acrylates, acrylamides, functionalized styrenes, dienes) meanwhile ROP catalyzed by organic bases with low nucleophilicity (e.g. 1,8-diazobicycloundec-7-ene, DBU) is suitable for monomers like lactide, glycolide, ring strained lactones and cyclic carbonates. In both cases preformed polymers, like poly(ethylene oxide), can be used as first block on which polymerize the second one.

The complex self-assembly behavior of two families of BCP, one obtained by RAFT, poly(styrene)-block-poly(dimethylacrilamide) (PDMA-b-PS), and one by ROP, PEO-*b*-PLA, will be described by means of Dynamic Light Scattering (DLS), Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM) and Cryogenic Electron Microscopy (Cryo-EM).

#151 - Effect of charged dendrimers on a model lipid membrane

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Dendrimers are highly ramified polymeric nanoparticles for the development of molecular level synthetic prototypes for the control of organization and dynamical properties on the colloid size scales [1, 2]. With the aim to study how different typology of charged dendrimer scaffolds can affect model bio-membranes, the self-assembly processes of a mixtures of charged polyamidoamine (PAMAM) dendrimers and dipalmitoylphosphatidylcholine (DPPC) lipids were investigated by means of Zeta potential analysis, Raman and Small Angle X-ray Scattering techniques. Interestingly DPPC liposomes showed different behaviours during their interaction with negatively charged sodium carboxylate terminated [$-COO^- Na^+$] or positively charged amino terminated [$-NH_2$] dendrimers. The obtained results evidence sensitive interactions between charged dendrimers and lipid molecules at the surface of the liposome (with an enhancement of the liposome zeta potential), as well as in the hydrophobic region of the bilayers (with a perturbation of the lipids alkyl chains of the liposome). Analysis of the dendrimers electrostatic potential allow an estimation of an effective charge of PAMAM dendrimers, while only a fraction of this charge (about 1/7) contribute to the liposome zeta-potential increase with increasing amount of included PAMAM dendrimers. The findings of our investigation may be applied to rationalize the effect of the nanoparticles electrostatic interactions in solution environments for the design of new drug carriers for drug delivery technology [2-4]

References

[1] M. A. Mintzer, M. W. Grinstaff, Chem Soc Rev. **40**, 173–90 (2011)

[2] D. Lombardo et al., BBA-Biomembranes, **1858(11)**, 2769–2777, (2016)

[3] D. Lombardo et al., Nanomaterials, **6**, 125(1-26), (2016)

[4] D. Lombardo et al., BBA-Gen Subjects, 2016 (in Press)

#152 - Encapsulation of dissolved guest molecules: a minimal model

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We investigate the low-temperature structure of a dilute mixture of amphiphilic dimers and spheres, a model relevant to the problem of encapsulating ``guest'' molecules in a dispersion. Dimers and spheres are taken to be hard particles, with an additional attraction between a sphere and the smaller monomer in a dimer. Using Monte Carlo simulation, we document the formation of aggregates of guests held together by dimers (``clusters''), whose typical size and shape depend on the relative guest concentration χ. For low χ values (less than 10%), most guests are isolated and coated with a layer of dimers. As χ progressively increases, clusters grow in size becoming more and more elongated; after reaching a maximum, the size of clusters again reduces upon increasing χ further. On heating, clusters shrink until at last the system becomes homogeneous on all scales. On the other hand, as the mixture is made increasingly dense at low temperature, clusters get larger until a percolating network is formed which spans the entire volume.

#153 - Engineered natural porous silica nanoparticles as drug delivery systems

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Nanomedicine is an innovative research field combining nanotechnology and medicine, radically changing the healthcare drug delivery scenario, in particular in the cancer treatment. Nanotechnology has provided the opportunity to get direct access to the cancerous cells selectively with increased drug localization and cellular uptake, making the therapy more patient compliant, efficientand painless. Moreover, nano-based systems allow delivery of poor water-soluble molecules (e.g., most of the anticancer drugs) difficult to administer, and can also protect the new therapeutics molecules, such oligonucleotide analogues (e.g., siRNA) from degradation, preserving their therapeutic efficacy while in the blood circulation. Thus, aim of nanomedicine in cancer therapy is the production of nanoparticles (NPs) able to deliver a drug to a specific site enhancing local drug molecules accumulation and reducing systemic toxicity. PSi is one of the most inorganic material used in biomedicine due to its unique properties such as high specific surface area, tunable pores size, biocompatibility, non-toxicity, high loading capability, controllable dissolution kinetic. In recent years, diatomite, a natural porous silica based material with similar physico-chemical properties to man-made fabricated PSi, has been suggested as feasible alternative to synthetic porous media for biomedical applications. Diatomite is a compound of sedimentary origin formed by remains of diatoms deposited on the bottom of seas or lakes. Due to its peculiar properties including highly ordered pore structure, high specific surface area, modifiable surface chemistry, biocompatibility, non-toxicity, low cost, optical and photonic properties, diatomite has been used in different applications ranging from optics and photonics to biosensing. Despite these properties and the recognition by the Food and Drug Administration (FDA) as Generally Recognized as Safe (GRAS) for foods and pharmaceuticals production, its use in nanomedicine is still surprisingly undervalued. In this work, the properties of diatomite nanoparticles, with an average diameter less than 350 nm, as potential drug delivery systems are described. Different surface functionalization strategies performed in order to transport molecules inside cancer cells and to improve diatomite NPs biocompatibility and cellular internalization are summarized.

#154 - New carrier systems for targeted antibiotics delivery

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The EU has published her Action Plan in 2011 against the rising threats from antimicrobial resistance. Developing new antibiotics is mandatory but takes years. A short-term alternative is the development of novel strategies to deliver existing drugs in an optimized way. In this frame, the use of engineered antibiotic nanocarriers is one of the most promising options. The objective of our research in the frame of the 7FP-ITN project Cyclonhit is to take full advantage of nanotechnology to efficiently encapsulate antibiotics in nanocarriers to kill both intracellular and extracellular bacteria. We have focused on two drugs, Ethionamide and Clofazimine, used for the treatment of TBC and Lepromatous Leprosy, respectively. Both suffer from very low solubility in water reducing drastically their bioavailability and complicating their administration. We have studied two different types of carrier systems consisting of polymeric cyclodextrins marked with fluorophores, on one hand, and porous fluorescent silica particles with size ranging from few hundreds of nm to 2 micrometers, on the other hand. We will discuss loading of the two drugs by these new fluorescent carrier systems, their antibacterial activity and their penetration in skin tissue.

#155 - NiO based nanostructures for low-cost, high sensitive glucometer devices

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Non-enzymatic glucose sensing is based on the direct catalytic oxidation of glucose and typically allows very high sensitivity at the expense of high fabrication cost, low selectivity and poor stability. Here we report on a novel NiO nanostructure fabricated by low-cost methods and successfully applied for non-enzymatic glucose sensing [1]. A Ni nanofoam (surface area of 25 m^2/g) is obtained by room-temperature chemical bath deposition followed by 350 °C annealing in reducing ambient. To activate glucose detection a catalytic layer of $Ni(OH)_2/NiOOH$ is formed onto the nanofoam by cyclic voltammetry (CV). Two glucose sensor electrodes, on flexible and on rigid substrate, were fabricated, both showing sensitivity in the range of 1.5-3 mA/cm^2mM, linear range of 0.01–0.7 mM, limit of detection (LOD) of 5 mM, resistance to chloride poisoning and excellent long-term stability (4% decrease in sensitivity after 64 days) and selectivity in the presence of common interfering species. Growth mechanism and related effects on the glucose detection effectiveness are presented and modeled. In addition, a full device was realized with a miniaturized electrochemical cell, based on a silicon chip with planar microelectrodes, connected to a PCB board (for the electrical driving and reading) and containing also a resistor for sensing test at high temperature. The sensing electrode was based on Ni oxy-hydroxide and glucose testing was performed with NaOH or PBS electrolytes [2]. The device sensitivity decreases with decreasing the electrolyte pH, with still some activity also at the physiological pH of 7.4.

[1] Iwu et al., Sensors and Actuators B 224 (2016) 764–771

[2] S. Petralia et al., submitted

#156 - Low-cost synthesis of hierarchical Ni nanoflakes /ZnO nanorods for non-enzymatic glucose sensing

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Nowadays an effective glucose level detection is a fundamental issue for human health and biotechnological applications. Nanostructured nickel hydroxide $Ni(OH)_2$has shown notable activity for amperometric non-enzymatic glucose sensing. Here, we present the synthesis of a hierarchical nanostructure composed of $Ni(OH)_2$nanoflakes electrodeposited onto ZnO nanorods grown by chemical bath deposition at low temperature. The morphological features of ZnO nanorods were varied by changing the chemical bath deposition parameters. These nanostructures serve as large surface area substrates for pulsed electrodeposition of $Ni(OH)_2$nanoflakes. We investigated the correlation between the morphology of the electrodes and their electrochemical properties in order to improve the glucose sensing performance by a simple tuning of the experimental parameters. The final electrode showed fast response time (1 s), high selectivity, resistance in chloride solution and long-term stability. The optimized structure showed the high sensitivity of 1.85 mA/cm^2 mM. The results suggest $Ni(OH)_2/ZnO$ hierarchical nanostructure can be a promising approach for low-cost glucose sensors.

#157 - Oxidation processes of Zn nanoparticles produced by pulsed laser ablation in aqueous solution

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ZnO nanoparticles (NPs), due to their high exciton binding energy (60 meV) and the presence of luminescent defects inside their direct band-gap (3.37 eV in bulk form), are characterized by two emission bands: 1) exciton related emission at 3.3 eV; 2) defect related emission at 2.2 eV. Hence, they are important for photonic applications like bioimaging probes and light emitters in the visible-UV range. Among the synthesis methods, Pulsed laser ablation in liquid (PLAL) allows to control the properties of the produced ZnO nanoparticles by changing several parameters (laser, solvent…). So far, the most part of studies have used *ex-situ* methods to study the endproducts of PLAL; these approaches only provide indirect information on the sequence of reactions ultimately yielding stable metal oxide NPs.

In this work, we report “online” absorption (OA) and photoluminescence (PL) measurements carried out during and after PLAL of a Zinc plate in aqueous solution. In a recent work (APL **107**, 013103 (2015)), we have demonstrated that ZnO NPs are formed by a sequence of two steps: (1) a defect-free superficial oxidation of Zn NPs, followed by (2) a slower oxidation that proceeds towards the inner Zn core leaving behind oxygen vacancies. Here, we extend that work to study the effects of the laser repetition rate (RR) and the liquid environment on the oxidation processes of ZnO NPs. The obtained results evidence that the fast oxidation dominates the initial production of ZnO species from Zn NPs and cannot be affected by the used laser repetition rate. Instead, the slower oxidation becomes relevant after 4000 pulses and fails to keep up with the zinc production rate. OA kinetics, during and after PLAL in a mixture of water and ethanol from 0 to 100%, reveal that it is possible to control the oxidation rate of the just produced Zn NPs. Moreover, the ethanol/water ratio also controls the concentration of oxygen vacancies inside ZnO NPs.

This investigation clarifies important aspects of the oxidation processes of Zn NPs in aqueous solution involved during PLAL which allow to control the endproduct of the synthesis in view of the use of ZnO NPs in technological applications.

#158 - Four visible deep level defect states in ZnO nanorods

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Visible luminescence from ZnO nanorods (NRs) is attracting large scientific interest for light emission and sensing applications. We study visible luminescent defects in ZnO NRs as a function of post growth thermal treatments, and find four distinct visible deep level defect states (VDLSs): blue (2.52 eV), green (2.23 eV), orange (2.03 eV), and red (1.92 eV). Photoluminescence (PL) studies reveal a distinct modification in the UV (3.25 eV) emission intensity and a shift in the visible spectra after annealing. Annealing at 600°C in Ar and O_2 cause a blue and red-shift in the visible emission band, respectively. All samples demonstrate orange emission from the core of the NR, with an additional surface related green, blue, and red emission in the the As-Prep, Ar600, and O600 samples, respectively. From PL excitation (PLE) measurements we determine the onset energy for population of the various VDLSs, and relate it to the presence of an Urbach tail below the conduction band due to a presence of ionized Zn_i or Zn_i complexes. We measured an onset energy of 3.25 eV for the as prepared sample. The onset energy red-shifts in the annealed samples by about 0.05 to 0.1 eV indicating a change in the defect structure, which we relate to the shift in the visible emission. We then used X-ray photoemission spectroscopy

(XPS), and elastic recoil detection analysis (ERDA) to understand changes in the surface structure, and H content, respectively. The results of the XPS and ERDA analysis explain how the chemical states are modified due to annealing. We summarize our results by correlating our VDLSs with specific intrinsic defect states to build a model for PL emission in ZnO NRs. These results are important for understanding how to control defect related visible emission for sensing and electroluminescence applications.

Based on:

E. G. Barbagiovanni, et al. Appl. Phys. Lett., (2015), 106, 093108

E. G. Barbagiovanni et al., Nanoscale **8**, 995 (2016)

E.G. Barbagiovanni et al., Appl. Phys. Lett. (submitted)

#159 - Electrical properties of semi-insulating CdTe radiation detectors: from a compensation model to the electric field distribution

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Due to their high atomic number, high resistivity and good transport properties, bulk semiinsulating Cd(Zn)Te crystals are largely used to fabricate X- and gamma-rays detectors. Despite the relevant advances in the recent years, there are still open issues concerning material defects and device performance. In this regard, the electric field uniformity and its stability are crucial for the full and reliable collection of the photogenerated carriers. It is worth reminding that, in semi-insulating materials, the space charge responsible for the specific electric field distribution is provided by deep levels. In turn, the predominant deep levels together with their ionization state are related to the compensation mechanism, which directly controls the resistivity. Furthermore, the device electrodes can directly affect the charge state of such deep levels and thus the electric field distribution.

It is then clear that a full comprehension of the electrical properties of these devices requires both a model for the material energy levels and the solution of the relevant charge carrier equations able to consistently account for the results from complementary experimental techniques.

Our contribution goes along this direction: we start by proposing a model for carrier compensation in CdTe, based on a single deep level placed, from spectral time of flight measurements, around mid-gap.The model is supported by an analysis of electrical resistivity at different temperatures, which returns ratios R= N_d/N_s in the range 1.9-2.4, where N_d and N_s are the deep level and shallow residual concentrations, respectively. Then, the model consistency is checked against the stationary electric field distribution in Schottky and Ohmic (injecting carriers under high applied voltages) CdTe detectors. This is done numerically within the drift-diffusion approach. Luckily, becoming CdTe birefringent under electric field, then the Pockels effect offers the remarkable opportunity to unveil its internal electric field, with high spatial and temporal resolution and without perturbing it. By using this effect, we have thus measured the stationary electric field distributions. A good agreement between experiments and simulations is found when considering Nd in the range 2.5-3.5 x 10^{12}cm^{-3} and R=2.1. Finally, the comparison has been extended to the (bias induced) transient regime, allowing us to evaluate the capture cross section of the mid-gap level, and thus completing the signature of the level responsible for compensation in CdTe.

#160 - Tensile strain in Ge membranes induced by SiGe nanostressors for optoelectronic applications

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Information and communication technologies eagerly need novel solutions to continue the improvement of the performance and integration level of silicon based electronic devices. Indeed, uniaxial strain obtained using local stressors has become part of mainstream Si-based technology. Next, a direct-gap semiconductor which is fully compatible with Si-based technology would suggest the possibility of highly efficient Si-compatible emitters of infrared radiation, which would greatly facilitate full integration of electronics and optoelectronics. Tensile strain in germanium reduces the separation between its indirect (L) and direct (Γ) conduction band minima. The application of 4% uniaxial strain applied along [100] to a Ge(001) layer is expected to lower the direct gap below that of the indirect gap and increases the radiative recombination rate of the material In this work we transfer our successful method using a patterned SiGe stressor layer on germanium [1,2] from bulk material to suspended micro-bridges. SiGe is grown pseudomorphically on Ge and is tensile strain loaded due to its smaller lattice constant with respect to Ge. Upon patterning of the SiGe layer, free side walls are created at which the SiGe layer can relax thereby compressing the germanium beneath [3]. However, the germanium inside a trench of the pattern, where SiGe was removed, is tensilely strained because the perimeter forces of the surrounding free SiGe side walls act as pulling forces. Specifically, a strained $Si_{1-x}Ge_x$ film has been grown on a relaxed Ge buffer on Si(001) substrates by low-energy plasma-enhanced chemical vapor deposition (LEPECVD). Several freestanding nanostructureshave been defined by electron-beam lithography (EBL) and reactive ion etching (RIE), and analysed by scanning electron microscopy (SEM). Micro-Raman spectroscopy has been used to obtain information on the strain state within the pattern [4]. FEM simulations are thereby used as guidelines for designing top-down nanostructures to optimize Ge strain engineering. A combination of dry and wet-anisotropic etching has been used for the fabrication of both suspended-bridge and substrate-anchored SiGe/Ge membranes on a Si(001) substrate. A systematic study of the etching parameters has been carried out for different Ge contents of the SiGe capping layer, in order to selectively etch the Si substrate and not the SiGe layer and, finally, to realize free-standing Ge structures for new class of tensile Ge micro substrates.

[1] M. Bollani et al. Applied Physics Letters 107, 083101 (2015)

[2] V. Mondiali et al. Microelectron. Eng. **141** 256--260 (2015)

[3] V. Mondiali et al., Microelectron. Eng. **153** 88--91 (2016)

[4] M.Barget et al. under submission.

#161 - Sensing properties of rhodium oxide nanoparticles prepared by pulsed laser ablation in liquids

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Recently, rhodium based nanomaterials have been proposed for Surface Enhanced Raman Scattering (SERS) substrates, energy conversion devices, electrocatalytic systems, biosensors and as catalysts in metal oxide gas sensors [1-3]. Actually, the chemical synthetic procedures require toxic reagents and harsh conditions which limited the control over NPs size and distribution and their applicability only to specific reaction–support combinations. To overcome these drawbacks, a direct manipulation of the Rh/Rh oxides NPs and the design of suitable stabilizers that indirectly modify the nanoparticles properties are adopted.

In this work, we propose an alternative approach to prepare rhodium oxide nanoparticles with well-defined chemistry, structure and morphology at the nanometric scale. The rhodium oxide colloids were prepared by pulsed laser ablation in liquid and characterized using different techniques such as X-Ray photoelectron spectroscopy, X-Ray Diffraction, UV-Vis absorption and micro-Raman spectroscopies. Characterization data revealed the growth of very small rhodium oxide nanoparticles (less than 10 nm in diameter), displaying a mixed metallic Rh/Rh oxide composition. For the first time, the gas sensing properties of the prepared nanostructures were investigated. An excellent sensitivity towards volatile organic compounds (VOCs) such as ethanol and acetone has been found and correlated to the chemical/structural properties of the samples.

[1] K.S. Lokesh et al., Bioelectrochemistry 75 (2009) 104.

[2] C. Moreno-Marrodan et al., Catal. Sci. Technol., 2015, 5 , 3762.

[3] N.-H. Kima, S.-J. Choi et al., Sensor. Actuat. B-Chem., 2016, 224, 185.

#162 - Towards the ultimate electron transparent graphene based membrane

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An alternative approach towards Ambient-Pressure Photoelectron Spectroscopy (APPES) and microscopy can be realized by using gas tight, but electron transparent membranes. Such membranes may be used to seal a non vacuum compatible compartment which is introduced into the ultra high vacuum environment of an electron spectrometer. It is then possible to investigate the interior of the sealed compartment by applying photoelectron spectroscopy, if the ejected photoelectrons can pass the electron window and enter into the electron analyzer. Due to the short inelastic mean free path of electrons in condensed matter, extremely thin and mechanically stable membranes are required for this application, especially if electron transparency for low energy electrons is needed. Graphene is a very promising membrane material as shown when testing its maximum achievable electron transparency. We also performed principle of proof experiments showing that indeed x-ray photoelectron spectroscopy through sealed cells can be performed. We found that it is mandatory to grow highest quality single crystalline graphene sheets (flakes) when aiming at building the ultimate electron transparent membrane. For this purpose, we thoroughly investigated the catalytic growth of monolayer graphene on Cu and found that a special pretreatment of the Cu foils is required to enable the growth of single crystalline g-flakes with diameters approaching the mm-range. Recent understanding on the involved processes during growth of high quality graphene as well as limits during membrane fabrication are reported.

#163 - Graphene/Ni(100) moiré structures: insight from atomic-scale simulations

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Graphene on Ni(100) forms a variety of Moiré patterns which can be well explained in atomistic models by the mismatch with the substrate, with periodicity depending on the relative angle between the hexagonal graphene and the square surface lattices. Evidence of the different Moiré structures is given by high resolution scanning tunneling microscopy images, that are well reproduced by ab-initio simulations. Beyond providing the detailed atomic-scale structures, the numerical simulations allow a deep local characterization of the chemical bonding between the graphene layer and the support. We also discuss the possible formation beneath the graphene of a surface-confined nickel-carbide in specific regions of particular Moirè structures, whose presence is suggested by experimental STM images.

#164 - Evidence for Germanene formation on epitaxial hexagonal (h)-AlN(0001)/Ag(111)

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2-Dimensional semiconductors, have recently received considerable attention and most of the work done so far has been on metal surfaces: 2D lattices of Ge have been observed on various metallic substrates such as Pt(111) [Li-14], or Au(111) [davila-14]. Metallic surfaces are poorly compatible with silicon technology and efforts are devoted for obtaining 2D layers on more appropriate substrates. 2D graphite-like hexagonal AlN (h-AlN), a metastable phase favored at small thickness against the most known bulk wurtzite-AlN phase, is a promising insulating substrate for germanene growth, since it has been theoretically predicted that the silicene counterpart remains stable when encapsulated between two 2D h-AlN layers. In this work, we present evidence of germanene formation 2D h-AlN insulating layers on Ag(111). By combining a number of experimental techniques such as RHEED, STM and UPS we first report the successful epitaxial growth of sp2-hybridized h-AlN layers on Ag(111) with a flat geometry by plasma assisted MBE. Subsequently, Ge layers were also deposited by MBE on an h-AlN buffer layer and were structurally characterized by RHEED, XAS and DFT calculations. RHEED data indicate a faint 4x4 superstructure with respect to (1x1) Ag(111), or a (3x3) reconstruction with respect to (1x1) germanene.

Grazing Incidence surface XAS measurements at the Ge-K edge [dacapito-16] were carried out at the LISA beamline at ESRF. Two kind of bonds are revealed: Ge-Ge and Ge-Ag. The former comes from Ge structures whereas the latter comes from a spurious alloy with the substrate. The Ge-Ge distance is 2.44(2) A in the deposit on Ag revealing that tetrahedral Ge islands are formed. On the other hand in samples obtained depositing Ge over Aln the Ge-Ge distance drops to dGe-Ge=2.38 Å. This distance is extremely short and can be explained only by the presence of sp2 hybridized Ge i.e. germanene. This idea is also supported by first-principles DFT calculations performed on the Ge/h-AlN/Ag(111).

References

[Li-14] Li L, Lu S Z, Pan J, Qin Z, Wang Y G, Wang Y, Cao G Y, Du S and Gao H J 2014 Adv. Mater. 26 4820–4

[davila-14] Davila M E, Xian L, Cahangirov S, Rubio A and Lay G L New J. Phys. 2014, 16 095002

[dacapito-16] d'Acapito, S Torrengo, E Xenogiannopoulou, P Tsipas, J Marquez Velasco, D Tsoutsou and A Dimoulas J. Phys.: Condens. Matter 28 (2016) 045002.

#165 - Stability of H- and O-functionalized graphene by first principle calculations

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Graphene is a two-dimensional material that exhibits unique electrical, mechanical and optical properties. More recently, derivatives of graphene have been of large interest because of the possibility to add new functionalities to graphene and tune its electronic properties. Among the possible derivatives, graphane, a graphene structure fully-hydrogenated on both sides of the plane, and graphene oxide (GO) have attracted great attention in the last years. GO is usually derived by graphite oxide via chemical routes which are observed to produce a material with a defective lattice. Using ab initio calculations we show that when graphene oxide is synthesized with alternative methods, such as chemical vapour deposition, the formation of regular and short period hydrogenated graphene oxide is possible. This material could be used as an insulating thin coating and/or as an insulating layer in conjunction with metals and semiconductors in electrical and optoelectronic devices.

#166 - Self-Assembly of Graphene Nanoblisters

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In addition to the impressive characteristics featured by extended, flat two-dimensional (2D) graphene, unusual intriguing behaviors appear when its electronic, tribological, and mechanical properties are modulated at the nanoscale.

By exploiting the possibility to intercalate rare gas atoms below metal-supported graphene, we have trapped remarkable quantities of Ar, equivalent to 15% of the substrate surface atoms, under epitaxial graphene monolayers on Ni(111) by means of irradiation with low energy Ar^+ ions. At high temperature, the Ar atoms below graphene assemble into solid clusters encased by the floating graphene regions, while graphene in direct contact with the Ni surface dissolves in the substrate bulk. In this way graphene nanosized blisters (GNBs) are produced, evenly distributed on the bare Ni(111) substrate surface and stable in a wide temperature range.

We used synchrotron radiation based time resolved X-ray photoelectron spectroscopy (XPS) to monitor the Ar^+ intercalation and follow in real time the nanoblisters self-assembling during the thermal annealing of the Gr/ Ni(111) sample. Scanning tunneling microscopy (STM) was employed to study the morphology of the interface loaded with Ar and the structure at the atomic scale of the GNBs formed after the thermal treatment.

The GNBs contain Ar aggregates compressed at high pressure arranged below the graphene monolayer skin that is decoupled from the Ni substrate and sealed only at the edges through stable C-Ni bonds. Their in-plane truncated triangular shapes are driven by the crystallographic directions of the Ni surface. The extremely high pressure of the gas inside the blister (hundreds of kbar) induces a lattice strain (10 - 15 %) of the graphene structure capping the GNBs. The non-uniform strain revealed along the blister profile is explained by the inhomogeneous expansion of the flexible graphene lattice that adjusts to envelop the Ar atoms stack. In order to explore the versatility of the GNBs, we have successfully tested their stability in atmosphere, which is a technologically relevant issue. The integrity of the graphene lattice in the air-exposed blisters opens the way to the application of this technology to the graphene stress engineering topic, aimed at the electronic properties and chemical reactivity modulation. Moreover, suitable transfer techniques from the substrate can be envisaged to produce graphene nano-disks with a narrow size distribution.

#167 - Initial growth stages of graphene from ethanol chemical vapor deposition

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The growth of crystalline graphene on copper by the chemical vapour deposition (CVD) of ethanol (C_2H_5OH) presents advantages over methane-based CVD in terms of safety, cost, and ease of processing [1-3]. With ethanol, the catalytic growth process is more efficient than with methane and a faster growth kinetics leads to the growth of continuous graphene films in seconds rather than in minutes. As a consequence, individually nucleated graphene islands could not be observed before forming a continuous film, and were thus not reported in literature for ethanol-CVD until recently. Hexagonal single-crystals of graphene with size in the mm range have grown by ethanol-CVD inside sealed copper “enclosures” [4, 5], where the copper surface was not directly exposed to the process gases.

In this work, the conditions of the ethanol-CVD process were optimized to observe the initial growth stages of graphene on plain copper foils. Quick growth processes, down to 15s, were performed at 1070°C and at total process pressure of 70 Pa, with an ethanol partial pressure as low as 0.025 Pa. Optical and atomic force microscopy (AFM), Raman spectroscopy and scanning electronic microscopy (SEM) were used to investigate the graphene domains directly on copper and also after the transfer on Si/SiO_2 substrates. After 15s, the Cu surface was not completely covered and showed graphene grains of a few micrometers in diameter. The transfer of such small graphene domains on the Si/SiO_2 surface was successfully performed by using cyclododecane ($C_{12}H_{24}$) as supporting material during the copper etching [6]. An accurate analysis by Raman mapping, confirmed by AFM measurements, showed that all graphene domains were predominantly single-layer, with hexagonal shape and very low defect density. Such results indicate that the use of ethanol can lead to the growth of highly crystalline single-layer graphene films in a fraction of the time required by the methane-based growth.

References

[1] A. Guermoune et al., Carbon 49 (2011) 4204.

[2] G. Faggio et al., The Journal of Physical Chemistry C 117 (2013) 21569.

[3] N. Lisi et al., Thin Solid Films 571 (2014) 139–144.

[4] X. Li et al., Journal of the American Chemical Society 133 (2011) 2816–2819.

[5] X. Chen et al., Carbon 94 (2015) 810–815.

[6] A. Capasso et al., Applied Physics Letters 105 (2014) 11310

#168 - Intercalating Co thin films between Graphene and Ir(111): structural and magnetic effects

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The challenging development of ultra-high density memory devices can be achieved using ultra thin Co films. Below a critical thickness t_c of about 7 monolayers, Co films may develop perpendicular magnetic anisotropy (PMA) especially suitable to shrink the magnetic bits size.

A Graphene (Gr) capping layer allows to prevent film oxidation and preserve its magnetic response. For this reason, the films intercalation between Gr and Iridium(111) was attempted [1]. Interestingly, intercalated Co films showed PMA even for thickness exceeding t_c [2] suggesting a Co-Gr coupling enhancing the magnetic anisotropy.

However the origin of such enhanced magnetic response could also be related to other parameters triggering the intercalation such as annealing temperature and time, Gr quality, film thickness and morphology, etc. Our research aims to get a deeper insight of the involved phenomena. In particular, we focussed on the role of Co-Ir interface upon different annealing conditions.

To this aim we exploited state of the art complementary techniques to probe and compare the behavior of bare Co/Ir and Gr/Co/Ir systems. We used Angular Resolved X-ray Photoemission Spectroscopy (AR-XPS), X-Ray Reflectivity (XRR), Grazing Incidence X-Ray Diffraction (GIXD), X-ray Absorption Fine structure (XAFS) spectroscopy for a deep structural characterization, and Magneto Optical Kerr Effect (MOKE) for characterizing the anisotropic magnetic response.

With a fine analysis of our results, we gained a detailed understanding of the intermixing process occurring at the Co-Ir interface in bared and Gr-capped films. This clarifies the graphene contribution to the modified magnetic response of the intercalated films [3,4,5].

Our results provide valuable information particularly useful for applicative purposes. They demonstrate how the intercalation parameters affect the Co-Ir intermixing and how this affects the overall magnetic properties, paving the way to optimized synthesis processes tailoring the magnetic response of the final device.

[1] J. Couraux et al., J. Phys. Chem. Lett. 3, 2059 (2012)
[2] N. Rougemaille et al., Appl. Phys. Lett. 101, 142403 (2012)
[3] J. Drnec, et al., Carbon 94, 554 (2015)
[4] I. Carlomagno et al., submitted to J. Appl. Phys. (2016)
[5] I. Carlomagno et al., in preparation

#169 - Synergistic combination of PEDOT with new lithographically patterned glassy carbon electrodes for stable neural interfaces

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Synergistic combination of PEDOT with new lithographically patterned glassy carbon electrodes for stable neural interfaces

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Among materials for developing highly sensitive and microscale neural probes, conducting polymers (CPs), especially poly(3,4-ethylenedioxythiophene) (PEDOT), represent the most important tool aimed to significantly reduce the impedance in a wide frequency region, while increasing the biocompatibility. Stability must be improved in order to permit both neural recording and stimulation, as it has been reported that for this kind of application the major issue for conductive polymers is their tendency to delaminate. One possible way to reduce or suppress this material loss could be represented by the optimization of the electrode|CP interface. For neural application the most used electrode underlayers are typically represented by Platinum or Gold, onto which PEDOT is deposited by conventional electrochemical methods. The high porosity of electrochemically prepared gold microelectrodes has been demonstrated to significantly reduce delamination PEDOT. This suggests that the nature of the underlayer is a very important factor to be taken into account in order to improve the stability of CPs. We recently reported on a new electrode material fabricated from lithographically patterned glassy carbon (GC) that combines superior electrochemical properties for neural recordings and better long-term stability under electrical stimulation than current metal microelectrodes. Surprisingly, in this study we also found that PEDOT:PSS deposited on GC exhibited both superior electrochemical properties and higher stimulation capability, if compared to PEDOT:PSS deposited on Pt, presumably thanks to the interaction between the phenyl rings of the polystyrene chains and the π-conjugated system of PEDOT interacting with the carbonaceous surface of the GC. In its oxidized and conductive state, the positively charged PEDOT is counterbalanced by the negative charge of the counter-ion, typically PSS or smaller anions. Moved by the encouraging results observed for the GC/PEDOT:PSS material we decided to explore the possibility of further increasing the interaction between PEDOT and GC. Thus, the surface of our GC electrodes has been chemically modified, under mild conditions, by electrochemical oxidation of amino-benzene-sulfonic acids leading to covalent attachment of amine cation radicals onto the GC surface. Finally, the resulting monolayer films containing free sulfonate groups on GC will give significant improvement of the electrostatic interaction between the positively charged PEDOT and the negatively charged GC surface.

#170 - Comparison between thermal Silicon Oxide and silicon Nitride surfaces for Biosensing applications

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In this work, we present a comparison between silicon oxide and silicon nitride surfaces prepared by thermal methods, to be applied to nucleic acids detection by hybridization technique. The two substrates were properly functionalized by 3-glycidoxypropryltrimethoxysilane to obtain a coating suitable for biomolecules grafting. The chemical process was fully characterized by contact angle, ellipsometry, AFM and TEM analysis. The sensing performances have been investigated by hybridization of immobilized single-strand DNA with perfect-match oligonucleotides and with PCR-products, by both optical and capacitive transduction methods. The data show the higher chemical resistance of nitride surface with respect to the oxide one after similar hybridization procedures. The results indicate the nitride as a potential active material for electrical signal transduction of DNA recognition.

#171 - Probing receptor architectures and molecular recogntion at interfaces by sum-frequency vibrational spectroscopy

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The demand for fast and reliable detection of biological and chemical hazards as well as early-stage diagnosis of diseases is continuously rising, because of the foremost relevance for global health. Boosting detection selectivity requires molecular receptors to be devised by tailoring specific interactions with the target analyte, but also to be structured in architectures which retain the designed complexation capability in the real-world sensor working conditions. Among different types of macrocylic receptors, cavitands[1], organic host-molecules with enforced cavity of molecular dimension, have demonstrated significant potential for chemical and biochemical sensing applications, thanks to their high selectivity towards a particular class of ligands.[2-3] However, in most promising sensor architectures molecular recognition events occur at the transducing interfaces between the target molecules in solution (gaseous or liquid) and the host molecules located at the solid surfaces. In these cases, efficient and selective binding often depends on the organization of receptors at interfaces with proper surface density, preserving the functional conformation and orienting the binding fragments towards the analyte-containing medium. Therefore, it is of paramount importance to complement host−guest association studies in solution, with analytical in-situ investigations of the molecular recognition event directly at the sensor interfaces, by probing the molecular architecture of the host-decorated surfaces and correlating it with guest uptake efficiency and orientation upon complexation.

Sum-Frequency generation Vibrational Spectroscopy (SFVS) is a promising candidate, being a versatile analytical tool for non-invasive probing of any interface accessible by light, with chemical selectivity, inherent surface specificity and sub-monolayer sensitivity. It has been successfully used to yield the molecular-level description of the conformational switching of a cavitand monolayer at liquid/air interface.[4] Here we unveil the molecular architecture of surface-bound cavitands-organosilane hybrid bilayer[5] and report the first investigation of the molecular recognition event at the solid-gas interface.[6] By probing the molecular fragment involved in the host-guest complexation, the study allows to correlate the conformation and orientation of receptors at the interface with the orientation of the complexed cognate analyte inside the binding pocket.

References:

[1] D. J. Cram *Science* (1983) 219, 1177–1183.

[2] F. Bianchi et al. *New J. Chem.* (2003) 27, 502–509.

[3] E. Biavardi et al. *Proc. Natl. Acad. Sci., USA* (2012) 109, 2263–2268.

[4] P. Pagliusi et al. *J. Am. Chem. Soc.* (2006) 128, 12610−12611.

[5] A. Aprile et. al. *Langmuir* (2014) 30, 12843−12849.

[6] A. Aprile et al. *J. Phys. Chem Lett.* (2016) 7, 3022-3026

#172 - DNA electrochemical detection strategy on miniaturized silicon sensor.

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A novel electrode modification strategy was investigated for the rapid and sensitive electrochemical detection of DNA, without the PCR step. The chemistry strategy is based on hybridization of pathogen DNA target with oligonucleotides probes covalently anchored on a metal working electrode. The hybridization was probed by the intercalation of the Os(II) redox-active compound (([Os(2,2'-bipyridine)(dipyrido[3,2-a:2',3'-c] phenazine)]Cl_2), specific for double strand DNA [1, 2]. The adopted electrode chemical modification strategy here presented allows i) the PCR-free detection, ii) a stable and reproducible hybridization process, iii) a reduction of background redox current. The modification strategy was integrated in a silicon miniaturized device containing three-planar-microelectrodes and a resistor for heating and temperature control. This device allows the detection of nucleic acids in few minutes without the laborious and dispending PCR steps, making this methods very appealing for the development of a Point-of-Care-testing devices.

References

[1] T. Defever, M. Druet, D Evrard, D. Marchal, B. Limoges, Anal. Chem. 83 (2011) 1815–1821;

[2] S. Petralia, M. E. Castagna, E. Cappello, Fausto Puntoriero, Emanuela Trovato, Antonio Gagliano and S.Conoci, Sensing and Biosensing Research, 2015, 6, 90-94;

#173 - Property modulation of pseudoelastic alloys for the manufacturing of personalised rehabilitation devices

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Pseusoelasticity is a very useful property of NiTi-based alloys, which can be exploited for the design of innovative wearable devices for neuromuscular rehabilitation, and the treatment of movement disorders.

The great interpersonal variability of body masses, muscular forces, desease type and severity require that the pseudoelastic characteristics of those materials be modulated to meet individual needs and produce the desired results.

The combination of alloy composition, plastic deformation and thermal ageing affects the microstructure of the final products. Thermal ageing is particular important in the fine tuning of martensitic transformation characteristics. This work presents a method to guide real-time property modulation while the pseudoelatic elements are thermally treated and shows the map of desirable and achievable characteristics for biomedical applications in rehabilitation.

#174 - Glass supported gold nanostars monolayers coated with ultrathin silica films: reusable and robust substrates for SERS sensing

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The optimal SERS substrate in analytical processes requires to find the best compromise between different features: homogeneous structure, sample-to-sample reproducibility, low cost synthetic pathway, stability and reusability. A popular way to build SERS substrates consists in taking a bulk, inexpensive surface such glass, coating it whit a Self Assembled Monolayer (SAM) of an amine bearing alcoxysilane, for example aminopropiltrimethoxysilane (APTES): subsequently negatively charged nano-objects like gold nanostars (GNS) can interact with positively charged ammonium groups, allowing the preparation of uniform and reproducible substrates. Anyway some crucial problems might appear: electrostatic interactions are quite weak, mechanical removal following manipulation, scratching or ultrasounds treatments must be taken into account. Moreover, binding of substances dissolved in used fluids (especially those of biological origin) to nano-objects could lead to competitive interaction and eventually nanoparticles detachment, with possible release in considered media. Furthermore, chemical reactivity of substances (mainly thiols) showing high affinity towards noble metal surfaces can affect substrate stability, response and/or reusability.

We have prepared SERS substrates composed of a monolayer of different nano-objects (gold nanostars or silver nanodisks, grafted on glass by means of electrostatic interactions with protonated amines) and their coating with ultrathin silica layers (ranging from 1 to 5 nm, using a methodology widely employed to protect gold island films for transmission localized surface plasmon sensing. The nano-objects monolayers are isolated and protected from the surrounding environment. We obtained a complete mechanical stabilization, protection and separation from the solution and inertness towards mechanical removal and chemical reactivity. The SERS response, as expected, is decreased by the ultrathin dielectric layer but a useful Analytical Enhancement Factor (AEF~10^5) can be in any case maintained at the lower used thickness. The homogeneity of the silica coated substrates has been verified by mapping the SERS response. The inertness of silica coated substrates toward mechanical degradation and chemical reactivity have been tested and we obtained a clear indication about the reusability of these SERS chips.

The SERS data have been obtained mainly from a typical model analyte, rhodamine 6G, but applications to real biological samples have been tested as well. The results seem to indicate the possibility to realize a prototype of a low cost, homogeneous, reproducible, robust and reusable SERS substrate. Furthermore the obtained EF's from different substrates and from different Raman modes of R6G have been discussed in relation with the increase of the silica coating layer thickness.

#175 - Towards cavity Quantum Electro Dynamics with hybrid photon-plasmon states

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The lack of nonlinearities in plasmonic nanostructures is a fundamental bottleneck in the development of active plasmonic components. For this reason phenomena of strong coupling between localized surface plasmons (LSPs) and excitons in semiconductor materials are gaining increasing importance in the field, due to the general interest in dressing plasmons with nonlinearities [1]. However, even if LSPs have shown unique capabilities in beating the diffraction limit—shrinking optical energy in dimensions much smaller than the wavelength of light—the high absorption losses in metals still remain a fundamental point to face, given their influence in lowering the LSP quality factor.

For this reason, in recent years a new route has been explored for the exploitation of LSP, based on the localization of the electromagnetic field outside of the metal. To do this ordered arrays of plasmonic nanoparticles have been studied, in which the LSP of the individual elements couples to the grazing propagating diffractive modes of the array. By this way narrow, high quality factor modes arise, called Surface Lattice Resonance (SLR) [2,3], exhibiting a much larger mode volume though. The open question is thus if these hybrid modes could offer an effective gain in terms of Q/V ratio, which governs the onset of the strong coupling regime and of many non-linear effects.

In this work we combined the high quality factor of diffractive waves in nanoparticle lattices, with the ultra-small mode volume of narrow-gap nanodisk dimers, to demonstrate, both experimentally and theoretically, that high quality factor and low modal volume optical modes can be simultaneously sustained when the gap plasmon of the dimer is excited. We probed this by looking at the strong coupling regime in a J-aggregate coupled system, where we measured an 80% increase of the Rabi splitting when the gap plasmon mode is excited compared to the plasmonic mode perpendicular to the dimer gap.

References

[1] Y. Sugawara, T.A. Kelf, J. J. Baumberg, M. E. Abdelsalam and P. N. Bartlett, “Strong Coupling between Localized Plasmons and Organic Excitons in Metal Nanovoids”, *Phys. Rev. Lett.* 97 (26), 266808, 2006.

[2] Rodriguez, S.R.K., A. Abass, B. Maes, O. T. A. Janssen, G. Vecchi and J. Gómez Rivas, “Coupling Bright and Dark Plasmonic Lattice Resonances”, *Phys. Rev. X*, Vol. 1, No. 2, 021019 (7), 2011.

[3] Väkeväinen, A.I., R. J. Moerland, H. T. Rekola, A.-P. Eskelinen, J.-P. Martikainen, D.-H. Kim and P. Törmä, “Plasmonic Surface Lattice Resonances at the Strong Coupling Regime”, *Nano Lett.*, Vol. 14, No. 4, 1721-1727, 2013.

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Wide band gap semiconductors for power electronics and sensor applications	Fabrizio Roccaforte
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#176 - Thermally activated phenomena in hybrid perovskites investigated by classical molecular dynamics

Alessandro Mattoni - CNR-IOM SLACS Cagliari

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The success of methylammonium lead trihalide (MAPI) for photovoltaics has given rise to an intense research effort to study the fundamental properties of hybrid perovskites. Though the photovoltaic activity of the crystal ultimately originates from the excellent semiconducting properties of the inorganic PbI sublattice[1,2], the dynamics of molecules at finite temperature and the hybrid interactions sizably affect the electronic transport, the thermal conductivity, the ferroelectric ordering, and many other properties of MAPI. In this perspective, hybrid perovskites are sometimes referred to as "dynamical" crystals to emphasize the role of structural fluctuations and of dynamic phenomena induced by temperature. This is important not only to study the thermodynamics of the material but also to understand more unconventional phenomena such as the hysteretic current-voltage transients.

Here, we make use of the MYP ionic interatomic model recently developed by the Authors[3] to study by all-atoms molecular dynamics the effect of temperature on: infrared absorption and phonons[4], intrinsic point-defects diffusivity[5], thermal transport[6] and degradation of hybrid perovskites in water[7].

After discussing the fundamental physical concepts underlying the ionic model we show that it is crucial to study large crystals over the nanosecond time scale to properly understand the effect of temperature on the above properties.

A relevant outcome of the modeling is the possibility to simulate the diffusion of point defects at finite temperature demonstrating the occurrence of ultra high and anisotropic diffusion of iodine interstitials (and not only vacancies), a result that is fully consistent with the involvement of iodide ions in hysteresis and have important implication for material improvement.

References

1. A. Filippetti, and A. Mattoni, Phys. Rev. B (2014), 89, 125203.
2. A. Filippetti, P. Delugas, and A. Mattoni, J. Phys. Chem. C (2014), 118, 24843.
3. A. Mattoni, A. Filippetti, M.I. Saba, and P. Delugas, J. Phys. Chem. C (2015),119, 17421.
4. A. Mattoni, A. Filippetti, M.I. Saba, C. Caddeo, and P. Delugas, J. Phys. Chem. Lett. (2016), 7, 529.
5. P. Delugas, C. Caddeo, A. Filippetti, and A. Mattoni, J. Phys. Chem. Lett. (2016), 7, 2356.
6. C. Caddeo, C. Melis, M.I. Saba, A. Filippetti, L. Colombo, and A. Mattoni, submitted (2016)
7. M.I. Saba, C. Caddeo, A. Filippetti, and A. Mattoni, in preparation (2016)

#177 - Ar, N2, O2 and humidity impact on the optical constants of CH3NH3PbI3 layers in the temperature range 40-80°C

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A great attention is progressively rising in the literature to face the stability of photoactive hybrid perovskites during simulated operation conditions, including temperature, water, oxygen, light illumination, UV, interfaces, texture, grain boundaries. [i],[ii],[iii],[iv]. The efforts are mostly devoted to the comprehension of the mechanisms governing the back-reaction of perovskites to the starting by-products (PbI_2, MAI) that pilot the devices to failure. We show that modifications of the optical constants occur in planar $CH_3NH_3PbI_3$ layers well before any structural change is observed by X-ray diffraction. We demonstrate that environment and temperature are key parameters driving changes in the dielectric function and therefore in the absorption coefficient. The measurements were performed in controlled atmosphere of non-reactive gas (dry Ar or N_2) and reactive gas (O_2 or humid air) as a function of the working temperature, in the range 40-80°C, indeed across the tetragonal-cubic transition. With respect to truly inert Ar used as benchmark to sign the thermal behavior of the material, N_2 ambient not only assures the reversibility of the optical behavior during thermal cycles, thus preventing/counteracting degradation effects, but also slightly improves the optical response during time. While it is clearly elucidated that the optical constants of the material can be recovered during thermal cycles in N_2 and Ar ambient, the presence of humidity in the air, instead, causes the absorption coefficient to monotonically and inexorably reduce, especially at the crossover of the phase transition (above 60°C). An intermediate case is represented by a saturated O_2

ambient. The use of N_2 to stabilize the layer indeed results as an effective strategy to preserve the optical response of the material under thermal operation conditions.

[i]D. Wang , M. Wright, N. Kumar Elumalai, and A. Uddin , Solar Energy Materials & Solar Cells 147 255 (2016);

[ii]G. Niu, X. Guo and L. Wang, J. Mater. Chem. A 3, 8970 (2015);

[iii]T. J. Jacobsson, W.Tress, J.-P. Correa-Baena, T. Edvinsson, and A. Hagfeldt, J. Phys. Chem. C, J. Phys. Chem. C**120**, 11382 (2016);

[iv]A. J. Pearson, G. E. Eperon, P. E. Hopkinson, S. N. Habisreutinger, J. Tse-Wei Wang, H. J. Snaith, and N. C. Greenham, Adv. Energy Mater. 1600014 (2016);

#178 - Morphological and optical modification in CH3NH3PbI3 planar layers at room temperature in air ambient

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In the last years, a fast development of new solar devices based on hybrid organic-inorganic perovskite structure took place due to their high performances. Nonetheless, their stability, especially with respect to humidity, is still a big issue for their industrial development. In this work we present a study on the impact of the ambient condition, and in particular of humidity, during time on $CH_3NH_3PbI_3$ (MAPbI3) films at room temperature. Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) and Ellipsometric Spectroscopy (SE) analyses were performed to investigate the morphological, structural and optical changes on $MAPbI_3$.

SEM analysis performed on fresh $MAPbI_3$ film shows that the layer has a bimodal distribution of grains being composed by large grain (≈2-5μm in diameter) with flat surface and by small grains with a well-defined cubic shape resulting from the tetragonal perovskite crystalline structure of the $MAPbI_3$ lattice. The degradation towards PbI_2 caused by the presence of moisture in the ambient air (60% RH) follows a surface dependent mechanism as attested by the progressive smoothing of the grains edges with time. This surface effect does not produce clear structural changes in the bulk as attested by XRD. Thereby, no additional amount of PbI_2 was detected in the diffraction pattern together with the typical peaks of the tetragonal $MAPbI_3$, even after 4 weeks of air exposure. SE analyses show the typical $MAPbI_3$ spectrum on the fresh sample, with the well recognizable peak at 1.64 eV due to the optical band gap. On the other hand, spectra collected after 3 and 4 weeks indicate a degradation path toward PbI_2 on the basis of modifications of the specific features in the absorption coefficient from the gap tail up to ~5eV .

#179 - Long-time living photoinduced polarons: the secret of high efficient perovskite solar cells.

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In less than 5 years of research activities on hybrid organic inorganic perovskites $CH_3NH_3PbI_3$ (MAPbI) based photovoltaic devices reached relatively high conversion efficiencies (22%) [1,2] comparable to the higher Si standards. Together with the wide optical absorption interval, the relatively long mean free path for both electrons and holes [3] determine the large efficiency of MAPbI solar cells. Until now, there is not a shared interpretation on the mechanism that governs charge carriers transport in this material.

Interactions between organic cations and the inorganic cage in MAPbI have been deeply investigated by vibrational spectroscopy as a function of temperature and optical excitation. IR and non-resonant Raman response in the broad frequency range from 30-3400 cm^{-1} were measured in temperature interval from 80-360 K (in all three crystallographic phases of the compound); moreover, we monitored at RT the steady state photoinduced variation of the FIR spectrum.

The organic cations and the inorganic cage interactions likely represent one of the principal elements that determine the very peculiar charge transport properties of this class of materials.

Photoinduced absorption (PIA) [4] was performed by exiting a MAPbI film in the visible and observing the variation of FIR spectrum. These measurements are steady state and can monitor only long lived excitations (of the order of microseconds). We observed the bleaching of infrared modes mostly associated with the inorganic cage and the appearance of new features in the same spectral region. Such spectral changes can be associated to a local deformation of the lattice around the photoinduced charges, in other words, the signature of photoinduced polarons.

*Ab initio*molecular dynamics simulation of "doped" MAPbI shows a deformation around the charge carriers that resemble the orthorhombic structure and the computed IR spectral difference between unperturbed tetra and perturbed ortho lattice shows a pattern very similar to the experimental PIA absorption.

These observations imply a primary role of electron-phonon and electron-MA interactions in charge transport in the $CH_3NH_3PbI_3$.

References

[1] J.-H. Im, C.-R. Lee, J.-W. Lee, S.-W. Park and N.-G. Park, Nanoscale (2011), 3, 4088.

[2] NREL, BEST RESEARCH-CELL EFFICIENCIES. latest chart Rec. cell Effic. 2016.

[3] Stranks, Samuel D.; Eperon, Giles E.; Grancini, Giulia; et al., Science, (2014), 6156, 341.

[4] C. Taliani, R. Zamboni, G. Ruani, F. Matacotta and K. Pokhodnya, *solid state commun.* (1988), 66, 487.

#180 - New organic small molecules as Hole Transporting Layer for efficient Perovskite Solar Cells

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Of the many new materials and methodologies aimed to produce low cost and efficient photovoltaic solar cells, the hybrid halide perovskite family appears as the highly promising way to achieve great photo conversion efficiency (PCE) mainly due to the unique optoelectronic properties of these materials.The great improvement in the PCE of Perovskite Solar Cells relies on the efforts made on the precise optimization of the active material coupled with the design of efficient selective charge transporting materials. In order to optimize the holes extraction and transport, organic small molecular Hole Transporting Materials (HTMs) have been widely investigated due to their chemical versatility and easy processability. SpiroOMeTAD, as the state-of-the art small molecule, shows very high performances, but its complex synthesis, high cost and the need of dopants affected its wide implementation.

Starting from this remarks, we designed and synthesized two simple, triphenylamine-based, organic HTMs, namely H1 and H2, characterized by a symmetrical structure with a carbazole and a phenothiazine core unit, respectively. The choice of a carbazole or phenothiazine core unit, which have been successfully used in organic optoelectronics [1,2], and the introduction of alkyl chains on the structures play an important role to determine the energy levels, the molecular geometry, the charge carrier mobility and solid film self-assembly. Finally, the alkyl chains and the small size ensure higher solubility at low temperature, which enables the suitable fabrication of devices with by low temperature (sub-100 °C) solution process. Moreover H1 and H2 have been applied as HTM PCSs achieving 14.3% and 13.2% efficiency, respectively, compared to the value of 14.8% obtained with the reference material SpiroOMeTAD.

[1] R. Grisorio, L. De Marco, G. Allegretta, R. Giannuzzi, G. P. Suranna et al., *Dyes and pigments* **98** (2013), 98, 221-231.

[2] A. Michaleviciute, E. Gurskyte, D. Y. Volyniuk, V. V. Cherpak, G. Sini et al., *J. Org. Chem.***77**(2012), 9120-9133.

#181 - Quantum confinement on a single object level: band structure modification in perovskite nanocrystals

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Colloidal $CsPbX_3$ (X= Cl, Br and I) nanocrystals attract much attention recently due to their potential application for light emitting diodes, along with opportunities for low-cost high efficiency photovoltaic devices. Such applications rely on the nature of optical transitions between the valence and conduction band edges. We investigate the variation in bandgap energies of single $CsPbBr_3$ nanocrystals and explicitly demonstrate the presence of an effective coupling between proximal nanocrystals in an ensemble, leading to band structure modification. We make use of valence-loss electron spectroscopy in a state-of-the-art low-voltage monochromatic scanning transmission electron microscope, providing a spatial resolution below 1.6Å. In that way, absorption of a single nanocrystal can be investigated in parallel with its structural parameters. We provide novel insights regarding the relation between the nanocrystal size and shape, and its bandgap energy. We explicitly demonstrate that the bandgap increase due to quantum confinement, is governed by the smallest dimension of the cuboidal perovskite nanocrystal. These unique insights are directly relevant to the engineering of custom-designed quantum structures and solids, that will be realized by purposeful assemblage of individually characterized and selected quantum dots, serving as building blocks.

#182 - Bioinspired calcium phosphate nanocarriers for cardiac delivery of therapeutic molecules

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Cardiovascular disease (CVD) is a worldwide growing problem that afflicts close to 1% of the population and causes 17.3 million annual premature deaths. Causes include ischemic, toxic, genetic, post-inflammatory, and structural defects, overall resulting in a mortality of ~50% within 5 years from diagnosis. This highlights the urgent need to overcome the difficulties associated with present pharmacological therapies by developing new ground-breaking therapeutic strategies that go far beyond any current regimens. New approaches for safe, efficient, and heart-specific delivery of therapeutics are required.

Nanoparticles (NPs) hold great promise for nanomedical systems and provide an alternative strategy for more efficient, controlled, and safe approaches of drug delivery. While largely investigated in the cancer field, the development and use of efficient NPs for the treatment of CVDs is still in its infancy. In fact, to the best of our knowledge, only dendrimers, liposomes, and NPs based on synthetic polymers have been investigated so far for the *in vivo* delivery of various therapeutic molecules to myocardial cells. The use is drastically limited due to the lack of biodegradability and biocompatibility of these kinds of nano-carriers, the uncontrolled drug release in the bloodstream, the poor encapsulation efficacy, and the poor stability. In summary, there is a strong need for the identification of new formulations based on biocompatible and biodegradable NPs to overcome the limitations of NPs currently used for CVD treatment.

In this study, novel biocompatible and bioresorbable negatively charged biodegradable calcium phosphate nanoparticles (CaP-NPs) were developed as an innovative therapeutic system for the delivery of bioactive molecules to the heart. Synthesis of CaP-NPs was performed according to a new, straightforward one-pot inspired biomineralization protocol employing citrate as a stabilizing agent and regulator of crystal growth. Via the classical clathrin-mediated path, CaP-NPs were shown to efficiently internalize into HL-1 cardiac cells without promoting toxicity. Additionally, acute and chronic administration of CaP-NPs did not interfere with Ca^{2+} handling properties and electrophysiological features of HL-1 cells and adult cardiomyocytes. Finally, preliminary experiments validated that CaP-NPs were successfully able to encapsulate bioactive synthetic microRNAs and mimetic peptides, which were efficiently delivered into cardiac cell line *in vitro* and surprisingly even into cardiac tissue when administered *in vivo* by inhalation.

To sum up, our results showed that the CaP-NPs generated in this work are safe and effective drug-delivery systems for a new potential therapeutic treatment of polarized cells such as cardiomyocytes.

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#183 - CaCO3 nano-crystals as promising drug delivery systems for human and plants health

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Inorganic nanoparticles are suitable for a wide range of biomedical and environmental applications in particular for delivery systems fabrication. In particular $CaCO_3$ is one of the most used material due its biocompatibility, bioabsorbability and the characteristic porous structure capable of trapping different bioactive compounds. Our Spray Drying Technique produces $CaCO_3$ nano-crystals powder with defined morphology and phase.

Their biocompatibility was established in different cancer cell lines through MTT test. Cellular uptake and intracellular localization were evaluated by Confocal microscopy and Transmission electron microscopy showing the presence of nano-$CaCO_3$ mainly in the cytoplasm, in the nucleus, mitochondria and in the lysosomes.

We investigated the use of these nanocrystals as vessel for anti-cancer therapy. The nano-$CaCO_3$ efficiently encapsulated two anticancer drugs improving their cell uptake and cytotoxic effect. In particular we studied the sustained release of cisplatin and BEZ 235. The encapsulation strategy provided an enhancement of drug activity up to 100 times higher then free administration at the same nominal concentration.

Furthermore the nano-$CaCO_3$ features allowed to investigate a surface functionalization in order to tune their bio-interaction. The nano-crystals were efficiently coated by synthetic phospholipids providing improved dispersibility and plasmatic membrane targeting.

The technology of nano-carrier is the last frontier of drug discovery as it allows to amplify the drug effect both in effectiveness that in selectivity. All this translates in the administration of low agrochemicals doses in agriculture.

Given the safety of the obtained nanomaterial, we also investigated the application of nano-crystals as carrier for crop protection to fight plants infections. In particular we studied an innovative strategy against the *Xylella fastidiosa* infection that affect the olive trees in the South of Italy. Preliminary studies conducted in our laboratory have demonstrated the mobility of the nano-carriers in xylem vessels, without any effect on the plant tissues nor uptake by the vegetable cells. The nano-carriers are therefore free to travel and selectively hit the bacteria as missiles, hopefully, releasing specific anti-*Xylella* substances. The absence of phyto-toxicity was verified in experiment with model plants in order to expect experimentation in olive grove.

#184 - Antimicrobial and Bioactive Ionic Liquid-Calcium Phosphate-Based Biocomposites for Tissue Engineering

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Bacteria and fungi can often adhere to biomaterials and have the capability of forming biofilms on foreign bodies. The subsequent detachment of cells from these biofilms can result in the development of highly resistant local or systemic infections in patients. It has been suggested that the local application of antimicrobials can provide higher local antibiotic concentrations than those through intravenous application, and can also avoid the toxicity accompanied with their high plasma levels. Thus, the aim of this study is creating a biomaterial with antimicrobial activity and able to regenerate the tissue in bone defects. It has been demonstrated that some imidazolium, pyridinium and quaternary ammonium ionic liquids (IL) have antimicrobial activity. The *in situ* application of IL into sol-gel processes allows nanoparticles' structure control, driven by the IL' self-assembling property and selective IL-substrate interactions, while preserving their specific properties. In this work IL were incorporated in Hydroxyapatite (HA) through the sol-gel process to obtain an injectable material with biocompatible and antimicrobial properties.

The HA/IL biocomposites were obtained by applying IL $[C_nMIm]Cl$ (1 and 2 wt%) with different chain-lengths in the sol-gel process at room temperature. This induced shorter gelification times in comparison with the neat HA system. IL interact with the growing particles through the hydrogen bond "co-π-π stacking" mechanism, which creates an IL-layer on the HA surface. Thus, differences in the size, geometry, polarity and Coulomb coupling forces between the IL' anions and cations contribute directly to the final HA particle size and morphology. Furthermore, X-ray analyses demonstrated that as the IL *N*-alkyl chain-length increases, the HA phase decreases and the contents of its precursors, such as brushite and monetite, increases. Meanwhile, biological investigations performed with human Mesenchymal Stem Cells (hMSCs) demonstrated that the biocomposites have a good biocompatibility, supporting the cell-proliferation up to day 14. Furthermore, the materials induced a pre-osteoblast differentiation at short time (ALP, 3 days) in basal conditions, and stimulated osteocalcin expression after 14 days of cell culture. In particular, the expression of biological markers increased with an increasing IL *N*-alkyl chain-length. The antimicrobial studies confirmed the antifungal activity (*Candida albicans, C. tropicalis*) of the biocomposites with $C_{10}MImCl$, $C_{16}MImCl$ and $(C_{10})_2MImCl$, while the best antibacterial properties (E. coli) were obtained with the $(C_{10})_2MImCl$-based biomaterial.

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#185 - Nanotheranostic tools engineered with Cyclodextrins and Photosensitisers assemblies

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Cyclodextrin are suitable host molecules especially used for drug entrapment and delivery. Our goals is to design and characterize biodegradable amphiphilic cyclodextrin able to host, deliver and especially target a drug in the sites of action. These carriers, have a size compatible with i.v. injection and posses high potential to optimize drug distribution in the body, and selectively deliver anticancer [1,2], photosensitiser for Photodynamic Therapy of Tumors (PDT) [3], metal nanoparticles [4], DNA for gene therapy [5] or combined dose of therapeutics [6] and /or diagnostic probe for theranostic [7].This multifunctional nanoconstructs can be engineered with stimuli-responsive probes i.e. pH, magnetic field, light , redox potential [8], or combined with nanoplatform based on graphene and/or MWCNT [9] to give dispositives for investigating cell behavior. Recent investigations and results will be here discussed.

References

1 Quaglia, F.; Ostacolo, L.; Mazzaglia, A.; Villari, V.; Zaccaria, D.; Sciortino, M.T. Biomaterials, 2009, 30, 374.

2 Bondì, M. L.; Scala, A.; Sortino, S.; Amore, A.; Botto, C.; Azzolina, A.; Balasus, D.; Cervello, M., Mazzaglia A. Biomacromolecules 2015, 16, 3784.

3 Conte, C.; Ungaro, F.; Mazzaglia, A.; Quaglia, F. In Nano-Oncologicals: New Targeting and Delivery Approaches. Advances in Delivery Science and Technology; Alonso, M. J., Garcia-Fuentes, M., Eds; CRS Springer: New York, 2014; pp 123−160.

4 Mazzaglia, A.; Monsù Scolaro, L.; Mezzi, A.; Kaciulis, S.; De Caro, T.; Ingo, G.; Padeletti, G. J. Phys. Chem. C 2009, 113, 12772.

5 Villari, V.; Mazzaglia, A.; Darcy, R.; O'Driscoll, C. M.; Micali, N. Biomacromolecules 2013, 14, 811. 6 Conte, C.; Scala A., Siracusano, G.; Sortino G.; Pennisi, R.; Piperno, A.; Miro, A.; Ungaro, F.; Sciortino, M. T.; Quaglia, F.; Mazzaglia A. Colloids and Surfaces B: Biointerfaces, 2016, 146, 590.

7 Mazzaglia, A.; Valerio, A.; Micali, N.; Villari, V.; Quaglia, F.; Castriciano, M. A.; Monsù Scolaro, L.; Giuffré, M.; Siracusano, G.; Sciortino, M. T. Chem. Commun. 2011, 47, 9140.

8 Foschi, G.; Leonardi,F.; Scala, A.; Biscarini, F.; Kovtun, A.; Liscio, A.; Mazzaglia A.; Casalini S. Nanoscale, 2015, 7, 20025.

9 Iannazzo, D.; Mazzaglia, A.; Scala, A.; Pistone, A.; Galvagno, S.; Lanza, M.; Riccucci, C.; Ingo, G.M.; Colao, I.; M. T. Sciortino, M. T., Piperno A.; Grassi, G. Colloids Surf., B, 2014, 123, 264.

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#186 - Multi-layer PEDOT electropolymerized system for superior electrochemical performance and drug release in neuroprosthesis applications

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Multi-layer PEDOT electropolymerized system for superior electrochemical performance and drug release in neuroprosthesis applications

Elisa Castagnola, Stefano Carli, Luciano Fadiga, Davide Ricci

The great challenge of neuroprosthesis is to obtain stable neural interfaces between neural tissue and implanted microelectrodes. The greatest obstacle to overcome is the complex tissue response, which involves a series of events that occur following implantation, strongly influencing the long-term device performances. The relationship between these events and the formation of a glial scar, i.e. the final result of acute and chronic tissue reactions that impairs both signal recording and neural stimulation,is still not completely understood. This is the reason why several alternative routes have been undertaken to reduce or prevent the tissue response, among which drug delivery, electrode miniaturization, use of soft and flexible substrates, surface bio-electrochemical properties improvements are the most sought after. In order to combine several of these strategies for avoiding of tissue reaction, we have previously engineered an original device composed by a low-impedance gold sphere microelectrode directly grown at the tip of an ultrathin and ultra-flexible tether wire.

In this study we report the optimization of a multi-layer Poly(3,4-ethylenedioxythiophene) (PEDOT) electrodeposition technique for the functionalization of such sphere microelectrodes: a first PEDOT-PSS-CNT layer, that provides superior charge- transport, mechanical and stability properties, is followed by a second PEDOT-DEX (Dexamethasone) layer, that guarantees an electrochemically controlled drug release. This electrochemical system is aimed to preserve the original superior properties of the PEDOT-PSS-CNT composite, while introducing the possibility to contrast acute imflammatory response through DEX delivery. We report here: (1) the electrochemical performance of the PEDOT multi-layer coating through electrochemical impedance spectroscopy and voltammetric analysis; (2) how the PEDOT-DEX layer influence the charge - tansport and stability properties of the PEDOT-PSS-CNT underlayer and (3) the electrochemically controlled in-vitro release of the DEX in PBS solution monitored by UV spectroscopy.

#187 - Srf siRNA Nanoparticle-Coated Coronary Stent for Prevention of Post-Angioplasty Restenosis

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Restenosis, the re-narrowing of a blood vessel after removal of atherosclerotic plaque, is a major limitation of surgical treatments for atherosclerosis.Indeed, injury of arteries during angioplasty and stenting causes cell migration and thrombosis in vessel tissue. The pharmacological conventional approaches are not fully effective for inhibiting restenosis, requiring new approaches to suppress and/or prevent restenosis *via* inhibition of migration/proliferation of smooth muscle cells (SMCs). Several types of carriers and technologies have been recently developed for controlled delivery/release of genes, siRNAs, miRNAs, and peptide structures, to the target damaged tissue. Agents to be delivered are either attached to the vector surface or entrapped in the bulk of the carrier. Serum response factor (Srf) is a widely expressed transcription factor that regulates the expression of SMCs marker genes, such as smooth muscle α-actin, calponin-1, ortransgelin (SM22a). The specific inhibition of Srf gene expression results in the retardation of cell growth and migration. To take advantage of these benefits, we developed a new delivery system for Srf siRNA-nanoparticles from chitosan-coated stent surface. For this purpose, polyhydroxybutyrate (PHB) nanoparticles were modified *via* aminolysis with low-molecular weight polyethylenimine (PEI) to obtain positively charged PHB nanoparticles, able to delivery Srf siRNAs (Srf-NPs). Synthetized siRNA nanoparticles were immobilized on the chitosan-coated stent surface, and analysed for transfection efficiency and intracellular uptake on A10 vascular smooth muscle cells. The immobilized Srf-nanoparticles exhibited negligible cytotoxicity against the adhering A10 cells and high gene silencing efficiency as determined by RT-PCR and western blot analyses. *In vitro* cell migration assay indicated that the silencing of the target genes achieved by the Srf-NPs resulted in a significant reduction of the migration potential of A10 cells. Our results demonstrate that Srf released from the stent was able to suppress the SRF protein and its downstream signalling proteins regulating SMC cell growth and migration.

#188 - Graphene heterostructures with Nitride semiconductors for high frequency electronics

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Group III Nitride semiconductors (III-N), including GaN, AlN, InN and their alloys, are materials of choice for many applications in optoelectronics and high-power/high-frequency electronics (e.g. LEDs, diodes, HEMTs,..). Due to its electrical, optical and thermal properties,graphene (Gr) integration with III-N has been considered in the last years to address some issues of the state-of-the-art GaN technology, e.g. as transparent conductive electrode for GaN LEDs, or as a heat spreader for thermal management in high power AlGaN/GaN HEMTs [1].

More recently, Gr integration with III-N has been proposed to realize novel device concepts for ultra-high frequency applications. In this context, Gr/AlGaN/GaN heterostructures deserve particular interest, since they offer the possibility to exploit the properties of Gr and AlGaN/GaN 2DEGs in close proximity. As an example, such a system can represent a building block for a Gr-Base Hot Electron Transistor (GBHET), a vertical device where Gr plays the role of the ultrathin base and the AlGaN/GaN 2DEG of the emitter [1].

In our work, different approaches to fabricate Gr heterostructures with III-N will be explored, including the transfer of Gr grown by CVD on catalytic metals (Cu) [2], and the directCVD growth of Gr on AlN [3] and AlGaN templates. Several structural/chemical, morphological and electrical characterizations have been employed to investigate these heterostructures. Micro-Raman spectroscopy was used to evaluate the number of Gr layers and defects density, while AFM provided information on the surface roughness of the transferred/grown Gr, which is crucial for GBHETs. Local electrical analyses by CAFM [2] and electrical measurements on properly fabricated test patterns were used to investigate vertical current transport across the Gr/III-N heterostructures. The experimental results have been compared with ab-initio calculations of the Gr/III-N interface structure and electronic properties. Furthermore, kinetic Monte Carlo simulations were employed to describe the mechanisms of CVD Gr growth on III-N templates.

Finally, some key processes for the fabrication of the GBHETs have been developed, such as isolation of Gr and AlGaN/GaN 2DEGs, Ohmic contacts formation, and the atomic layer deposition of ultra-thin dielectrics with high structural/electrical quality on Gr.

All these results represent important advances towards the assessment of a Gr/Nitrides hybrid technology for next generation high frequency electronics.

[1] F. Giannazzo, G. Fisichella, G. Greco, A. La Magna, F. Roccaforte, B. Pecz, R. Yakimova, R. Dagher, A. Michon, Y. Cordier, Physica Status Solidi A (2016), in press.

[2] G. Fisichella, G. Greco, F. Roccaforte, F. Giannazzo, Nanoscale 6 (2014) 8671.

[3] A. Michon, A. Tiberj, S. Vezian, E. Roudon, D. Lefebvre, M. Portail, M. Zielinski, T. Chassagne, J. Camassel, Y. Cordier, Appl. Phys. Lett. 104, 071912 (2014).

#189 - Electronic structure of hydrogenated diamond: Microscopical insight into surface conductivity

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Although intrinsic diamond is an insulator, it is well known that hydrogen-terminated diamond (HD) surfaces exposed to air exhibit surface p-type conductivity [1] up to 7 orders of magnitude larger than the bulk one. Such excellent electric conductivity is a very attractive property for high- power and high-frequency applications [2], nonetheless the basic mechanism of this well-known phenomenon is still awaiting to be fully characterized and explained in detail.

We have correlated the surface conductivity of HD to the electronic structure in the Fermi region. Significant density of electronic states (DOS) in proximity of the Fermi edge has been measured by photoelectron spectroscopy (PES) on surfaces exposed to air, corresponding to a p-type electric conductive regime, while upon annealing a depletion of the DOS has been achieved, resembling the diamond insulating state. The surface and subsurface electronic structure has been determined, exploiting the different probing depths of PES applied in a photon energy range between 7 and 31 eV. Ab initio density functional calculations including surface charge depletion and band-bending effects favorably compare with electronic states measured by angular-resolved photoelectron spectroscopy. Such states are organized in the energy-momentum space in a twofold structure: one, bulk-derived, band disperses in the Gamma-X direction with an average hole effective mass of (0.43 ± 0.02)m_0, where m0 is the bare electron mass; a second flatter band, with an effective mass of (2.2 ± 0.9)m_0, proves that a hole gas confined within 1nm in the topmost layers is responsible for the conductivity of the (2 × 1) hydrogen-terminated diamond (100) surface. [3]

References

[1] F. Maier, M. Riedel, B. Mantel, J. Ristein, and L. Ley, Phys. Rev. Lett. **85**, 3472 (2000).

[2] V. Camarchia, F. Cappelluti, G. Ghione, M. C. Rossi, P. Calvani, G. Conte, B. Pasciuto, E. Limiti, D. Dominijanni, and E. Giovine, Solid-State Electron. **55**, 19 (2011).

[3] S. Iacobucci, Paola Alippi, P. Calvani, M. Girolami, F. Offi, L. Petaccia, and D. M. Trucchi, Phys. Rev. B 94, 045307 (2016) .

#190 - Mosaic diamond detectors for fast neutrons and large ionizing radiation fields

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First neutron and X-ray beam tests on a novel 12-pixel single-crystal diamond mosaic detector are presented and discussed. Preliminary characterization of single-pixel electronic properties, performed with alpha particles, results in charge carrier mobilities > 2000 cm^2/Vs and saturation velocities of the order of 10^7 cm/s. Signal stability over time, measured with a ^{241}Am source (37 kBq activity), is longer than 5 h. Tests under an intense X-ray beam (1 Gy/h dose-rate) show a very good response uniformity (down to about 1% of relative standard deviation from mean value), suggesting a high level of pixel reproducibility at intermediate bias voltages (ranging from 20 to 100 V). Response uniformity reduces at voltages >200 V, due presumably to radiation-assisted detrapping effects. Preliminary results of 12-pixel simultaneous acquisitions of X-ray beam profiles and pulse height spectra under a fast neutron beam (14 MeV) are also presented.

#191 - Graphite distributed electrodes for diamond-based photon-enhanced thermionic emission solar cells

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Graphite conductive vertical microchannels, fabricated by femtosecond laser treatment, are proposed as distributed electrodes in defect-engineered (“black”) single-crystal diamond cathodes for innovative solar cells. Energy conversion is based on photon-enhanced thermionic emission, where the reduction of the cathode series resistance is crucial to preserve conversion efficiency. Process yield higher than 80% and resistivity as low as 0.75 ± 0.15 Ω cm were achieved by the optimization of laser parameters and the use of a multi-pass writing technique. A 100x100 array of graphite electrodes was integrated in a diamond-based cathode prototype, reducing the series resistance of more than 10 orders of magnitude with respect to bulk diamond.

#192 - SiC based photodetectors for UV-A sensing

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Exposure to ultraviolet radiation is a major risk factor for most skin cancers. The sun is our primary natural source of UV radiation. The strength of the sun's ultraviolet radiation is expressed as Solar UV Index (UVI). UV-A (320-400 nm) and UV-B (290-320 nm) rays mostly contribute to UVI. UV-B is typically the most destructive form of UV radiation because it has enough energy to cause photochemical damage to cellular DNA. Also overexposure to UV-A rays has been associated with toughening of the skin, suppression of the immune system, and cataract formation. The use of preventive measures to decrease sunlight UV radiation absorption is fundamental to reduce acute and irreversible health diseases to skin, eyes and immune system. In this perspective UV sensors able to monitor in a monolithic and compact chip the UV Index and relative UV-A and UV-B components of solar spectrum can play a relevant role for prevention, especially in view of the integration of these detectors in close at hand portable devices. Here we present the preliminary results obtained on our UV-A sensor technology based on the use of hydrogenated Silicon Nitride (SiN:H) thin passivating layers grown through Plasma Enhanced Chemical Vapor Deposition (PECVD) on the surface of thin continuous metal film Ni_2Si/4H-SiC Schottky detectors, already used for UV-Index monitoring. The use of thin passivating SiN:H films, allow to reduce the detectors responsivity in the UVC range (< 280 nm) and shift the detection spectrum of 4H-SiC photodiodes in the UVA range with a peak responsivity around 330 nm-340 nm. The first UV-A detector prototypes fabricated on 4H-SiC substrates exhibit a good uniformity of the electro-optical performances with a very low leakage current density of about 0.2 pA/mm^2 and a peak responsivity value of 0.027 A/W at 330 nm, both measured at 0V bias. Quite recently the same SiN:H layers dielectric stacks have been integrated also on the first thin metal film Ni_2Si-6H-SiC Schottky photodiodes prototypes fabricated on 2” diameter 6H-SiC substrates. The 6H-SiC lower energy gap (Eg=3.05 eV, λcut-off=405 nm) with respect to 4H-SiC (Eg=3.26 eV, λcut-off=380 nm) is expected in fact to further shift the detector’s peak responsivity spectrum in the middle of the UV-A range. First measurements performed on these devices show a maximum optical responsivity of about 0.07 A/W at 330 nm and 0V bias on the bare Ni_2Si-6H-SiC Schottky photodiodes. The use of the SiN:H absorbing layer on the top of the Ni_2Si surface of these detectors allow to shift the maximum responsivity spectrum at 360 nm (0.055A/W measured at 0V bias). In summary the integration of SiN:H thin passivation layers on Ni_2Si/SiC Schottky photodiodes has been shown extremely promising for the development of a low cost UV Index-UVA/UVB intensity monolithic detector, considering the compatibility of SiN:H deposition process with current UV detectors manufacturing process.

#193 - Schottky SiC diodes for X-ray, UV and low and medium energy ions detection

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SiC has been long identified as a radiation hard material with superior electronic properties which are appropriate for applications involving elevated temperature in high radiation environments. Moreover, due to the intrinsic visible blindness SiC detectors can operate without any external filters at high intensity visible light.

In recent years, the availability of high quality SiC bulk and epitaxial layers have allowed the realization of high performances detectors based on Schottky diodes and p-n junction. In past years, Schottky SiC diodes with continuous front electrode were proposed to detect high energy ions (1-3 MeV) emitted from plasmas generated by high intensity lasers (~10^{16} W/cm^2) . In that case, the SiC diodes are able to detect and distinguish the photo-peak, the electron and the ion components, showing a high sensitivity to ion detection. However, due to the metal surface contact, they cannot detect ions with energy below 100 keV/amu.

Recently, the scientific community focused the attention on plasma generated with lower lasers intensity (~10^{10} W/cm^2) and to the monitoring of all components of the plasma such as UV, X-ray low and medium energy particles.

In this work we then propose our experiments conducted using Schottky SiC detectors with interdigit front electrode and active epilayer 4 um thick and devices with thin continuous front electrode and active epilayer 25 um thick for plasma monitoring and detection of ions with hundreds of keV energy.

We demonstrated interdigit devices are able to detect soft X-ray, UV radiation and to monitor with good sensitivity the ions generated in plasma, and eventually post-accelerated by a suitable system, at energy ranging within 1 keV and 30 keV.

Concerning thin continuous front electrode detectors, they were tested using a standard three peaks alpha particle source obtaining an energy resolution (expressed in percentage) of 1.3% for the 5.48 MeV peak (^{241}Am) and using a Helium beam in an ion implanter in a backscattering configuration from different metallic targets, demonstrating that our SiC detectors are able to detect particle in the energy range 200 – 600 keV, with a resolution of about 8 %, very near to the values obtained with commercial Si detectors in this energy range.

In conclusion, our tests demonstrate that proposed devices are promising for plasma monitoring and for detection of ions with energy of hundreds of keV and they are particularly suitable for applications in presence of visible light, such as in case of ion backscattering from dielectrics materials, and in harsh environments thanks to the visible blindness and radiation hardness typical of 4H-SiC.

#194 - Gold Nanoparticles on 3C-SiC substrates by Electroless Deposition

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SiC-based electronic devices and sensors can operate in demanding conditions and where conventional silicon-based electronics cannot. Among the polytypes, the 3C-SiC has the zinco-blende crystalline arrangement and so it could be grown by hetero-epitaxy on silicon substrates, combining large area and low temperature production if compared to the other polytypes. It is also bio-compatible and, with a band-gap of 2.2 eV, it could be used as a photo-anode in photo-electrochemical (PEC) reactions, such as water splitting. However, it has been shown that to improve the PEC processes and also the sensing ability, metallic nano-particles should be used. Gold or platinum are particularly promising because they are very stable against corrosion and have a very high work function (more than 5 eV). Here we propose the well known electroless deposition, based on a simple immersion in a solution containing a metal salt and HF, as a method to obtain gold nanoparticles on 3C-SiC layers. The deposition was investigated by varying the immersion time in the solution. Electron microscopy showed that the arrangement of gold particles replicates the substrate surface, according to a self selective deposition mechanism and it is more pronounced on defects sites. From RBS (Rutherford Backscattering Spectrometry of 2MeV He^+) we measured the gold areal density and we found that in our time range the growth is diffusion limited, consistently with the model observed on silicon substrates. From Electron Microscopy analyses we calculated the evolution of density and size of the particles as a function of time. After an incubation time, the gold particles are progressively nucleated, and the radius grows with the square root of time, indicating a direct attachment of ions to the growing island with no interacting diffusion fields. Reflectivity measurements and Raman spectroscopy have been employed in order to evidence plasmonic effects and we found that the deposited particles exhibit properties modulated by the clusters size and density. This technique appears very promising for applications in which the plasmonic effect has a relevant role, such as biomedicine and sensors devices, as well as for photo-electrochemistry.

#195 - Synthesis of MoS2 nanosheets from Molybdenum oxide film precursors

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The impact of Molybdenum disulphide (MoS_2) is rapidly increasing because of its unique physical and chemical properties at the ultrathin thickness scale, down to a two-dimensional monolayer. Such properties are exploited to integrate MoS_2 as active material in prototypical devices, such as field-effect transistors and photodetectors, for low-power, ultra-scaled nano-, opto- and spin-electronics.

MoS_2 with lateral size in the micrometer range and thickness down to the monolayer can be easily obtained in the form of flakes by mechanical/chemical exfoliation from geological crystals, taking advantage of its bulk structure at ultrathin thickness characterized by weakly interacting layers, as in other transition metal dichalcogenides. However, this approach has severe limitations in terms of technology transfer, where wafer-size synthesis of MoS_2 in the form of a thin film with atomic control of thickness is required. How to overcome this limitation is still an open issue.

In this frame, we synthesized MoS_2 nanosheets by using S powder and sub-stoichiometric oxidized Molybdenum thin films in a heterogeneous vapor–solid reaction at high-temperature. In this chemical vapor deposition approach, the morphology of the precursor film plays a crucial role in dictating MoS_2 structural properties, as observed considering the granular nature and grain size in MoS_2 layers obtained from the sulfurization of electron-beam deposited precursor films [1]. To gain a deeper insight into this aspect, we also carried out sulfurization starting from thin solid precursor Molybdenum oxide films grown by atomic layer deposition (ALD), where extremely high conformality and thickness control are achievable in the film growth [2].

We found that the thickness dependence of the MoS_2 structural properties is directly connected with the observed granularity of the MoS_2, which derives from the precursor film morphology. The basic mechanism governing MoS_2 crystalline order relies on the connection–disconnection between adjacent grains. Further, ALD based synthesis of MoS_2 has a quality comparable to the natural crystals at thicknesses down to four layers, while at very low thicknesses the interface energetics between the ALD precursor film and SiO_2 substrate dramatically affects the evolution of the sulfurization process leading to MoS_2 nanoclustering. Such limitation is overcome by exploiting monocrystalline sapphire substrate as support for the precursor.

Our results evidence the potential of a heterogeneous vapor–solid reaction process to synthesize MoS_2 nanosheets with high conformality, uniformity and thickness control on the cm^2 scale. Further, precursor/substrate interface engineering represents a promising way to control the physical/chemical properties of the MoS_2 nanosheet.

[1] S. Vangelista et al., Nanotechnology **27** 175703 (2016)

[2] C. Martella et al., Adv. Electr. Mater. (in press)

#196 - Dephasing in strongly anisotropic black phosphorus

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Black phosphorus (bP) is a direct gap semiconductor which, thanks to its layered structure, can be exfoliated down to the monolayer, called phosphorene. This material recently attracted great interest thanks to the band gap tunable with the number of layers, which can provide an opportunity to fill the gap among graphene and transition metal dichalcogenides [1]. Moreover, anisotropic transport, optical, and thermoelectric properties have been recently observed and related to the puckered structure of bP layers [2].

Here, we will report measurements of weak localization on a 65 nm thick black phosphorus field effect transistor [3]. Weak localization is a quantum effect, related to coherent scattering at low temperatures. Using the Hikami-Larkin-Nagaoka model [4],

the dephasing length L_ϕ (or inelastic scattering length) can be inferred from weak localization. Our study is performed for various gate voltages, in the hole-doped regime, in a closed cycle ^{3}He cryostat, at temperatures down to 250mK.

The dephasing length is found to increase with increasing hole density, attaining a maximum value of 55 nm at a hole density of approximately 10^{13}cm^{-2}, obtained from the Hall effect.

The temperature dependence of L_ϕ was also investigated. Above 1K it decreases, with a weaker temperature dependence than $T^{-1/2}$, the one expected for electron-electron interaction in two dimensions. Rather, the observed power law was found to be close to that observed previously in quasi-one-dimensional systems such as metallic nanowires and carbon nanotubes. We attribute our result to the crystal structure of bP which host a `puckered' honeycomb lattice forming a strongly anisotropic medium for localization. Therefore, we found a further effect where the anisotropic structure of black phosphorus plays a crucial role.

[1] H. O. H. Churchill and P. Jarillo-Herrero, “Two-dimensional crystals: Phosphorus joins the family,” *Nat. Nanotechnol.*, vol. 9, no. 5, pp. 330–331, 2014.

[2] F. Xia, H. Wang, and Y. Jia, “Rediscovering black phosphorus as an anisotropic layered material for optoelectronics and electronics.,” *Nat. Commun.*, vol. 5, p. 4458, 2014.

[3] N. Hemsworth, V. Tayari, F. Telesio, S. Xiang, S. Roddaro, M. Caporali, A. Ienco, M. Serrano-Ruiz, M. Peruzzini, G. Gervais, T. Szkopek, and S. Heun, “Dephasing in strongly anisotropic black phosphorus,” *arXiv:1607.08677*, Jul. 2016.

[4] G. Bergmann, “Weak Localization in Thin Films,” *Phys. Rep.*, vol. 107, pp. 99–99, 1984.

#197 - Large scale production of 2D crystals by wet jet milling

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Efficient and scalable two-dimensional (2D) crystals production methods are urgently required for a rapid clearing of technological hurdles towards the development of a 2D crystals-based industry, satisfying the specific requirements of different application areas.[1] The outstanding properties of the 2D crystals is boosting the research activity in several application areas, ranging from polymer composites for aircraft to quantum computers, and applications in biology, electronics, and medicine.[1] However, the practical realisation of any commercial application requires efficient production methods.[2] Although many production techniques have been developed,[2] the most promising approach for large-scale production of 2D crystals relies on liquid phase exfoliation (LPE) of their bulk counterparts. However, the main limitation of this method is the time-consuming process, i.e. in the exfoliation using sonic waves, the sonication time ranges from 6 to 90 hours,[3,4] achieving concentrations in order of grams per litre; or the shear mixing process[5], which can produce graphene dispersions with a concentration of 0.1 gL^{-1} after more than 60 hours.[5]

Here, we show a novel approach we recently developed for the exfoliation of layered crystals. The process is based on high-pressure wet jet milling (WJM). This technique allows us to produce large quantities of single and few layer 2D flakes in dispersion. The WJM has been successfully applied to graphite, *h*-BN, transition metal dichalcogenides, and black phosphorus. By using WJM we can produce more than 2 litres per hour of 2D crystals in dispersion with a concentration exceeding 10 gL^{-1}. In the case of graphene, the exfoliated crystals show low defectiveness (Raman peak intensity ratio ID/IG = ~0.5). A further purification by centrifugation allows us to prepare dispersions discriminating the thick or un-exfoliated flakes, keeping a concentration as high as 1 gL^{-1}. Finally, we will present the results obtained with the integration of the as-produced dispersions in different applications. We have indeed used them as active material in lithium ion battery anodes, as reinforcement in Nylon-graphene composite, and as flame-retardant additive in fibre glass.

References

1. A. C. Ferrari, et al., Nanoscale, **7** (2015) 4598.

2. F. Bonaccorso, et al., Mater. Today, **15**(2012) 564.

3. Y. Hernandez, et al., Nature Nanotechnology, **3** (2008) 563.

4. N. Nicolosi, et al., Science, **340** (2013) 1226419.

5. K. R. Paton, et al., Nature Materials, **13** (2014) 624

#198 - Protein induced self-assembly of GO

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Graphene has been acclaimed as a cutting edge material since its discovery [1]. Because of its noteworthy properties [2] it has attracted and is still attracting major interest. Moreover, graphene's benefits have further expanded after obtaining related materials such as graphene oxide (GO) [3] that features tunable electro-optical and chemical properties, high hydrophilicity and ease of production and functionalization. Yet the possibility of obtaining reduced GO (rGO) by processing contributed greatly to its outstanding potential, as rGO can partially restore the properties of graphene while enabling its dispersion in surfactant-free solution [4].

However, using graphene for practical applications remains to be fully realized. One main issue is the integration of its 2D structure into accessible and scalable 3D materials, a need that has inspired a growing field of research [5].

We accomplish the task of building 3D GO structures by Peroxiredoxins (Prx), a family of multi-tasking enzymes with ring-like architectures. Taking advantage of the proteins capabilities of interacting with both GO and rGO through weak interactions due to their exposed surfaces [22], as well as of their symmetric structure [6], 3D rGO-based composites are hereby built up.

The Prx rings adhere flat on single GO layers and induce partial reduction, driving their stacking into 3D multi-layer rGO-Prx composites, even when using very few amounts of GO. Further, protein engineering allows divalent metal ions to bind the Prx's lumen and this is exploited to capture pre-synthesized gold nanoparticles (AuNPs) and grow in situ palladium nanoparticles (PdNPs) using the protein ring as physical confinement, thus paving the way to straightforward and "green" routes to 3D rGO-metal composites.

GO quickly gets clumped in the presence of Prx during mixing experiments in solution. Such clumps progressively push together leading to a soft colloid which can be hanged as compact material. The colloid can form again even after breaking by shaking, hence suggesting that a reversible self-assembly process occurs. The so-formed rGO-Prx colloid can be easily dried as a free-standing material by freeze-drying while keeping a microporous internal architecture.

Addition by protein engineering of metal-binding sites on the lumen of the Prx ring allows the protein to bind divalent metal ions. By this way, Prx can trap Ni(II)-functionalized AuNPs with ~2 nm diameter and carrier them inside the multi-layer rGO-based composite. The versatility of the system is also demonstrated for Pd(II) and for Co(II) [7].

References

[1] K. S. Novoselov et al. Science 306 (2004), 666
[2] A.C. Ferrari et al. Nanoscale 7 (2015), 4598
[3] X. Huang et al. Small 7 (2011), 1876
[4] R. L. D. Whitby, ACS Nano 8 (2014), 9733
[5] M. Zeng et al. Chin. Phys. B 22 (2013), p098105
[6] F. Angelucci et al., J. Mol. Biol. 425 (2013), 4556
[7] M. Ardini et al. Nanoscale 8 (2016), 6739

#199 - Electronic properties of Chevron-like graphene nanoribbons: a combined experimental and theoretical investigation

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On-surface synthesis is presently representing a powerful and promising approach to achieve atomic-precise graphene-based nanostructures[1], as in particular graphene nanoribbons (GNR) with specific width, edge terminations and chemical composition[2]. By choosing the proper molecular precursor, a precise tuning of the nanostructure properties can be achieved. Indeed, effective control over bandgap values and electronic doping opens the way to the fabrication of complex nanostructures, such as for instance nano-heterojuctions[3]. Despite the recent advancements, the investigation of the GNR properties is still at the early stages and a throughout characterization of the electronic and optical properties of different GNR types remains an open issue.

In this work, we present the results of a combined experimental and theoretical investigation on chevron-like armchair-GNRs, grown by on-surface synthesis technique. X-ray Photoemission Spectroscopy and High-Resolution Energy Loss Spectroscopy have been used to characterize their growth and electronic properties. The EELS electronic spectra were analysed applying the three phase dielectric model, thus obtaining the adsorbate dielectric function ε_{ads}. The experimental ε_{ads} has been modelled with four damped harmonic oscillator located at 2.3, 2.8, 3.4 and 4.4 eV, respectively. The good agreement with theoretical results - based on DFT calculations - demonstrates the fundamental role played by excitons in determining the optical and electronic properties of chGNRs. Comparison with results obtained by Reflectance Difference Spectroscopy [4] will be also discussed.

References

[1] L. Lafferentz et al. Nat. Chem 4, 215 (2012)

[2] J. Cai et al., Nat. 466, 470, (2010)

[3]J. Cai et al Nat. Nano. 9, 896, (2014)

[4] R. Denk et al. , Nat. Comm. 5, 4253 (2014)

#200 - Recent developments in calcium phosphate cements for bone graft substitution

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Since the first clinical application of a calcium phosphate (CaP) hydraulic cement for bone void filling in 1982, these injectable and self-setting materials have been widely adopted and are now found in the portfolios of most manufacturers of synthetic bone graft substitutes. Injectable cements are appreciated for their minimally invasive application, and the ability to fill defects of any shape. A vast number of compositions based on one or two CaP phases and a liquid component have been developed in the early 1990s. All formulations recrystallize to one of the following biocompatible and biomimetic CaP phases: brushite (DCPD), monetite (DCPA), or hydroxyapatite (HA) with a variable degree of Ca deficiency (CDHA). However, despite their undeniably attractive features, conventional CaP cements are criticized for some shortcomings as compared to more generic porous preforms and granules. Firstly, cured cements are microporous but do not contain any controlled macroporosity, as such the vascularization rate, cell proliferation, fluid circulation, and hence the resorption rate are considerably slower compared to macroporous implants. Secondly, large volumes of DCPA or DCPD tend to hydrolyze to HA before complete resorption is accomplished. This process releases acidic phosphates which interfere with bone regeneration, and results in cores of non-resorbable HA. Thirdly, cements are packaged as separate powder and liquid components which need to be thoroughly mixed before application. Once mixed the setting reaction starts and requires a strict work schedule in order to avoid premature setting in the application device. This last issue is particularly adverse as it imposes additional pressure on the surgeon in an already stressful situation.

The complicated mixing and application procedures of conventional CaP cements have recently been addressed by many developers. New products are designed as pre-mixed pastes in order to eliminate the mixing step. Different concepts have been applied to suppress premature setting in the application device, such as: using organic liquid components, separating the reactive powder components into two pastes, or adding a reaction inhibitor which is eliminated by an activator component admixed during injection through a static mixer. Shelf life and sterilization requirements also present major challenges for the development of commercial products. During a shelf life period of typically 2 years or more, the pastes must be physically and chemically stable; hence no sedimentation, phase separation, recrystallization, or premature setting can be allowed to occur. A feasible sterilization method must be available, which does not degrade organic additives in an uncontrolled manner. Despite these challenges significant progress has been made in the recent years, and a new generation of ready-to-use cements is in the process of reaching market clearance.

#201 - Versatile designing of the performance of calcium phosphate bone cements

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Calcium phosphate bone cements (CPCs) are considered as promising injectable biomaterials for mini-invasive procedures addressed to the treatment of bone diseases, especially when substantial bone regeneration is pursued. Among the several reported routes to prepare CPCs, the precipitation of nano-size HA particles through the hydrolysis of αTCP phases (i.e. a-$Ca_3(PO_4)_2$) offers certain advantages, including hardening at body-temperature without significant pH fluctuations that prevent harmful effects in body environment. Nevertheless, the achievement of CPCs with rheological and setting properties adequate to meet the requests of clinicians still represents a remarkable challenge, especially due to the multitude of correlated processing parameters to be simultaneously adjusted. In this work, for the first time, a Design of Experiment (DoE) approach was used to evaluate the effect of several processing parameters on the final properties of Sr-doped hydroxyapatite cement (Sr-HA), obtained by Sr-doped αTCP phases, selected as unique inorganic precursor.In particular, three different DoE schemes were implemented to investigate the correlated effects of relevant process parameters such as the synthesis process and in particular of the ion doping, the subsequent powder milling process, the composition of the setting solution and the liquid-on-powder ratio, on the features of the Sr-doped αTCP precursors and, hence, on the final Sr-HA product. The results reported in this work described both qualitatively and quantitatively the interaction among the various parameters, thus obtaining preliminary equations predictive of the properties of the final cements. In particular, the effect of the synthesis process and ion doping on the composition and crystallinity of the cement precursors and on the setting times was described; in addition, a significant increase of the cement strength with maintenance of a high overall porosity was obtained by decreasing the diameter of the powder milling balls. On this basis, this work paves new ways towards the modeling of CPCs and, more generally, of calcium phosphate pastes as injectable fillers for the treatment of bone defects.

#202 - Photothermal properties of gold nanostar and copper sulfide patterns inkjet printed on latex coated paper substrate

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Inkjet printing has been successfully applied to pattern various functional materials (including biomaterials) for applications in biology and medicine. Metal nanoparticle based inks are widely used in inkjet printing technology due to their important conductive and thermal properties. Anisotropic gold nanoparticles, namely gold nanostars, with tunable in Near Infrared Region (NIR) Localized Surface Plasmon Resonance were printed on coated paper surfaces as sources of local photothermal effect. However, their cost would prevent a wide spread use in nanotechnology and in nanomedicine. Therefore, copper sulfide nanoparticles, that display a broad NIR absorption arising from the d–d transition of CuS, offer a valuable alternative to gold nanoparticles. In this work stable inks of these nanoparticles were inkjet printed on biocompatible latex coated paper substrates. Pronounced photothermal effect was observed under NIR irradiation of resulted patterns. The photothermal effect depends on laser intensity and on printing parameters. The results indicated that a significant photothermal effect can be reached even under relatively low laser intensities. Beside the direct photothermal effect NIR-triggered release of model compounds from printed surfaces was achieved as additional and valuable effect.

#203 - DNA templated selfassembly of bio-inorganic devices

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The talk outlines briefly the power offered by DNA nanotechnology, coupled to bio-inorganic material specific interactions, in the fabrication of nanodevices hierarchically selfassembled on different scales. First results obtained by the ENEA group in collaboration with the cDNA Aarhus University and with the Oak Ridge Center for Nanostructured Materials Science, will be reported: selfassembled DNA nano-breadboards for organic and inorganic molecular components were successfully suspended across sets of four conductive nanodots. The importance of simulating the details of bio-inorganic interaction, as well as of artificial lithographic technologies in assisting the drive toward full bottom-up selfassembly, will be also discussed.

#204 - Modular functionalization of reactive self-assembled monolayers the fabrication of multilevel optical storage media

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A widely exploited strategy to fabricate functional and responsive surfaces relies on the fabrication of Self-Assembled Monolayers (SAMs), which, in the last two decades, have been a crucial breakthrough in for surface chemistry and, also by the combination with soft lithography, have given an extraordinary contribute to the development of nanotechnology.

We report a further breakthrough in SAM technology demonstrating that iterative micro contact printing (µCP) allows additive grafting of different functional molecules in the same area of a reactive SAM, preserving molecular individual functional properties. We used the additive µCP process to fabricate a multi-level fluorescent TAG (multi-TAG), which consists of two overlapping micrometric patterns containing a digital information (e.g. Aztec code). The multi-TAG is fabricated by printing two interpenetrating fluorescent molecules that can be independently visualized; it allows the storage of digital information optically accessible at different level by individually accessing each pattern. Multi-TAGs were obtained both on rigid and flexiblesubstrates.

The process was demonstrated by using one of the most investigated reactive SAMssuch as the (3-aminopropyl)-triethoxysilane(APTS), which is widely employed in surface chemistry applications for its ability to react efficiently with hydroxy-rich surfaces. The APTS-SAM was then chemically functionalized with two fluorescent oligothiophenes, namely bis(2,5-dioxopyrrolidin-1-yl) [2,2':5',2''-terthiophene]-5,5''-dicarboxylate and bis(2,5-dioxopyrrolidin-1-yl) 5,5'-(benzo [1,2,5]thiadiazole-4,7-diyl)bis(thiophene-2-carboxylate) bearing succinimidyl-ester ends that can be coupled to amino groups of the APTS-SAM.

#205 - Adiabatic quantum information transfer between three-level emitters, assisted by localised surface plasmon polaritons of a spherical metal nanoparticle

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Plasmonic Quantum Electrodynamics analyses and uses the strong coupling of quantum emitters (QEs), for example quantum dots used as effective optical nanosources, with the surface plasmon polariton (SPP) field, whose quantized modes act as highly confined cavity modes. Nevertheless, the strongly lossy nature and the multiplicity of the SPP modes limit so far the utility of the high confinement for the achievement of a reversible exchange of energy between the emitters and the SPP field.

Our project of research has the aim to bypass this limitation in order to take full advantage of the strong coupling between matter and the SPPs for quantum information processes. We have analysed if and in which circumstances the localised SPPs can be used as mediators of an efficient population transfer between two not-directly interacting 3-level QEs, placed at few nanometers from the surface of a subwavelength spherical metal nanoparticle (MNP) and strongly coupled with it. We have developed the mathematical language necessary to write continuous and discrete effective models describing the compound hybrid system in terms of fermionic and bosonic degrees of freedom, for the QEs and for the localized plasmonic field respectively. We have proposed a method of orthogonalization of the field operators to obtain an effective description of the bosonic nature associated to the plasmonic field, exploiting in an operatorial context the *sequential* Gram-Schmidt method and the democratic *Löwdin* approach of orthonormalization used for vectors. The latter approach is a very promising technique to treat a large number of QEs. The physical technique that we have exploited to verify if it is possible to circumvent the problem of plasmonic dissipation is a generalization of the Stimulated Raman Adiabatic Passage (STIRAP).

We have found that, under adiabatic conditions, a high transfer efficiency can be reached for very small angles between the position vectors of the two QEs (the origin of the reference frame is placed at the center of the MNP). The populations of the plasmonic modes remain effectively negligible for all the dynamics, giving to the plasmon polaritons the role of a dark subsystem: only its empty modes play a role in the transfer. Increasing the angular distance, an interference effect of the n plasmonic modes effectively involved in the interaction creates a blockade of the population transfer, more pronounced when the QEs are positioned at opposite sides of the MNP. In order to obtain an efficient transfer over longer angular distances, we have introduced an intermediate QE between the two ones directly involved in the STIRAP-like process. Numerical results show that, in the configurations with only two QEs in which no transfer occurs, the introduction of another QE doesn't improve the efficiency of the transfer, but it reduces the effect of the interference caused by the plasmonic modes

#206 - A simple and fast protocol to quantify the oxidation degree of graphene-based materials

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Graphene-based materials (GRMs) are a wide class with different chemical/electronic/electrical behaviors.1,2,3Controlling and tuning of their chemical composition is one of the key for success of such materials in the industrial applications Despite of X-ray Photoemission Spectroscopy (XPS) is one the most powerful and commonly used technique to study the chemical analysis of surfaces,4a quantitative and reliable approach to study GRM is still lacked. For example, there is not a standard way to quantify the oxidation degree of GRM (called alternately O/C or C/O). Describing the ratio between the number of carbon and oxygen atoms, in bulk materials the value is simply given by the ratio between the XPS peaks of O 1s and C 1s. This approach can be extended for thin films (

#207 - Hybrid halide perovskites: targeting material properties for device innovation

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Hybrid halide perovskites have become benchmark active material in several cutting-edge optoelectronic applications. This innovation originates from the unique properties of the material, which are direct band gap semiconductors, very easy to prepare, owning strong light absorption coupled to high charge carrier lifetime and impressive diffusion lengths. Despite the simple wet chemistry leading to an intrinsically disorder material-assembly process, superior optoelectronic properties, in line with ultrapure inorganic semiconductors, distinguish halide perovskites.

From conceptually new devices, we have been exploring viable routes for an intelligent mastering of material preparation targeting various optoelectronic applications. From solution focused approaches to post-deposition treatments, we aim to achieve a fine tuning and a profound comprehension of the material's physical-chemical properties.

#208 - Demonstration of the order-disorder character of the CH3NH3PbI3 polymorphic transition and its implications on the lattice stability

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Issues on stability and durability of hybrid perovskites are dramatically delaying the large dissemination of low cost/high yield related technologies for photovoltaic, light sensing and emitting purposes. Although several combinations of cations and anions are currently under investigation, the advance of the technologies is forced to pass through the rationalization of the phenomena occurring into the hybrid lattice under conditions which mimic the material operation (e.g temperature, external species).

In this framework, we study the structural modifications of the $MAPbI_3$ lattice upon recursive thermal cycles from 30°C to 80°C in different annealing ambient. Although it is known that the lattice experiences a tetragonal to cubic polymorphic transition above 55°C, here we reveal that a profound lattice modification starts even from room temperature and proceeds with continuity by approaching the transition temperature. This modification is driven by the progressive change of the rotational state of the organic MA^+ cations that gradually gain off-xy-plane components. Since the atomic positions of Lead and Iodine atoms are tightly related to the MA^+ configurations, the whole lattice experiences a progressive continuous transition which culminates (55-65°C) in the symmetrisation of the three crystallographic axes after full MA^+ randomization.

In this respect, we demonstrate that this order-disorder transition creates a weakness-point in the structure since external species are thus more facilitated to enter the cage. It is rather irrelevant for inert species such as for N_2 molecules, but enormously dangerous for aggressive/interacting species. As a matter of fact, we show that, thermal cycles in air causes a sudden degradation towards PbI_2 above 55-60°C, which correspondently sings the tetragonal to cubic lattice transition. Degradation is, instead, significantly embanked during cycles in dry N_2, notwithstanding the crossover of the tetragonal/cubic transition. With this prerequisite, the polymorphic transition becomes fully reversible.

Our description can help rationalising new solutions to prolong the device durability, with special attention to restrain the temperature during operation and to the encapsulation with nitrogen as possible actions. Our findings also extend to predict the transition temperature to be critical also with regards to the diffusion of atomic species from boundary materials, often responsible for hysteresis issues.

#209 - Supramolecular control over hybrid perovskite self-assembly for efficient solar cells

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Perovskite Solar Cells (PSC) have been one of the most promising alternative to Silicon-based photovoltaics in the last 10 years and big efforts have been devoted to the development of new efficient materials and innovative architectures for this class of devices. Their outstanding properties in terms of easy processability, transport and low recombination rate led to very fast development of research activities both on the device implementation and on the characterization sides. This material has recently aroused great interest in the scientific community, as it enabled power-conversion efficiencies of over 20%. Deposition methods and morphological study have also been developed in the common effort of the scientific community to control the crystallization and correlate structure and energy conversion properties in these devices. Here a supramolecular control of the morphology and perovskite crystal growth is presented, aiming at highlighting the profound dependence in the growth mechanisms of these materials if influenced by nucleating agents. A particular attention is devoted to the study of intermolecular interactions occurring in solution deeply modifying the self-assembly process, and their relationship with the properties of the deposited thin film. The function of the additives in PSC is found to be crucial in influencing crystalline order, morphology and photo-physical properties of the final material. Experimental characterization and photovoltaic applications of different perovskite-based nanocomposites perovskite-additives is presented.

#210 - Atom kinetics and phase transitions in organic-inorganic lead halide perovskites

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The unexpected rise of the photovoltaic efficiency above 22% for the hybrid lead iodide perovskite during the last years has triggered a widespread interest for the development of solar panels and solar cells based on organic-inorganic perovskites. However, such rapid technological growth has not been accompanied by a robust understanding of the physical properties of these materials. For example, the polymorphic behavior of $CH_3NH_3PbI_3$, which manifests with an orthorhombic-to-tetragonal and a tetragonal-to-cubic transition upon temperature annealing, is still a matter of debate. A generic explanation often found in the literature attributes these phase transitions to an order-towards-disorder shift, without giving any information on the atomistic mechanisms that may contribute to the structural alterations. Here, we employ *ab initio* molecular dynamics calculations in order to understand the kinetic aspects that give rise to the polymorphic shaping of the material's lattice at different temperatures. We find clear correlations between the spontaneous movement of the organic ions and the tetragonal-to-cubic transition, whereas we address the energetic aspects related with the lattice rearrangements. Finally, we expand our discussion for other lead halide perovskites.

#211 - Robustness and electrical reliability of AZO/Ag/AZO thin film after bending stress

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The increasing interest in thin flexible and bendable devices, particularly for the flexible photovoltaic module, the flat panel display and touch screens technologies,has led to a strong demand for mechanically robust and electrically reliable transparent electrodes. Indium doped Tin Oxide (ITO)films are mostly used due to their superior electrical transport properties. But, the toxicity, scarcity and high price of In, pushes to replace ITO with other In-free compounds. To this aim, Aluminium doped Zinc Oxide (AZO) has extensively been investigated and employed as transparent electrode.However, a high flexibility is usually achieved at very low thickness, which, unfortunately, compromises the electrical conductivity. Several articles have been published dealing with the appearance and evolution of structural defects after bending processes. In particular, they report an increase of the electrical resistivity of ITO and AZO single layers (200 nm to 700 nm thick) after bending cycles (1 to 1000 cycles) as a function of film thickness or applied stress.

Here we report the effect of mechanical bending cycles on the electrical and optical properties of ultra-thin AZO/Ag/AZO multilayers (45nm/10nm/45nm) and, for comparison, of two AZO single layers whose thickness was 100 nm and 700 nm, respectively, deposited at room-temperature on flexible polyethylene naphthalate (PEN) plastic substrates. The electrical stability of the films after several cycles of bending were evaluated by monitoring the relative variation of the electrical resistance with respect to the as prepared sample; crack size and density were detected by Scanning Electron Microscopy (SEM). We observed excellent electrical stability and high mechanical flexibility in the AZO/Ag/AZO sample even after 100 cycles, whereas for the single AZO films the resistivity rapidly increases. We also presented a simulation of the bending process to calculate the stress distribution and intensity in our samples. The simulations show as the presence of the 10nm thick Ag intralayer in the AZO film produces a reduction of the stress, so increasing the flexibility of the overall structure and the robustness to bending processes. Our results support the idea of using very thin AZO/Ag/AZO multilayers as a reliable transparent conductor material for flexible devices.

#212 - Chemical etching for the boron rich layer and its impact on the electrical properties of n-type c-si wafers for solar cells application

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N-type crystalline silicon based solar cells have attracted considerable attention in the recent few years from researchers and solar cells manufacturers due to its high bulk lifetime, as well as to the absence of the light induced degradation lifetime caused by the presence of the boron-oxygencomplexes.The elaboration of ap-type emitter on n-type wafer can be performed by several methods, in this work, the boron spin on diffusant source (B155) was chosen for this end, however,borosilicate glass (BSG) and an undesirable boron rich layer (BRL) were formed during the boron diffusion, this latter acts as a recombination site for the charge carrier due to the inactive boron atoms containing in this layer, therefore, it is necessary to remove the BRL by a chemical etching treatment in nitric acid solutionby varying different parameters such as: duration of the diffusion process, duration of the etching treatment and the temperature of the chemical solution.The current study reports on the impact of the chemical etching treatment for the boron rich layer (BRL) removal on the sheet resistance, emitter saturation current and effective lifetimeusing the four point probe measurements and the quasy-steady state photoconductancetechnique, respectively.

#213 - Self-assembled monolayers of molecular precursors for silicon doping

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Common methods for the semiconductor doping are: a) Ion implantation (I.I.), where the interaction between the doping source and the target to be doped is between energetic ions and a solid substrate, b) the so called diffusion based methods where the dopant sources are solid, liquid and gaseous but the final interaction with the solid target is gas/solid, c) the Spin on Dopant (SOD) in which the initial source is liquid and then it solidifies, as a consequence the interaction is between two solid systems. I.I shows together with the crystal damage, some critical aspects as poor doping conformality, safety issues and high costs of the process and the equipment. Diffusion based methods, as in the previous case, show high costs of the system and the use of dangerous gases. Finally, SOD suffers from a lack of dose control and uniformity over large areas and leaves behind undesirable residues. Recently a new low cost technique for controlled nanoscale doping of semiconductors has gained attention [J. Ho et al., Nature Nanomater. 7 (2008) 62; R. A. Puglisi et al., Phys. Stat. Sol. A212 (2015) 1685]. This method consists in forming a monolayer of dopant-containing molecules from liquid solutions followed by the deposition of an oxide cap layer and successive diffusion via thermal annealing. With this process itis possible to obtain n- or p- type doping [Garozzo et al., Mater. Sci. Eng. B178 (2013) 686] and to modulate the doping characteristics by changing the coating time without changing the precursor molecules [R. A. Puglisi et al. Phys. Stat. Sol. A212 (2015) 1685]. The contribution of the carbon atoms constituting the precursor molecules and their diffusion inside the silicon substrate have been studied by investigating the chemical properties of the surface, also in terms of the role of the cap layer. Moreover, their contribution on the sheet resistance as a function of the sample depth has been explored through a new method based on four probe point (4PP) measurements [Caccamo et al., Mat. Sci. Semic. Proc. 42 (2016) 200]. Here we present a study about the role of the cap layer on the diffusion of the dopant atoms, in this case phosphorus, inside the substrate. It is found that the main parameters in the samples with and without the cap are not the same. Surprisingly samples without cap layer showed better parameters than samples with the cap layer. One possible explanation of these results will be discussed in terms of the diffusion of the dopant atoms and their evaporation.

#214 - Hybrid Polymeric-Protein Nano-Carriers (HPPNC) for targeted delivery of TGFβ inhibitor to hepatocarcinoma cells

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The strategy applied to solve genetic therapy issue using bacterial vector suffers from several drawbacks, since un-methylated CPG of bacterial DNA can elicit strong host immune responses. Nanotechnology has proven its ability to encapsulate DNA, siRNA, and P-17 and to functionalize nano-carrier surface to be selective for its target. Folic acid (FA) has good binding affinity to folate receptors and Bovine Serum Albumin (BSA) has special affinity property to easily bind hepatocytes. Our aim is to create site-chemical conjugation of (FA-BSA) and use this complex to coat SHT-DNA, siRNA and P-17 attached with Polyethylene glycol (PEG). The activation of FA has been investigated by FTIR spectroscopy and spectrophotometry. Successful BSA-FA attachment was detected by X-ray diffraction and electrophoretic mobility of Agarose gel-FA bands. HPPNC-FA colloidal stability was measured by photon correlation spectroscopy. SHT-DNA, siRNA and P-17 entrapment was demonstrated byuranyl acetate-TEM. HPPNC-FA topography was measured by AFM. HPNP-FA cellular internalization was demonstrated by ELISA fluorescence spectrum Reader. The efficiency of SHT-DNA, siRNA and P-17 cellular uptake was quantified by confocal microscopy. Activated FA has shown good absorbance, high fluorescence intensity and revealed isolated bands compared to that one dissolved in MilliQ water. FTIR and X-ray diffraction show successful conjugation of for BSA-FA. Photon correlation spectroscopy result indicates a good stability of HPNP-FA as colloidal suspension. Microplate reader of HCC confirms successful internalization of HPNP-FA. Uranyl acetate-TEM photomicrograph shows encapsulation of SHT DNA, siRNA and P-17 inside HPNP-FA layers. Confocal microscopy shows good efficiency of SHT DNA, siRNA and P-17. HPPNC-FA demonstrated to be a specific target for HCC because of high affinity binding of FA and BSA to folate receptor and cell membrane. Additionally PEG conjugation increased time circulation in blood stream.

#215 - SERS detection of Biomolecules at Physiological pH via aggregation of Gold Nanorods mediated by Optical Forces

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We report on a novel scheme that exploits the radiation pressure to locally push gold nanorods and induce their aggregation in buffered solutions of biomolecules, achieving biomolecular SERS detection at almost neutral pH [1]. The sensor (LIQUISOR) is applied to detect non-resonant amino acids and proteins, namely Phenylalanine (Phe), Bovine Serum Albumin (BSA) and Lysozyme (Lys), reaching detection limits in the μg/mL range. We tailored the methodology to add molecular specificity, by functionalizing the nanorods with aptamers and testing the results on MnSOD, a pathology biomarker, and ochratoxin, a fungal toxin knwn to occur in food commodities and wine. The performances shown are compared to other in-vitro schemes of SERS detection thay employ optical nanonatennas and operate in dry condictions [2]. Being a chemical free and contactless technique, our methodology is easy to implement, fast to operate, needs small sample volumes and has potential for integration in microfluidic circuits for biomarkers detection.

[1] B. Fazio et al. Sci. Rep. 26952 (2016)

[2] M. Cottat et al. J. Phys. Chem C 119, 15532 (2015)

#216 - Disordered array of Au covered Silicon nanowires for SERS biosensing combined with electrochemical detection

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We report on highly disordered array of Au coated silicon nanowires (Au/SiNWs) as surface enhanced Raman scattering (SERS) probe combined with electrochemical detection for biosensing applications. SiNWs, few microns long, were grown by plasma enhanced chemical vapor deposition on common microscope slides and covered by Au evaporated film, 150 nm thick. The capability of the resulting composite structure to act as SERS biosensor was studied via the biotin-avidin interaction: the Raman signal obtained from this structure allowed to follow each surface modification step as well as to detect efficiently avidin molecules over a broad range of concentrations from micromolar down to the nanomolar values. The metallic coverage wrapping SiNWs was exploited also to obtain a dual detection of the same bioanalyte by electrochemical impedance spectroscopy (EIS). Indeed, the SERS signal and impedance modifications induced by the biomolecule perturbations on the metalized surface of the NWs were monitored on the very same three-electrode device with the Au/SiNWs acting as both working electrode and SERS probe.

The combination of an optical and electrochemical signal transduction in the same Au/SiNWs can offer an improved method to identify and quantify the bio-analytes over either technique independently. Indeed, EIS is widely used in diagnostic biosensing, because it allows to detect a wide range of analytes with high sensitivity by using chip and miniaturized devices. On the other hand, the impedance biosensors do not provide chemical identification of the analyte and can detect also non-target biomolecules stuck to the probe causing a false positive signal. This is a critical issue when biological fluids containing a large background of on specific interferents (blood, salive etc.) are analyzed. The SERS offers the complementary chemical information due to the ability to identify analytes from unique Raman signatures reducing the issue of false positive signal.

#217 - SNOM spectroscopy for tissue imaging and cancer diagnostics

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We present a fully implemented Infrared (IR) Scanning Near-field Optical Microscopy (SNOM) in spectroscopic mode for tissue imaging and early cancer diagnostics. The SNOM has been coupled with an infrared light source, based on Free Electron Laser at the ALICE facility in Daresbury.

The potential of IR spectroscopy to characterise cancerous tissues has long been recognised and studies of various cancers by many groups have established that regions of malignant tissue can be easily identified on the basis of its IR spectrum. The oesophageal adenocarcinoma, the cancer with the fastest rise in incidence in the Western world, requires an instrument providing specific chemical images at sub-cellular level of oesophagus tissue. This approach demonstrates the potential of the IR-SNOM spectroscopy for yielding an accurate diagnostic test for oesophageal and other types of cancers.

The SNOM employed in this work was developed on the IR FEL at Vanderbilt and established on the IR FEL on the ALICE energy recovery linear accelerator at Daresbury [1]. Results of IR-SNOM on oesophageal adenocarcinoma have shown that the system can operate at nanometer resolution and has been able to distinguish between healthy and malignant tissues [2]. The optical fibre has been driven in particular areas of the oesophageal tissue and topographical and optical images have been collected simultaneously at different wavelengths. In particular, SNOM images were collected at wavelengths of 7.0 micron (no strong biomarker), 7.3 micron (protein/glycoprotein), and 8.05 micron (DNA).

This combination of InfraRed radiation and Scanning Near-field Optical Microscopy, in its spectroscopic mode, can be an important tool for tissue imaging and early cancer diagnostics. It is expected to produce a major advance in imaging of malignant tissues [3], leading to the development of portable diagnostic devices for hospital use for various types of cancer. It is also planned to utilise the powerful combination of high spatial resolution and chemical specificity of the mentioned methodologies to study the key components, responsible for cancer formation.

References:

[1] Cricenti A, Luce M, Tolk NH, Margaritondo G; Nanosci. Nanotechnol. Lett.; 3 (2011) 913;

[2] Smith AD, Siggel-King MRF, Holder GM, Cricenti A, Luce M, Harrison P, Martin DS, Surman M, Craig T, Barrett SD, Wolski A, Dunning DJ, Thompson NR, Saveliev Y, Pritchard DM, Varro A, Chattopadhyay S, Weightman P; Applied Physics Letters; 102 (2013) 053701.

[3] Halliwell Diane E, Morais Camilo LM, Lima Kássio MG, Trevisan Julio, Siggel-King Michele RF, Craig Tim, Ingham James, Martin David S, Heys Kelly A, Kyrgiou Maria, Mitra Anita, Paraskevaidis Evangelos, Theophilou Georgios, Martin-Hirsch Pierre L, Cricenti Antonio, Luce Marco, Weightman Peter, Martin Francis L; Nature Scientific Reports; 6 (2016) 29494.

#218 - Aggregation and stability in solution of plasmonic active nano-biocolloids

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The capability of gold nanoparticles (AuNps) to form hybrid assemblies with biomolecules provides the basis to engineer innovative systems with potential applications in nano-medicine and nano-biotechnology [1,2]. Great interest in these systems arose in recent years due to the peculiar optical properties of gold at the nanoscale, whose interaction with electromagnetic radiation can be tuned by manipulating the dielectric constant of the environment or the size and shape of the assembly [2,3]. Biocompatibility, versatility, and "tunability" of these systems make them suitable for applications in sensing and therapy [4]. We recently employed mesoscopic aggregates of AuNps on solid support as substrates for Surface Enhanced Raman Spectroscopy and demonstrated their capability to provide huge signal enhancements in sensing applications [3,5,6]. Here we focus on the colloidal aggregation in solution of anionic AuNp (60 nm and 100 nm sized) mediated by lysozyme: a robust, globular and functional protein, with a pH-dependent positive charge. The process was studied by Dynamic Light Scattering (DLS) and Z-potential measurements at varying the AuNps-lysozyme relative molar ratio for different pH of the solution. The aggregation was also monitored following the Surface Plasmon Resonance (SPR) of the aggregates by UV-Visible Absorption Spectroscopy (UV-Vis). A study of the reversibility of the process was carried on by varying the pH of the solution after the clusters were formed. Analogously to the aggregation of biocolloids mediated by linear polymers [7], experiments showed that stable clusters can be obtained with a finite size depending on the AuNps-lysozyme relative molar ratio and on the pH of the solution. The comparison between DLS and UVVis measurements enlightened the higher sensitivity of the plasmonic absorption to disentangle the adsorption of lysozyme on the gold surface and the AuNps aggregation. Interestingly enough, we obtained intriguing protein-AuNp bioplasmonic assemblies with a size within few hundred nanometers, exhibiting colloidal stability in physiological condition and a large dynamic range of SPR frequencies from visible to near-infrared spectral region.

[1] A. Polman, Science, 2008, 322, 868.

[2] P. K. Jain et al., Accounts of Chemical Research, 2008, 41-12, 1578.

[3] F. Domenici et al., Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2016, 498, 168.

[4] F. Domenici et al., Analytical Biochemistry, 2012, 421, 9. [

5] C. Fasolato et al., AIP Conference Proceeding, 2015, 1667, 020012.

[6] F. Brasili et al., IEEE-NANO 2015 - 15th Int. Conference on Nanotechnology, 2016, 33323, 1023.

[7] S. Sennato et al., Soft Matter, 2012, 8, 93.

#219 - Sorafenib Delivery Nanoplatforms Based on Superparamagnetic Iron Oxide Nanoparticles for Magnetically Targeted Therapy of Hepatocellular Carcinoma

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Hepatocellular carcinoma (HCC) is the third most common cause of cancer-related death. Advanced HCC has a poor therapeutic outcome and treatment options are limited. Sorafenib, an orally active multikinase inhibitor, is the only systemic drug that has shown to provide survival benefits in randomized control studies [1]. However, many side effects decrease its tolerability and therefore limit the therapeutic response that can be achieved [2]. Superparamagnetic iron oxide nanoparticles (SPIONs) are very attractive for drug delivery as they can be targeted to specific sites in the body through the application of a magnetic field, thus improving intracellular accumulation and reducing adverse effects [3]. Here, the development of nanoformulations based on polyethylene glycol modified phospholipid micelles [4,5], loaded with both SPIONs and sorafenib, was successfully realized. The nanovectors were investigated by means of several complementary techniques, resulting effective drug delivery systems with good stability in aqueous medium and controlled drug loading. An in vitro dynamic system was specifically designed to prove that the micelles loaded with SPIONs can be efficiently held by using magnetic field under the flow conditions typically found in the human liver. The tumor cell targeting efficacy of the superparamagnetic micelles loaded with sorafenib were evaluated on human hepatocellular carcinoma (HepG2) cells, highlighting that the delivery platform is able to enhance the drug antitumor effectiveness when magnetically targeted. The herein presented nanovectors represent promising candidates for the magnetic targeting of the chemotherapeutic agent to tumor sites towards an efficacious treatment of HCC.

[1]. A. Villanueva, et al. Gastroenterology 2011, 140, 1410

[2]. H. B. El-Serag et al. Gastroenterology 2008, 134, 1752

[3]. P. Liang et al. International Journal of Nanomedicine 2016, 11, 2021

[4]. G. Valente, N. Depalo et al. Nano Research 2016, 9, 644

[5]. N. Depalo Langmuir 2011, 27, 6962

#220 - Synthesis strategies for the realization of decorated polymeric nanocarriers

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In the field of innovative anticancer therapies, nanoparticles (NPs) have attracted significant attention in recent years. The most common approach to selectively improve their accumulation in tumor tissues remains surface decoration with different targeting moieties recognizing specific receptors that are over-expressed in cancer cells.

Surface decorated NPs can be prepared by either post-modification of the surface, or by synthesizing tailored all-in-one amphiphilic copolymers. With this approach, the number and nature of molecules on the surface of the resulting NPs can be finely tuned, also avoiding the premature release of drug cargo.

Here we describe two different synthesis approaches: NPs made by self-assembling amphiphilic copolymers bearing the target unit covalently linked on the hydrophilic chain end, and cationic NPs, able to deeply penetrate inside tumors, decorated with hyaluronic acid (HA).

In the first case, copolymers are made up of PEG as hydrophilic block and PCL as hydrophobic one; in this way, methods of synthesis aimed to asymmetrically modify PEG in order to introduce ethero end groups are largely explored in literature. Here, a simple route of synthesis to selectively obtain PCL-PEG-gFolate (Fol) copolymer with high yield and purity is described.It is note from literature that only g-folate conjugates retain affinity towards folate-receptor, that is overexpressed in the majority of cancer cells. Furthermore, we demonstrate that the extent of specific internalization of targetednanoparticles can be improved by regulating the length of the PEG chains in PCL-PEG to attain stealth properties (1000 Da) and in PCL-PEG-gFol to improve Fol exposition on NPs surface (1500 Da). Formulations of NPs using amphiphilic copolymers with different length of PEG blocks turned to be a good strategy to enhanceexposition of Fol~~ate~~on their surface.

In the second case, amino-terminated homopolymer PCL was synthesized to obtain PCL- or PEG-PCL-based NPs with cationic surface.Cationic can be “covered” with anionic molecules, like HA, through non–covalent interaction. HA encourages NPs uptake in cell overexpressing CD44 receptors. We show how modulation of surface charge density influences cell uptake.

#221 - Silicene: free-standing vs. supported properties

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The rich physical properties of graphene motivate the study of 2-D materials with honeycomb structure. Silicene, a 2-D honeycomb lattice of silicon, is theoretically predicted to be stable as a free-standing monolayer in a low-buckled geometry. While evidence for free-standing silicene has not yet been experimentally obtained, synthesis of silicene has been recently realized on a few substrates. A key issue is whether silicene preserveson supporting substrates the properties of the free-standing lattice. We addressed this question for silicene on Ag(111), the simplest and most extensively studied silicene form, by mean of various experimental methods and by electronic structure calculations. We find that the electronic interaction between silicene and the substratehas much stronger consequences than assumed in former studies on this system. The results question the validity of the claim that graphene-like silicene and silicene multilayers are in fact formed on Ag(111). Results and perspectives regarding the possible formation of 2-D silicene on other supporting substrates will be briefly reviewed and discussed.

#222 - Layer-dependent quantum cooperation of electron and hole states in the anomalous semimetal WTe2

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We report angle and spin-resolved photoemission spectroscopy of WTe_2 transition metal dichalcogenide with titanic nonsaturating magnetoresistance [1]. Supported by first-principles calculations and high-resolution surface topography, we reveal the existence of a layer-dependent electronic behaviour. The balance of electron and hole states which is believed to lead to nonsaturating magnetoresistive behaviour, is found only when considering at least three Te-W-Te layers, showing that the behavior of WTe_2 is in between those expected for 2D and 3D electronic systems [2].

The behaviour of electrons and holes in a crystal lattice is a fundamental quantum phenomenon, accounting for a rich variety of properties in solids. Boosted by the remarkable electronic and physical properties of two-dimensional (2D) materials such as graphene and topological insulators, transition metal dichalcogenides (TMDs), long of interest in materials science, have recently received renewed attention in this context. Among TMDs, the anomalous bulk properties of semimetallic WTe_2 have attracted considerable interest [1]. Here we report angle and spin-resolved photoemission spectroscopy of WTe_2 single crystals, through which we are able to disentangle the role of W and Te atoms in the formation of the band structure and to identify the interplay of the charge, spin and orbital degrees of freedom [2]. Supported by first-principles calculations and high-resolution surface topography, we reveal the existence of a layer-dependent electronic behavior. The balance of electron and hole states is found only when considering at least three Te-W-Te layers, showing that the behavior of WTe_2 is in between those expected for 2D and 3D electronic systems. The observed evolution as a function of depth from the surface indicates that WTe_2 provides an excellent platform to study the effect of dimensionality on the quantum properties of matter.

References

[1] M. N. Ali et al., Nature 514, 205–208 (2014).

[2] P.K. Das et al., Nature Communications 7, 10847 (2016).

#223 - Interaction-induced thermoelectric effects in 2D topological material

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We consider thermoelectric transport properties of the edge states of a two dimensional topological insulator in a double quantum point contact geometry. Here the two constrictions allows for the breaking of particle-hole symmetry and thus for finite thermoelectric signals.
We take into account electron-electron interactions and different tunneling processes.
We will show that the simultaneous presence of spin-flipping processes and interactions gives rise to a finite longitudinal
spin current. Moreover, its sign and amplitude can be tuned by means of gate voltages with the possibility to generate a pure spin current, with a vanishing charge current.

#224 - From n-type to ambipolar current transport in MoS2 field effect transistors by nanoscale modification of source/drain contacts

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Transition metal dichalcogenides (TMDs), such as MoS_2, recently attracted considerable interest for future electronic and optoelectronic applications. In particular, field effect transistors (FETs) with very interesting performances (on/off current ratio $>10^7$ and low subthreshold swing ~70 mV/decade) have been demonstratedboth using single-layer [1] and multi-layer MoS_2[2]. In spite of these progresses, several processing issues (Ohmic contacts, gate dielectrics, passivation, doping,…) need to be addressed in order to fully exploit the potentialities of this 2D material. Virgin MoS_2 is an unintentionally n-type doped semiconductor and most of the metals exhibit a Fermi level pinning below MoS_2 conduction band [3]. Hence, only accumulation mode n-channel field effect transistors (FETs) with Schottky source/drain contacts are easily obtained with pristine MoS_2. On the other hand, p-type doping under the contacts and/or tailoring of the metal/MoS_2 Schottky barrier (SB) are required for efficient hole injection, in order to obtain the complementary inversion mode p-channel FETs.

In this work, we investigated different processes allowing the observation of p-type current transport in back-gated multilayer MoS_2 with Ni source drain contacts.

Firstly, it will be shown that, after a temperature-bias annealing performed at T=200°C (under the application of a positive gate bias ramp), the subthreshold characteristics of the FET show a low current hole branch, indicating a modification of the Ni/MoS_2 interface with the formation of a low density of regions with reduced SB for holes [4].

A second and more efficient process is represented by O_2 plasma functionalization of the MoS_2 regions where Ni source/drain contacts are subsequently fabricated. A dominant p-type transport or an ambipolar behaviour is achieved in FETs with O_2 plasma modified Ni/MoS_2 interface. High resolution current mapping by conductive atomic force microscopy (CAFM) [5] shed light into the current injection mechanisms from the metal to the O_2 plasma treated MoS_2 surface. These local electrical measurements, combined with high resolution transmission electron microscopy (HRTEM), electron energy loss spectroscopy (EELS), micro-Raman and X-ray photoemission spectroscopy (XPS) analyses, as well as ab-initio simulations, allowed to clarify the role of O_2 plasma induced modification of the MoS_2 topmost layers on the observed p-type behaviour of the MoS_2 transistors.

[1] B. Radisavljevic, et al., Nat. Nanotechnol. 6, 147 (2011).

[2] S. Kim, et al., Nat. Commun. 3, 1011 (2012).

[3] S. Das, et al., Nano Lett. 13, 100 (2013).

[4] F. Giannazzo, G. Fisichella, A. Piazza, S. Di Franco, G. Greco, S. Agnello, F. Roccaforte , Physica Stat. Solidi RRL 2016, DOI:10.1002/pssr.201600209.

[5] F. Giannazzo, G. Fisichella, A. Piazza, S. Agnello, F. Roccaforte. Phys. Rev. B **92**, 081307(R) (2015).

#225 - The influence of crystallographic defects on the electrical and optical properties of MoS2 flakes

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The class of the semiconducting transition metal dichalcogenides (TMDC), such as MoS_2 or WS_2, has emerged thanks to their high mechanical flexibility, compositional stability and crystal quality coupled with potentially inexpensive production methods[1] as a promising substitutes for graphene.

One of the advantages of the two dimensional (2D) TMDCs comes from quantum confinement effects that enable an indirect-to-direct band-gap transition in single layers[2] that makes TMDC monolayers promising two-dimensional semiconducting materials for nanoelectronic and optoelectronic applications as well as for FET-based bio-sensors.[3]

The lattice defects in 2D TMDCs, including point defects, ripplocations and grain boundaries, have been studied mainly from a structural point of view, while their optical and electrical properties currently remain mostly unexplored. Therefore, the analysis of the crystal defects in 2D nanoflakes is still in its early stage and deserves a focused approach to understand how novel electronic and optical properties can be engineered by controlling the defect nucleation.

In this work we report on the first experimental evidence of near-infrared (NIR) emissions from crystalline defects in MoS_2 multi-layer flakes exfoliated from bulk molybdenite via the conventional tape method.

Different kinds of crystal defects have been investigated by aberration corrected Scanning Transmission Electron Microscopy (STEM), Electron Energy Loss Spectroscopy (EELS), microRaman spectroscopy, Cathodoluminescence (CL) spectroscopy complemented by *ab-initio* Density Functional Theory (DFT) calculations in order to assess their influence on the optical properties.

In particular, CL mapping reveals that the MoS_2 flake' edges present an intense emission peaked at about 0.75 eV. According to EELS results and *ab-initio* calculations the origin of this emission is ascribed to the high concentration of sulfur vacancies (V_S). Moreover, the ripplocations have been found to induce a strong red-shift and broadening of the indirect band-to-band transition of MoS_2, peaked at 1.25 eV.[4]

Lastly, structural and compositional modifications induced by controlled electron beam irradiation experiments have been performed to understand how novel electronic and/or optical properties can be engineered by controlling the nucleation of crystal defects.[5]

[1]Q.H. Wang, *et al.* Nat. Nanotech. 7, 699-712 (2012)

[2]A.Splendiani, *et al.* Nano Letters **10**, 1271-1275 (2010).

[3]D. Sarkar *et al.* ACS Nano **4**, 392-4003 2014

[4]F. Fabbri *et al.* Nature Comm. DOI: 10.1038/ncomms13044

[5]E. Rotunno *et al.* 2D Materials 3 2016 025024

#226 - Electronic and optical properties of Weyl semimetals based on transition metal monopnictides: Ab initio studies of TaAs, TaP, NbAs and NbP

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We investigate electronic, optical and loss properties of the Weyl semimetals TaAs, TaP, NbAs and NbP crystallizing in bct geometry for small and larger energies by means of the *ab initio* density functional theory with spin-orbit interaction and within the independent-particle approximation. Chemical trends are discussed. The four band structures show well energetically separated Ta5*d*/Nb4*d* conduction and As4*p*/P3*p* valence bands. Their small energetical overlap leads to electron and/or hole pockets near the Fermi energy at the 8 W_1 and 16 W_2 Weyl nodes, the parameters of which are computed, in particular for the linear bands and the small energy distances between the Fermi energy and the Weyl nodes. The bands and their occupation near the Weyl nodes determine the infrared optical properties. They give rise to almost constant values of the imaginary part of the dielectric function and, hence, a linear increase of the real part of the optical conductivity. The high-energy spectra are dominated by interband transitions in the band structure. The energy zeros of the real part of the dielectric function define plasmon frequencies, at which the energy loss function exhibits a pronounced peak. Whereas the details of the Weyl nodes are compared with recent ARPES results for TaAs and NbP, we directly compare with measured optical spectra for TaAs.

#227 - Non-linearity at the single particle level: an entangled state of a polariton with a single photon

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The development of a purely quantum computing device, even at the proof-of-principle level, has proved to be an extremely challenging task due to the difficulties in combining good isolation from the environment and strong interactions between qubits. Exciton-polariton, a quasi-particle formed by the superposition of light and matter, can display the desired characteristics and it has been deeply investigated for this reason, but a genuine quantum effect with polaritons remained elusive still now. In this work we show for the first time the entanglement between a single photon and a single polariton in a solid state device, opening the page of quantum polaritonics.

For systems able to confine electron-hole pairs in two dimensions (quantum wells), the polariton exhibits some of the best features of its composing subsystems: the coherence and on-chip propagation of light, together with the capability of interaction inherited by excitons, which gives enhanced control on the system. Up to now, the quantum nature of polaritons had been only demonstrated for quantum dots, in which the 3D confinement of the electron generates antibunching in the emitted light. To allow an easy interaction between qubits, in this work, we experimentally show the quantum nature of 2D polaritons in an optical microcavity-quantum well system. A tomographic measurement shows that an entangled state between photon and polariton is generated: since this effect has no classical counterpart, it proves univocally the quantum nature of the polariton. Importantly, we have been able to control the level of entanglement of the single polaritons by a weak external laser, proving the interaction at the single particle level. This opens a wide range of possibilities in the way towards the development of a quantum information device.

#228 - Soft X-ray probes for ultrafast femtochemistry and catalysis.

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The study of charge dynamics in chemical processes at surfaces by measuring in real time the changes of the electronic structure of the materials is nowadays possible thanks to the advent of free-electron lasers FELs. We studied phtocatalytic reactions at surfaces by recording electronic structure changes in the femtosecond and picosecond timescale after an optical excitation. I will briefly present our time resolved resonant x-ray emission (RXES) study at FELs of the first picoseconds in CO desorption and oxidation reactions triggered by optical pulses. Besides photon in-photon out probing techniques like RXES, photon in-electron out techniques like PES can also be employed for the electronic structure study. I will discuss the advantages and limitations on the usage of time resolved photoemission (PES) for such measurements at FELs. I will present a preliminary time resolved PES experiment performed at a synchrotron facility to explore the charge dynamics induced by sunlight in donor/acceptor molecular systems and describe the set-up for optical pump- PES probe we are are currently building at ALOISA beamline of the Elettra synchrotron.

#229 - Diamond optical waveguides and NV centers formed by focused femtosecond laser pulses

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Diamond's nitrogen-vacancy (NV) centers show great promise in sensing applications and quantum computing due to their long electron spin coherence time and their ability to be located, manipulated and read out using light. The electrons of the NV center, largely localized at the vacancy site, combine to form a spin triplet, which can be polarized with 532-nm laser light, even at room temperature. The NV's states are isolated from environmental perturbations making their spin coherence comparable to trapped ions. An important breakthrough would be in connecting, using waveguides, multiple diamond NVs together optically. However, the inertness of diamond is a significant hurdle for the fabrication of integrated optics similar to those that revolutionized silicon photonics.

In this work we show the possibility of buried waveguide fabrication in diamond, enabled by focused femtosecond high repetition rate laser pulses. We use mRaman spectroscopy, post-etching methods, transmission electron microscopy and stress-field simulations to gain better insight into the structure and refractive index profile of the optical waveguides. Using optically detected magnetic resonance and confocal photoluminescence characterization, high quality NV properties are observed in waveguides formed in diamond. In addition, we show the possibility of creating vacancies in bulk diamond using focused femtosecond laser pulses. After annealing, NV centers are formed in both optical and electronic grade diamond. The integration of NV centers and optical waveguides in diamond could open the door for applications in sensing and quantum information.

#230 - Four wave mixing experiments in the extreme ultraviolet regime

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The analysis of non-linear optics allowed the birth of a class of experimental techniques based on the mixing of various wavelength. In details, Four Wave mixing (FWM) processes are of particular interest for their versatility in the studies of dynamical properties of matter. Since few years ago, only optical laser based FWM experiments were possible, due to the lack of coherent sources in the shorter wavelength regime. Thanks to the development of Free Electron Lasers (FEL), a fundamental extension of FWM techniques towards the Extreme Ultraviolet (EUV) and soft x-ray regime is now available, building up the frequency and wave vector range exploitable by such methods, as well as provide atomic-selectivity. We hereby report on the first FWM experiments based on FEL sources, where Transient Grating and Coherent Anti-Stokes Raman Scattering signal have been produced and recorded.

The measurements include information on vibrational relaxations, but also on the electron-phonon coupling and thermal diffusion in amorphous and crystalline structure, allowing also a resonant and non-resonant excitation, thanks to the FEL energy tunability. Bulk acoustic waves and surface acoustic waves can be easily detected contemporary on the sample, thanks to the transmission and reflection geometries employed in the experimental setup.

The measurements demonstrate the unique prospects to exploit the dynamics and coupling between “low-energy” modes, such as vibration and valence electronic states, and “high-energy” excitation involving core levels.

We also report the actual state of the new high repetition laser based high harmonics generation laboratory under the NFFA-SPRINT project, devoted to the studies on photoemission and spin dynamics on magnetic materials, as a valid alternative to the FEL sources for studies in the EUV spectral region, where high repetition rate (not available for FEL) is required.

#231 - Heat Dissipation and Melting of Metal Nanoparticle Systems and Arrays

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When the plasmon band or the interband spectral region of gold nanoparticle (AuNP) systems is excited by an intense pulse, the photon energy absorbed by the electrons is transferred to the lattice of the NP as heat through electron-phonon coupling. Depending on the intensity of the light pulse and thus the initial electron temperature a number of outcomes are possible. At low intensities the heat of the lattice is fully transferred to the environment of the particles (surfactant molecules and solvent) through phonon-phonon coupling on the time-scale of 100s of picoseconds with the Au NPs returning to room temperature before the arrival of subsequent light pulses [1]. In this case the morphology of the NP system remains unchanged. At medium intensities the initial temperature is sufficient to lead to melting of the NPs, which can lead to morphological changes of the NP structure. Higher intensities can lead to other effects such as photofragmentation of the NPs, release of stabiliser molecules from the surface of the NPs or even Coulomb explosion due to multiple ionisation events.

In this work we concentrate on the effects of low and medium intensity laser excitation of synthesized self-assembled dye-stabilised AuNP systems in aqueous solutions [2], using the interaction of the light with AuNPs to modify their morphology, by reshaping them in gold nanorods, larger nanospheres [3] or other metallic nanostructures [4, 5]. The NP system is excited by a femtosecond laser pulse of different wavelengths allowing selective deposition of energy and the subsequent heat dissipation through phonon-phonon coupling and morphological changes are monitored in time by recording transient absorption spectra in 400-800 nm range, that makes it possible to follow the phonon-phonon coupling effects on the recovery of the bleaching of both the transverse and extended plasmon resonances of the AuNP system. Changing the wavelength and intensity of the light allows the structures formed subsequent to photoinduced melting of the nanoparticles to be carefully controlled. This experimental approach to nanostructure assembly by the combination of chemical synthesis of aggregates of spherical NPs and photothermal melting will allow the construction of nanostructures with properties not attainable using traditional techniques.

References

[1] M. Hu, X. Wang, G. V. Hartland, V. Salgueirino-Maceira, and L. M. Liz-Marzan, Chemical Physics Letters 372, 767 (2003).

[2] I. Venditti, L. Fontana, I. Fratoddi, C. Battocchio, C. Cametti, S. Sennato, F. Mura, F. Sciubba, M. Delfini, M.V. Russo; J. Colloid Interf. Sci. 418,52 (2014)

[3] S. Link, C. Burda, B. Nikoobakht, and M. A. El-Sayed, The Journal of Physical Chemistry B 104, 6152 (2000).

[4] R. Jin, Y. Cao, E. Hao, G. Metraux, G. Schatz, and C. Mirkin, NATURE 425, 487 (2003).

[5] D. Liu, C. Li, F. Zhou, T. Zhang, H. Zhang, X. Li, G. Duan, W. Cai, and Y. Li, Scientific Reports 5 (2015).

#232 - Ultrafast Manipulation of Dimerization by Photodoping

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The ultrafast control of physical properties on the nanoscale provides an understanding of the primary processes leading to particular material properties and strategies to develop new nanotechnology. To realize this goal, one needs to observe and control dynamics in solids to reveal
the mechanism of exotic quantum phenomena with the interweaving of spin, charge, orbital, and phonon degrees of freedom. Here, we provide a report from both experimental and theoretical studies on 5d iridates using femtosecond electron diffraction (FED) and density functional theory (DFT) to investigate structural dynamics during the onset of the multi-orbital ordered phase transition.
This study provides direct evidence illustrating that the ultrafast manipulation of dimerization is possible via photodoping. Photoexcitation can be used to control orbital occupations, thereby leading to ultrafast control of the bonding pattern. The Ir-Ir dimerization shows an unexpected fast
break and recovery due to the filling of the antibonding d xy orbital in the 1/5 phase. The atomically-resolved experimental technique developed here reveals a previously unforeseen pathway of a structural phase transition and could pave the way to ultrafast switching between metastable
structures by controlled breaking and creation of bonds in solids.

#233 - Density and structural anomalies in soft-repulsive dimeric fluids

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The class of systems known as network-forming fluids, i.e. fluids characterized by intermolecular bonds strictly dependent by the orientation, has always captured great interest in the field of chemical physics. Such interest is mainly due to the large variety of anomalies found in the phase behaviour and in the fluid structure of these systems when subjected to conditions of high pressure and low temperatures. In this context, the possibility to develop simple models able to reproduce such anomalies even via spherically symmetric potentials constitutes a fascinating challenge. To this aim, the particular class of intermolecular interactions called core-softened potentials [1] may play a significant role: these potentials are characterized by the softening of the hard-core plus an attractive tail and it has been observed that such a softening may give rise to anomalous behaviours, such as a temperature of maximum density [2] typical of water-like fluids. Here we report Monte Carlo results for the fluid structure of a system of dimeric particles interacting via a core-softened pair potential of inverse-power form, modified in such a way that the repulsion strength is softened in a given range of distances [3]. The aim of such a study is to investigate how both the elongation of the dimers and the softness of the potential affect some features of the model. Our results show that the dimeric fluid exhibits both density and structural anomalies even if the interaction is not characterized by two length scales. Upon increasing the aspect ratio of the dimers, such anomalies are progressively hindered, with the structural anomaly surviving even after the disappearance of the density anomaly. These results shed light on the peculiar behaviour of molecular systems of non-spherical shape, showing how geometrical and interaction parameters play a fundamental role for the presence of anomalies. [1] P. C. Hemmer and G. Stell, Phys. Rev. Lett. 24, 1284 (1970). [2] S. V. Buldyrev, G. Malescio, C. A. Angell, N. Giovambattista, S. Prestipino, F. Saija, H. E. Stanley and L. Xu, J. Phys.: Condens. Matter 21, 504106 (2009). [3] G. Malescio, S. Prestipino and F.Saija, Mol. Phys. 109, 2837 (2011).

#234 - High-Pressure Synthesis Of New Multiferroic Materials

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Multiferroics are a family of materials where two or more of the so-called 'ferroic' order parameters (ferroelectricity, ferromagnetism and ferroelasticity) simultaneously coexist; they are extremely rare in nature for a number of factors, including symmetry and electronic constraints.

New synthesis techniques such as high pressure/high temperature (HP/HT), represent a powerful tool both for the understanding of the complex mechanisms leading to multiferroism and for the fabrication of new compounds, in particular magneto-electric (ME) phases, potentially suitable for technological applications.

We present some new metastabile phases (often perovskite-based oxides) obtained and characterized at IMEM-CNR. Basically, HP/HT synthesis allows to stabilize highly distorted structures and the delicate interplay among structural distortions and spin/lattice degrees of freedom might support the ME coupling [1].

Noticeable examples are: *simple*- or *double*-perovskite compounds containing Bi^{3+} ($BiMnO_3$ [2] and Bi_2FeMnO_6 [3], respectively), or Pb^{2+} (Pb_2FeMoO_6[4]) and *quadruple*-perovskite (i.e. $(BiMn_3)Mn_4O_{12}$ [5]) magnetic oxides in which the ferroelectricity arises by the asymmetrical coordination induced by the stereochemical effect of the Bi^{3+}/Pb^{2+} 'lone-pair' electrons, while magnetism is related to the unpaired electrons carried by the transition metal ions.

Large polarisation has been recently observed in the isostructural $(LaMn_3)Mn_4O_{12}$ polycrystals where exchange striction is expected to play a dominant role [6]. The iron fluorides crystals synthesized by hydrothermal synthesis, with tetragonal tungsten bronze (TTB) structure of general formula general formula $K_xFe_5F_{15}$ ($2<x<3$), a rare example of complete MF, being simultaneously ferrimagnetic, ferroelectric and ferroelastic [7] .

A further possibility is provided by the chemical substitutions made possible under pressure, as in $(Pb,K)_2FeMnO_6$, where K^+ partially substitutes Pb^{2+} on the perovksite A site, transforming a semimetal into a (polar) dielectric material to get a multiferroic phase [8].

References

[1] E. Gilioli and L. Ehm, *IUCrJ*, **2014**, 1, 590–603

[2] E. Montanari et al., *Physical Review B,* **2007***,*75, 220101**R**

[3] D. Delmonteet al.,*Physical Review B*, **2013**, 88, 014431

[4] F. Mezzadri et al., *Journal of Material Chemistry C*, **2016**, 4, 1533-1542

[5] A. Gauzzi et al., *J. Appl. Phys.,* **2013***,* 113, 043920

[6] R. Cabassi et al., *Physical Review B,* **2010,**81, 214412

[7] F. Mezzadriet al., *Physical Review B*, **2011**, 84, 104418

[8] D. Delmonteet al., *in preparation*

#235 - Gravure printing as industrially viable method for the production of flexible optoelectronics

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In the last decade roll-to-roll printing techniques were considered as viable method for the low cost industrial production of flexible large area optoelectronic devices. Among the roll-to-roll printing techniques the gravure printing appears the most promising coupling the advantages of high speed production and high quality resolution. However, to date, the application of the gravure printing to the optoelectronic filed is very limited due to the difficulties of low viscosity inks for the production of functional layers having suitable characteristics. In fact, till now, gravure printed layers encounters some technological limitations such as low thickness, inhomogeneity and high surface roughness often resulting in a printed layer not suitable for electronic devices. This work shows the possibility to overcome the problems related to the ink formulation and gravure printability of different functional materials promoting the only high speed, high resolution printing technique for the production of large area electronic devices.

One of the most important success was obtained in the production of a polymeric electrode. The research on the optoelectronics is in fact also focused on the substitution of the widely used expensive and brittle Indium Tin Oxide (ITO). The most promising candidate, the highly conductive PEDOT, was for the first time successfully gravure printed and tested in organic photovoltaic solar cells. A multilayer approach with variable ink concentration, using IPA as process solvent allowed to improve the anode characteristics. The adopted multilayer easy approach can be applied to other functional materials for the production of different layers necessary in the realization of the optoelectronic devices, pushing more and more the possibility of employing the gravure printing to the partial or complete fabrication of optoelectronic devices.

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#236 - Inkjet printing of polymeric microlenses for otpoelectronic applications

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In the recent years, the micro-optics technology has been increasingly explorated for its potential in large area application fields. In particular, microlenses are now incorporated in many systems and commercial applications such as optoelectronics and photonic devices.

Several fabrication techniques have been proposed for the realization of differently shaped microlenses. In particular, the printing techniques have attracted increasing interest as single-step processes with wide versatility in the definition of the patterns and in the employable substrates for optical devices, making the fabrication rapid and cost-effective. The present work is focused on the manufacturing of inkjet printed microlenses and on the study of the effect induced by the post-printing thermal treatment on the optical parameters. Poly(methyl methacrylate) (PMMA), an optical grade polymer with good mechanical properties, and its composite with TiO_2 nanoparticles have been used as materials to fabricate the microlenses. The inks have been printed on glass substrates covered by highly hydrophobic tetraethyl orthosilicate 1H,1H,2H,2H-perfluorodecyl-triethoxysilane (TEOS/PFTEOS) films. The optical and geometrical characterizations of the microstructures have been performed by interferometric and profilometric analyses. Specifically, in order to evaluate the optical properties a Mach-Zender system in confocal and cut-eye configuration has been employed. The results indicated that the optimized printed parameters allow to control the optical quality of the realized polymer microlenses further improved by applying the proper thermal post-treatment process.

#237 - Inkjet printing of an aqueous graphene suspension for sensing applications

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In the present work we present a feasibility study of graphene-based chemi-resistive gas sensors inkjet printed onto different substrates.

The inkjet printing (IJP) technology, among the deposition methods from liquid phase, allows to selectively deposit small ink volumes in controlled way: this patterning capability permits an efficient use of different functional inks so reducing the amount of waste products; additionally, this technique operates in no-vacuum, no-temperature and contactless conditions resulting totally versatile for the employable inks and substrates.

All these items make IJP an eco-sustainable fabrication process especially if combined with low-cost and low-environmental impact materials, both functional inks and substrates.

In this perspective, the aim of the current research is to address the potential of IJP for manufacturing gas sensor devices according to an green approach, where a suspension of graphene dispersed in a mixture of isopropanol and ultrapure water has been IJ-printed as sensing material onto glossy paper. Moreover, the same graphene-based ink, prepared through the Liquid Phase Exfoliation (LPE) method, has also been deposited onto other substrates, Al_2O_3 and Si/SiO_2, in order to investigate the effect of the substrate morphology and, more specifically, of the ink/substrate interaction on the device performances. The comparison analysis has been performed in terms of relative conductance variations upon exposure to NO_2 in standard conditions and correlating them to surface characteristics of the sensing films differently grown onto the different substrates.

#238 - 4-layer sprayed polymer solar cells based on thick active layer processed with non-chlorinated solvents

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The scientific and technological interest on polymer solar cells (PSCs) has been arisen from the possibility to fabricate photovoltaic devices by solution processing, thus allowing cost reduction, lightness and versatility in terms of transparency and shape. These features increase their potential in application fields as solar-powered consumer electronics, building-integrated photovoltaics (BIPV) and greenhouses [1-3], where conventional photovoltaics is difficult to apply. Although new photoactive materials have markedly improved the power conversion efficiency (PCE) of lab-scale devices, exceeding 10%, a great effort needs to be performed to transfer such performance on large-area by using industry-compatible coating techniques and materials.

This work has been focused on spray coating technique, performed by an automated spray machine in air, which allows, according to the setting of several spray parameters, an easy and low cost process with good reproducibility and high yield. The optimized parameters able to deposit the charge transport layers and the active layer with the desired properties in terms of coverage, morphology, and thickness have been found. 4-layer sprayed inverted polymer solar cells with an active layer comprising of a commercial low band-gap donor (PTB7-Th) have been fabricated, achieving a significant PCE of 2.9%.

The active layer based on donors belonging to PBDTTT family is characterized by low thickness of about 80-100nm. This is not advantageous for high throughput manufacturing of large-area organic photovoltaics. Firstly, thin layers lead to poor product yields as thin films are highly susceptible to point defects. Secondly, they result in poor reproducibility as relatively small variation in layer thickness produce large difference in solar cell performance [4]. To overcome these issues, PffBT4T-2OD donor polymer has been investigated, due to its property to allow high efficiency with thicker films. The introduction of such donor in the 4-layer sprayed structure have increased the PCE up to 3.8%. Notably, the active layer has been processed from ortho-xylene, which is more tolerated in the industry than the typically used chlorinated solvents.

[1] N. Espinosa et al., *J. Mater. Chem. A*, 2013, 1, 7037-7049.

[2] Bas van der Wiel et al., *MRS Proceedings*, 2014, vol.1639.

[3] C. J M Emmott et al., *Energy Environ. Sci.*, 2015, **8**, 1317-1328.

[4] C. Duan et al., *Polym. Chem.*, 2015,6, 8081-8098.

#239 - Low-temperature solution-processed electron transport layers for high-efficiency inverted polymer solar cells

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During the last years, there was an increasing interest in the development of materials for polymer solar cells (PSCs). This kind of photovoltaic devices shows promising advantages such as flexibility, light weight, low cost and processability with roll-to-roll printing techniques compared to conventional silicon solar cells. In order to compete with these inorganic devices in real-world applications, high power conversion efficiency (PCE) and environmental stability are also important. The performances and the stability of such devices mainly depend from the photoactive layer and the architecture of the device. In fact, it has been demonstrated that PSCs, with the so-called inverted device architecture (i.e. a cell where the polarity of the electrodes is reversed compared to the standard configuration), show better photovoltaic properties. The interface materials used between the ITO cathode and the active layer, which act as electron transport layers (ETL), have a great impact on the performance of PSC in term of electronic and optical properties.

In this work, we realized inverted PSCs using various ETLs realized by solution processes and with low-temperature treatments. The architecture of all the devices was glass/ITO/ETL/blend/MoO_3/Ag. The photoactive layer was a blend of poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*;4,5-*b'*]dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-*b*]thiophene-)-2-carboxylate-2-6-diyl)] (PTB7-Th) and [6,6]-phenyl C_{71} butyric acid methyl ester ([70]PCBM). Solar cells were realized and characterized by external quantum efficiency (EQE) and current-voltage (IV) measurements in dark and under AM1.5G illumination (100 mW/cm^2). Power conversion efficiency surpassing 10% has been obtained.

Thursday December 15

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#240 - Magnetic Nanomaterials in Bio-medical applications

Valentin Alek Dediu (I) - CNR-ISMN

Nowadays the interest to the tissue engineering is continuously increasing in both scientific and application fields. In particular, scaffolds have become fundamental tools in bone graft substitution and the research in this direction has achieved impressive accomplishments. On the other hand, the need to support the scaffold with cells, growth factors and others evidenced a long-standing problem consisting on the difficulty to reload after implantation the scaffolds with the bio-agents. Recently proposed magnetic scaffolds represent a conceptually new solution to this problem. The magnetic scaffold is able, via magnetic driving, to attract and take up in vivo growth factors, stem cells or other bio-agents bound to magnetic particles.

I will discuss the potential posibilities of these new smart biomaterials and will illustrate some recent achievements. In addition to this I will overview the prospectives for the employmet of magnetic nanostructured materials in advanced diagnostics and theranostics.

#241 - Polymer based superparamagnetic scaffolds for tissue engineering

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Magnetic feature have been recently incorporated into polymer based multifunctional scaffolds for tissue engineering. The rationale relies on the possibility to deliver, on demand, bioaggregates such as drugs and growth factors, by switching on and off an external magnetic field. Moreover, cell seeding into these scaffold may be improved through external magnetic fields. Nanocomposite magnetic scaffolds consist of a thermoplastic polymeric matrix reinforced and functionalized with magnetic nanoparticles (MNP). These composites show a superparamagnetic behavior, as they magnetize in the presence of a magnetic field in a similar fashion of ferromagnetic materials, but removing the external magnetic field the residual magnetization is almost null.

Iron oxide and iron doped hydroxyapatite MNPs have been incorporated into aliphatic polyester matrix, and these nanocomposites were processed according to rapid prototyping techniques. A multiphysical approach based on magnetic measurements, simulations, mechanical testing and contact angle measurements has been carried out for characterizing these fully interconnected scaffolds. Cell-material interaction has been evaluated in vitro through cell assays, while preliminary in vivo behavior has been assessed through animal models.

Nanocomposite magnetic scaffolds have been successfully processed through rapid prototyping techniques. These scaffolds show a superparamagnetic behavior. MNPs allow to tailor mechanical properties and to improve wettability. Compared to neat aliphatic polyester based scaffolds, an enhancement of cell-material interaction and of tissue regeneration is observed. It seems that this approach is the only one possible to release, on demand, bioaggregates through an external physical signal.

Nanocomposite superparamagnetic scaffolds provide very unique features. Used in combination with magnetically labeled cells and/or magnetic functionalized bioaggregates, these scaffolds allow to trigger biological events by using static or dynamic magnetic fields. Custom made superparamagnetic nanocomposite scaffolds have the potential to guide the regeneration process of damaged biological tissues.

#242 - NEW MAGNETIC BIOACTIVE NANOPARTICLES: A NEW PLATFORM FOR NANOMEDICINE

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The ever increasing need of more effective and targeted therapies for the treatment of various degenerative pathologies is pushing material scientists to develop new solutions associating enhanced safety with smart functionality, also permitting the establishment of personalized therapeutic approaches. In this respect, the development and use of nanoparticles is today limited by several factors among which: i) low biodegradability and biocompatibility; ii) toxic by-products; iii) uncontrolled drug release into the bloodstream; iv) limited cell-target specificity and v) low efficiency in crossing biological barriers.

In this respect a novel magnetic apatitic nanoparticle (FeHA) has been recently developed, through controlled substitution of Ca^{2+} ions with $Fe^{2+/3+}$ ions, with specific Fe/Ca and Fe^{2+}/Fe^{3+} ratios. Fe-HA exhibits excellent biocompatibility and biodegradability both in vitro and in vivo, as well as intrinsic superparamagnetic properties that enable remote activation by magnetic signals. Due to its unique features, FeHA can replace SPIONs for a variety of breakthrough applications in regenerative medicine and theranostics. In particular, the new nanoparticles offer a promising opportunity in selective cell targeting and in the translation of magnetic cell-based therapies from laboratory to clinical studies. In fact mesenchymal stem cells can easily endocytose FeHA becoming “magnetic stem cells”. After injection, the magnetic labelled cells could be driven by a static magnetic field and localised to the target site where they can perform their specific role.

This approach can also aid tissue engineering approaches forcing the scaffold colonisation overcoming several limitationsin critical tissuedefects, thus enhancing/shorteningthe regenerative processes. Besides, such new nanoparticlescan link several bio-molecules such as anti-cancer drugs, proteins(e.g. anabolic factors), nucleic acids (i.e. miRNA, siRNA, DNA fragments), and drive them to targeted tissues and released on demand by applying weak magnetic fields.

Moreover, we recently proved the capability of FeHA to work as contrast agent in imaging applications giving to us the great chance to offer a smart tool in medicine. It will be possible, at the same time, live monitoring the injected cells and/or biomolecules, guiding them only to the target site and tuning on demand their release and bioactivity opening brilliant perspective in personalised medicine applications.

#243 - Interacting superparamagnetic Fe-doped calcium-phosphate nanocomposite: combining different magnetic contributes to achieve highly efficient nanosystems for therapeutic and diagnostic applications

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Magnetic nanoparticles (MNPs) have strongly emerged in nanomedicine since their successful application in magnetic drug delivery, hyperthermia and contrast agent for diagnostic imaging. In order to maximally accomplish their function, MNPs are required to be targeted to a particular tissue/organ leading to high concentrations in a localized area and thus to the possible arising of toxic implications[1]. For example, dextran-coated SPIONs (i.e. FeridexTM) used as contrast agent in magnetic resonance imaging (MRI) were associated with sufficient complement-related side effects in patients to discontinue them from clinical use. To circumvent these issues, numerous studies were focused on doping well-known biocompatible materials with magnetic ions to obtain magnetic biomaterials endowed with better biological features than SPIONs.

Here, we report on the production and characterization of iron-doped hydroxyapatite (FeHA) NPs having intrinsic biocompatibility and endowed with exceptionally high nanomagnetism, generated by the specific positioning of Fe ions. The association of several investigation techniques such as X-ray absorption, Mössbauer, magnetometry and TEM allowed to unveil that the magnetic properties of FeHA occur by a synergy of two different phenomena, i.e.: (i) interacting superparamagnetism due to the interplay between iron-doped apatite and iron oxide nanoparticles, as well as to the occurrence of dipolar interactions, (ii) interacting paramagnetism due to Fe^{3+} ions present in the superficial hydrated layer of the apatite nanophase and, to a lesser extent, paramagnetism due to isolated Fe^{3+} ions in the apatite lattice. The potential use of FeHA as a novel and safer multifunctional platform for several applications in nanomedicine is supported by the results obtained on (i) magnetically-triggered release of chemotherapeutics (i.e. Doxorubicin) and (ii) magnetic resonance imaging (MRI).

Due to its intrinsic bioresorbability, its ability to act as carrier for controlled drug release by external magnetic stimuli and as a contrast agent in MRI, FeHA represents a novel alternative to SPIONs to develop new magnetic nanosystems with remotely controlled multi-functionalities for personalized nanomedical applications.

#244 - Short, long term fate and biodegradation of SPIONs in vivo

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Once a nanoparticle (NP) is administered *in vivo*, it interacts with components of a physiological environment what results in a formation of so called protein corona.[1]Surrounding the NP corona can dramatically change the nanomaterial size, aggregation state and interfacial properties.[2]As a result NP acquires a new biological identity that would dominate the behaviour of NPs *in vivo*.[3] Therefore, investigation of the PC is a benchmark in understanding and controlling NPs performance *in vivo*. Moreover, long term studies encompassing the whole NP lifecycle are necessary to clarify the fears concerning NPs safety. Thoroughly, unravelling of the interactions of commonly known nanomaterials with living organisms could diminish the huge discrepancy between the produced numerous nanoscale size therapeutics and scarce clinical outcomes.

Here we report the effect of the superparamagnetic iron oxide NPs (SPIONs) surface modification with two hydrophilic molecules, either glucose (glc) or poly(ethylene glycol) (PEG), on protein adsorption, NPs fate and their biotransformation over 4 months. Although NPs@glc and NPs@PEG bound similar amount of proteins *in vitro*, the differences found in the composition of both PCs corresponded to the NPs biodistribution *in vivo*. Whereas NPs@glc were mostly accumulated in the liver and spleen, NPs@PEG were detected in various organs. Moreover, by employing magnetic measurements we have found, that the biodegradation kinetic and therefore clearance of both NPs types was unequal. 4 months after the administration, NPs@PEG suffered a complete disaggregation and/or reduction of size, and were totally removed from the spleen, but not from the liver. On the other side, NPs@glc clearance kinetic was higher in the liver than in the spleen, albeit here the degradation of the NPs in both organs was only partial. Interestingly, degradation tested *in vitro* was faster for NPs@glc than for NPs@PEG demonstrating that the attached molecule is implicated in the protection against degradation in NPs with the same core-shell structure. The variation in the degradation rate observed *in vivo* could be therefore related not only with the attached molecules, but also with the associated PC, which composition may directly affect the degradation rate by lysosomal enzymes or indirectly by driving NPs accumulation in different cells.

(1) Monopoli, M. P.; Aberg, C.; Salvati, A.; Dawson, K. a. Biomolecular Coronas Provide the Biological Identity of Nanosized Materials. *Nat. Nanotechnol.* **2012**, *7*, 779–786.

(2) Walkey, C. D.; Chan, W. C. W. Understanding and Controlling the Interaction of Nanomaterials with Proteins in a Physiological Environment. *Chem. Soc. Rev.* **2012**, *41*, 2780–2799.

(3) Gunawan, C.; Lim, M.; Marquis, C. P.; Amal, R. Nanoparticle-Protein Corona Complexes Govern the Biological Fates and Functions of Nanoparticles. *J. Mater. Chem. B* **2014**, *2*, 2060–2083.

#245 - H-Ferritin-based Multifunctional Nanoparticles: A Smart Thernaostic Platform

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Iron oxide nanoparticles, NPs, mineralized within human H chain ferritin, HFt, protein represent a viable platform to develop novel theranostic agents as they offer multiple advantages in terms of stability, biocompatibility and easiness of functionalization. However, a major limitation is that their size cannot exceed the protein shell inner diameter (ca. 8 nm), which is not large enough to produce a significant hyperthermic efficiency.

In order to overcome this drawback while still exploiting the advantages provided by HFt, we developed two different approaches: first, we increased the magnetic anisotropy of 6-7 nm NPs@HFt by doping with small amount of Co^{2+} ions (Co-NPs@HFt);[1] second, we conjugated HFt-NPs on larger (15 nm), chemically synthesized, maghemite NPs (HFt-NP).

In vitro tests showed that both constructs were highly biocompatible. The hyperthermic properties of Co-NPs@HFt and HFt-NPs were investigated through calorimetric technique and related to structural and magnetic properties. A doping of 5% was found to enhance the hyperthermic efficiency of Co-NPs@HFt and to induce a significant reduction of cell viability when exposed to an alternating field, with clear indications of an advanced stage of apoptotic process. On the other hand, despite of the much larger hyperthermic efficiency, HFt-NP were found to affect cell viability only when internalized in large amount, as confirmed by confocal microscopy performed on rhodamine labeled samples. These results enlighten the primary role of cell-NP interactions besides the large hyperthermic efficiency of the inorganic core.

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[1] E. Fantechi et al., ACS Nano 8 (2014) 4705.

#246 - A polymer-based interface modulates neuronal activity and restores light sensitivity in blind rats

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Engineering biocompatible devices to interface neural networks is a standing challenge for the fields of bioengineering and materials science. In the past years, our group became interested in biocompatible functional materials. We developed a neural interface based on photovoltaic polymers able to modulate neuronal activity upon light stimulation. The devices have been proven to elicit a modification of the activity of both primary neurons cultures and more complex networks like retinal explants or brain slices.Sight restoration represents one of the new frontiers for prosthetic devices enabling the electrical stimulation of neurons. In particular, diseases that affect the retina pigmented epithelium and/or photoreceptors, but preserve the inner retinal layers are preferential targets for implantation of visual prostheses. Thus, we started an in vivo study by implanting the prosthesis in the eye of rats bearing photoreceptor degeneration due to mutation in the MERTK gene (Royal College of Surgeons rats), a recognized animal model of human Retinitis pigmentosa. Preliminary experiments performed in a first cohort of animals showed that: (i) the retina remains well attached over the entire region of the sub-retinal implant without inflammation or fibrosis; (ii) pupil constriction in the implanted blind rat was similar to the response of the non-dystrophic animal and significantly higher than non-implanted dystrophic animals; (iii) visually evoked field potentials were detected in the V1 cortex in implanted blind rats, whereas they were undetectable in non-implanted dystrophic animals. These results broaden the possibility of developing a new generation of fully organic prosthetic devices for sub-retinal implants. In conclusion, we exploited the use of conjugated polymers to generate an organic photovoltaic retinal prosthesis. Our research indicates that organic materials, in particular photovoltaic semiconducting polymers, are suitable for the generation of fully organic interfaces with live cells to be exploited in neuroprosthetics.

#247 - Study of Graphene - Supported Lipid Bilayers interaction for applications in novel electrochemical biosensors

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In our work we investigate the development of a novel electrochemical biosensor using graphene as transducer and electroactive membrane proteins as biological recognition elements.

Graphene is used as transducer because of its unique properties, namely high surface area, electrical conductivity, ultra-high electron mobility, wide electrochemical potential window, low charge-transfer resistance, and reduction of overvoltage: all these properties are responsible for the enhancement of the direct electron transfer between graphene and the membrane proteins.

Membrane proteins are the chosen biosensing element since they are the key factors in cell metabolism, e.g., in cell-cell interactions, signal transduction, and transport of ions and nutrients. Thanks to this important function, membrane proteins are a preferred target for pharmaceuticals, with about 60% of consumed drugs addressing them. The main problem is that the contact with electrode surface causes the denaturation of membrane proteins, so they need to be embedded in a system mimicking their native environment, the supported lipid bilayers (SLBs).

This study is focused on the synthesis of graphene through chemical vapour deposition (CVD), on the surface treatments of graphene through a mild oxidation – to improve its biocompatibility – and on the investigation of its interaction with SLBs.

High quality graphene is synthetized by chemical vapour deposition and it is characterized by using scanning electron microscopy (SEM) imaging, Raman spectroscopy and by measuring the water contact angles (WCAs) before and after surface treatments.

The interaction of graphene with lipids (DOPC - 1,2-dioleoyl-sn-glicero-3-phosphocholine), in particular the formation of SLBs is investigated via electrochemical impedance spectroscopy (EIS), which is a valuable tool for characterizing surface modifications, such as those occurring during the immobilisation of biomolecules (i.e. lipid membrane) on the transducer.

A way of interpretation of EIS data is to use an equivalent circuit: its parameters are determined from the best fitting of theoretically calculated impedance plots to experimental ones.

#248 - Cell durotactic behaviour on surfaces with controlled stiffness

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The need of materials that can control cell adhesion and viability on implanted devices such as biosensors or scaffolds for tissue engineeringis a key tenet to assess and optimize the biocompatibility of implantable devices. The cell external environment (physical and chemical signals) is complex and dynamic governed by several stimuli acting simultaneously which affects cell activities such as survival, adhesion, differentiation, motility, proliferation and apoptosis or necrosis. Biomaterials capable to mimic this environment can contribute in understanding how cells respond to more than one stimulus and when one cue dominates over the other. The trend of cells to move from a soft to a stiff matrix is renowned as durotaxis. As cells migrate from a soft to a stiffer matrix, the stability of adhesions increases. However, the molecular mechanisms of durotaxis are still unexplored. The purpose of this study is to investigate, dual structured PDMS substrates that exhibit uniform topography and chemistry with controlled gradient of stiffness.We illustrate this approach by patterning different types of cells with different geometric patterns, to investigate how these substrates influence adhesion and motility. The well-known durotactic migration of adherent HeLa, NIH 3T3 and BJ cells and non-adherent myeloid blood KU812 cells on biocompatible polydimethylsiloxane (PDMS)-membranes in response to a rigidity gradient was validated on substrates that only exhibit a gradient in modulus. Cells exhibited directed migration toward the stiff regions of the substrate. Cell displacements, cytoskeleton and focal adhesions were investigated. These features were affected by the elastic modulus of the substrate and were not observed when using unpatterned substrates. Future incorporation of multiple gradients within a single substrate will lead to a deeper and more comprehensive understanding of cells dynamics through the complex *in vivo* microenvironment.

#249 - Pyro-electrified polymer membranes for direct cell patterning

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Understanding how the interfacial effects influence cell adhesion and morphology is of fundamental interest for controlling function, growth, and movement of cells in vitro and in vivo. In particular, the influence of surface charges is well-known but still controversial, especially when new functional materials and methods are introduced. With the aim to understand the importance of surface charges, in our preliminary study, for the first time, NIH-3T3 behavior was investigated on c-cut Lithium Niobate (LN) crystals. Significant differences in cell behavior were observed on the faces of LN crystals with opposite polarities. The study suggest the potential of LN as a platform for investigating the role of charges on cellular processes.Afterwards, the electrostatic fields generated spontaneously over the crystal was used to induce permanent and 2D patterned dipoles into polymer films, thus producing freestanding bipolar membranes, by a voltage-free pyro-electrification (PE) process; the lithium niobate (LN) crystal is the key component that plays the multi-purpose role of sustaining, heating and poling the polymer layer that is then peeled-off easily in order to have a free-standing charged membrane. Through our proposal technique, it's possible to obtain spontaneous organization and a driven growth of SH-SY5Y cells that is solely dictated by the nature of the charge polymer surface. In fact, the multidomain pyro-electrified (MD-PE) membrane clearly appears to favour the cell adhesion and spreading onto the regions with positive polarity of patterned surface, with the additional advantage of being supported by a flexible membrane that open, in this way, the innovative chance to manipulate and transfer biological samples on a free-standing polymer layer. The results show the fascinating application for the living cell patterning.

#250 - True spirals at microscale by µ-pyro-electrospinning

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Spiral shapes occur extensively in nature and inspire many technological devices that take advantage of this kind of silhouette. In particular, lots of efforts were made to control the electrospinning (ES) process to form polymer microspiral fibres, but the structures obtained, even exhibiting a spiral shape, lack in regularity at microscale. We present here the µ-pyroelectrospinning (µ-PES), an innovative approach belonging to the ES family, able to condition the driving pyro-electric field, generated through a µheater (µH) integrated in a lithium niobate ferroelectric crystal, favouring the tendency of the fibre in spinning spirally and generating true spirals at microscale. Spiral structures are obtained by an easy and versatile approach based on a mask free and single step process, thus avoiding repetitive, time consuming and expensive lithographic procedures. The peculiarity of this method is its ability to keep under control those fibres bending effects that, instead, occurs chaotically in traditional ES. This result is the combination of different key features: (1) a tip support for the ink reservoir that allows to draw little volumes and therefore thin fibres at shorter distances (2) a µheating process providing an efficient thermal stimulus that, translated in a controlled increase in temperature by regular intervals, ensures a fibre spinning regulated by a stationary electric field, analogously to standard ES. PMMA is used here as ink for demonstrating the reliability of the technique and the results show that the polymer concentration plays a key role in producing reliable and long spirals (i.e. PMMA @9% in anisole). The self-sustained spiral structures obtained, thanks to their true regularity, would be useful for addressing the cell adhesion via a versatile and multiscale technique, opening the route to a potential new platform for cell morphogenesis studies and for cochlea regeneration scaffolds.

#251 - Protein hydrogels as new biomaterials for advanced scaffolds

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Recently the fabrication of gels from biological molecules has received increasing interest in the field of biomaterials. Indeed these gels, especially the hydrogels, can be biocompatible and biodegradable, can entrap large amounts of water or biological fluid, have a microporous structure and provide an excellent mechanical support through their three-dimensional structure. These properties make them the ideal biomaterials for applications in the biomedical field.

Here we report our results, obtained exploiting the proteins' natural tendency to self-organize in a 3D network, for the production of new protein-based materials. The main aim of our work has been to determine the best experimental conditions to obtain a hydrogel of protein aggregates of BSA, a human-compatible and well-known protein. Our experimental procedure was to characterize the nature of the aggregates created at different pH and the mechanical properties of the gel formed during the incubation time; finally we tested the obtained protein hydrogels on a cellular model to verify their application as 3D scaffold.

We analyzed the conformational and structural changes of the protein during all the steps of the thermal aggregation and gelation through FTIR and AFM measurements. The macroscopic hydrogel features have been tested by rheological measurements. SEM images have given a picture of the different arrangement of the protein aggregates created at different pH at the end of the incubation time. Biological tests on LAN5 cell culture have been performed. Our results indicate that BSA hydrogels can be a promising material for biological application in the field of tissue engineering.

#252 - Laccase thin films produced by MAPLE and ESI techniques: Effect of some solvents

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Matrix Assisted Pulsed Laser Evaporation (MAPLE) and ElectroSpray Ionization (ESI) can represent useful techniques for producing enzyme thin films [1-2] exploitable in biosensors. Previous studies were carried out to deposit Laccase thin films by MAPLE using water or benzene as solvents [3-4]. Laccase was chosen since it is a redox enzyme widely used as a biological recognition component in biosensors for the detection of polyphenols. In this work, Laccase films deposited by MAPLE using water or benzene were compared and Laccase films deposited by ESI using acetonitrile or ethanol, both at 10% concentration, were also investigated. The efficiency of the deposition processes as well as the preservation of the biomolecular structure and functionality strongly depend on the solvent. The Laccase film funzionality in terms of enzymatic activity, was determined by spectrophotometric analysis by using syringaldazine as the enzyme substrate. These analysis highlighted that MAPLE using benzene allows obtaining more active films in a shorter time with respect to those obtained with water. Also ESI using ethanol allows obtaining more active Laccase films than those obtained by ESI using acenonitrile. Therefore a successful deposition of Laccase by MAPLE or ESI requires a careful choice of the solvent.

[1] A.P. Caricato and A. Luches, Appl. Phys. A 105 (2011) 565-582.

[2] V.N. Morozov and T.Ya. Morozova, Anal. Chem. 71 (1999) 1415-1420

[3] N. Cicco et al., Sensors, Proceeding of Second National Conference on Sensors, Series: Lecture Notes in Electrical Engineering, Vol 319 (2015) 47-51.

[4] M. Verrastro et al., Talanta 154 (2016) 438-445

#253 - Cs impurities and metal-insulator transition in MoS2 natural crystals

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In the realm of layered materials beyond graphene, MoS_2 gained a primary role due to its semiconducting nature and *n*-type transport down to the two-dimensional limit that makes it extremely appealing for electronic and optoelectronic applications. The intrinsic presence of defects causes MoS_2 to undergo localization effects. In the present work, we propose an extended compositional characterization of MoS_2 natural crystals and we bring solid evidence of Cs impurities in bulky MoS_2 crystals in a concentration well beyond the sensitivity threshold of independent compositional spectrometry probes. Unlike conventional intercalation of alkali in MoS_2, on the basis of the measured crystal structure and *ab initio* calculations we propose that the incorporation of Cs is stabilized by complex where one Cs atom is associated with a double S vacancy therein resulting in an overall *n*-type doping of the MoS_2. The field effect transistor based on this kind of Cs-doped MoS_2 multilayer flake exhibit a clear hallmark of metal-insulator transition as a function of temperature in different bias configuration (high gate bias and forward bias). The insulating regime at low temperature is qualified by a variable range hopping transport with a two-dimensional character throughout the MoS_2 planes. This study is intended to provide tips on how to engineer the doping in MoS_2 nanosheet so as to manipulate the transport features.

#254 - Electronic and optical properties of topological semimetal Cd3As2 from first principles

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Using *ab initio* density functional theory the band structure and the dielectric function of a bct $Cd3_3As_2$ crystal are calculated. We find a

Dirac semimetal with two Dirac nodes near the Gamma point on the tetragonal axis. The bands near the Fermi level exhibit a linear behavior in a

small energy interval. The resulting Dirac cones are anisotropic and the electron-hole symmetry is destroyed along the tetragonal axis.

Along this axis the band linearity only exists in a small energy interval. The Dirac cones seemingly found by ARPES in a wider energy range is interpreted in terms of pseudo-linear bands.

The behavior as 3D graphene-like material is traced back to As *p* orbital pointing to Cd

vacancies, in directions, which vary throughout the unit cell. Because of the Dirac nodes the dielectric functions (imaginary part) indeed show a plateau for vanishing frequencies whose finite value varies with the light polarization. Consequently, two different slopes of the optical conductivity (real part) are derived. The results are critically discussed and compared with those of reflectivity and photoemission experiments.

#255 - Two dimensional Nitrides: an ab-initio study

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Group-III nitrides have received considerable attention for high-power electronic devices and for optoelectronic applications such as light-emitting and laser diodes. In particular in 2014 Akasaki, Amano e Nakamura were awarded for bright and highly efficient blue LEDs with the Nobel Prize in Physics [1]. In addition in recent years theoretical and experimental studies of graphene provided a wide range of knowledge for a new class of 2D materials [2-3-4-5-6]. Motivated by this recent developments we present here a sistematic ab-initio study of the electronic and optical properties of two-dimensional Nitrides (BN, AlN, GaN, InN, TlN). In particular our results about the geometry are obtained within Density Functional Theory (DFT-LDA), while the electronic properties are calculated with the GW approximation. These materials are predicted to have a honeycomb flat structure like graphene [4]. Our results show that with increasing group-III atomic number, a decrease of the gap from 6.7 eV to a few meV takes place. In particular, 2D GaN and InN present a direct gap at Γ. As regards the optical properties we have estimated the excitons behavior of this class of materials using a simple analitical model for 2D systems [7],[8]. The results demonstrate that 2D sheets possess strongly bound excitons due to the interplay of low dimensionality, depressed screening and the presence of a gap. By exploiting the reduced dimensionality and the chemical trend, we demonstrate that it is possible to engineer their electronic and optical response, and suggest that the possible emission range of optoelectronic devices based on 2D group-III Nitrides vary from deep UV to visible. Additionally, it is well-known that heterostructures and alloys open the possibility of tailoring device properties by taking advantage of the characteristics of individual materials, so that new practical applications can arise. In this regard to understand what kind of heterostructures we can have with 2D Nitrides we have compared their band alignments and we display that BN/AlN form an heterostucture of type II . We also have investigated the $In_xGa_{(1-x)}N$ and $In_xTl_{(1-x)}N$ In alloys properties. A very interesting result is that mixing GaN and TlN with InN we can tune the gap from UV to IR. As regards heterostructures also in these case type II alignment can be formed. These tipe II novel heterostructures based on the vertical stacking of different hexagonal 2D crystals may be important for photovoltaic applications.

References:

[1] Amano H et al. Appl. Phys. Lett. 48 (1986) 353;

[2] Novoselov K.S. et al. Science 306,(2004) 666;

[3] Nagashima A et al. Phys. Rev. B 51, (1995) 4606;

[4] Sahin H et al. Phys. Rev. B 80, (2009)155453;

[5] Bacaksiz C et al. Phys. Rev. B, 91,(2015) 085430;

[6] Tsipas P et al. Appl. Phys. Lett. 103 (2013) 251605

[7] Cudazzo P et al; Phys. Rev. B 84 (2011) 085406;

[8] Pulci O et al. Phys. Status Solidi b; 252 (2015) 72-77;

#256 - Co-depositing graphene oxide and exfoliated manganese thiophosphate: a simple route to new 2D nanocomposites

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Lately, 2D layered materials have attracted much interest with their highly anisotropic structural and physicochemical properties. Often, these materials are easily processable as stable colloidal suspensions,[1] allowing to benefit from solution processing and to fabricate functional thin films.[2] Among the most technologically-relevant 2D materials, graphene, graphene oxide and their nanocomposites have exerted a pivotal role for their broad applicability.[3] Here, we report the production of thin films of a new hybrid nanocomposite obtained through the intercalation of graphene oxide (GO) into manganese thiophosphate ($MnPS_3$) layers by a simple "mixing and casting" protocol at room temperature. $MnPS_3$ is a member of the transition metal thiophosphates family[4] and it is an inorganic, pore-layered semiconductor which can behave as a flexible host lattice. The thin films were studied through the combined use of microscopy, diffraction and spectroscopy techniques, obtaining information on the interaction between the two nanocomponents. In particular, the XPS, XRD and Raman spectroscopy data indicate that a partial reduction of GO is obtained upon its interaction with manganese thiophosphate layers. Further electrical and optical analyses will be carried out in the future to determine if the observed partial GO reduction is reflected on such properties.

References

1. (a) V. Nicolosi, M. Chhowall, M. G. Kanatzidis, M. S. Strano and J. N.Coleman, *Science* 2013, **340,** 1226419. (b) G. R. Bhimanapati, *et al.*, *ACS Nano* 2015, **9**, 11509. (c) J. N. Coleman, *et al.*, *Science* 2011, **331**, 568. (d) W. Nie, *et al.*, *Science* 2015, **347**, 522.

2. R. M. Pasquarelli, D. S. Ginley and R. O'Hayre, *Chem. Soc. Rev*. 2011, **40**, 5406.

3. (a) A. Schlierf, P. Samorì and V. Palermo, *J. Mater. Chem. C* 2014, **2**, 3129. (b) T. S. Sreeprasad, M. S. Maliyekkal, K. Deepti, K. Chaudhari, P. L. Xavier, T. Pradeep, *ACS Appl. Mater. Interfaces* 2011, **3,** 2643.

4. V. Grasso, L. Silipigni, *Rivista del Nuovo Cimento* della Società Italiana di Fisica 2002, **25** (1), 1.

#257 - Formation of a Quasi-Free-Standing Single Layer of Graphene and Hexagonal Boron Nitride on Pt(111) by a Single Molecular Precursor

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Hexagonal boron nitride (h-BN) and graphene (G) are honeycomb atomic monolayer materials with similar atomic structure (lattice parameter mismatch less than 1.7%). Graphene has gained a clear prominence among materials thanks to its superb carrier mobility, high transparency, excellent thermal conductivity, chemical inertness. Hexagonal BN shares many of these properties with G, but, differently from it, h-BN is an insulator with a wide bandgap.

One of the most attractive goals is the possibility to merge these two materials in stacked layers or in-plane hybrid heterostructures for the realization of 2D atomic-layer circuits, and novel spintronic devices tailoring the semiconducting properties of graphene[1–3].

Up to now, h-BN-G in-plane hybrid structures have been obtained using chemical vapour deposition (CVD) starting from two or more precursors[4], plasma-assisted deposition[5], by mechanical transfer or hydrogen etching of G layers[2]or by a two step process consisting in the growth of h-BN on existing graphene patches[1,3,6]

We propose a novel bottom-up approach to grow continuous hybrid hexagonal heterostructures combining h-BN and G in 2 dimensional (2D) sheets on single crystals in ultra-high-vacuum (UHV) environment using only one molecular precursor, dimethylamine borane (DMAB).

This novel growth route allows an easy and controlled preparation of perfectly merging domains of G and h-BN of different size and relative concentration or hybridized B-C-N materials on the clean surface of a crystal in UHV just adjusting the substrate temperature.

In particular, G-BN layer grown on Pt(111) at 1000 K was investigated by high resolution X-ray spectroscopy (XPS and NEXAFS), scanning tunneling microscopy (STM), low energy electron microscopy (LEEM) combined with electron energy loss spectroscopy (EELS) and micro-low energy electron diffraction (μ-LEED).

The measurements have shown the formation of a continuous hybrid layer of h-BN and graphene that fully covers the Pt(111) surface. The layer has revealed a complete inertness towards molecular oxygen up to 10^{-6} mbar partial pressure in the temperature range 300 K-600 K.

Our findings have demonstrated that the dehydrogenation of a simple molecular precursor, such as DMAB, is an efficient and easy method for obtaining a continuous h-BN and graphene atomically thin lateral heterostructure on a metal substrate, such as Pt(111).

References

1. Sutter, P., et al, *Nano Lett.* **12,** 4869–4874 (2012).

2. Rajasekaran, S., et al. *Phys. Rev. B* **85,** 045419 (2012).

3. Liu, L. *et al. Science* **343,** 163–167 (2014).

4. Ci, L. *et al. Nat. Mater.* **9,**430–435 (2010).

5. Yang, W. *et al. Nat. Mater.* **12,** 792–797 (2013).

6. Levendorf, M. P. *et al. Nature* **488,** 627–632 (2012).

#258 - High electronic quality Al2O3 on graphene by atomic layer deposition with in-situ seed layer

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The integration a dielectric material on top of Graphene (Gr) is essential for several device architectures, such as Gr Field Effect Transistors (GFETs) as well as for Gr vertical devices, such as the Gr Base Hot Electron Transistors (GBHET). Thickness uniformity, conformal coverage and high structural/electrical quality of the insulator/Gr interface are essential requirements for the final device performances. The deposition technique has a key role both on the final dielectric quality and on the Gr properties preservation. In this sense the Atomic Layer Deposition (ALD) is the ideal technique in order to achieve such kind of dielectric fabrication control without introducing damages or killing modifications in Gr.

ALD can be adopted as the method of choice to deposit the top-gate dielectrics on Gr. However, due to the surface inertness of Gr, chemical pre-functionalization or ex-situ physical deposition of a seed layer, are commonly employed, which can in turn degrade Gr or result in an insufficient film quality. Here we investigate a fully-in-situ activated ALD process for Al_2O_3 on Gr transferred on a Al_2O_3/Si substrate, starting with a seed layer deposition at 100°C with trimethylaluminum (TMA) and H_2O precursors, followed by Al_2O_3 thermal growth at 250°C. The structural and electrical quality of Al_2O_3 such as the effects on the Gr properties are analyzed by AFM, Raman spectroscopy and properly designed microelectronic test devices. Al_2O_3/Gr lateral FETs are employed to investigate the impact of the dielectric integration on the Gr mobility.

Finally, the integration of Al_2O_3 into a Gr coated AlGaN/GaN heterostructure is evaluated. Such as system, comprising Gr and AlGaN/GaN 2DEGs separated by namometer-thick AlGaN barrier layer, hold great promises for the realization of new concept vertical transistors (such as the graphene-base-hot-electron transistors [1]) for ultra-high frequency electronics. Vertical current transport at the Gr/AlGaN/GaN heterointerface has been analysed in previous works [2,3] revealing the presence of a Schottky barrier depending on the thickness, Al concentration and structural properties of the AlGaN layer. The integration of a thin and high quality barrier layer over Gr is required for the implementation of a GBHET. The deposition conditions to achieve uniform coverage and high electrical quality Al_2O_3 on the Gr/AlGaN/GaN heterostructure will be discussed.

[1] G. Fisichella, G. Greco, S. Di Franco, R. Lo Nigro, E. Schilirò, F. Roccaforte, F. Giannazzo, Materials Science Forum, 858, 137, (2016)

[2] G. Fisichella, G. Greco, F. Roccaforte, and F. Giannazzo, Nanoscale **6**, 8671 (2014).

[3] G. Fisichella, G. Greco, F. Roccaforte, F. Giannazzo, Appl. Phys. Lett. **105**, 063117 (2014).

#259 - Room-temperature superfluidity in a polariton condensate

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Superfluidity—a characteristic property of a quantum fluid resulting in a frictionless flow—is one of the most fascinating phenomena studied in physics. Starting from the first demonstration in He 4, superfluidity has been obtained in different systems such as Bose-Einstein condensates (BEC) of sodium atoms[1] and exciton-polaritons—bosonic quasi-particles arising from strong light-matter interactions between excitons and photons—in semiconductor microcavities (MCs)[2,3]. Polaritonic systems have achieved great importance for studies on BEC[4], superfluidity and quantum vortex[5], but also for the realization of ultrafast logic devices thanks to their strong nonlinearities[6]. However both atomic BECs and polaritonic superfluids are tipically achieved at cryogenic temperature. Low temperature, obviously, limits the potential applications of such quasi-particles, while room temperature (RT) superfluidity effects had never been observed in any physical system (due to the ionization of the exciton in inorganic systems). For this reason, organic materials, with their huge oscillator strength, are achieving a great interest for their capability to create stable polaritons at RT. Recently, condensation[7,8] has been demonstrates in MCs embedded organic materials and different experimental configurations have been proposed to obtain long propagation distances—i.e. coupling with evanescent modes[9]—for the realization of polaritonic devices. Here, for the first time, we observe a transition from normal to superfluid flow of polaritons in an organic MC (thanks to the stable Frenkel exciton-polaritons of such system). The crossover between normal and superfluid regime is observed exciting a flow of polaritons around a defect and decreasing the velocities below a critical value. Our observations highlight the presence of scatterless flow both in real and momentum space and are in good agreement with numerical simulations. This result represents a milestone in giving access to next-generation platforms for the study of quantum hydrodynamics and the implementation of RT polariton devices.

1. Onofrio R. et al., PRL 85-11, 2228-2231 (2000)

2. Amo A. et al., Nature Physics 5, 805 - 810 (2009)

3. Sanvitto D. et al., Nature Physics 6, 527–533 (2010)

4. Kasprzak J. et al., Nature 443, 409–414 (2006)

5. Lagoudakis K.G. et al. Nature Physics 4, 706-710 (2008)

6. Ballarini D. et al., Nature Communications 4, 1778 (2013)

7. Plumhof J. D. et al., Nature Materials 13, 247–252 (2014)

8. Daskalakis K. S. et al., Nature Materials 13, 271–278 (2014)

9. Lerario G. et al., Light: Science & Applications 6, e16212 (2017)

#260 - Design of additive-manufactured scaffolds for regenerative medicine applications

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A key factor in scaffold-based tissue and organ regeneration relies on enhancing (stem) cell-material interactions to obtain the same original functionality. Different approaches include delivery of biological factors and surface topography modifications. Although both strategies have proved to augment cell activity on biomaterials, they are still characterized by limited control in space and time, which hampers the proper regeneration of complex tissues. Here, we present a few examples where the integration of biofabrication technology platforms allowed the generation of a new library of 3D scaffolds with tailored biological, physical, and chemical cues at the macro, micro, and nano scale. By engineering their topological properties, these porous biomaterials influence the activity of seeded cells, thereby initiating the regeneration of skeletal, vascular, and neural tissues. Future efforts should aim at further improving our understanding of scaffold topological properties to achieve a fine control on cell fate at multiple scales. This will enable the regeneration of complex tissues including vasculature and innervation, which will result in enhanced *in vivo* integration with surrounding tissues. By doing so, the gap from tissue to organ regeneration will be reduced, bringing regenerative medicine technologies closer to the clinics.

#261 - Influence of microstructure on the improved mechanical performances of metallic biomaterials produced by laser sintering

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Direct Metal Laser Sintering (DMLS) technology, based on a layer-by-layer production process, was used to produce Co-Cr-Mo-W and Ti-6Al-4V alloys specifically developed for biomedical applications. The alloys mechanical response and microstructure were investigated in the as-sintered state and after post-production thermal treatments, including those required for ceramic coatings on dental prostheses. Roughness and hardness measurements, as well as tensile and flexural mechanical tests, were performed to study the mechanical response of the alloys; while X-ray diffraction (XRD), electron microscopy (SEM, TEM, STEM) techniques and microanalysis (EDX) were used to investigate the microstructure in different conditions. The alloy microstructure as well as its response to thermal treatments depend on the specific composition.

The Co-Cr-Mo-W alloy shows an intricate network of ε-Co (hcp) lamellae in the γ-Co (fcc) matrix, responsible of the high UTS and hardness values in the as-sintered state. Thermal treatments increase volume fraction of the ε-Co (hcp) martensite, but slightly modify the average size of the lamellar structure. Nevertheless, thermal treatments are capable of producing a sensible increase in UTS and hardness and a strong reduction in ductility. These latter effects were mainly attributed to the massive precipitation of an hcp $Co_3(Mo,W)_2Si$ phase and the contemporary formation of Si-rich inclusions.

For the Ti-6Al-4V alloy, results evidenced a mechanical behaviour of tensile samples dependent on the building orientation during the sintering process. In terms of microstructure, the as-sintered sample shows a single phase acicular α’-Ti (hcp) structure, typical of metal parts subject to high cooling rates. After thermal treatments, samples show a reduction of hardness and strength due to formation of β-Ti (bcc) laths at the boundaries of α’-Ti plates and to variation of lattice parameters of the hcp phase. Element partitioning plays a role during the thermal treatments giving rise to high concentration of V atoms (up to 20 wt%) at the plate boundaries where the β-Ti phase preferentially forms.

#262 - Design and development of 3D printed scaffolds with advanced functional features for tissue engineering

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Interfacial tissue engineering (ITE) aims to regenerate tissues through the mimicking of continuous biological, physico-chemical gradients. The introduction of additive manufacturing techniques can be useful to obtain continuous gradient of mechanical, mass transport and morphological features, however the possibility to functionalize such three-dimensional (3D) structures by introducing biochemical signal gradients has not fully been investigated. The goal of the present study was to optimize a two-step functionalization method in which, a 3D poly(ε-caprolactone) (PCL) scaffold was aminolysed with a continuous gradient of amine concentration (NH_2 groups) and, successively, a collagen gradient was created via carbodiimide reaction[1-3]. As reported in the literature, the aminolysis represents a simple method to covalently bind NH_2 groups, free to interact with other biomolecules. Furthermore, a protein immobilization, such as collagen, has a clear influence on cell attachment, proliferation and differentiation. To this aim, 3D additive-manufactured scaffolds were produced by means of a rapid prototyping technique. PCL surfaces were modified by dipping the structures in a 1,6-hexanediamine/isopropanol solution. NH_2 density gradient was obtained along the length of the structure through the control of the time and the surface exposure to the reactive solution. Lyophilized collagen type I was covalently bind using a carbodiimide reaction. Ninhydrin and hydroxyproline assays, contact angle measurements, microscopy imaging, Fourier transform infrared spectroscopy (FTIR), collagen staining and biological analyses were carried out in order to characterize the surfaces and the gradients. Results showed that the NH_2 concentration, as well as the immobilized collagen, increased over the reaction time. Microscopy imaging evidenced NH_2 and the collagen gradient distribution whilst FTIR confirmed its grafting. Biological analyses highlighted that MG63 cells showed better adhesion/proliferation on collagen-based structures. Future trends will be focused on the design and development of 3D additive-manufactured scaffolds with combined structural and chemical gradients for ITE applications.

References

[1] Z. Yang, M. ZhengWei, S. H.Yu and G.C. You. "In-depth study on aminolysis of poly(ε-caprolactone): Back to the fundamentals"**.** *Sci. China Chem.*Vol.55 No.11, pp. 2419–2427, 2012.

[2] F. Causa, E. Battista, R. Della Moglie, D. Guarnieri, M. Iannone and P. A. Netti. Surface investigation on biomimetic materials to control cell adhesion :The case of RGD conjugation on PCL. *Langmuir,* 26 (12), pp. 9875–9884, 2010.

[3] K. Y. Chang, L. H. Hung, I. M. Chu, C. S. Ko and Y. D. Lee. "The application of type II collagen and chondroitin sulfate grafted PCL porous scaffold in cartilage tissue engineering". *J. Biomed. Mater. Res. A.* 92(2), pp. 712-23, 2010.

#263 - NANOCOMPOSITES FOR RAPID PROTOTYPING APPLICATIONS

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A new set of manufacturing technologies has emerged in the past decades to address market requirements in a customized way and to provide support for research tasks that require prototypes [1]. These new techniques and technologies are usually referred to as rapid prototyping (RP) and they allow prototypes to be produced in a wide range of materials with remarkable precision in a couple of hours [2-3]. The introduction of rapid prototyping techniques into the biomedical field has allowed to obtain 3D well-defined and morphologically-controlled structures with suitable mass transport and mechanical properties [4-5]. RP systems such as Selective Laser Sintering (SLS), and Stereolithography (SLA) have been shown to be feasible for producing nanocomposite porous structures for use in tissue engineering [6-7]. There are also many restrictions of RP procedures, primarily in the number of available materials and their properties [8], so part of our research in the field of rapid prototyping has been pointed to the development of innovative materials with specific properties like improved biocompatibility, bioactivity and electrical conductivity. Resins based on chemical modified polyesters bioactivated with hydroxyapatite nanoparticles were developed and applied in stereolithography. Thermoplastic polyurethane (TPU) powder has been mixed with graphene nanopowder in order to synthesize the base material to realize electrically conductive 3D structures by SLS. In this work we proposed the integration between composite materials and RP technique to easily create 3D composite scaffolds with a wide range of biological and physical properties for biomedical applications.

References

[1]. AD Lantada et al. Annu. Rev. Biomed. Eng. 2012, 14, pp. 73–96.

[2]. FPW Melchels et al. Biomaterials, 2009,30, pp. 3801-3809.

[3]. WY Yeong et al. Trends in Biotechnol. 22, 12, 2004, pp. 643–652.

[4]. A Ronca et al. Acta Biomaterialia, 9, 4, 2013, pp. 5989–5996.

[5]. A Gloria et al. J Appl Biomater Biom, 7, 3, 2009, pp.141-152.

[6]. FPW Melchels et al. Biomaterials, 31, 2010, pp. 6121-6130.

[7]. A Ronca et al. J Appl Biomater Biom Funct Mat, 10, 3, 2012, pp. 249-258.

[8]. A Pilipović et al. Int J Adv Manuf Tech. 2009, 40, 1, pp. 105–115.

#264 - Additive Manufacturing of metallic nanoparticles structures by 2-photons Direct Laser Writing

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The 2-photons Direct Laser Writing (2P-DLW) is the most advanced optical technique for creating arbitrarily complex 3D materials featuring details well below the diffraction limit, in organic resists.

The possibility to include metallic details with a comparable resolution in the polymeric structures would pave the way for the realisation of metallic/polymeric nanocomposites by 2P-DLW for plasmonics, advanced optics and innovative bio-sensing platforms.

Here we report about the study on the physical features of gold nanoparticles created by 2-Photons Direct Laser Writing[1] in a polymeric or hydrogel matrix, doped with tetrachlorauric acid as the gold precursor.

We show that a coarse control on the GNPs size distribution and density can be achieved with the delivered optical energy dose [2]. This control has been very recently exploited in building substrates for SERS with a tunable enhancement factor, ranging from 10^2 - 10^4 [3].

With the aim to get a finer control on the created structures, we've performed a series of experiments aimed to elucidate the involved physical phenomena, beyond the bare photochemistry. In particular, we report about preliminary results pointing out the key-role of thermal diffusive and convective processes.

In fact, the 2-photons absorption processalso determines the local heating of the sampleand the generation of athermal shock-wave,causing the dehydration ofthe spottedarea.

Because of the concentration gradients of the $AuCl_4^-$ ions, due to their reduction upon the exposure, and of water, due to the thermal effects, distinct diffusive processes, on timescales differing by an order of magnitude, take place.

With the aim to separate the two effects, we created GNPs by dosing the delivered energy in multiple shots, considering different waiting times between them, in order to allow the system to recover the initial conditions.

Our experiments demonstrate that a time interval between shots shorter than typically 10^{-1} s doesn't causes any relevant changes with respect to the single shot case.
However, with intervals between 10^{-1}s and 1 s, we observe a considerable variation in the voxel diameter and the creation of a denser cluster of GNPs [4].

Time intervals longer than 1 s allow the complete rehydration of the area of interest [5]; under these conditions each laser shot causes the local evaporation of water and the consequent shockwave that ejects radially the GNPs from the spot to the near area, causing a voxel contraction and the formation of a ring made of GNPs and precipitated tetrachlorauric acid.

[1] M. Sakamoto et al., J. Photochem. Photobiol. C: Photochem. Rev., (2009)

[2] T. Ritacco et al, JEOS, (2016)

[3] V. G. Ivanov et al, to appare in JPCS, (2016)

[4] T. C. Smith, Master's Thesis, University of Richmond, (1963)

[5] T. L. Porter et al., Sensors, (2007)

#265 - Development of Soft 3D Intricate Microstructures via Direct Laser Lithography Fabricated Flexible Molds

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Three-dimensionally (3D) micropatterned surfaces are attracting increasing interest in soft robotics owing to the potential of mimicking natural morphologies[1]at the microscale and nanoscale. In particular, roboticists are looking to new technologies for designing soft robots with bioinspired capabilities.[2]

In this work we present an innovative micromolding technique that employs direct laser lithography (DLL) for the fabrication of complex 3D micropatterned flexible molds for shaping moldable materials. DLL allows creating arbitrarily complex 3D designs (e.g. reentrant geometries)with high spatial resolution[3],not achievable with standard methods.

Molds have been fabricated in positive photoresist (AZ9260, AZ Electronics materials, GmbH) on Mylar flexible sheets. We designed several shapes in order to investigate the potentiality of the presented technique, obtaining 3D intricate microstructures in poly-(dimethylsiloxane) (PDMS): hollow truncated hemispheres (nominal diameter of 33 µm, height of15 µm and nominal aperture diameter of 15 µm) that do not collapse due to their hemispherical geometry; microgrippers, consisting of couples of sloping trapezoidal-shaped arms (major and minor bases of 20 and 10 µm respectively, height of 9 µm and a bottom to top decreasing thickness starting from 3.6 µm at the baseline), inclined toward each other of a 60° angle with respect to the base; microchannels, consisting of half-pipes of length 150 µm and diameters of 10 and 12 µm, demonstrating the possibility to fabricate elements covering relatively wide areas; crossing arches of diameters 32 and 37 µm and nominal thickness of 2.5 µm, demonstrating the possibility to fabricate self-standing tiny structures. Also, we fabricated a soft cylinder with 3D surface microstructures through one molding step, demonstrating the possibility to obtain 3D patterns at the microscale even on curved surfaces with radius of curvatures of few millimeters. Furthermore, we exploited the hyperelastic behavior of PDMS to deform some of the 3D architectures, demonstrating the possibility of fabricating surfaces with soft gripping and trapping capabilities. The proposed micromolding technique proved to be effective in terms of resolutions and reproducibility, and it can also be applied to any moldable compatible material, in addition to PDMS.

REFERENCES

(1) Bhushan, B. Biomimetics: Lessons from Nature–an Overview. Philos. Trans. R. Soc. Lond. Math. Phys. Eng. Sci. 2009, 367, 1445–1486.

(2) Kim, S.; Laschi, C.; Trimmer, B. Soft Robotics: A Bioinspired Evolution in Robotics. Trends Biotechnol. 2013, 31, 287–294.

(3) Sun, H.-B.; Kawata, S. Two-Photon Photopolymerization and 3D Lithographic Microfabrication. In NMR • 3D Analysis • Photopolymerization; Advances in Polymer Science; Springer Berlin Heidelberg, 2006, 169–273.

#266 - 3D printing of thermosetting/photocurable resins and composites

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Nowadays, additive manufacturing (AM) technology is largely diffused in many different fields: design, customization, engineering, prototyping, biomedical and more. AM fabricates objects by adding material layer by layer, in contrast with traditional manufacturing that operates following a subtractive logic. In fact, AM has many advantages compared to traditional manufacturing: less material waste, complex allowed geometries, customization and less overall costs. In the last few years, AM has been identified with the 3D printing, which can explain itself by many different techniques. The most diffused is the fused deposition modelling (FDM), that allows to print a thermoplastic material from a heating chamber and depositing it layer by layer creating the object. To extend the range of printable polymeric materials also to thermosetting systems, another technique has been developed, the liquid deposition modelling (LDM): liquid resins with appropriate rheological profiles are directly processed through a syringe, followed by post-treatments that allow the curing reaction and the creation of the solid 3D object. An evolution of the LDM approach is represented by UV-assisted 3D printing, in which the feed material is constituted by photocrosslinkable resin systems that can be cured at room temperature right after exiting the extrusion nozzle by means of UV-light irradiation. Hence a dual curable system has been developed, made by a thermosetting resin (epoxy based) and a photocurable one (acrylate based):the simultaneous presence of these two resins in the formulation allowed to achieve fast curing of this ink during the printing process (thanks to the acrylate resin) while concurrently ensuring the formation of a fully crosslinked 3D structure upon subsequent thermal curing of the epoxy-based resin. By incorporating reinforcing fibers into this dual curable matrix, CFR and glass-fiber reinforced (GFR) composite formulations can be obtained. To achieve the transfer of the stress from the matrix to the fibers, and so to improve mechanical properties, a good adhesion between the matrix and the reinforce has to be reached. This innovative approach is in principle extensible also to other 3D printing technique as stereolithography (SL): it creates solid parts by selectively solidifying a liquid photopolymer using a UV laser. This technique is largely spread into biomedical world, because allows to produce customizable medical devices (for example, stents) with completely biocompatible and biodegradable polymer systems. Among these, smart polymers like shape memory polymers (SMPs) are earning a great attention in the biomedical field for their ability to response to difference kind of stimuli, and then returning to their original shape. The additional filling with micro and nanoparticles is a promising application of SMPs with enhanced features.

#267 - Printing of small molecule/polymer semiconducting blends for high performing organic field-effect transistors (OFETs)

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Organic-based devices are currently attracting great attention for applications where low-cost, large area coverage and flexibility are required. The best performing electronic devices to date are those comprising single crystals of organic semiconductors, although they are neither suitable for large-area applications nor compatible with fast high-throughput industrial-scale fabrication. Thus, engineering processing techniques that could give rise to highly crystalline and homogenous semiconducting films potentially resulting in reproducibly high mobility devices is a current challenge. We report here the bar-assisted solution shearing (BAMS) of organic semiconductor blends based on small semiconducting molecules and the insulating polymer polystyrene.[1-3] This technique results in highly crystalline thin films that showed ideal OFET characteristics. Further, the devices were also tested in aqueous media employing the Electrolyte-Gated Field-Effect Transistor (EGOFET) configuration. Our EGOFETs reach excellent performances in terms of mobility as well as subthreshold slope and, additionally, show an outstanding stability, which makes them suitable candidates for addressing actual challenges in (bio-)electronics.[4]

[1] F. G. del Pozo, S. Fabiano, R. Pfattner, S. Georgakopoulos, S. Galindo, X. Liu, S. Braun,M. Fahlman, J. Veciana, C. Rovira, X. Crispin, M. Berggren, M. Mas-Torrent, *Adv. Funct. Mater.* **2016**, *26*, 2379.

[2] S. Georgakopoulos, F. G. del Pozo, M. Mas-Torrent, *J. Mater. Chem. C* **2015**, *3*, 12199.

[3] I. Temiño, F. G. del Pozo, M. R. Ajayakumar, S. Galindo, J. Puigdollers, M. Mas-Torrent, *Adv. Mater. Technol.***2016**, DOI 10.1002/admt.201600090.

[4] F. Leonardi et al. Submitted results.

#268 - Flexible X-ray detectors based on organic thin films

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The research interest on alternative materials for innovative ionizing radiation detection is rapidly growing, in particular to envisage the need of large-area conformable sensor flat panels for applications that span from cultural heritage preservation to the security of public buildings. Organic materials have a strong potential for such an application, thanks to their mechanical flexibility and the possibility of deposition over large and bendable substrates by means of low-cost wet-technologies as printing techniques. Therefore, these feature permits to overcome the constraint of traditional inorganic materials, i. e. expensive or complex growth techniques and stiff mechanical properties. Recently, the employment of solution-grown organic materials as reliable direct X-ray detectors, operating at room temperature, have been demonstrated [1-3]. These studies opens the way to the development of a new class of fully flexible organic-based direct detectors with higher performances. In this work, we will report about results on organic thin-films based, fully bendable, devices as direct X-ray detectors, obtaining sensitivity values up to several hundreds of nC/Gy at ultra-low bias of 0.2 V. We developed an analytical model accounting for the signal amplitude and sensitivity values achieved and describing the mechanisms of collection and transport of the X-ray generated charges. Finally, we assessed the possibility to use the detector under mechanical strain and gave the first demonstration of a 2×2 pixelated matrix organic detector used as an imager. [1] B. Fraboni et al., Adv. Mater., 24, 17, 2289–2293, 2012. [2] B. Fraboni et al., Faraday Discuss., 174, 219, 2014. [3] L. Basiricò et al., IEEE Trans. Nucl. Sci., 62, 4, 1791–1797, 2015. [4] L.Basirico' et al. Nature Comm , in press 2016.

#269 - Highly Conductive Open Networks of Poly(3-hexylthiophene)/ single-walled carbon nanotube hybrids

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Conjugated polymeric composites with carbon nanotubes are well known to provide a good conductive path at relatively low carbon content as these have high aspect ratio specific surfaces and are cost effective. Many applications have indeed been proposed for conjugated polymer/carbon nanotube hybrid materials including conductive and high-strength composites, energy storage and energy conversion devices, sensors etc.In particular, poly(3-hexylthiophene)/carbon nanotube composites (P3HT/NTs) are at the forefront of being widely used in the development of organic photovoltaic devices, chemical sensors etc. In this contribution, we present the preparation of new high conductivity nanohybrid open networks of poly(3-hexylthiophene) and single-walled carbon nanotubes by spin coating depositio . The novel open 2Dnetworks prepared at high spinning speed showed a conductivity three orders of magnitude higher than that measured for networks deposited at low spinning speed although the individual nanotubes are not seen to form a direct connection between the electrodes.[1] The strong improvement of the conductivity performances is explained in terms of the formation of a new nanohybrid system consisting of thin sheaths of P3HT wrapped around NTs forming complex NT/P3HT/NT junctions yielding a soldering effect of the interposed P3HT sheath.

[1] G. Sfuncia, N. Tuccitto and G. Marletta RSC Adv., 2016,6, 51485-51492

#270 - Femtosecond electron transfer at core-excited adsorbed molecules

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Charge transfer phenomena at metal/organic interfaces are a crucial step affecting the efficiencies of devices for organic based electronics and photovoltaics. A quantitative study of electron transfer rates, which take place on the femtosecond timescale, is often difficult, especially since in most systems the molecular adsorption geometry is unknown. Electron core-level spectroscopies have emerged as effective tools to investigate several aspects of the hybrid interface between organic molecules and a substrate. In particular, X-ray resonant photoemission spectroscopy can measure interfacial electron transfer times down to the femtosecond timescale. Furthermore, the strong perturbation induced by the core hole opens up the several questions on how the properties of the interface are modified, calling for a theoretical description of the core-excited system.

Here, we use X-ray resonant photoemission spectroscopy to measure ultrafast charge transfer rates across pyridine/Au(111) interfaces while also controlling the molecular orientation on the metal [1]. We demonstrate that a bi-directional charge transfer across the molecule/metal interface is enabled upon creation of a core-exciton on the molecule with a rate that has a strong dependence on the molecular adsorption angle.

We adopt a theoretical framework based on density-functional theory (DFT), where the excitation is introduced explicitly in the core-level occupation of an atom in a molecule, to investigate the electronic structure and electron transfer from/to the molecules adsorbed on a semi-infinite metal, whose continuum of states is described by a Green's function method [2]. We show that the alignment of molecular levels relative to the metal Fermi level is dramatically altered when a core-hole is created on the molecule, allowing the lowest unoccupied molecular orbital to fall partially below the metal Fermi level opening to substrate-to-molecule electron transfer in X-ray photoemission experiments. We also calculate charge transfer rates as a function of molecular adsorption geometry and find a trend in semiquantitative agreement with the experiment [1].

References:
[1] D. Cvetko, G. Fratesi, G. Kladnik, A. Cossaro, G.P. Brivio, L. Venkataraman, and A. Morgante, Phys. Chem. Chem. Phys. 18 (2016) 22140
[2] G. Fratesi, C. Motta, M. I. Trioni, G. P. Brivio, and D. Sánchez-Portal, J. Phys. Chem. C 118 (2014) 8775

#271 - Direct Imaging of defect formation in strained organic flexible electronics by Scanning Kelvin Probe Microscopy

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Reliable performance under mechanical deformation is a central goal for flexible electronic sensors. The realization of mechanically rugged materials and device architectures depends crucially on the understanding of how strain affects electronic material properties and leads to defect formation. Scanning Kelvin-Probe Microscopy (SKPM) is a formidable technique for nanoelectronic investigations as it combines non-invasive measurement of surface topography and surface electrical potential. Here we show that KPFM becomes feasible on free-standing, deformed flexible samples when operated in the low-interaction regime of non-contact mode thereby providing the opportunity to study strain effects on nano-electronic properties.

As an example we apply the technique to investigate strain effects and failure of flexible thin film transistors containing TIPS-pentacene during bending. We find that the step-wise reduction of device performance at a critical bending radii is related to the formation of nano-cracks in the microcrystal morphology of the TIPS pentacene film. The cracks are easily identified due to the abrupt variation in SKPM surface potential caused by a local increase in resistance. Importantly, the strong surface adhesion of microcrystals to the elastic dielectric allows to maintain a conductive path also after fracture thus providing the opportunity to attenuate strain effects. We support our findings by numerical simulations of the bending mechanics of the hole transistor structure allowing to quantify the tensile strain exerted on the TIPS-pentacene micro-crystals as the fundamental origin of fracture.

#272 - New carbazole based copolymers and Rhenium-based metallo-copolymers for optoelectronic applications

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Photovoltaic (PV) utilisation of solar energy is one of the least exploited and more promising carbon.neutral thecnology available today. Over recent years, organic solar cells have been perfected at laboratory level with a record PCE of 10.6%[1] for polymer solution processd devices and a large area module PCE of 5.5% which may challange a-SI PV technology.[2]

In recent years, conjugated polymers have actracted more and more attention due to their growing efficiency in plastic solar cells.[3] Donor low band-gap copolymers which combine carbazole wirh electronwithdrawing dithienylbenzothiadiazole[4] or benzothiadiazole (**P1**) units have been reported.

In order to increase PV efficiency, we have designed and synthesized new electrowithdrawing comonomers containing bis-imine aromatic ligands (1.2-diazine) to exploit metal coordination for lowering the LUMO level and increasing absorption in the visible region. Here , we report the synthesis of 5,8-dibromophenothiazine (**M2**) and 5,7-dibromothieno[3,4-d]pyridazine (**M3**). The monomers have been polymerized with the boronic derivative of carbazole comonomer by the Suzuki-Miyaura coupling reaction, otaining the corresponding **P2** and **P3** copolymers in goog yield. Later, **P2** and **P3** have been used as ligands in neutral Rhenium (1) complexes of formula $[Re_2(CO)_6(m\text{-}x)(m\text{-}y)(m\text{-diazine})]^5$ (x and Y are bridging anionic ligands), thus obtaining the metallo-copolymers **ReP2** and **ReP3**, respctively. Metal coordination also enhanced photo induced charge-separation and thermal stability. Spectroscopic (NMR,FTIR, UV_Vis, PL) and electrochemical (cyclic-voltammetry) characterizations of new monomers **M2** and **M3** ,and of **P2**, **P3**, **ReP2**, and **ReP3** materials have been performed and the data have been compared with those of the "reference" copolymer **P1**. NMR and MALDI-TOF characterizations reveal a diffrent comonomer enchaiment in the polymer backbone depending on the electronwithdrawing unit and affecting electronic and thermal properties.

1. Dou et al. *Nature Photonics* **2012,** *6*, 181

2. IMEC and Solway **2012**

3. a) H. Chen et al *Nature Photonics* **2009**, 3, 649; b) N. Blouin et al. *Adv. Mater*. **2007**, *19*, 2295

4) M. Leclec et al *J. Am. Che. Soc*. **2008**, *130*, 732

5) M. Panigati et al. *Coor. Chem. Rev.* **2012**, *256*, 1621

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273 - Solar energy conversion performed by solution-processed silicon nanocrystals

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Silicon nanocrystals (SiNCs) in the quantum size range (2-12 nm) are attracting an increasing interest: on the contrary of bulk silicon, they display a bright emission, which can be tuned from the visible to the near-infrared spectral region by increasing their size. Compared to more traditional quantum dots, such as CdSe, SiNCs offer the following advantages: silicon is abundant, easily available and essentially non toxic, it can form covalent bonds with carbon, thereby offering the possibility of integrating inorganic and organic components in a robust structure[1]. Moreover, being Si an indirect band gap semiconductor, the photophysical properties of SiNCs are characterized by an extremely large Stokes shift, long phosphorescence lifetimes and photoluminescence quantum yield as high as 45%. These properties, together with the interest in materials compatible with the Si-based technology, promote SiNCs as ideal candidates for sensing and photovoltaic applications. In particular for the conversion of sunlight to electrical energy, the energy provided by the UV component of the solar spectrum can be down-converted by SiNCs to visible light, matching the typical high responsivity region of conventional Si-based or dye sensitized solar cells.

In this contribution, the implementation of SiNCs in cutting-edge photovoltaic technologies will be discussed. Specifically, the embedding of these nanocrystals in polymer matrix was exploited to prepare semi-transparent polymer waveguides and the photophysical properties of embedded SiNCs were deeply investigated[2]. In addition to this, the photovoltaic performance of the prepared plates as solar concentrators will be reported, demonstrating the feasibility and the promising features of SiNCs based integrated photovoltaics.

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References:

1. Mazzaro, R. *et al.* Photoinduced Processes between Pyrene-Functionalized Silicon Nanocrystals and Carbon Allotropes - SI. *Chem. Mater.* **27,** 4390–4397 (2015).

2. Coropceanu, I. & Bawendi, M. G. Core/Shell Quantum Dot Based Luminescent Solar Concentrators with Reduced Reabsorption and Enhanced Efficiency. *Nano Lett.* **14,** 4097–4101 (2014).

#274 - Harvesting infra-red light in thin film silicon solar cells using upconversion-based strategies

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Spectral upconversion is one of the new nanotechnology-based strategies that can address the issue of unabsorbed sub-bandgap light that normally passes through the solar cell without being absorbed. A spectral-upconversion layer can be conveniently placed at the back of a solar cell without any change in the existing solar cell architecture. Upconversion quantum efficiencies are, however, not high enough to significantly enhance the photovoltaic performance, which is a hindrance for the commercial application of upconversion in solar cells. Light trapping using nanotextures is an established method to enhance carrier generation by increasing the absorption of above-bandgap light in solar cells. Textures that are large enough to scatter and increase multiple reflection of the IR light can be useful to enhance the upconversion yield, and may in fact be more beneficial than the near-field effects of plasmonic nanostructures for larger sized upconverter crystals.

In this work, we demonstrate a patch, which contains upconverting crystals of $Gd_2O_2S{:}Yb^{3+}$, Er^{3+} mixed with a UV curable gel, integrated with a textured back-reflector that can be externally affixed to a bifacial thin-film silicon solar cell.The patch serves to provide the benefit of light trapping as well as spectrum upconversion to the solar cell fabricated on a flat substrate. The photogenerated short-circuit current densities of the solar cell show a power-law dependence on the illuminated laser light intensity when an upconverter patch is attached to the solar cell (exponent 1.5-1.6) while a linear dependence is observed for the solar cell without the upconverter patch. The upconverting patch is shown to enhance the solar cell performance and offers a new stick-on technique to apply upconversion-based strategies to existing solar cells.

#275 - Cathodoluminescence study of single GaAs/AlGaAs core-shell nanowire heterostructures grown by MOVPE

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III-V semiconductors nanowires (NWs) are considered as functional building-blocks for the fabrication of future quasi-1D nanoelectronics, nanophotonics and photovoltaic devices [1-3], such as diodes, field effect transistors, LEDs, lasers and solar cells, due to their unique geometry and superior physical properties.

In this work we report GaAs-$Al_xGa_{1-x}As$ ($x \approx 0.33$) core-shell nanowires epitaxially grown on (111)B-GaAs substrates by Au-catalyst assisted metalorganic vapour phase epitaxy (MOVPE).

The growth of a AlGaAs shell around a GaAs NW allows to suppress the effects of surface states, controls carrier confinement within core material and improves photon optical confinement by acting as an optical cavity.

However, the optimization and control of the electronic and optoelectronic properties of both single NWs and NW arrays is a prerequisite for the fabrication of high quality devices. Thus, a better comprehension of their growth and morphological, geometrical and optical properties is fundamental.

Optimized growth conditions allowed us to fabricate highly-dense arrays (1E8-1E9 cm-2) of vertically-aligned nanowires, with regular hexagonal cross-section and a length of about 1 µm.

The GaAs core diameter remains constant (≈ 60 nm) for all samples, while the overall core-shell NW diameter decreases with increasing the nanowire densities. This effect can be explained based on a vapour mass-transport model of the AlGaAs shell grown around a dense nanowire array [4].

The optical properties of single GaAs/AlGaAs heterostructure nanowires have been studied using low-temperature cathodoluminescence (CL) performed in a field emission scanning electron microscopy (FE-SEM).

The combination of FE-SEM and CL measurements on individual nanowires allows to directly correlate the nanowire specific photon emission with values of the shell-thickness to core radius ratio.

A comparison of experimental results with theoretical calculations based on an equilibrium elastic energy model of AlGaAs/GaAs nanowires [5] allowed determining the origin of the dominant luminescence emission and evaluating the contributions of elastic strain. The dominant emission ascribed to the emission of the nanowire GaAs core.

References

1. G. Chen, E. M. Gallo, O.D. Leaffer, T. McGuckin, P. Prete, N. Lovergine, J. E. Spanier, Phys. Rev. Lett. 107, 156802 (2011).

2. G. N. Chen, G. Sun, Y. J. J. Ding, P. Prete, I. Miccoli, N. Lovergine, H. Shtrikman, P. Kung, T. Livneh, J. E. Spanier, Nano Lett. 13, 4152-4157 (2013).

3. E. M. Gallo, G. Chen, M. Currie, T. McGuckin, P. Prete, N. Lovergine, B. Nabet, and J. E. Spanier, Applied Physics Letters 98, issue 24, 241113 (3 pp) (2011).

4. Miccoli, I., Prete, P. and Lovergine, N., CrystEngComm, 17, 5998-6005, (2015).

5. P. Prete, I. Miccoli, F. Marzo, N. Lovergine, Phys. Status Solidi RRL, 7, 874–877(2013).

#276 - Progress on Low-Temperature Pulsed Electron Deposition of CuInGaSe2 Solar Cells

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The quest for single-stage deposition of $CuInGaSe_2$ (CIGS) is an open race to replace very effective but capital intensive thin film solar cell manufacturing processes like multiple-stage coevaporation or sputtering combined with high pressure selenisation treatments. In this paper the most recent achievements of Low Temperature Pulsed Electron Deposition (LTPED), a novel single stage deposition process by which CIGS can be deposited at 250 °C, are presented and discussed. We show that selenium loss during the film deposition is not a problem with LTPED as good crystalline films are formed very close to the melting temperature of selenium. The mechanism of formation of good ohmic contacts between CIGS and Mo in the absence of any $MoSe_2$ transition layers is also illustrated, followed by a brief summary of the measured characteristics of test solar cells grown by LTPED. The 17% efficiency target achieved by lab-scale CIGS devices without bandgap modulation, antireflection coating or K-doping is considered to be a crucial milestone along the path to the industrial scale-up of LTPED. The paper ends with a brief review of the open scientific and technological issues related to the scale-up and the possible future applications of the new technology.

#277 - Efficiency improvement of amorphous silicon single junction and tandem solar cells through DC electric field stress

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The Staebler and Wronski light soaking effect [1-3] in hydrogenated amorphous silicon (a-Si:H) solar cells leads to a performance reduction mainly attributed to dangling bond defects whose density under light illumination increases compared to the initial value. Recently, it has been shown that the application of the reverse bias stress not only slows down the ageing kinetics [4, 5], but even produces an improvement of the cell parameters as a function of stress time [6]. In this work we report on such improvement by comparing the behavior of single p-i-n junctions and of double-junction (amorphous Si / microcrystalline Si) solar cells.

Single-junction p-i-n hydrogenated amorphous silicon (a-Si:H) solar were prepared by PECVD. The deposition was performed on AGC ASAHI GLASS VU-type with ≈ 700 nm thick SnO2:F (FTO) as TCO. Another set of cells consisted in tandem amorphous Si / microcrystalline Si solar cells fabricated on the FTO AGC glass substrates by PECVD.

The a-Si:H cells under prolonged stresses in short circuit show a JSC decrease due to the Staebler-Wronski effect proportional to the illumination intensity. The application of a reverse bias changes dramatically the behavior: under reverse bias stress the solar cell characteristics improve, and the rate of such improvement increases with the applied reverse bias. Also we found that by increasing the light intensity the cell parameters improvement rates increase very significantly. Such improvements clearly show reversibility, dependent on the stress voltage sign [6]. In fact, under consecutive stresses under Maximum Power Point (MPP) condition (+0.6 V, i.e. in forward bias) followed by reverse bias stresses (-12 V) we find that under MPP the efficiency decreases with time due to the Staebler-Wronski effect, while under reverse bias it improves. We also observe a strong overall improvement of efficiency.

A possible cause of the above described instability / improvement is the motion of ions in and out from the FTO to the p-type a-Si:H layer. Such interpretation is actually confirmed by the effects given by the type of substrate. To further confirm such interpretation we have studied the case of tandem (amorphous Si / microcrystalline Si) solar cells. The results confirm quite well the above model [7]. In the complete paper we will show further data on the role of electric field intensity, illumination, substrate type and temperature.

References

[1] D.L. Staebler, C.R. Wronski, Appl. Phys. Lett. 31 (1977) 292. [2] H. Fritzsche, Ann. Rev. Mater. Res. 31 (2001) 47. [3] H.M. Branz, Phys. Rev. B 59 (1999) 5498. [4] D.E. Carlson, K. Rajan, Appl. Phys. Lett. 70 (1997) 2168. [5] D.E. Carlson, K. Rajan, Appl. Phys. Lett.

83 (1998) 1726. [6] A. Scuto, M. Foti, C. Gerardi, A. Battaglia, and S. Lombardo, Sol. Energ. Mat., 141, 203-209 (2015). [7] A. Scuto, C. Gerardi, A. Battaglia, and S. Lombardo, manuscript in preparation.

#278 - Shedding light on graphene using core level spectroscopy

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Since long time core level photoelectron spectroscopy is widely used to probe physical and chemical processes taking place at solid surfaces. As core levels are highly localized, changes in core electron binding energies can be used as a local probe of the variation in the electrostatic potential of atoms located in different chemical and geometrical environments.

In the case of epitaxial graphene this is valid for both, carbon atoms forming the two-dimensional honeycomb lattice, and first-layer substrate atoms. Indeed the core-level energies of the substrate atoms reflect the changes in the electronic distribution because of interaction with the graphene layer. Since core level binding energy shifts can be calculated with a high level of accuracy using density functional theory, the close comparison between experimental and theoretical results represents a key ingredient to obtain precious information about the properties of epitaxial graphene.

In this talk I will show how this approach can be used in order to study the growth mechanism, the interaction and the thermal stability of graphene grown on a wide range of transition metals [1-4], oxide films [5] and bimetallic surface alloys [6].

[1] P. Lacovig et al., Phys. Rev. Lett. 103, 166101 (2009).
[2] D. Curcio et al., J. Am. Chem. Soc. 138, 3395 (2016)
[3] E. Miniussi et al., Phys. Rev. Lett. 106, 216101 (2011).
[4] M. Pozzo et al., Phys. Rev. Lett. 106, 135501 (2011).
[5] L. Omiciuolo et al., Nature Communications 5, 5062 (2014).
[6] D. Alfè et al., Scientific Reports 3, 2430 (2013).

#279 - Oxygen functionalities evolution in thermally treated graphene oxide featured by EELS and DFT calculations

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Graphene on a large scale could be obtained by the removal of oxygen functional groups of graphene oxide (GO). The main functionalities contained in GO flakes are hydroxyl (C-OH) and epoxy (C-O-C) groups in the basal planes and hydroxyl, carbonyl (C=O) and carboxylic (O=C-OH) groups at the edges. The presence of oxygen functionalities opens an electron energy gap that can be modulated modifying the amount of oxygen in the structure by thermal processes, chemical treatments or UV irradiation.

Furthermore, while graphene is hydrophobic, the polar carbon-oxygen bonds of GO render it strongly hydrophilic. GO forms stable solutions in water, it can be easily processed for further derivatization and it finds application in water purification, biomedical technology, sensor technology and microelectronic devices.

The composition and the structure of GO and reduced GO (RGO) depend on the synthesis and reduction methodologies.The different strategies of derivatizationof GO for subsequent applications can be improved by the identification of the distribution at atomic resolution of the various oxygen functional groups on the GO surface.

For this purpose, the local atomic configuration of GO was investigated by identifying the different oxygen functionalities and following their evolution induced by thermal treatments in various environments (vacuum, nitrogen or argon flow). X-ray photoelectron spectroscopy and scanning transmission electron microscopy analyses were performed and electron energy-loss (EEL) spectra were acquired in different regions of GO and thermally reduced GO flakes. Experimental results show a series of characteristic peaks related to C and O K-edge shells with different intensities depending on the analyzed zoneand different features depending on the annealing environments.

In order to understand the experimental core-loss EEL spectra, density functional theory calculations have been performed in order to compute core-loss EEL spectra of graphene oxide (C and O K-edges) with different oxygen functional groups at different concentrations by using the WIEN2K full-potential augmented-plane-wave code. EEL spectra were computed with the TELNES3 post-processing program.

The simulationsofthe high-loss EEL spectra at atomic level allow to associate the observed experimental peaks to the presence of different oxygen functional groups on the graphene surface and the corresponding atomic configurations (C-OH, C-O-C, O in vacancies). This methodology allows to obtain the mapping of the different functionalities of GO at the spatial resolution of the EELS probe (< 1 nm) and to establish the atomic configurations that prevail in different ranges of annealing temperatures and environments.

#280 - Chessboard Nanopatterning of Ruthenium Phthalocyanine Layer(s) on Graphite Driven by Molecular Rotamerism

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Nanoarchitectonics, a new paradigm of materials science and nanotechnology, recognizes as a fundamental task in the creation of novel materials the harmonization of nanoscale parts through the control of spontaneous processes such as self-assembly. Such harmonization requires bricks whose reciprocal complex interactions create unexpected order and unpredictable collective phenomena up to the microscale. We show here that ultrathin films of ruthenium phthalocyanine $(RuPc)_2$ on graphite go beyond simple schemes of two-dimensional self-assembling, presenting a three-dimensional (3D) ordered structure which makes this system a paradigmatic example of supramolecular nanoarchitecture, suitable for integration in innovative new materials.

Ruthenium phthalocyanine is not stable as a single (RuPc) unit, spontaneously forming stable dimers kept together by direct Ru-Ru bonds. $(RuPc)_2$ films and amorphous powders have interesting properties: as opposed to monomeric MPc films, in which the layer by layer growth is often driven by vertical metal-nitrogen interactions between layers, $(RuPc)_2$ molecules pile up in vertical pillars. Such $(RuPc)_2$-based structures show one of the highest room temperature conductivities measured for undoped Pc ($10^{-5}\Omega^{-1}cm^{-1}$), likely due to the presence of highly oriented stacks of π-conjugated ligands. Moreover, due to its dimeric structure connected by a direct Ru-Ru bond, $(RuPc)_2$ can act as a rotameric switch.

We have deposited submonolayer to multilayer $(RuPc)_2$ films on a highly oriented pyrolitic graphite (HOPG) substrate with the aim of obtaining a highly ordered assembling of $(RuPc)_2$ and, in turn, of elucidating at and below the nanoscale the interesting properties of such a unique molecule. Such properties include an unexpected peculiar pattern of the molecular films, resulting from intermolecular interaction. Our STM and PES results, interpreted with the assistance of parallel ab initio simulations based on DFT calculations, show that a first flat $(RuPc)_2$ layer self-assemble on HOPG by forming a chessboard-like pattern made out of two different rotamers of the molecule, whose fingerprint is clearly visible by all the employed techniques. In addition, the first interfacial layer induces a columnar stacking of further molecules in the same fashion, thus confirming all the potentialities of $(RuPc)_2$ as building block of highly conductive and magnetically active ordered organic films. These results are compared to preliminary measurements using graphene as a substrate.

#281 - Tailor made functionalization of graphene layers

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Nanosized carbon allotropes with sp^2 carbon atoms are main characters in the advanced research on materials. Carbon nanotubes, both single and multiwalled, graphene, few layer graphenes and graphite nanoplatelets are hugely investigated due to their outstanding mechanical and electrical properties. They are able to substantially improve the properties of polymeric materials, provided that they can be evenly distributed and dispersed. In the light of this objective, functionalization of carbon allotropes is a crucial step. In particular, chemical reactions on nanosized graphite is adopted as a way to promote exfoliation and to prepare graphene. However, many of such chemical reactions involve harsh experimental conditions and dangerous or toxic reagents.

This work had the objective to reduce the synthetic footprint in nanotechnology.

A biobased *Janus* molecule was prepared with very high atom efficiency, without solvents, catalyst and work up procedure, and was used to obtain facile and sustainable functionalization of sp^2 carbon allotropes. Such *Janus* molecule was 2-(2,5-dimethyl-1*H*-pyrrol-1-yl)-1,3-propanediol (serinol pyrrole, SP), a serinol derivative obtained through the reaction of 2,5-hexanedione with 2-

amino-1,3-propandiol [1]. Adducts of high surface area graphite (HSAG) [2] and SP were prepared through simple methods such as ball milling or heating of the reaction mixture [3, 4].

Polyhydroxylated few layer graphene (G-OH) were prepared by simply milling or heating a mixture of HSAG and KOH [5]. Successive reactions allowed to selectively introduce aldehyde and carboxy functional groups.

X-ray diffraction and Raman analysis revealed that both reactions left substantially unaltered the order in the graphitic layers and the interlayer distance. Stable water dispersions were obtained, in a wide range of concentration, from 0.1 to 200 mg/mL, and few layer graphene was isolated by simple centrifugation, up to about 40% of starting HSAG. Water dispersions were used to prepare conductive coatings, flexible and conductive carbon papers and monolithic aerogels, with biobased polymeric matrix such as chitosan.

References:

[1] V. Barbera, A. Citterio, M. Galimberti, G. Leonardi, R. Sebastiano, S.U. Shisodia, A.M. Valerio; WO 189411 A1, 2015

[2] M. Mauro, V. Cipolletti, M. Galimberti, P. Longo, & G. Guerra, *The Journal of Physical Chemistry C*, 2012, *116*(46), 24809-24813;

[3] M. Galimberti, V. Barbera, S. Guerra, L. Conzatti, C. Castiglioni, L. Brambilla, A. Serafini, *RSC Adv.,* 2015, 5, 81142-81152;

[4] M. Galimberti, V. Barbera, R. Sebastiano, A. Citterio, G. Leonardi, A.M. Valerio WO 2016 050887 A1;

[5] V. Barbera, A. Porta, L. Brambilla, S. Guerra, A. Serafini, A. Valerio, A. Vitale, M. Galimberti, *RSC Advances*, 2016, DOI: 10.1039/C6RA19078B

#282 - Curvature-dependent reactivity of graphene for storage applications

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Graphene's strength and extreme flexibility allow sustained ripples in a wide range of amplitudes and wavelengths [1]. This circumstance can be exploited for applications: ripples produce a modulation of the local curvature, which in turn is strongly correlated with the stability of chemisorbed hydrogen atoms [2]. Curvature induced local pyramidalisation, i.e. pushing a carbon site towards the sp^3 configuration, contributes to the increase of its reactivity [3]. Thus, the functionalization of curved graphene with hydrogen, or other adatoms, gives the possibility to tune its chemical and adsorption properties for storage applications, as well as capture and purification of pure gases and mixtures [4].

While atomic hydrogen adhesion is a spontaneous process with a very small barrier, molecular hydrogen (H_2) chemisorption process is characterized by a barrier high on the order of ~1.5ev/atom [5], making the kinetics of loading very slow. Moreover, H tends to stick onto convexities [2,5] and to detach from concavities on the curved graphene. In this work, we address the H_2/graphene interaction useful for H-storage applications [4] as well as for the general understanding of graphene morphology/reactivity relationship. We propose that curvature manipulation could be used to improve the adhesion kinetics. To this aim, we perform a systematic DFT based study to evaluate the dependence of chemi(de)sorption barriers on curvature. We use different kinds of functionals with various levels of electronic density gradient and London dispersion [6] corrections. We also highlight the role of the dispersion effect in the adsorption energies, in the barrier high and the orientation of the molecules relative to the surface. We use model systems with various levels of corrugation generated by lateral compression of the isolated sheet [3], chosen to approximate the symmetry of natural rippling of graphene grown on SiC. We evaluate the chemi(de)sorption profiles by means of nudged elastic band technique [7] with and without effects of an external electric field. We believe that the barrier can be manipulated by changing the curvature, and estimate the levels of curvature needed to use this effect in a real device [8].

References

[1] Z F Wang et. al., Phys Rev B **83** (2011) 041403(R)

[2] V Tozzini, V Pellegrini J Phys Chem C **115** (2011) 25523

[3] A Rossi, S Piccinin, V Pellegrini, S de Gironcoli, V Tozzini J Phys Chem C **119** (2015) 7900

[4] F Bonaccorso et. al., Science **347** (2015) 1246501

[5] S Goler, C Coletti, V Tozzini et. al., J Phys Chem C **117** (2013) 11506

[6] a) M Dionet et. al., Phys Rev Lett **92** (2004) 246401 b) K. Leeet. et. al., Phys Rev B **82** (2010) 081101 c) S Grimme J Comp Chem **27** (15) (2006) 1787

[7] G Henkelman et. al., J Chem Phys **113** (22) (2000) 9978

[8] K Kakhiani, V Tozzini "Activation barriers for chemi(de)sorption on corrugated graphene: mapping morphology dependence of graphene reactivity", in preparation.

#283 - Plasma strategies for graphene functionalization and tuning of transport properties

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The chemical modifications of graphene have been the subject of several works aimed at the tuning of the intrinsic material properties or at the introduction of new ones: opening of a band gap; improving wettability toward other materials of technological interest, providing selective interactions with analytes, etc.. Since graphene is characterized by a high chemical inertness, its functionalization processing typically involves the exploitation of free radicals addiction reactions. Several strategies have been investigated for providing the generation of radical species in a controlled way including thermal, photochemical, and plasma processes. In particular, plasma chemistry offers a high potential in terms of process scalability but it often resulted in a low control of the functionalization processes as well as in the structural damaging of the materials.

In this contribution, we present mild modulated plasma processes for tailoring transport properties of large area chemical vapor deposition (CVD) graphene by functionalization with hydrogen [1], fluorine [2] and oxygen species. The functionalization processes have been developed and optimized with the twofold aim: the fine control of graphene functionalization kinetics while minimizing the induced structural damage. This, together with the real time monitoring of graphene optical properties by spectroscopic ellipsometry, allows for an unprecedented control over the degree of functionalization.

The suitability of our functionalized graphene with engineered transport properties for applications in electronics, optoelectronics and photovoltaics is experimentally demonstrated.

[1] M. Grande, G.V. Bianco, et al, Optics Express (2016), in press.

[2] G. Bruno, G.V. Bianco, Phys.Chem.Chem.Phys., 16 (2014) 13948.

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#284 - The long way to the discovery of new materials made it short

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The development of novel materials is a strong enabler for any technology, and in fact technology and materials innovation cannot be separated. Unfortunately the process of finding new materials, optimal for a given application, is a lengthy, often unpredictable and has a low throughput. Here we describe a systematic pathway to the discovery of novel materials, which demonstrates an unprecedented throughput and discovery speed. The method can be applied to any materials class and any potential application, so that can enable progress in quantum and classical technologies alike. Here I will use the example of magnetism to introduce the main features of the method, and I will demonstrate the discovery of several new high-performance magnets.

Based on an extensive electronic structures library of Heusler alloys containing 236,115 prototypical compounds, we have filtered those alloys displaying magnetic order and established whether they can be fabricated at thermodynamical equilibrium [1]. Specifically, we have carried out a full stability analysis for intermetallic Heuslers made only of transition metals. Among the possible 36,540 prototypes, 248 are found thermodynamically stable but only 20 are magnetic. The magnetic ordering temperature, T_C, has then been estimated by a regression calibrated on the experimental T_C of about 60 known compounds. As a final validation we have attempted the synthesis of a few of the predicted compounds and produced two new magnets. One, Co_2MnTi, displays a remarkably high T_C in perfect agreement with the predictions, while the other, Mn_2PtPd, is a complex antiferromagnet. Our work paves the way for large-scale design of novel magnetic materials at unprecedented speed.

[1] Stefano Sanvito, Corey Oses, Junkai Xue, Anurag, Tiwari, Mario Zic, Thomas Archer, Pelin Tozman, Munuswamy Venkatesan, J. Michael D. Coey and Stefano Curtarolo, *Accelerated discovery of new magnets in the Heusler alloy family*, under review.

#285 - Optimization of SAW devices for spintronic applications

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The achievement of the magnetization orientation control through non-magnetic parameters (such as electric fields) is one of key target for the development of novel spintronic devices. Recently, magneto-elastic interactions were exploited to control the magnetic degree of freedom in SAW-based piezoelectric/ferromagnetic hybrid devices. In particular, surface acoustic waves were employed to drive the ferromagnetic resonance, trigger the magnetization dynamics, writing magnetic patterns and spin pumping. Targeting the characterization of SAW-based hybrid devices, we worked on the optimization and realization of SAW delay lines and resonators. In particular, we performed a systematic study to investigate the dependence of the transmitted signal on the device geometry, changing the interdigital transducer (IDT) features such as shape (single, double), number of finger pairs, distance between emitter and receiver, overlap finger length. This investigation was also important to identify the geometry with less electromagnetic noise. In fact, upon applying a rf voltage to the input IDT, an electromagnetic wave (EMW) is launched since an IDT works as an antenna as well as an electromechanical transducer. By adjusting the delay line geometry, it was possible to enhance the SAW signal and to reduce but not to eliminate the electromagnetic noise. This problem was solved by means of time resolved measurements that allowed to distinguishing between the electromagnetic and acoustic contributions to the signal thanks to their different propagation velocity. This result is important for experiments in which the electromagnetic contribution is significant and the detection of SAW signal has to be quantitative.

#286 - Exactly solvable time-dependent models of two interacting two-level systems

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Two coupled two-level systems placed under external time-dependent magnetic fields are modeled by a general Hamiltonian endowed with a symmetry that enables us to reduce the total dynamics into two independent two-dimensional subdynamics. Each of the subdynamics is shown to be brought into an exactly solvable form by appropriately engineering the magnetic fields and thus we obtain an exact time evolution of the compound system. Several physically relevant and interesting quantities are evaluated exactly to disclose intriguing phenomena in such a system.

#287 - Asymmetric band gaps in a Rashba film system

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The joint effect of exchange and Rashba spin-orbit interactions is examined on the surface and quantum well states of Ag$_2$Bi-terminated Ag films grown on ferromagnetic Fe(110). The system displays a particular combination of time-reversal and translational symmetry breaking that strongly influences its electronic structure. Angle-resolved photoemission reveals asymmetric band gap openings, due to spin-selective hybridization between Rashba-split surface states and exchange-split quantum well states. This results in an unequal number of states along positive and negative reciprocal space directions. We suggest that the peculiar asymmetry of the discovered electronic structure can have significant influence on spin-polarized transport properties.

#288 - Spin-textured topological surface state on Bi$_{2}$Se$_{3}$ thin films grown by Pulsed Laser Deposition: impact of the substrates onto the surface structural properties

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Over the last decade, topological insulators (TIs) have attracted a great interest of the scientific community for their intriguing conduction mechanisms. Even though insulating in the bulk, at the surface, they show a strong metallic state characterized by a unique surface spin texture. Beyond the perspectives in fundamental studies on transport phenomena in 2D spin-textured systems, the strong spin-orbit coupling of electric carriers makes them extremely attractive for spintronic application. Therefore, for both fundamental studies as well as electronic applications, high-quality single-crystalline Bi2Se3 thin films, exhibiting surface topological states, are mandatory. Furthermore, since it is equally mandatory to have access to ad-hoc tailored multi-layered heterostructures, it is necessary to use flexible thin film deposition technique which would allow the growth of the highest possible number of functional materials. With respect to this, the Pulsed Laser Deposition (PLD) combines the capability to provide highly oriented epitaxial thin films and the largest flexibility in the possible materials to grow (e.g. oxide materials). We here report on the growth of high quality epitaxial Bi2Se3 thin films at very high Ar pressure (i.e. 0.1mbar). We show that the substrate, while not influencing the structural properties of the bulk, does have a tremendous impact at the surface of the films. Highly-textured single domain (001)-oriented Bi2Se3 can be successfully grown on (001) Al$_{2}$O$_{3}$ substrates. The combination of low deposition temperatures (290°C) and low deposition rate are the key element to obtain superior Bi2Se3 epitaxial thin films. Even though metallic-like behaviour of the bulk transport properties as well as core-level spectra investigated by X-ray photoemission spectroscopy point to a slight Se-deficiency, spin-resolved angle-resolved photo-electron spectroscopy investigation of Bi2Se3 thin film shows a single Dirac cone with a well-defined spin polarization texture. To the best of our knowledge, this is the first experimental report demonstrating the stabilization of spin-textured topological states at surface of PLD-grown Bi2Se3 thin films. Such a capability can open intriguing perspectives in emerging spintronics planar devices based on multi-layered heterostructures in which one functional layer is the topological insulator Bi2Se3.

#289 - Perspectives on quantitative nanomagnetometry with magnetic force microscopy

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Advancements in the use of magnetic nanomaterials for scientific and technological applications require the capability of quantitatively characterizing their magnetic properties at the nanometer scale. Magnetic force microscopy (MFM) has been proposed for the magnetic imaging of different materials, including magnetic recording media, magnetic thin films, and nanomaterials. MFM has been also exploited for the visualization of magnetic nanomaterials in complex systems, such as in the case of magnetic nanoparticles internalized in cells or other nano-biosystems [1]. Despite being a relatively widespread technique, the use of MFM to accurately determine quantitative magnetic parameters of sample is still a challenge. The main limitation can be recognized in the presence of topography-induced electrostatic artifacts [2]. Thus, overcoming this limitation is currently one of the hottest nanometrological open issues in MFM. Here, we present a novel experimental approach to remove such artifacts from MFM images [3] and discuss its possible applications in the quantification of magnetic parameters of some nanosystems of technological interest.

References

[1] Passeri, D. et al. Magnetic force microscopy: Quantitative issues in biomaterials. Biomatter 4, e29507 (2014)[2] Jaafar, M. et al. Distinguishing magnetic and electrostatic interactions by a Kelvin probe force microscopy-magnetic force microscopy combination. Beilstein J. Nanotechnol. 2, 552–560 (2011)[3] Angeloni, L. et al. Removal of electrostatic artifacts in magnetic force microscopy by controlled magnetization of the tip: application to superparamagnetic nanoparticles. Sci.Rep. 6, 26293 (2016)

#290 - Developed and characterization of PZTN-CFO particulate ceramic composites

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The surge of interest in multiferroic materials over the past 15 years has been driven by their fascinating physical properties and huge potential for technological applications such as sensors, microwave devices, energy harvesting, photovoltaic technologies, solid-state refrigeration, data storage recording technologies and multiferroic random access multi-state memories (MFRAM) [1]. Remarkable efforts have been done to develop laminated bi-layer and multilayer multiferroic composites as bulk or thin films. Such structures lead to remarkable magneto-electric coupling coefficients of a few Volts / cm·Oe because in such configuration the ferroic layer is a “full dielectric” which can be completely polarized in the conventional way [2]. On the other hand in the particulate ceramic composites the requirement for “full dielectric” is no longer applicable, since the ferroic phases are fully separated within the composite. The strengths of particulate ceramic composites are low cost, simple production technology, higher strain mediated magneto-electric coupling (since electric order phase/magnetic phase interface density can be higher) and easy control of electrical and magnetic properties if the ferroelectric phase (generally a perovskite) and the ferromagnetic one (a ferrite with spinel structure) are mixed in a favourable proportion under the percolation threshold of the ferromagnetic phase.

A great research effort is in progress to improve the fabrication of PZT–$CoFe_2O_4$ (PZT–CF) composites in order to avoid theunwanted reactions, which occur during densification of PZT–CF materialsat 1100-1200 °C, and to achieve the electric saturation during the poling. Up to date, by setting a quite-fast sintering, full densification and prevention of unwanted reactions were achieved for the PZT:CF 74:26 composites [3], but the achieving of electric saturation is still a challenging. Further important achieved results were: the understanding that the main cause of reactions is the PbO loss [3]; the proposal of an equation to calculate the PbO loss through XRD analysis, considering the amount of ZrO_2 and variation of perovskite's tetragonality [3]; and the ability to design the ceramic process to control the CF grain size distribution, which can be mono- or bi-modal, and overgrowth [3, 4].

[1] M. M. Vopson. Crit. Rev. Solid State 4:40 (2015) 223-250 doi:10.1080/10408436.2014.992584

[2] P. Galizia, et al. J. Eur. Ceram. Soc. 36 (2016) 373-380. doi:10.1016/j.jeurceramsoc.2015.07.038

[3] P. Galizia, et al., *PZT-cobalt ferrite particulate composites: Densification and lead loss controlled by quite-fast sintering*. J. Eur. Ceram. Soc. (2016). doi:10.1016/j.jeurceramsoc.2016.08.025

[4] P. Galizia, et al., *Multiple parallel twinning overgrowth in nanostructured dense cobalt ferrite*. Mater. Design109 (2016) 19–26. doi:10.1016/j.matdes.2016.07.050

#291 - New concept for the development of Bi-2212 wires for high field applications

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Bi-2212 is an extremely interesting superconducting material for application at high fields and low temperature, in a range where the Nb-based superconductors can not be used. If on one side it has the important advantage to be processed as round wires, on the other side an improvement of the transport properties is still needed especially over long lengths. The first step towards high critical currents in Bi-2212 wires was the comprehension that the supercurrent is blocked over long lengths by filament-diameter bubbles grown during the melt stage, which cause expansion of the wire diameter and dedensification of the superconducting filaments. Whereas the previous successful approach to reduce the problem of voids related to bubbles was based on the application of a high overpressure during the heat treatment, we fabricated Bi-2212 wires by applying a new concept of suitably alternating groove-rolling and drawing techniques with the aim of densifying the phase already during the working procedure prior to the heat treatment.

We here for the first time were able to reach in wires reacted with closed ends – i.e. with no way to escape for the possible residual gas trapped in the wire as it happens in long-length wires – and on long samples the very same values of critical current shown in short wires reacted with open ends. This is the evidence that, only by acting on the deformation technique, we were able to raise the critical current by properly densifying the superconducting powder inside the filaments already before the melt stage. Whole-conductor current densities in our long length simulation wires already reach 400 A/mm^2 at 4.2 K and 5 T, which can be still easily increased through architecture optimization. The actual breakthrough is that the densification is optimized without further complex treatments through a technique which can be straightforwardly applied to long-lengths wires.

#292 - Probing efficient electric current transport in superconducting materials

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Superconductors can conduct electricity at a very low temperature where no energy is dissipated by resistive heating, so superconductors can carry current with 100% efficiency. Indeed superconductivity can be an ultimate energy-saving technology. Commercial products based on superconductors include transformers, electric motors, generators, fault current limiters, power cables and energy storage systems, now in the testing stage, and electric cable producers, electricity suppliers, and electrical manufacturers are investing in the future of this technical knowledge. Actually the use of High Temperature Superconductors technology can make smaller, lighter, and more powerful equipments that can improve a power system's stability, reliability, quality, and safety. As far as power applications are concerned, the stability of the superconducting state becomes relevant for the operation of these devices. Unfortunately, superconductivity becomes unstable under sufficiently high bias currents. Not only the highest critical currents are required, but also quenching phenomena need to be prevented in order to get the best performance of any superconducting device. Typically this instability is observed in the current-voltage characteristics as an abrupt voltage jump to the normal state, which turns into a current driving quench event. Therefore such instability study arises as a valuable tool to test the high current carrying capability of a superconductor. On top of that the flux flow instability can also be used as a sensitive probe of unconventional superconductors by field-angle dependent measurements. Although a general well established theory is able to predict such an instability in an ideal superconductor, real superconductors can be modeled in the presence of material pinning. Indeed we show that the critical parameters can be phenomenologically addressed from a flux flow instability analysis, basically a study of the current-voltage (I-V) characteristics and the magnetic field dependence of the critical current density Jc(B). Remarkably, this experimental technique provide a direct method to classify superconducting materials from strong to weak pinning superconductors, as well as from intrinsic to extrinsic mechanisms leading to the quenching events. Measurements were performed in extremely high magnetic fields and low temperatures, as a function of the direction of the applied magnetic field in our advanced Material Science and TEchnology Research – MaSTER – labs. We report our overall study on different materials, from Low to High Temperature and Iron-Based Superconductors too. The presented technique can be employed as a direct tool to validate the stability of superconducting materials for energy-efficient technology. We acknowledge financing by MIUR PON2007/2013 under Grant Agreement PON NAFASSY and technical support from S. Abate.

#293 - The multi-well phase field model of the explosive crystallization phenomenon

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Pulsed laser irradiation in the nanosecond regime is applied to process locally ultra-thin films of the device structures in several electronic technologies. In particular, when amorphous films in the region near the sample surface are processed, the irradiation often leads to the explosive crystallization phenomenon, where the driving force of the phenomenon is the formation of under-cooled liquid layers.The material properties after the irradiation and the material evolution during the process are difficult to predict and analyze, due to the complexity and the rapidity of the phenomenon. This difficulty is also caused by the lack of a consistent model able to simulate the concurrent kinetics of the amorphous-liquid and liquid-crystal interfaces.Here we propose a multi-well phase-field model specifically suited for the simulation of explosive crystallization induced by pulsed laser irradiation in the nanosecond regime. The model is robust despite the coexistenceat least of two sharp interface and three materials with domain that evolve in time. The predictive potential of the simulations is demonstrated by means of comparison of the modeling predictions with the results of dedicated experiments in term of in situ reflectivity measurements and ex-situ micro-structural, chemical and electrical characterizations.

#294 - Radiation Tolerant Flexible Large-Area Electronics Based on Oxide Semiconductors

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Large area electronics provides revolutionary means to integrate electronic functionality in formerly passive surfaces. Transfer of this technology to space applications, medical X-ray detectors or areas with radioactive contamination requires the materials and devices to resist to the continuous exposure to ionizing radiation. Here we demonstrate the radiation hardness of oxide semiconductors such as Gallium Indium Zinc Oxide (GIZO) which combine unique advantages in processing with robust electrical performance in thin-film transistors (TFTs) [1]. In contrast we find that a material platform based on organic electronics shows degradation under ionizing conditions. In the experiments we subjected oxide as well as organic transistors to X-ray radiation and monitored the transistor performance metrics as a function of total ionizing dose. Flexible oxide TFTs maintained a constant mobility of 10 cm^2/Vs even after exposure to doses of 410 krad(SiO2) whereas OTFT lost 50% of their transport performance. Relevant temporary damage originates in oxide TFTs only due to the trapping of ionization charges in dielectric layers. However, these effects are only observed at high dose-rates and recover on a time-scale of hours. In addition they scale with the thickness of the dielectric, thus allowing to fabricate radiation transparent flexible transistors by employing thin dielectrics. We attribute these exceptional resistance of oxide semiconductors to ionization damage to their intrinsic properties such as independence of transport on long-range order and large ionic lattice energy.

[1] T.Cramer et al. Adv. Elec. Mat. 2016, DOI: 10.1002/aelm.201500489

#295 - Pulsed Bessel beam-induced high aspect-ratio microchannels on diamond surface for microfluidics applications

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Material processing with ultrafast laser pulses [1] is a powerful technological platform which supports numerous applications in the field of photonics and microfluidics [2]. While structural modifications in the material can be induced by tightly focusing a Gaussian laser wavepacket, processing can be enhanced by suitable spatial, temporal, or spatio-temporal tailoring of the optical wave-packet.

In this context, when an intense laser beam is focused by a conical lens in a transparent dielectric medium, it generates a Bessel filament in the focal region, i.e. a light string with a narrow core over a distance that may slightly exceed the Bessel zone. In the stationary regime characterized by a uniform light channel [3,4], the laser pulse leaves in its wake a uniform plasma track which is essential for an efficient microfabrication of transparent materials. This plasma track is indeed the main support for laser energy deposition, before energy is transferred to the lattice and induces thermo-mechanical constraints leading to void nanochannels or to high aspect ratio inscribed microstructures [5].

In the present work we describe the versatile generation of Bessel beams, and their application to the laser surface micromachining of synthetic monocrystalline diamond, showing the possibility to create low-roughness three-dimensional microfluidic structures (featured by a depth of tens of microns and one micron width). The morphology of the microfluidic channels obtained has been characterized by a scanning electron microscope. Raman spectroscopy indicates that the irradiated area is covered by graphitic material, which after a suitable chemical etching can be almost completely removed.

The results show the advantage of using quasi-stationary beams in ultra-fast laser inscription technology to fabricate high aspect-ratio microfluidic channels on biocompatible diamond substrates, thus offering a great potential for biomedical sensing applications.

1. R. R Gattass and E. Mazur, *Nat. Photonics* **2**, 219 (2008).

2. K.C. Phillips et al. *Advances in Optics and Photonics* **7**, 684 (2015).

3. P. Polesana et al. *Phys. Rev. Lett.* **99**, 223902 (2007).

4. J. Fan, E. Parra, and H. M. Milchberg, *Phys. Rev. Lett.* **84**, 3085 (2000).

5. M. K. Bhuyan et al. Appl. Phys. Lett. **97**, 081102 (2010); Eur. Phys. J: Spec. Top. 199, 101 (2011).

#296 - Ge doping by ion implantation and melting laser annealing

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Achieving highly-doped shallow layers in germanium is a major challenge for advanced device development in many fields such as nano- and opto-electronics, photonics, sensors, etc. To this purpose pulsed laser melting, subsequent to ion implantation, is studied as being able to promote ultra-fast liquid phase epitaxial regrowth in a shallow layer. As a consequence, dopants are activated well above the equilibrium solid solubility while confining the diffusion within the molten layer. Latest results on electrical activation, diffusion, residual defects, contaminations, thermal stability will be presented for both *p*- and *n*-type doping of Ge in a wide range of experimental conditions.

#297 - Defects and dopant activation in laser annealed Si and Ge

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Defect evolution and dopant activation are intimately related to the use of ion implantation and annealing, traditionally used to dope semiconductors during device fabrication. However, during the last decade, the increased difficulties to maintain the transistor miniaturization pace have led to a diversification of both the basic device architecture and processes.

In this context, the recent advances in nanosecond laser annealing have opened the way to solve a wide spectrum of difficult challenges in semiconductor technology, well beyond the traditinal source/drain fabrication issues. Indeed, thanks to the low thermal budget of a laser pulse (with duration in the nanosecond regime), laser annealing is very attractive not only for the achievement of abrupt and highly doped junctions, but more generally for all semiconductor technologies in which dopants need to be activated while preserving the integrity of the surrounding areas, as in the case of CMOS backside imagers or 3D integration technologies.

After giving an overview of some relevant published studies in this domain, we will present some recent investigations focused on damage evolution and its impact on dopant distribution and electrical activation during nanosecond laser thermal annealing of ion-implanted group-IV semiconductors, with particular emphasis on the structural modifications occurring in preamorphised Germanium during melt laser annealing.

#298 - Study of high temperature superconducting coatings for beam impedance mitigation in the Future Circular Collider at CERN

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The high energy proton beams circulating in the Future Cicolar Collider (FCC), currently in the design phase at CERN, will produce several tens of watts per meter of synchrotron radiation due to their 50 TeV energy. To prevent this power from impinging on the 16 T dipoles, which are cooled to Liquid Helium temperature, they have to be protected, like in the LHC, by a beam screen. Many considerations related to vacuum stability dictate that the beam screen has to be kept at a temperature between 40 and 60 K. At these temperatures, common electrical conductors such as copper may have not low enough impedance for GHz beam induced eddy currents, resulting in beam energy losses and instability. High temperature superconductors materials, cupper based oxides with critical temperature well above 77 K, may offer the only viable solution to overcome this obstacle. However, a study of the required performance under these extreme condition has shown that Bismuth based cuprates (that can be produced by simple powder in tube technique) would be inadequate whereas $YBa_2Cu_3O_x$ could cope with the requirements, but is currently available only in the form of thin coated ribbons. Scaling the YBCO fabrication procedure to the beam screen shape remains a tough challenge, and would require a thorough rethinking of the coating technology. Among the high-temperature superconductors Tl-cuprates stand out due to their very high critical temperatures and upper critical fields. In particular $TlSr_2Ca_2Cu_3O_x$ with a T_c of about 120 K, very high H_{c2} and H_{irr}, and moderate anisotropy is a promising material for the realization of a low surface resistance coating for the FCC beam screen. This superconducting material can be grown textured on pure silver by much simpler and cheaper techniques, and has the additional advantage of a potentially lower surface resistance (since $R_S \propto (H/H_{C2})^{1/2}$). The behaviour of high temperature superconductor under these extreme conditions of temperature, magnetic field,frequencies and radiation will be discussed and the experimental feasibility of using this material for coatings suitable for the FCC beam screen is currently being explored by CNR-SPIN, TU Wien, and CERN in a joint project.

#299 - Polar conjugated polymers: eco-friendly materials as new frontier of organic semiconductors

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The development of new materials plays a key role for the exploitation of the new technologies. One important class of emerging semiconducting materials is represented by conjugated polyelectrolytes (CPEs) comprising an electronically delocalized π-conjugated backbone with pendant groups bearing polar or ionic functionalities [1]. CPEs bring together the typical properties of polymeric semiconductors, such as easy processability, chemical tunability, lightness and flexibility with the growing demand for environmentally friendly materials. In fact, the incorporation of polar/ionic side groups increases the solubility in water and alcohols, which can potentially provide increased biocompatibility for sensor applications and more environmentally friendly manufacturing options. Moreover, the possibility for orthogonal solvent processability opens the way to all-solution-processed organic multilayer devices. Interfacial engineering has been identified recently as an essential approach for maximizing efficiency and stability of electronic devices. In this contest, the intrinsic hybrid characteristics of CPEs make them promising candidates for tuning the interface properties of inorganic materials too. We have recently shown that the insertion of a thin CPE film between active layer and cathode in organic electronic devices results in the energy level tuning at the CPE/metal interface, which is crucial for achieving a high-performance device, due to the formation of permanent dipoles [2]. In this view, we have designed, synthesized and tested CPEs featuring a fluorene-based backbone with pendant phosphonate and/or amine groups and we have tested them in different types of devices. In particular by comparing the effect of CPEs on OLEDs and OPVs behaviour, we focus on the influence of the electrical conditioning of the CPE layer on the device performance. The same class of CPEs, thanks to their conjugated backbone and ionic functionality have shown to remarkably enhance the pseudocapacitance of MXene-based hybrid 2D materials [3]. [1] Hu Z., Zhang K., Huang F. & Cao Y. (2015). Water/alcohol soluble conjugated polymers for the interface engineering of highly efficient polymer light-emitting diodes and polymer solar cells, Chem. Commun., 51, 5572-5585. [2] Castelli, A., Meinardi, F., Pasini, M., Galeotti, F., Pinchetti, V., Lorenzon, M., ... & Brovelli, S. (2015). High-Efficiency All-Solution-Processed Light-Emitting Diodes Based on Anisotropic Colloidal Heterostructures with Polar Polymer Injecting Layers. Nano letters, 15(8), 5455-5464. [3] Lukatskaya, M. R., Mashtalir, O., Ren, C. E., Dall'Agnese, Y., Rozier, P., Taberna, P. L., ... & Gogotsi, Y. (2013). Cation intercalation and high volumetric capacitance of two-dimensional titanium carbide. Science, 341(6153), 1502-1505.

#300 - H-shaped arylamine compounds coupled through the 2,5-bis((dibenzofulvene))thiophene bridge: New Near Infrared absorption electrochromic organic materials

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H-shaped arylamine compounds coupled through the 2,5-bis((dibenzofulvene))thiophene bridge: New Near Infrared absorption electrochromic organic materials

Near-infrared (NIR)-absorbing electrochromic (EC) materials are receiving great attention due to their potential applications in optical communications, biomedicine, camouflage materials in warfare, and thermal control and thermal emission detectors for spacecraft. UV-vis electrochromic materials have been well studied but few NIR electrochromic materials are known to date.

Organic materials offer many advantages over their inorganic counterparts. Most notably, thanks to easily and various functionalization strategy, they have the ability to tune the colour of the two states allowing color transitions spanning the visible spectrum and into the NIR. Therefore, a wide range of colors is possible both with their on and off states. In addition, the organic electrochromic materials outdo inorganic ones in term of low-cost, large area flexibility, good solution processability and high colour contrast.

In this presentation, we take this opportunity and we introduce organic Mixed-Valence compounds based on a novel "H-shaped" design like a new molecular class of organic NIR-electrochromic materials. In such a configuration four diarylamine redox centers are connected via a bis-(dibenzofulvene)-thiophene conjugated bridge. In this way, it is possible to exploit the electronic coupling between the redox centers both "vertically" along each dibenzofulvene (DBF) moiety and "horizontally" along the thiophene central bridge. To show in practice the potential of the H-shaped" MV compounds we consider two prototypes differing for the anchoring position on the DBF (they are labeled **TKMV1** for 2,7-position and **TKMV2** for 3,6-position, respectively).

Interestingly, we find that the placement of redox sites on different positions of the DBF core gives rise to significantly different degrees of coupling resulting in markedly different electrochromic properties of the compounds.

Finally a color/structure relationships provides valuable insights on molecular design principles for this class of molecules, putting forth the importance of jointly playing the electron coupling factor as position function of the redox centers on the π-conjugated backbone in order to choose appropriate molecular architectures.

#301 - Polymer Bricks for Photonic Devices

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Within the last 20 years, photonic crystals have been extensively employed for many applications ranging from sensing to optical computing. The wide spreading of these structure own to the possibility to control the flow of light using simple dielectric lattices where the refractive index is periodically modulated in the submicrometric scale. Intuitively, the ability to allow or forbid light propagation is directly related to the dielectric contrast provided by the lattice building blocks. Therefore, thanks to the high dielectric contrasts possible with inorganic materials, polymer structures have often been restricted to decorative purposes.[1]

In the last decades, the fast rising of organic electronics made the fabrication of flexible and light photonic structures increasingly researched. Moreover, the possibility to reduce the fabrication time and costs increased the attractiveness of polymers. In this work, we demonstrate that the low dielectric contrast typical of polymers allows relatively narrow stop-bands which are very advantageous for application requiring the detection of small spectral variation. For instance, embedding a photoisomerizable azobenzene within two planar dielectric mirror to form a microcavity, it is possible to induce a reversible spectral shift of the cavity mode via a simple laser writing-erasing process allowing a ON-OFF optical switch.[2] Narrow stop-bands are also advantageous for sensing purposes allowing the detection of very small concentration of vapor analytes, usually forbidden with inorganic structures. We will demonstrate the use of optical nanocomposite and poly(p-phenylene oxide) to allow fast absorption of analytes and selective response without any chemical target.[3]We will then show that despite the low dielectric contrast available, polymer structures can be used for to achieve photoluminescence enhancement and directional control[4]or lasing[5]with a variety of dyes including J-aggregates, quantum dots and small molecules.

References

1. Comoretto, D., *Organic and Hybrid Photonic Crystals*. 2015: Springer.

2. Knarr III, R.J., et al., Polymer, 2016. **84**, 383-390.

3. Lova, P., et al., ACS Photonics, 2015. **2**(4), 537-543.

4. Frezza, L., et al., J. Phys. Chem. C, 2011. **115**(40), 19939 - 19946.

5. Canazza, G., et al., Laser Phys. Lett., 2014. **11**(3), 035804

#302 - Contact-resistance effects in n-type organic transistors investigated by Kelvin-probe microscopy

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In this contribution, we analyzed the electrical behavior of n-type organic field-effect transistors (OFET) based on thin films of PDI8-CN_2 and PDIF-CN_2: two perylene diimide derivatives with excellent air-stable charge transport properties[1]. Bottom-contact bottom-gate devices were fabricated by evaporating PDI8-CN_2 and PDIF-CN_2 films by Knudsen cells on highly-doped Silicon/Silicon Dioxide (SiO_2) substrates equipped with gold electrodes (Drain/Source contacts). In order to get layers with enhanced structural and electrical quality, SiO_2 surface was pre-functionalized by the application of Hexamethyldisiloxane (HMDS) monolayers and the deposition parameters (i.e. substrate temperature and evaporation rate) were carefully optimized.

While transfer-curves recorded in saturation (i.e. under high Drain-Source, V_{DS}, voltages) were found to follow an almost ideal behavior with maximum mobility values of 0.05 and 0.4 cm^2/volt*sec for PDI8-CN_2 and PDIF-CN_2 devices, respectively, the OFET response in linear region (i.e. low V_{DS}) was quite far from the MOSFET theory predictions. This occurrence was attributed to the so-called contact resistance (R_c) effect which, in many cases, influences considerably the charge injection and/or extraction processes between the Source/Drain electrodes and the OFET active channel. To clarify the physical reasons ruling this phenomenon, accurate scanning Kelvin probe microscopy (SKPM) experiments were performed as a function of the organic film thickness and also in the light of the electrode treatment with an aromatic thiol monolayer.

SKPM measurements revealed that, independent on the electrode functionalization, R_c values increase exponentially when progressively lower drain-source (V_{DS}) voltages are applied along the active channels. Moreover, we observed that the active channel thickness reduction tends to furthermore magnify the effect and makes less efficient the electrode treatment.

Finally, we have found that the R_c-related voltage drops occurring at the Drain electrode are larger than those taking place at the Source contact. This finding indicates that, for the investigated devices, the R_c effect is not simply due to the presence of a reverse-biased Schottky junction limiting the electron injection process into the active channel. As a whole, our data suggest rather that the R_c phenomenon is related to a combination of morphological disorder in the organic/electrode transition regions and of still unclear details about the energy level alignment at the perylene/gold interfaces[2].

References

[1] B. A. Jones et al., Effects of Arylene Diimide Thin Film Growth Conditions on n-Channel OFET Performance, Adv. Funct. Mater., 18 (2008), 1329–1339.

[2] F. Chiarella et al., Contact-resistance effects in PDI8-CN_2 n-type thin-film transistors investigated by Kelvin-probe potentiometry Organic Electronics, 28 (2016), 299-305.

#303 - Electronic and optical properties of organically functionalized Silicon surfaces: uracil-like nucleobases on Si(001)

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Organically functionalized solid surfaces have acquired a fundamental role in many fields of research, ranging from semiconductor devices with novel properties(1) to DNA sequencing(2). A large variety of molecular assemblies can form upon adsorption of organic molecules on metal, semiconductor, and insulating surfaces, with different geometries depending on the experimental conditions during the growth. In this work we consider the silicon(001) surface, functionalized by the adsorption of the pyrimidinic uracil-like nucleobases thymine (THY), uracil (URA) and 5-fluorouracil (5-FU) in the energetically favored “dimer bridging” configuration, with the two oxygen atoms of the nucleobase bound to two surface silicon atoms from Si dimers of adjacent rows. Using density functional theory (DFT) with pseudopotentials and plane wave basis set, we investigate the effects of molecule adsorption, chemical substitutions and adsorption geometry on the electronic and optical properties of the Si(001) surface. The electronic bandstructure of the Si(001):X systems (X=THY,URA,5-FU) in the region of the bulk silicon gap is found to display a strong dependence on the molecular tilt angle with respect to an upright adsorption geometry(3). Uracil-like nucleobase adsorption on Si(001) in the "dimer bridge" configuration gives rise to a characteristic shape of the reflectance anisotropy spectra (RAS)(4), with negligible dependence on molecule type and geometry, up to ~4 eV. We trace back the origin of the observed spectral features by singling out RAS structures directly associated with molecular states, and those induced by relaxation and passivation effects on the underneath Si surface. Some sensitivity to molecule type and tilt angle appears only for higher energies. Our results may be of interest for applications in hybrid silicon/biomolecule-based nanodevices, and call for a RAS experimental study of Si(001):nucleobase systems in the UV region extending up to 7 eV. References: (1) A. Vilan et al., Adv. Mater. 22, 140-159 (2010). (2) D. Fologea et al., NanoLetters 5, 1905-1909 (2005). (3) E. Molteni, G. Onida, and G. Cappellini, Eur. Phys. J. B 89, 98 (2016). (4) E. Molteni, G. Cappellini, G. Onida, and G. Fratesi, in preparation.

#304 - Ballistic electron and photocurrent transport in Au/organic/Si(001) diodes with PDI8-CN2 interlayers

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We use ballistic electron emission microscopy (BEEM) [1] to probe hot-electron and photocurrent transport in Au/organic/n-Si(001) diodes incorporating the *n*-type perylene diimide semiconductor PDI8-CN_2 [2]. For the case of an ultrathin organic interlayer, hot-electron injection is weak and can be detected only at randomly-distributed nanosized domains, where BEEM provides electronic barrier heights of ~0.67eV and ~0.94eV respectively [3]. No ballistic transport is detected for devices with a 10nm-thick interlayer. Regardless of the organic layer thickness, BEEM reveals laterally-uniform contributions due to scanning tunnelling microscopy-induced photocurrent (STM-PC), with a characteristic energy onset at ~1.2eV and a broad intensity peak in the 2-4eV range. We give insight on such spectroscopic features by examination of temperature-dependent spectra and of literature data. This study shows that PDI8-CN_2 limits the penetration of Au towards Si, likely due to stiff intermolecular interactions and reactivity of the cyano groups. Moreover, ballistic transmittance is remarkably suppressed and photocurrent transport takes place via defects or recombination centres. Our analysis of electronic and STM-PC fingerprints appears useful for the characterization of several organic-on-inorganic heterostructures [4].

References

[1] W. Yi, A.J. Stollenwerk, V. Narayanamurti, *Surf. Sci. Rep.* **64** (2009) 169.

[2] B.A. Jones *et al.*, *J. Am. Chem. Soc.* **129** (2007) 15259.

[3] R. Buzio, A.Gerbi, D. Marré, M. Barra, A. Cassinese, Organic Electronics **18** (2015) 44.

[4] R. Buzio, A.Gerbi, D. Marré, M. Barra, A. Cassinese, J. Vac. Sci. Technol. B **34** (2016) 041212.

#305 - Structural control of ultra-thin polymeric layers deposited by Langmuir-Schaefer technique for bi-layer ambipolar field-effect transistor applications

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The need of large-area and flexible electronic applications has considerably enlarged the interest on conjugated semiconducting polymers. Despite the efforts, a comprehensive understanding of the correlation between polymers microstructures and their electrical performances is still demanding. Indeed, too many parameters affect the polymer self-assembly, such as polymer weight, polydispersivity, and backbone rigidity,and consequently the role of inter- and intra-chain charge transport is still under debate. [1]

In this work we show that the Langmuir-Schaefer (LS) technique allows to depose ultra-thin polymeric layers with controlled orientation and therefore to study the effect of the above mentioned parameters to the organic thin film transistor (oTFT) based on them.

Single- and bi-layer structures composed by ultra-thin polymeric active layers of the p-type polymer derivative of isoindigo,IIDDT-C3, [2] and the n-type P(NDI2OD-T2) [3] polymer were deposited by LS technique onto SiO_2 substrates. Grazing incidence X-ray diffraction measurements revealed that LS deposition technique coerces the polymers to adopt an edge-on organization with respect to the substrate surface, which is a particularly suitable configuration for charge transport in oTFTs. We found that in the case of P(NDI2OD-T2) the presence of a bulky and planar NDI core ensures rigidity to the polymer backbone, even at high polymer weight,thus favoring the intra-chain charge transport. An opposite result was obtained for IIDDT-C3: LS technique induces the formation of crystalline fibers where the strong π-π interaction promotes the inter-chain transport mechanism.

These structural features are observed regardless the nature of the substrate and therefore they persist when polymers are deposited one over the other, i.e. in bi-layer structures. This configuration is particularly suitable for charge transport and contributes to the achievement of remarkable electrons and holes mobilities as well as balanced threshold voltage values in bi-layer ambipolar architectures. These remarkable results represent an enormous improvement in view of future large-area and low-cost device fabrication compatible with flexible substrates.

References

[1] D. T. Duong et al., *Adv. Funct. Mater*. **24** (2014) 4515–4521

[2] T. Lei, J. H. Dou, J. Pei, Advanced Materials, **24** (2012) 6457-6461

[3] R. Steyrleuthner, R. Di Pietro, B. A. Collins et al. *JACS*, **136** (2014) 4245-4256

#306 - Enhanced emission of organic light emitting diodes working in ultra-strong light-matter coupling regime

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Organic semiconductor molecules, well known for Organic Light Emitting Diodes (OLED), are excellent materials to study and exploit different light-matter coupling regimes, namely weak (WC), strong (SC) and ultrastrong coupling (USC). The devices can be fabricated inserting an organic electroluminescent stack into an optical resonator (i.e. a Fabry-Perot microcavity): WC regime leads to a strong enhancement of efficiency and color tunability of OLEDs, while in SC and USC regimes emitting molecules rapidly exchange energy with the cavity generating two hybrid states between light and matter called polariton states. The research on electroluminescent dynamics of organic polaritons is a fundamental step towards the realization of the first electrically pumped organic polariton laser, which in principle can emit coherent light at very low power thresholds. Nevertheless all of the experiments reported so far showed that the efficiency of polaritons OLEDs are much lower than those of standard devices without a general and exhaustive explanation.[1,2] In our recent works [3,4] we report about electroluminescent metal-clad microcavities with a squaraine dye as active material that reached the USC regime. In particular we pushed the light-matter coupling ratio up to values that are twice the largest ones so far reported for organic microcavities (g=60 % under optical excitation and g=48 % under electrical pumping). We also clearly observed new features of the USC regime, id est the appearance of a polariton energy-gap and a strong narrowing of the polariton modes well below the line-width of both the bare emissive molecule and the weakly coupled cavity. Furthermore an unexpected increment of external quantum efficiencies (EQE) of strongly coupled squaraine OLEDs (Sq-OLEDs) was observed, reaching the reference device ones at the maximum coupling ratio. Owing to the USC properties, Sq-OLEDs produce also monochromatic emission nearly angular independent, which could be important for future technological applications. To fully understand the dynamics behind such results we compared these features with those of different OLEDs in SC regime made with another fluorescent compound revealing the parameters connected to the EQE enhancement. The increased polariton OLEDs efficiencies shows how emissive dynamics of organic compounds can be strongly modified exploiting ultra-strong light matter coupling between metal-clad microcavities and proper molecules, and paves the way to the fabrication of novel efficient organic polariton devices in high Q-factor microcavities.

[1] N. Christogiannis et al., Advanced Optical Materials, 1, 503-509 (**2013**)

[2] C. R. Gubbin et al., Applied Physics Letters 104, 233302 (**2014**)

[3] S. Gambino et al., ACS Photonics. 1 (10), 1042-1048 (**2014**)

[4] S. Gambino et al., Applied Materials Today, 1 (1), 33-36 (**2015**)

#307 - Quantum-Confined and Enhanced Optical Absorption of Colloidal PbS Quantum Dots at Wavelengths with Expected Bulk Behavior

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Nowadays it is well-accepted to attribute bulk-like optical absorption properties to colloidal PbS quantum dots (QDs) at wavelengths above 400 nm. This assumption has relevant implication permitting the use of formalisms derived from classical electromagnetism, such as the Maxwell-Garnett effective medium theory, to determine optical absorption coefficients of PbS QDs and consequently their concentration in colloidal solutions. Here we demonstrate that PbS QDs experience the quantum confinement regime across the entire near UV-Vis-NIR spectral range, therefore also between 350 and 400 nm already proposed to be sufficiently far above the bandgap to suppress quantum confinement. This effect is particularly relevant for small PbS QDs (with diameter of ≤3.5 nm) leading to absorption coefficients that largely differ from bulk values (up to 40 % less). As a result of the broadband quantum confinement and of the high surface-to-volume ratio peculiar of QDs, suitable surface chemical modification of PbS QDs is exploited to achieve a marked enhancement of the absorption coefficients (up to 250 %) compared to bulk values. We provide empirical relations to determine the absorption coefficients at 400 nm of as-synthesized and ligand-exchanged PbS QDs, accounting for the broadband quantum confinement and suggesting a heuristic approach to qualitatively predict the ligand effects on the optical absorption properties of PbS QDs. Our findings highlight the limitations of formalisms derived from classical electromagnetism and permit to spectrophotometrically calculate the concentration of PbS QD solutions avoiding underestimation due to deviations from the bulk. In perspective, we envisage the use of extended π-conjugated ligands bearing electronically-active substituents to enhance QD solid optical absorption for photovoltaic and photodetection applications and note the inadequacy of the representation of ligands at the QD surface as dipoles.

#308 - Pyran based photosensitizers for DSSC

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Among the classes of dyes more investigated in the last 20 years for applications in organic electronics, pyran containing derivatives hold a relevant position. Theversatilityofthestartingbuildingblockofthiskindofcompounds,2,6-dimethyl-γ-pyrone, characterized by two kinds of reactive sites (i.e., the ketonic group and the two acidic methyl moieties),has allowed the synthesis of several different molecular structures and led to the preparation of materials featuring interesting properties in various fields of organic electronics and photonics. In the last years, the use of this class of compounds as photosensitizers in dye sensitized solar cells (DSSC) has shown encouraging results.Dye Sensitized Solar Cells (DSSC) represent a relatively new generation of photovoltaic technologies; as compared to traditional photovoltaics based on silicon, the appeal of DSSCs lies on economical and aesthetic reasons: the fabrication of DSSCs is in fact affordable by using cheap solution techniques. They can be moreover be prepared in a wide range of different colors, are compatible with flexible substrates and offer a better integrability with architectonic elements different from the roof.In this context, we investigated the properties of a set of novel pyran based dyes and their application, as photosensitizers in DSSC. The dyes feature a common molecular structure, based on a pyran core, functionalized with different electron acceptor groups, symmetrically linked to carbazole or phenothiazine electron donor moieties; the end-functionalization with two carboxylic groups allow a tight adhesion to the semiconductor oxide surface in the fabrication of the device. The optical absorption of the dyes is strongly modulated by the strength of the different acceptor used and, in a less extent, by the donor ability of the carbazole or phenotiazinic rings. As a consequence, the dyes overall cover the most part of the visible spectrum, providing colours ranging from orange to green. They are moreover characterized by high molar extinction coefficients, up to a value of 1.0·105 cm·M-1. The dyes have been used as photosensitizers in DSSC affording devices with a maximum power conversion efficiency of 2.82 %. The most promising device underwent an accelerated ageing test, performed at 85 °C for 50 days: no variation of the main electrical parameters and of the optical spectrum of the DSSC was observed during the test, indicating an excellent stability for this kind of device.

#309 - Molecular Imprinting Technology applied into photoelectrochemical device

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Traditionally, Molecular Imprinting Technology (MIT) was applied into a lot of different research and application areas. In particular, highest selectivity versus target molecule was achieved by materials based on MIT process used in high performance sensors, materials used for chromatographic application and finally also in the pre-treatment process of liquid and gas media. A particular class of these materials called Molecular Imprinting Polymers (MIPs) can be easily synthetized by a low cost and environmental friendly processes. In this work, an application of MIPs materials as counter-electrode in Dye-Sensitized Solar Cells (DSCs) was introduced to enhance the selectivity towards triiodide molecule contained in the electrolyte. The latter is commonly a complex matrix containing other than triiodide (the target molecule) also other compounds used as additives and stabilizers that can interfere with the triiodide reduction lowering the cell efficiency. The application of MIPs counter-electrode allowed a definite increase in the photovoltaic efficiency of the device as a consequence of the lowering of charge transfer resistance at the counter-electrode side. These results open the possibility to apply MIP materials into energy systems based on photoelectrochemical cell improving their properties.

#310 - Excess electrons distribution in TiO2(110) and Mg:TiO2(011) surfaces

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Titanium dioxide is a metal oxide with many relevant technological properties for photocatalysis, chemical reactivity, electrical conductivity and solar energy harvesting. TiO2 is an inert insulator in stoichiometric form and it can be easily reduced into an n-type semiconductor TiO2-x with the trasformation of Ti4+ to Ti3+ ions. This reduction is also characterized by the excess electrons populating localized Ti3d states in the band gap [1]. These electrons can be well characterized by the presence of a defect state at about 0.8 eV below the Fermi level [2]. Moreover, in the case of very low defect content, Ti3d states can be exalted through resonant valence-band photoemission process where, at resonance, the direct photoemission of a valence-band electron interferes with the two-step autoionization process leading to the same final state. It has been measured the angular distribution and the corresponding PhotoElectron Diffraction (PED) pattern of the defect state in resonant conditions for the rutile TiO2(110) surface and mapped its distribution in the case of a non-stochiometric surface [3] and after deposition of Na on a stoichiometric surface [4]. The main finding was the demonstration that charge distribution of the band gap state is essentially an intrinsic property of the TiO2 (110) surface, because largely independent of the way excess electrons are created. Within this framework we moved to study another rutile surface – the (011) - in the presence of Mg. Mg is a common contaminant of TiO2 and, by thermal annealing of the sample, it is possible to make it segregate from the bulk of the sample up to the surface. Both core level and valence band photoemission experiments were performed and the spectra show a decrease of the defect state linked to Mg presence. PED patterns were also recorded in order to study the localization of magnesium in the TiO2 surface layers. The experimental data set allows to exclude the formation of metallic Mg clusters on the surface and, rather, to point to the substitution of Mg into the Ti lattice sites. The decrease of the defect state intensity in the band gap observed in the presence of Mg is due to the formation of MgO which takes the role of “metal oxide dopant” for the TiO2 , since doping with a metal oxide (i.e. ionic doping) does not induce electron excess.

References

[1] T. L. Thompson and J. T. Yates, Jr., Chem. Rev. 106, 4428 (2006).

[2] R.L. Kurtz,R. Stockbauer, T.E. Madey,E. Roman, J.L. de Segovia, Surf. Sci. 218 (1989) 178.

[3] P. Krüger, S. Bourgeois, B. Domenichini, H. Magnan, D. Chandesris, P. Le Fèvre, A. M. Flank, J. Jupille, L. Floreano, A. Cossaro, A. Verdini, and A. Morgante, Phys. Rev. Lett. 100, 055501 (2008)

[4] P. Krüger, J. Jupille, S. Bourgeois, B. Domenichini, A. Verdini, L. Floreano, and A. Morgante, Phys.Rev. Lett. 108, 126803 (2012).

#311 - Synthesis and chracterization of amphiphilic block-copolymers low band gap rigid segment-block-P4VP

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Two homologous series of rod-coil b[lock copolymers, composed by a low band gap rod moiety (poly[2,6-(4,4 bis-(2ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) anda flexible poly(4-vinylpyrydine) (P4VP) based polar block, were synthesized by two different approaches. Step Grwoth-like procedure provided copolymers with longer coil, whilst copolymers with longer rod arise from Chain Growth-like process. Both the series were deeply investigated with different analytical tecniques (^{1}H NMR, SEC-DV, and MALDI-TOF MS) in order to prove the coupling process and elucidate of the obatined materials. Chemical composition was evaluated by ^{1}H NMR analysis. DSC heating traces of rod-coil copolymers synthesized by Step Growth-like route present two well resolved glass transition temperatures corresponding to the rod and coil blocks. The low band-gap rod-coil copolymers especially these with short coil can find application in hybrid solar cells.

The length of the coil block is strongly limited by the low reactivity of the macroiniziator related two the rigid ity of the conjugated systems with respect to the poly(3-hexyl thiophene) (P3HT). The shortness of a coil segmente (P4VP) allows to perform a proper MALDI-TOF MS characterization which is in agreement with ^{1}H-NMR data. A series of rod-coil copolymers was prepared with predominance of the rod block (>86%w) stating from a fixed ro block and tuning the length of the rod moiety, by varying both the Macroiniziator/4VP ratio and the time of the nitroxide mediated radical polymerization (NMRP).

The two series of obtained materials aggregate indifferent manners and show ditinct organizations in solid stat films depending of the respective length of the two blocks in the copolymers, from globular micelle-like to lamellar segregation as highlighted by AFM images with the increasing of the length of the coil segment.

#312 - Coherence with hard X-rays at the ESRF beamline ID10

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Coherence is one of the key properties of the new X-ray sources such as X-ray Free Electron LASERs and ultimate storage rings. The beamline ID10 at the European Synchrotron Radiation Facility exploits coherence in scattering measurements with hard X-rays with techniques like X-ray Photon Correlation Spectroscopy (XPCS) and Coherent X-ray Diffraction Imaging (CXDI). XPCS probes the microscopic dynamics in a large variety of systems [1], from soft matter (colloidal suspension [2,3], liquid surface dynamics [4]...) down to those related to atomic motions in glasses [5] and alloys [6]. CXDI is a high-resolution imaging technique based on numerically retrieving the missing phase information in oversampled speckle patterns recorded in the far field [7, 8]. At ID10 the potential of CXDI for 3D imaging with hard X-rays have been recently demonstrated in inorganic systems [9] and biological samples [10].

Here we will give a flavour of the main developments at ID10 involving coherence with hard X-rays. For XPCS we show examples of non-conventional applications, e.g. an induced atomic dynamics of metallic glasses under a hydrogen flow [11] and a study of colloidal dynamics in confinement with high-energy coherent X-rays [12]. For CXDI we report about applications in characterizing nano-structured materials in 3D, e.g. based on TiO_2 for photovoltaic applications and porous Si clusters [13].

Finally, XPCS and CXDI will largely benefit from the next advent of the Extremely Brilliant Source at ESRF with its 100 times increase in brilliance, opening the field to many new scientific opportunities.

[1] G. Grübel and F. Zontone, J. Alloys Comp. 362 (**2004**) 3.

[2] C. Caronna, Y. Chushkin, A. Madsen, and A. Cupane, Phys. Rev. Lett. 100 (**2008**) 055702.

[3] L.B. Lurio et al., Phys. Rev. Lett. 84 (**2000**) 785.

[4] D. Orsi, E. Guzmán, L. Liggieri, F. Ravera, B. Ruta, Y. Chushkin, T. Rimoldi & L. Cristofolini, (**2015**) Sci. Rep. 5, 17930.

[5] Giordano, V.M. & Ruta, B. (**2016**). Nat. Comm., 7, 10344.

[6] M. Leitner et al., Nature Mater. 8 (**2009**) 717.

[7] J. Miao, P. Charalambous, J. Kirz, D. Sayre, Nature, 400, (**1999**), 342.

[8] H.M. Chapman et al, J. Opt. Soc. Am. A, 23, (**2006**), 1179.

[9] Y. Chushkin, F. Zontone, E. Lima, L. De Caro, P. Guardia, L. Manna and C. Giannini, J. of Synchrotron Rad. 21 (**2014**) 594.

[10] J. A. Rodriguez, R. Xu, C.-C. Chen, Z. Huang, H. Jiang, A. L. Chen, K. S. Raines, A. Pryor Jr., D. Nam, L. Wiegart, C. Song, A. Madsen, Y. Chushkin, F. Zontone, P. J. Bradley and J. Miao l, IUCrJ Vol. 2, Part 5 (**2015**) 575.

[11] B. Ruta, S. Sarker, D. Viano, F. Zontone, W.M. Chien, M. Dolan, and D. Chandra, Sci. Rep. (submitted)..

[12] K. Nygård, J. Buitenhuis, M. Kagias, K. Jefimovs, F. Zontone and Y. Chushkin, Phys. Rev. Lett. 116 (**2016**) 167801.

[13] E.M.L.D. de Jong, G. Mannino, A. Alberti, R. Ruggeri, M. Italia, F. Zontone, Y. Chushkin, A.R. Pennisi, T. Gregorkiewicz. & G. Faraci, (**2016**) Sci. Rep., 6, 25664.

#313 - Synthesis of MoS2 monolayer using promoter

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Nanosheet materials such as graphene, boron nitride and Transition Metal Dichalcogenides (TMD) have gathered a lot of interest in recent years thanks to their outstanding properties and promises for future tecnology, energy generation and post-CMOS device concepts. Amongst this class of materials, MoS_2 has been studied because of its semiconducting properties, its direct bandgap and the possibility to be synthesized by bottom up techniques.

MoS_2 flakes were obtained on SiO_2/Si using chalcogen and sulfur powders in a quartz tube heated at between 680 and 750 °C. In order to promote flakes nucleation, an organic precursor, namely perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), was drop-casted on a Si substrate and placed near the SiO_2/Si substrate on which the growth of flakes occurred.

It was observed that the presence (or absence) of PTCDA in the growth chamber has a profund effect on MoS_2 flakes nucleation and size.

Several growth parameters were varied in order to find the optimal conditions for flakes nucleation: powder weight, sulfur temperature, promoter concentration, substrate temperature, flows. The flakes were observed using a Nomarksi optical microscope and then *characterized* by means of Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Raman and Photoluminescence.

The relationships between growth parameters, flakes thickness and optical properties are discussed.

#314 - Monitoring of graphene thermal doping in controlled atmosphere by Raman spectroscopy

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Graphene (Gr) doping is a key aspect for the application of this 2D material in electronic or optoelectronic devices. Among the different doping methods reported to date, those based on thermal treatments in controlled atmosphere hold many advantages, such as the compatibility with semiconductor production lines and a low density of defects introduced in Gr. As recently shown, it is indeed possible to obtain large doping levels (~10^{13} cm^{-2}) by Gr treatments in oxygen ambient at temperatures <500°C [1]. However, it has not yet been fully clarified the role of the substrate and the nature of the interaction between Gr and doping molecules present in the treatment atmosphere. In particular, two critical aspects have emerged: (i) strain/stresses related to the different thermal expansion coefficients of Gr and substrate, (ii) specific role of given molecules of the ambient in Gr doping and its stability.

In this study, the effects of thermal treatments in controlled atmosphere up to 400°C of single layer of CVD grown Gr transferred on SiO_2 coated Si samples are investigated. A comparison between the effects of high purity N_2, CO_2, H_2O or O_2 atmosphere, or vacuum during the treatment is done by atomic force microscopy (AFM) and micro-Raman spectroscopy measurements in order to evidence those effects attributable to stress/strain and separate them from the doping effects [2, 3]. In-situ micro-Raman (mR) spectroscopy during the thermal treatments enables to clarify the time and temperature dynamics aspects of doping. Moreover it sheds light on the type of doping as well as its dependence on the atmosphere during the treatment. Furthermore doping stability tests and aging of materials were explored by thermal treatments in controlled atmosphere. Our data highlight an efficient p-type doping of Gr by thermal treatments in O_2 at T>200°C and a temperature effect on the 2D band at about 2680 cm^{-1} inducing its red shift and widening before returning to room temperature. This latter effect could be attributed to the thermal sensitivity of vibrational modes somehow masking the doping effect. However, the net doping was confirmed by electrical measurements on transmission line model test structures, from which we obtained Gr sheet resistance.After treatment in O_2 atmosphere it has been proven that the graphene sheet resistance decreases fully consistent with the enhanced p-type doping induced by O_2 [3].

[1] Piazza A., Giannazzo F., Buscarino G., Fisichella G., La Magna A., Roccaforte F., Cannas M., Gelardi F.M. and Agnello S., J. Phys. Chem. C; **119**, 22718-23 (2015).

[2] Verhagen T.G.A., Drogowska K., Kalbac M., and Vejpravova J., Phys. Review B; **92**, 125437 1-9 (2015).

[3] Piazza A., Giannazzo F., Buscarino G., Fisichella G., La Magna A., Roccaforte F., Cannas M., Gelardi F.M., Pignataro B., Scopelliti M. and Agnello S,.Carbon **107,** 696-704 (2016)

#315 - A Versatile Graphene-Plasmonic Metals-Porphyrines Platform

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New opportunities for energy harvesting, plasmonics, biomimetic catalysis, chemosensing, biosensing, immunosensing and cellular recognition are offered by novel hybrid heterojunctions combining, semiconductors, graphene, plasmonic metals and porphyrines. In those hybrids, graphene activates interfacial charge transfer, metal nanoparticles, in turn, activate the plasmonic electromagnetic coupling of light, and the porphyrines act as redox-mediators in view of their various properties, such as reversibility, regeneration at low potential, and generation of stable redox states. In order to design these platforms to take advantage of applications exploiting interfacial charge transfer, we need to better understand the surface and interfacial electronic phenomena in graphene-based hybrids. This contribution presents examples of: - graphene coupling to various plasmonic metals that extend far beyond gold, allowing charge transfer to and from graphene; we introduce hybrids that can extend plasmonic applications to THz and UV ranges and that can exploit charge transfer at interfaces to enhance or quench or shift the frequency of the plasmon resonance providing a fully tunable plasmonic platform. [1-2] - further functionalization with porphyrins, highlighting aspects of the interfacial charge transfer controlling activation of redox catalytic processes; - applications of the graphene supported porphyrines as a high efficient peroxidase-mimic catalyst, with high catalytic activity and substrate binding affinity approaching that of natural enzymes; - functionalization strategies for the graphene-based hybrids to activate the response of human fibronectin to its antibody monoclonal anti-human fibronectin. The graphene is grown by CVD at the Apulian Graphene Lab, which is part of the CNR-Nanotec in Bari and then transferred to the substrates of technological interest, which span from semiconductors, glass to ultrathin plastics. [1] M. Losurdo, C. Yi, A. Suvorova, S. Rubanov, T.-H. Kim, M.M. Giangregorio, W. Jiao, I. Bergmair, G. Bruno, A. S. Brown, ACS NANO, 8, 3031 (2014) [2] M.M. Giangregorio, W. Jiao, G. V. Bianco, P. Capezzuto, A. S. Brown, G. Bruno, M. Losurdo, Nanoscale, 7, 12868 (2015) Acknowledgement: We acknowledge the project TWINFUSYON. This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 692034.

#316 - Preparation of Reduced Graphene Oxide by controlled explosion of lyophized Graphene Oxide.

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Graphene can be prepared through different methods among which the material synthesis trough a reduction of graphene oxide is one of the best candidates for industrial applications. The goal of the method is obtaining the largest exposed Specific Surface Area (SSA), being the theoretical value of a single graphene sheet about 2600 m^2/g. The process consists in exfoliation of graphene sheets from bulk graphite, through oxidation-derived intercalation expansion, followed by a sucessive quick reduction, that removes the previously inserted oxygen groups.

In this work, two different graphene samples have been synthesized by thermal reduction of Graphene Oxide (GO) following a controlled and an explosive pathway, respectively.

GO suspension was obtained by exploiting a modified Hummers method.(1) After washing 100 ml of neutral solution with concentration of 2 mg/ml was frozen and then subjected to a lyophilization (freeze drying)(2) process to obtain Lyophilised Graphene Oxide (LGO). The reduction of LGO was then promoted by thermal activation exploiting a controlled reduction pathway, obtaining thus a Reduced Graphene Oxide (RGO hereafter), and an explosive reduction pathway, producing an Exploded Graphene Oxide (EGO). Both samples were obtained under a vacuum of 10^{-2} mmHg. The materials were characterized by means of FTIR Spectroscopy by Attenuated Total Reflection (ATR) *IRPrestige 21 Shimadzu*, high brilliance LEO 1530 Field Emission Scanning Electron Microscope (FESEM). Nitrogen adsorption isotherms have been measured at 77K by using a Quantachrome AutoSorb iQ apparatus and the BET method(3) was applied to calculate the SSA.

Differences in the reduction process of GO can drastically alter morphological properties of the samples. Nitrogen adsorption measurements show that the EGO sample possesses a significantly higher specific surface area (~580 m^2/g) than the RGO sample

(~90 m^2/g), due to a higher degree of disorder and larger spacing between graphene sheets. On the opposite, the low area measured for the RGO sample can be ascribed to a shorter separation between the graphene sheets.

References

1. Hummers WS, Offeman RE. Preparation of Graphitic Oxide. J Am Chem Soc. 80(6) (1958), 1339.

2. A. Capobianchi, S. Foglia, P. Imperatori, A. Notargiacomo, M. Giammatteo, T. Del Buono, E Palange. Carbon 45 (2007), 2205.

3. Brunauer S, Emmett P, Teller E. Adsorption of gases in multimolecular layers. J Am Chem Soc. 1938 Feb;60(2):309–19.

#317 - Exfoliation of graphite in green solvents: Scalable graphene production for polymer composites

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Graphene-based polymer composites have attracted great attention in the field of materials and polymers science during the last decade, due to the improvements in mechanical, electrical, and thermal properties with respect to the pristine polymers [1]-[2]. However, large scale production of graphene flakes [3] and their optimal dispersion in polymer matrices are the main issues to be tackled for the realization of high-performance graphene-based composites [1].

The most efficient solvent to produce graphene through liquid phase exfoliation (LPE) of graphite is N-Methylpyrrolidone (NMP), due to its surface tension value matching the graphene's surface energy [4]. In fact, the solvent can minimize the interfacial tension between the solvent and the exfoliated flakes, avoiding them to restack in the dispersion. [5] However, because NMP is teratogenic [6], other solvents, for example water [7], ethanol [8] etc. have been exploited to find a more environmentally friendly path for the graphene production. Although their surface tension does not match the graphene flakes' surface energy, it can be increased using surfactants [7] and polymers [8]. Moreover, the LPE process of 2D materials can be coupled with solution blending to prepare polymer composites. This is key for the realization of devices demonstrating flexibility and scalability [2].

In this study, we propose a new approach consisting in the exfoliation of graphite using low boiling point solvents and their mixtures, adding a low percentage (below 5 wt%) of poly methyl methacrylate (PMMA). The latter one can reduce the solvent/graphene agglomeration, enhancing the exfoliation process efficiency. Graphene dispersions are prepared using common solvents, such as ethyl acetate, methyl ethyl ketone, and ethanol/acetonitrile mixture, using different PMMA loadings (1, 2, and 4 wt%).The lateral size of the graphene flakes is analyzed by transmission electron microscopy (TEM), the exfoliation efficiency is studied through Raman spectroscopy, and the graphene loading is determined by thermogravimetric analysis (TGA).

The dispersions containing 1% of PMMA show the best results in terms of exfoliation, where the lateral size of flakes is found in the range between 400-600 nm. This novel polymer assisted graphite exfoliation provides a new approach, which can combine the two-dimensional materials up-scalable production and the polymer composites preparation through solution blending.

References

[1] J. R.Potts, et al., *Polymer*, 52 (2011) 5

[2] A.C. Ferrari et al., *Nanoscale*, 7 (2015), 4598

[3] F. Bonaccorso et al., *Adv. Mater*. 28 (2016) 28, 6136

[4] Y. Hernandez et al., *Nature Nanotech.,* 3 (2008), 563

[5] F. Bonaccorso et al., *Materials Today* 15 (2012) 12, 564

[6] H. M. Solomon, *Drug Chem. Toxicol*., 18 (1995), 271

[7] M. Lotya et al., *J. Am. Chem. Soc.,*131(2009) 10, 3611

[8] T. Y.LiangandM. C. Hersam, *J. Am. Chem. Soc.*,132 (2010)50, 17661

#318 - Investigation of Zinc(II) tetraphenylporphyrin adsorption on Au(111) and graphene/Cu surfaces: from monolayer to multilayer transition

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In recent years, the study of self-assembled monolayers (SAMs) of organic molecules on various substrates has assumed an increasingly important role in surface physics [1-3]. These systems are very attractive, and the main reason concern the possibility to synthesize various advanced functional materials and devices through molecular manipulation. Among all organic compounds, porphyrins are a well-known and versatile popular class of molecules, which has significant properties that can be exploited in a wide variety of electronic devices [4,5] such as dye-sensitized solar cells [6,7]. In particular the tetraphenylporphyrins (TPPs), one porphyrin derivatives, have the interesting property to self-assemble on noble-metal surfaces into highly ordered and extended arrays at room temperature [8]. Starting from these results, TTPs depositions can be extended to graphene surface, an interesting 2D material of well-known properties, in order to study at first the molecular packing and then the possible effects of the functionalization due to weak interaction between molecules and substrate. Indeed, TTPs molecules could be act as extrinsic dopants donating or accepting electrons, modifying graphene Fermi level [9]. Our work investigates the Zinc(II) tetraphenylporphyrin (ZnTPP) molecules behavior on Au(111) and graphene surfaces using scanning tunnel microscopy. In particular, to have a reference model, deposition was performed before on Au(111) and after on graphene surface. Study on the molecular packing of ZnTPP was performed going from low coverages up to multilayer through monolayer self-assembly. The binding behavior and the mobility of the molecules were inspected as well. References 1. K. Banerjee, A. Kumar, F.F. Canova, S. Kezilebieke, A.S. Foster and P. Liljeroth, The Journal of Physical Chemistry C 120 (16), 8772-8780 (2016). 2. R. Addou and M. Batzill, Langmuir 29 (21), 6354-6360 (2013). 3. M. Lackinger, S. Griessl, W.M. Heckl, M. Hietschold and G.W. Flynn, Langmuir 21 (11), 4984-4988 (2005). 4. C.B. Winkelmann, I. Ionica, X. Chevalier, G. Royal, C. Bucher and V. Bouchiat, Nano Letters 7 (6), 1454-1458 (2007). 5. D.S. Hecht, R.J.A. Ramirez, M. Briman, E. Artukovic, K. S. Chichak, J.F. Stoddart and G. Grüner, Nano Letters 6 (9), 2031-2036 (2006). 6. L.-L. Li and E.W.-G. Diau, Chemical Society Reviews 42 (1), 291-304 (2013). 7. A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, Chemical Reviews 110 (11), 6595-6663 (2010). 8. C. Ruggieri, S. Rangan, R.A. Bartynski and E. Galoppini, The Journal of Physical Chemistry C 120 (14), 7575-7585 (2016). 9. A.A. Castellanos-Gomez and B.J.van Wees, Graphene 02 (03), 102-108 (2013).

#319 - A novel hybrid Graphene oxide nanomaterial: photoreleasing nitric oxide

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Graphene oxide (GO) is a low cost material that is synthesized from graphite and has a wide range of potential uses in many research areas, including energy storage,1 nanoelectronics,2 molecular biosensing3 and catalysis.4 Here we present the development of a new photoresponsive nanosystem for nitric oxide (NO) photodelivery, achieved by the chemical functionalization of graphene oxide (GO) with an NO photodonor (NOP1) 5. In this material, the photoactive component has been covalently grafted at the periphery of the GO platform, leading mainly to single nanosheets of GO–NOP1 that can be dispersed in aqueous media, are stable in the dark and can supply NO under exclusive control of visible light. The GO–NOP1 nanomaterial has been fully characterized by SEM, TEM, AFM, XRD, FTIR and UV-Vis absorption spectroscopy. Our experiments proves that NO photoreleasing occurs with an efficiency similar to that observed for a free model compound ruling out any significant quenching effect (i.e. photoinduced energy/electron transfer) and accounting for the excellent preservation of its photochemical properties upon grafting. A combination of amperometric detection and indirect measurements based on a fluorometric assay prove that the remote-controlled release of NO from the GO–NOP1 nanosystem is exclusively tuned by visible light stimuli. Our experiment indicate also an excellent preservation of NO releaser photochemical properties upon grafting. Overall, this is one of the first and most promising reports of graphene-based hybrid materials for light-triggered NO delivery and can open intriguing opportunities for further studies in biomedical research, due to the multiple fascinating properties of the NO radical in medicine and biology. 1 M. D. Stoller, S. Park, Y. Zhu, J. An and R. S. Ruoff, Nano Lett., 2008, 8, 3498. 2 X. Li, X. Wang, L. Zhang, S. Lee and H. Dai, Science, 2008, 319, 1229. 3 J. T. Robinson, F. K. Perkins, E. S. Snow, Z. Wei and P. E. Sheehan, Nano Lett., 2008, 8, 3137. 4 J. Pyun, Angew. Chem., Int. Ed., 2011, 50, 46. 5 N Marino, S Petralia, M Perez-Lloret, J Mosinger, S Conoci and S Sortino. Graphene oxide nanohybrid photoreleasing nitric oxide. Journal of Material Chemcistry B (2016), 4, 5825--5830

#320 - Production and characterization of exchange coupled Co/Pt and Co/Pd based pseudo spin-valves

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Pseudo spin-valves (PSVs) based on giant and tunneling magnetoresistance (GMR and TMR, respectively) heterostructures with perpendicular magnetic anisotropy (PMA) are attracting an ever increasing attention due their potential use in magnetic random access memories based on the spin transfer torque effect (STT-MRAMs), being also of interest for other applications including magnetic field sensors and logic ports. However, the increasing demand for miniaturization of magnetic devices requires to specifically address the effect of size confinement, down to the nanoscale, on PSVs with perpendicular anisotropy.

In this context, the NANOREST project has addressed the problem of enhancing the magnetic stability of nanostructures, to be employed as electrodes in spin-valves of the MRAM architecture. The approach is to build both the reference layer (RL) and the free layer (FL) as two-phase dots in which a key role in determining the magnetic behaviour is played by the interface exchange coupling.

In this contribution,we present the activitieson perpendicular [Co/M] (M=Pt, Pd) based PSV aimed at establishing the best conditions to obtain both the deposition of continuous multilayers and the shaping of the same systems in the form of nanosized dot arrays by using FIB based processes. To this purpose a [Co/M]n/FeCo/Cu/FeCo/[Co/M]n PSVs structure with PMA is proposed, in which a key role is played by the exchange coupling at the soft/hard FeCo/[Co/M] interface. By properly changing the thickness of Co and M layers and the number of repetition *n*, the PMA can be finely modulated thus allowing two electrodes with different coercivity to be obtained, as required in a SV system.

The results showed that, when a [Co/Pd]n layer is used as the hard phase in the continuous bilayers, the desired rigid exchange-coupled system, consisting of hard and soft phases with PMA, was obtained. However, when two bilayers with different coercivity are chosen as RL and FL and assembled in a PSV stack, the behavior of such a system was not a simple superposition of the hysteresis loops of the individual electrodes (as expected for ideal PSV stacks), the overall shape suggesting a strong dipolar coupling between the constituent layers across the Cu spacer. The effect of the nanostructuring process on the magnetic properties of patterned bilayers and PSV systems will be illustrated.

Acknowledgments:

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#321 - Magnetic anisotropy in Co/Pt multilayers: ab initio calculations and experiments

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Co/Pt magnetic multilayers (MLs) are attractive systems for applications as storage media in high-density magneto-recording media and spintronic devices. Strong perpendicular magnetic anisotropy (PMA) of $[Co_n/Pt_m]_x$ superstructures, mainly due to the prominent presence of symmetry-breaking elements (interfaces) in the layered structure [1], is their key characteristic. Various studies have demonstrated that the strength of the PMA can be tuned by varying structural and micro-structural features, such as thickness of the Co_n/Pt_m unit, superstructure periodicity, and crystallographic orientation [2] of growth. In particular, the magnetic anisotropy is highly sensitive to Co thickness: the highest values of PMA have been obtained for 1−2 monolayers of Co [2], while different thickness thresholds (n_{thr},) for in-plane magnetization flipping have been found, mainly depending on the MLs crystallographic orientation.

In this work, *ab initio* electronic structure investigations have been performed to determine the magnetic anisotropy energy (MAE) of $[Co_n/Pt_m]_x$ MLs. MAE is obtained from non-collinear spin-polarized total energy calculations within Density Functional Theory (DFT) in the Generalized Gradient approximation [3], using plane-waves and projector augmented-wave method implemented in the VASP code [4]. We varied Co and Pt thickness as well as the number of repetitions in a (1x1)-fcc Pt_{sub}-$[Co_n/Pt_m]_x$ supercell with two possible orientations of *z*-axis, i.e., [100] and [111]. A Pt substrate is explicitly included in the calculations, at fixed bulk atomic positions; all other atomic distances have been relaxed by force minimization. DFT MAE values show indeed that the stability of out-of-plane magnetization is primarily dependent on the number of Co layers and on ML orientation, with a larger Co thickness threshold (n_{thr}≈ 8Å) found for [111]-oriented MLs with respect to [100]-oriented ones (n_{trh}≈4Å).

Theoretical results are compared to experimental characterizations (both structural and magnetic) of Co/Pt MLs grown by magnetron sputtering. We interpret the magnetic anisotropy features through *ab initio* MAE, in terms of a possible decomposition of the total magnetic anisotropy into bulk-like and surface/interface contributions. The competition between the anisotropy of internal Co layers (mainly favoring out-of-plane crystalline directions resembling Co hcp-(0001) easy axis) and in-plane interface anisotropy is discussed, with the aim of setting up a predictive model to optimize MLs compositions realizing high PMA.

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[1] M. T. Johnson et al., Rep.Progr.Phys. **59**, 1409, (1996)

[2] C. Lin et al., JMMM **93**, 194, (1991); H. Nemoto and Y. Hosoe, JAP **97**, 10J109 (2005)

[3] J. P. Perdew et al., PRL **77** (1996) 3865

[4] G. Kresse and J. Hafner, PRB **47** (1993) 558; P. E. Bloechl, PRB **50** (1994) 17953

#322 - Highly textured FeCo thin films deposited by low temperature pulsed laser deposition

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Pulsed Laser Deposition (PLD) technique has been widely and successfully used to deposit complex metal oxide materials [1], while only few examples are reported on metallic thin films grown by PLD. In this work we demonstrated that properly choosing the experimental conditions, high quality continuous $Fe_{50}Co_{50}$ thin films, of great interest for a number of applications including spintronics, can be prepared at room temperature, thus paving the way to a simple process to fabricate advanced multifunctional films and heterostructures combining metallic and oxide materials [2].

The effect of the deposition temperature on the crystallographic orientation was investigated by combining XRD and HRTEM analyses and correlated with the magnetic anisotropic properties measured by angle dependent hysteresis loops. Highly textured films with a bcc structure and a very smooth surface were obtained, the film being [100] and [110] oriented at T_{dep} = 25 °C and 150 °C, respectively. The cubic symmetry is reflected in the angular dependence of remanent magnetization, showing a 4-fold feature, whose in-plane distribution is consistent with the different crystallographic orientations of the films. The high structural quality, observed even at room temperature, is reflected in a high value of the saturation magnetization (~1.88 MA/m) and a low coercivity (~2 mT at 25 °C and ~4 mT at 150 °C, along the easy-axis), matching the requirements for technological applications. The thin film growth mechanism is also discussed. (This work was supported by MIUR, under the project FIRB2010 – NANOREST).

[1] P.R. Willmott, *Prog. Surf. Sci.* 76, 2004 163

[2] G. Varvaro, D. Peddis, G. Barucca, P. Mengucci, V. Rodionova, K. Chichay, A. M.Testa, E. Agostinelli, S. Laureti, *ACS Appl. Mater. Interfaces* 7, 2015 22341

#323 - Supporting magnonic multimode resonances of YIG in 3D microwave cavity

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Recently, the hybridization of microwave-frequency cavity modes with collective spin excitations attracted large interest. The final goal of these studies is the implementation of quantum computation protocols exploiting the transfer of information among these two physical systems. In this frame, important results were obtained, such as the demonstration of magnon-based memories at room temperature [1]. Another major advance was the implementation of hybrid systems among ferromagnetic magnons and superconducting qubits, where the microwave cavity acts like a bus that enables correlation between electronic transport in dielectric materials and magnetization precession in high spin density crystals [2]. Recently, Tang et al. described coherent photon-phonon interactions within a magnonic resonator working as an information trasductor device [3].

Here, we report the strong coupling of magnetization precession modes in a small Yttrium Iron Garnet (YIG) sphere to the microwave photons resonating in a tridimensional aluminum cavity. YIG is a very interesting material having a spin-wave decay length as large as several centimeters which allows magnons to propagate over a long distance. In our experiments, an YIG sphere was sequentially placed in cavity magnetic antinodes of the first two electric modes, respectively at 8.401 GHz for TE101 and 10.361 GHz for TE102. In each case, as a function of the applied magnetostatic field, we recorded the cavity response in stationary regime and evaluated the cavity signal relaxations after a MW excitation pulse.

For both the investigated modes, hybridization between magnons in the ferrimagnetic crystal and photons in the cavity was demonstrated by the observation of clear avoided crossings in strong coupling regime and an identical cooperativity value (11.2 MHz), which was evaluated by fitting the output signal envelope decay by a Rabi’s oscillation function.

[1] X. F. Zhang, C. L. Zou, N. Zhu, F. Marquardt, L. Jiang, and H. X. Tang. Magnon Dark modes and gradient memory. Nature Communications 6, 8914 (2015).

[2] Y. Tabuchi, S. Ishino, A. Noguchi, T. Ishikawa, R. Yamazaki, K. Usami, and Y. Nakamura. Coherent coupling between ferrimagnetic magnons and a superconducting qubit. Science 349, 405 (2015).

[3] X. Zhang, C. Zou, L. Jiang, and H.X. Tang, Cavity Magnomechanics. Science Advances 2, 3, e1501286 (2016).

#324 - Bi5T5O17: a (hyper) ferroelectric metal

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We report that the layered perovskite Bi5Ti5O17 is a metal that is also, natively, ferroelectric, i.e. exhibits coexisting metallicity (Fermi surface and conductivity) and switchable spontaneous polarization. Also, it is able to support a depolarizing field in thin film form [1]. In this sense this material is also an example of hyperferroelectric. Its behavior is due to the peculiar partial self-screening due to the response of free charge.

[1] A. Filippetti, V. Fiorentini, F. Ricci, P. Delugas, and J. Iniguez: Prediction of a native ferroelectric metal, Nature Commun. 8, 11211 (2016)d.

#325 - Magneto-piezo-resistive composites optimization in prospect of micro-devices development

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Magneto-piezo-resistive composites are made of magnetic microparticles homogeneously dispersed into an elastomer matrix preventing their direct contact during the production process even at volume fractions slight above the percolation threshold. Bar shaped samples exhibit two main properties: noteworthy deformation induced by a moderate external magnetic field (direct elastomagnetic effect) and giant change of resistivity produced by a moderate strain (piezoresistivity). The coexistence of elasto-magnetism and piezo-resistivity has give rise to the so-called magneto-piezo-resistive (MPR) effect: giant change of sample resistance due to the application of a magnetic field gradient [1]. Several applications of this effect have been developed, as position or local magnetization sensors [2,3].

The MPR effect performance depends on particle average size, shape and preferential orientation. This work constitutes an insight on the role of particle orientation in the case of Fe microparticles optimized in size and shape on the basis of previous investigations [1-3]. In particular, they look as thin chips, exhibiting a moderate planar shape anisotropy. Longitudinal hysteresis loops, elastomagnetic strain, piezoresistive and MPR sensitivities were compared in the case of homogeneous filling particles distribution, but random, longitudinal or transversal preferential orientation of their plane of easy-magnetization.

This investigation show that the longitudinal pre-orientation of the particles is able to give a 20% enhancement in the sensitivity compared to recent MPR sensors for detecting magnetic field direction [3].

MPR effect in recently produced elastomagnetic nanofibers (ENF) is presented. Silicone/PVP Core/Sheath ENF have been fabricated by using a home-made electrospinning equipped with a metal ultra-coaxial needle (inner channel 27G outer channel 18 G - MECC, Japan). The presence of Ni nanoparticles (NPs) in the silicone fiber core influences the process of fiber formation, inducing a drastic decay of mesh size – ca. 50% of average fiber diameter reduction respect unloaded ones. Despite the not homogeneous distribution of NPs, ENF show a noticeable stretching accompanied by reversible longitudinal and transversal strains under applied longitudinal magnetic field gradient.

The reported new data clarify the intriguing coupling of elasticity, magnetization and electric conduction in innovative miniaturized MPR composites, furnishing fundamental data in view of their application as transducer material in biomedical or magnetic field sensors.

Ref.

[1] G. Ausanio, C. L. Hison, V. Iannotti, L. Lanotte jr, and L. Lanotte, J. Appl. Phys. 110, 063903 (pp. 5) (2011).

[2] G. Ausanio, V. Iannotti, E. Ricciardi, L. Lanotte jr, L. Lanotte, Sensor Actuat A-Phys 205, 235-239 (2014).

[3] V. Iannotti, G. Ausanio, L. Lanotte jr, L. Lanotte, Express Polym Lett 10, 65-71 (2016).

#326 - Magnetic states of MnP under hydrostatic pressure

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The discovery of superconductivity (SC) in MnP in late 2014 has attracted much interest since it constitutes the first observation of a manganese based superconductor. In the normal state, MnP is characterized by a complex magnetic phase diagram [1-4] which alternates ferromagnetic and helimagnetic orders as a function of pressure and temperature. When the magnetic order disappears, above 70 kbar hydrostatic pressure, a small superconducting dome with TC, max ~ 1 K sets in. The superconducting state appears close to the pressure induced magnetic to paramagnetic transition thus resembling the unconventional superconductors phase diagrams. It is therefore clearly important to clarify the details of the long range order which could be involved in the pairing mechanism. We have investigated the magnetic part of the phase diagram with both experimental and theoretical methods. We confirmed [3-4] that the high pressure helical magnetic state is different from the one observed at ambient pressure below 50 K, thus validating recent neutron scattering results and against X-ray scattering based observations. We have finally obtained, from density functional theory simulations, indications of the presence of competing magnetic states close to the magnetic phase boundary, again in support of the hypothesis of unconventional SC. [1] J. G. Cheng et al, Phys. Rev. Lett. 114, 117001 (2015). [2] E. E. Huber and D. H. Ridgley, Phys. Rev. 135, A1033 (1964) [3] R. Khasanov et al, Phys. Rev. B 93, 180509(R) (2016) [4] M. Matsuda et al, Phys. Rev. B 93, 100405(R) (2016)

#327 - Magnetic Excitations in Multiferroic GdMn2O5

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RMn_2O_5 compounds recently attracted attention due to complex frustrated ground state and unconventional excitations. YMn2O5 with non-magnetic rare earth shows incommensurate spiral state with spins in the neighboring chains aligned at 90-degrees to each other[PRL]. Here we model the phase diagram and magnetic excitations in GdMn2O5, with magnetic rare earth.

#328 - Ab initio molecular dynamics study of aqueous solutions under an electric field

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We report on an ab initio molecular dynamics study of aqueous solutions (LiCl, NaCl, KCl) under the effect of static electric fields. We found that at low-to-moderate field intensity regimes chlorine ions have a greater mobility than cations which, being a sort of ‘‘structure makers’’, are able to drag their own coordination shells. However, for field strengths exceeding 0.15 V/Åthe mobility of cations overcomes that of chlorine ions as both types of ions do actually escape from their respective hydration cages. The presence of charged particles lowers the water dissociation threshold (i.e., the minimum field strength which induces a transfer of protons) from 0.35 V/Åto 0.25 V/Å; moreover, a protonic current was also recorded at the estimated dissociation threshold of the solution. The behaviour of the current–voltage diagram of the protonic response to the external electric field is Ohmic as in pure water, with a resulting protonic conductivity of about 2.5 S/cm. This value is approximately one third of that estimated in pure water (7.8 S/cm), which shows that the partial breaking of hydrogen bonds induced by the solvated ions hinders the migration of protonic defects.

#329 - Oxidation protective coatings by pack cementation for Cf/C composites

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Carbon-carbon composites are attractive materials for several industrial and transport applications, but their use is limited by low oxidation resistance. Different protective solutions have been studied for many years and the most promising method, especially at high temperature applications, implies an overlay coating. Pack cementation represents an interesting solution, mainly because is a simple and low-cost method to protect materials against oxidation. Pack cementation was developed in the past to protect metal components, but in more recent years it has been also applied to ceramic materials. A process, based on the two-step pack cementation, was applied to the C_f/C composites obtained by the Chemical Vapour Infiltration (CVI) pilot plant, located in our laboratory. In the first step, a porous layer of SiC was obtained by using a pack mixture of Si and C powders, whereas Si, C and $MoSi_2$ mixed powders were used in the second step in order to densify the protective coating. Thermal analysis, scanning electron microscopy investigations and X-ray diffraction analysis were carried out to study the behaviour of coated C_f/C composites after oxidation tests.

#330 - Nitride films produced via HiPIMS for extreme conditions

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AlTiN is a promising anti-oxidation and corrosion protective material. Thanks to its good chemical stability, the blocking oxygen diffusion ability, the formation of a coherent, compact and adherent alumina scale, it is suitable to operate in harsh environments and in extreme conditions.

In this work, the intrinsic properties of AlTiN films produced by reactive High Power Impulse Magnetron Sputtering (HiPIMS) have been deeply investigated. HiPIMS is an emerging PVD technology, which produces an ultra-dense plasma leading to high-density coatings with reduced columnar structure, residual stress and deposition temperature, improved toughness and enhanced adhesion, even for complex-shaped surfaces.

Different materials were chosen as substrates, considering their technological purposes: AISI 304 stainlesssteel, T91 martensitic steel, which is proper as structural material for nuclear fusion and fission plants and for future generation nuclear fast reactors, and γ-TiAl, a light alloy designed for aeronautic applications, which is a promising candidate to replace Ni based super-alloy in aircraft turbine engines.

Morphology, microstructure, mechanical properties and residual stress state were evaluated by means of high-resolution techniques. Microstructural and compositional analyses were carried out by Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS). Moreover, nano-mechanical properties of films, such as hardness (H) and elastic modulus (E), were estimated by means of nano-indentation, whereas adhesion was evaluated by scratch tests. In order to investigate the average residual stress in the produced coatings, a recently proposed approach was exploited. It involves an incremental FIB milling of annular tracks at material surface, combined with high resolution SEM imaging.

Equipments simulating the real harsh operating conditions were used to evaluate performances of produced coatings. Thus, AlTiN/T91 films were exposed to long duration corrosion tests (550°C for 1200 h) in a molten Pb bath. Instead AlTiN/γ-TiAl films for gas turbine components, they were treated in a burner-rig apparatus for repeated thermal shock cycles up to 950°C, in oxidizing atmosphere.

Furthermore, the tribological properties of films deposited on T91 substrates were characterized by means of linear wear tests. Similarly, also films grown on γ-TiAl were evaluated tribologically before and after cyclic thermal shock treatments.

The promising outcomes resulting by the extensive characterization of the different coatings permit to state that the HiPIMS technique is an enabling technology to produce high quality films for extreme conditions.

#331 - Effect of SiC addition on the microstructure and mechanical properties of UHTCMCs based on ZrB2 – SiC – Cf

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The demand for advanced Thermal Protection Systems (TPS) related to hypersonic flight and rocket propulsion, where temperatures as high as 2000 °C are reached, has fostered the development of a new class of materials. The currently available Ceramic Matrix Composites (CMC), based on Carbon/Carbon and Carbon/SiC composites, display excellent thermomechanical properties but the carbon fibers start oxidizing at temperatures as low as 500°C. On the other hand, Ultra-High-Temperature-Ceramics (UHTC), such as transition metal diborides, are characterized by high ablation and oxidation resistance in extreme conditions and high thermal conductivity, but their low fracture toughness limits their use.

By combining the good damage tolerance of CMCs and the oxidation and ablation resistance of UHTCs, these limitations could be overcome.

In this work, UHTCMCs based on ZrB_2 – SiC – Cf were prepared by hot pressing at 1900°C under a uniaxial pressure of 40 MPa and a holding time of 10min.

SiC in amounts ranging from 5 to 20% was introduced in order to improve the densification, oxidation resistance and mechanical properties of the composite. Continuous carbon fiber preforms were used as reinforcement in order to increase damage tolerance.

The microstructure was analyzed by SEM-EDS and image analysis. Bending strength was determined by 4-point bending tests while fracture toughness was evaluated by Chevron-Notch-Bending test.

Results show that an increase in SiC amount promotes the densification of the composite. SiC particles are finely dispersed in the matrix with an average particle size of 524 nm, as ascertained by image analysis. The sample with 5% SiC shows comparatively higher values of bending strength but lower values of fracture toughness.

#332 - Protective transition metal nitride coatings

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Coated cutting tools may allow a significant increase in cutting speed, decreasing the machining times and their relative cost. The coatings can facilitate the processing of difficult-to-machine materials such as aluminum, titanium and magnesium alloys, and high-alloy steels, providing low friction coefficient, high wear resistance, low tendency to adhere, thermal stability, hardness and oxidation resistance.

Hard coatings based on ternary Ti–Al–N are commercial products currently employed in many industrial applications and replaced TiN coatings due to their chemical and physical features.

With the further increase of requirements, a lot of efforts are made to increase mostly the properties of Ti–Al–N by adding alloying elements X to develop the quaternary Ti–Al–X–N coatings.

With this aim, we have undertaken a systematic study about the quaternary TiZrAlN coatings and relative binary ZrN and ternary TiAlN realized using innovative PVD techniques such as Dual Magnetron Sputtering and High power pulsed magnetron sputtering.

The coating process is conducted at relatively low temperature (substrate temperature below 500 °C) in co-deposition configuration. The chemical composition depended on the process parameters such as relative distance from the two targets, gas pressure, substrate temperature, powers and pulse duration.

On the other hand, the chemical composition influences the crystalline structure: the coatings crystallize in a face centered cubic (fcc) NaCl-type or a hexagonal close packed (hcp) or wurtzite-type (w) phase varying the TiAl content.

The combination of diagnostic analysis as x-ray diffractometry, Raman spectroscopy and nanoindentation allows for identifying, describing, and understanding the mechanisms and processes that govern the coating performance.

For the main engineering applications, the cubic structure is preferred due to the superior mechanical and tribological properties.

#333 - Extreme ion irradiation of oxide nanoceramics

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Oxide nanoceramics combine the enanced radiation tolerance of nanocrystalline materials with the chemical inertness of oxides, and are promising materials for highly corrosive and intense radiation environments. In this work, the properties of oxide nanoceramic thin films are evaluated as radiation damage approaches extreme levels, reaching or even exceeding those anticipated for advanced nuclear systems. In particular, taking Al2O3 as a model material, an effort is made to establish a correlation between the irradiation spectrum and the observed evolution of the oxide's structural features and mechanical properties. The irradiation conditions are relevant for advanced nuclear systems, and consist in low, moderate, high and extreme radiation damage levels at 600°C -namely, 20, 40, 150, 250, and 450 displacements per atom. A comprehensive analysis of the irradiated nanoceramic is accomplished by XRD, TEM, STEM and nanoindentation. The results confirm that grain growth is the main structural change induced by irradiation in oxide nanoceramics. This structual change maifests mechnically through an initial increase of hardness that is well fitted by the Hall-Petch relationship, and eventually through softening in the extreme damage range. Stiffness increases sub-linearly with damage before reaching a plateau. Further, both hardness and stiffness depend on the phase present. The phase evolution may be depth-dependent, and depends strongly on the ion utilized and on the irradiation spectrum. To conclude, it is shown that the coatings successfully provide negligible hydrogen permeation and superior corrosion resistance to structural steels at high temperature in chemically aggressive media. All these features are of particular interest for accident tolerant fuel concepts for current generation nuclear reactors, and for future fuel concepts in Generation IV and fusion systems.

#334 - High performance alumina bsed tritium permeation barrier coatings

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Concerning nuclear fusion systems, namely ITER (International Thermonuclear Experimental Reactor) and DEMO (DEMostrator Reactor), which take the tritium deuterium reaction as a reference, tritium breeding from Pb-16Li eutectic is one of the focus point of technological R&D activities worldwide. The permeation of tritium through the foreseen steels of eutectic Pb-Li Breeder Blanket (BB) concepts is a challenge for the tritium balance in the reactor. Once tritium is produced, it must be appropriately extracted from the Pb-16Li eutectic, precluding losses by permeation through the steels towards the Helium or Water cooling systems. In order to avoid such losses, an adequate permeation barrier is required. We report on the barrier performance of advanced Al_2O_3 ceramic coatings, which are suitable for this task owing to their chemical inertia, high density and amorphous character. Permeation tests are performed at the ENEA Research Center of Brasimone (Italy). In particular, hydrogen gas is used in order to simulate tritium. Tests are performed with a fixed barrier thickness (5 µm) and under a fixed hydrogen partial pressure (100 mBar). The temperature of the tests is varied within the range 523-923 K. Hydrogen permeation through coated disc specimens is detected using a quadrupole mass spectrometer. Our results show that the Al_2O_3 coatings tested are a promising tritium permeation barrier, with permeation reduction factors (PRF) approaching 10^5. Last, but not the least, we show that the coatings perform well as anti-corrosion barriers in harsh environments relevant for BB concepts, such as liquid lead.

#335 - Investigating the thermoelectric response of individual nanostructures

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Nanowires are ideal for exploring the thermoelectric response of nanostructured materials, in particular for what concerns the impact of carrier density, of low-dimensionality and of the suppression of thermal conductivity by interface scattering. In my talk, I will review our recent activities on the thermoelectric benchmarking of individual nanostructures and discuss the technical/scientific challenges and opportunities it entails. I will in particular introduce techniques based on the field-effect modulation of the Seebeck coefficient and on spatially-resolved Raman spectroscopy for the measurement of thermal conductivity. Results on the full thermoelectric assessment of Se-doped InSb and InAs nanowires will be presented.

#336 - Pulsed Laser Deposition of doped zinc antimonide thin films for thermoelectric applications

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Zinc antimonide (ZnSb)-based nanostructured thin films were produced by Pulsed Laser Deposition (PLD) using a multi-target deposition system. ZnSb is a promising thermoelectric material for low-medium temperature applications.The spontaneous tendency to deposit nano-structured materials by PLD has been exploited to grow thin films characterized by crystallite size smaller than 35 nm, in agreement with the specific dimensions useful to drastically lower the thermal conductivity.The thin films were prepared according to a multi-layer structure, obtained by adding different dopants within the ZnSb matrix. The influence of different deposition parameters (such as repetition rate, pulse energy, and substrate temperature), and the effect of the dopant introduction on the structural, compositional, and electronic properties of the deposited films were studied in the temperature range 300-600 K. The evaluation of the performance of the nanostructured films for the thermoelectric conversion was carried out by the determination of the Power Factor (*PF*).

#337 - Effect of processing routes on the synthesis and properties of Yb0.25Co4Sb12

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Yb-filled Co_4Sb_{12} n-type skutterudite is among the most promising thermoelectric (TE) materials for automotive applications with a value of ZT ranging around 1 at 600 K [1]. Manufacturing of reliable TE modules requires dense materials with good mechanical and thermal stability.

In this work, we study the effect of different processing routes on the synthesis of the $Yb_{0.25}Co_4Sb_{12}$ compound and its properties. Precursors materials were prepared from the melt by 1) casting of a bulk, 2) rapid solidification of thin ribbons.

The kinetics for obtaining the Yb-filled Co_4Sb_{12}single phase by annealing the precursor materials was studied both for bulk and rapidly solidified samples.

As prepared and annealed precursors materials were powdered for the subsequent sintering process. Sintering was performed on the different precursors materials by Open-Die-Pressing [2] and Electro-Sinter-Forging [3].

The structural, microstructural, mechanical and thermoelectric properties of the sintered bulk samples were correlated to the different precursors materials and the different sintering techniques.

[1] G. S. Nolas, M. Kaeser, R. T. Littleton, T. M. Tritt, Appl. Phys. Lett., 77 (2000) 1855

[2] S. Ceresara, C. Fanciulli, F. Passaretti, D. Vasilevskiy, J. Electron. Mater. 42 (2013) 1529

[3] A. Fais, M. Actis Grande, I. Forno, Mater. Des. 93 (2016) 458

#338 - MEMS thermoelectric generators based on top-down silicon nanowires for micro-energy harvesting

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A new technology for fabricating MEMS thermoelectric generators based polycrystalline silicon nanowires fabricated with top-down technology is presented. The devices are built integrating dense arrays of nanowires on bulk micromachined silicon structures that are used to obtain a significant thermal gradient on the nanowires and generate electrical energy. In order to increase the energy conversion performance, dense nanowires arrays are fabricated by stacking the nanowires on three levels using a multilayer Si3N4/SiO2 thin film template. A thermal heat sink can be mounted on the bulk micromachined masses of the MEMS in order to enhance the thermal exchange with the environment and increase the thermal gradient across the nanowires. The devices have a size of 10x10x0.5 mm^3 and are able to generate a power around 1 µW when placed on a heat source at 200 °C. The generated power is sufficient for powering a wireless sensor node composed by a temperature sensor and a low-power wireless unit applied to an industrial fryer

#339 - Interacting QD heat engine in the linear response regime and beyond

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In this work we study the thermoelectric properties of an interacting quantum dot (QD) weakly coupled to two or more electronic reservoirs, aiming at assessing its heat-to-work conversion properties. In particular, we revise the sequential tunnelling formalism to deal with generic multi-level, multi-terminal interacting QDs in the linear response regime and beyond.

In the linear response regime we derive, for a two-terminal system in the quantum limit (small temperatures), analytical expressions for the transport coefficients and for the figure of merit *ZT* which allows us to determine analytically the optimal system parameters in order to maximize the maximum power, the maximum efficiency, and the efficiency at maximum power. We also numerically study a three-terminal system to point out the advantages, in terms of efficiency and power output, brought by the additional (third) terminal.

Moreover, we extend the investigation by going beyond the linear response regime to assess the influence of the various parameters defining the system on the efficiency and power output. We find in general that both quantities can be greatly enhanced with respect to their linear-response values. In particular, we identify the conditions under which the efficiency at the maximum power goes above the Curzon-Ahlbornlimit, while the power remains close to its maximum value.

#340 - Structural texture induced in SnSe thermoelectric compound via open die pressing

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The publication of an unprecedented result for ZT value on bulk material observed on SnSe single crystal, has recently renewed the interest in this material. The result reported by Zhao *et al*[1] is associated to a structural transition of the material at high temperature and is displayed only along one of the directions of the crystal lattice. The anisotropy observed in the other directions could explain the low results observed up to now on polycrystalline samples of the same compound. In fact, beside a ZT value equal to 2.6, at the same temperature, a value of 0.8 has been observed along another axis. Investigations performed by other groups on polycrystalline samples have still not been able to reproduce the same results reported for single crystals.

This work is focused on the possibility to obtain a polycrystalline sample with structural properties close to the single crystal ones and thermoelectric properties improved by the improved phonon scattering promoted by the grain boundaries. To obtain this result, the polycrystalline material has to be strongly textured along a crystallographic direction able to take advantage of the natural anisotropy reported. The material has been prepared following a standard synthesis route, but instead of a slow growing process proposed in literature for single crystal production, the produced ingots have been powdered and sintered using open die pressing process. The resulting bulks display good compaction, improved mechanical properties and strong texture of the phase.

Structural and morphological analyses have been performed to verify the successful orientation according to the (*4,0,0*) cleavage plane. The structural transition responsible for the ultra-low thermal conductivity, has been investigated and possible irreversible effects on the starting phase due to thermal cycling have been evaluated. Preliminary measurements of thermal conductivity display a lower value as respect to the one reported in literature for the same material.

1 L.-D. Zhao, S.-H. Lo, Y. Zhang, H. Sun, G. Tan, C. Uher, C. Wolverton, V.P. Dravid and M. Kanatzidis, Nature 508 (2014) 373

#341 - III-V heterostructured nanowires for thermoelectric applications

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III-V semiconductor nanowires (NWs) and their related heterostructures have been intensively investigated in view of their potential interest for different applications. In particular the peculiar shape and dimensions of the NWs have opened the way to their exploitation in thermoelectric devices. Compared to bulk materials, NWs show important advantages such as the increase of power factor and thermal conductivity suppression, boosting the thermoelectric efficiency (ZT). At present, relatively small values for ZT at 300K have been obtained for NWs with respect to bulk crystal: this is mostly due to the impact of surface effects on electron mobility. These limitations are likely to be solvable by the design of suitable heterostructures that protect electrons from scattering, However, the growth of heterostructured NWs with good morphology and sharp interfaces between the two materials is still challenging and many growth issues have to be addressed yet. Moreover, the development of NW-based thermoelectric devices depends on the ability to tightly control properties such as morphology, crystal structure, and composition, which can be obtained only if growth parameters and protocols are properly optimized. Among the different methods exploited for the NW growth, the chemical beam epitaxy (CBE) is a very appealing technique since it offers important advantages such as monolayer thickness control, high flexibility and reproducibility. Here, we present the synthesis of heterostructured NWs by means of CBE using different approaches: catalyzed growth using Au nanoparticles and catalyst-free methods. By employing these two methods and by suitable tuning the growth parameters, such as metalorganic pressures and growth temperature, we have successfully grown axial InAs/InP and radial InAs/GaSb heterostructured NWs with controlled morphology and crystal structure.

#342 - Portable Thermoelectric Power Generation based on Catalytic Combustor for Low Power Electronic Equipment

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During the last years, the miniaturization of mechanical and electromechanical engineering devices has received growing attention, thanks to the increasing interest in the areas of microelectronics, biomechanics, and also to the progress made in microfabrication techniques. The advances in miniaturized mechanical devices open new opportunities in the field of micro power generation, allowing the development of power-supply devices with high specific energy (small size, low weight, long duration). The growing interest in miniaturized devices is further boosted by the desire to replace batteries with hydrocarbon-based fuels for portable power sources.

The coupling of thermoelectric modules with catalytic combustors has been explored in several works. The advantage of this approach is the fine tunability of combustion conditions allowing a precise temperature control of the heat source coupled to the thermoelectric modules. As a result, catalytic combustors allow taking advantage of the high power density associated to hydrocarbon fuels in a controlled and safe process. A further advantage is the possibility to produce small devices, having lower input power requirement, and being therefore compatible with modern mobile/portable technologies.

In this work a novel catalytic meso-scale combustor fuelled with propane/air mixture has been coupled with two conventional thermoelectric modules. The wafer-like combustor is filled up with commercially-available catalytic pellets of Platinum (1% weight) on alumina. In order to calibrate the operating conditions, the analysis of the temperature values and distribution across the combustor surfaces have been carried out.

Characterization of exhaust gases concentration and of pellet aging were performed in order to investigate combustor properties. The results of the combustor characterization have guided the coupling of the combustor with commercially available thermoelectric modules using at the cold side a water cooled heat exchanger. The system obtained has been characterized measuring the delivered electric power in different operating conditions. Efficiency estimation proves that the system is suitable for small portable power generation.

Following the results obtained, the system has been scaled down with the aim to design a portable system suitable for common batteries replacement for small device powering.

From the preliminary results the system can provide about 1.5 V and 2.2 A by a fuel consumption of about 5 g/hr, an output close to common portable batteries used for electronic devices.

Tests are undergoing in order to further improve the system in terms of power production by using high power generation modules. Moreover, in order to increase automaticity and portability, passive cooling is going to be implemented in the system.

Friday December 16

Session title	Chairman
Magnetic materials for medicine	Valentin Alek Dediu
Novel 2D materials based devices	Khatuna Kakhiani
Fuel cells	Aurora Rizzo
Optical fiber materials and devices	Giuseppe Gigli
Active packaging materials	Cosimo Carfagna

#343 - Novel superparamagnetic iron-doped hydroxyapatite nanoparticles to direct cellular fate

Samuele Dozio - CNR-ISTEC

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INTRODUCTION: Strong coupling between nanotechnology and cell/molecular biology leaded to a breakthrough in medicine in the last decade due to the exiting opportunities in designing and developing a tailored approach in response to different disease. Magnetic nanoparticles (NPs) have attracted the attention of scientific community for biological and medical purposes as promising materials in drug or gene delivery, DNA/biomolecules separation, hypothermal treatment of tumours, contrast agents for imaging, and recently in tissue engineering and theranostic applications. Here novel biomimetic, fully biodegradable and cytocompatible NPs fabricated by doping hydroxyapatite (HA) with Fe ions (FeHA), avoiding the presence of magnetic secondary phases and coating, were biologically tested. A live monitoring of intracellular fate of FeHA NPs and the biodistribution with a pilot study *in vivo* were deeply investigated.

METHODS: FeHA NPs were prepared by a neutralization process using $FeCl_2$ and $FeCl_3$ as a source of Fe2+ and Fe3+ doping ions; HA NPs and two commercial fluidMag NPs (Chemicell) were used as control groups. Mouse pre-osteoblast cells line (OBs), MC3T3-E1, used as a normal osteoblast in vitro models and human Osteosarcoma cell line, MG63, used as a cancer cells in vitro model, were cultured with 100 µg/ml NPs up to 72 hours. The molecular pathways of cellular response (apoptosis/necrosis, ROS production and autophagy) to NPs were investigated. Moreover the mechanism of internalization by Caveolae-mediated endocytosis was studied. In a pilot in vivo experiment the biodistribution of different concentrations of NPs was evaluated.

RESULTS: The *in vitro* results showed that FeHA NPs were rapidly and easily internalized by both cell lines without producing significant cell damages and death. A different behaviour induce by FeHA NPs were observed in cancer cells respect to normal OBs. The OBs uptake of FeHA NPs seems to be mediated by Caveolae-mediated endocytosis, while a different endocytic mechanism is required by MG63 cell line. Moreover, FeHA NPs seem to act as modulator of autophagy pathway. The *in vivo* pilot study showed the absence of systemic toxicity even with the higher concentration.

DISCUSSION & CONCLUSIONS: The data obtained on the cellular uptake of FeHA NPs lay the basis to clarify the intracellular fate of the FeHA NPs and open brilliant prospective for their use as innovative tools for nanomedicine. FeHA NPs could be injected and guided to a desired body site by an external magnetic field, avoiding any toxicity. Moreover, FeHA NPs could be easily functionalized with several biomolecules or drugs to direct cell fate in medical applications.

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#344 - Aggregation of magnetite nanoparticles: the influence on the magnetic hyperthermia properties c hyperthermia properties of magnetite nanoparticles

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Magnetic nanoparticles are considered key nanomaterials for future information storage, energy and biomedical and pharmaceutical applications. In particular in the biomedicine, they are suitable for both diagnostics, therapeutics and delivery. They are proposed as contrast agents to enhance the magnetic resonance imaging signal, while in the field of therapeutics, they can be used as magnetic vectors in drug delivery and/or as heat mediators in hyperthermia treatment. In this last application, the apoptosis of cancer cells is produced by the local increase of the temperature thanks to the heating of the magnetic nanoparticles contained in the cells under a oscillating magnetic fields. The physic-chemical mechanisms and effects that give rise to the magnetic energy losses are under study. One of the most discussed questions is the role of the interparticle and intraparticular interactions induced by the different aggregation levels, which can be different in the laboratory conditions and into the cells.

In this study different classes of aggregates of magnetite nanoparticles have been synthesized using several techniques at which corresponds different magnetic hyperthermia strength. First, monodispersed magnetite nanoparticles of very similar sizes (7 nm) have been synthesized using coprecipitation and thermal decomposition routes. Thanks to the different steric stabilizations, the nanoparticles are isolated or forming aggregates of around 140 nm of size, respectively. On the other hand magnetite nanoparticles have been prepared by oriented aggregation, exploiting the action of calix[8]arene, an organic macrocycle capable to complex Fe ions, during the synthesis. The control over the aggregation degree allows tuning the morphology of the product that can vary from multi-core aggregated nanoparticles to nano-octahedra, with a dramatic change in the magnetic properties. Octahedral magnetite nanoparticles present a ferrimagnetic behavior, typical of magnetite above 40 nm in size. Conversely, multi-core nanostructures present a narrower hysteresis loop, and remarkable heating capacity under an alternating magnetic field.In the investigated synthesis the aggregates in which dipolar interparticle interactions are dominant exhibit better hyperthermia features than its counterparts. Nanostructural and Lorentz Force microscopy characterizations and magnetic studies have been performed to understand the mechanisms that determine the observed hyperthermia properties.

#345 - Perspectives in the design of polymer-based MRI contrast agents

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Magnetic Resonance Imaging (MRI) represents the first-line diagnostic imaging modality for numerous indications. Signal intensity in MRI is related to the relaxation rate of in vivo water protons and can be enhanced by the administration of a contrast agent (CA) before the examination.

These CAs utilize paramagnetic metal ions to enhance the contrast in an MR image by positively influencing the relaxation rates of water protons in the surroundings of the tissue in which they localize.

Among different CAs, Gadolinium (Gd) contrast medium is used in up to 30% of MRI scans. However, like most of the clinically-used CAs, it is characterized by a relaxivity well below its theoretical limit, lacks in tissue specificity and causes allergic effects and nephrotoxicity.

In 2006, the impact of chemical rigidification on relaxivity of a “free” Gd-chelate was introduced by Port et al. [1] and later Decuzzi et al. [2] proposed an alternative strategy to improve relaxivity based on the geometrical confinement of Gd-based (CAs) within the porous structures of silicon microparticles. Furthermore, we have recently published an article [3] about the impact of biopolymer matrices on the relaxometric properties of CAs.

We propose a general strategy based on the formation of nanostructures for boosting the efficacy of commercial Gd-based CAs by using FDA approved biopolymers and that, at the same time, can also provide tissue specificity and reduce nephrotoxic effects.

Indeed, there are some general advantages in using nanotechnologies for enhanced MRI because of their capability to reach a specific target and to accumulate in the tissue or the possibility to reduce nephrotoxic effects. Furthermore, they can be useful to increase the relaxivity of the CAs.

Our strategy consists of increasing the rigidification of readily-available Gd-complexes within biopolymer matrices by controlling water dynamics, physicochemical interactions and polymer conformations. Some fundamental studies have been conducted to understand the thermodynamic modifications induced by the polymer–CAs interactions and, later, this optimized and characterized polymer matrix can be used for the rational design of nanostructures to recognize and accumulate within the diseased vasculature.

[1] M. Port, et al. C*ontrast Media & Molecular Imaging*, 2006, **1(3)**, 121-127.

[2] A. Gizzatov, et al. *Cancer Letters*, 2014, **352(1)**, 97-101.

[3] A. M. Ponsiglione, et al. *Interface Focus*, 2016, 6:20160061, *(in press)*

#346 - Electrostatically assembled Gold Nanorods and Silica-coated Magnetic nanoparticles for Targeted Photothermal Therapy

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Metallic Nanoparticles with Plasmonic properties have been widely studied in the last decade because of their tunable optical properties that allow to absorb or scatter light of a particular wavelength range depending on material and geometry of nanoparticles. Among other, gold nanoparticles (of different shapes) have widely proposed in literature for different biomedical applications, including photo-thermal ablation of cancerous masses with near-infrared laser (prior internalization), as demonstrated in several *In vitro* and *in vivo* trials.[1] However, cancer cell targeting is limited by several biological variables even with proper ligand surface functionalization, thus posing problems in dosimetry and difficulties in clinical translation of this technology. On the other hand, superparamagnetic iron oxide nanoparticles (SPIONs) have been demonstrated to have the capability to be accumulated by a magnetic field gradient directly inside the body thus enabling the possibility of implementing a magnetic targeting.[2]

Here we present a single nanoparticulate assembly (namely AuMag) that couple the plasmonic behavior of gold nanorods with the magnetic properties of silica-coated iron oxide nanoparticles, allowing magnetic targeted photothermal activity.

NIR-resonant gold nanorods have been fabricated by longitudinal growth of a gold nanoparticles seed solution and subsequently coated with poly styrenesulfonate (PSS) to acquire an average negative surface charge (- 50 mV). Iron oxide nanoparticles have been covered with a silica shell and subsequently coated with poly ethyleneimine (PEI) obtaining positive surface charge (+40 mV). Afterwards these particles has been mixed together to create the AuMag nanoassembly. Further BSA coating has been provided to increase colloidal stability in biological environment. In addition to spectroscopic characterization, complete morphological characterization has been done by transmission electron microscopy (TEM). Magnetic behavior of these particles has been also validate with a permanent neodymium magnet, allowing particles accumulation within a minutes. Temperature increase upon NIR laser stimulation has been also assessed with an infrared thermocamera and revealed almost instantaneous temperature rise with maximum temperature of 100 °C upon particles magnetic accumulation and NIR stimulation (70 mW optical power), showing excellent photothermal properties of the assembly.

Overall our experiments showed the possibility to use AuMag nanoparticles for targeted temperature increase upon magnetic accumulation and laser stimulation. Further *in vitro / in vivo* experiments will investigate the feasibility of the use of these nanoparticles for photothermal treatment of cancerous masses.

1. Huang, X., *et al.*, Lasers in medical science 23.3: 217-228 (2008)

2. Pankhurst, Q. A., et al., J. Phys D: Appl. Phys., 36, R167 (2003)

#347 - New magnetic microspheres obtained by bio-inspired synthesis, for controlled release of BMP-2 in bone tissue engineering

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The development of biomaterials enabling linking of bioactive molecules and characterised by stimuli-responsive release mechanisms is among the major research topics in biomaterial science. Bio-inspired synthesis processes can be applied to control the assembly of natural polymers and simultaneous mineralization with nano-apatites into hybrid gels that can be turned into biomimetic bone scaffolds [1] or also, into carriers for controlled drug release *in vivo*, thanks to the high density of exposed charged sites. Bone morphogenetic proteins (BMPs) are the most studied growth factors in bone tissue engineering, due to their claimed osteoinductive effect. However, the delivery of supra-therapeutic doses can result in severely harmful side effects, therefore a major effort is in the development of innovative systems able to bind anabolic factors and to guarantee their controlled release *in vivo* [2]. Recently magnetic materials have risen the interest of scientists as they enable remote control by magnetic signalling; in particular the recent development of a biocompatible superparamagnetic nanophase made of iron-substituted apatite (Fe-HA) promises new safer approaches in the development of magnetic materials for controlled drug delivery [3, 4].

Herein, a bio-inspired synthesis based on [5] was translated to a different natural polymer, i.e. a recombinant peptide based on human collagen type I (RCP) (commercially available as Cellnest^{TM}, by Fujifilm Manufacturing Europe B.V.), to generate mineralized hydrogels, then engineered into hybrid superparamagnetic microspheres proposed as smart carrier to control the BMP-2 release, by an oil-in-water emulsification process. A thorough investigation of chemical-physical composition, magnetic properties, cytocompatibility and expression of genes relevant in the bone regeneration cascade was presented. The new hybrid microspheres showed bone-like composition with intrinsic magnetic properties, and no toxic effect in presence of murine pre-osteoblasts

(MC3T3-E1), up to 7 days of culture was detected. Preliminary investigation on BMP-2 release was carried out in cell culture media, under two conditions, static and pulsed electric magnetic field (PEMF). The effect of PEMF slightly increased the release of BMP-2 from hybrid magnetic microspheres. The peculiar properties of those hybrid magnetic microspheres can be tailored by means of external magnetic fields and applied as smart device to assist bone tissue regeneration.

[1] Tampieri et al. (2008) *Biomat.* 29(26), 3539-3546

[2] Kim et al. (2016) *Biomacromolec. 17*(5), 1633-1642

[3] Tampieri et al. (2012) *Act. biom. 8*(2), 843-851

[4] Iafisco et al. (2016) *J. Mat. Ch. B 4*(1), 57-70

[5] Tampieri et al. (2014) *ACS Ap. Mat. & intrf.* 6(18), 15697-15707

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#348 - Surface chemical reactions at epitaxial graphene and materials "beyond graphene"

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Graphene (Gr) is a promising material in the fields of energy and catalysis. By means of a combination of surface-science spectroscopies and density functional theory [1], we have investigated the mechanisms ruling the catalytic role of epitaxial Gr grown on transition-metal substrates for the production of hydrogen from water. Water decomposition at the Gr/metal interface at room temperature provides a hydrogenated Gr sheet, which is buckled and decoupled from the metal substrate. We have evaluated the performance of Gr/metal interface as a hydrogen storage medium, with a storage density in the Gr sheet comparable with state-of-the-art materials (1.42 wt.%). Moreover, thermal programmed reaction experiments show that molecular hydrogen is released upon heating the water-exposed Gr/metal interface above 400 K. The Gr hydro/dehydrogenation process might be exploited for an effective and eco-friendly device to produce (and store) hydrogen from water, i.e. starting from an almost unlimited source. The role of defects in the intercalation and decomposition processes will be discussed.

Moreover, the analysis of the chemical reactivity of surface defects of two-dimensional materials provides important information for the nanofabrication process of electronic devices with active channels of ultrathin flakes of black phosphorus (few-layer phosphorene) [2, 3] or InSe [4], which require the use of capping layers in order to avoid surface degradation in ambient conditions. In particular, we find high reactivity of phosphorene toward water, oxygen and CO [5], while water decomposition at room temperature occurs at Se vacancies of InSe [4].

Finally, the chemical inertness of high-quality single crystals of topological insulators toward ambient gases [6] will be discussed. The subsequent ambient stability of uncapped topological insulator-based nanodevices [7] paves the way for the technological exploitation of topological insulators in the fields of plasmonics [8] and Terahertz photodetection [7].

References

[1] A. Politano et al., ACS Nano 10 (2016) 4543.

[2] L. Viti, J. Hu, D. Coquillat, W. Knap, A. Tredicucci, A. Politano and M. S. Vitiello, Adv. Mater. 27 (2015) 5567.

[3] L. Viti, J. Hu, D. Coquillat, A. Politano, W. Knap and M. S. Vitiello, Sci. Rep. 6 (2016) 20474.

[4] A. Politano et al., Nanoscale 8 (2016) 8474.

[5 A. Politano, M. S. Vitiello, L. Viti, J. Hu, Z. Mao, J. Wei, G. Chiarello and D. W. Boukhvalov, Nano Res. 9 (2016) 2598.

[6] A. Politano et al., J. Phys. Chem. C 118 (2014) 21517.

[7] L. Viti, D. Coquillat, A. Politano, K. A. Kokh, Z. S. Aliev, M. B. Babanly, O. E. Tereshchenko, W. Knap, E. V. Chulkov and M. S. Vitiello, Nano Lett. 16 (2016) 80.

[8] A. Politano, V. M. Silkin, I. A. Nechaev, M. S. Vitiello, L. Viti, Z. S. Aliev, M. B. Babanly, G. Chiarello, P. M. Echenique and E. V. Chulkov, Phys. Rev. Lett. 115 (2015) 216802.

#349 - Engineered graphene for optically transparent microwave devices

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The most current and lowest reported experimental values of graphene sheet resistance invalidate the possibility to use this two-dimensional material as a conducting layer in microwave applications. Conversely, *quasi-metallic* grapheneshowsa very low sheet resistance providing full microwave reflection and behaving as an optically transparent metal [1].

In this contribution, we report on the realization of a new class of optically transparent microwave devices based on engineered Chemical Vapour Deposition (CVD) graphene demonstrating the tuning of the graphene response to the microwave radiation by engineering its sheet resistance from the *lossy-dielectric* to the *quasi-metallic* region [1]. This approach enables the fabrication of novel microwave devices, such as polarizers, shields and absorbers. In particular, we propose an innovative approach for the realization of a microwave absorber fully transparent in the optical regime exploiting a Salisbury screen configuration. This device consists of a lossless spacer sandwiched between two graphene sheets whose sheet resistances are properly engineered by means of a $SOCl_2$ treatment and hydrogen-based plasma-chemistry [2]. Experimental results show the possibility to achieve near-perfect electromagnetic absorption in the microwave X-band along with an optical transparency equal to 85%.

These results allow circumventing some of the major limitations of opaque microwave absorbers paving the way for the realization of optically transparent novel devices for military camouflage, satellite applications, shielding systems and photovoltaics.

References

[1] M. Grande, G. V. Bianco, M. A. Vincenti, D. de Ceglia, P. Capezzuto, M. Scalora, A. D'Orazio, G. Bruno, "Optically transparent microwave polarizer based on quasi-metallic graphene", *Scientific Reports*, **5** - 17083 (2015).

[2] M. Grande, G. V. Bianco, M. A. Vincenti, D. de Ceglia, P. Capezzuto, V. Petruzzelli, M. Scalora, G. Bruno, A. D'Orazio, "Optically transparent microwave screens based on engineered graphene layers", *Optics Express*, *in press* (2016).

#350 - Inter-Edge Backscattering in Buried Split-Gate-Defined Graphene Quantum Point Contacts

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Graphene provides a formidable opportunity for the investigation of one-dimensional quantum Hall edge states. Thanks to the fact that electron conduction occurs directly at the surface, a wide range of scanning probe techniques can be used to track the nature and the behavior of electronic states with nanometric precision [1]. In our work, we demonstrate the control of edge state trajectories in the quantum Hall regime thanks to a split-gate structure buried under a dielectric layer [2]. Devices were fabricated starting from monocrystalline graphene flakes obtained by chemical vapor deposition [3,4]. Different n-type and p-type regions can be induced in our devices and used to create a controllable interaction between co-propagating and counter-propagating edge channels at the boundaries of the various quantum Hall regions. We show that the observed resistance values can be understood in terms of edge conduction and mixing relative to three different filling factors in the bulk of the sample, on top of the split-gate, and in the gap between the split-gates. Differently from previous reports [5], the graphene surface is completely accessible from above, and the gating geometry allows an easier electrostatic control of the filling configurations. Perspectives for scanning probe investigation of edge channels [6] are discussed.

[1] G. Li et al., Evolution of Landau levels into edge states in graphene, Nature Comm. 4, 1744 (2013).

[2] S. Xiang et al., Inter-Edge Backscattering in Buried Split-Gate-Defined Graphene Quantum Point Contacts, arXiv:1608.07503 [cond-mat.mes-hall].

[3] V. Miseikis et al., Rapid CVD growth of millimeter-sized single crystal graphene using a cold-wall reactor, 2D Mater. 2, 014006 (2015).

[4] S. Xiang et al., Low-temperature quantum transport in CVD-grown single crystal graphene, Nano Res. 9, 1823 (2016).

[5] S.Nakaharai et al., Gate-Defined Graphene Quantum Point Contact in the Quantum Hall Regime, Phys. Rev. Lett. 107, 036602 (2011).

[6] N.Paradiso et al., Imaging Fractional Incompressible Stripes in Integer Quantum Hall systems, Phys. Rev. Lett. 108, 246801 (2012).

#351 - Flexible Graphene based NFC Antenna

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Graphene is currently one of the most extensively studied materials in the world, both at scientific and industrial level. It consists of microscopic sheets of carbon atoms, having the thickness of a single atom and a lateral size which may reach several tens of microns. Since its discovery in 2004, graphene has shown different exceptional properties usually not present all together in the same material: extremely high mobility of electric charge, transparency, high mechanical strength, excellent thermal conductivity, high surface area and it is impervious to all common gases. In recent years the number of scientific publications and patents on graphene has grown exponentially.

CNR-ISOF, Nokia R&D and ST Microelectronics have realized flexible Near Field Communication (NFC) antennas with different graphene derivatives. Radio frequency identification (RFID) is nowadays more and more used to identify objects, especially NFC tags are used in the tracking and management of inventories, assets, people, animals, in security cards, etc. Several designs, materials and configurations were studied and tested. The graphene antennas were laminated on different substrates like PET, PVC, Kapton, furthermore a silk/graphene paper wearable antenna was prepared. The completely flexible graphene NFC device demonstrators were tested with a mobile phone showing good functionality whether flat or fixed on curved objects. Finally, some fully working graphene smart cards were prepared in order to be used as electronic keys, business cards and other typical NFC applications.

The graphene NFC antennas open a new scenario in the field of the flexible electronics and communication technology. The high conductivity and high flexibility of graphene paper allows the processing and transfer of the paper on a wide variety of substrates materials with no need of high temperature processes and can be applied both on flat or curved objects. Being composed of carbon, the paper will be chemically and thermally stable; it is resistant to acids, oxidation, high temperature and saline environments. The processes used for the realization of these applications are scalable, environmentally friendly and make use of a technology already present in the industries. Another advantage is related to the final waste disposal of the RFID tag, being composed of carbon (as the underlying polymeric film) the paper will not give restrictions for disposal that are instead common for heavy metals.

#352 - Shape approaches for enhancing plasmon propagation in graphene

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Graphene plasmonics is a promising alternative for high speed communication devices that integrate optics and electronics. [1] A key advantage for graphene plasmons (GPs) over surface plasmons (SPs) on metal dielectric interfaces is related to the strong confinement of electromagnetic energy at sub-wavelength scales, which can be tuned and controlled via the charge carrier density through a gate voltage. A major disadvantage for graphene plasmons is their rather short decay length in the infrared range, due to plasmonic losses intrinsic to graphene and induced by defects related to the underlying substrate. This drawback makes the realization of integrated optoelectronic devices extremely challenging. Therefore, viable approaches for launching and conveying graphene plasmons towards efficient and reliable communication on a device scale are needed. One means for overcoming this limitation is represented by the combination of graphene plasmonic waveguides and noble metal antennas. [2] Here we discuss and analyze, using numerical simulations, different designs of metal antennas and their coupling to graphene plasmons, as well as graphene based nanopatterned waveguides that can lead to a more efficient GP propagation. A Yagi-Uda antenna [3] leads to stronger coupling to GPs and allows for directive propagation as compared to a simple dipole antenna. This is especially advantageous to launch plasmons in graphene nanowire waveguides, where propagation up to 3 microns and frequency and phase control can be achieved. In tapered graphene waveguides the constructive interference of the plasmon reflection at the edges can lead to strong plasmon signals up to 8 microns distant from the launching dipole antenna. Nanostructuring of rectangular waveguides into asymmetric chains of truncated triangles greatly enhances directionality of GP propagation and conserves phase information. A comparison of the propagation length and electric near-field strength of these different approaches is presented, and confronted with the efficiency of GP launching by light scattering on scanning near field optical microscopy (SNOM) tips.

References

[1] A. N. Grigorenko, M. Polini and K. S. Novoselov, Graphene plasmonics, Nature Photonics, 2012, 6, 749–758

[2] P. Alonso-González, A. Y. Nikitin, F. Golmar, A. Centeno, A. Pesquera, S. Vélez, J. Chen, G. Navickaite, F. Koppens, A. Zurutuza, F. Casanova, L. E. Hueso, R. Hillenbrand, Controlling graphene plasmons with resonant metal antennas and spatial conductivity patterns Science, 2014, Vol. 344, Issue 6190, pp. 1369-1373

[3] Terukazu Kosako, Holger F. Hofmann and Yutaka Kadoya, Directional control of light by a nano-optical Yagi–Uda antenna, Nature Photonics 4, 312 - 315 (2010)

#353 - S/TEM challenges beyond the nanoscale

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Imaging and chemical analysis at atomic-level spatial resolution with single-atom detection sensitivity is one of the ultimate goals in materials characterization. Such atomic-level materials characterization would be feasible by Z-contrast and electron energy-loss spectrometry (EELS) in the latest aberration-corrected scanning transmission electron microscopes (STEMs) because more probe current can be added into the incident probe by aberration-correction. Especially for EELS analysis, sufficient amounts of core-loss signals can be generated within a short acquisition time by higher current probes, and hence atomic-resolution EELS mapping has already been applied. In this presentation, a review of applications will be presented going from nanoscale to the single atom characterization. Then, recent results at atomic-level obtained on epitaxial graphene on SIC, MoS2, electronic structure and structural characterization of Phosphorene, will also be presented

[1] G.Nicotra, Q. M. Ramasse, I. Deretzis, A. La Magna, C. Spinella, and F. Giannazzo. Delaminated graphene at silicon carbide facets: atomic scale imaging and spectroscopy. *ACS Nano* **7**, 3045–3052 (2013)

[2] G. Nicotra, I. Deretzis, M. Scuderi, C. Spinella, P. Longo, R. Yakimova, F. Giannazzo, and A. La Magna. Interface disorder probed at the atomic scale for graphene grown on the C face of SiC.

Phys. Rev. B 91, 155411

[3] F Fabbri , G. Nicotra et al Novel near-infrared emission from crystal defects in MoS2 multi-layer flakes.

Nat. Comm. in press

[4] G. Nicotra, A.Politano et al Probing excited states of black phosphorus with electron energy-loss near-edge structure spectroscopy. ACS Nano submitted

#354 - Controlled growth of self-assembled 2D ZnO nanosheets

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Two dimensional (2D) ZnO nanostructures exhibit huge surface-to-volume ratio and extremely interesting sensing properties due to semiconducting nature of ZnO. Among the methods used for their synthesis, solution based techniques are favorable due to the low temperatures, high deposition rate and cost effectiveness. Here we report on the growth mechanism of nanowalls (NWLs), composed of ZnO based nanosheets (~10 nm thick) and grown vertically on Al (covered) substrates by chemical bath deposition. It is believed that hydroxyl ions of the synthetic solution react with Al to form the $Al(OH)_4^-$ complex, which promotes the nanosheet shape. The use of anodized Al was demonstrated to be a way to enhance the growth rate, density and quality of the NWLs film. In addition, we report on the synthesis of ZnO microflowers (MFLs), obtained by centrifugation and sonication of a solution containing Zn nitrate, HMTA and NH_4F. These MFLs are also composed of ZnO nanosheets, self-assembled in sphere-like package (1-3 um in size) and homogeneously nucleated in the synthetic solution. F^- ions are believed to act as binder to the Zn^{2+} terminated surfaces causing the nanosheet shape. Sensing tests of ZnO NWLs [1,2] and MFLs will be presented and discussed.

[1] Maiolo et al., Appl. Phys. Lett. (2014)

[2] Iwu et al., Cryst. Growth Des. (2015)

#355 - Fostering Hydrogen Technologies in Smart Cities Application

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The present abstract describes the design, realization and validation of a solar powered hydrogen fueling station in smart cities applications. CNR-ITAE together with other industrial partners has developed, under the Italian research project called i-NEXT (innovation for greeN Energy and eXchange in Transportation), the on-site hydrogen production plant. The plant is fed by a micro grid able to receive energy, from solar radiation by a 100 kW roof-top photovoltaic plant and connected with a battery energy storage of 300 kWh (composed by 16 sodium nickel chloride high temperature batteries) and it is able to deliver hydrogen and electricity for an electric and hydrogen vehicles fleet. The hydrogen plant consists of four sub systems: hydrogen production by electrolysis, compression system, high-pressure storage system and hydrogen dispenser for automotive applications. The experimental plant is able to generate in the hydrogen production sub system, through alkaline electrolyzer of 30 kWh: 6,64 Nm^3/h of H_2 with a gas purity of 99,995% (O_2 < 5ppm and dew point < -60°C). The compression sub system consisted by three stage compressor with gas flow rate of 5,2 Nm^3/h and a delivery pressure of 360 bar. After that, the compressed H_2 gas is stored in high-pressure tanks of 350 liters capacity allowing, in this way, a supply through dispenser system of two automotive's tank of 150 liters @ 350 bar in less than thirty minutes.

This paper shows the design, the development and the efficiency results coming from a first test campaign.

#356 - Porphyrin enhancing performance of functionalized sPEEK membranes for Polymer Electrolyte Membranes portable applications

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Fuel cells are clean and highly efficient electrochemical systems for energy conversion. In particular, polymer electrolyte fuel cells (PEFC) are more efficient and less bulky than currently available systems for the fabrication of portable systems, due to the high energy density with respect to the traditional batteries.

In this field, one of the goal is to obtain low cost materials able to improve the performance of the device.

The polyaromatic membranes based on sulphonated polyetheretherketone (sPEEK), due to its properties such as high solvent resistance, high thermo-oxidative stability, excellent mechanical properties, good proton conductivity, can be considered as an alternative and good candidate to conventional membrane. In order to stabilize the membranes maintaining a proton path for the conduction mechanism and improving the characteristics of the sPEEK material, opportunely selected porphyrins[1] able to specifically interact with the polymeric matrix, were added.

To identify the best composition as a function of the interactions between the components, membranes with different porphyrin load and functionalization polymer degree have been obtained by a standardized doctor-blade method. Spectroscopic investigation has been carried out to investigate the interactions among the chromophoric units and the polymeric matrix as well as the porphyrin aggregation state into the membranes. Physical-chemical characterizations in terms of ionic exchange capacity, water uptake, dimensional variations and swelling, structural and morphological analyses have been performed. Proton conductivity measurements at low temperatures allowed investigating the role of the interaction between polymer and porphyrin on the proton transport mechanism. Moreover, the composite membranes were tested in a PEFC 25 cm^2 single cell showing very good electrochemical performance and excellent stability operating in experimental conditions optimized for application in portable devices.

1. A. Carbone, A. Saccà, R. Pedicini, I. Gatto, A. Romeo, L. Monsù Scolaro, M.A. Castriciano, Int. J. Hydrogen Energy, 2015, 40, 17394–17401.

#357 - Nanostructured Palladium films as methanol crossover-blocking barriers for high efficiency Direct Methanol Fuel Cells

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One of the critical issues in Direct Methanol Fuel Cells (DMFC) technology is the crossover of liquid methanol from anode to cathode side. Due to its high affinity with water, methanol crosses the Nafion® membrane reaching the cathode, where it oxidizes in presence of oxygen without electron injection in the external circuit causing severe energy loss.

In 2014, Casalegno et.al developed a palladium barrier deposited directly on the Nafion 115® membrane by PLD [*Int. J. Hydrogen En.* 2014, 39(6), 2801-2811]. Although the protonic resistance was increased, the cell efficiency improved due to a strong decrease in methanol crossover.

In this work, we present a compact Pd barrier deposited on a thinner Nafion XL® membrane (25.7µm) by means of different PVD techniques. The choice of a 4 times thinner membrane, compared to state of art Nafion 115® is to compensate the decrease in proton conductivity due to the presence of the palladium.

Our nanocomposite membranes show a strong hydride fraction, which suggests it could be possible to tune the composition of the film towards high concentration of hydrogen interstitials in the Pd lattice, optimizing and fine-tuning the proton conductivity.

For the fuel cell testing, they are sandwiched between two commercial DMFC electrodes and tested in fuel cell configuration. Voltammetric and spectroscopic analyses are performed.

With an efficient way to block the crossover, it could be possible to improve the cell performances along with the efficiency, filling partially the gap to large-scale commercialization of this technology.

#358 - Advanced carbon materials as electro-catalyst supports for fuel cells application

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The electro-catalytic materials used at the electrodes of low temperature fuel cells play a key role in determining the performance, stability and cost-effectiveness of the system. Noble metals are generally used to lower the overpotential of the half-reactions. To maximize the utilization of these precious metals, they are supported on carbon materials in the form of small nanoparticles (2-3 nm). Carbon materials should present a good electrical conductivity, a high surface area, an open porous structure (mesopores are preferred) and a good resistance to electrochemical corrosion. Recent studies have revealed that carbon supports can not only provide a high dispersion of Pt nanoparticles, but also facilitate the electron transfer processes, affecting positively the fuel cell performance [1]. Novel non-conventional carbon materials have attracted a great interest as electrocatalyst support, including graphene, carbon nanotubes, carbon nanofibers, carbon nanocoils, carbon nanospheres, carbon aerogels, carbon xerogels, ordered mesoporous carbons, etc. The wide variety of carbon morphologies and the possibility to tune their porosity and surface chemistry opens a broad spectrum of possibilities to optimize the performance of fuel cell catalysts. Due to corrosion phenomena in carbon, also non-carbon supports are investigated, such as stable metal sub-oxides. The main problems regard their relatively low surface area and electrical conductivity when compared to commonly used carbon supports. In this contribution we will present recent results regarding the utilization of advanced supports for noble metals and the effect of the support features on activity and stability [2-7]. 1. E. Antolini, Applied Catalysis B: Environmental 1-2, 1 (2009). 2. D. Sebastián, A.G. Ruiz, I. Suelves, R. Moliner, M.J. Lázaro, V. Baglio, A. Stassi, A.S. Aricò, Applied Catalysis B: Environmental 115-116, 269 (2012). 3. D. Sebastián, M.J. Lázaro, I. Suelves, R. Moliner, V. Baglio, A. Stassi, A.S. Aricò, International Journal of Hydrogen Energy, 37, 6253 (2012). 4. D. Sebastián, I. Suelves, R. Moliner, M.J. Lázaro, A. Stassi, V. Baglio, A.S. Aricò, Applied Catalysis B: Environmental 132-133, 22 (2013). 5. C. Alegre, D. Sebastián, M.E. Gálvez, R. Moliner, A. Stassi, A.S. Aricò, M.J. Lázaro, V. Baglio, Catalysts 3, 744 (2013). 6. D. Sebastián, M.J. Lázaro, R. Moliner, I. Suelves, A.S. Aricò, V. Baglio, International Journal of Hydrogen Energy 39, 5414 (2014). 7. D. Sebastián, C. Alegre, M.E. Gálvez, R. Moliner, M.J. Lázaro, A.S. Aricò, V. Baglio, Journal of Materials Chemistry A 2, 13713 (2014).

#359 - Hierarchical Titanium Nitride Nanostructures as highly stable catalyst support for Fuel Cells

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To overcome the high cost of the catalyst in Direct Methanol Fuel Cell (DMFC) technology, research is moving towards the reduction in the Pt loading in the electrodes by increasing the electrochemical surface area. To date, the state of the art of catalyst supports is dominated by mesoporous carbon. It shows high conductivity but suffer from stability issues especially on long term operation. As shown in various works, titanium nitride (TiN) has a metal-like conductivity with an outstanding chemical stability, making it a possible candidate to replace carbon.

In this contribution, we report about Pt-TiN catalysts support with self-assembled, hierarchical mesoporous nanostructure, grown by Pulsed Laser Deposition. This approach controls the gas dynamics of the nanoclusters-inseminated supersonic jet in order to differentiate the resulting impaction deposition, affecting the growth of the film. For the Pt-functionalization of the thin film, pulsed electrodeposition is performed. From the electrochemical characterization towards methanol oxidation, it is shown the potential of the titanium nitride scaffold to remove the poisonous intermediates from the platinum, suggesting that it can substitute the more expensive Ru co-catalyst, which is currently present in state DMFC electrodes.

These results show the potential of a PVD based technique that opens the doors of the nanoscale to the fabrication of high performing and functional electrodes, whose morphology and composition are easily tuned.

#360 - Three Dimensional Silicon Crystalline Growth in Plasma Reactor

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Exploiting the versatile opportunity offered by plasma synthesis technique, nowadays it is possible to obtain, within a single and fast synthesis process, isolated crystal nanostructures whose nature, size and shape depend on the plasma parameters. Researchers are now explored new possible applications as in the case of silicon crystalline nanoparticles (Si-NPs) which is rediscovered as promising candidate as anode material for next-generation rechargeable lithium ion batteries. The research priority is the optimizing of material performances by means a comprehensive study of size and shape evolution during Si-NPs synthesis.

In this perspective, we have synthetized isolated Si nanoparticles by using non-thermal plasma. We have obtained homogenous sets of mono-disperse and single shape silicon nanoparticles each set having sizes in the range 20-200 nm, well exceeding the largest size reported so far. We have identified the transition of equilibrium shape from spherical to octahedral and investigated the growth rate evaluating the effect of impurity on the growth. Contrary to the typical dynamic of nucleation and growth in solid phase experiments, where first the growth rate is slower waiting for supercritical nucleus formation, in plasma synthesis the grow rate becomes slower with increasing plasma time. This means that the smaller Si-NPs the faster is the grow rate. In fact, the grow rate goes from 3700 Å/min for 20 nm spherical Si-NPs to 500 Å/min for 200 nm octahedral Si-NPs.In presence of phosphorus, the grow rate is systematically slower. We have simulated the plasma process, realizing that the Si-NPs grow rate tends towards the 2D grow rate of a Silicon layer. We also have explored the shape effect on the diffraction pattern interpreted the wedge diffraction artefacts. Finally, we have mapped the distribution of incorporated phosphorus giving the proof of its effective activation.

#361 - Lab on Fiber Technology: a promising platform for multifucntional all fiber nanoprobes

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Optical fibers technology has experienced a tremendous growth and advancement over the past several decades, not only in transmission systems for communications (where nowadays totally dominate especially at the high performances level) but also in the sensing field. For this reason, there is an ever increasing need to add new functionalities and improve the performances, through the integration on the optical fibers of advanced functional materials providing the control and manipulation of light at nanoscale.

Lab-on-Fiber" technology may constitute a valid solution to satisfy this ever increasing request for advanced photonic devices, components and systems. Lab on Fiber is indeed an emerging field envisioning a novel class of advanced, multifunctional photonic devices and components arising from the integration onto optical fibers of different materials at micro and nano-scale with suitable physical, chemical and biological properties. This new fascinating and intriguing research field thus proposes a new technological platform where functionalized materials, devices and components are constructed, embedded all together in a single optical fiber providing the necessary physical connections and light matter interaction, exploitable in both communication and sensing applications. This technological innovation would open the way for the creation of a novel technological world completely integrated in a single optical fiber conferring unique and unprecedented performances and functionality degree. This lecture reviews the strategies, the main achievements and related devices in the "Lab on Fiber" roadmap discussing perspectives and challenges that lie ahead.

#362 - Self-assembly approach to optical fiber sensors

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The realization of optical fiber tip sensors is attractive forwide a range of strategic application fields including environmental monitoring, life science, food monitoring, safety and security.In recent years, significant advances have been achieved in the development of novel fabrication processes devoted to patterning the tip of optical fibers[1-2]. The most conventional methods used to produce micro- and nanostructures on the optical fiber tip, such as electron beam or focusing ion beam lithography, demonstrated their efficacy in precision and size control, but all of them are inherently time consuming and require complex and expensive fabrication procedures with a relatively low throughput. By contrast, self-assembly approaches provide a much simpler, faster and inexpensive alternative to nanolithography in creating micro- and nanostructures in ordered fashion.

Our studies aim to attain advanced nanostructured optical fiber tip sensors by exploiting simple and low-cost fabrication processes suitable to be employed in massive production of technologically advanced devices. Here we propose two different fabrication approaches based on self-assembly: breath figure patterning and nanosphere lithography. The first approach consists in the preparation of a honeycomb-like microstructured polymeric film directly on the optical fiber tip, obtained in a few seconds by a simple solution casting under controlled conditions. The successive metal deposition leads to metallo-dielectric honeycomb patterns which are sensitive to the surrounding refractive index changes, demonstrating their potentialities for chemical and biological sensing applications. In the second approach, polymer microspheres are assembled at the air/water interface and then transferred on the fiber tip. By applying to the fiber further treatments like particle size reduction, metal coating and sphere removal, different periodic structures are conveniently realized, from regularly distributed metallic-dielectric sphere arrays to differently shaped metallic patterns with dimensional features down to a submicron scale. Finally, as proof of concept, we demonstrate that the realized patterns are able to work as efficient Surface Enhanced Raman Spectroscopy (SERS) fiber probes, legitimizing the self-assembly approach as valid option for the realization of ultra-sensitive tools for *in vivo* molecular recognition.

[1] Cusano, A., Consales, M., Crescitelli, A., Ricciardi, A. (Eds.), Lab-on-Fiber Technology, Vol. 56. **2015**, XXII, 359.

[2] Kostovski, G., Stoddart, P. R. and Mitchell, A. *Advanced Materials* **2014**, 26(23), 3798-3820.

[3] Pisco, M., Galeotti, F., Quero, G., ... & Cusano, A. *Acs Photonics* **2014**, *1*(10), 917-927.

[4] Pisco, M., Galeotti, F., Quero, G., ... & Cusano, A. *Light: Science & Applications* **2017**, 6, e16229.

#363 - Birefringence and strain distribution analysis in silicon photonics structures

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The application of an asymmetric strain on silicon crystal, by depositing a high intrinsic stress layer on top, can enable the presence of significant electro-optic effect and second harmonic-generation. These nonlinear effects can be leveraged for the realization of optical functionalities such as routing, switching and filtering in photonic integrated circuits (PIC). In this work we report a study on the lattice deformation induced by a silicon nitride (Si3N4)film deposited onto silicon photonics structures (450 nm x 220 nm). In particular, simulations of stress and strain distributions on single and coupled ribs structures across the nitride-to-silicon interface were performed along with an estimation of the optical properties of strained SOI optical waveguides. Finally, Convergent Beam Electron Diffraction (CBED) technique was carried out to perform locally accurate strain measurements on the microfabricated structures. A simulative model employing a finite element method (FEM) was carried out in order to estimate the amount and the distribution of stress and strain induced by the stoichiometric Si3N4 layer in the single and coupling silicon rib structures. Moreover a variational model, based on FEM, was also applied to estimate the crystal deformation-induced optical properties of SOI structures with manufactured geometry for different Si3N4 film thicknesses. Planar silicon rib structures were manufactured on 4 inches <100> silicon wafers employing a spacer technology that allowed fabrication of sub-micrometric silicon waveguides starting from conventional near-UV micrometric photolithography. Then, a stoichiometric LPCVD Si3N4 film was deposited onto them, showing good adherence on silicon with no cracks or fractures. Several sets of structures with different dimensions and spacing were manufactured, for instance single and coupled rib structures (450 nm x 220 nm) with a 300 nm gap with surrounding Si3N4-straining layer (average 375 nm thickness). The lattice deformations induced by the Si3N4 film deposition in microfabricated silicon rib structures were measured. The Convergent Beam Electron Diffraction (CBED) technique, carried out in the TEM operated in scanning (STEM) mode Transmission Electron Microscope (TEM) facility, was employed showing nanometer-scale resolution and very high strain sensitivities. Owing to the nanometric dimension of the analyzed structures, CBED, unlike other commonly used strain measurements techniques, fits the needs of our study. The amount and the distribution of the measured strain and the optical properties attained in the electromagnetic simulations highlight promising features for the application of strained silicon technology in lightwave processing devices exploiting the asymmetric strain-induced birefringence.

#364 - Er3+ doped monolithic 1-D dielectric microcavity fabricated by rf-sputtering for coherent emission at 1500 nm

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Er^{3+} doped 1-D monolithic glass microcavity was fabricated by rf sputtering technique. The microcavity was constituted by half wave Er^{3+} doped SiO2 active layer inserted between two Bragg reflectors consists of ten pairs of SiO_2/TiO_2 layers also doped with Er^{3+} ions. Morphology and optical features of the sample were investigated by scanning electron microscopy and transmittance measurements. The photoluminescence measurements were obtained by optically exciting at the third order cavity resonance using 514.5 nm Ar^+ laser with an excitation angle of 30°. The Full Width at Half Maximum of the emission peak at 1560 nm decrease with the pump power until the spectral resolution of the detection system of ~ 1.0 nm. Moreover the emission intensity present a non-linear behavior with the pump power and a threshold at about 24 mW was observed with saturation of the signal at above 185 mW of pump power.

This research was performed in the framework of MaDEleNA PAT project, COST MP1401 “Advanced Fibre Laser and Coherent Source as tools for Society, Manufacturing and Lifescience” (2014 - 2018), PAS-CNR (2014-2016) and PLANS - Centro Fermi projects, R.R. Gonçalves and M. Ferrari acknowledge Brazilian Scientific Mobility Program “Ciências sem Fronteiras”.

#365 - Heavily n doped germanium epitaxially grown on silicon for mid-infrared plasmonics

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Heavily-doped semiconductor films are very promising for application in midinfrared plasmonic devices because the real part of their dielectric function is negative and broadly tunable in this wavelength range. In this work we investigate heavily n-type doped germanium epilayers grown on silicon by infrared spectroscopy, first principle calculations, pump-probe spectroscopy and DC transport measurements to determine the relation between the plasma edge and the carrier density and to quantify mid-infrared plasmon losses. We demonstrate that the screened plasma frequency can be tuned up to 2000 cm^{-1}and that the electron scattering rate is dominated by scattering with optical phonons and charged impurities. We also found weak dependence of losses and tunability on crystal defect density, temperature, inactivated dopant density and optical pump wavelength in the near infrared. Our results suggest that plasmon decay times in the picosecond range can be obtained in Ge. In order to assess the potentiality of our approach, we have processed nano-antennas out of the epitaxially grown n-type Ge films and demonstrated a strong signal enhancement for the molecules located in the antenna hot spots. This result paves the way toward low-cost integration of plasmonic sensing platforms into the existing CMOS technologies. The research leading to these results has received funding from the European Union’s Seventh Framework Programme under grant agreement no. 613055.

#366 - Glass-Ceramic Photonic Systems

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The development of optically confined structure is a major topic in both basic and applied physics not solely ICT oriented but also concerning lighting, laser, sensing, energy, environment, biological and medical sciences, and quantum optics. Glasses and glass-ceramics activated by rare earth ions are the bricks of such structures. Glass-ceramics are nanocomposite systems that exhibit specific morphologic, structural and spectroscopic properties allowing to develop new physical concepts, for instance the mechanism related to the transparency, as well as novel photonic devices based on the enhancement of the luminescence. The dependence of the final product on the specific parent glass and on the fabrication protocol still remain an important task of the research in material science. Looking to application, the enhanced spectroscopic properties typical of glass ceramic in respect to those of the amorphous structures constitute an important point for the development of integrated optics devices, including optical amplifiers, monolithic waveguide laser, novel sensors, coating of spherical microresonators, and up and down converters. The present lecture covers the properties and current state of transparent glass-ceramics for guided-wave devices, including the discussion of the preparation methods and of their spectral and luminescent properties.

#367 - Production and characterization of transparent yttrium aluminum garnet (YAG) ceramics: materials for laser sources

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Yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG) doped with rare earth ions is one of the most widely used laser gain media in bulk solid state lasers and due its good thermal and mechanical properties in comparison with glasses it is very attractive for applications in high-power laser devices. The main approach used for the production of YAG is single crystal growth, but in the recent years another group of materials, transparent ceramics, has proved to be useful and promising, thanks to the advantages provided by ceramic technology compared to that of single crystals.

The two types of materials have identical chemical and phase composition, and the main difference between them is their microstructure: unlike single crystals transparent ceramics are polycrystalline materials composed of grains usually microns to tens of microns in size. Not only the production process of transparent ceramics requires lower processing temperature and shorter times in comparison to the Czochralski growth, but a further advantage is the possibility to produce materials with near-net shape and with a controlled and well-defined distribution of doping ions to improve the homogeneity of temperature distribution and thus significantly reduce the temperature gradients and the resulting undesired thermal and thermo-mechanical effects (thermal lensing, surface deformation, etc.)[1]. This is particularly important for the production of gain media for high power lasers, where significant amount of heat is generated during the lasing process.

Transparent Yb:YAG ceramics with uniform or layered doping distribution were produced from high purity oxide powders via two different shaping methods. The first consists in granulation of a homogeneous stoichiometric mixture of oxide powders and pressing of the granulate into the desired shape at room temperature. In the latter approach, tape casting is used to produce thin sheets from the suspension of oxide powders. The tapes are then stacked and pressed at elevated temperature in order to produce a bulk compact. In both cases the shaping is followed by heat treatment in air at 800 °C and sintering under high vacuum.

The microstructure and Yb distribution were analyzed by SEM-EDX, optical quality characterized by measurements of transmittance and transmittance mapping, and the laser efficiency characterized in a laser cavity under quasi-CW and CW pumping. Slope efficiencies higher than 50 % were obtained.

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References

[1] L. Esposito et al., Multilayered YAG-Yb:YAG ceramics: manufacture and laser performance. *J. Mater. Chem. C* **2** (2014) 10138-10148.

#368 - Release from Polymer Films of Active Compounds Loaded into various Inorganic Carriers. A Comparison among Mesoporous Silica SBA, Montmorillonite and Halloysite

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One of the possible approach to delay or inhibit the mechanisms responsible for the degradation of the packed foodstuff is the development of active packaging materials exhibiting a slow and controlled release of active compounds from the film/container to the food. This has the advantage to overcome the drawbacks related to their direct addition into the food. Due to recent progress in material chemistry and material science, advanced nanoscale systems used to control the release of active compounds have recently received tremendous attention. In recent years, many inorganic nanomaterials used as nanocarriers have been intensively studied. Among these, many investigation efforts focused on the exploitation of the porous network provided by such materials as a reservoir for the accommodation of drug molecules. In fact, the well-known opportunity to chemically functionalize the surface of siliceous mesostructures with different organic moieties constitutes a route for controlling the drug release by diffusion under specific conditions. Drug release from mesoporous materials is generally controlled by diffusion. Nevertheless, when the interactions between desorbing molecules and silica pore walls are significantly strong and/or show some kind of specificity, the release also depends by the stability of the complex between the functional groups of the drug and those of the substrate. This phenomenon allows then to fine tune the release of specific molecules from a given mesostructure by simply changing the functional groups that are attached to its pore walls during the synthesis process. In addition to the production of smart drug delivery systems, such approach can be also used in the field of food packaging due to the increasing interest in the concept of "active packaging" materials as compounds which, interacting with the packaged foodstuff, are able to control quality as well as to increase shelf-life. The aim of the present work is the study and the comparison of the release kinetics from active polymer films of various active compounds embedded or supported into/onto three inorganic carriers: SBA (Santa Barbara Amorphous), Montmorillonite and Halloysite. Migration tests were performed at 25 °C, using 96% v/v ethanol and water as food simulant, using polymer films obtained by embedding active inorganic carriers into LDPE, chitosan and PCA matrices. Obtained results show the influence of functionalization of the inorganic carriers on the diffusion of active compounds and thus on their release kinetics into the liquid media.

#369 - Surface-coated polylactide films as active food packaging materials

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Polylactic acid (PLA) is a biodegradable thermoplastic aliphatic polyester derived from renewable resources. It is safe food contact, highly transparent to visible light and flexible polymer. It is also environmental friendly and commercially available, therefore PLA has potential for use in the packaging industry [1-2].

The combination of suitable surface coatings on PLA film can provide functionalities, such as antimicrobial activity. With this purpose, thin aluminum-doped zinc oxide (AZO) coatings have been deposited employing rf magnetron sputtering technique at room temperature and at different sputtering power onto extruded PLA film [3-4].

The morphology of the coatings was analyzed by scanning electron microscopy (SEM). The structural properties of the AZO-coated PLA films were studied using X-ray diffraction and the transparency of the films by optical transmission measurements in the UV-Vis range.

In order to evaluate the food contact migration of AZO particles from PLA surface, release tests were conducted monitoring the aqueous food simulant solution in contact with the coated samples at different times, up to 3 months by spectrophotometric measurements.

Antibacterial tests against Escherichia coli demonstrated very fast activity for all the AZO-coated PLA films.

The obtained results indicate that the deposition of AZO coatings by magnetron sputtering onto extruded PLA films can be promising to prepare composite systems for active packaging applications.

References

[1] L.T. Lim, R. Auras, M. Rubino. Processing technologies for poly(lactic acid). Progr Polym Sci 33, 820–852, 2008.

[2] K.M. Nampoothiri, N.R. Nair, R.P. John. An overview of the recent developments in polylactide (PLA) research. Bioresource Technol 101, 8493–8501, 2010.

[3] I.S.M.A. Tawakkal, M.J. Cran, J. Miltz, S.W. Bigger. A review of poly(lactic acid)-based materials for antimicrobial packaging. J Food Sci 79, R1477-R1490, 2014.

[4] M. Murariu, A. Doumbia, L. Bonnaud, A.L. Dechief, Y. Paint, M. Ferreira, C. Campagne, E. Devaux, P. Dubois. High-performance polylactide/ZnO nanocomposites designed for films and fibers with special end-use properties. Biomacromolecules 12, 1762−1771, 2011.

#370 - Structural characterization of reacted PC/PEN blend.

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Chemical reactions occurring during reactive melt mixing of equimolar blend of poly(ethylene naphthalate) (PEN) and poly(bisphenol-A carbonate) (PC) at 280°C in presence of a catalysts (0.1%w) such as $Ti(OBu)_4$ were studied. Beside expected direct inner-inner and outer-inner exchange reactions, consecuitive reactions that lead to the elimination of CO_2 and ethylene carbonate (EC) from backbone, were also detected. The composition and the architecture of the formed copolymers change as the mixing time increases.

Initial PC-PEN block copolymers formed at lower mixing time (2 min) evolve towards the formation of naphthalate based random copoly(ester-ether)s at reaction time higher than 45 min, owing to the total elimination of carbonate units. Determination of composition and microstructure of copolymers formed was attempted by (^{1}H and ^{13}C)-NMR analyses applying appropriate chemical microstructure model. Dyads and triads sequences determined here give detailed information of the change in the molar fractions of the sequences with increasing the reaction time. DSC analysis shows that block copolymer formed at 2 min mixing present two glas transition (Tg) temperatures close to those of initial homopolymers (PC and PEN), whereas the other ones show a single Tg that changes as a functions of their dyads molar compositions. Thermogravimetric (TGA) analysis shows that the more thermally stable copolymers are random copoly(ester-ether)s formedat thigher reactiontime.

#371 - Characterization of PET-MXD6 Copolyesteramides from Reactive Blending of Homopolymers

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Poly(ethylene terephthalate)-poly(m-xylylene adipamide) (PET-MXD6) copolymers were prepared by reactive blending of the equimolar PET/MXD6 blends at 240 *C for different times in presence of terephthalic acid (1%w). First, the partial hydrolysis of PET and MXD6 polymers occurs, yielding oligomers terminated with the reactive aromtic carboxyl groups. These oligomers quickly react wit ester and amide inner groups producing PET-MXD6 copolymers that may compatibilize the initial biphasic blend. In these homogeneous enviroment, the aliphatic carboxyl-terminated MXD6 chains, inactive in the initial biphasic blend, may promote the exchange rections determining the formation of a random copolymer a longer reaction time (120 min). The progress of thje exchange reactions and the microstructure of the formed copolyesteramides, versus the reaction time was followed by (^{1}H and ^{13}C)-NMR analyses using a CDCl3/TFA-d/$(CF_3CO)_2O$ mixture as solvent and applying appropriate mathematical models. Dyads and triads sequences were thoroughly characterized by NMR. Semicrystallyne block copolymers were obtained at reaction time lower than 45 min. All PET-MXD6 copolymers show a single glass transition temperature (Tg) that change as a function of the dyads molar composition in the copolymers. The measured Tg values match with those calculated by a proposed modified Fox equation that take into account the weight fration of the four dyads components the of PET-MXD6 copolymers.

#372 - Combined Techniques for the Characterization of Linear–Hyperbranched Hybrid Poly(Butylene Adipate) Copolymers

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Linear-hyperbranched hybrid poly(butylene adipate) (HPBA) copolymers were synthesized though a branching reaction between the linear tailored prepolymer terminated with methyl ester groups and different mol% of the 1,1,1-tris(hydroxymethyl)-propane

(TMP) as branching agent using the titanium(IV)isopropoxide as catalist, a 180°C under vacuum for different times, All samples were characterized by NMR and matrix assisted laser desorption/ionization time of flight mass spectrmetry (MALDI-TOF MS). In particular, MALDI-TOF mass spectra of the unfractionated and size exclusion chromatography (SEC) - fractionated hyperbranched (HB) samples gave information of their composition, on the end groups as well as on the TMP units present in each family of the HB macromolecules. HB chains containing cyclic branches and ether bonds formed by intermolecular transesterification and intramolecular and intermolecular trans-etherification side reactions, respectively, were also revealed by MALDI-TOF MS analysis. All samples were also investigated by SEC. The averge molar masses (MMs) evalutaed by SEC calibrated with the polystyrene (PS) narrow standards were overestimated with respect to those calculated by the SEC-MALDI-TOF MS self calibration method, which gave reliable values. Moreover, it also showed that the hydrodinamic volume of the HPBA polymers was higher than that of the linear PSs with similar MMs.

Posters

#P001 - Colloidal suspensions of Goethite (α-FeOOH) nanorods: effect of synthesis parameters on morphology and NIR absorption tunability under magnetic field

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Goethite colloids are known mineral liquid crystals and due to their peculiar magnetic properties, their optical properties can be tuned under suitably oriented magnetic field.

In this work, we show that it is possible to tune the transmittance of polarized light, mainly in the NIR range, by properly applying a magnetic field. This property could open new applications for these colloids such as on Smart Windows or Laser-Induced Thermotherapy.

Goethite (α-FeOOH) nanorods have been synthetized using two different methods, by the aging of ferrihydrite suspensions obtained through co-precipitation in different conditions, or by fast conversion of ferrihydrite through ultrasonic irradiation. The synthesis parameters influence the morphology of nanoparticles and the optical properties of nanorods colloidal suspensions in water.

The nanopowders have been characterized by Powder X-Ray Diffraction and Scanning Electron Microscopy, while the colloidal suspensions by Dynamic Light Scattering and ζ-potential measurements. Transmittance of colloids in the UV-Vis-NIR range has been determined under different magnetic field intensities and directions with respect to light polarization.

#P002 - A Study on Graphene Oxide Properties as Contrast Agent for NMR Imaging

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Nuclear Magnetic Resonance Imaging (MRI) is a non-invasive technique used to visualize anatomical structures in biomedical research and clinical medicine. The use of complexes of paramagnetic metal ions such as gadolinium (Gd^{3+}), manganese (Mn^{2+}), or iron (Fe^{2+}) as MRI contrast agents (CAs), capable of varying the intrinsic relaxation times of water protons *in vivo*, has enabled clinical diagnostic improvements [1-2]. However, enhanced contrast and safety issues call for novel classes of CA. Recently, the use of graphene-oxide (GO) based CA has been proposed as a new tool for MRI biomedical applications [3]. However, the full characterization and understanding of the GO relaxation mechanisms is still not fully understood [4-6]. In this talk, after reviewing the current literature on MRI CAs, we will present longitudinal and transverse relaxivity data of GO in water solutions obtained in our lab by means of a 2.35T MRI scanner.

[1] de Haen C. “Conception of the first magnetic resonance imaging contrast agents: a brief history”, Top Magn Reson Imaging. 2001;12(4):221-30.

[2] Lohrke J, Frenzel T, Endrikat J, Alves FC, Grist TM, Law M, Lee JM, Leiner T, Li KC, Nikolaou K, Prince MR, Schild HH, Weinreb JC, Yoshikawa K, Pietsch H. “25 Years of Contrast-Enhanced MRI: Developments, Current Challenges and Future Perspectives”. Adv Ther. 2016;33(1):1-28.

[3] Paratala BS, Jacobson BD, Kanakia S, Francis LD, Sitharaman B. Physicochemical characterization, and relaxometry studies of micro-graphite oxide, grapheme nanoplatelets, and nanoribbons. PLoS One. 2012;7(6):e38185.

[4] Nair RR, Sepioni M, Tsai IL, Lehtinen O, Keinonen J, Krasheninnikov AV, Thomson T, Geim AK, Grigorieva IV, “Spin-half paramagnetism in graphene induced by point defects”, Nature Physics, 2012;8:199-202.

[5] Panich AM, Shames AI, Sergeev NA, ”Paramagnetic Impurities in Graphene Oxide”, Appl Magn Reson 2013;44:107–116.

[6] Wong CHA, Sofer Z, Kubešová M, Kucera J, Matejková S, and Pumeraa M, “Synthetic routes contaminate graphene materials with a whole spectrum of unanticipated metallic elements”, PNAS, 2014;111:13774–13779.

#P003 - Solid State NMR analysis of materials for photovoltaic applications

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Photovoltaic (PV) cell technology has been experiencing a continuous development during last years, with new device architectures and improved performance claims being published at a very fast rate [1]. The recent emergence of solution processed halide perovskite-based solar cells represents one of the lowest cost technologies, capable of the highest sunlight conversion efficiencies [2], even though well established technologies such as solid state dye-sensitized solar cells (SS-DSSCs) are still widely investigated.

The complex nature of the micro and nano-structured materials employed in solar cell fabrication and the strong influence of organization, surface/bulk defects and interface structure on device performances makes the characterization of such materials an important challenge.

Solid state (SS) NMR is a powerful technique that can be applied to a broad range of compounds, providing information on molecular structure and mobility. It is particularly suited for the analysis of multiphase, hybrid organic/inorganic structures as it can probe different nuclei (allowing to observe both organic and inorganic phases) and can provide a molecular-level focus on the interfacial phenomena that plays a key role in the definition of final properties. Here some example of the application of NMR to the analysis of solar cell materials are reported.

SS NMR was employed to clarify the impact of lithium salt doping on the conductivity of the hole-transport layer (namely Spiro-OMETAD) in SS-DSSCs [3]. An active redox behavior of Li-TFSI salt was observed that lead to a doping of the hole transporter, involving also oxygen absorbed from the atmosphere. The formation of lithium oxide species was suggested by ^{7}Li NMR recorded on the Spiro – LiTFSI system after exposure to oxygen.

^{19}F and ^{13}C NMR experiments were used to investigate the coordination of iodopentafluorobenzene (IPFB) on halide-lead perovskite crystals [4]. The IPFB treatment of perovskite film, before the deposition of the organic layer, led to a clear improvement of the efficiency that was ascribed to the passivation of the uncoordinated halide anions at the surface. The shift observed in NMR spectra proved the formation of a halogen bond between the iodine of IPFB and the surface ions of perovskite.

References

[1] Yu, J.; Zheng, Y.; Huang J. *Polymers* **2014**, 6, 2473.

[2] Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. *J. Am. Chem. Soc.***2009**, 131, 6050.

[3] Abate, A.; Leijtens, T.; Pathak, S.; Teuscher, J.; Avolio, R.; Errico, M.E.; Kirkpatrik, J.; Ball, J.M.; Docampo, P.; McPherson, I.; Snaith, H.J. *Phys. Chem. Chem. Phys.***2013**, 15, 2572.

[4] Abate, A.; Saliba, M.; Hollman, D.J.; Stranks, S.D.; Wojciechowski, K.; Avolio, R.; Grancini, G.; Petrozza, A.; Snaith H.J. *Nano Letters* **2014**, 14, 3247.

#P004 - CaCO3 nano-crystals as smart materials for sustainable protection from the Olive Quick Decline Syndrome

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The Olive Quick Decline Syndrome, denoted **CoDiRO**, is the Olive Trees disease observed in Salento (Apulia, southern Italy) that is associated to ***Xylella Fastidiosa*** (*Xf*) infection. The impact of infection by *Xf* is devastating for the local economy, especially considering the high value of the ancient monumental olive trees (trees older than 100 years). Although the traditional approach versus bacterial diseases is the infected plants eradication but the economic value of each tree requires the research of alternative strategies.

Our aim is the development of **innovative phyto-therapy** based on nano-carriers to efficiently reach the target and to amplify the agrochemical effect.

We have developed a new Spray-drying synthesis of pure and thermodynamically stable calcium carbonate nano-crystals (**nano-$CaCO_3$**). We investigated the potential of using nano-$CaCO_3$ as delivery systems to target bioactive compounds in infected plants. First for all we have studied the penetration and transport of the nanoparticles into the xylema that is the target site of *Xf*. Preliminary phyto-toxicity assays are carried out to study the safety of nano-$CaCO_3$. The interaction between nano-$CaCO_3$ and *Xf* cells was studied through ultrastructural analysis by transmission electron microscopy (TEM).

$CaCO_3$ nano-crystals don't result phyto-toxic in preliminary assays with model plants. Our nano-crystals show good mobility in xylem vessels, without any effect on the plant tissues nor uptake by the vegetable cells. The TEM observation of *Xf* cells reveal an evident effect of nano-crystals without any bactericidal cargo. Nano-$CaCO_3$ are uptaken by cells and they cause a drastic alteration of **bacteria wall** structure.

In conclusion, our synthetic process is easy and versatile, can be usable on large scale and allows a rigorous control of nano-$CaCO_3$ shape, dimensions and crystalline phase, without using surfactants. The application of nano-$CaCO_3$ as phyto-drugs delivery systems against *Xf* infection results a promising strategy. The nano-$CaCO_3$ easily move into xylema without any toxic effect. At present we are demonstrated a great effect of nano-crystals on pathogen cells vitality, in particular on bacteria wall integrity. The action mechanism is yet to be understood through specific biological assays. We will investigate also the effect of encapsulated phyto-drugs using the nano-$CaCO_3$ carries.

#P005 - New bioactive coatings with enhanced osteogenic and antibacterial activity

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The polyether ether ketone (PEEK) is a very promising material in the field of bone implant substitutes for its chemical stability, thermal stability, lightness and excellent mechanical properties. In this respect, one of the most frequent problems is the achievement of adequate adhesion and osteointegration of the implant to the native bone. To this purpose bone implants can be subjected to coatings with materials ensuring enhanced bioactivity, among which Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) is considered as the golden standard, due to its close similarity with the inorganic bone. HA phases with enhanced bioactivity can be obtained by selective ion doping in the HA structure. For instance, Strontium (Sr) is well known as anti-osteoporotic agent, able to enhance new bone formation and bone mineral density, whereas reducing at the same time bone resorption. Strontium ions can be successfully introduced in the apatite lattice and used as a biomaterial with ability of ion delivery in the physiological environment. Among the secondary effects that can prejudice the lifetime and performance of bone implants the occurrence of bacterial contamination that may yield the formation of bacterial biofilms at the interface between the implant and the bone is among the most serious concerns.In this respect the coating of implants with hydroxyapatite phases with specific antibacterial properties is a topic of increasing interest. Zinc ion has been investigated as an antibacterial agent against one of the most present bacteria in post-surgical infection, *Staphylococcus Aureus*, and can be introduced in the lattice of HA phase.Besides preventing infections, preliminary studies indicate that zinc release in physiological environment could also have the effect of osteoblast activation, thus stimulating new-bone formation.

For the deposition of these apatitic phases it was thought to use pulsed plasma deposition (PPD). PPD is a technique able to transfer material from a target to a substrate using a plasma and creating thin films. This technique is particularly suitable for the use on PEEK because the material transfer, although with high energy impact, is at low temperature, thus avoiding damage on PEEK structure. Furthermore is very suitable for substituted-HA transfer because is able to transfer quantitatively the different elements. The coating of PEEK with thin film of substituted-hydroxyapatite should unite the mechanical properties, stability and low weight of the PEEK with osteoconductivity of HA. Furthermore the insertion of doping ions should increase is osteogenic properties and eventually provide antibacterial properties.

Syntheses of substituted HA doped with Sr or with Zn was successfully conduced and preliminary experiments on deposition and crystallization of Sr-HA with pulsed plasma deposition on PEEK were conducted.

#P006 - PHOTONICS FOR ENERGY CONVERSION AND HEALTHCARE

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The goal of our research is to design, prepare and characterize advanced organic, inorganic and hybrid materials that process or produce light signals useful for technological applications in the areas of energy conversion and healthcare. Our research is based on a multidisciplinary approach that embraces theoretical chemistry, organic synthesis, photophysics, photochemistry, biochemistry, electrochemistry and materials science. We present some recent results concerning:

- Multi-component systems mimicking artificial photosynthesis for the collection and conversion of light radiation into chemical energy containing organic, inorganic and bio-inorganic subunits.

- Devices for converting solar energy into electrical energy (LSC, DSSC).

- Photo- and electroluminescent materials for flat and diffuse light sources (OLED, LEC) and sensors, such as organic molecules and metal complexes.

- Two-photon absorbers for biomedical and sensor applications.

- Polymeric or hybrid nanoparticle systems for drug delivery, traceable in a biological environment by means of fluorescence imaging techniques.

- Molecular modelling to predict the photochemical and photophysical properties of the systems under investigation.

#P007 - High-efficiency Dye-Sensitized Solar Cell co-sensitized with Gold Nanoparticles Embedded in mesoscopic TiO2

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Dye-sensitized solar cells (DSSC) have been studied since 1991 and, since then, a lot of work has been done for improving each constituent of this photoelectrochemical device, and, in particular, several functional elements have been added to the initial simple structure of the photoanode, with the aim of improving light harvesting and charge transport, decreasing dark current and reducing charge carriers recombination. The use of plasmonic effects is extremely interesting for improving light harvesting. In order to implement it, a co-sensitizer is added to the DSSC in the form of metal nanoparticles or clusters which are known to possess surface plasmon resonance (SPR) effect. This concept has been successfully applied to DSSCs only recently [1,2]. It is assumed that the SPR effect increases the coupling of light and the amount ofphoton energy transferred to the dye, increasing the generation of charge carriers. In the present work, a method is proposed which, by the first preliminary study where the conversion efficiency was 10,7 %, is showing to enhance the efficiency DSSCs up to 15,1 %. The short circuit current, J_{sc}= 26.0 mA cm^{-2}, has increased by 18%, the open circuit voltage, V_{oc}= 0.864 V, by 8.9% and the fill factor, *FF*= 67.2% by 10%.The method consists in incorporating gold nanoclusters directly into the nanometric TiO_2 particles used to build the anode nanoscopic layer, thus obtaining a sort of single functional units for light harvesting and electron transport. The preliminary results indicate a large enhancement of the DSSC efficiency, through an increase of all of the three significant parameters promise to produce a large boosting effect on a fully optimized system.

[1] M. A. Al-Azawi, N. Bidin, M. Bououdina, S. M. Mohammad, Preparation of gold and gold– silver alloy nanoparticles for enhancement of plasmonic dye-sensitized solar cells performance, Solar Energy 126 (2016) 93–104.

[2] H. Choi, Y. S. Chen, K. G. Stamplecoskie, P. V. Kamat, Boosting the Photovoltage of Dye- Sensitized Solar Cells with Thiolated Gold Nanoclusters, *J. Phys. Chem. Lett.* 6 (1) (2015) 217-223

#P008 - Characterization of PCPDTBT-P4VP amphiphilic block-copolymers

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Two homologous series of rod-coil block copolymers, composed by a low band-gao rod moiety (poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene)-alt-4,7-(2,1,3benzothiadiazole)] (**PCPDTBT**) and a flexible poly(4-vinylpyridine) (**P4VP**) based polar block, were synthesized by two different approaches. *Step growth-like* procedure provided copolymers with longer coil, whilst copolymers with longer rod arise from *chain growth-like* process. Both th series were deeply investigated with different analytical techniques (^{1}H-NMR, SEC-DV and MALDI-TOF MS) in order to prove the coupling process and elucidate the composition of the obtained polymeric materials. Chemical composition was evaluated by ^{1}H-NMR analysis. DSC heating traces of rod-coil copolymers synthesized by step growth-like route present two well resolved glass transition temperature (Tg) corresponding to the rod and coil blocks. The low band-gap rod-coli block copolymers especially those with short coil can find application in hybrid solar cells. The length of the coil block is strongly limited by the low reactivity of the macroinitiator (**M1**) related to the rigidity of the conjugated system with respect to the poly(3,hexyl thiophene) (P3HT) cases reported. The shortness of a rod segment allows to perform a proper MALDI-TOF MS characterization which is in agreement with ^{1}H-NMR data. A series of a rod-coil copolymers was prepared with predominant of the rod block (> 86%w) starting from a fixed rod block and tuning the length of the coil moiety, by varying both the **M1/4VP** molar ratio and the time of the nitroxide mediated radical polymerization (**NMRP**). The two series of obtained materials aggregate in different manner and show disinct organizations in soli state films dependingon the respective lengths of the two blocks in the copolymers, fromglobular micelle-like to lamellar segregation as highlighted by a AFM images, with the increasing of the length of the coil segment.

#P009 - Quantum oscillation in electric and thermal transport properties of 2DEG in ZnO based heterostructures

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In recent years, two-dimensional electron gas (2DEG) in wide bandgap semiconductors has attracted much attention for electrical device applications such as high electron mobilitytransistors (HEMTs) and quantum spin transport devices. Most of previous studies focused on III–nitride materials, but only a few attempts were made on II–oxide materials [1,2]. Both materials have wurtzite structure and the heterostructures are usually grown along the polar caxis direction. At the heterointerfaces, for example $Al_xGa_{1-x}N$/GaN and $Mg_xZn_{1\_x}O$/ZnO, a strong built-in potential arises from macroscopic polarization mismatch and bands align because of different bandgaps in the two layers, causing the formation of 2DEGs at the interface.

Here we present a characterization of electrical and thermoelectrical transport properties of 2DEG in $Mg_xZn_{1\_x}O$/ZnO heterostructures. ZnO and $Mg_xZn_{1\_x}O$ (x=0.05; 0.15) layer were deposited by pulsed laser deposition on ZnO single crystal on Zn polar side. A difference of the band gap of about 0.6 eV for the doped and undoped layer was measured, indicating the possibility to form a quantum well at the interface.

The realized heterostructures have a carrier concentration of 1012 e-/cm2 and a large mobility (up to 4000 V/cm^{2}s).

Measurements up to 32.5 T of electrical and thermoelectrical transport properties performed at HMFL (Nijmegen). Quantum Hall Effect and Shubnikov–de Haas oscillations confirmed the existence of the 2DEG at the interface and have been observed at temperatures up to 20 K. Quantum oscillation were observed, for the first time in a oxide based 2DEG, also in the Seebeck and Nernst effects.

[1] A. Tsukazaki, A. Ohtomo, T. Kita, Y. Ohno, H. Ohno, and M. Kawasaki, Science **315**,1388 2007

[2] A. Tsukazaki, A. Ohtomo, M. Kawasaki, S. Akasaka, H. Yuji, K. Tamura, K. Nakahara,T. Tanabe, A. Kamisawa, T. Gokmen, J. Shavani, M. Shayegan Physical Review B **78**,233308 (2008).

#P010 - Quantum oscillation in electric and thermal transport properties of 2DEG in ZnO based heterostructures

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#P011 - Impact of local oxides on the nanoscale electrical conductivity of laser-sintered Ge nanoparticle layers

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For thermoelectric applications micro- and nanostructured materials based on group-IV semiconductors are a promising approach to diminish the use of traditional materials being harmful to the environment. To further increase the efficiency of such devices, their thermal conductivity needs to be reduced while at the same time Seebeck coefficient and electrical conductivity should be increased or at least remain unchanged. In this work, scanning probe microscopy methods and scanning transmission electron microscopy (STEM) are discussed to study structural and electrical properties of laser-sintered highly crystalline Ge nanoparticle layers.

SEM studies already showed a strong effect of the laser fluence on the sinter process resulting in meander structures with variations in structure size. These additional non-uniformities act as scatter areas for phonons reducing the thermal conductivity. The electron backscatter diffraction (EBSD) study of the meander structure of these films revealed that the laser fluence has no substantial impact on the grain size distribution. STEM images showed that the sinter process takes place predominately in the top level of the layer forming larger formations whereas the nanoparticles keep their original crystal structure with amorphous components in between, explaining the low confidence index of the EBSD measurements.

Conductive atomic force microscopy and scanning spreading resistance microscopy (SSRM) is applied to study correlations between film morphology and 2D current distribution. The alteration of the local electrical conductivity of differently doped samples (undoped, n-doped low and high) is shown with current distributions measured with SSRM and local IV-characteristics performed with doped full diamond tips. For undoped (only HF treated) thin films individual grains show a significant drop of their local conductivity. Additionally, the local IV-characteristic curves show a diode-like behaviour on these areas. This is caused by oxide layers at the boundary of larger formations which have been revealed by EDS mappings in STEM mode.

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#P012 - Epitaxial growth of gapped graphene and tungsten disulfide

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In contrast to the progresses achieved in the graphene production methodologies (mechanical and chemical exfoliation as well as chemical vapor deposition), the development of a new 2D electronics is still limited. The main drawback can be related to the lack of an energy gap in graphene which prevents its application in logic transistors. For this reason, several research paths are being targeted at opening a bandgap in graphene including nanoribbon, biased bilayer graphene, chemically modified graphene, bent graphene, etc.. However, the availability of gapped graphene for concrete technological applications results still missing. This lack has strongly motivated the scientific interest toward other 2D materials, such as transition metal dichalcogenides, which already present energy gap. Indeed, the synthesis of a wafer scale graphene with an intrinsic energy gap has been demonstrated since 2007 when a gap of 0.26 eV has been measured in single layer graphene growth on silicon carbide, SiC, by silicon sublimation (namely, epitaxial graphene)[1]. The presence of an energy gap derives from interface interactions between graphene and its growing substrate. For increasing graphene thickness (layer number) such interface effect is minimized and the material results gapless.

We presents a new “chemical route” for the growth of epitaxial graphene. This methodology, in contrast to the simple Si sublimation process, allows a better control of the graphene growth kinetics and, hence, of thickness as well as an improved material quality. We report the full structural and electrical characterization of the as grown epitaxial graphene including the energy gap estimation.

Moreover, we use epitaxial graphene as substrate for the epitaxial growth of tungsten disulfide, WS_2, monolayer for the fabrication of Van der Waals heterostructure integrating 2D materials with complementary properties [2]. Specifically, WS_2 in the monolayer form is a semiconductor with direct gap and strong photoluminescence in the visible and its integration with graphene finds applications in optoelectronic devices. We demonstrate that epitaxial graphene is a perfect template for the growth of few layer WS_2 with homogeneous PL by minimizing interface defects and strain.

[1] S. Y. Zhou, et al, Nature Materials, 6 (2007) 770.

[2] G.V. Bianco, et al, RSC Adv., 5 (2015) 98700.

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#P013 - Morphological and Compositional Modifications of NiTinol surface by Femtosecond Laser Texturing

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Thanks to high biocompatibility and complete recoverable strain up to 8-10%, superelastic NiTi (Nitinol) is the most used shape memory alloy for industrial biomedical applications. The surface processing of NiTi medical components play a fundamental role for guarantee both Ti oxide passivizing layer for avoiding Ni ion release in the human body and surface morphology for controlling the cell proliferation.

Mechanical polishing, electro-chemical, chemical and thermal treatments are performed for surface modifications; recently short and ultrashort laser texturing has been successfully applied for this issue on NiTinol devices.

In the present work an ultrashort laser source, producing 100 fs long laser pulses, was employed for the surface texturing of commercial superelastic NiTinol plates. The plates were prepared with the surface required for biomedical applications. The effect of process parameters, such as average power and scanning rate, on the morphology, surface chemical composition and calorimetric response was studied through SEM and XPS respectively. Surface morphology and Ni/Ti ratio were modified from the initial surface, depending on the process parameters adopted, as different thermal cycles were induced on the Nitinol surface.

#P014 - Spontaneous and assisted self-assembling of silicon nanocrystals on SOI substrates

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Silicon-based nanocrystals represent a promising resource both for next generation electronic devices and for nano-photonics applications but require precise size, shape and position control. Previous work demonstrated the fabrication of ordered arrays of Ge-NCs with relevant electronic properties for microelectronic applications [1,2,3]. In this work a fabrication of silicon nanocrystals by templated solid-state dewetting of thin silicon films (SOI) will be proposed [4, 5, 6]. The process makes use of solid state dewetting of a thin film templated through alloy liquid metal ion source focused ion beam (LMIS-FIB) nanopatterning or by electron beam lithography (EBL) process. The solid state dewetting initiated at the edges of the patterns controllably creates the ordering of NCs with ad hoc placement and periodicity. The NC size is tuned by varying the nominal thickness of the film while their position results from the association of film retraction from the edges of the lay out and Rayleigh-like instability. Islands formation, organization, positioning and composition are studied by dark-field, atomic force and transmission electron microscopy. In optimised conditions the shape of the islands, their number and their relative position can be controlled with a precision of better than 10%. We consider that the capabilities of this top-down/bottom up hybrid method in engineering the SOI dewetting fronts should be open new ways of playing with ordered and disordered metamaterials for thin-film antireflection coating and broad-band and wide angle light-coupling.

[1] A. Karmous, et al., Phys. Rev. B 73, 075323 (2006)

[2] M. Scarselli et al., Appl. Phys. Lett. 91, 141117 (2007)

[3] K Gacem et al. Nanotechnology 21 (2010)

[4]M. Aouassa et al, Appl. Phys. Lett. 101, 013117 (2012)

[5] I. Berbezier et al., J. Appl. Phys. 113, 064908 (2013)

[6] M. Abbarchi et al., ACS Nano 8, 11181 (2014)

#P015 - Optical source for fiber optic distributed sensing based on Brillouin scattering

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Distributed optical fiber sensors have raised a significant interest in the last few years thanks to their inherent measurement capability allowing spatial resolved measurements over long distances with applications ranging from energy to security, defense and structural health monitoring. Among distributed sensors, those exploiting Brillouin scattering effect occurring in silica fiber core are becoming of widespread use since they enable strain measurements as well as temperature assessment. In particular, mostly adopted schemes are based on pump-probe techniques such as Brillouin optical time-domain analysis (BOTDA) or Brillouin frequency-domain analysis (BOFDA), and exploit the temperature and strain dependence of the Brillouin frequency shift parameter, allowing for distributed temperature and strain sensing over tens of km of single-mode optical fibers (SMF). In this paper we show a simple and efficient light source providing pump and probe lights to be employed in Brillouin sensor systems. Generation of a pump-probe light pair with wavelength spacing and tunable capabilities suitable for Brillouin sensing is implemented through a recirculation loop employing a fiber ring structure and bi-directional Erbium-doped fiber amplification (B-EDFA). The theoretical and experimental study shows low threshold values, good tunability properties and a small linewidth of the generated probe light. A distributed feedback laser (DFB) laser (~1.25 MHz linewidth) has been employed for generating the pump light, centered around λ = 1.55 µm, which is then injected in single mode fiber (SMF) on an optical circulator. A bi-directional Erbium Doped Fiber Amplifier (B-EDFA) is then placed in order to boost the seed power and amplifying the generated SBS light, then effecting lowering the threshold level and enhancing the system efficiency. Compared to other solutions, the proposed source has a number of interesting advantages: no expensive parts (no microwave modulation or optical PLL), no critical alignment (the wavelength-shift of the probe is intrinsically locked to the pump), increased sensitivity (narrow-linewidth generated light can be more effective in probing Brillouin Stokes for BOTDA). Source characterization indicates an adequate probe output power (~0.5 mw), large tunability capabilities (up to ~200 MHz), and a narrow linewidth (

#P016 - Synthesis of MoS2 monolayer using promoter

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Nanosheet materials such as graphene, boron nitride and Transition Metal Dichalcogenides (TMD) have gathered a lot of interest in recent years thanks to their outstanding properties and promises for future tecnology, energy generation and post-CMOS device concepts. Amongst this class of materials, MoS_2 has been studied because of its semiconducting properties, its direct bandgap and the possibility to be synthesized by bottom up techniques.

MoS_2 flakes were obtained on SiO_2/Si using chalcogen and sulfur powders in a quartz tube heated at between 680 and 750 °C. In order to promote flakes nucleation, an organic precursor, namely perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), was drop-casted on a Si substrate and placed near the SiO_2/Si substrate on which the growth of flakes occurred.

It was observed that the presence (or absence) of PTCDA in the growth chamber has a profund effect on MoS_2 flakes nucleation and size.

Several growth parameters were varied in order to find the optimal conditions for flakes nucleation: powder weight, sulfur temperature, promoter concentration, substrate temperature, flows. The flakes were observed using a Nomarksi optical microscope and then *characterized* by means of Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Raman and Photoluminescence.

The relationships between growth parameters, flakes thickness and optical properties are discussed.

#P017 - Hetero-epitaxy of epsilon-Ga2O3 layers by MOCVD and ALD

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Gallium oxide, Ga_2O_3, attracted renewed attention in recent times as large single crystals and high-quality homo- and hetero-epitaxial layers became available. The possibility of growing high-quality crystals and films permitted to use this material for new application areas such as substrates for GaN-based LEDs, high-power transistors and UV detectors.

In this work we studied the deposition of Ga_2O_3 films on c-oriented sapphire and we report on the structural characterization of the layers. The deposition was performed on a custom MOVPE reactor that uses trimethyl gallium and water as reagents, either in a standard MOVPE reactor or, by alternating the oxygen and gallium supply, as atomic layer deposition (ALD) process.

We report the crystallographic and structural characterization of the epsilon - Ga_2O_3 phase. Analysis of the growth mechanisms of epsilon - Ga_2O_3 on sapphire shows that growth proceeds via formation of small oriented nuclei that expand up to give large flat hexagonal islands, which ultimately merge producing a flat and homogeneous film. Epilayers of the same epsilon - Ga_2O_3 phase were also successfully deposited on alternative hetero-substrates ((0001)-GaN and (111)-SiC) with good results.

The epsilon - Ga_2O_3 phase was identified by XRD analysis: the structural quality was assessed by high-resolution reciprocal lattice map measurements. A 0.3° mosaicity and 0.01° Omega – 2 Theta peak width demonstrated the high quality of the epilayers. The c axis of epsilon - Ga_2O_3 and sapphire were seen to be coincident, but the Ga_2O_3 lattice is rotated by 30° about the c-axis with respect to the Al_2O_3 substrate. This arrangement allows for a strong reduction of the lattice mismatch. Single-crystal diffraction experiments carried out on a "composite" Ga_2O_3/Al_2O_3sample permitted an in-depth study of the epsilon - Ga2O3 structure. Thanks to XRD data and TEM investigations, a model of the crystal structure characterized by statistical occupation of the gallium sites is proposed.

Finally, a sharp transition from epsilon to beta-$Ga_2O_3$was observed when the growth temperature was increased from 650 to 715 °C. This means that the epsilon phase may be considered stable up to about 650 °C. Although not extremely high, this threshold is high enough to open new perspectives in terms of device applications, which makes this unusual phase of gallium oxide very attractive.

#P018 - Physical vapor deposition of thin films: applications in optoelectronics and OLED technologies and in graphite protection with 2D porphyrin layers

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Physical vapor deposition (PVD) is an extremely versatile thermal evaporation technique which allows for the growth of organic, inorganic and hybrid thin films under controlled conditions. PVDs find wide application in optoelectronic technologies and devices, such as OLEDs, OPVs, OFETs and sensors, because of the potentials for realizing multilayer stacks and codepositions. In addition, PVDs allow for the growth of highly ordered 2D (or pseudo 2D) thin film suitable as surface protecting agents.

Here we present the development/optimization of protocols suitable for the deposition of organic/inorganic materials and their use in: *i)* the realization of multi-color OLEDs devices, and *ii)* deposition of tetra-phenyl-porphyrins (H_2TPP) on a highly oriented pyrolytic graphite, HOPG, to study its protective effect during anion intercalation in graphite.

i) Blue to nearIR OLEDs are fabricated in a multilayer stacks with a doped emissive layer (ITO/NPD/host-Iridium/BCP/LiF/Al). Cyclometalated Ir(III) complexes are selected according to the color and doped onto a semiconductor host.[1] This maximize the charge trapping and exciton recombination in the emissive layer. *ii)* Graphite crystals play a key role in current technology as an electrode and for graphene production.[2] Under electrochemical oxidation condition graphite undergoes degradation in process known as *blister* growth due to anion intercalation. We deposited an ultra-thin (nominal 0.5 Å thick) and a thin (12 Å) H_2TPP film onto HOPG substrate and studied their effect. The thicker film is characterized by coexistence of 3D and 2D phase, while the thinner shows only the 2D wetting-layer. Electrochemical-AFM investigations highlight the protective effect of H_2TPP.[3]

We employed a Kenosistec PVD system, coupled to a glove box, which works at 10-7 mbar pressure and is equipped with four effusive Knudsen type sources for the evaporation of small molecule organic materials and two Joule thermal sources for the deposition of inorganic materials. Two quartz crystal microbalances allow the control, simultaneity, both the deposition rate and thickness of the films while a double zone thermocouples enable careful control on the evaporation temperature of the Knudsen sources especially in the low/medium range.

1) S. Kesarkar, W. Mroz, M. Penconi, M. Pasini, S. Destri, M. Cazzaniga, D. Ceresoli, P. R. Mussini, C. Baldoli, U. Giovanella, A. Bossi, *Angew. Chem. Int. Ed.***2016**, *128*, 2764-2768. 2) R.C. Alkire, P.N. Bartlett, J. Lipkowski, Advances in Electrochemical Science and Engineering. Electrochemistry of Carbon Electrodes. **2015**, 16 (Wiley). 3) R. Yivlialin, G. Bussetti, M. Penconi, A. Bossi, F. Ciccacci, M. Finazzi, L. Duò, Protective Porphyrin Film for Graphite during Anion Intercalation, *submitted*.

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#P019 - Synthesis and characterization of nanocomposite materials for green buildings

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Nowadays an increase in glazing surface is observed in the design of architectural structure, and it’s known that main heat losses are due to glasses and windows. The energy conservation is assuming a key role in “green buildings”, a concept concerning in find new sustainable ways to construct house and building. For example, many efforts are spent in the development of windows with nanocomposite coating acting as solar shield and heat insulator.

In this work nanocomposite materials are prepared starting from two different polymer matrices and antimony tin oxide (ATO) nanoparticles as filler, in order to obtain heat insulator coating for windows. Ionomer polyurethanes, synthesized in our labs and a commercial polymer commonly used in laminate glass, named as polyvinylbutyral (PVB), are used as polymer matrices.

Ionomer polymeric matrices are based on linear thermoplastic polyurethane composed by soft (polytetramethylene oxide) and hard (aromatic diisocyanate) segments. Two different synthetic approaches are then compared. In route A, after quaternarization of PU via Menshutkin reaction by quaternarisation of the chain extender nitrogens with alkyl halide, PU-cationomer is water dispersed and then ATO nanoparticles are added. In route B, ATO nanoparticles are firstly functionalized on the surface with a suitable molecule, then modified-ATO nanoparticles are used to quaternarize PU and finally PU-cationomer based nanocomposite is obtained after water addition.

The possibility to synthesize nanocomposites with a different hard/soft content ratio, different % of ionic content, different type of quaternarising agent, and different content of nanoparticles is proved. The nanocomposites are characterized by TEM in order to correlate as different composition of polymeric matrices can affect morphology, thermal, mechanical and spectral properties of the nanocomposites.

PVB-ATO nanocomposites are obtained by spray deposition of ATO suspension onto PVB commercial film, and by casting of PVB solution with ATO nanoparticles dispersed. The spray deposition led to couple glass/nanocomposite/glass in order to obtain laminated glass with insulating property in a scalable manner for industry purpose. The film by cast deposition led to nanocomposite able to be characterized by thermal, spectroscopy and polymer dynamics techniques.

References

1. C. G. Granqvist, Sol. Energ. Mat. Sol. Cells 2007, 91, 1529-1598

2. O. Jaudoin, J. Robin, J. Lopez-Cuesta, D. Perrin, C. Imbert, Polym. Int. 2012, 61, 495-510

3. K. Nanda, D. A. Wicks, S. A. Modbouly, J. U. Otaigbe J. of Appl. Polym. Scie. 2005, 98, 2514-2520

4. Z. Dai, Z. Li, L. Li, G. Xu Polym. Adv. Technol, 2011, 22, 1905-1911

5. Fang, X. Zhou, Q. Yu, S. Lin, D. Guo, R. Yu, J. Hu Prog. Org. Coat 2014, 77, 61-71.

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#P020 - Synthesis of innovative graphene structures by chemical vapor deposition

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C-based materials cover a central role in the field of modern nanoelectronics, sensing and energy. In particular, graphene seems to be one of the most promising materials thanks to its many fascinating properties, such as giant electron mobility, extremely high thermal conductivity and extraordinary elasticity and stiffness. Recently, a great attention has been focused also to three dimensional (3D) graphene structures, able to integrate this material into three dimensional functional architectures for new macroscopic applications.

Our research activity is hence focused on the realization of these C-based materials by a dedicated Thermal and Plasma Enhanced Chemical Vapor Deposition. In particular, we deal with the synthesis and characterization of 3D structures (e.g. graphene foams, GFs) by using substrates of different nature and morphology as templates. Indeed, these 3D structures provide graphene-based materials with high specific surface areas (~850m^2/g), strong mechanical strengths and fast mass and electron transport kinetics. All these properties make them interesting for applications in many fields (e.g. sensing, Li batteries, etc.) where the available surface area plays a central role. Many efforts have been devoted to optimize both the growth process and the following steps aimed to remove the template to obtain a free standing GFs. This step is very critical in order to prevent the collapse of the final graphene foam due to the difficult in bearing the liquid capillary force caused by the evaporation of the common solvents used during the various steps. The obtained GFs were characterized both morphologically and structurally. Part of the study is also devoted to the realization and characterization of hybrid structures with other nanostructured materials (e.g. metals or oxides) that can open further promising ways of applications.

#P021 - Protective coatings for monolithic ceramics by oxidation assisted pack cementation

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Pack cementation is a simple and low-cost method to protect materials against oxidation. It has been developed many years ago to obtain an oxidation resistant coating on the nickel alloys. In more recent years, it has been also applied both to the monolithic and to the composite ceramics. The experimental results, aimed to the development of different coatings, are presented. In the case of monolithic ceramics, a modified pack cementation method called OXidation-assisted PAck Cementation (OXPAC) was successfully applied to silicon carbide-based materials. This method is based on the reaction of the powder pack with the surface layer composed of the oxidation products of the SiC -based materials. Rare earth oxides were used as pack powder in order to obtain rare earth silicates after OXPAC

#P022 - Photoluminescence-structure correlations in ferroelectric Eu:Ba(Ti,Zr)O3 ceramics: study of phase transitions

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$BaTiO_3$-based ferroelectric ceramics show interesting properties such as high dielectric constant, low losses, high hydrostatic piezoelectric coefficient and positive coefficient of resistivity. For these reasons, barium titanate is widely used in the electronic industry for manufacturing miniaturized multilayer ceramic capacitors, underwater transducers and self-regulating thermistors. $BaZr_xTi_{1-x}O_3$ (BZT) solid solution shows a series of phase transitions (PT) and a progressive evolution of ferroelectric order, from long-range order typical of classic ferroelectrics (y = 0) to short-range order typical of relaxors ($x \geq 0.25$), which consequently affects the functional properties. This material can be considered as a model system for understanding the composition-property correlations in ferroelectric ceramics. The trivalent europium ion (Eu^{3+}) is well known for its strong luminescence in the red spectral region. Even very small variations in the coordination sphere of europium ions induce major changes in the emission spectrum. Thanks to these features, Eu^{3+} is a unique and powerful local structural probe. In this framework, we used photoluminescence (PL) as a tool to investigate phase transitions and the ferroelectric order in BZT using Eu^{3+} as active centre. Dense ceramics (relative density: 96-99%) with composition $Eu_xBa_{1-x}Zr_yTi_{1-y-x/4}O_3$ (x = 0.01, y = 0, 0.05, 0.15 and 0.30) were prepared by the classical solid-state route and sintered at 1450-1500 °C. The dielectric permittivity of the samples was measured from -150 to 150 °C and at 10^2-10^6 Hz to determine reference values of the phase transition temperatures. The study of PL spectra as function of the temperature, in the interval -100/140 °C, revealed strong shape variations in the PT proximity thus allowing the identification of the stability range of the different crystalline phases.

#P023 - Synthesis and modification of silver and BaTiO3 particles as fillers for polymeric composites with high dielectric constant

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There is an increasing demand of high permittivity (high-k) materials due to the rapid development of the electronic industry and the need of more efficient energy storage devices. The combination of dissimilar components in composites is expected to be an effective approach to better dielectric materials. The inclusion of high-k particles, such as Ag and $BaTiO_3$, in a polymeric matrix can significantly increase the dielectric constant while preserving the flexibility and the high breakdown voltage typical of polymers. The combination of high-permittivity and large breakdown fields is a fundamental requirement to store electrostatic energy with high density.

Ferroelectric $BaTiO_3$ nanoparticles (50-100 nm) were obtained by a hydrothermal-like method starting from cheap inorganic precursors ($BaCl_2$ and $TiCl_4$). The size of the particles was tailored by changing the precursor concentration. Silver particles (20-200 nm) were synthesized by a solvothermal method using ethylene glycol as a solvent and $AgNO_3$ as a precursor and adding polyvinylpyrrolidone (PVP) as growth modifier to control the particle size.

The nature of the inclusion-polymer interface has a strong impact on the dispersion of the inorganic particles and the dielectric properties of the resultant composite. The compatibility between the two phases was improved by functionalizing the particles with specific coupling molecules, such as silane-based compounds. As a further strategy to improve the dielectric properties of the composite, the particles were coated with a thin TiO_2 shell, which has a dielectric constant intermediate between the filler and the polymer matrix and thus realizes a more homogeneous distribution of the electric field.

#P024 - Ruthenium-based dye-sensitized solar cells: future and perspective.

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There is currently a large effort to improve device performances and stability in order to meet with the requirement for greener energy generation. Dye-sensitized solar cells (DSCs) are actually one of the most promising low cost photovoltaic technologies, addressing "secure, clean and efficient solar energy conversion" [1]. Here we show and compare our recent progress on the exploitation of hybrid-organic dyes ruthenium based (N719, K19, C101, C106, N749 and Z907) for application in DSCs. Furthermore, we provide an in depth discussion on the main limitations in the use of these dyes, outlining future developments for their use both in DSCs and large area modules [2]. We also discuss the cost of DSCs and how their can boost the advancement for new power management solutions in living environments integration and economically viable routes. Finally, we present our view on future prospective in the development of advanced materials for more efficient DSCs. References [1] Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H.; Dye-sensitized solar cells. Chem. Rev. 2010, 110, 6595-6663. [2] Calogero, G.; Bartolotta, A.; Di Marco, G. ; Di Carlo A.; Bonaccorso, F. Vegetable-based Dye-Sensitized Solar Cells. Chem Soc Rev. 2015.

#P025 - Towards air stable field-effect transistors based on few-layer black phosphorus

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Two-dimensional crystals have emerged as a class of materials that may influence future electronic technologies. Recently, black phosphorous (BP) was reintroduced from the perspective of a 2D layered material. BP presents a puckered single layer geometry that consists of two atomic layers and two kinds of P-P bonds. The anisotropic in-plane lattice structure gives rise to highly anisotropic properties[1]. Moreover, the direct energy bandgap in few-layer BP increases monotonously with reducing number of layers, eventually reaching 2 eV for monolayer crystals, called *phosphorene*. High carrier mobility and ambipolar transport have been recently reported for phosphorene[2,3]. Thus, BP has demonstrated intriguing properties and promising potential for applications in infrared optoelectronics and photonics, which may enable the realization of conceptually new devices. While many efforts are devoted to develop cost-effective methods to produce mono/few-layer BP[4], mechanical exfoliation from bulk BP crystals remains the favorite fabrication protocol towards pure 2D BP for basic physical investigations.

Un-encapsulated BP flakes were found to be prone to chemical degradation in environmental conditions. Alumina is the commonly used coating, proved effective towards BP oxidation[5], and preserving its electrical properties. In order to answer the needs of air-stability improvement, we will report about the electrical and structural investigation, of few-layer BP flakes coated with different materials, both organic (like PMMA, SU8) and inorganic (like SiO_2, Al_2O_3, SiN). We will exploit field-effect transistors (FETs), fabricated with electron beam lithography on individual BP flakes, as a platform for the investigation of the active interfaces between BP surface and both the metal contacts and the insulating layers. We will show i) the results of the FET electrical characterization and ii) the structural and chemical investigation of the interfaces combining high-resolution transmission electron microscopy, micro-Raman spectroscopy and confocal microscopy on devices cross-sections prepared with focused ion beam methods.

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References

[1] F. Xia, et al., *Nat. Commun.* **2014**, *5*, 4458.

[2] L. Li, et al., *Nat. Nanotechnol.* **2014**, *9*, 372.

[3] S. Das, et al., *ACS Nano* **2014**, 11730.

[4] M. Serrano-Ruiz, et al., *Adv. Mater. Interfaces* **2016**, *3*, 1500441.

[5] J. D. Wood, et al., *Nano Letters*. **2014** 14 6964.

#P026 - Polymeric blend of gelatin and cellulose nanofibrils: a nanobiomaterial with controlled mechanical performances and degradability

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Introduction:

In recent years, new regenerative approaches for the healing of diseased tissues and organs have aimed to recover the original functionality and reduce healthcare costs and patient's pain. Furthermore, different studies shows as some substrate characteristics (stiffness, mechanical stimulation, surface topography etc.) can influence cellular functions and direct stem cell differentiation.

In the present work, blending and cross-linking processes are designed to combine the best properties of two bio-polymers and to obtain hybrid materials with improved mechanical performances without losing biocompatibility, chemical stability and flexibility. In particular, several blend compositions were studied to obtain specimens with different mechanical properties and biodegradability in simulated body conditions suitable to induce different cell differentiation. Gelatin has been selected due to its high biocompatibility, easy production and low cost, while cellulose nano-fibers (CNF) have been selected due to their biocompatibility, exceptional mechanical properties, high crystallinity and surface areaand availability.The polymeric blends were obtained by dissolving porcine gelatin in CNF water suspension at 40°C under mechanical stirring keeping constant the final blend concentration and varying the polymers weight ratio. The blends were than freeze-dried to achieve 3D porous structures and cross-linked applying a dehydrothermal cross-linking treatment (DHT) at 160°C in vacuum. Evaluation of morphological, chemic-physical and viscoelastic properties of the different specimens were carried out. Preliminary in vitro tests were performed to evaluate scaffolds cytotoxicity.

Results & Discussion:

Different CNF/gelatin weight ratio were evaluated: 1:0, 1:1,2:1, 1:2, 0:1 respectively, and all blends were cross-linked by DHT. The samples show similar interconnected porous structures and suitable chemical stability in physiological conditions, this prove that the polymeric ratio does not affect significantly the scaffold morphologies and stability. DMTA analyses demonstrate that by changing the polymeric ratio it is possible to obtain scaffold with different mechanical performances in terms of stiffness and Young modulus in function of the content of CNF. In vitro evaluation demonstrates the biocompatibility of the scaffolds and their good interaction with cells.

Acknowledgments

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#P027 - A Low-temperature Solvent-free Chemical Strategy for the Direct Synthesis of L10 FePt Nanoparticles from Layered Precursor

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The binary FePt alloy in the high magnetic anisotropy $L1_0$ phase is one of the most promising magnetic materials for applications in the field of magnetic recording for media capable to sustain areal density larger than 1 Tbit/in^2. This is due to the large magnetic anisotropy energy of $7{\times}10^7$ J/m^3 [1], which allows stable ferromagnetic particles with size as small as 2.8 nm, to its resistance to oxidation and its stability at room temperature. The chemically ordered tetragonal $L1_0$ FePt phase is usually obtained by thermal treatment of the chemically disordered cubic phase A1. The degree of phase transformation A1 -> $L1_0$ increases with the treatment temperature, but usually, even in optimized processes, temperatures higher than 500-600°C are required.

In this work, a new green chemical approach to synthesize magnetically hard $L1_0$ FePt nanoparticles at lower temperature (400 °C) is described. A crystalline saline complex hexaaquairon(II)hexachloroplatinate, $[Fe(H_2O)_6]PtCl_6$ was employed as the precursor for the synthesis. [2] This complex is the ideal starting point for a low temperature synthesis, since it is characterized by a chemically ordered crystal structure [3] with alternate layers of Fe and Pt atoms, that very much resembles the chemical order of Fe and Pt elements in the $L1_0$ tetragonal cell.

The precursor was mixed with NaCl in different proportion (50mg/20g, 25mg/20g, 10mg/20g) and milled in a planetary milling. The powder was then heated up to 400 °C under reducing atmosphere (5% H_2 and 95% Ar). Then, after annealing at the final temperature for 2 h, the formation of FePt nanoparticles in the highly ordered $L1_0$ phase was observed, as confirmed by XRD and HRTEM investigations. This method can be considered " green" due to the low temperature of the process and to the absence of organic solvents or surfactants. Indeed only non-hazardous materials were used in the synthesis, the milling step being performed using NaCl as media and water as solvent. By varying the precursor/NaCl ratio, particles with size in the range of 6.2 – 13.2 nm were obtained. With the decrease of particle size, the room temperature coercivity of FePt nanoparticles also decreased from 10.9 kOe to 4.7 kOe.

[1] K. Inomata, T. Sawa and S. Hashimoto, J Appl Phys, 1988, 64, 2537-2540; J. P. Wang, P Ieee, 2008, 96, 1847-1863.

[2] X. C. Hu, E. Agostinelli, C. Ni, G. C. Hadjipanayis, and A. Capobianchi, Green Chemistry 2014, 16 (4), 2292-2297

[3]A. Capobianchi, G. Campi, M. Camalli and C. Veroli, Z Kristallogr, 2009, 224, 384-388.

#P028 - Electrodeposition and Characterization of thin films of MoS2

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Nowdays, the research is more and more moving towards the develop of low cost affordable techniques to produce thin films of inhexpensive materials that have promising characteristics to be used in direct solar cells. The Electrochemical Atomic Layer Deposition (E-ALD) is one of these techniques allowing the production of ordered thin films of semiconductors. E-ALD method was used to obtain semiconductor compounds in the form of very thin films (below 100nm) . The method is based on an alternate underpotential deposition (UPD) of monolayer of the elements forming the compound. The UPD is a surface phenomenon that occurs when the deposition of one element precedes the massive electrodeposition. The UPD allows the perfect control of deposition of different kind of elements making possible to deposit highly defined nanostructures with a layer-by-layer control. The technical advantage is the possibility to modulate and to modify the parameters that influence the electrodeposition. That means that conditions for deposition can be adjusted concerning potential, pH, reactants and so on. Among the material suitable for electrodeposition from aqueous solutions, MoS_2 is an important IV–VI semiconductor, diamagnetic and with bandgap very close to silicon (1.7 eV), thus perfectly fitting with solar emission. Moreover, MoS_2 with particle size in the range of 1–100 µm is used as a common dry lubricant. Few alternatives exist that confer high lubricity and stability up to 350°C in oxidizing environments.

UPD anodic electrodeposition of Na_2S on crystalline Ag[111] electrode is well-known process, so starting from this technical background we investigated the system in order to discover the optimal conditions to depose Mo on sulfur covered Ag[111]. From a solution of MoO_4^{2-} in alkaline buffer the electroreduction process can be controlled limiting the the deposition of molibdenum to just a monolayer. By means of cyclic voltammetry, a very low coast technique, it is possible to accurately control the deposition process.

In this communication the preliminary results of an investigation devoted to determine the optimal condition for the electrodeposition of Mo on Ag[111]/S in buffered alkaline solution are described.

#P029 - Space and Time coherence properties of 2D driven-dissipative polariton condensates

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Polariton condensation has been observed in many different systems, ranging from standard inorganic 2D microcavities [1] and 1D wires to confined pillars [2]. Recently the same phenomenon has been reported using hybrid or organic dyes as active materials [3]. The condensation dynamics and the formation of a spatially extended coherent state of polaritons are nowadays well understood [4], but the consequences of the balancing between pumping and losses together with the finite lifetime of these quasi-particles bring on stage unexpected behaviours [5].

In this work, we have studied the time and spatial coherence properties of an extended 2D polariton condensate, a paradigmatic realization of an open, driven-dissipative system. Actually, the theory behind the coherence build up processes is well established in 2D atomic BEC, although no sign of correlation between temporal and spatial coherence has been observed in such systems. On the other hand, it remains a matter of debate whether a genuine Berezinskii-Kosterlitz-Thouless (BKT) phase can be reached in open-driven dissipative systems, such as exciton-polaritons [6]. Indeed, the condition for the establishment of the thermal equilibrium when crossing the phase transition is still an open question. Here, we have investigated these phenomena using the first order cross-correlation function for the spatial correlation and the auto-correlation function for the temporal decay. For the first time we evidence the same power-law decay in both domains, in agreement with the theory prediction for a true equilibrium BKT. The experimental findings are backed up by numerical stochastic simulations demonstrating that the pairing mechanism of topological defects is responsible to the crossover.

These results show that in large enough 2D polariton condensates it is possible to determine if the thermal equilibrium is established, upon observing simultaneously the spatial and temporal decay of the correlation. This unique type of estimation could open new possibilities of investigation and applications not accessible to the atomic counterparts.

[1] Wertz, E. *et al.* Spontaneous formation and optical manipulation of extended polariton condensates. *Nature Phys.* **6**, 860864 (2010).

[2] Bajoni, D. *et al*. Polariton laser using single micropillar GaAsGaAlAs semiconductor cavities. *Phys. Rev. Lett.* **100**, 047401 (2008).

[3] Daskalakis, K. S. et al. *Nonlinear interactions in an organic polariton condensate, Nature Materials* **13**, 271–278

[4] Timofeev, V. & Sanvitto, D. (eds) Exciton Polaritons in Microcavities Vol. 172 (Springer, 2012)

[5] L.Dominici *et al*.Vortex and half-vortex stability in coherently driven spinor polariton fluid, arXiv: 1403.0487(2014)

[6] Roumpos *et al.* Power-law decay of the spatial correlation function in exciton-polariton condensates, **109**.

#P030 - Optical and electronic properties of eumelanin: from monomer to tetramer structures

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In the present work we report a systematic comparison, based upon a computational study between the electronic and optical properties of four monomers and those of two tetramers recently proposed as possible protomolecules of eumelanin. Eumelanin is the most important form of melanin which is one of the most universal natural pigments present in living organisms. For the isolated monomers and for the tetramers we performed all-electrons Density Functional Theory (DFT) and Time Dependent DFT (TDDFT) calculations with a localized Gaussian basis-set. For each molecule here studied we determined a series of molecular properties, namely electron affinities, ionization energies, fundamental energy-gaps, optical absorption spectra, and exciton binding energies. In the case of the DHI monomer we were able to perfom also direct e.m. absorption measurements in ethanol solution. We discuss these results in comparison with the corresponding theoretical counterparts and, moreover, the possible implications of the above electronic and optical properties of the single monomers and of the tetramers with respect to the long-standing debate on the structure of eumelanin molecule

#P031 - Aging of Polyamide 11 nanocomposites

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Thermal and photo-oxidative degradation processes occurring on PA11 nanocomposites (NC) with Cloisite™30B were investigated to establish the eventual contribution of organo nanoclay modifier on degradation mechanisms. It is well known that polyamides are not intrinsically stable in the presence of oxygen and/or humidity especially at high temperature. The literature identified as most relevant the *a-CH hydrogen abstraction*oxidative mechanism followed by the Karsten and Rossbach pathway for the interpretation of residue formation.Contradictory opinions about the degradation processes involving PAs NC materials were found. Furthermore, was not clear as nanoclays affect the degradation pathways of PAs based NC. Thermal-oxidation of PA11NC was performed in a glass vessel at 215°C under flow or atmospheric air up to 150 minutes, whereas the photo-aging was carried out on QUV apparatus at 60°C using UV lamps (340nm) up to 7 days. The oxidized materials were analyzed by size exclusion chromatography (SEC), viscometry and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOFMS). Data obtained for thermo-oxidised PA11 NC, ascertained an active contribution of organo-modifier clays in accelerating cross-linking reactions. PA 11 NC samples degraded faster than virgin PA11 material producing a higher amount of insoluble residue. The formation of gel fraction was accomplished by the appearance of a characteristic peak in the MALDI spectra. We suppose that olefins produced by Hofmann elimination reaction from Cloisite™30B were responsible for the increase of rate of cross linking reactions. In fact, olefins are very susceptible to air and moisture, producing oxygenated (aldehydes, acids) as final products. During initial step of auto-oxidation, the formation of aolefin hydroperoxides is accomplished by the capture of available hydrogens; the favourable attack is without doubt to the aamino methylene positions of PA11 chains. At this point, the well known *a-CH hydrogen abstraction*mechanism proceeds, accelerating the formation of amide terminal chain groups and consequently the gel fraction. The amide degradation products were identified and revealed as a characteristic peak in the MALDI spectra. Data obtained from photo-oxidation of PA11 nanocomposites suggested that organo-modifier clays do not significantly contribute to modify photoreaction pathways of polymeric material. Differently from PA6 and PA66, MALDI peaks deriving from NORRISH photo-cleavage were absent from the PA11 spectra collected at different exposure time. The only mechanism active during photo-exposure of PA11 samples appears to be the *a-CH hydrogen abstraction.*

#P032 - Vertically-Illuminated Resonant Cavity Graphene/Silicon Schottky Photodetectors at 1550 nm

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Graphene is an appealing materials for photonics, optoelectronics and sensors because they offer a wide palette of advantages compared to other materials. Indeed, graphene properties include ultrafast carrier dynamics, wavelength-independent absorption, tunable optical properties via electrostatic doping, low dissipation rates and high mobility, and the ability to confine electromagnetic energy to unprecedented small volumes. The dispersion relation remains quasi linear up to ~±4eV from the Fermi energy. It is therefore possible to generate charge carriers by optically stimulating inter-band transitions over a wide energy spectrum, unmatched by any other material. This includes commercially important telecommunication wavelengths, the FIR/THz, the SWIR (short-wave infrared) and MIR (mid-infrared) ranges. The high carrier mobility enables ultrafast conversion of photons or plasmons to electrical currents or voltages. By integration with local gates, this process is actively tunableand allows for sub-micron detection resolution and pixelization. A variety of prototype optoelectronicdevices have already been demonstrated, such as transparent electrodes in displays and photovoltaic modules, optical modulators, plasmonic devices, microcavities and ultra-fast lasers. Amongst these, a significant effort has been devoted to photodetectors (PDs). Various photodetection schemes and architectures have been proposed to date. The simplest configuration is the metal-graphene-metal (MGM) PD in which graphene is contacted with metal electrodes as source and drain. Further, these PDs can be enhanced with plasmonic metal nanostructures employing local surface plasmons for increased absorption, increasing responsivity.

In this work we report on the fabrication and characterization of a vertically-illuminated Fabry-Perot photodetector based on a graphene-silicon Schottky junction working at 1550 nm. Device absorption mechanism is based on the internal photoemission effect through a metal-silicon junction where chemical vapor deposition-grown graphene plays the role of the metal. Taking advantage of multiple reflections inside the resonant structure, a wavelength-dependent external responsivity of 20 mA/W at -10V and 1550 nm, has been reported. This paves the way to graphene integrated silicon photonics for free space optical communications, coherence optical tomography and LIDAR applications.

#P033 - Force field simulations of particle subjected to dielectrophoresis interactions

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Particles (with sizes in range from sub-micrometer to about 1 millimeter) whit particular electrical and/or magnetic properties, experience mechanical forces and torques when are subjected to electromagnetic fields (this type of particles are called “electromechanical particles”). Some of the phenomena that affect electromechanical particles are: electrostatic adhesion, magnetic separation, electrophoresis and dielectrophoresis (DEP). A branch of emerging application relates to manipulation of biological particles, such as cells or DNA.

The theoretical study of these large class of complex systems is possible thanks to the development of real systems' models and numerical simulations of the stable (multi-particle) configurations and their dynamics; whereas the electric permittivity and electric conductivity (both of the particles and of the medium), the amplitude of the externally imposed field and its frequency are important parameters of such approach. The forecasts will be compared with the behavior of real systems.

This contribution focuses on the theoretical study of the dynamics of spherical particles suspended in a colloidal solution, in the presence of non-homogeneous and non-uniform variable electric fields, which are subjected to dielectrophoresis. DEP forces are estimated by integrating the Maxwell tensor, whilst dynamics is simulated by Molecular-Dynamics like techniques. Hard wall potential is included to take into account the steric interactions between particles and wall. Gravity and hydrodynamic forces are also considered if necessary.

We apply this numerical code to study motion of cells and inorganic particles. Interestingly these simulations may relate to statistical mechanics experiments. It is possible to simulate experiments related to Szilard model, according to which one bit of information, which is obtained through a measurement on the system, can be converted into a quantity of free energy equal to KTln2.

#P034 - Valorization of hemp fibres in eco-composites from bioplastics

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Hemp is generally grown for its bast fibres, used as a raw material for cordage and textile products, and for its pulp used for specialty papers. For many years, hemp has been a traditional crop in Italy; from the late ‘90s hemp cultivation has been reintroduced due to an increasing demand for non-food crops in farming systems and a renewed interest in the use of natural fibres, also for non-woven industrial products. From hemp processing derive significant amounts of secondary products with a low value. Hemp fibres possess some of the best mechanical properties of all natural fibres and, apart textile applications of bast fibres, up to now the short fibres are mainly used for building insulation and composite materials. In the latter case, the market of reference is the automotive interior, and the composites are based on synthetic plastics.

Within this frame, of particular interest it appears the development of fully compostable eco-composite materials based on biodegradable or compostable bioplastics as matrices and low value hemp fibres and/or shives as reinforcing agents. In the present work, raw hemp fibres were used to reinforce a commercial biopolyester, namely poly(1,4-butylene adipate-*co*-terephthalate) thus improving its mechanical properties. To this purpose, an appropriate surface treatment of the fibres was necessary to enhance the fibre/matrix adhesion.

To reduce the intrinsic hydrophilicity of the hemp fibres, they were preliminary washed with diluted $NaOH_{aq}$ in mild conditions and then treated with a green process based on a novel soft plasma jet (developed by Nadir Srl). In the present case, this system allowed the use of a Ar + O_2 gas mixture, coupled with deposition of methyl metacrylate. Thermogravimetric analysis (TGA) was carried out to evaluate thermal and thermo-oxidative stability of the ensuing composites and determine the fibre content. Morphological analysis of fibres and composites was performed by scanning electronic microscopy (SEM). The eco-composites were investigated in terms of rheological, mechanical, and dynamic-mechanical behaviour in comparison with the neat biopolyester matrix. Specific mechanical testing were performed on fibres before and after surface modification treatments.

#P035 - Functionalization of nanoporous Gold obtained by dealloying of amorphous precursors

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Nanoporous metals are constituted by ligaments and pores interconnected with size of tens or hundreds of nanometers. They can be produced by dealloying, a process in which less noble elements are chemically or electrochemically dissolved from a crystalline or an amorphous alloy leaving apart the noble element.

Nanoporous Gold can found applications in various fields such as catalysis, electrocatalysis, sensing, electronics, and optics, due to its structural, morphological and chemical flexibility.

In this work, the production of NPG via dealloying of Au-based amorphous precursors is outlined, showing how the final morphology can be tailored by controlling processing parameters and alloy composition. The morphology and structure of nanoporous Gold obtained from an amorphous and a crystalline precursor ($Au_{40}Cu_{28}Ag_7Pd_5Si_{20}$ and $Au_{31}Cu_{41}Zn_{12.8}Mn_{15.2}$ respectively) is studied by means of Scanning Electron Microscopy, Transmission Electron Microscopy and X-ray Diffraction. The differences are explained in terms of mechanism of dealloying that can differ when the precursor is amorphous with respect to a crystalline solid solution.

Moreover, the functionalization of nanoporous Gold obtained from $Au_{40}Cu_{28}Ag_7Pd_5Si_{20}$ amorphous precursor electrochemically dealloyiedwill be addressed describing a variety of possible applications.

#P036 - Hydrides for energy storage

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Hydrides are investigated for various energy storage applications, including hydrogen storage, solid-state electrolytes, heat storage, etc. With a careful tailoring of composition and a refinement of the microstructure on a nanoscale, properties related to different applications can be significantly improved. In all cases, thermodynamic properties and phase diagrams have to be known in details. In this work, examples of hydrides for different applications will be provided.
Solid state hydrogen storage based on hydrides has been investigated in recent years with the goal to improve hydrogen gravimetric density and to match thermodynamic requirements necessary for dehydrogenation reactions with an equilibrium close to ambient conditions. Results of assessments of thermodynamic properties for metal hydrides (e.g. MgH2 [1]), intermetallic compounds (e.g. La(Ni,Al)5H7 [2]), complex hydrides (e.g. LiBH4 [3], Mg(BH4)2 [4]) will be reported. Experimental data can vary significantly depending on experimental conditions, because several metastable products can be formed during dehydrogenation reactions [5]. Combining ab-initio calculations and experimental investigations, possible dehydrogenation paths were outlined [4]. On the basis of hydrogen sorption properties, applications of solid state hydrogen tanks coupled with PEM fuel cells will be shown [6].
The description of thermodynamic properties of the liquid phase in hydrides remains a big challenge, because of lacking of experimental data. Examples of phase diagrams will be provided for eutectic mixtures (e.g LiBH4-NaBH4 [7]), often infiltrated into porous scaffolds to enhance hydrogen sorption properties
LiBH4 exhibits Li superionic conduction due to a structural transition at around 390 K and it has been suggested as solid-state electrolyte for Li-ion batteries. The combination of different complex hydrides (e.g. LiBH4 and LiNH2) provides the stabilization of the high conducting phase or the development of new crystal structures, characterized by open channels for fast Li-ion mobility. Examples will be provided for Li4(NH2)3(BH4) and Li2(NH2)(BH4) compounds [8].

[1] M.W.Rahman, A.Castellero, S.Enzo et al., J. All. Comp. 509S (2011) S438–S443
[2] E.R.Pinatel, M.Palumbo, F.Massimino, P.Rizzi, M.Baricco, Intermetallics, 62 (2015) 7-16
[3] A.El Kharbachi, E.Pinatel, I.Nuta, C.Chatillon, M.Baricco, CALPHAD 39 (2012) 80-90
[4] E.R. Pinatel, E. Albanese, B. Civalleri, M. Baricco, J. All. Comp. 645S (2015) S64-S68
[5] J.G.Vitillo, S.Bordiga, M.Baricco, J. Phys. Chem. C 119 (2016) 25340-25351
[6] P.Rizzi, E.Pinatel, C.Luetto et al., J. All. Comp. 645S (2015) S338-S342
[7] E.M.Dematteis, E.Roedern, E.R.Pinatel et al., RSC Advances 6 (2016) 60101–60108
[8] A.Wolczyk, E.Pinatel, M.Chierotti et al., Int. J. Hydr. Ener. (2016) doi:10.1016/j.ijhydene.2016.03.040

#P037 - Lithographic control of chirality in supramolecular aggregates

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Chirality is one of the most intriguing property of matter related to the lack of mirror symmetry. Molecules can exist in the two mirror-image structures due to the occurrence of at least one chiral center or a chiral structural arrangement. The transmission of chirality from the molecular up to the macroscopic scale has major implication in life sciences but it is relevant for many applications ranging from catalysis to spintronic. However, its control at nano- and meso-scale is still an open issue that limits its technological application. Here, we demonstrate by a simple approach how chirality can be specifically transferred to a supramolecular system. We describe the formation of stripe features consists of chiral aggregates of a porphyrin derivative on solid substrate in a sub-micrometer-order precision using a modified protocol of a soft lithography. Different from the conventional methods, the polymeric stamp is swelled with an ethanol solution of a chiral inducer reagent and upon contact with a porphyrin aqueous solution J-aggregates are formed. By slow evaporation of the solvent, the solution remains into the protrusions between the substrate surface and stamp, whereas the remaining surface becomes dry. Removal of the stamp results in the formation of a patterned solid features made of porphyrin chiral aggregates. The proposed method successfully allows the fabrication of an ordered distribution of sub-micrometric porphyrin structures in precise and controllable position with programmed chirality, providing a fundamental breakthrough toward the exploitation of chiral materials in technological applications.

#P038 - Logic-gate devices based on printed semiconducting nanostripes

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The applications of organic semiconductors in complex circuitry such as printed CMOS-like logic circuits demand miniaturization of the active structures to the sub-micrometric and nanoscale level while enhancing or at least preserving the charge transport properties upon processing. Here, we addressed this issue by using a wet lithographic technique, which exploits and enhances the molecular order in polymers by spatial confinement, to fabricate ambipolar organic field effect transistors and inverter circuits based on nanostructured single component ambipolar polymeric semiconductor. In our devices, the current flows through a precisely-defined array of nanostripes made of a highly-ordered diketopyrrolopyrrole-benzothiadiazole copolymer with high charge carrier mobility (1.45 $cm^2V^{-1}s^{-1}$ for electrons and 0.70 $cm^2V^{-1}s^{-1}$ for holes). Finally, we demonstrated the functionality of the ambipolar nanostripe transistors by assembling them into an inverter circuit that exhibits a gain (105) comparable to inverters based on single crystal semiconductors.

#P039 - Vibrational Fingerprints of Atomically-precise Graphene Nanoribbon

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Graphene nanoribbons (GNRs) – i.e. quasi one-dimensional narrow stripes of graphene – are semiconductors trough quantum confinement, their bandgap depending on nanoribbon width and edge shape [1]. Indeed, the ability to tune GNR electronic properties by controlling their shape and dimensions makes them extremely promising materials for optoelectronic, as well as spintronic applications. Surface-assisted self-assembly of suitable molecular precursors have been introduced as a bottom-up approach to obtain atomically precise control on GNRs width, shape and chemical composition [2]. In this method, the features that influence GNRs properties (i.e. width, shape and edge terminations) are completely determined by the choice of the precursor monomer. Several techniques, such as in particular STM, Raman, and synchrotron-radiation spectroscopies, are currently used to characterize GNR properties and their formation process. High Resolution Electron Energy Loss Spectroscopy (HREELS) is a surface-sensitive technique, which can precisely characterize the vibrational properties of overlayers, especially when infrared absorption is weak. For this reason, it is particularly suitable to investigate the self-assembling of GNRs on metal surfaces. In this work we present a combined experimental and theoretical investigation, analyzing and comparing different types of GNRs (i.e. Armchair, Chevron-shaped armchair and N-doped chevron), grown on Au(111). In all cases, GNR HREELS spectra are dominated by the out-of-plane γ(C-H) mode manifold, located in the 700-850 cm-1 region. Comparison between experimental data and theoretical calculations based on a DFT approach, unveils that this manifold is a superposition of peaks assignable to different molecular edge topologies (i.e., TRIO, DUO and SOLO structures [3][4]). The manifold profile thus reflects the shape and edge terminations of the GNRs, representing a clear fingerprint of the different GNR types. It also provides useful information on GNR average morphology and on the presence of structural defects. Considering the amount of information which can be obtained by a careful analysis of HREELS vibrational spectra, we propose it as a powerful tool for the characterization of GNRs, and more generally of all graphene-based nanostructures which can be synthesized exploiting the on-surface approach. References [1] Yang, L. et al. Phys. Rev. Lett. 99, 186801 (2007). [2] J. Cai et al. Nature 466, 470 (2010). [3] Centrone, A. et al. Carbon 43, 1593-1609 (2005). [4] Tommasini, M. et al. Spectrochimica Acta A 152, 134-148 (2016).

#P040 - Relevance of LiPF6 as Etching Agent of LiMnPO4 Colloidal Nanocrystals for High Rate Performing Li-ion Battery Cathodes

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$LiMnPO_4$ is an attractive cathode material for the next-generation high power Li-ion batteries, due to its high theoretical specific capacity (170 mAh g^{-1}) and working voltage (4.1 V vs Li^+/Li). However, two main drawbacks prevent the practical use of $LiMnPO_4$: its low electronic conductivity and the limited lithium diffusion rate, which are responsible for the poor rate capability of the cathode. The electronic resistance is usually lowered by coating the particles with carbon, while the use of nanosize particles can alleviate the issues associated with poor ionic conductivity. It is therefore of primary importance to develop a synthetic route to $LiMnPO_4$ nanocrystals (NCs) with controlled size and coated with a highly conductive carbon layer. We report here the combination of a new colloidal approach to $LiMnPO_4$ NCs and an effective surface etching process (using $LiPF_6$) that makes the NCs miscible in the aqueous glucose solution used as carbon source for the carbon coating step. Also, it is likely that the improved exposure of the NC surface to glucose facilitates the formation of a conductive carbon layer that is in intimate contact with the inorganic core, resulting in a high electronic conductivity of the electrode, as observed by us. The carbon coated etched $LiMnPO_4$-based electrode exhibited a specific capacity of 118 mAh g^{-1} at 1C, with a stable cycling performance and a capacity retention of 92% after 120 cycles at different C-rates. The delivered capacities were higher than those of electrodes based on not etched carbon coated NCs, which never exceeded 30 mAh g^{-1}. The rate capability here reported for the carbon coated etched $LiMnPO_4$ nanocrystals represents an important result, taking into account that in the electrode formulation 80 % wt. is made of the active material and the adopted charge protocol is based on reasonable fast charge times.[1]

[1] Lin Chen, et al. ACS Appl Mater. Interfaces 2016, 8, 4069-4075.

#P041 - UV photocathodes based on MWPECVD undoped and nitrogen-doped diamond films

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Diamond represents an interesting material for its low electron affinity that becomes negative (NEA) if the surface is hydrogenated by treating it in H2 plasma. Specifically, synthetic diamond in film form, produced for example by microwave plasma enhanced chemical vapour deposition (MWPECVD) and starting from CH4-H2 gas mixture, exhibits hydrogenated surface and therefore a NEA character. Besides, the nitrogen addition to the gas mixture allows to dope (n-type) the diamond because nitrogen contains one additional electron as compared to carbon atom. Thus, the n-doping can change the electron density, can also tune the chemical-structural properties and create defect sites. This versatile property of nitrogen to engineer the electronic and structural properties of the diamond network makes this material suitable for photo- and thermo-emission applications such as photocathodes, neutralizer cathode in thrusters for space propulsions, energy converters in solar concentrating systems and so on. In the present contribution, undoped and nitrogen-doped films were produced by MWPECVD technique starting from CH4-H2 gas mixture and adding variable nitrogen percentages of 0, 0.2, 0.5, 1, 3.5, 5 and 6 %. The chemical-structural, electrical and photoemissive properties of films were determined by XPS, Raman and photoluminescence spectroscopies, two points technique for I-V characteristics and photoemission measurements, respectively. The examined films exhibited an evolution of chemical-structural features, of electrical and photoemissive properties as a function of the nitrogen addition. The Raman results showed that the increasing N2 amount in the gas phase promotes the sp2 hybridization of the carbon with respect to sp3 one in the resultant diamond films. The photoemission quantum efficiency (QE), a merit figure for photocathode applications, was assessed in the UV range from 140 to 210 nm for all the samples, before and after plasma treatments in pure H2 and H2-N2 (25-75%) plasmas. Both the hydrogenated and hydro-nitrogenated films showed an enhancement of the QE with respect to the untreated aged ones.

#P042 - SUSTAINABLE BIOCOMPOSITES BASED ON POLYMERS AND NATURAL FIBRES FROM RENEWABLE RESOURCES

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The utilization of “bio-polymers” for the production of “bio-plastic” has became worldwide an assessed priority with the aim of reducing dependence from petro sources, and handle the concern for disposal of waste generated from not degradable plastics. Their use for production of bio-based composites has attracted interest of various application sectors ranging from packaging to automotive components and other high value applications.

Advantages of wood derived fibres on conventional reinforcements such as glass and aramid fibres are their relative cheapness, their ability to recycle, and the fact that they can compete well with them in terms of strength per weight of material. However the strength of the bond between fibres and matrix is substantial for the best mechanical performances of a composite. Many factors interacting with each other affect the complex process of the fibre/matrix adhesion. It can be influenced by the chemical nature of the polymeric matrix, manufacturing methods, processing parameters, surface modification of the fibres or by additives like adhesion modifier agents. In particular for production of composites with bio based biodegradable polymers it is important to address fibres pre-treatment and use of compatibility agents. The present research is focused on the valorisation of natural fibres by products of forest or agriculture industries such as wood fibres, micro cellulose fibres or fibres derived by potato and wheat by-products. In our research unit production of bio-based composites was addressed with different compostable polymeric matrices such as polylacticacid (PLA) and polyhydroxybutyrate (PHB), or recyclable polymers such as polypropylene (PP). As representative examples we report in this abstract the results of composites production with PP, and PHB as polymeric matrix and wood fibres as filler. Modification of fibres by pre-treatment with waxes were attempted to improve adhesion and performances of the composites based respectively on PP or PHB as polymeric matrix. In PHB based composites the presence of PEG1500 improves processing and in both composites prepared with PP or PHB as polymeric matrices pre-treatment with waxes resulted efficient in improving mechanical properties in the composites.

#P043 - SUSTAINABLE BIOCOMPOSITES BASED ON POLYMERS AND NATURAL FIBRES FROM RENEWABLE RESOURCES

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#P044 - Analytical and preparative enantioseparation and main chiroptical properties of Iridium (III)bis(4,6-difluorophenylpyridinato)picolinato

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Almost all Iridium(III) complexes employed both as dopants in PhOLEDs and as pharmaceuticals and fluorescence bioprobes are racemic mixtures. In this study the single enantiomers of the most stable diastereomeric form *fac-trans-N-N*,bis[2-(4,6-difluorophenyl)pyridinato-C^2,*N*](picolinato)iridium(III) (FIrpic) were separated and analysed. The data obtained showed that the complex can be separated into stable optically active Λ and Δ isomers employing cellulose based chiral stationary phase both in normal and polar phase mode. Their chirality was confirmed and their absolute configuration assigned employing several methods (DFT and TDDFT calculations, CD and VCD).The CPL spectroscopy of the isolated enantiomers of FIrpic was also recorded due to its possible value in the OLEDs field. The chromatographic method was applied for a semipreparative purpose demonstrating that polar organic solvent chromatography (POSC) could be used to avoid the low-solubility issues associated with these Iridium(III) complexes. Finally, the chemical and stereochemical stability of the single isomers was evaluated under thermal stress by liquid chromatography coupled to high-resolution mass spectrometry (LC-QTOF) on both chiral and achiral columns. No racemization and/or isomerization was observed; however, the dissociation of the ancillary ligand was demonstrated employing LC-QTOF.

#P045 - Nanoparticles as probe to characterize transient oligomeric state of amyloid protein

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The presence of insoluble fibrillar deposits in the pancreas and in the brainis one of the most common pathological features in patients affected respectively by diabetes mellitus type IIand Alzheimer's disease. The fibrillogenesis process of the two proteins β-amyloid peptide (Aβ(1-40)) and islet amyloid polypeptide (IAPP) or amylin follows a nucleation-dependent mechanism. The mechanism comprises a first phase in which monomers form small, soluble, unstructured aggregates, called oligomers, followed by a second phase, in which unstructured aggregates transform into β-sheet-rich structures that form the mature fibrils through a self-assembling process . Moreover, it has been suggested that the main mechanism for cell cytotoxicity can be ascribed to membrane permeabilization, through the formation of membrane channels by soluble oligomers. Oligomers, are fast transient unstructured species, so experimentally not structurally characterized.

In this work, we highlight an accurate spectral detection of the soluble oligomers by using Surface-Enhanced Raman Scattering (SERS) nanoparticles based on silver, gold and their alloys. Metal colloids were obtained by a pulsed laser ablation process using the 532 nm irradiation wavelength of a Nd:YAG laser. We demonstrate that optimizing the size and the composition of nanostructures we can obtain SERS spectra of proteins at low concentration in the soluble phase. Our data show in the oligomeric species of ABeta

(1-40) and IAPP, the presence of both α-helix and β-sheet secondary structures. This data agree with previous molecular dynamics simulation. Moreover, our data evidence oligomeric species of both proteins shared common future secondary structures

#P046 - Fluoride and Quaternary Ammonium Exert Synergistic Antibiofilm and Tissue Regenerative Action.

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Dental restoration materials are widely used in the treatment of dental caries. However, half of all dental restorations fail within 10 years, mainly due to secondary caries, bulk fracture and dental plaque biofilm formation. Indeed, in periodontium and tooth surfaces, bacteria associate to form one of the most complex biofilm systems in nature, the human dental plaque, that causes a variety of oral infections including caries, pulp and periapical diseases. Nowadays, the research field on dental restorative resins has been expanding, mainly targeting the development of composites loading inorganic ions having anticariogenic and antimicrobial properties. In this contest, the development of composites that can fight biofilms has become increasingly necessary. Here we report the incorporation into visible light-cured commercial dental resin of quaternary ammonium methacrylate (QAM) and layered double hydroxide containing fluoride (LDH-F) to obtain antibiofilm and tissue regenerative composite materials. The antibacterial/antibiofilm properties of QAM are due to its “contact killing” ability by binding to the cell membrane causing bacteria lysis and cytoplasmic leakage. In addition, the LDH-F controlled release of fluoride might reduce demineralization, enhance remineralization, inhibit microbial growth, and recruit undifferentiated dental pulp stem cells, promoting dental pulp regeneration. Different mass fractions (0, 1.5, 3% and 4.5%) of [2-(Methacryloyloxy)ethyl] trimethylammonium chloride (METAC) and 10% LDH-F were incorporated into the visible light-cured commercial dental resin (METAC/LDH-F). The materials chemical-physical characteristics and fluoride release were tested. A *Streptococcus mutans* biofilm model was used. Congo Red Agar staining was used to analyze the inhibitory effect of synthetized materials on the biofilm matrix. In addition, biofilm metabolic activity, lactic acid metabolism and the expression of glucosyltransferase genes gtfB, gtfC and gtfD were measured. Dental materials containing up to 3% METAC and 10% LDH-F had surface charge density and fluoride release increased than the commercial control. Biological assays demonstrated that the METAC/LDH-F material significantly reduced biofilm formation in a concentration dependent manner. Moreover, the presence of LDH-F confers not only antibacterial properties to the material but also promotes dental pulp stem cells recruitment and differentiation toward osteoblast-like phenotype. In conclusion, METAC/LDH-F improves commercial dental material performance contributing to the better management of secondary caries and tissue regeneration.

#P047 - Room temperature processing for solid-state electrochromic devices on single substrate: from glass to flexible plastic

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Flexible, solid-state, room temperature processed electrochromic (EC) devices, with a simplified architecture could represent a relevant chance for the industrial exploitation of smart windows: a technology with multiple benefits, spanning from energy-saving to reduction of greenhouse gas emissions, allowing high levels of visual comfort indoor due to optimized daylighting use[1,2]. In the experimental work presented hereafter, we report the features of a full solid-state electrochromic (EC) device fabricated on a single substrate, made of glass as well as plastic, by adopting a facile, low-cost, non-toxic, eco-friendly, and room-temperature (RT) fabrication process[3]. By combining a solvent-processing of Nafion electrolyte film and the radio-frequency (RF) sputtering deposition at RT of ITO films on the solid Nafion, we obtained monolithic systems with a simplified architecture (substrate/ITO/WO_3/Nafion/ITO) in which a suitable Nafion film (8 mm thick) tightly shares its interfaces with the WO_3 layer and the highly transparent and conductive RF-sputtered ITO film. Compared to conventional sandwich type EC devices using semi-solid or liquid electrolytes, the resulting monolithic devices (substrate/ITO/WO_3/Nafion/ITO) exhibited a strong enhancement in terms of interface properties, robustness, cyclic stability, and long-term durability (at least 1000 chronoamperometric cycles). Moreover, electro-optical characterizations highlighted high transmittance modulation (49% at 650nm), astonishing results in terms of coloration efficiency ($139cm^2/C$), and low energy absorption ($80mWs/cm^2$).

Bibliography

1. Roger J. Mortimer, David R. Rosseinsky, Paul M. S. Monk. Electrochromic Materials and Devices, ed. Wiley-VCH Verlag GmbH & Co 2015 doi:10.1002/9783527679850

2. Alessandro Cannavale, Pierluigi Cossari, Giles E. Eperon, Silvia Colella, Francesco Fiorito, Giuseppe Gigli, Henry J. Snaith and Andrea Listorti, Forthcoming perspectives of photoelectrochromic devices: a critical review. Energy & Environmental Science, 2016 Accepted Manuscript, doi: 10.1039/C6EE01514J

3. Pierluigi Cossari, Alessandro Cannavale, Salvatore Gambino, Giuseppe Gigli. Room temperature processing for solid-state electrochromic devices on single substrate: From glass to flexible plastic, Solar Energy Materials & Solar Cells 155 (2016) 411-420.

#P048 - Single Wall Carbon Nanotubes induce molecular and ultrastructural changes in endothelial cells. The potential impact on the atherosclerotic process

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Single Wall Carbon Nanotubes (swCNTs) may have the potential to contribute to the development and progression of cardiovascular disease, atherosclerosis included, as shown by Li et al. [1] in Apo E-/- mice. Atherosclerosis is an inflammatory disease, in which, since the earlier stages, a feature of the pathophysiology is the "endothelial dysfunction" [2]. In this work we wanted to check if swCNTs could accelerate the atherosclerosis process. At this end, we treated the Ea.hy926 human endothelial cell line with pristine CNTs, and studied different end-points to understand if the cells acquired an inflammatory phenotype. We also imaged the cells with atomic force microscope (AFM) to detect possible ultrastructural alterations. To check the oxidative stress, we performed the Oxygen Radical Antioxidant Capacity (ORAC) [3] and malondialdehyde (MDA) [4] tests. In our hands, as the concentration of CNTs increased, in ORAC test there was an average reduction of about 30% of the anti-oxidant capacity of the cells, while there was a significant rise of MDA. Overall, these results indicate that cells undergo a significant increase in oxidative stress. We made an extensive investigation of various classes of metalloproteinases (MMPs) and Tissue inhibitors of metalloproteinases [5]. The MMPs play a key role in regulating the degradation of the extracellular matrix. In many studies the clearest evidence is for a positive relationship between MMP-9 expression and plaque instability. Instead TIMPs inhibit the enzymatic activity of MMPs. A tight balance between MMP proteolysis and TIMP expression is necessary for tissue homeostasis. In atherosclerosis, TIMPs are unregulated, especially at the base of plaques, and in part counteract the destructive potential of MMPs. To verify ultrastructural changes in cell surface, we used atomic force microscopy (AFM). Because the AFM can generate images of the plasma membrane structure in great detail, the instrument can be used to estimate the surface roughness. This parameter is a tool for investigating the membrane–cytoskeleton integrity. A large decrease in the surface roughness value is indicative of alterations produced by destabilization of the filament cytoskeleton network. This is our case: both in the central and peripheral regions, the roughness of treated cells decreased in a statistically significant way indicating that CNTs may influence the process of atherosclerosis. [1] Li Z, Hulderman T, et al., Environ Health Perspect. 2007 Mar;115(3):377-82. [2] Gimbrone MA Jr, García-Cardeña G. , Circ Res. 2016 Feb 19;118(4):620-36. [3] Amorati R, Valgimigli L, Free Radic Res. 2015 May;49(5):633-49. [4] Czerska M, Mikołajewska K, Zieliński M, Gromadzińska J, Wąsowicz W, Med Pr. 2015;66(3):393-405. [5] Amin M, Pushpakumar S, Muradashvili N, Kundu S, Tyagi SC, Sen U. Front Biosci (Landmark Ed). 2016 Jan 1;21:89-118.

#P049 - Detection and localization of gold nanoshells inside cells: near-field approximation

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The optical properties of metal nanoparticles play a fundamental role for their use in a wide range of applications. In hyperthermia treatment, for example, gold nanoshells (NSs, dielectric core+gold shell) pre-embedded in a cancer cell absorb energy when exposed to appropriate wavelengths of a laser beam and heat up, thereby destroying the cancer cell. In this process, nevertheless, healthy tissues (not targeted by the NSs) along the laser path are not affected; this is because most biological soft tissues have a relatively low light absorption coefficient in the near-infrared (NIR) regions—a characteristic known as the tissue optical window.

Over such a window, NIR light transmits through the tissues with scattering-limited attenuation and minimal heating, thereby avoiding damage to healthy tissues. As a consequence, the identification of NSs assumed a fundamental role for the further development of such cancer treatment. Recently, we have demonstrated the possibility to identify 100–150 nm diameter gold NSs inside mouse cells using a scanning near-optical microscope (SNOM). We provide a numerical demonstration that the SNOM is able to locate NSs inside the cell with a particle–aperture distance of about 100 nm. This result was obtained by developing an analytical approach based on the calculation of the dyadic Green function in the near-field approximation. The implications of our findings will remarkably affect further investigations on the interaction between NSs and biological systems. [1]

[1] Mario D’Acunto, Antonio Cricenti, Serena Danti, Simone Dinarelli, Marco Luce, Davide Moroni, and Ovidio Salvetti,**Applied Optics,** 55, D11-D16, (2016), doi: 10.1364/AO.55.000D11

#P050 - Flame synthesis of nanoscale carbonaceous materials

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Flame is an ideal reactor for the production of well-controlled nanostructured materials. By changing combustion parameters, i.e., fuel composition, the mixture of fuel and oxidizer, the inert diluents, pressure and residence time, it is possible to control the gas-to-particle conversion, thus producing a large variety of nanostructures having different chemical characteristics and morphologies.

In this study, we focus on the process of carbonaceous particle formation via the mechanism of homogeneous nucleation of aromatic molecules followed by agglomeration/growth owning to the competing mechanism of collision-coalescence among nascent particles and gas-phase compounds.

It is demonstrated that, starting from gaseous and pre-vaporized hydrocarbons, gas-phase aromatic compounds and atomically-thin disk-like structures composed of aromatic compounds connected by non aromatic bonding are formed during hydrocarbon oxidation in fuel-rich conditions. The magnitude of the p-electron extension in the nano-disks and the possible inclusion of heteroatom bonding may be controlled by flame operating conditions. Multi-layered nano-disks can be also obtained; their formation precedes the formation of nanoparticles containing stacked aromatic layers. All of these nanoscale carbonaceous materials possess interesting optical and electronic properties that make these materials potentially interesting for new applications, as in the field of the organic electronic, both in the form of powder and thin nano-coatings.

A variety of diagnostic techniques are used to follow and control their formation/evolution process. They include in-situ laser induced emission spectroscopy with ultrafast laser sources in the UV (fluorescence and incandescence), laser light scattering and broadband light absorption, and ex-situ on-line measurements with differential mobility analyzers. Off-line atomic force microscopy, operated in both semi-contact and force spectroscopy mode, HR-TEM, Raman spectroscopy, X-ray and ultraviolet photoemission spectroscopy complement the on-line measurements. A molecular dynamics approach coupled to a detailed model of hydrocarbon oxidation and pyrolysis is also used to explore the flame operating conditions which allow the obtaining of the desired morphology of the particles.

#P051 - Structural investigations of sputtered GeTe/Sb2Te3 superlattices for iPCRAMS

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Chalcogenide Phase Change Materials (PCM), mainly based on Ge/Sb/Te alloys (GST), have been widely investigated in resistive-switching non-volatile memory with Phase Change Random Access Memories (PCRAM). Recently, a new type of phase-change memory device, called “Interfacial Phase-Change Memory” (iPCM) has shown a dramatically improved performance in terms of reduced switching energies, write-erase cycle lifetimes and commutation speed [1]. These materials consist in a superlattice (SL) structure of alternated ultra-thin GeTe and Sb2Te3 crystalline layers. The origin and the underlying mechanism of the resistance change in iPCM devices are still under debate: Tominaga et al. [2] suggested a short-range motion of Ge atoms at the interface of GeTe/Sb2Te3 layers. This Ge umbrella-flip between two coordination sites is expected to produce a transition between a Dirac semimetal and a ferroelectric material. Other studies [3, 4] have instead suggested that GeTe layers tend to be intermixed in the within the Sb2Te3 block. The aim of the present study is to get a better insight on the structure of GeTe/Sb2Te3 via EXAFS measurements at Ge K-edge and X-ray diffraction.

GeTe/Sb2Te3 SL samples were deposited by magnetron co-sputtering deoxidized Si (100) substrates; the thickness of each GeTe layer 0.7 nm to correspond to the (GeTe)2 unit needed for a Dirac semimetal to ferroelectric material transition [2]. The structure of the SL samples was studied as a function of the thickness of Sb2Te3 spacing layer, which was fixed at 1, 2, 4 and 8 nm, respectively.

The EXAFS data reveal a high atomic ordering around Ge atoms. The data could be fitted with a model based on the Ferroelectric structure thus confirming the structure suggested in [2]. These measurements were completed by grazing incidence XRD to access the lattice parameters in the in plane of the sample surface.

REFERENCES
[1] R.E. Simpson et al., Nature Nanotechnology 6 (2011) 501-505
[2] J. Tominaga et al., Adv. Mater. Interfaces 1 (2014) 1300027
[3] J. Momand et al., Nanoscale 7 (2015) 19136-19143
[4] B. Casarin et al., Scientific reports 6 (2016) 22353

#P052 - Electron beam-induced transformations of colloidal CsPbBr3 Nanocrystals at low temperature

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Lead halide perovskites are attractive materials due to their optical properties, making them promising in applications in photovoltaics and optoelectronics. Besides being used for imaging, elemental and chemical analysis, electron microscopy is also a powerful tool for engineering of nanomaterials. In-situ TEM observations have demonstrated that electron beam can either induce formation of metal nanoparticles from relevant compounds, [1]or convert the solid nanoparticles to hollow [2]. Our recent observations revealed electron beam induced formation of metallic lead nanoparticles on colloidal $CsPbX_3$ nanocrystals at -20°C or higher temperature. [3] . In those conditions, the structure of $CsPbX_3$ nanocrystals is eventually damaged. However, when the temperature is not high enough for the formation of Pb nanoparticles (below -40°C), further electron bombardment causes the remaining atoms to crystallize instead.

In this study, electron beam induced transformation of colloidal $CsPbBr_3$ nanocuboids of average edge length of 40 nm is studied in detail at low temperature. The electron beam irradiation experiments were carried out on a 200 kV TEM microscope (JEOL JEM-2200FS) equipped with a spherical aberration corrector (CEOS) for the objective lens, an in-column image filter (Ω-type) and a Bruker Quantax 400 energy dispersive X-ray spectrometry (EDS) system with an XFlash 5060 detector. A Gatan cryotransfer holder with a Model 900 Smartset cold stage controller with liquid nitrogen cooling was used for observing the electron beam induced transformation at low temperatures in the range of -160°C to -40°C. The colloidal $CsPbBr_3$ nanocuboids exhibit orthorhombic phase (lattice parameters at room temperature matching with ICSD # 97851) in this low temperature range, enclosed by {1-10}, {110} and {001} facets. Under parallel beam illumination condition (TEM), along with the reduction of Pb^{2+} to Pb^0 atoms the nanocuboids firstly lose part of Br from the edge regions and become amorphous. These regions recrystallize into CsPb (ICSD # 617071, tetragonal phase) with further electron irradiation. Especially in the temperature range of T=-70°C to -50°C, the shape of the final nanostructure composed of CsPb tends to stabilize in a new structure exhibiting 45°- rotated faceting with respect to the original $CsPbBr_3$ nanocuboids, probably due to surface energy minimization. (i.e. The resulting CsPb oriented in [100] exhibits {040} and {004} facets, and CsPb (040) // $CsPbBr_3$ (020), which is 45° rotated with respect to the {1-10} and {110} facets of the [001] oriented $CsPbBr_3$ nanocuboid.) Under convergent beam illumination condition (STEM), formation of yolk-shell nanoparticles has been observed at -60 °C.

[1] S. Sepulveda-Guzman et al, *Nanotechnology*, vol. 18, no. 33, p. 335604, 2007

[2] A.-A. El Mel et al, *Nanoscale*, vol. 8, no. 21, pp. 10876–10884, 2016

#P053 - Innovative process for recovering high value raw materials from CRT glass waste.

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Innovative process for recovering high value raw materials from CRT glass waste.

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The high lead content of CRT glass waste has caused a serious environmental problem throughout the world. The difficulties removal lead in CRT glass have left landfilling as the only viable disposal optionfor CRT glass Waste. However, landfilling of this type of waste has been banned because ofleaching of lead might result in contamination of the ground water and soil.

To recover high value raw materials (metallic lead and sodium/potassium silicate) from CRT glass waste, a company located in Siracusa (IT) has been developed an innovative environmentally sustainable process involving a cold hydro-metallurgical methodology. The grounded CRT glass waste is dissolved under controlled conditions of time, temperature and pressure together with a concentrated sodium hydroxide solution. The suspension is cooled to room temperature, diluted and transferred to a temporary tank where it is further diluted. The solid and liquid phases are separated in a filter press. The solid phase mainly constituted of a mix of insoluble silicates of polyvalent not amphoteric metals can be further treated with concentrated sodium hydroxide to reduce residual lead content.

The liquid phase containing sodium-potassium silicate and lead is transferred to a electrolytic cell for lead electro-winning. After recovering the metallic lead from the electrolytic cell, the sodium-potassium silicate solution is treated with zinc powder or sodium sulfide to allow the precipitation of the remaining traces of soluble lead. Precipitated lead and any other suspended solid are filtered and the final sodium-potassium silicate solution is transferred to the storage tank, ready for sale.

This process allows the production of high purity metallic lead and sodium/potassium soluble silicate from CRT glass waste with a high market value.

The solid residues with fine particle size may be used to prepare glass foam in an economically and environmentally friendly way.The describe process and electro-winning methodology for recovering of lead from soluble silicates is a simple process, with a high recovery (about 90%) of LEAD metal.

#P054 - Innovative functionalization of polyamide fabrics with a natural biopolymer

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Microplastics pollution of marine environments has arisen particular attention in recent years. Such marine litter (< 5 mm) can derive from the deterioration of scraps of large dimensions (bags, packaging), from abrasives (sandblasting) or from cosmetics (such as microbeads used for skin scrubs). Recently, washing processes of synthetic clothes have been identified as one of the major source of microplastics due to the friction of the detergent with the fabrics. In order to mitigate this problem, this work aims to develop functional finishing treatments of fabrics that can reduce the amount of microplastics released. The formation of a uniform and resistant coating on the surface of the fabric can prevent the detachment of microfibers from the yarns as effect of mechanical stresses during washings. Among the materials used for the finishing, natural polymers represent a promising and interesting alternative to synthetic ones. In particular, the present work focuses on the use of pectin, a natural polysaccharide mainly extracted from suitable agro-by-products like citrus, peel and apple pomace, with high reactivity and biocompatibility.

In order to develop a pectin based coating on polyamide fabrics, pectin was chemically modified by the reaction with glycidyl methacrylate (GMA) that introduces vinylic groups in the polysaccharide structure. Such reactive functionality was exploited to graft the pectin on the surface of polyamide fabric by crosslinking reaction. Different ratios of pectin:GMA were tested in order to obtain a homogeneous coating that does not affect the hand of the textile. The effectiveness of the treatment was investigated through scanning electron microscopy (SEM), solid state nuclear magnetic resonance spectroscopy (NMR) and Attenuated Total Reflectance (ATR) Fourier Transform InfraRed (FT-IR) spectroscopy.

#P055 - XPS and XAS investigation of stability and reactivity in perovskite organic-inorganic halides/TiO2 interfaces

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Solar cells based on perovskite organic-inorganic halides are emerging as extremely promising devices, due both to the high conversion efficiencies that have been obtained, up to > 20%, and to the relatively easy realization protocols [1,2]. High efficiency is essentially due to the perovskite material, that combines a high absorption coefficient with good carrier mobility. Nowadays, improving the stability of the materials and devices is demanding for effective applications. A a key issue to be addressed is therefore a precise understanding of the aging processes occurring when the cell is placed in working environments.

In the present study, we exploit synchrotron radiation techniques to investigate the composition, stability and reactivity of both the electron transporting layer (TiO_2 – either mesoporous or in compact planar form) and the organic perovskite (either $CH_3NH_3PbI_3$ or $CH_3NH_3PbI_{1-x}Br_x$) thin film as a function of possible degradation agents: prolonged air exposure, heating in oven at 60°C, exposure to sun simulator. Perovskite/TiO_2 thin films (100-200 nm) were prepared on fluorine-doped tin oxide (FTO) conductive glass. High resolution X-ray photoelectron spectroscopy (XPS) was combined with X ray absorption (XAS) - acquired both in total electron yield and in fluorescence yield modes – to discriminate between near-surface and bulk effects and gain access to the perovskite/TiO2 buried interface. In particular, concerning XPS, Pb4f, I4d, Br3d, C1s, N1s, O1s, Ti 2p, core levels and the evolution of the valence band were followed to identify chemical reactions and presence of interface defects and impurities which can play a crucial role in a real device performance. XAS at the Ti $L_{2,3}$ edges, O K edge and N K edge were measured, providing information on the degradation of the methylammonium cations in the perovskite and on the presence of O vacancies in the TiO_2 layer.

[1] D. Liu, T. L. Kelly, Nat. Photonics 2013, 8, 133

[2] http://www.nrel.gov/ncpv/images/efficiency_chart.jpeg.

#P056 - Chemical stability study on BaCe0.65Zr0.20Y0.15O3-δ-Ce0.85Gd0.15O2-δ ceramic composites for hydrogen separation

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Title:Chemical stability study on $BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-\delta}$-$Ce_{0.85}Gd_{0.15}O_{2-\delta}$ ceramic composites for hydrogen separation

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The production of pure hydrogen usually requires its extraction from a gas mixture. In fact, one of the critical stages related to the use of hydrogen as an energy carrier is the development of efficient and competitive techniques that separate hydrogen from other by-products such as steam, hydrocarbons, carbon dioxide and other gases. Membranes for hydrogen purification represent an appealing alternative to the current commercially available pressure swing adsorption (PSA) technology. In this context, mixed proton and electron conductors (MPEC) oxides are attractive candidates to be used as dense ceramic membranes for H_2 separation due to their particular properties. These materials incorporate hydrogen into their lattice as charge protonic defects which means that, theoretically, they are 100% selective towards hydrogen separation. Furthermore, the properties of these oxides (i.e. working temperatures, durability) endow membranes that could be directly integrated into industrial processes or used in the so-called catalytic membrane reactors.

Recently, $BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-\delta}$ (BCZ20Y15) and $Ce_{0.85}M_{0.15}O_{2-\delta}$ (M = Y and Gd) dual-phase membranes were explored by our group [1] reaching hydrogen permeability values among the highest ever reported for bulk MPEC membranes. The highest permeation flux was attained for the 50:50 volume ratio $BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-\delta}$ and $Ce_{0.85}Gd_{0.15}O_{2-\delta}$ membrane, reaching values of 1.27 $mL \cdot min^{-1} \cdot cm^{-2}$ at 755°C and 2.40 $mL \cdot min^{-1} \cdot cm^{-2}$ at 1040°C.

The long term stability and degradation mechanisms are critical issues for these systems.Working conditions are really challenging: hydrogen purification is carried out at high temperatures in harsh environments containing H_2O vapour, CO, CO_2, and sulphides. Structural changes, chemical reactions, cation diffusion and other undesired phenomena could occur damaging the performance of membranes, even if TGA analysis and permeation tests indicate that the composites were stable in CO_2. In this work, BCZ20Y15-GDC15 composites were exposed to different environments at high temperatures and then characterized by means of XRD and SEM techniques. The objective of this study is to systematically examine the chemical stability of the membranes in order to obtain a better understanding of their capability for practical applications.

[1] E. Rebollo, C. Mortalò, S. Escolástico, S.Boldrini, S. Barison, J. M. Serra, and M. Fabrizio, Exceptional hydrogen permeation of all-ceramic composite robust membranes based on $BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-\delta}$and Y- or Gd-doped ceria, Energy and Environmental science 8, 3675-3686, (2015)

#P057 - DFT simulation of electron holography response in folded graphene membranes

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The analysis of the response in transmission electron holography depends on the electromagnetic field experienced by the electron beam within the sample. In nanostructures it is not always clear how to relate quantitatively the observed phase shifts to the average value of the inner potential integrated across the sample thickness. The Density Functional Theory (DFT) approach provides a set of numerical tools to compute various properties of bulk and nanoscopic materials. By retaining a sufficient number of basis elements, one can quantify the inner potential and density fields with a sub-angstrom resolution.

However the actual possibility of carrying out an analysis of this type is limited by three factors:

-in a plane-wave scheme the infinitely extended directions are easily treated but for the spatially limited ones a supercell treatment is needed;

-one has to adopt a suitable transferable form of the exchange-correlation terms and associated pseudopotential;

-the total number of atoms in a unit supercell is necessarily limited by computational resources, ranging from hundreds to a few thousands with current high-performance parellel machines.

In this contribution we perform a systematic study of the first two aspects on flat multilayer graphene sheets with up to ten layers, in different relative stacking configurations, employing different proposals of van der Waals exchange-correlation schemes, to check how the binding energies, interlayer distances, vacuum fields and integrated profiles compare to experimental data. In these cases the approach is fully of DFT nature, meaning that first the nanostructures are relaxed towards minum energy configurations and then the self-consistent fields are post-processed. The resulting dependence on the layers separation and number provides an estimate of a surface- and an interlayer term to be taken as references values in holographic experiments, especially close to folded edges where the layers distance locally increases. Moreover it is seen that the dependence on the relative orientation is weak, probably below the current experimental reach.

As regards the third point above, we have extended and tested the method above using an effective two-stage strategy. When the number of atoms is prohibitively large for a full DFT relaxation, the optimal configurations are first determined by means of a molecular dynamics approach using suitable force fields that yield practically the same shapes as with DFT for samples where the data are available. The larger structures we are interested in are both multilayer folded graphene membranes and large squeezed chiral nanotubes that can be viewed also as folded graphene sheets with chiral folding axis. Once the optimal configuration is available the inner charge and potential field can be extracted fully at the quantum level in a final self-consistent "snapshot", allowing for a quantitative numerical estimate

#P058 - One-step fabrication of Carbon coated MoS2 nanoflakes anode for high performance lithium ion batteries

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Lithium-ion batteries (LIBs) are becoming one of the main power sources for future portable electronic devices and hybrid electric vehicles due to their high energy density and long cycle life.[1]To date, graphite is extensively utilized as commercial anode materials for LIBs due to its low potential profile versus lithium (~0.2 V) and structural stability during charge/discharge cycling.[2]However, graphite suffers low capacity value (372 mAh g^{-1}) [1]hindering the development of high-performance LIBs. In this context, molybdenum disulfide (MoS_2), having a specific capacity of 670 mAh g^{-1} [3]is becoming a promising candidate for LIBs.[4]In fact, the layered structure with a larger interlayer distance (0.64-0.69 nm) with respect to graphite allows favorable Li ions intercalation.[5, 6] However, the MoS_2-based anodes suffer limited cyclability and poor rate performance owing to their inherently low electrical conductivity and large volume changes during lithiation/de-lithiation processes.[7]The latter results in electrode pulverization, which strongly affect the current collector electrical properties.[3]

Here, we present a simple one-step method for the realization of a hybrid MoS_2/amorphous carbon (MoS_2/C) anode. The MoS_2 nanoflakes are produced by liquid phase exfoliation of bulk MoS_2,[8]achieving flake size in 100-200 nm range. The binder-free MoS_2/C anodes are prepared by annealing at 750°C a mixture of MoS_2 NFs, Super-P carbon black and polyacrylic acid (PAA). Galvanostatic cycling tests of MoS_2/C in half-cell configuration indicates a high initial specific capacity (1358 mAh g^{-1}) compared to that of bulk MoS_2 (877 mAh g^{-1}). Additionally, the MoS_2/C anodes retain 80% of its initial specific capacity after 20 cycles, which is much higher with respect to that retained by bulk MoS_2 anode (only 10%). The significant improvement in electrochemical performance demonstrates that MoS_2 nanoflakes promote the diffusion of Li^+ by reducing the diffusion length comparing to the bulk material. Additionally, Cyclic Voltammetry (CV) measurements show that the cathodic/anodic peaks of MoS_2 nanoflakes anode maintains the same potential upon cycling. On the contrary, in the case of bulk MoS_2 anode, there is a potential shift of cathodic/anodic peaks with cycling, which is attributed to the increase in electrical resistance of the electrode. Thus, the carbon coating improves the electrical conductivity of the electrode by providing the connecting network between the MoS_2 nanofakes and the current collector, even after pulverization of MoS_2. Our research is paving the way towards the fast fabrication of high-performance 2D metal sulfides electrodes for high-energy lithium ion batteries.

1 M. Tarascon Nature 2001

2 Flandrois Carbon 1999

3 Stephenson Energ Envi. Sci 2014

4 Z. Liu, M Nat Com. 2014

5 Hwang Na. Lett 2011

6 D. Du, Chem Comm. 2010

7 L. An Adv Fun. Mat., 2015

8 Nicolosi,Science 2013

#P059 - PREFABRICATED CONSTRUCTION SYSTEM MADE UP OF CARDBOARD

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Corrugated cardboard is a wood derivative material which is lightweight and resistant. Currently, its main employment is packaging field. Mechanical, thermo-acoustical and environmental performances of corrugated cardboard makes it useful as building construction material in form of advanced prefabricated systems. Hence the idea of developing Archicart, a prefabrication system whose base element consist in an alveolar corrugated cardboard panel, able to reduce transport and installation costs and usable in case of self-construction. This panel present low weight and optimal manoeuvrability and inherits environmental sustainability, recyclability and biodegradability from wood. In the proposal paper, after a description of Archicart system, the authors will show a possible application to realize an emergency village for Civil Protection, in one of the strategical area of Catania. The type module is a terraced unit of two floors made up of structural members filled with cellulose fiber to increase thermic performances.

Furthermore, they will be presented the results of an experimentation conducted to compare the performances of base component in some alternative fillings.

#P060 - 3D Cell Cultures in Porous Scaffolds with Oriented Microtubules Designed for Dental Regeneration

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INTRODUCTION: Tooth loss is a common result of a variety of oral diseases due to physiological causes, trauma, genetic disorders and aging, and can lead to physical and mental suffering that markedly lower the individual's quality of life [1-3]. Tooth is a complex organ that is composed of mineralized tissues and soft connective tissues. Dentin is the most voluminous tissue of the tooth and its formation (dentinogenesis) is a highly regulated process displaying several similarities with osteogenesis.

METHODS: In this study a low-cost scaffold made by gelatin biomineralized with magnesium-doped hydroxyapatite and blended with chitosan, was developed for hard tissue engineering. We synthetized a dentin-like scaffolds using a controlled freeze-drying process permitting the formation of microscopic channels comparable to dentin tubules and appropriate for cell penetration and matrix deposition.

Mesenchymal stem cells (MSCs) and dental pulp steam cells (DPSCs) were seeded in direct contact with the scaffolds and cultured with medium supplemented with osteogenic factors. Cell viability and cell morphology were analysed up to 14 days of cultured. Moreover gene and protein quantification were investigated.

RESULTS: The scaffolds show an aligned porosity suitable for the colonization of its inner part by the seeded cells (Fig. 1). The scaffold had no cytotoxicity, cells morphology was accordant to a non-stress cell condition and a good adhesion to the scaffold. The SEM observations showed the scaffold's aligned porosity and rugosity, cells were found through almost the entire height of the scaffold.

DISCUSSION & CONCLUSIONS:3D cell culture with MSCs and DPSCs showed the promising properties of the new scaffolds for tooth regeneration. In detail, the chemical composition of the biomineralized gelatin facilitate the cell adhesion, the aligned porosity is suitable for cell colonization and fine cell/materialinteractions together with mineral component permit the cells differentiation and matrix deposition.

This preliminary study indicate the potential of a low-cost biomineralized gelatin scaffold as a novel tool for 3D cell culture in dental regeneration.

REFERENCE:[1]Y. Chai, H.C. Slavkin (2003) *Microscopy Research and Technique* **60(5):**469-479. [2]S.P. Ho, B. Yu, W. Yun, et al. (2009) *Acta Biomater* **5(2):**707-718. [3]A.Linde, M. Goldberg (1993) *Crit Rev Oral Biol Med* **4(5):**679-728.

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#P061 - Design of Bioelastic Materials

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Design of Bioelastic Materials

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Elastic protein-based polymers fold and assembly by relatively unrestricting contacts involving bulky hydrophobic side chains. This leaves most of their backbone peptide moieties without structurally constraining inter- and intramolecular hydrogen bonding, and so these moieties are free to undergo large amplitude high-entropy rocking motions that become damped on extension. These protein-based elastomers are nearly ideal elastomers, with limited straining and breaking of bonds on extension resulting in the potential for extraordinary functional lifetimes. This decrease in entropy, caused by the damping of internal chain dynamics on extension (i.e. a decrease in the amplitude of the peptide-moiety rocking motions) has been called the peptide-librational-entropy mechanism of elasticity. The literature data and analyses affirm that components of elastin, and purified elastin fibre itself contain dynamic, non-random, regularly repeating structures that exhibit dominantly entropic elasticity by means of a damping of internal chain dynamics on extension. The resulting structure is termed a β-spiral, as the β-turn is the dominant repeating secondary structural feature. The term spiral is used instead of helix to emphasize in the structure that there is not obligatory hydrogen bonding between repeating units as in the classical helical structures of polypeptides. The interturn interactions are hydrophobic; there is water within the β-spiral; and the β-turns function as spacer between the turns of the β-spiral. Experimental studies on the inverse temperature transitions exhibited by elastic protein-based polymers, as they relate to the performance of various forms of work or energy conversions of relevance to biology, have resulted in some axioms: “Variables including temperature, pressure, chemical concentration, and light-elicited changes in chemical structure can be used to alter the value of temperature transition to perform mechanical work by producing folding and assembly” and “The above energy conversion can be demonstrated to be more efficient when carried out using more-hydrophobic protein-based polymers”. On these bases, we have observed the conformational behaviour of different sequences containing hydrophobic amino acids in order to design news bioelastic polymers.

References

Urry D.W., Phil. Trans. R. Soc. Lond. B (2002) 357, 169-184

Fenude Schoch E., Römer U.D., Lorenzi G.P., Int. J. Peptide Protein Res.(1994) 44, 10-18

Römer U.D., Fenude Schoch E., Lorenzi G.P., Helv. Chim. Acta (1993) 76, 451-458

Navarro E., Fenude E., Celda B., Biopolymers (2001) 59, 110-117

Navarro E., Fenude E., Celda B., Biopolymers (2002) 64, 198-209

#P062 - Polymerization of Structural Elements lead to Tubular Biopolymers

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Polymerization of Structural Elements lead to Tubular Biopolymers

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The remarkable range of chemical capabilities that evolution has elicited from proteins suggests that it might be possible to design analogous capabilities into unnatural polymers that fold into compact and specific conformations. A fundamental challenge in the design of synthetic polypeptides that folds in defined ways is the generation of a sequence of monomer buildings blocks that will manifest the correct fold. In this work, I will focus upon the properties of gramicidin A analogues with the aim to design and synthesize complex channel-forming heteropolymeric structures which may reveal novel structural and functional properties not observed in nature. Several studies have indicated that the ion-conducting transmembrane channels formed by gramicidin A in lipid bilayer originated through a dimerization process, and *Urry* [1] has proposed that the channels are helical dimers consisting of two single stranded β-helices connected head-to-head (formyl-end-to-formyl-end). These helices should be $\beta^{6.3}$-helices but also $\beta^{4.4}$-helices, $\beta^{8.2}$- helices, and $\beta^{9.0}$-helices have been considered. *Urry*’s proposal is consistent with a number of experimental observations, and the ability of single- and double-stranded β-helices to give head-to-head dimers has been demonstrated either with gramicidin A [1,2] as with synthetic N-formyl oligopeptides[3-5]. Systematic studies on the novo design of β-spiral using the 20 naturally occurring α-amino acids have resulted in the formulation of a set of rules for the construction of stable helices [6]. On these bases here, we report the results of a study on the tendency to polymerization of ‘models’ peptides with large propensity to assume helical structures.

We have synthetized and observed heteropeptides (with different length and compositions) that, after polymerization, can assume tubular structure. Conformational analysis of this oligopeptides provides important information about polymerization method, balance between hydrogen bonds and hydrophobic interactions, modulation of number of residues per turn of helix, insertion of functionalized residues without alter the stability of backbone structure, that will be here discussed,

References

[1] Urry D.W, Proc.Natl. Acad. Science U.S.A. (1983) 68, 672

[2] Benoit Roux, Acc. Chem. Res. (2002) 35, 366

[3]Lorenzi G.P., Muri-Valle V., Bangerter F., Helv.Chim. Acta (1984) 67, 1588

[4] Lorenzi G.P., Jackle H., Tomasic L., Rizzo V., Pedone C., J. Am. Chem. Soc. (1982) 104, 1728

[5] Fenude Schoch E., Römer U.D., Lorenzi G.P., Int. J. Peptide Protein Res.(1994) 44, 10

[6] Urry D.W., Phil. Trans. R. Soc. Lond. B (2002) 357, 169-

[7] Navarro E., Fenude E., Celda B., Biopolymers (2001) 59, 110

#P063 - Amphiphobic coatings for antifouling in marine environment

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Amphiphobic materials created for marine applications could be an innovative solution where technological and ecological aspects allow to be merged, taking into account the limitations imposed by international laws in terms of environmental protection. In the marine field the use of highly hydro and olephobic (amphiphobic) materials is relatively young and not very explored. In this work a coating with amphiphobic/superamphiphobic behaviour for marine applications has been characterized and tested in both laboratory and field conditions, since investigations in real seawater are crucial to evaluate the behaviour of SH/SO surfaces because of a complexity not reproducible in laboratory. Because of the real conditions where the surface can operate, preliminary tests of wearing, thermal stress and durability have been also performed in order to study amphiphobic systems for different applications related to the marine environment.

#P064 - Hybrid sulfonated pentablock copolymer membranes with titania and graphene oxide for azo-dye removal from water.

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We report an easy and low cost procedure for the preparation of reusablesulfonated pentablock copolymer (s-PBC)nanocomposites with promising ability in water purification application as adsorbent or photocatalytic material.The s-PBC is a thermoplastic elastomer with discrete sequences of ionic (sulfonated) and non-ionic (unsulfonated) blocks.Titanium dioxide (TiO_2) and graphene oxide (GO) were dispersed in the polymeric matrix and nanocomposite membranes (named s-PBC-TiO_2 and s-PBC-GO,respectively) were prepared by drop casting.

The chemical, structural and morphological properties of the nanocomposite membraneswere characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The composites were tested as adsorbents or as photocatalysts for the removal of dyes from water. In particular, the photocatalytic activity of such nanocomposite membranes was investigated by measuring the degradation of methylene blue (MB) and methyl orange (MO) under UV-Visible light irradiation. Comparing the nanocomposites degradation ability towards the two different dyes, the key role played by the direct interaction of the polymer itself with the contaminant is shown. Both the s-PBC-GO and s-PBC-TiO_2 nanocomposites, show high efficiency in dyes adsorption and photocatalytic degradation. In particular, all the materials are able to remove more than the 90% of the initial MB concentration either in dark or under irradiation. The removal of MB occurs immediately in the first few minutes within the formation of MB aggregates. The same polymer and its composites are able to adsorb protonated MO molecules. The MO degradation ability is increased under irradiation by a factor of 50% for the composite with TiO_2 and of 30% for the composite with GO, with respect to MO removal in dark conditions. Finally, these two composites show the same degradation efficiencyalthough the use of s-PBC-GO membrane for MO dye removal from water seems to be a safer method than the use of s-PBC–TiO_2 membrane. The possibility to recover easily the materials at the end of the processes, regenerating them and reusing for consecutive process is also shown.

#P065 - Silicon nitride as graphene substrate in device design

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One of the most severe limits in future design of graphene-based electronic devices is that, when supported on a substrate, the carrier mobility of graphene (G) is often reduced by an order of magnitude or more. Ultra-thin β-Si_3N_4 can be used as high-K dielectric to overcome this problem. In this work we present the results of the first experimental characterization of the G/β-Si_3N_4(0001)/Si(111) interface. First, the β-Si_3N_4 film was grown under UHV conditions and thoroughly investigated by scanning tunneling microscopy (STM). Subsequently, a G flake has been transferred on top of it by a PMMA-based transfer technique. The structural and electronic investigation of this prototypical interface has been conducted by STM and μ-Raman spectroscopy showing a high quality of the graphene layer with a low number of defects. This study demonstrates that β-Si_3N_4(0001)/Si(111) has strong potential as platform for future graphene-based electronic device applications.

#P066 - A WEARABLE ELECTRO-CHEMICAL SENSOR FOR THE DETECTION OF REDOX-ACTIVE BIOMOLECULES

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A tremendous and growing interest is focused on the development of new wearable technology for physiological monitoring, in order to obtain a novel class of personalized point-of-care devices that could be integrated into the daily life of a patient in the form of wireless body sensors. Although most of the research efforts are converged on the production of miniaturized wearable appliances based on relatively mature technologies, such as motion tracking, a remarkable ability would be the chemical sensing of bio-markers in body fluids. Several wearable sensors, mainly based on an electrochemical transduction, have been developed, however they often require the implantation of electrodes and the use of a relative-bulky read-out electronics. To overcome these drawbacks a good solution is the monitoring of biomarkers in sweat through wearable sensors that are merged with the textile, obtaining a device that really "disappears" inside the cloth. Recently, the potentiality of textile Organic electrochemical transistors (OECTs) for the detection of ions and adrenaline has been shown [Coppedè et al., J. Mater. Chem. B, 2 (2014) 5620], but the sensing process should be studied in depth in order to control and fully exploit their properties and performance . This contribution reports on the huge potential of OECTs as wearable chemical sensors for the detection of bio-compounds in sweat [I.Gualandi et al Sci.Reports in press (2016)]. In an OECT the current flowing in the channel (a stripe of conductive polymer) can be modulated through the voltage applied to the gate electrode by electrochemical reactions that take place in an electrolytic solution. Since the device is the combination of a sensitive element and an amplifier, OECTs directly amplify the electro-chemical signals. These transistors are made by screen printing on different textiles and they exhibit very appealing features for wearable sensors: 1) the operating potentials are very low (< 1 V), a key point considering that the device must be placed in direct contact with skin; 2) since the current used as signal is quite high (> 1 mA), it requires a simple readout electronics ; 3) the absorbed power is very low (< 10-4 W); 4) it can be deformed without observing a degradation of its electrical features. Moreover the stability of the OECT we have developed has been assesed under washing conditions. The potentialities of the here described OECT as a sensor were tested using different redox active bio-molecules (adrenaline, dopamine and ascorbic acid). All tested analytes react with PEDOT:PSS by extracting charge carriers from the transistor channel and leading to a logarithmic decrease of the drain current for increasing concentration. The OECTs sensing capability has been assessed in two different experimental contexts: i) totally dipped in an electrolyte solution, to evaluate their performance in the ideal operation; ii) in air, by sequentially adding few drops of electrolyte solution in the sensing area in order to simulate the exposure of the fabric to human sweat in real applications.

#P067 - Bottom-up approaches based on block copolymer self-assembly for the fabrication of nanoscale RRAM

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Oxide-based resistive switching devices (RRAM) represent today an emerging class of devices with a significant potential in memory, logic, and neuromorphic circuit applications. These devices have a simple capacitor structure and promise superior scalability together with favorable memory performances. Although isolated RRAM devices down to a few nm have been demonstrated, the gathering of multiple nanoscale memory cells in high density arrays is a fundamental step toward the development of ultra-dense memories. Bottom-up fabrication approaches may prove effective in providing a flexible platform for the investigation of highly scaled devices with unprecedented packing density at the laboratory level. Moreover, their integration with current top-down technologies is currently under investigation since it offers new strategies to overcome some of the limitations faced by traditional fabrication approaches. In particular, block copolymers can self-assemble in nanoscale periodic domains with a tight control over the size and density of the defined features and their compatibility with microelectronics fabrication processes has been demonstrated.

In this work, bottom-up fabrication approaches based on the self-assembly property of di-block copolymers are explored in combination with different fabrication methodologies for the development of large arrays of resistive switching devices based on metal oxides. Using this technique, we tested the scalability limit of ultra-dense memory arrays with density up to 10^{11} dev/cm². Multiple devices were defined over a large area in regular arrays by defining the top electrode using cylinder-forming di-block copolymers and a lift-off approach, while the switching oxide was deposited by atomic layer deposition in thin film. In this way, a device stack similar to the one of the best performing devices was defined. After fabrication, the selective addressing of individual nanodevices was achieved using conductive atomic force microscopy. Electrical measurements probed the non-volatile switching of the resistance and the device variability was also examined and related to the inherent oxide non-homogeneity at the nanoscale. The analysis drew the attention to a crosstalk phenomenon occurring between nanoscale memory cells in a continuous thin film geometry. Structural analysis and an electrical model were elaborated to explain the observed phenomenon. Alternative system configurations and fabrication strategies were envisaged to fully exploit the scalability potential offered by resistive switching devices in combination with bottom-up fabrication approaches.

#P068 - Magnetic and structural investigations on undoped and substituted zinc ferrites nanopowders

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MFe_2O_4 (M=Ni, Co, Zn, Mg, etc.) spinel ferrite nanoparticles can be widely used in various fields of science and technology, as well as in medicine, in particular for magnetic hyperthermia. The properties of the ferrites mainly depend on the cation distribution that in turn is related to the composition and synthesis methods. Among all ferrites, zinc ferrite exhibits unusual behavior in nanoregime. Bulk $ZnFe_2O_4$ has a normal spinel structure, in which all Zn^{2+} ions occupy tetrahedral positions (A-sites) and all Fe^{3+} ions octahedral positions (B-sites). At room temperature, zinc ferrite is paramagnetic and the transition to a magnetically ordered state occurs only at temperatures of about 10 K. The magnetic properties change significantly when the particle size decreases to a few tens of nanometers: at this scale, a partial cation inversion occurs. Thus, there is a structural transformation from normal to mixed spinel, which can lead to a superparamagnetic behaviour at room temperature.

In this work we present XRD, EPR and micro-Raman data collected from a series of undoped and substitued zinc ferrites obtained from classical solid state synthesis and microwave combustion and co-precipitation methods. The cation substitution involved both A site (Ca or Sr for Zn) and B site (Gd or Al for Fe). The Raman data, in particular the A1g mode due to the motion inside the tetrahdral AO_4 units, allow to derive an inversion degree of the structure. The temperature behaviour of Fe^{3+} EPR signals from different samples has been correlated to the structural information derived from XRD and micro-Raman experiments. On this basis, the magnetic behaviour has been measured and discussed. The results seem to validate an intrinsic nature of the observed superparamagnetic behavior accompanying the superparamagnetic contribution caused by the formation of maghemite nanosized clusters.

#P069 - PVA-GTA Fricke gel dosimeters exposed to clinical photons beams: Nuclear Magnetic Resonance Relaxometry and Imaging

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Fricke Gel (FXGs) dosimetric system is based on the radiation induced oxidation of ferrousto ferric ions.

The application of Fricke gels for ionizing radiation dosimetry is continuously increasing worldwide due to their many favorable properties. However, one of their shortcomings is that ferrous and ferric ions diffuse in the gel matrix. To maintain the spatial integrity of the dose distribution, Fricke gels must be undergoing measurement within a few hours of their irradiation, so that ferric ions remain close to their point of production. Thus, the spatial integrity of the dose distribution in the Fricke gel is maintained (Schreiner, 2015).

The gel matrix also contributes to the oxidation of ferrous ions during irradiation, increasing the chemical yield of ferric ions in aqueous solution and increasing the sensitivity of the dosimeter.

The oxidation of ferrous ions also causes a reduction of the longitudinal nuclear magnetic relaxation time T_1 which can be measured by means of Nuclear Magnetic Resonance Relaxometry (NMR) and Magnetic Resonance Imaging (MRI) (Marrale, 2014).

The results here presented are related to an experimental investigation conducted on Fricke Gels characterized by gelatinous matrix of Polyvinyl alcohol (PVA)cross-linked with a Glutaraldehyde (GTA) (Marini, 2016).

The main dosimetric features of the NMR signal were investigated. The gels were irradiated in the clinical dose range between 0 and 20 Gy. In order to assess the photon sensitivity we analyzed the dependence of NMR relaxation times on radiation dose with varying ferrous ammonium sulfate content inside FXGs. Furthermore, signal stability was followed for several days after irradiation.

These measurements were preliminary to MRI analysis which can permit 3D dose mapping. In order to maximize the MRI response a systematic study was performed to optimize acquisition sequences and parameters. In particular, we analyzed for inversion recovery sequences the dependence of MRI signal on the repetition time T_R and on the inversion time T_I.

The dose calibration curves are reported and discussed from the point of view of the dosimeter use in clinical radiotherapy. This work has highlighted that the optimization of additives inside gel matrix is fundamental for maximizing photon sensitivity of these detectors. We can conclude that FXG dosimeters with optimal ferrous ammonium sulfate content can be regarded as a valuable dosimetric tool to achieve fast information on spatial dose distribution.

A. Marini et al., Diffusion and sensitivity characteristics of a chemically cross-linked PVA-Fricke gel dosimeter, Physica Medica (2016), 32, 41.

M. Marrale et al., Correlation between ferrous ammonium sulfate concentration, sensitivity and stability of fricke gel dosimeters exposed to clinical x-ray beams. NIM B (2014b) **335** 54–60.

J. Schreiner, MRI true 3D chemical dosimetry: development and clinical role. Jpc. (2015) **573.**

#P070 - Phenol compounds as new materials for Electron Paramagnetic Resonance dosimetry in clinical photon and electron beams

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In the last decades several research laboratories have shown an increasing interest aimed at extending the applicability of Electron Paramagnetic Resonance (EPR) dosimetry to radiotherapy with different types of radiation beams. EPR is a spectroscopic method for investigating the structure and dynamics of such paramagnetic species. Free radicals are known to be produced when a compound is irradiated with ionizing radiations. The concentration of radiation-induced free radicals is proportional to the energy released inside in the medium and this allows for dosimetric measurements through EPR technique. The use of alanine as a dosimetric material gave the possibility to apply EPR spectroscopy for high-dose standardization and dose control in radiation processing (Marrale 2016).

The EPR dosimetric method has many advantages such as simple and rapid dose evaluation, the readout procedure is non-destructive, linear response of many organic and inorganic compounds. EPR detectors show a behavior that suggest possible applications for various kinds of beams used for radiation therapy. Nowadays, the most widely used organic compound as a dosimeter is the alanine. However, many researches are in progress with the aim at improving sensitivity of EPR dosimetry for doses much smaller than 1 Gy. More sensitive materials than alanine are needed to make the EPR dosimeter competitive with other dosimetry systems.

Our research group has started an investigation of the EPR response of some phenols compounds for possible EPR dosimetric applications suitable features, such as high efficiency of radiation-matter energy transfer and radical stability at room temperature.

Phenols are compounds possessing a benzene ring attached to a OH group. After irradiation the final product is a stable phenoxy radical. The stability of such radical can be improved by adding other alkyl chains which can be attached to the benzene ring.

The phenol octadecyl-3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate gave interesting results. Moreover, its high molecular weight, the low volatility and the compatibility with the dosimeter binding material (wax) are advantages with respect to lower molecular weight phenols.

In this work we report the EPR investigation of phenols exposed to clinical photon and electron beams (Gallo, 2016).

The dosimetric features of these EPR dosimeters (dependence on microwave power and modulation amplitude, their response after gamma and electron irradiations, dependence on beam type and energy, the detection limits for both beam typologies, signal stability after irradiation) were investigated and the results are reported.

M. Marrale et al., EPR/alanine dosimetry for two therapeutic proton beams, Nuclear Instruments and Methods B, vol 368 (2016).

Gallo et al., Phenol compounds as new materials for electron spin resonance dosimetry in radiotherapy, Physica Medica, vol 32 (2016).

#P071 - Electron Spin Resonance dosimetry using organic compounds (alanine and ammonium tartrate) for mixed neutron-gamma fields

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Alongside with the development of Neutron Capture Therapy (NCT) and the use of thermal neutrons for radiotherapeutic purposes, many efforts have been devoted to the characterization of the beam in order to optimize therapy procedures. Reliable dose measurements should be able to determine the various (neutrons and photonic) components of the mixed beam usually employed for therapy.
This paper studies the effect of additives such as Bboric and Ggadolinium nuclei on the sensitivity of neutron organic (alanine and ammonium tartrate) dosimeters analyzed through Electron Spin Resonance (ESR) technique (Marrale, 2014). These dosimeters were exposed to a mixed (neutron-gamma) field mainly composed of thermal neutrons. The choice of 10B and 64Gd as nuclei additives is due to their very high capture cross section for thermal neutrons. Also, after the nuclear reaction with thermal neutrons are emitted particles, which in turn release their energy in the vicinity of the reaction site (Marrale, 2008).
The irradiation with mixed field (neutron-gamma) were performed within the thermal column of the TRIGA reactor, University of Pavia. Dosimeters readout was performed through the Electron Spin Resonance spectrometer Bruker ECS106 located at the Laboratory of Dosimetry ESR / TL of the Department of Physics and Chemistry - University of Palermo.
We found that the addition of Gadolinium allows to largely increase the sensitivity of the dosimeters for thermal neutrons. In

particular, a low concentration (5% by weight) of gadolinium oxide leads to an improvement of the sensitivity of neutrons more than 10 times. In addition, for this low content of gadolinium the photon tissue equivalence is not heavily reduced. This experimental analyses are compared with computational analyses carried out by means of Monte Carlo simulations performed with the MCNP (Monte Carlo N-Particle) transport code. A good agreement was observed for alanine dosimeters.

M. Marrale et al., Exposure of Gd2O3-alanine and Gd2O3-ammonium tartrate ESR dosimeters to thermal neutrons: experiments and Monte Carlo simulations, Radiation Measurements, volume 43, number 2 (2008).

M. Marrale et al., Neutron ESR dosimetry through ammonium tartrate with low Gd content, Radiation protection dosimetry, volume 159, number 1-4 (2014).

#P072 - Phenol compounds for Electron Spin Resonance (ESR) dosimetry in gamma and neutron field

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The use of neutrons for cancer treatments has stimulated the research for beam characterization in order to optimize the therapy procedures in Neutron Capture Therapy (Altieri, 2008). Several research laboratories have shown an increasing interest aimed at extending the applicability of Electron Spin Resonance (ESR) dosimetry to radiotherapy with different types of radiation beams. In particular, ESR spectrometry provides absorbed dose measurements through the detection of the stable free radicals produced by ionizing radiations. The ESR dosimetric method has many advantages such as simple and rapid dose evaluation, the readout procedure is non-destructive, linear response of many organic and inorganic compounds (Baffa,2014).

In this work we study the response of phenolic compounds with and without gadolinium addition for electron spin resonance (ESR) dosimetry exposed to a gamma and mixed (n, gamma) field mainly composed of thermal neutrons.

The compound IRGANOX 1076 phenol gives a phenoxy radical stabilized by the presence of two bulky groups [3]. Moreover, its high molecular weight, the low volatility and the compatibility with the dosimeter binding material (paraffin) are advantages with respect to lower molecular weight phenols.

In this work we report the ESR investigation of phenols pellets and thin films with and without Gd2O3 (5% by weight) exposed in the thermal column of the Triga Mark II reactor of LENA of Pavia.

Thanks to their size, the phenolic films here presented are good devices for the dosimetry of beams with high dose gradient and which require accurate knowledge of the precise dose delivered. The choice of Gd as the additive nucleus has been made because we are interested in applications for mixed field (neutrons/photons) Gd-ESR dosimetry has an high neutron capture cross section and, furthermore, the high LET secondary particles release their energy entirely in the dosimeter. The low content of gadolinium guarantees a good tradeoff between the sensitivity to thermal neutrons. However, the use of gadolinium reduces or abolishes tissue equivalence because of its high atomic number (Marrale, 2015).

The dosimetric features of these ESR dosimeters have been investigated. In particular, we analyzed the ESR spectra of these compounds and their dependence on microwave power and modulation amplitude, their response after gamma and neutron irradiations, the detection limits for both beam typologies, signal stability after irradiation.

The results of ESR experiments are compared with Monte Carlo simulations aimed at obtaining information about the total dose measured by means of ESR dosimeters.

[1] S. Altieri et al., App. Rad. Isot. (2008) – doi: 10.1016/j.apradiso.2008.05.007

[2] O. Baffa, A. Kinoshita, Rad. and env. Bioph. (2014) – doi: 10.1007/s00411-013-0509-2.

[3] M. Marrale et al., Rad. Mes. (2015) – doi: doi:10.1016/j.radmeas.2015.02.019.

#P073 - Vortex control and dynamics in a quantum fluid of a polariton condensate.

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In this work we generate and observe intriguing new dynamics of time-oscillating and swirling quantum vortices in a two-dimensional polariton fluid. These new topological states are achieved through means of powering Rabi oscillations in the polaritons and upon implementing fine coherent control of pulsed singular beams.

Polaritons are bosonic quasiparticles that arise from the strong coupling between photonic modes and quantum well excitons in high Q microcavities. Microcavity polaritons also allow to reach Bose-Einstein condensation under opportune conditions, creating a quantum fluid of light that can be easily manipulated [1].

In the present case we resonantly excite the system initializing a superposition state of both the polariton eigenstates (which is, the upper polariton and lower polariton branches, UP and LP, respectively). This gives rise to periodic energy transfer between the excitonic and the photonic field, resulting in the oscillations of the photoluminescence intensity, which are collected and resolved thanks to the coherence of the polariton wavefunction [2].

The resonant excitation gives us also the possibility to use non trivial phase patterns to be directly impressed onto the condensate. In particular, we are able by means of a patterned liquid crystal retarder, the Q-plate [3], to create photonic Laguerre-Gaussian modes of non-zero orders which convert into the polaritonic quantized vortex and to track their dynamics by means of a Digital Holography technique [4].

The initialized state is subsequently perturbed by a delayed coherent pulse that induces the Rabi desynchronization of the polariton field, triggering the twist of the phase-singularity (which is the vortex core) in the 2D fluid. The peculiarity of this state is the continuous exchange of energy and angular momentum between the photonic and excitonic fields. Such an exchange, together with the different dephasing times of the UP and LP, result in the damped spiraling of the vortex core. These dynamics are also impressed in the outcoupled emitted photons, acquiring the original features of time- and space-structured singular light, with potential interest in advanced optical tweezer and femtochemistry applications.

[1] D. Sanvitto and S. Kéna-Cohen, The road towards polaritonic devices, Nat. Mater. (2016)

[2] L. Dominici et al., Ultrafast Control and Rabi Oscillations of Polaritons, Phys. Rev. Lett. 113, 226401, (2014)

[3] L. Marrucci et al., Spin-to-orbital conversion of the angular momentum of light and its classical and quantum applications, J. Opt. 13, 064001 (2011)

[4] L. Dominici et al., Vortex and half-vortex dynamics in a nonlinear spinor quantum fluid, Sci. Adv. 1, e1500807 (2015)

#P074 - The Dynamic Organic/Inorganic Interface of Colloidal PbS Quantum Dots

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Colloidal quantum dots are constituted by nanometer-sized crystallites of inorganic semiconductor materials bearing organic molecules at their surface. The organic/inorganic interface markedly affects forms and functions of the quantum dots, therefore its description and control have paramount importance towards effective application. Here we demonstrate that archetypal colloidal PbS quantum dots adapt their interface to the surroundings, thus existing in solution-phase as equilibrium mixtures with their (metal-)organic ligand and inorganic core components. The interfacial equilibria are dictated by solvent polarity and concentration, show striking size dependence (leading to more stable ligand/core adducts for larger quantum dots) and selectively involve nanocrystal facets. This notion of ligand/core dynamic equilibrium may open novel synthetic paths and refined nanocrystal surface chemistry strategies for optoelectronic applications.

#P075 - High-resolution wide-range dynamic neutron monochromators based on AlN/diamond acoustic resonators

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This work proposes the concept of a high-resolution wide-range dynamic neutron monochromator able to operate up to a few eV, thus significantly extending the reliable operating neutron energy range of the state-of-the-art crystal-based devices, and to improve energy resolution in the epithermal range if compared to mechanical choppers. The proposed device is based on a radiation-hard aluminium nitride (AlN)/diamond heterostructure, operating as a super-high-frequency (> 3 GHz) high-speed (> 10000 m/s) acoustic resonator. The resulting surface acoustic wave (SAW) acts as a dynamic grating for the incoming neutrons: as long as neutron speed is lower than (or at least comparable to) SAW speed, diffraction angles are significantly enhanced, thus allowing for neutron beam monochromatization to be effective up to the eV energy range. SAW amplitude can be electrically tuned to increase first-order reflectivity, leading to an enhanced intensity of the monochromatized beam.

#P076 - A biomimicry strategy for developing collagen-hydroxyapatite hybrid scaffolds crosslinked with D-ribose for bone tissue regeneration

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Developing, biomimetic, bone-like scaffolds with analogous chemical and mechanical properties of the native bone is of clinical importance to substitute the current technologies which has limited capability to treat bony defects. An approach to reconciliate this clinical demand is to tailor scaffolds with osteogenic cues and strengthened the mechanical properties through crosslinking reactions. Apart, from the plethora of crosslinking strategies, D-ribose crosslinking is of greater importance nowadays, as it is a biocompatible and low-cost coupling agent used to obtain highly stable, solid and durable scaffold for hard tissue engineering application. This study exploits the opportunity of using D-ribose as crosslinking agent to improve the mechanical performance and the chemical stability of magnesium-doped-hydroxyapatite/collagen (MHA/Coll) based scaffolds obtained through a bioinspired biomineralization process. To this aim, the crosslinking mechanism in terms of pre-ribose glycation (before freeze drying) and post-ribose glycation (after freeze drying) was investigated. The study results explicate that with controlled freeze-drying highly anisotropic porous structure with opportune macro-micro porosity was obtained. The physical-chemical features of the scaffolds characterized by XRD, FTIR, ICP and TGA demonstrated high level of structural mimicry analogous to the native bone. The influence of ribose greatly assisted in decreased solubility and increased enzymatic resistivity of the scaffolds. In addition, a favourable mechanical behaviour in response to compressive force was achieved. The preliminary cell culture experiments represented a satisfying biocompatibility with good cell adhesion, proliferation and colonization. As a proof of concept we have demonstrated that D-ribose crosslinking is cost-effective, safe and effective. This study also offers new insights and opportunities in developing promising scaffolds for bone tissue engineering.

#P077 - 3D porous collagen scaffolds reinforced by glycation with D-ribose for tissue engineering application.

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Collagen type I is in the centre of the most common biomaterials used in tissue engineering because of its biodegradability, low toxicity and promotion of cell adhesion and signalling. Nonetheless, without suitable stabilization, collagen can degrade quickly in the physiological conditions as well as under mechanical load. In order to enhance structural integrity and stiffness of the material D-ribose was proposed as a promising, non-toxic, low cost crosslinker. The objective of this study was to determine optimal conditions of glycation with D-ribose to improve stability, mechanical properties and biocompatibility of 3D porous collagen scaffolds for cartilage tissue engineering application. Two different crosslinking strategies were investigated including variety in concentration of ribose and the time of reaction: pre-crosslinking (before freeze-drying) and post-crosslinking (after freeze-drying). All types of ribose-glycated collagen scaffolds demonstrated good swelling properties and porous microstructure suitable for cell growth and colonization. Higher porosity and higher crosslinking degree were observed for post-crosslinked samples compared to pre-crosslinked. Collagenase degradation test showed that ribose-crosslinking increased the resistance to enzymatic digestion with the highest extent for samples crosslinked for a longer time. Moreover, mechanical properties of the scaffolds were significantly improved upon glycation when compared to non-crosslinked collagen. Cell-scaffold interaction and scaffold's impact on cell differentiation were evaluated using mouse mesenchymal stem cells cultured in chondrogenic medium. The study showed scaffolds biocompatibility with higher cell viability and cell proliferation as well as higher glycosoaminoglycans secretion indicating enhanced extracellular matrix production for post-crosslinked scaffolds respect to pre-crosslinked. This study demonstrated feasibility of developing 3D collagen scaffolds by ribose glycation for cartilage regeneration.

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#P078 - Topographical and Electrical Stimulation of Neural Cells through Micro-Nanowrinkled Conducting Polymer Substrates

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A variety of physical and chemical stimuli are able to induce complex responses in cells in their natural environment (extracellular matrix, ECM). Therefore, combining different functions in a single smart biointerface for in vitro cell studies could help in understanding cell-material interactions. Surfaces with micro/nanoscale **anisotropic topographical features**, **mimicking the hierarchical structural organization of ECM**, and used as substrates for in vitro cell culture, have shown **to promote contact guidance phenomena, cell alignment, and differentiation** [1-2]. On the other hand, introducing in the biointerface the capability to electrically stimulate cells or to record electrical signals related to cell activity has fundamental importance. To this aim, organic semiconductors and conducting polymers (CPs) are foreseen as soft, biocompatible, functional materials in the emergent area of **organic bioelectronics**.[3-4] In order to promote the axonal alignment and outgrowth by synergistically exploiting topographical and electrical cues, we developed **conductive and wrinkled organic biointerfaces** based on the conducting polymer poly(3,4-ethylenedioxythiophene) :poly(styrenesulfonate) (PEDOT:PSS). Thanks to the **surface wrinkling** technique, a rapid and convenient **self-assembly** method, uniaxially aligned microwrinkles were formed on the surface of PEDOT:PSS nanoscale films by thermally-induced shrinking of commercial polystyrene sheet (Polyshrink) used as substrate [5]. The topographic pattern was tunable by setting film deposition parameters (spin-coating speed), as predicted by the theoretical model for surface wrinkling [6]. Biointerfaces characterized by uniaxial wrinkles with an average spacing of around 1 µm, used for differentiating neuron-like cells (human SH-SY5Y neuroblastoma), were found to be **remarkably effective in orientating the neurite outgrowth**. Moreover, by subjecting the neurons to a biphasic pulsed voltage along the wrinkle alignment direction for 8 hours/day during 5 days of differentiation, a significant enhancement of the neurite length, with respect to the unstimulated controls, was achieved.

References

1) G. Genchi, J Tissue Eng Regen Med 9, 151 (2015).

2) A. Marino, ACS Appl Mater Inter 5, 13012 (2013).

3) G. G. Malliaras, Biochimica et Biophysica Acta (BBA) - Gen. Subj. 1830, 4286 (2013).

4) M. Berggren, A. Richter-Dahlfors, Adv. Mater. 19, 3201 (2007).

5) F. Greco et al., ACS Applied Materials & Interfaces 5, 573 (2013).

6) J. Genzer and J. Groenewold, Soft Matter 2, 310 (2006)

#P079 - Roll to Roll Processing of Ultraconformable Conducting Polymer Nanosheets and Their Application as Skin-Contact Electrodes

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Human-device interfaces and unperceivable skin-contact personal health monitoring systems can rely on ultra-thin polymeric films combined with conductive materials and/or embedding electronic devices.[1] In particular as regards skin-contact applications, ultra-low thickness (few micrometers or less) of such polymer films allows for an intimate contact and conformal adhesion. Our previous studies demonstrated the fabrication and patterning of free-standing conducting polymer nanosheets which could be transferred onto target surfaces, including skin; nanosheets were prepared by spin-coating on small scale substrates [3-4] However, the adoption of industry-ready, high throughput, large area fabrication processes is demanded for achieving cost-effectiveness and speed of execution, towards mass-scale manufacturing.

Here we report a roll-to-roll (R2R) process which permits the upscaling to large area and continuous manufacturing for the production of conducting polymer nanosheets. R2R conductive nanosheets comprise a functional layer of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and a support layer of poly(D,L lactic acid) (PDLLA). These bilayer structures having overall thickness 60 < t < 350 nm were prepared by R2R gravure printing onto a temporary substrate (PET or PP film roll) from which they can be released as free-standing films by peeling off in dry conditions. They can be then transferred in conformal contact to any target surface with arbitrary shape, curvature and surface topography (including biological tissues and skin). R2R nanosheets strongly adhere to surfaces without the use of an adhesive, as evaluated in adhesiveness tests. High-conductivity nanosheets were produced by using dimethylsulfoxide or butylene glycol (BG) as secondary dopants of PEDOT:PSS. As regards BG, it was introduced, as a dermatologically approved ingredient, for skin-contact applications of nanosheets. R2R nanosheets were tested as unperceivable and dry surface electromyography (sEMG) electrodes able to record muscle electric activity on the skin of human subjects and their performances were compared with standard pregelled electrodes used in clinical practice. Remarkable performances were obtained, especially in terms of signal to noise ratio of the recorded bioelectric signals. Moreover, very good mechanical and electrical stability against body movement and sweating could be assessed for R2R nanosheets worn on the skin, even after prolonged use (several hours).

References

1. M. Kaltenbrunner*et al.*, *Nature* **499**, 458 (2013).

2. D. H. Kim*et al.*, *Science* **333**, 838 (2011).

3. F. Greco *et al.*, *Soft Matter* **7**, 10642 (2011).

4. F. Greco *et al.*, *ACS Appl. Mater. Interf.* **5**, 9461 (2013).

#P080 - Experimental and theoretical study of thiophene-based oligomers interacting with silver surfaces and role of condensed benzene rings

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A comparative study of DTBT (1,3-di(thiophen-2-yl)benzo[c]thiophene), Br-DTBT-Br (1,3-bis(4,5-dibromothiophen-2-yl)benzo[c]thiophene) and 3T (2,2':5',2–terthiophene) oligothiophenes has been performed by following the nature of interactions occurring between these compounds and Ag (both polycrystalline and single crystal) surfaces. For this purpose, RAMAN and SERS spectra have been acquired for the isolated pure bulk molecules and for the same molecules in contact with a nanostructured Ag film. After the observation of quite different chemical behaviour, high-resolution XPS carbon 1s and sulfur 2p core levels data of molecules deposited onto a Ag single crystal surface (Ag(110)) after Ultra-High Vacuum (UHV) deposition have been also acquired. The results suggest that, in general, DTBT-like compounds interact in a peculiar way with the Ag surface compared with the model

3T molecule. In the same time, some evaluations about the possible orientations of these compounds on Ag surfaces have been experimentally performed, especially through NEXAFS carbon K-edge synchrotron based measurements depositing the molecules on Ag(110) surface. In parallel, theoretical DFT calculations have been run to confirm the hypothesized reactivity, interactions and molecular conformations/orientations at the metal Ag(110) interface. Though still preliminary, our results can provide fundamental information for predicting the reactivity and stability of compounds in which a benzo-fused ring is present such as in our DTBT-like oligothiophene compounds after the deposition on top of silver substrates. The results show that the DTBT-like compounds/Ag systems are not simply formed by unreacted and/or polymerized chains in contact with metal substrate; rather, the formation of oligothiophene dissociated species by C-S bond cleavages has been ascertained.

#P081 - Ageing mechanisms of nickel based n-type silicon photoanodes for photoelectrochemical water splitting

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A significant and promising approach to solve the energy challenges on the world is the transformation of renewable solar energy to chemical energy by the formation of fuels. Photoelectrochemical (PEC) water splitting based on solar cells utilize sunlight and water to produce hydrogen (H_2). Silicon, one abundant material on the world, attracts lots of researchers to do water splitting, because it's a good photon absorber, with appropriate band-gap (1.1 eV). However, due to the susceptibility to corrosion in the acid and basic solutions, a protective and catalytic coating on the surface is necessary to avoid the corrosion in the electrolyte for PEC water splitting.

It has been shown that n-type Si covered by thin layers of nickel or NiOx can be successfully used for water splitting, up to 1200 h in basic electrolyte. However, the degradation mechanisms producing reduction in activity and device failures in water splitting solar cells are still not understood.

In this work we have investigated the aging mechanisms of ultrathin nickel coated silicon photoanodes. We fabricated the photoanodes by electron beam evaporation of Ni layers with different thickness, on the surface of oxidized n-type Si. We have then performed long-time PEC characterizations in basic electrolyte (KOH). In addition, we comprehensively analyzed the photoanodes at nano and atomic scales using atomic force microscopy (AFM) and electron microscopy. By investigating the morphology changes and the chemical composition of the photoanodes after long operation times, we find that the ageing mechanisms extremely rely on the thickness of the Ni coating layer. The activity of the 2 nm nickel coated silicon photoanode decays faster than thicker ones, whilst photoanodes with more than 5 nm Ni coatings show longer stability, and the degradation is due to the formation of holes in the NiO_X layer.

#P082 - Screen printed ITO-free flexible OLED devices

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In this study, flexible organic light emitting devices (OLED) with general structure PEN/PEDOT:PSS/emitting polymer/Metal prepared by a roll to roll (R2R) compatible screen printing method are demonstrated. For the realization of single layers the inks were diluted to a suitable density in order to be screen printed with good uniformity and thickness of 100-200 nm. In particular, the highly transparent (transmittance≈90%) and conductive (700 S/cm) anode is processed from aqueous solution and 5wt% of dimethyl sulfoxide (DMSO) and is heat treated to ensure proper printing results and a proper wetting of the PEN substrate. The light emitting polymers used in this work are red emitting and white emitting polymers. The pLED structure was completed with screen printed silver paste or alternatively evaporated silver.

All processing steps excluding metal evaporation are performed in air.

In order to estimate the performance of the devices, OLEDs with the same structure were also fabricated by spin-coating and compared with those fabricated by screen printing.

#P083 - Enhancing polycarbonate performances by adding environmentally friendly liquid-phase exfoliated boron nitride flakes

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The outstanding improvements of two-dimensional (2D) crystals-based composites in mechanical, electrical and thermal properties compared to pristine polymer matrices [1,2], have boosted the research activity in both 2D-crystals and polymer science fields. A key requirement for the application of 2D-crystals in the composites field is their large scale production [1]. In this view, liquid phase exfoliation (LPE) of layered-crystals [3,4] is the most promising approach for the scalability of high-quality 2D-crystals, such as graphene,molybdenum disulfide (MoS_2), and hexagonal-boron nitride (*h*BN), just to cite a few.

Herein, we propose an environmentally friendly approach for the exfoliation of bulk *h*BN, by exploiting water/surfactant solution. The as-exfoliated flakes are used as filler in a polycarbonate (PC) matrix, obtaining nanocomposites, with enhanced properties with respect to the pristine polymer.

Exfoliation of bulk *h*BN is carried out by ultra-sonication [5] in a water/surfactant solution, obtaining *h*BN flakes, which are then sorted by lateral size and thickness by using ultra-centrifugation [6-8]. A cascade centrifugation [9] is exploited in order to prepare two dispersions containing *h*BN flakes having average lateral sizes of 200 and 400 nm, respectively. After the ultra-centrifugation, a solvent exchange process is used for the re-dispersion of *h*BN flakes in 1,3-dioxolane, the same solvent used for the dissolution of PC pellets.

Composites, with 0.5 wt% of loading of *h*BN, are morphologically and structurally characterized using atomic force and scanning electron microscopies, and Raman spectroscopy. Mechanical, thermal and oxygen-barrier measurements are carried out to investigate the effect of *h*BN filler in PC matrix. We found an improvement of ~30% in Young’s modulus and a decrease of ~35% in oxygen permeability with respect to the bare polymer. Correlating the oxygen permeability respect to filler concentration it is possible to probe the aspect ratio and state of dispersion of the *h*BN fillers in the PC matrix [10], opening novel insights discovering the blend compatibility.

References

[1] A. C. Ferrari, et al., Nanoscale, **7** (2015) 4598

[2] J. R. Potts, et al., Polymer, **52** (2011) 5

[3] J. N. Coleman, et al., Science, **331** (2011) 568

[4] F. Bonaccorso, et al., Adv. Mater., **28** (2016) 6136

[5] Y. Hernandez, et al., Nat. Nanotechnol., **3** (2008) 563

[6] O. M. Maragó, et al., ACS Nano, **4** (2010) 7515

[7] J. Hassoun, et al., Nano Lett., **14** (2014) 4901

[8] A. Capasso, et al., Solid State Commun., **224** (2015) 53

[9] C. Backes, et al., ACS Nano, **10** (2016) 1589

[10] L. E. Nielsen, J. Macromol. Sci. A, **1** (1967) 929

#P084 - Correlation between chemical ordering and magnetic properties in binary magnetic alloys

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Nowadays, the development of new advanced technologies in the field of information storage and electronic devices requires a great effort in improving the performance of magnetic materials that are at the basis of the device’s functioning. Among the magnetic materials, chemically ordered binary alloys ($L1_0$, $L1_2$) are of significant interest due to the peculiar atomic arrangement within the crystallographic cell, which induces in the material, through the spin-orbit interaction, a high magnetocrystalline anisotropy [1].

The BAG project (2015-2016) at LISA Beamline (ESRF) aims at investigating by X-ray Absorption Spectroscopy (XAS) the degree of chemical order within different magnetic alloys and to understand the influence of specific process conditions (growth and annealing temperature, addition of a third element) on the transformation from the chemically disordered state (fcc structure) to the chemically ordered structure (fct-$L1_0$or fcc-$L1_2$). Among the characterization techniques applied to investigate the structural properties at the local-scale, XAS is an effective tool to probe the chemical environment around an absorber element, and to get information on the average structural features of the materials, thus being complementary to conventional X-ray diffraction (XRD) techniques [2]. Due to its peculiar characteristics, i.e. selectivity and high sensitivity, Extended X-ray Absorption Fine Structure (EXAFS) analysis represents the main technique to investigate the local properties in many systems whose behaviour is strongly affected by the atomic arrangement, as in the case of the $L1_0$ or $L1_2$ chemically ordered alloys, where the degree of chemical order influences significantly the magnetocrystalline anisotropy [3]. In particular, the main results obtained from four experiments on different systems (Ferromagnetic FePt nanoparticles, Ferromagnetic $(Fe_{1-x}Mn_x)_{50}Pt_{50}$ thin film, Antiferromagnetic IrMn thin films and $(Fe_{1-x}Cr_x)_{50}Pt_{50}$ thin films) will be presented, illustrating the great versatility of the LISA beamline in characterizing a variety of magnetic system under different experimental conditions.

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References:

[1] A. Cebollada et al., Magnetic nanostrucures, H. Nalwa (Ed), American Scientific Publishers, 2002, ch. 3 (2002) 93

[2] Srajer et al., J. Magn. Magn. Mater. 307, (2006) 1

[3] Laureti, et al., J. Appl. Cryst. 47 (2014) 1722

#P085 - Fabrication and Characterization of ALK1Fc-Loaded Fluoro-Magnetic Nanorods for inhibiting TGF β1 in Hepatocellular Carcinoma (HCC).

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Fluoro-magnetic nanoparticles are needed urgent as contrast agent for bio-medical- fluorescence imaging. Indeed, their size and concentration in the tumor allow a very high resolution and an accurate mapping of lesions. Fluorescence isothiocynate that was added during fabrication has been entrapped inside crystal of MNPs during crystallization. These led to change of crystal architecture to form elongated rods. Ferric atoms were distributed over the length of crystal leading to strength magnetic value. TEM and SEM-EDX show that elongated crystals were produced with high ferric atoms scatter. The intensity of fluoro-MNPs fluorescence was detected by fluorescence photometer and confocal microscope. The benzene ring structure of FITC and its carboxylic group were clearly detected on fluoro-MNPs spectrum by using FTIR, compared to MNPs prepared in absence of FITC. Fluoro-MNPs rods were functionalized by hydrogel crosslinking structure (PEG-CMC) onto fluoro-MNPs surface by using LbL alternative adsorption. These hydrogel properties are used as preserver for protein delivery. ALK1fc as specific TGFβ1 inhibitor, is encapsulated inside (PEG- CMC) layers during Layer by Layer assembly (LbL). Zeta potential measurement, X-rays diffraction and SDS page-silver staining results confirm encapsulation of ALK1fc. Efficiency of encapsulated ALK1fc was detected by Immune-fluorescence assay against localization of TGFβ1.Stained TGFβ1 appeared as purple color, distributed in cytoplasm of HLF cells (control). Hence it disappeared in HLF sample treated by encapsulated ALK1fc.

#P086 - Scale-dependent fragmentation mechanisms of graphene oxide: A quantitative morphological analysis as new approach for metrology of 2D materials

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The production of large quantities of 2D materials in solution with well-controlled morphological properties of the nanosheets is not only a technological challenge but also a fundamental one, because several scientific aspects still need to be clarified for a detailed understanding of the fragmentation mechanisms and the control of the final products. Furthermore, it is necessary to develop fast and reliable protocols to measure and analyze a large number of 2D objects and as well as to find a set of "robust" parameters to achieve an accurate multi-scale description of the system.

Here we show how these problems can be fruitful solved by using a statistical approach. In particular, the study of the distribution of the morphological parameters represents the key-factor i) to understand the physical mechanisms of the fragmentation in liquid, ii) to test the theoretical models and iii) to explore the mechanical and the structural properties of both the starting material and the final fragments.[1] Recently, we developed a fast and automatic procedure based on topographic images to measure, one by one, the exact shape and size of thousands of nanosheets obtained by exfoliation and fragmentation in general.[2] Combining the analysis of images acquired with different techniques such as Fluorescence (FM), Scanning Electron (SEM) and Atomic Scanning Probe (AFM) microscopies, we monitored the time evolution of the area and the shape distribution of 2D single sheets of graphene oxide (GO) in water during extended sonication treatment. Combining the analysis of images acquired with different microscopies, we monitored the 2D fragments from the millimeter to the nanometer scale. In particular, we showed that the quantitative analysis provides to measure the mechanical properties of the GO sheet such as the fracture strength. Moreover, the analysis of the fragment distributions gives detailed information on the dynamics of the 2D fragmentation providing direct evidence of different regimes given by the interplay of two breaking mechanisms, such as core fragmentation and peripheral erosion. Finally, based on the high-skewed size-distribution of the GO sheets, we propose a new approach to parametrize the polydispersity of the 2D materials. The capability to monitor and to control the morphological and the mechanical properties at nanoscale of large quantities of 2D materials in solution will pave the way towards using these materials as fillers for industrial-scale production of graphene- and 2D-based composites.[3]

References:

[1] D. E. Grady, "Length scales and size distributions in dynamic fragmentation," International Journal of Fracture, vol. 163, pp. 85-99, (2010)

[2] K. Kouroupis-Agalou et al., "Fragmentation and exfoliation of 2D materials: a statistical approach," Nanoscale, vol. 6, pp. 5926-5933, (2014)

[3] This research was supported by Graphene Flagship (Grant Agreement No. 604391)

#P087 - 4H-SiC detectors for nuclear physics

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Silicon carbide (SiC) is one of the compound semiconductor which has been considered as a potential alternative to Silicon for the realization of charge particles detectors and dosimeters in high energy physics. SiC is predicted to be radiation harder than Si due to the high displacement threshold energy and potentially used for radiation detectors in high radiation conditions. High performances SiC detectors, based on Schottky diodes and p-n junction, have been used to detect neutrons, X-rays, protons, alpha particles and heavier ions.

In this work we describe the performances of 4H-SiC Schottky diode detectors that will be used as an innovative and very promising detection system for next generation nuclear physics experiments at high beam luminosity, that can operate at high energy (~ 1 GeV) with high fluxes (10^7 pps/m^2) and fluences (10^{14} cm^{-2}) of heavy-ions in order to determine the cross sections of very rare nuclear phenomena. Silicon carbide technology offers today an ideal response to such challenges, since it gives the opportunity to cope the excellent properties of silicon detectors (resolution, efficiency, linearity, compactness) with a much larger radiation hardness (up to five orders of magnitude for heavy ions), thermal stability and insensitivity to visible light. However a significant upgrade of present devices is required in terms of thickness of the active region and detection area. So it is in progress the development of thick (>100 µm) and large area (1 cm^2) SiC detectors with two typologies of design: Schottky and the p-n junctions. The Schottky diodes represent today the state of art for SiC detectors, the p-n represents a novel solution for SiC, that is particularly promising in analogy to similar junctions based on Silicon devices. The first step for the development of this research is the realization of some 4H-SiC prototype detectors with performances suitable to monitor heavy ions at high energy. So in the present paper we have studied the effects of very high energy irradiation on SiC and Si detector electrical characteristics. We performed energy resolution analysis on SiC Schottky diode using alpha particles beams to evaluate the detectors performances and studied the effects of very high energy irradiation on SiC and Si detector electrical characteristics. The detectors were irradiated with 740 MeV C^+ at a dose of 94 KGy, and current-voltage I-V measurements of not irradiated and irradiated diodes were compared.

#P088 - Crystallographic defects detection in 3C-SiC by micro-Raman and micro-PL analysis

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Cubic Silicon Carbide (3C-SiC) is a wide band-gap material regarded as a most promising candidate for high power and high frequency devices application since 3C-SiC allows a highest speed of electron transport within the crystal. In this work a new technique with micro-Raman and micro-PL analysis is proposed to detect defects in 3C-SiC epitaxial films because a detailed study of defects in 3C-SiC has not yet been performed. The technique uses above band-gap high-power laser densities to induce a local increase of free carriers in un-doped epitaxies ($n<10^{16}$ at/cm^3), creating an electronic plasma that couples with the longitudinal optical (LO) Raman mode. This effect is due to the longitudinal electric field, related to the atomic displacements associated with the LO phonon mode (connected to the SiC lattice ionic nature and to the difference in electro-negativity between Silicon and Carbon atoms), which interacts with the neighbouring electrons. The Raman shift of the LO phonon plasmon-coupled mode (LOPC) increases as the free carrier density increases. Crystallographic defects induce a modification of the free carriers density determining a change in the coupling LOPC, a different Raman shift and PL emission from 3C-SiC gap. Thus we suppose that the results observed are connected to crystallographic defects and we propose this technique as a very efficient solution for the analysis of defects in 3C-SiC material. This technique is non-destructive and detects defetcs not evidenced by KOH etching.

#P089 - Biofuel fed SOFC: a clean energy and efficient technology

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This communication complies with the general trend on Solid Oxide Fuel Cells (SOFCs) about the utilization of low cost fuels. A possible scenario for the near future is the direct utilization of biofuels in SOFCs. At the present, the conventional Ni-YSZ/YSZ/YDC/LSFC cells are affected by several constraints in the direct utilization of such fuels mainly consisting in the carbon formation and sulphur contamination of the anode. For this reason, in the short and medium terms a possible solution to these issues is the utilization of a barrier layer attached to the outermost side of the anode. The pre-layer materials must show properties that may comply requirements such as mechanical, thermal and electrochemical properties at least similar to the Ni-YSZ. In addition, the catalyst must be deposited at very thin levels in order to mitigate the ohmic constraint of an addition layer. Ni-based alloys (Ni-M, M=Ni, Co, and Fe) in combination with gadolinia-doped ceria is reported to be a valuable material for the oxidation of biofuels including the oxidation of sulphur compounds. Therefore, the investigation of such catalysts as protective layer becomes of interest in order to maintain the well established manufacturing technology around the SOFCs. With this preface, this communication will report the strategy adopted for the preparation of a catalyst with a proper composition at the atomic level, the catalytic properties and physico-chemical properties of catalyst, as well as the electrochemical investigation of performances for the protected cells in comparison to that achieved for a bare cell. In the final part of this communication, the realization and testing of a proof-of-concept system based on a 500 W_{el} SOFC stack fed by biogas will be reported.

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#P090 - Structural-chemical assessment and electro-optical investigation on InAs/AlGaAs quantum dot structures for Enlarged Bandgap Intermediate Band Solar Cells

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In this work we present the results of structural, chemical and electro-optical investigation on an Intermediate Band Solar Cell (IBSC) structure, where the concept of *intermediate-band*is exploited by a high energy barrier AlGaAs material with embedded InAs quantum dots via a multistep growth approach. In this way the intrinsic issues related to different surface kinetics of involved species (Ga, In and Al adatoms) and affecting crystal quality, namely rough interface between AlGaAs and InAs which negatively affects the growth of uniform and pseudomorphic QDs, are overcome.

This growth procedure leads to a complex chemical and structural profile both on QDs and WL, which acts as a 2D quaternary *template layer*, strongly affecting the electro-optical properties of the system. A detailed scanning transmission electron microscopy (STEM) study was carried out in order to assess the structural and chemical properties of the QDs and 2D template layers. In particular, high resolution STEM images and energy dispersive X-ray point spectra, scan profiles and maps allowed to define the compositional and strain distribution within these complex nanostructures and to correlate these results with the electro-optical performances of the related IBSCs. The optical role of the 2D template layer with respect to device operation has been deeply investigated by means of different cw and modulation spectroscopy techniques, along with temperature studies of the photocurrent spectral generation by additional optical and electrical external bias, showing the occurrence of carrier thermal transferring and inter-level filling processes between this state and the QD related energy positions.

#P091 - Emulsions in grooved channels: dynamics, rheology and applications

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Emulsions are complex systems which are formed by a number of droplets dispersed in a solvent. Such droplets do not coalesce but rather push against each other leading to non-trivial effects in the overall flowing dynamics. In fact, such systems possess a so-called yield stress below which the system has an elastic response to an external forcing, i.e. it deforms but it does not flow. While above the yield stress the system flows, the rheological properties are those of a non-Newtonian fluid, i.e. the stress is not proportional to the shear. In the solid-like regime the network of the droplets interfaces stores the energy coming from the work exerted by an external forcing. This energy can also be used to actually move the droplets in a non-reversible way named plastic event. The simplest bulk event involves four droplets and it is called T1. More formally plastic events are related to topological changes of the droplets configurations. There are some phenomenological models aiming at describing the collective behaviour of such systems that assume the proportionality between the rate Γ of T1 events and the so-called fluidity field $f = \dot{\gamma}/\sigma$, where $\dot{\gamma}$ is the shear rate and σ is the stress: $f \propto \Gamma$ [1]. Indeed, droplets rearrangements are the basis of the overall flowing behaviour.

However such theoretical models mainly describe bulk phenomena so that the subject of boundary conditions remains an open subject. While it is well known that in the presence of a smooth surface the main effect is the development of a slip velocity at the boundaries little is known for more complex geometries. In this talk we present some recent results concerning the dynamics of emulsions in microchannels characterized by a rough surface. The rough surface is described by a set of parameters which have been varied in our studies. We report and compare results both from laboratory experiments and from numerical simulations aiming at providing detailed information about plastic events. In order to sustain a high rate of detection of such events without hampering the underlying Lattice Boltzmann model simulations for emulsions we resorted to a GPU implementation for the detection of topological changes. Specifically, we are able to track and study plastic events everywhere in the channel (bulk and boundary) allowing us to relate a detailed plastic activity study close to the rough wall to the experimentally measured flow profiles.

#P092 - Novel complexes for the sol-gel synthesis of perovskites CsCaF3 thin films

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Metal-halide perovskites have recently attracted great attention due to their remarkable potential applications in the field of optoelectronic devices including solar cells, light-emitting diodes and lasers. This interest is mainly due to the challenging potentialities of these perovskites, that may substitute the organic-inorganic lead halide based perovskites if they possess a suitable band-gap.

In particular, the ternary compounds, belonging to the group of fluoro-perovskites, having the general formula ABF_3, where A and B are alkaline and alkaline earth metals respectively, have been studied over the past decade. Their band-gap is actually too large to be applied in solar cells, but fluoro-perovskites, such as $CsCaF_3$, arevery interesting for optoelectronic applications. The main advantage is that these materials can be used as light emitting materials in the deep ultraviolet regime.

In the present study, the synthesis of a novel precursor containing Cs and Ca is reported and applied to the sol-gel fabrication of cesium based fluoro-perovskite thin films.The complex acts as a single source of the metals and of fluorine. A systematic study has been carried out to optimize the sol-gel process for the fluoro-perovskite phase formation and the effect of deposition conditions on the film structural, morphological and compositional properties has been investigated by X-Ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray analysis (EDX). Our characterization shows that the applied approach is a suitable method to deposit polycrystalline $CsCaF_3$ films with the correct stoichiometry and a very uniform surface.

#P093 - Electronic and optical properties of hexathiapentacene in the gas and crystal phases

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Using density functional theory (DFT) and its time-dependent (TD) extension, the electronic and optical properties of the hexathiapentacene (HTP) molecule, a derivative of pentacene (PNT) obtained by symmetric substitution of the six central H atoms with S atoms, are investigated for its gas and solid phases. For the molecular structure, all-electron calculations are performed using a Gaussian localized orbital basis set in conjunction with the Becke three-parameter Lee-Yang-Parr (B3LYP) hybrid exchange-correlation functional. Electron affinities, ionization energies, quasiparticle energy gaps, optical absorption spectra, and exciton binding energies are calculated and compared with the corresponding results for PNT, as well as with the available experimental data. The DFT and TDDFT results are also validated by performing many-body perturbation theory calculations within the GW and Bethe-Salpeter equation formalisms. The functionalization with S atoms induces an increase of both ionization energies and electron affinities, a sizable reduction of the fundamental electronic gap, and a redshift of the optical absorption onset. Notably, the intensity of the first absorption peak of HTP falling in the visible region is found to be nearly tripled with respect to the pure

PNT molecule. For the crystal structures, pseudopotential calculations are adopted using a plane-wave basis set together with the Perdew-Burke-Ernzerhof exchange-correlation functional empirically corrected in order to take dispersive interactions into account. The electronic excitations are also obtained within a perturbative B3LYP scheme. A comparative analysis is carried out between the ground-state and excited-state properties of crystalline HTP and PNT linking to the findings obtained for the isolated molecules.

R. Cardia, G. Malloci, G.-M. Rignanese, X. Blase, E. Molteni, and G. Cappellini, Phys. Rev. B 93, 235132 (2016)

#P094 - Label-free Investigation of the Effects of Lithium Niobate Polarization on Cell Adhesion

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The determination of contact area is pivotal to understand how biomaterials properties influence cell adhesion[1].In particular, the influence of surface charges is well-known but still controversial, especially when new functional materials and methods are introduced[2,3]. Here, we use for the first time Holographic Total Internal Reflection Microscopy (HoloTIRM) to study the influence of the spontaneous polarization of ferroelectric lithium niobate (LN) on the adhesion properties of fibroblast cells. The selective illumination of a very thin region directly above the substrate, achieved by Total Internal Reflection, provides high-contrast images of the contact regions. Holographic recording, on the other hand, allows for label-free quantitative phase imaging of the contact areas between cells and LN. This work shows that cells adhering on negatively polarized LN present a significant increase of the contact area as long as an intensification of contact vicinity. This confirms the potential of LN as a platform for investigating the role of charges on cellular processes and highlights the potential of HoloTIRM as a non-invasive, high-throughput technique for the investigation of cell/material interaction.

(1) Burmeister, J. S.; Olivier, L. a; Reichert, W. M.; Truskey, G. a. *Biomaterials* **1998**, *19*, 307–325.

(2) Baxter, F. R.; Bowen, C. R.; Turner, I. G.; Dent, A. C. E. *Ann. Biomed. Eng.* **2010**, *38*, 2079–2092.

(3) Choi, W. J.; Jung, J.; Lee, S.; Chung, Y. J.; Yang, C.-S.; Lee, Y. K.; Lee, Y.-S.; Park, J. K.; Ko, H. W.; Lee, J.-O. *Sci. Rep.* **2015**, *5*, 9974.

#P095 - Critical Casimir forces tailor the growth of quantum dot superstructures

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Quantum dots represent one of the most interesting and versatile systems of modern nanoscience, unravelling the interaction of light with crystalline matter squeezed down to a few nanometers in size. On one hand, several synthesis approaches have been proposed, featuring different materials, heterostructures, shapes and surface functionalization [1]; on the other hand, a major effort has been placed in trying to understand how to self - assemble these building blocks in a programmable way in order to access a new class of materials by design [2, 3].

We propose a novel type of assembly method for colloidal quantum dots that does not depend on the specific type of material, structure, shape or surface of quantum dots and is therefore completely general. We manage to induce controlled nanoparticle assembly by making use of the attractive critical Casimir interaction [4]; this force exploits the role of temperature dependent solvent density fluctuations present in a binary solvent close to its critical point. By carefully tuning magnitude and length scale of attractive Casimir and repulsive Coulombic interactions, we are able to grow large quantum dot superstructures. We study the assembly process as it takes place by scattering techniques (DLS, SAXS) and the final product by electron microscopy (SEM, TEM). Furthermore, we scavenge the optoelectronic properties of growing superstructures by simultaneous topological and spectral mapping via AFM combined with bright field photoluminescence microscopy.

We expect the results here described to stimulate the attention of the scientific community in a novel method to achieve large area quantum dot based superstructures for application in light emitting diodes and solar cells.

[1] Talapin, Dmitri V., et al. "Prospects of colloidal nanocrystals for electronic and optoelectronic applications." Chemical reviews 110.1 (2009): 389-458.
[2] Bishop, Kyle JM, et al. "Nanoscale forces and their uses in self-assembly." small 5.14 (2009): 1600-1630.
[3] Hanrath, Tobias. "Colloidal nanocrystal quantum dot assemblies as artificial solids." Journal of Vacuum Science & Technology A 30.3 (2012): 030802.
[4] Nguyen, Van Duc et al. "Controlling colloidal phase transitions with critical Casimir forces." Nature communications 4 (2013): 1584.

#P096 - Engineered Materials from Poly(lactic acid) with Cardanol Deriving Additives

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Engineered Materials from Poly(lactic acid) with Cardanol Deriving Additives

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Biopolymers or Green-Plastics are environment-friendly materials based on biodegradable very promising matrices (film or bulk) that have similar, and often better, properties than traditional synthetic plastic materials.

These materials also contribute to the reduction of CO_2 emissions during their production cycle, the weight of the material, the cost of the final product and above all are easily processable, recyclable and biodegradable.

Among of these materials, we realize new films based on Poly(lactic acid) (PLA) that is a very attractive polymer for food packaging application because in addition of being thermoplastic, biodegradable, compostable, and produced from renewable resources, it shows comparable behavior in mechanical, thermal and barrier properties to the most used synthetic polymers [1,2].

Cardanol (CA) is a natural and renewable organic raw material well known as product of the cashew industry. Its component, easily obtained by distillation under vacuum, have been used as antioxidants, antifungal, antibacterial, as well as for the synthesis of fine chemicals [3].

In this context the preparation of functional PLA film opportunely modified with cardanol derivatives, in order to improve their potential applications in food and biomedical packaging, will be reported.

REFERENCES

[1] Drumright, R. E.; Gruber, P. R.; Henton, D. E.; Adv. Mater. 2000,12, pp.1841−1846.

[2] Auras, R. A.; Harte, B.; Selke, S.; Hernandez, R. J.; Plast. Film Sheeting 2003, 19, pp.123−135.

[3] Mele, G.; Vasapollo, G. Mini-Rev. Org. Chem., 2008, 5, 243-253.

#P097 - Direct Laser Lithography as a Tool for Producing Biomimetic Functional Surface

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Biomimetics is the study of natural systems in order to find out smart solutions for complex technological challenges, taking inspiration by the solutions already developed by nature.[1] The cutting edge application of biomimetics regards the micro- and nanoscale, since inherent limitations of fabrication techniques prevent the replication of complex hierarchical microstructures. We present some examples of artificial bioinspired surfaces that can be employed in several fields such as self-cleaning, air retention, water drag reduction and dry adhesion. Surfaces were patterned with a negative tone, IPL-780 (Nanoscribe GmbH),. through direct laser lithography (DLL), based on two-photon absorption, allowing the three-dimensional fabrication in the microscale with nanometric resolution.

The first type of artificial surface, patterned in the micro- and nano-scale, is inspired by *Salvinia Molesta* leaves. This plant shows the ability of self-cleaning, due to super-hydrophobicity, and air retention when submerged by water.[2] These capabilities are performed by hairs capped with a crown-like head of about 500 µm in height. The hairs of the salvinia were reproduced about 100 times smaller, showing not only the same properties of the salvinia leaves in terms of air retention and hydrophobicity, but also the capability of promoting the condensation of atmospheric moisture. In particular, in the natural model, the performance is due to the interplay of morphology and chemical coating, while in the artificial hair only the morphology was reproduced, thus succeeding in making an hydrophobic surface made up of an hydrophilic material, i.e. the negative tone resist. It is possible to assume that the realization of different patterns on the same surface, in terms of geometry, dimension and spatial organization, can lead to a new type of functional structured surfaces, simply by modulating the entity of the three properties.

Structures for dry adhesion were fabricated taking the gecko foot skin as inspiration. The multilevel hierarchical conformal structure of the artificial gecko setae can enhance, thanks to nanometric features, short range interactions, producing attractive Van der Waals forces.[3] The setae of the gecko were reproduced by DLL following the morphology of the natural ones. Several adhesion tests, by means of force sensors operating in the µN scale,were carried out in order to compare the parallel and perpendicular adhesion forces of the artificial setae to the natural ones.

1. Bhushan, *Philos. Trans. R. Soc. Math. Phys. Eng. Sci. 367*: 1445-1486 (2009).

2. Barthlott *et al.*, *Adv. Mater. 22*: 2325-2328 (2010).

3. Autumn *et al,. Nature 405*: 681-685 (2000).

#P098 - Smart Sulfonated Polystyrene Opals for Ionic Strength Sensing

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Stimuli-responsive photonic crystals (PCs) represent an intriguing class of smart materials, very promising for sensing applications, whose optical properties can be modulated by using external triggers, including, among other, chemical, thermal and electrical[1] stimuli. Here, selective ionic strength responsive polymeric PCs are reported. They are easily fabricated by partial sulfonation of polystyrene (PS) opals, without using toxic or expensive monomers and etching steps. In details the sulfonation of PS opals was carried out by treating dry colloidal crystals with concentrated sulfuric acid. PS opal were obtained by evaporative deposition method on a horizontal substrate from an aqueous PS particle dispersion (diameter about 160 nm). The sulfonation reaction of self-assembled PS opals involved the external shell of each sphere, providing a well ordered lattice of partially fused core-shell particles . As a result of this reaction, each particle consisted of a core of highly hydrophobic polystyrene and a shell of polystyrene sulfonate (PSS), which is highly hydrophilic. The shell thickness of PSS depends on several factors, such as reaction time, temperature and particles size. The introduction of charged sulfonic groups ($-SO_3^-$) in the polymeric chain resulted in the formation of a polyelectrolytes network, which is able to absorb a large amount of water and produced an important swelling of the photonic structure, with consequent red-shift of the diffracted light with respect to the pristine material, passing from 405 nm (pristine opal) to 760 nm (after 3 h of sulfonation).

The presence of a polyelectrolyte network in these PCs introduces the possibility to modulate the opals swelling and thus their color by changing the ionic strength (IS). Indeed, as expected for a polyelectrolytes gel, the gel volume can be reduced by the presence of salts in the surrounding solution for the creation of the Donnan equilibrium. The latter provides the relationship between the equilibrium concentrations of salt ions within the gel and in the surrounding solution. In particular, by increasing the salt content of the solution, the osmotic pressure in the network decreases and the hydrogel matrix tends to collapse. In the case of an ordered photonic structure, this process corresponds to a blue-shift of the reflected wavelength. In particular in our case the color of the opal can be continuously shifted over the entire visible range (405-760 nm) by changing the content of ions over an extremely wide range of concentration (from 67 mM to 4 M).

The optical response is completely independent from pH and temperature and the initial color can be fully recovered by washing the sulfonated opals with pure water. These new smart photonic materials could find important applications as ionic strength sensors for environmental monitoring as well as for healthcare screening.

[1] Nucara *at al.,* J. Mater. Chem. C, 3:8449 (2015).

#P099 - A fully organic retinal prosthesis restores vision in a rat model of degenerative blindness

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The progressive degeneration of retinal photoreceptors due to single mutations in any of over 240 identified genes (RetNet, Retinal Information Network) is one of the major causes of adult blindness in humans. Among these pathologies, *Retinitis pigmentosa*, a collective name for a set of genetic disorders that cause death of photoreceptors, afflicts 1 person in every 4,000 worldwide. At the moment, no effective clinical treatment exists for this pathology. Here we report on the fabrication and functional validation of a fully organic three-layered prosthetic device for *in vivo* subretinal implantation in the eye of Royal College of Surgeons rats, a widely recognized model of *Retinitis pigmentosa*. Electrophysiological and behavioral analyses revealed a significant and prosthesis-dependent recovery of light-sensitivity and visual acuity that persists up to 6 months after surgery. The rescue of the visual function was accompanied by an increase in the basal metabolic activity of the primary visual cortex, as demonstrated by positron emission tomography imaging. Our results highlight the possibility of developing a new generation of fully organic, highly biocompatible and functionally autonomous photovoltaic prostheses for subretinal implants to treat degenerative blindness.

#P100 - Nanomagnets based on Peptides-decorated Cyclodextrin for Amyloid-β targeting.

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Magnetic nanoparticles (MNPs) are widely utilized in magnetic-field-assisted bio-separation, bio- interaction, imaging and drug delivery, due to their large surface area and easy manipulation by an external magnetic force. Nanomagnets constituted by polymers, dendrimers and cyclodextrins functionalizing magnetite have been widely developed for therapy and diagnosis.[1-2] Amphiphilic cyclodextrin (aCD) are largely employed to deliver different types of therapeutic and diagnostic molecules.[3-4] Here we propose novel nanomagnets based on non ionic amphiphilic cyclodextrin heptakis (2-oligo(ethyleneoxide)-6-hexadecylthio-)-β-CD (SC16OH) -capping Fe_3O_4 NPs and decorated with Adamantanil-(PEG)4-KLVFF, (Ada-Pep), as nanoconstructs based on the self-recognizing sequence of the Amyloid-β (Aβ) peptides.

Fe_3O_4@SC16OH was prepared by mixing Fe_3O_4 NPs with an aqueous dispersion of SC16OH and then isolated by settling down with a magnet. Fe_3O_4@SC16OH/Ada-Pep was prepared by hydration of an organic film of Ada-Pep, and isolated by centrifugation. In order to assess the recognition properties of the KLVFF active peptide, a magnetic cyclodextrin decorated with the scrambled units adamantanil-(PEG)4VFLKF (Ada-PepSCR) was fabricated. Peptide-tailored nanomagnets were characterized at solid state by TGA, STEM, AFM, X-Ray Diffraction, XPS and magnetization mass measurements. In aqueous physiological solutions, DLS and Z-potential measurements, point out a size of @200 nm and a negative surface potential (-30 mV) dependently by the co-presence of aCD olygoethylenglycol chains and peptide units on the external fringe. The ability of these novel nanomagnets to target the Aβ peptides was studied either in Aβ containing aqueous samples by means of Maldi-Tof-Ms or in the medium of cultured cells over-expressing the Aβ peptides, by using an ELISA based assay. Our results indicate that in both the experimental conditions the nanomagnets can perform an unbiased Aβ-targeted fishing, thereby suggesting their potential use as efficient diagnostic agents.

1E. Amstad, M. Textor, E. Reimhult Nanoscale, 2011, 3, 2819

2U. J. Menon, P. Jadeja, P. Tambe, K.Vu, B. Yuan, K. T. Nguyen Theranostics, 2013, 3,152

3A. Mazzaglia, A. Valerio, N. Micali, V. Villari, F. Quaglia, M. A. Castriciano, L. Monsu` Scolaro, M. Giuffre` ,

G. Siracusano, M. T. Sciortino Chem. Commun., 2011, 47, 9140

4M. L. Bondì, A. Scala, G. Sortino, E. Amore, C. Botto, A. Azzolina, D. Balasus, M. Cervello, A. Mazzaglia, Biomacromolecules 2015, 16, 3784

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#P101 - Solar energy conversion performed by solution-processed silicon nanocrystals

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Silicon nanocrystals (SiNCs) in the quantum size range (2-12 nm) are attracting an increasing interest: on the contrary of bulk silicon, they display a bright emission, which can be tuned from the visible to the near-infrared spectral region by increasing their size. Compared to more traditional quantum dots, such as CdSe, SiNCs offer the following advantages: silicon is abundant, easily available and essentially non toxic, it can form covalent bonds with carbon, thereby offering the possibility of integrating inorganic and organic components in a robust structure[1]. Moreover, being Si an indirect band gap semiconductor, the photophysical properties of SiNCs are characterized by an extremely large Stokes shift, long phosphorescence lifetimes and photoluminescence quantum yield as high as 45%. These properties, together with the interest in materials compatible with the Si-based technology, promote SiNCs as ideal candidates for sensing and photovoltaic applications. In particular for the conversion of sunlight to electrical energy, the energy provided by the UV component of the solar spectrum can be down-converted by SiNCs to visible light, matching the typical high responsivity region of conventional Si-based or dye sensitized solar cells.

In this contribution, the implementation of SiNCs in cutting-edge photovoltaic technologies will be discussed. Specifically, the embedding of these nanocrystals in polymer matrix was exploited to prepare semi-transparent polymer waveguides and the photophysical properties of embedded SiNCs were deeply investigated[2]. In addition to this, the photovoltaic performance of the prepared plates as solar concentrators will be reported, demonstrating the feasibility and the promising features of SiNCs based integrated photovoltaics.

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References:

1. Mazzaro, R. *et al.* Photoinduced Processes between Pyrene-Functionalized Silicon Nanocrystals and Carbon Allotropes - SI. *Chem. Mater.* **27,** 4390–4397 (2015).

2. Coropceanu, I. & Bawendi, M. G. Core/Shell Quantum Dot Based Luminescent Solar Concentrators with Reduced Reabsorption and Enhanced Efficiency. *Nano Lett.* **14,** 4097–4101 (2014).

#P102 - Biocompatible cationic polymeric cryogel: smart material for biomedical applications

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Heparin is a highly sulfated glycosaminoglycan commonly used as anticoagulant drug during clinical procedures, such as cardiovascular surgery or extracorporeal blood purification (dialysis), to avoid the unfavorable formation of clots.[1] High concentrations of circulating heparin require neutralization due to possible serious bleeding complications. The intravenous administration of the heparin antagonist protamine sulfate is routinely clinically performed, but is frequently associated with adverse reactions.[2] Therefore, there is a need for a valid and safe alternative to achieve heparin removal from blood or plasma, such as an extracorporeal filter, a matrix, or an adsorbent.

Recently we have developed and characterized a functionalized cationic polymeric macroporous material able to selectively adsorb the anticoagulant drug heparin both in vitro and in human plasma.[3] This material showed a high heparin capture efficiency and a good blood compatibility, as indicated by negligible adsorption of albumin, antithrombin III, and total protein, and may thus be suitable for the design and development of extracorporeal heparin removal device.

In this contribution we will report the latest results concerning the development of a new synthetic procedure that allows to obtain a set of macroporous cationic polymeric cryogels with various compositions and different performances towards heparin neutralization.

The same material, due to its macroporous structure, biocompatibility and high affinity for heparin, has also been preliminary tested as support for application in cell growth and tissue engineering.

References

1. Hirsh, J.; Anand, S. S.; Halperin, J. L.; Fuster, V. *Circulation* **2001**, 103, 2994-3018

2. Weiler, J. M.; Freiman, P.; Sharath, M. D.; Metzger. W. J.; Smith, J. M.; Richerson, H. B.; Ballas, Z. H.; Halverson, P. C.; Shulan, D. J.; Matsuo, S.; Wilson, R. *J. Allergy Clin. Immunol.* **1985**, 75, 297-303

3. La Spina, R.; Tripisciano, C.; Mecca, T.; Cunsolo, F.; Weber, V.; Mattiasson, B. *J. Biomed. Mater.Res. B: Appl. Biomat.* **2014**, 102, 1207-1216.

#P103 - PLA as a sustainable candidate for CO2 sorption: Effect of polymer morphology

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In a world where reduction of CO_2 emissions appears necessary to manage greenhouse effect and global warming, two main strategies have been considered: Carbon Capture and Storage (CCS) and Carbon Capture and Utilization (CCU). [1] The latter employs the carbon dioxide as a C1-building block in synthetic reactions, such as the Fischer-Tropsch reaction in combination with renewable H_2 used by Audi for their e-fuels. [2] Polylactide (PLA) is a renewable polymer, obtained from corn and commercially available, representing one of the most promising eco-friendly alternatives to petrobased plastics, being applied not only in temporary but also in more durable applications, [3] and literature data suggest it as a valid CCS/CCU candidate. [4]

We report on PLA sorption properties and their possible relationship with polymer morphology. Experimental parameters employed were: gaseous CO_2 (up to 1.5 MPa), low operative temperature (RT), mild preparation/regenerative conditions (333 K), different morphology (powder, flakes and pellets). PLA samples were characterized by helium picnometry to estimate the skeletal density; by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) to obtain structural and morphological data; by an home-made Sievert-type apparatus [5] to obtain adsorption/desorption data. Regeneration effect was investigated.

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References

[1] P. Markewitz, W. Kuckshinrichs, W. Leitner, J. Linssen, P. Zapp, R. Bongartz, A. Schreiber, T. E. Müller, *Energy Environ. Sci.*, **2012**, *5*, 7281-7305.

[2] http://www.audi.com/corporate/en/sustainability/we-live-responsibility/product/synthetic-fuels-Audi-e-fuels.html

[3] (a) C. Vilela, A. F. Sousa, A. C. Fonseca, A. C. Serra, J. F. J. Coelho, C. S. R. Freire, A. J. D. Silvestre, *Polym. Chem.* **2014**, *5*, 3119-3141. (b) V. Nagarajan, A. K. Mohanty, M. Misra, *ACS Sustainable Chem. Eng.* **2016**, *4*, 2899-2916.

[4] Studies in supercritical CO_2:(a) R. Pini, G. Storti, M. Mazzotti, H. Tai, K. M. Shakesheff, S. M. Howdle, *Macromol. Symp.* **2007**, *259*, 197-202; (b) S. P. Nalawade, F. Picchioni, L. P. B. M. Janssen, D. W. Grijpma, J. Feijen, *J. Appl. Polym. Sci.***2008**, *109*, 3376-3381; (c) M. Champeau, J.-M. Thomassin, C. Jérôme, T. Tassaing, *J. Supercrit. Fluids* **2014**, *90*, 44-52. Studies via indirect measurements: (d) T. Komatsuka, A. Kusakabe, K. Nagai, *Desalination* **2008**, *234*, 212-220. High preparation/regenerative energy: (e) N. S. Oliveira, J. Dorgan, J. A. P. Coutinho, A. Ferreira, J. L. Daridon, I. M. Marrucho, *J. Polym. Sci., Part B: Polym. Phys.* **2007**, *45*, 616-625; (f) S. H. Mahmood, M. Keshtkar, C. B. Park, *J. Chem. Thermodyn.* **2014**, *70*, 13-23.

[5] A. Policicchio, E. Maccallini, G. N. Kalantzopoulos, U. Cataldi, S. Abate, G. Desiderio, R. G. Agostino, *Rev. Sci. Instrum.* **2013**,*84*, 103907.

#P104 - Double-Wall Nanotubes and Graphene Nanoplatelets for Hybrid Conductive Adhesives with Enhanced Thermal and Electrical Conductivity

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Improving the electrical and thermal properties of conductive adhesives is essential for the fabrication of compact microelectronic and optoelectronic power devices. Here we report on the addition of a commercially available conductive resin with double-wall carbon nanotubes and graphene nanoplatelets that yields simultaneously improved thermal and electrical conductivity. Using isopropanol as a common solvent for the debundling of nanotubes, exfoliation of graphene, and dispersion of the carbon nanostructures in the epoxy resin, we obtain a nanostructured conducting adhesive with thermal conductivity of ∼ 12 W/mK and resistivity down to 30 μΩ cm at very small loadings (1% w/w for nanotubes and 0.01% w/w for graphene). The low filler content allows one to keep almost unchanged the glass-transition temperature, the viscosity, and the curing parameters. Die shear measurements show that the nanostructured resins fulfill the MIL-STD-883 requirements when bonding gold-metalized SMD components, even after repeated thermal cycling. The same procedure has been validated on a high-conductivity resin characterized by a higher viscosity, on which we have doubled the thermal conductivity and quadrupled the electrical conductivity. Graphene yields better performances with respect to nanotubes in terms of conductivity and filler quantity needed to improve the resin. We have finally applied the nanostructured resins to bond GaN-based highelectron- mobility transistors in power-amplifier circuits. We observe a decrease of the GaN peak and average temperatures of, respectively, ∼ 30 ° C and ∼ 10 ° C, with respect to the pristine resin. The obtained results are important for the fabrication of advanced packaging materials in power electronic and microwave applications and fit the technological roadmap for CNTs, graphene, and hybrid systems.

#P105 - Electron transfer dynamics from carbon dots to copper ions in solution

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Electron transfer dynamics from carbon dots to copper ions in solution.

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Carbon dots are a class of optically-active carbon-based nanomaterials, consisting in sub-10 nm nanoparticles composed by carbon, oxygen, nitrogen and hydrogen only. Their structure is variable, but often consists in a nanocrystalline core having a graphite or carbon nitride structure, decorated by a variety of polar functional groups on the surface. Carbon dots behave as wide bandgap nanomaterials, and are capable of a strong fluorescence which can be tuned in the visible range. The latter, combined with ease of synthesis, water solubility, low cost and lack of toxicity, is very interesting for applications such as bioimaging and optoelectronics, currently motivating an intense research in the field. Moreover, the photoluminescence of carbon dots is extremely sensitive to the local environment, and to interactions with nearby metal ions, very promising in view of nanosensing applications.

In this context, several works have highlighted that carbon dots fluorescence is easily quenched by the proximity of transition metal ions, supposedly due to excited-state charge transfer from the dot to the metal which often occurs in a very short time. Yet, only a few works have addressed the fundamental interaction mechanisms responsible of such a quenching, or provided direct measurements of the time scales of these events, directly detectable by ultrafast spectroscopies only. Here we report a study of the interaction between carbon dots and copper ions in water. The combination of steady-state fluorescence and absorption measurements, time-resolved fluorescence on the nanosecond domain, and femtosecond pump/probe spectroscopy, provides a comprehensive view of the intrinsic dynamics observed upon photo-excitation of the dots, involving a combination of so-called static and dynamic quenching events related to the presence of metal ions. In particular, sub-picosecond time-resolved spectroscopy is able to reveal for the first time the intrinsic time scales of electron transfer from photoexcited carbon dots to nearby copper ions, substantially advancing our current description of these processes.

#P106 - MORPHOLOGICAL AND ELECTRICAL MODIFICATIONS ON ELECTROLESS DEPOSITED GOLD CLUSTERS BY HF TREATMENTS

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Gold nano-particles on silicon substrates are of interest in many scientific areas, from sensors to standard miniaturized electrical devices. Among the different methods adopted to deposit Au nano-clusters on a Si substrate, electroless deposition based on galvanic displacement reactions is an efficient and versatile technique. It consists in a manual dip of samples in the plating bath for few seconds without having to provide external current or potential. The system Gold-Silicon is well known in the literature and generally the morphology of the gold clusters, regardless of the deposition technique, is characterized by both flat regions and by semispherical particles, consistent with a layer by layer plus islands growth mode. Usually particles shall be subjected to post deposition annealing to change their distribution with involved temperatures ranging from 300°C up to 900°C. In our work we demonstrated that a dip in an HF solution for few seconds has the same effect of long time, high temperature thermal processes. If prior deposition it affects the predominant gold growth mode. For 10s of HF pre-treatment we obtained mainly flat regions, few tens nm long. The prevalent 3D growth instead, is achieved after a cleaning procedure of 4min; it results in many spherical particles with a diameter of roughly 15nm and residual square layers few nm in side. The samples were also treated with HF after the deposition and we found out a general thickening of flat regions as revealed by TEM and AFM analyses. The presence of HF probably dissolves the silicon oxide layer formed on top of the thin flat clusters and promotes the partial atomic re-arrangement of the layered gold atoms, driven by a reduction of the surface energy. The XRD investigation pointed out also changes in the crystalline orientation of the flat regions that lose in part their initially hetero-epitaxial relationship with the substrate. Nanoscale electrical characterization was carried out by the conductive biased tip of an atomic force microscope to point out the changes induced in the electrical response.

#P107 - Enhanced light absorption in Ge quantum dot multilayers

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Ge quantum dots (QD) embedded in insulating matrix show the appealing features of a confined system with interesting properties in the light absorption processes. In particular, among quantum confinement effects, there are the increase of the optical bandgap and the enhanced oscillator strength which can be successfully used for increasing the light absorption in PV cells. In this respect, since in Ge QDs the exciton Bohr radius is larger than in Si QDs (24 nm vs. 5 nm), the modulation of the light absorption coefficient can be easier and stronger, with large potential benefits in several applications. In this work, we present an experimental investigation of light absorption in small Ge QDs (2-3 nm in diameter) grown by PECVD in a multilayer configuration (3-6 nm thick film with Ge QDs, separated by 20 nm thick SiO_2 barrier). An unprecedented high light absorption efficiency, 15 times larger than in the bulk, has been observed for these systems. Structural and optical characterizations have been employed to describe the QCE-induced enhancement of optical bandgap (from 0.8 in bulk up to 2.5 eV in multilayer structure) and of oscillator strength (one order of magnitude). Through a detailed electron energy loss spectroscopy (EELS) analysis we characterized the structural and chemical properties of Ge QD. A comparison with Ge QDs in single thick layer is also performed. These results add new insights into the role of QD packaging on confined systems, and open the route for reliable exploitation of QC effects.

#P108 - Single Walled Carbon Nanohorns synthesized by arc discharge and their potential applications

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Graphene-based materials include all nanostructures in which graphene is present rolled or bended in tubular or conical forms owing to large densities of defects, like pentagons, heptagons etc. Single walled Carbon Nanohorns (SWNH) are carbon nanostructures where the graphene is in a convoluted structure with the shape of cone. This nanostructure has been reported by S. IIJima in 1999 for the first time. Ideal SWNHs present a conical tip with angle of about 20° and with five pentagons. They are generally observed in aggregates with diameters of about 100 nm. Two kind of aggregates are often found: "bud-like" and "dahlia –like". In the former case, the nanohorns are nested together in a compacted form, while in the latter case the tips of the nanohorns protrude from the aggregate surface, like in a chestnut. Owing to their properties, SWCNH are interesting materials for many applications. In particular it has been demonstrated that their specific surface could be tuned by opening holes in their walls. Due to this property SWNH have been proposed also like molecular sieving and gas storage. SWCNH can behave as support for catalysts, material for drug delivery, fillers for nanofluids, for application in fuel cells, supercapacitors, batteries and as biocatalysts of bioanode in enzymatic BFCs. SWNH could be produced by processes based on the sublimation of carbon at high temperature. Mainly, laser ablation and arc discharge have been used to produce SWNH but it has also been reported the synthesis by electromagnetic induction heating. It has been proven that this material can be produced without any catalyst support so that a pure material can be easily synthesized. Moreover recent results report about their low toxicity. In this work, we report about the synthesis of SWNH by arc discharge. The process has been optimized by using AC powering, instead of the usual DC fed arc. In this way the quantity of soot rich of SWNHs largely increases. The synthetic process has been further improved by selecting a symmetric configuration of the electrodes and by the use of an external collector. By this procedure, the deposition of a hard crust containing, among other structures, Multi-Walled Carbon Nanotubes (MWNT), generally observed in the arc discharge process, is hindered and the carbon sublimated is mainly recovered as SWCNH, whose properties in different technological applications are reported.

#P109 - Novel superparamagnetic iron-doped hydroxyapatite nanoparticles to direct cellular fate

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INTRODUCTION: Strong coupling between nanotechnology and cell/molecular biology leaded to a breakthrough in medicine in the last decade due to the exiting opportunities in designing and developing a tailored approach in response to different disease. Magnetic nanoparticles (NPs) have attracted the attention of scientific community for biological and medical purposes as promising materials in drug or gene delivery, DNA/biomolecules separation, hypothermal treatment of tumours, contrast agents for imaging, and recently in tissue engineering and theranostic applications. Here novel biomimetic, fully biodegradable and cytocompatible NPs fabricated by doping hydroxyapatite (HA) with Fe ions (FeHA), avoiding the presence of magnetic secondary phases and coating, were biologically tested. A live monitoring of intracellular fate of FeHA NPs and the biodistribution with a pilot study *in vivo* were deeply investigated.

METHODS: FeHA NPs were prepared by a neutralization process using $FeCl_2$ and $FeCl_3$ as a source of Fe2+ and Fe3+ doping ions; HA NPs and two commercial fluidMag NPs (Chemicell) were used as control groups. Mouse pre-osteoblast cells line (OBs), MC3T3-E1, used as a normal osteoblast in vitro models and human Osteosarcoma cell line, MG63, used as a cancer cells in vitro model, were cultured with 100 µg/ml NPs up to 72 hours. The molecular pathways of cellular response (apoptosis/necrosis, ROS production and autophagy) to NPs were investigated. Moreover the mechanism of internalization by Caveolae-mediated endocytosis was studied. In a pilot in vivo experiment the biodistribution of different concentrations of NPs was evaluated.

RESULTS: The *in vitro* results showed that FeHA NPs were rapidly and easily internalized by both cell lines without producing significant cell damages and death. A different behaviour induce by FeHA NPs were observed in cancer cells respect to normal OBs. The OBs uptake of FeHA NPs seems to be mediated by Caveolae-mediated endocytosis, while a different endocytic mechanism is required by MG63 cell line. Moreover, FeHA NPs seem to act as modulator of autophagy pathway. The *in vivo* pilot study showed the absence of systemic toxicity even with the higher concentration.

DISCUSSION & CONCLUSIONS: The data obtained on the cellular uptake of FeHA NPs lay the basis to clarify the intracellular fate of the FeHA NPs and open brilliant prospective for their use as innovative tools for nanomedicine. FeHA NPs could be injected and guided to a desired body site by an external magnetic field, avoiding any toxicity. Moreover, FeHA NPs could be easily functionalized with several biomolecules or drugs to direct cell fate in medical applications.

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#P110 - Large area fabrication of self-standing nanoporous graphene-on-PMMA substrate

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Nanoporous graphene (NPG) materials have been widely exploited not only to open the band gap or increase the specific surface area, but also to improve the optical, catalytic and sensing properties [1,2]. Recent advancements in the synthesis of NPGs and their applications in field effect transistors (FETs), sensors, electrochemical capacitors, nucleic acid analysis and molecular sieving have been reported [3].

Top-down techniques using focused electron beam and lithography are commonly used in fabricating NPGs. However, these techniques cannot be applied to pattern large-area graphene sheets. In order to produce NPGs more efficiently, new techniques that can be extended to large areas are required. So-called large-scale techniques have been reported [4] and they are all based on graphene-on-substrate transfer. The limitation for industrially scalable NPG fabrication comes from the nanoporous mask used to pattern the graphene into NPG, that must be inorganic, to resist O2 plasma etching, and intimately attached to the graphene. To comply with these requirements, different multilayer strategies, sometimes based on lithographic processing have been developed mostly employing SiO2 or Al2O3 nanoporous masks [5,6]. These approaches are still complex, limited to a few square centimeters and require several steps, hindering thus their industrial applications.

Here we report a new fabrication strategy to obtain large area continuous NPGs-on-substrate combining graphene-on-substrate industrial techniques and swift-ion beam irradiation (SHI). Graphene membranes were synthesized on the Cu substrate and afterwards a 600 nm layer of PMMA was spin-coated on the surface to complete the PMMA-Graphene-Cu stack. The PMMA-graphene-Cu trilayer was exposed to a flow of Au heavy ions that penetrate through the entire thickness of both polymer layer and the graphene sheet creating ion-tracks and damages. A consecutive track-etching technique is used with an adequate revealing agent for PMMA, Isopropyl Alcohol (IPA), to selectively dissolve the latent tracks and damages created during SHI irradiation in the insulating material and the graphene sheet. Resulting from SHI irradiation and track-etching, the graphene nanopores are thus perfectly aligned to the PMMA nanopores, providing, after cupper dissolution, a composite that features both well-defined and truly 2-dimensional nanopores in the graphene layer but that can be handled as a normal polymer film [7].

References

[1] H. Bai et al. Adv. Mater. 23 (2011), 1089
[2] X. Huang et al. Small 7 (2011), 1876
[3] W. Yuan, et al. Materials Today 17 (2014), 77
[4] M. Wang et al. Sci. Rep. 3 (2013), 1238
[5] J. Bai et al. Nat. Nanotechnol. 5 (2010), 190
[6] N. S. Safron et al. Adv. Mater. 24 (2012), 1041
[7] M.C. clochard et al. Mat. Lett. 184 (2016), 47

#P111 - Low temperature ethanol-based CVD growth of graphene derivatives as high-performance hole transport materials for organic photovoltaics

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The CVD growth of graphene on metal foils from precursors other than methane may offer several advantages [1,2]. Using Ethanol vapor not only makes the process simpler, safer and more efficient but it also allows the growth of other 2D carbonaceous forms which extend the range of graphene properties.

By lowering the growth temperature, an electrically insulating and optically transparent film was obtained. The single to a few layer carbonaceous film resulted to consist of functionalized graphene, or of a graphene based derivative, probably with hydrogen atoms inserted in the lattice at sp3 sites. The film could then be transferred onto target surfaces using the same protocols of graphene.

Results concerning the transfer of the growth film on glass/indium tin oxide and its use as hole transport layer in organic solar cells based on a PBDTTT-C-T:PCBM blend will be reported. The cells attained a maximum power conversion efficiency of 5%, matching reference cells made with state-of-the-art PEDOT:PSS as the hole transport layer [3]. Our results indicate that functionalized graphene could represent an effective alternative to PEDOT:PSS as hole transport/electron blocking layer in solution-processed organic photovoltaics [4].

Moreover, since the carbon films form directly on the copper surface at the equilibrium growth conditions rather than by the post-growth non-equilibrium processes reported for graphene (such as plasmas which can induce lattice damage), we believe that our findings can lead to the practical synthesis of several novel and stable graphene based derivatives. In a far vision the derivatives can be made to accommodate selected functional groups at specific lattice sites to confer tailored functional properties to arbitrary surfaces.

References

[1] D.C. Elias et al. Science 323 (2009), 610
[2] R. Nair et al. Small 6 (2010), 2877
[3] F. Machui et al. Energy Environ. Sci. 7 (2014), 2802
[4] A. Capasso et al. ACS Appl. Mater. Interfaces 8 (2016), 23844

#P112 - Influence of the bromide content on the properties of CH3NH3PbI(3−x)Brx perovskite films

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$MAPbI_{3-x}Br_x$ ($MA=CH_3NH_3$) perovskites have been studied mainly because adjusting the component I/Br ratio allows the bandgap to be tuned to cover almost the whole visible spectrum, [1,2] so that an intermediate band gap semiconductor can be obtained and used as the high-band-gap material in tandem/spectrally split cells. Besides, Br inclusion results in a significant improvement of the short term stability of nanostructured solar cells for x=0.6 [1].

We report about the properties of $MAPbI_{3-x}Br_x$ films having different compositions x obtained by mixtures of $MAPbI_3$ and $MAPbBr_3$ solutions that allow synthetic processes suitable for solar cell production being fast and reproducible. Tuning the Br content and measuring the bandgap energy by the Tauc analysis of diffuse reflectance measurements allow us to achieve an $E_G(x)$ relation that does not depend on film properties other than composition, contrary to the one previously reported in the literature [1]. Besides, in those films we evaluate the dependence on x of the disorder through the Urbach energy E_0, finding a close relation between E_0 and grain size, which points out that defect states responsible for the sub-bandgap absorption are localized at the grain boundaries in these materials. Photoluminescence (PL) spectra are dominated by a peak whose position (∼1.7 eV) is independent of the composition in the range $0.6<x<3$. The origin of this peak is discussed considering the main hypotheses proposed so far, paying particular attention to photo-induced halide migration [3,4]. Besides, we report preliminary results of an investigation about the influence of electron irradiation on mixed I/Br perovskite films, aiming to assess if studying possible ion migration under electron irradiation is feasible.

Work is in progress to prepare I/Br perovskite films by flash evaporation in order to assess how this promising preparation procedure affects film properties.

References

[1] J.H. Noh, S.H. Im, J.H. Heo, T.N. Mandal, S.I. Seok, Nano Lett. (2013), 13, 1764–1769

[2] P. Fedeli, F. Gazza, D. Calestani, P. Ferro, T. Besagni, A. Zappettini, G. Calestani, E. Marchi, P. Ceroni, R. Mosca, *J. Phys. Chem. C* (2015), 119, 21304–21313

[3] E.T. Hoke,D.J. Slotcavage, E.R. Dohner, A. R. Bowring, H.I. Karunadasa, and M.D. McGehee, *Chem. Sci.* (2015), 6, 613-617

[4] C. G. Bischak, C. L. Hetherington, H. Wu, S. Aloni, D. F. Ogletree, D. T. Limmer, N. S. Ginsberg, `arXiv:` 1606.07366v2

#P113 - Synthesis of CoxOy/graphene oxide and CoxOy/functionalised graphene oxide composites for rechargeable battery applications

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Graphene has attracted considerable attention in energy storage technologies due to its unique physicochemical properties, such as high specific surface area, chemical inertness, great mechanical strength, excellent electrical and thermal conductivity [1]. Conversely, the poor transport properties and low electronic conductivity of transition metal oxides (e.g. Co_3O_4) commonly utilized as anode materials have encouraged the use of conductive additives such as carbon black or graphene. In this scenery, the synthesis of nanocomposites based on metal oxides and graphene may represent the winning strategy for the preparation of highly performing electrode materials. Actually, graphene oxide (GO), easily produced on a large scale by chemical exfoliation method, is currently used inplace of graphene because of its better dispersibility and low-cost.GO exhibits remarkable hydrophilic character and chemical reactivity. Covalent functionalisation allows improving its properties by modifying the typology and the spatial distribution of the oxygenated functional groups that act as anchoring sites for the adsorption of metal oxide NPs [2].

This work deals with preparation ofnanostructured materials consisting of cobalt oxide nanoparticles (NPs) anchored on GO or on functionalized graphene oxide (f-GO) to beused as electrodes in rechargeable batteries. Several complementary characterization techniques were used to systematically analyze all the materials at each step of their preparation.

GO was prepared by following a slightly modified Hummers method [3] and subsequently functionalised viawith 4-carboxyphenyl groupsdiazonium chemistry [2].

The composite materials were obtained by means of two synthetic approaches:

1) in decoration, via a phase-transfer method [2], of GO and f-GO with previously prepared through the benzyl alcohol route Co_xO_y NPs coated with undecanoic acid (UA);

2) solvothermal treatment of GO and f-GO with the addition of Co(II) precursor.

The results of XRD, Raman and XPS analyses proved the successful preparation of GO, as well as the change in the relative proportions of the oxygenated functional groups present on its surface in f-GO. The formation of Co_xO_y NPs in both GO and f-GO based composites was evidenced. A more homogeneous distribution of Co_xO_y NPs over f-GO with respect to pristine GO was obtained.

[1] F. Li, X. Jiang, J.Zhao, S. Zhang, *Nano Energy*16 (2015) 488.

[2] V. Rebuttini, E. Fazio, S. Santangelo, F. Neri, G. Caputo, C. Martin, T. Brousse, F. Favier, N. Pinna, *Chem.– Eur. J.* 21 (2015) 12465.

[3] W.S. Hummers, R.E. Offeman, *J. Am. Chem. Soc.* 80 (1958) 13.

#P114 - Gas sensing properties of 2D - SnS2 nanoflakes

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Recently, layered nanostructures consisting of one, few o multilayers of atomic planes, thanks to their fascinating and technologically useful properties are showing potentialities in catalysis, electronic, optoelectronic devices and high performance electrodes [1]. Moreover, due to the large surface area, these two-dimensional (2D) nanostructures provide large number of reactive sites for gas adsorption. In addition, the fast charge transfer ability, eventually tunable, makes 2-D nanomaterials efficient in chemical sensing application therefore suggesting them among the best suitable candidates for the fabrication of chemoresistive gas sensors [2].

As an alternative to the metal oxides, metal sulfide semiconductors display interesting peculiarities such as facile synthesis, low band gaps, absence of oxygen in the lattice and low activation energy of surface reactions, which may result in improvement of the sensing performance as well as selectivity and stability. Therefore, recently, they are receiving special attention by researchers in this field [3]. Among various metal sulfides, tin disulfide (SnS_2), a n-type semiconductor with a band gap of 2.18–2.44 eV, has been proposed as a promising material for gas sensing [4].

With the aim to combine the peculiarity of the 2D nanostructure with the properties of metal sulfide, we synthesized 2D-SnS_2 flakes via a facile wet chemical route. The effect of different annealing temperatures on their morphological and microstructural characteristics has been evaluated and investigated by a variety of techniques such as XRD, SEM-EDX and Raman. The behavior of the differently annealed 2D-SnS_2 flakes as sensing materials has been tested and an optimization study has been undertaken to develop high performance chemosensors based on these nanomaterials.

[1] A. Gupta, T. Sakthivel, S. Seal, *Prog. Mater. Sci.*, 2015, 73, 44–126.

[2] S. S. Varghese, S. H. Varghese, S. Swaminathan, K. K. Singh, V. Mittal, *Electronics*, 2015, 4, 651-687.

[3] A. Gaiardo, B. Fabbri, V. Guidi, P. Bellutti, A. Giberti, S. Gherardi, L. Vanzetti, C. Malagù, G. Zonta, *Sensors*, 2016, 16, 296.

[4] J. Z. Ou , W. Ge, B. Carey, T. Daeneke, A. Rotbart, W. Shan, Y. Wang, Z. Fu, A. F. Chrimes, W. Wlodarski, S. P. Russo, Yongxiang Li, K. Kalantar-zadeh, *ACS Nano*, 2015, 9,10313-10323.

#P115 - Metal-Organic Frameworks (MOFs)-Graphene Composites for gas storage applications

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Metal-Organic Frameworks (MOFs) emerged during the last twenty years as a new class of functional solid materials characterized by: *i*) highly crystalline 1-, 2- or 3-dimensional coordination networks; *ii*) porous structures with extremely high surface area and with tunable pore size dimensions; *iii*) network topologies that can be easily functionalized with different chemical groups; *iv*) many different technological fields of applications that range from gas storage/separation and catalysis to drug delivery and to many others [1]. One of the next challenges in this research area is the preparation of MOF composites with improved thermal and electrical conductive properties [2]. MOF composites with graphene oxide (GO) and functionalized reduced graphene oxide (rGO) have been recently reported in the literature [3].

The work presented here has the aim to develop new graphene/MOF composites to be used in methane storage technologies. MOFs are characterized by very low thermal conductivity and the preparation of composites with graphene, should give the opportunity to develop more energy efficient adsorbing materials. For the preparation of graphene/MOF composites, among all the MOFs prepared so far, we selected HKUST-1 [4] or $[Cu_3(BTC)_2(H_2O)_3]_n$ (H_3BTC = benzene-1,3,5-tricarboxylic acid), and to facilitate the preparation of the composites, we used a benzoic acid functionalized reduced graphite oxide (BFG) that was prepared according to literature procedures [5]. HKUST-1 was synthetized with different methods in the presence of variable amounts of BFG and the obtained materials were characterized by spectroscopic methods, X-Ray diffraction, SEM, TEM and nitrogen adsorption isotherms. Preliminary results indicate the formation of MOF/BFG composites.

REFERENCES:

1. H.-C Zhou, et al. Chem. Rev., 112 (2012) 673.

2. S. Li, et al. Nanoscale, 7 (2015), 7482.

3. C. Petit, et al. Adv. Mater., 21 (2009) 4753; C. Petit, T. J. Bandosz, Adv. Funct. Mater., 21 (2011) 2108.

4. S. S.-Y. Chui, et al. Science, 283 (1999) 1148.

5. M. Jahan, et al. J. Am. Chem. Soc., 134 (2012) 6707.

#P116 - Efficient Surface Enhanced Raman Substrates for analytical and biological applications.

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Surface Enhanced Raman Spectroscopy (SERS) is one of the leading techniques for molecular analysis with sensitivity up to the single molecule. SERS consists of the enhancement of the Raman scattering intensity by molecules when these are absorbed or in close proximity to nanometer-sized metallic particles. The Raman enhancement is attributed to electromagnetic and chemical enhancement mechanisms although the signal amplification derives mainly from the electromagnetic interaction of radiation with metals (generally gold and silver), which produces a large field enhancement from laser source by exciting localized surface plasmon resonance (LSPR) characteristics of nanoscale metal structures. In the past few decades, the main challenge has been to fabricate SERS-active substrates with highly sensitivity, reproducibility and low concentrations detection capability for trace analysis and biological tags. Representative SERS substrates, are structured noble metal surfaces typically manufactured by: i) Electron beam lithography (EBL) that is an ideal method for the fabrication of engineered uniform SERS substrates with high repeatability; ii) colloidal metal nanoparticle aggregates/assemblies; iii) individual metal nanoparticles. The latter two types of SERS substrates require synthesis of colloidal metal nanoparticles. It has been demonstrated that key structural parameters such as particle sizes and compositions play a critical role in determining SERS efficiency.

In this work we demonstrate highly sensitive and reproducible SERS substrates that can be obtained by different fabrication techniques. The first step was to study the performances of the gold SERS substrates. At this aim, to verify the SERS response, the Raman enhanced signal of a self-assembled molecular monolayer of pMA (p-mercaptoaniline) was measured. pMA is a typical probe molecule for identifying the electronic properties of the SERS substrates since it can be strongly adsorbed on gold producing very unique and strong surface-enhanced Raman signals. Furthermore, in order to probe the devices sensitivity and reproducibility for analytical and biological applications the SERS response of pesticides and human cells were investigated.

#P117 - Ice-templating of geopolymer architectures

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Geopolymers are produced by reacting an aluminosilicate powder (metakaolins, blast furnace slags, fly ashes, pozzolana etc.) with an aqueous alkali hydroxide and/or alkali silicate activating solution. The water based production process of geopolymers allows the tailoring of the intrinsic mesoporosity of the material and the possibility to apply different process techniques, commonly used for the production of ceramics, to induce ultra-macroporosity.

In particular, geopolymers with controlled lamellar macroporosity and total porosity ranging from 60% to 70% were obtained through the ice-templating (water based freeze casting) of partially geopolymerized slurries.

Ice-templating is an environmentally friendly process that implies the use of ice as sacrificial pore template. The unidirectional freezing of the aqueous geopolymer suspension determines the lamellar growth of ice crystals. Then, ice sublimation finally produces porous architectures with unidirectional channel-like (lamellar) pores that are the replicas of the ice crystals.

The study on the production process highlighted as the macrostructure (lamellar pores morphology) was strongly affected by several process parameters, such as: viscosity of the starting slurry, maturation treatment, amount of water targeted for ice-templating, mould geometry.

Lamellar monoliths, boards and tubes were realized by varying these parameters, showing as the process can be adopted for the realization of samples with different size and geometry suitable for novel tailor-made catalyst supports.

#P118 - Transport and Microstructural Properties of Inkjet-printed Conductive Silver Patterns from Saline Precursors

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Inkjet printing is a precise, quick and inexpensive technique with multiple capabilities [1,2] . One application concerns the printing of conducting patterns over different surfaces. Inks are generally prepared by different approaches such as metallic nanoparticles suspensions, that consist of metal organic precursors in appropriate solvents [2-4] and metal organic decomposition, which is synthesized from metallic salt and formed solutions [5-6].

In this work, we report a study on a simple, economical and low-toxic fabrication route of conductive silver (Ag) patterns obtained from aqueous ink solutions of silver nitrate (AgNO3) [7]. AgNO3 patterns were printed on three substrates of technological interest: flexible polyimide (Kapton), Alumina and a machinable glass ceramic (Macor). We printed 12M AgNO3 aqueous inks using a DMP 2831 Dimatix-Fujifilm inkjet apparatus. To increase the adhesive force between the printed patterns and the substrate, an extreme small amount of dishwashing detergent was added as surfactant. Conductive Ag patterns were finally achieved via thermal annealing at about 200 °C under argon-5% hydrogen gas flow. We report a systematic analysis of the printed patterns in terms of morphology and behavior of electrical resistivity as a function of temperature in the 4.2 K to 300 K range. We use magnetotransport characterization as a tool to investigate independently the respective intergrain and intragrain contributions to conductivity. The comparison of the measured resistivity with that of bulk silver allows to extract the degree of porosity in each sample, indicating that Ag/Alumina is the least porous among the samples.

[1] T. H. J. van Osch, J. Perelaer, A. W. M. de Laat, U. S. Schubert, Adv. Mater. 2008; 20: 343–345.

[2] K. Rajan, I. Roppolo, A. Chiappone, S. Bocchini, D. Perrone, A. Chiolerio, Nanotechnology, Science and Applications 2016; 9: 1–13.

[3] H. Meier, U. Löffelmann, D. Mager, P. J. Smith, J. G. Korvink, Phys. Status Solidi A 2009; 206: 1626–1630.

[4] J. Perelaer, B. J. de Gans, U. S. Schubert, Adv. Mater. 2006; 18: 2101–2104.

[5] K. F. Teng, R. W. Vest, IEEE Trans. Comp. Hybrids Manu. Tech. 1988; 11: 291-297.

[6] A. L. Dearden, P. J. Smith, D. Y. Shin, N. Reis, B. Derby, P. O’Brien, Macromol. Rapid Com-mun. 2005; 26: 315–318.

[7] J-T. Wu, S. L-C. Hsu, M-H. Tsai, W-S Hwang Thin Solid Films 2009; 517: 5913–5917.

#P119 - The effect of strain on Ag+ cation substitution in CdSe nanocrystals

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Cation exchange (CE) reactions allow for the selective replacement of the cations of preformed ionic nanocrystals (NC) with new desired guest cations, while retaining their size, shape and anion framework. CE is lacking a full theoretical understanding despite the vast amount of research it has been object of since last decade [1,2]. In a prototypical case, incoming Ag+ cations can rapidly (within 100 ms) substitute Cd2+ cations in a CdSe NC [3]. In a general view, the incoming Ag+ cations diffuse into the NC from a solvent and, after reaching a certain (very low) critical concentration, they enter a Cd2+ vacancy or a substitution with a host cation takes place. At this point the activation energy for an exchange reaction decreases dramatically near the first exchange site [4], and successively with more substitutions, igniting a cooperative reaction [5]. It has been suggested that the cation exchange is driven by the Coulomb forces arising from the change in the charge state of cations through the reaction pathway [3]. Since these forces should impose an atomic readjustment of atomic positions, a local strain can be supposed to appear in the reaction [4]. In this work we study the effect of local and non-local strain on the reaction rate of the Ag+- Cd2+ cation exchange reaction in CdSe NC and sketch possible technological implications as well as systems where it could be critical. [1] Son D. H., Hughes S. M., Yin Y., Alivisatos A. P., Science 2004, 306, 1009-1012 [2] De Trizio L., Manna L., Chem. Rev.(in press) DOI: 10.1021/acs.chemrev.5b00739 [3] Chan E. M., Marcus M. A., Fakra S, ElNaggar M., Mathies R. A., Alivisatos A. P., J. Phys. Chem. A, 2007, 111 (49), pp 12210–12215 [4] Ott F. D., Spiegel L. L., Norris D. J., and Erwin S. C., Phys. Rev. Lett. 113, 156803 [5] White S. L., Smith J. G., Behl M., Jain P. K., Nat. Commun. 4:2933 doi: 10.1038/ncomms3933 (2013).

#P120 - Synthesis and characterization of selenium-substituted hydroxyapatite nanoparticles for applications in tissue engineering

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Hydroxyapatite (HA) is used as a bone graft material in orthopedic implants since it possesses exceptional biocompatibility and bioactivity properties. Nanosized HA is the main component of mineral bone. [1] The possibility to use HA doped with ions and to improve some features, such as osteointegration and bone mechanical properties, has recently attracted much attention [2].

One of the most important microelements is selenium, one of the essential constituents of the human diet[3]. Selenium plays an important role in several metabolic processes as a constituent of selenoproteins, may prevent carcinogenesis and may inhibit the growth of tumor cells[4-6]. For this reason nano-crystalline selenite-substituted HA has been studied for the inhibiting effect on the growth of osteosarcoma cells. [7]

In this work, selenium-substituted hydroxyapatite nanoparticles (nHA_Se) with different Se/P ratios were synthesizedto study the effect of different concentrations of nHA_Sein order to accurately evaluate the amount of selenium that inhibits the growth of different cells type.

nHA_Se were synthetized by a co-precipitation method, using sodium selenite (Na_2SeO_3) as a selenium source.The physical and chemical properties of the nanoparticles have been investigated by SEM, TEM, DLS and XRD. The obtained selenium-substituted nHA products are needle-like nanoparticles with size and crystallinity similar to those of pure HA nanoparticles. It has been observed that when the P/Se ratio increases the crystallinity reduces mimicking the biological HA.

Cytocompatibility studies with both primary and osteoblastoma-derived Saos2 cells showed different cytotoxic effect of nHA_Se depending on the nanoparticles concentrations.

These nHA_Se may be utilized to produce biocomposite material for applications in bone tissue engineering.

References

[1] M.P. Ferraz et al. Appl. Biomater. Biomech. 2(2), (2004) 74

[2] D. Laurencin et al. Biomaterials. 32 (2011)1826.

[3] A. Fernandez-Martinez et al. Rev. Environ. Sci. Biotechnol. 8 (2009) 8.

[4] G.F. Combs et al. Pharmacol. Ther. 79 (1998) 179.

[5] E.N. Drake. Hypotheses 67 (2006) 318.

[6] H. Zeng et al. Nutrients 5 (2013) 97.

[7] Y. Wang et al. Interface Focus, 2 (2012) 378.

#P121 - Deposition of PEDOT:PSS layers for application in homo-junction Si solar cells

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A large number of publications on Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) and its applications as hole transport layer or as buffer layer in organic and hybrid solar cells is present in literature. Only a few papers propose this material as transparent metallic contact in homo-junction devices. However, its good optical properties, adjustable electrical characteristics, low cost deposition methods and interesting tribological properties make it a good candidate for this type of unconventional application. PEDOT:PSS is a mixture of two ionophores (PEDOT and PSS) in aqueous solution not covalently linked to each other. The two polymer chains interact with each other through the ionic electrostatic forces due to interaction between the positive charges on the PEDOT chains and the negative charges of the sulfonate groups of the PSS. The intrinsic conductivity of the polymer is linked to the hole transport on the PEDOT chains and to the inter-chain hopping. The PSS stabilizes the positive charges generated on the PEDOT chains and guarantees the solubility of the chain, normally hydrophobic, in the aqueous environment. Many papers in this field of literature correlate the polymer electrical properties to their morphological characteristics. Previous studies have found the existence of conductive domains of PEDOT arranged within a dielectric matrix of the PSS where the conductivity takes place through the holes inside the PEDOT domains, while the conductivity of the entire polymer layer is due to the hopping between the conductive domains. Here we present results on the morphological, optical and electrical properties of PEDOT:PSS deposited, from commercial solutions, over Si, glass or SiO_2 substrates by spin coating with different deposition and post-deposition conditions. Preliminary experiments on the integration of the polymeric layers in homo-junction Si solar cells will be also presented.

#P122 - From Flax Fibers to porous materials

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Flax-based aerogel (AFs) and cryogels (CFs) was prepared from Flax Fibers (FF) without any pretreatment using 1-ethyl-3-methylimidazolium acetate (EMIMAc) as a solvent via regeneration and environmentally friendly supercritical and freeze-drying methods.After having been regenerated with distilled water, the resulting Flax hydrogels were rendered highly porous materials. The results show that the Flax fibers concentration in the EMIMAc solutions and the supercritical drying process influence the materials Flax properties (morphology, porosity, bulk density, Brunauer-Emmett-Teller surface area (a_{BET}), crystallinity and energy of hydrogen bands).Adirect correlation between the crystallinity of materials and the concentration of Flax fibers in the ionic liquid solutions has been established by Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) characterizations. Mechanisms of nanofibrils reorganization have been suggested so as to explain the variation of the porosity, the bulk density and mainly the crystallinity of the materials during the supercritical process.

Keywords

Aerogel, cryogel, crystallinity, Flax fibers, SEM, ionic liquid, biopolymer.

#P123 - CIGS-based Bifacial Solar Cells

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Although the photovoltaic (PV) market is still dominated by the Si-based solar cells, thin film technology is considered to be a viable solution, in particular for unconventional applications such as flexible, transparent or bifacial solar cells, which represent an great opportunity in the field of the integrated PV (BIPV). Cu(In,Ga)Se_2 (CIGS) represents a good compromise between conversion efficiency, stability and possibility to be grown on different substrates therefore is considered to be the most promising material for thin-film PV. We report on the fabrication of CIGS-based bifacial thin film solar cells by means of the Pulsed Electron Deposition (PED) technique, using transparent substrates (glass) and back contacts based on In_2O_3:Sn (ITO), SnO_2:F (FTO) or ZnO:Al (AZO). In the last years, PED has been developed at IMEM-CNR for high-quality CIGS deposition; recently, small solar cells with PV efficiency exceeding 17% have been obtained by controlling the absorber doping and by optimizing the cell architecture and the device processing. Interestingly, high-quality CIGS absorber layers can be deposited at much lower temperature (250-270°C) compared to alternative techniques, enabling the use of a large number of substrates, including polymeric thermo-labile ones. This makes the PED a very effective method to grow “complex” materials and to explore unconventional devices, such as flexible or transparent solar cells. The studied cells have the typical bifacial configuration: substrate (glass)/back contact (ITO, FTO and AZO by sputtering)/absorber (CIGS, by PED)/buffer layer (CdS, by CBD)/front contact (ZnO-AZO, by sputtering). We will report on the performance of PV cells with a total exceeding 15% of efficiency and significantly higher than recently published results under different types of illumination (direct, diffused, back reflected) for thick and thin CIGS layers.

#P124 - ZnO Thin Films Deposited by RF-Magnetron Sputtering for thermoelectric applications

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ZnO and Al-doped ZnO thin films were deposited on silicon and silica substrates by using a RF magnetron sputtering system under Ar, Ar+N_2 and Ar+O_2 atmospheres. ZnO thin films were deposited by sputtering a sintered ZnO target, while Al-doped ZnO films were deposited by co-sputtering a ZnO and an Al target. In the latter case, the Al percentage was varied changing the power ratio between the two targets from 0.1 to 0.7. Optical emissions from the plasma during the deposition, measured using a high resolution spectrometer in the wavelength range of 360-800 nm, showed that the constituents of each target were successfully sputtered off. X-ray diffraction (XRD) analysis confirmed the formation of ZnO and Al-doped ZnO thin films of hexagonal crystal structure. X-ray photoelectron spectroscopy (XPS) technique was carried on all doped thin films with the aim of micro-analytical and compositional characterization. The Al amount was evaluated inside the films, using quantitative depth profiling, while the chemical states revealed on the Zn 2p, O 1s and Al 2p acquired spectra allowed to define the different chemical bonds. Finally, functional thermoelectric characterizations were performed in order to investigate possible applications of these thin films as n-component in thermoelectric generator (TEG).

#P125 - Highly efficient ultra-thin and ultra-light-weight amorphous Si solar cells separated from the growth substrate

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Amorphous silicon (a-Si:H) photovoltaic technology is the oldest among all the thin film solar cells (TFSC) technologies and has additional advantages like being based on a non-toxic and abundant raw material, and compatibility with high yield and low-cost manufacturing. However, a huge obstacle to even larger applicability of Si TFSCs is that they are best fabricated on selected few substrates that are compatible with the deposition requirements of temperatures up to 350C and surface smoothness. There is a large market potential for substrate-independent TFSCs, especially with the advent of pervasive computing and related devices and sensors. However, as long as solar cell fabrication is not substrate-independent or the cells cannot function on a wider range of surfaces, we will not see ubiquitous applications of solar cells like we have seen with thin film semiconductor based displays which have penetrated every aspect of human life.

In this work, we have successfully demonstrated a transfer method where highly efficient ultra-thin amorphous silicon solar cells were separated from their growth substrate and latter attached to a plastic kitchen foil (9 micron thick), without affecting their performance. The thickness of the absorber layer in the p-i-n type a-Si:H solar cells was 100 nm and the power conversion efficiency was 8%. It is evident from our results that solar cells capable of functioning on different surfaces can have a great market potential, especially with the advent of pervasive computing and related devices and sensors. Our method is not limited to silicon based solar cells but can also be applied to the other types of thin-film solar cells in general.

#P126 - Utilizing photon trapping from quasi-periodic nano-wrinkle textured surfaces in ultra-thin amorphous silicon solar cells

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Stability and efficiency are two important issues in the thin film silicon solar cell technology. Reducing the thickness of the thin-film silicon solar cell increases its stability and cost-effectiveness, but it decreases its conversion efficiency. This loss of efficiency can be compensated by applying light management techniques that decrease the reflective photon losses and increase the path of the photon within the cell, thus increasing carrier generation. In this work we present an inexpensive, scalable and non-lithographic approach for the fabrication of sub-wavelength scale wrinkled surfaces, using shape memory thermoplastics. The obtained nano-wrinkle features are tunable to various nanoscale sizes and quasi-periodic in nature. The features were later imprinted on glass substrates using UV curable lacquer followed by transparent conducting oxides coating atop the features to produce the front-electrode for solar cells.

The ultra-thin p-i-n type amorphous silicon solar cells fabricated on these nano-wrinkle textured surfaces consist of only 100 nm thick absorber layer. The power conversion efficiencies of such ultra-thin solar cells are above 8%. Our experimental results show significant enhancements in the photocurrent, up to 32%, and in the efficiency, up to 25%, for the solar cells fabricated on these nano-wrinkle front-electrodes compared with the ones deposited on flat surface. This approach not only addresses the current challenges of micro/nanofabrication, but also introduces a revolutionizing shift from a sophisticated manufacturing to a desktop approach.

#P127 - Laser-based fabrication of lumpy Pd and Pt nanoparticles on transparent conductive oxide substrates

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In this work we report on the formation of lumpy Pd and Pt nanoparticles on fluorine-doped tin oxide/glass (FTO/glass) substrate by a laser-based approach. In general, complex-surface morphology metal nanoparticles can be used in several technological applications exploiting the peculiarities of their physical properties as modulated by nanoscale morphology. For example, plasmonic metal nanoparticles presenting a lumpy morphology (i. e. larger particles coated on the surface by smaller particles) can be used in plasmonic solar cell devices providing broadband scattering enhancement over the smooth nanoparticles leading, so, to the increase of the device efficiency. However, the use of plasmonic lumpy nanoparticles remains largely unexplored due to the lack of simply, versatile, low-cost and high-throughput methods for the controllable production of such nanostructures.

Starting from these considerations, we report on the observation that nanoscale-thick Pd and Pt films (17.6 and 27.9 nm, 12.1 and 19.5 nm, respectively) deposited on FTO/glass surface irradiated by nanosecond pulsed laser at fluences E in the 0.5-1.5 J/cm^2 range, produce Pd and Pt lumpy nanoparticles on the FTO surface. In addition, using scanning electron microscopy analyses, we report on the observation that starting from each metal film of fixed thickness h, the fraction F of lumpy nanoparticles increases with the laser fluence E and saturates at the higher fluences. For each fixed fluence, F was found higher starting from the Pt films (at each starting film thickness h) with respect to the Pd films. For each fixed metal and fluence, F was found to be higher decreasing the starting thickness of the deposited film. To explain the formation of the lumpy Pd and Pt nanoparticles and the behavior of F as a function of E and h both for Pd and Pt, the thermodynamic behavior of the Pd and Pt films and nanoparticles due to the interaction with the nanosecond laser is discussed. In particular, the photothermal vaporization and Coulomb explosion processes of the Pd and Pt nanoparticles are invoked as possible mechanisms for the lumpy nanoparticles formation.

#P128 - Experimental study on the coalescence process of SiO2 supported colloidal Au nanoparticles

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The controlled growth of nanoparticles (NPs) on surfaces is a powerful tool to create nanostructured materials with desired properties for several technological applications. In particular, metal NPs have attracted much interest due to their potential application in many areas (plasmonics, photovoltaics, sensing, nanoelectronics, etc.). The metal NPs shape and size are crucial parameters in determine their physical properties. For example, in metal NPs the wavelength of localized surface plasmon resonances can be controllably tuned through the visible to near infrared region by controlling their shape and size. In single electron transistor devices, as further example, NPs shape and size determines the charging energy. So, the key step towards reliable solid-state technological applications of metal NPs-based systems is the development of simple, versatile, low-cost, high-throughput methods for the fabrication and manipulation of metal NPs directly on surface. Key requirement to this end is the quantitative understanding of the physical mechanisms governing the NPs growth dynamics. On the basis of these considerations, with the present work, we report on an experimental investigation of the growth dynamics, induced by thermal processes, of colloidal Au NPs on SiO_2. We deposited size-mono-dispersed Au colloidal NPs on SiO_2 surface and performed annealing processes in the 573-1173 K temperature (T) range and 900-3600 s time (t) range. The evolution of the mean NPs size was quantified as a function of T and t by scanning electron microscopy analyses. In particular, we studied the experimental temporal evolution of the NPs size using the relations prescribed by the particles coalescence theoretical framework. Fits of the experimental data by such relations allowed us to determine a size-dependent activation energy for the coalescence process of the SiO_2-supported Au NPs (from about 0.21 eV to about 0.36 eV when the starting NPs diameter increases from 30 nm to 100 nm). The size-dependence of the activation energy is discussed on the basis of the size-dependent cohesive energy of the atoms in the Au NPs, supporting, so, the essential role of a high-mobility (liquid-like behavior) of the NP surface atoms for the coalescence process.

#P129 - Ultra-fast conformational dynamics in liquid of an oligothiophene compound

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Thiophene oligomers are stable compounds with high fluorescence quantum yields and a large degree of electron delocalization along the chain. For these reasons, such systems have been widely studied because of their potential applications for organic solar cells (OSCs) [1,2]. The starting point of our study has been the 1,3-di(2-thienyl)benzo[c]thiophene (DTBT) compound. In order to characterize the photophysics, relevant for the possible applications, the dynamic properties are of utmost importance. For these reasons, both time-resolved photoexcitation and optical spectroscopy of this oligothiophene have been performed trying to describe the possible conformational dynamics related to this small and unsubstituted oligothiophene compound. Through fs pump-probe experiments performed in solution it has been possible to investigate the effect of the molecular conformation on the evolution of the excited state following its intra-band relaxation. This fast process has been monitored by transient stimulated emission (SE) experiments. Fitting the rise- and the decay-time of this SE signal it has been possible to study the vibrational relaxation associated to the excited state geometry and dynamics of the slower torsional rearrangement of the molecular conformation, respectively. The former process, generally, gives a geometrical rearrangement in hundreds of fs; while, the latter gives molecular geometry planarization of the excited state which occurs generally in the ps time-scale [3]. With this study we demonstrate that these rearrangements can be justified through experimental evidences and, moreover, by theoretical TD-DFT calculations that are already in progress. References: [1] F. Zhang, D. Wu, Y. Xua and X. Feng J. Mater. Chem., 2011, 21, 17590. [2] Y.-J. Cheng, S.-H. Yang and C.-S. Hsu Chem. Rev., 2009, 109 (11), 5868. [3] T. Benincori, G. Bongiovanni, C. Botta, G. Cerullo, G. Lanzani, A. Mura, L. Rossi, F. Sannicolò, and R. Tubino, Phys. Rev. B, 1998, 58, 9082.

#P130 - Fs laser ablation of noble metal targets: generated nanomaterials' characterization

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Fs laser ablation of noble metal targets offers wide advantages especially for obtaining plasmonic effects due to the noble metal nanoparticles' properties deposited by this approach. N. Tsakiris et al. [1] reporting that about 90% of the material ablated by 800 nm, 50 fs Ti:Sa laser is characterized by a large fraction of nanoparticles having diameter smaller than 20nm and median of 5nm, it can be expected that varying the experimental parameters used the deposited nanoparticles features can be tuned. We address our attention in evaluating how the plasmonic properties of Cu, Ag and Au deposited nanoparticles can be affected by changing laser frequency rate, deposition time, target-substrate distance and, overall, angular distribution of the deposited nanoparticles. In this work the role played by the nanoparticles' angular distribution, coalescence and growth is highlighted so that their optical properties can be exploited which are directly related to the feature peculiarities of the ultrashort laser ablation process itself. UV-vis transmission data together with SEM and TEM observations are presented in order to estimate on one side the size distribution of the generated nanoparticles and on the others side the different plasmonic properties. The aim of the work is to tune the deposited NPs' features by choosing the operative condition with respect to the plasma plume expansion, caused by the ultra-short ablation process, and, consequently, correlating the collected NPs with the occurring agglomeration processes. The agglomeration of the produced NPs which occurs during the collection on a substrate can be useful employed for improving and enlarging plasmonic resonance which can be beneficial for either applications such as biosensors [2] or optoelectronics systems.

[1] N. Tsakiris, K. K. Anoop, G. Ausanio, M. Gill-Comeau, R. Bruzzese, S. Amoruso, L.J. Lewis, Ultrashort laser ablation of bulk copper targets: Dynamics and size distribution of the generated nanoparticles, J. Appl. Phys. 115 (2014) 243301.
[2] P.D. Howes, R. Chandrawati, M.M. Stevens, Colloidal nanoparticles as advanced biological sensors, Science 346 (6205) (2014) 1247390.

#P131 - Microstructural changes induced by working life cycles on 3D additive manufactured components, role of the laser parameters

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The ability of processing through laser beams different kinds of metallic powders for direct production of 3D components with complex geometries has been gaining an impressive and growing attention for specific industrial applications. The process which can be distinguished as Selective Laser Sintering or Selective Laser Melting is even considered, more generally, as Additive Manufacturing where layer by layer material is built by the interaction between a laser beam and a powder bed. The rapid heating of the powder due to the laser beam energy transfer process followed by a rapid cooling rate induces within the manufactured material a cellular structure with fine sub-grains, which are in the range of few hundred of micrometers. These metastable structures, which are smaller than the grain size in conventionally manufactured 316L stainless steel components, can undertake towards a recrystallization process due to either heat or mechanical treatments. For instance when sub-grain boundaries of the cells are enriched with Mo and higher concentration of dislocation, dynamical processes occur generating local residual stresses. In these circumstances the segregation of Mo in cell boundaries is out of thermodynamic equilibrium conditions so that microstructures and phases are metastable. In the range of 1100°-1400°C heat treatments a complete dissolution of Mo in the Fe matrix with a gradual disappearance of submicrons cell is observed feeding the growth of larger austenitic sub-grains formation. It follows a higher degree of Mo dissolution in the material matrix and a decrease of dislocation's concentration. In the work here presented we point out the occurrence of a similar behaviour where a microstructural evolution is caused after experiencing to fatigue of 80000 cycles some door joints stainless steel 316L produced by Additive Manufacturing. A decrease of dislocation's number, an increase of twinning due to the growth of grains and to the release of local stresses has been observed for which an important role could be played by the presence of dislocations in cell boundaries as well as oxides nano-inclusion formed in-situ during the additive manufacturing process. From these outcomes it is going to be presented how the 3D components produced by additive manufacturing could change and improve their features for potential industrial applications during life cycles and enhance such a behaviour by taking carefully into account the laser parameters and its scanning speed.

#P132 - Silicon Miniaturized micropillars for Nucleic Acid Extraction

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New microfluidic biofilter based on silicon micropillars have been tested in their aptitude to extract pathogen DNA. The device is composed by a silicon microchannel containing micropillars. The extracted DNA solutions were analysed by RT-qPCR method. The results here reported indicate that pillars geometrical dimensions influence the DNA binding and elution efficiency, moreover these increase proportionally with the surface/volume ratio. Finally the device exhibiting the best extraction efficiency was tested in a miniaturized silicon real time PCR amplification device as preliminary step towards the development of genetic Point-of Care device.

#P133 - Magneto sensitive composite foams

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A new class of composite polymeric foams that are lightweight and multifunctional, with magneto-mechanical properties and macroscopic behavior that can be controlled by a suitable applied magnetic field (MF) has been developed. These Magneto Active Foams (MAFs) are made by embedding magnetic particles, micrometric or nanometric in size, spread into the polymeric matrix during the foaming process. In presence of a suitable MF, particles align themselves along magnetic field lines leading to an anisotropic structural reinforcement. For example, a fibrous aggregation of particles along the force lines of a uniform MF can easily be obtained. The consequent structural behavior is anisotropic, reinforced along the alignment direction. Moreover, the constitutive relationships show a magneto-mechanical coupling: once produced, MAFs can be controlled through an adequate MF. This further smart functionality makes the porous material a sort of "active" one where the mechanical variables can be contactlessly controlled by the MF. This feature may be used for actuation purposes. MAFs exhibit other interesting features: - they can be lightweight, - they can be made out of polymeric matrices with low environmental impact, - they can be developed with a gradient of magneto-mechanical properties. MAFs development started since 2008, when some preliminary works have been published [1–3] on lightweight porous structures with embedded reinforcing MAFs. Recently this topic is gaining great interest from some international research groups confirming the potential of polymeric magneto-sensitive foams. Sorrentino et al. have produced reinforced foams based on a polyurethane (PU) matrix by aligning magnetic particles during the foaming process under the application of a low intensity MF [1]. These foams not only showed relevant increments of both Young's modulus and compressive strength (up to 300% with respect to reinforced samples with unaligned particle) but also a potential "active" behaviour due to mechanical relaxations induced by the application of a MF [3,4]. Brief bibliography [1] Sorrentino L, Aurilia M, Forte G and Iannace S 2008 Adv. Sci. Technol. 54 123–6 [2] Sorrentino L, Aurilia M, Forte G and Iannace S 2011 J. Appl. Polym. Sci. 119 1239–47 [3] Davino D, Mei P, Sorrentino L and Visone C 2012 IEEE Trans. Magn. 48 3043–6 [4] D'Auria M, Davino D, Pantani R and Sorrentino L 2016 Smart Mater. Struct. 25 55014

#P134 - Non-Lithographic Approach to SiO2 Mask Patterning for Selective-Area MOVPE Growth of GaAs Nanowires based Photovoltaics

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The highest efficiencies (up to 15.3%) demonstrated for third generation photovoltaics are achieved by III-V based nanowire solar cells [1]. Three main methods are well known for the growth of III-V nanowires (NWs): metal catalyst-assisted growth by Vapour Liquid Solid (VLS) mechanism [2], self-catalyzed nanowire growth [3] and selective-area metalorganic vapor phase epitaxy (SA-MOVPE) [4]. The latter one has been shown to be promising for the fabrication of photovoltaic devices due to higher material purity and optical absorption with respect to Au-catalyst based ones. The most commonly-used method for III-V NW self-assembly is based on the fabrication of thin SiO_2 masks nano-patterned by electron beam lithography (EBL), which is time consuming and limits the patterned areas to a few hundred squared-microns. We developed a novel approach to SA-MOVPE growth of GaAs nanowires on (111)Si employing self-patterned SiO_2 masks obtained by liquid phase deposition (LPD). The method requires the initial nucleation of (111)B-oriented GaAs nanoislands which are randomly deposited by MOVPE on (111)Si. Subsequently LPD is used to deposit a thin (few tens of nm) SiO_2 film directly on as-grown samples. Optimization of LPD process conditions allows to reach a high degree of selectivity for SiO_2 deposition onto Si and GaAs, thus achieving a compact SiO_2 film onto the bare Si surface and almost no growth on the GaAs nanoislands. The structure and morphology of as-fabricated samples were analyzed by field emission scanning electron microscopy (FE-SEM), Atomic force microscopy (AFM), X-ray diffraction(XRD) and X-ray photoelectron spectroscopy(XPS). (111)-aligned GaAs NWs were grown by SA-MOVPE on as-prepared samples, obtaining dense (10^7 cm^{-2}) NWs arrays over wafer areas of several squared centimetres.

[1] I. Aberg, G. Vescovi, D. Asoli, U. Naseem, James P. Gilboy, C. Sundvall, A. Dahlgren, K. Erik Svensson, N. Anttu, Mikael T. Bjork, L. Samuelson, IEEE Journal of Photovoltaics, vol.6, no.1 (2016)

[2] P. Prete, F. Marzo, P. Paiano, N. Lovergine, G. Salviati, L. Lazzarini, T. Sekiguchi, J. Crystal Growth 310, 5114 (2008)

[3]S. Plissard , KA Dick, G. Larrieu , S. Godey, A. Addad, X. Wallart, P. Caroff, Nanotechnology 21, 385602 (2010)

[4]K. Tomioka, J. Motohisa, S. Hara, K. Hiruma, T. Fukui, IEEE Journal of selected topics in quantum electronics, vol.17, no.4 (2011)

#P135 - Optoelectrical detection of quantum confinement in Si quantum dots in SiC matrix

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Quantum confinement in Si quantum dots (Si QD) in dielectric matrices such as silicon dioxide is a consolidated result since several years. However, when they are embedded within an SiC matrix, the demonstration is hindered by severe limitations. This is undesirable, because the SiC dielectric matrix guarantees a much better electical performance with respect to silicon dioxide, which makes it the preferred choice in electrooptical applications. The difficulties in directly detecting the occurrence of quantum confinement are essentially residual absorption of the disordered SiC matrix, which prevents from detecting the anticipated blue shift of the absorption edge, and the quenching of photoluminescence observed in the Si QD/SiC material, which prevents to use the technique to monitor the band gap enlargement.

However, carriers photogenerated within the Si QD subdomain, if inserted on a proper photovoltaic structure, retain information on the origin of the absorbed photon. Based on such consideration, in this contribution we show how the combined detection of optical absorption of the SiQD/SiC material, and the optoelectrical behaviour of p-i-n devices based on the same material, gives evidence of quantum confinement in Si QD in SiC matrix. Using this procedure, an energy gap of 1.7 eV is identified for 4 nm diameter Si QD. Details on the absorption of the different material subdomains are also given, and the implications in the determination of the absorption properties of a material which by definition cannot be physically isolated, are discussed.

#P136 - Lessons learned in organic dyes synthesis

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The communication will focus on the results obtained in the course of the research activities of the PON2 MAAT project, concerning fully organic dye synthesis. The research has been aimed at sharpening design rules and synthetic procedures of a series of DSSC organic dyes.

Fully organic dyes continue to stir considerable interest due to their great potential in terms of design flexibility and amenability to optimization.[1] Having individuated a base structure showing potential, two organic dyes have been conceived with a D–A–π–A structure with a triarylamine group as the donor, a dithienyl-benzothiadiazole as the chromophore to which, in a first set of experiments, an extension was placed, constituted by an ethynylene-thiophene (**G1**) or ethynylene-benzene (**G2**) π-spacer. The anchoring ability was provided by the classic cyano-acrylic acid group. Obtained DSSC efficiencies pointed to **G2** as the better performing dye (η=7.9 %) [2]

In a subsequent development stage, the structure-property relationships connected to the presence of the ethynylene bond were evaluated modifying G2, by depriving it of the ethynylene group. The synthesis of this π-extended D-A-π-A dye (**G3**) has been accomplished by applying the green chemistry pillars, aiming at substituting traditional organometallic chemistry with innovative synthetic strategies, cutting down waste burden and costs. A sensible DSSC efficiency improvement (η=8.64%) was also recorded along with a remarkably higher stability respect to N719 in 10-fold larger area devices. [3]

Based on the structural motif of G3, organic sensitizers **G4** and **G5** have been designed to optimize the interactions between the dye/TiO_2 layer and the redox electrolyte. The molecular tailoring of the **G3** scaffold was performed by positioning an alkyl chain onto the p-spacer (**G4**) and increasing the bulkiness of the electron-donor (**G5**). A deep theoretical investigation revealed that the main electronic transitions of **G3**-**G5** own only a weak charge-transfer character. Notwithstanding this unusual photo-excitation dynamic, impressive photovoltaic performances have been obtained, reaching PCE up to 9.8% under 1.0 sun for **G5**, remarkably higher than the N719 standard.[4] This result, crowning the experimental development activities of the aforementioned PON2 MAAT project, represents one of the highest performances exhibited by fully organic sensitizers employing the I^-/I_3^- redox shuttle.

[1] Wu, Y.; Zhu, W. Chem. Soc. Rev.2013, 42, 2039

[2] Grisorio, R.; De Marco, L.; Agosta, R.; Iacobellis, R.; Giannuzzi, R.; Manca, M.; Mastrorilli, P.; Gigli, G.; Suranna, G. P. ChemSusChem 2014, 7, 2659.

[3] Grisorio, R.; De Marco, L.; Baldisserri, C.; Martina, F.; Serantoni, M.; Gigli, G.; Suranna, G. P. ACS Sustainable Chem. Eng. 2015, 3, 770.

[4] Grisorio, R.; De Marco, L.; Giannuzzi, R.; Gigli, G.; Suranna G. P. Dyes Pigments 2016, 131, 282.

#P137 - Sharpening the Suzuki cross-coupling reaction conditions for well-defined organic electronics polymers

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Conjugated polymers constitute the main class of organic semiconductors for organic electronics applications. Traditional organometallic chemistry methods for their obtainment typically involve a step-growth mechanism that does not allow a control over molecular weights and dispersity. Conversely, a considerably higher control over MWs and PDIs can be achieved by forcing a polymerisation pathway towards a chain-growth mechanism.[1]

Pd-catalysed Suzuki cross-coupling polymerisation has emerged as one of the most appropriate protocol to exalt the prerogatives of a chain-growth pathway, due to the straightforward attainability of extremely pure, stable and non-toxic mono-functionalised boron-based AB-type monomers. To date, in fact, all chain-growth Suzuki polycondensations have necessarily required the preparation or the in situ generation of chain-initiators – of general structure $ArPd(t\text{-}Bu_3P)X$ – to suitably direct the polymerisation towards low PDI products. However, the preparation of chain-initiators is time-consuming and the tri-coordinated Pd initiators in particular are relatively unstable thus negatively affecting the polymer PDIs. Achieving full control of a chain-growth polymerisation bypassing the additional step of the chain-initiator preparation remains a challenge.

The idea that motivated our research is that the use of a pre-formed chain-initiator could be avoided if a suitable $LnPdX_2$ complex can be used to promote the homo-coupling of the aryl-boronic esters and if, at the same time, the reductive elimination is followed by the preferential oxidative addition on the halogen atom belonging to the growing chain. We chose palladium(II) acetate as precursor and the bulky and electron-rich $t\text{-}Bu_3P$ as ligand. The communication will deal with the main result obtained in the course of this investigation. In particular the control over the molecular weights and polydispersities of the Suzuki polymerisation products of a 9,9-dioctylfluorene AB-type monomer could successfully be achieved without the use of a formal chain-initiator.[2] Extremely fast (1 min) polymerisations and low polydispersities (Mw/Mn=1.16) could be reached using the chosen $Pd(AcO)_2/t\text{-}Bu_3P/K_3PO_4$ catalytic system upon the fine-tuning of the initiation step of the chain-growth pathway. Moreover, molecular weights nicely dependent on the monomer/catalyst molar ratio were observed, linearly ranging from 14 to 27 KDa.

The results of this study clear the path for the investigation of a new generation of Pd(II) sources, reaction conditions and substrates for the obtainment of a wide range of well-defined pi-conjugated polymers for task specific organic electronic devices.

[1] Grisorio, R; Suranna, G. P. Polym. Chem., 2015, 6, 7781 and references therein

[2] Grisorio, R.; Mastrorilli, P.; Suranna, G. P. Polym. Chem. 2014, 5, 4304.

#P138 - Natural treatments on hemp fibres: physical characterization and accelerating weathering tests

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A significant contribution to the climate change is given by buildings because their construction is responsible for a huge consumption of both natural resources and energy as well as for the emissions to air, water and soil, across the planet. As a consequence, in the last years, many researchers have carried out studies aimed at searching new materials and technologies in the building sector in order to find ways for the enhancement of the global sustainability. Such studies have demonstrated that the use of natural materials represents one of the pathways to achieve energy efficiency and environmental sustainability in buildings.

In the laboratories of ENEA Research Centre of Brindisi (Italy), it was investigated the ageing behavior of insulating mats based on hemp fibres in presence of moisture and microbial attacks and the impact of several pre-treatments onto the degradation of the fibres as well as on their physical properties. In particular, locally sourced hemp fibres treated with two natural substances were prepared and characterized in the framework of EFFEDIL Project.

Anti-fungal, anti-mold and water-repellent treatments in aqueous solutions and with natural substances were performed on hemp fibres. Hemp mats were artificially contaminated with two different fungal microorganisms, in order to investigate their sensitivity and resistance to contamination by fungi. These organisms were chosen among those associated with the presence of mould indoors, a common cause of the deterioration of insulating materials. To evaluate the effects on thermal, biological, chemical and mechanical characteristics, the mats of hemp fibres were then subjected to accelerated weathering cycles in a climatic chamber. After the aging tests, nofungal contamination was observed and we can conclude that the weather conditions simulated in this study did not cause significant macroscopic changes in hemp mats: the mass, color and appearance of the material remained unvaried.

The structural properties of hemp fibres were investigated by using the X-Ray Diffraction (XRD) technique. Three types of samples were analyzed: carded hemp fibres and carded hemp fibres treated with acid salicylic and the natural monoterpenes phenol, in order to assess the influence of the treatments on the fibres crystallinity. FTIR spectroscopy has been used as a simple technique for obtaining rapid information on the structure of the fibres constituents and chemical changes taking place in hemp fibres due to the two employed treatments. The morphology and microstructure of the hemp fibres surface were observed by using a Field Emission Scanning Electron Microscope (FE SEM).

#P139 - Ion irradiation of AZO thin films for flexible electronics

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Transparent conductive oxides (TCO) are strategic materials due to their combination of high optical transparency and good electrical conductivity, which make them essential components for a large variety of key devices such as solar cells, displays, E-paper, touch-screens. The expanding use of tin-doped indium oxide (In_2O_3:Sn or ITO) for the production of transparent electrodes is endangered by the scarcity and increasing price of In. Nowadays, aluminum-doped zinc oxide (Al:ZnO or AZO) is considered a true alternative to ITO due to the lower cost of the source materials, non-toxicity and good electro-optical properties.AZO resistivity is typically improved by thermal annealing, not applicable to plastic substrates, for thin flexible and bendable devices. Here we present a non-thermal route to improve the electrical and structural properties without deteriorating the optical ones, by using O^+ or Ar^+ ion beams (30 - 350 keV, $3x10^{15}$ - $3x10^{16}$ ions/cm^2) on AZO deposited on glass and polyethylene naphthalate (PEN). Ion beams and thermal processes produced similar modifications of the lattice strain, crystalline domain size and optical band-gap. The electrical resistivity also strongly depends on the post growth treatments and a reduction of the electrical resistivity of more than 2 orders of magnitude was obtained by using high temperature thermal annealing or appropriate ion beam irradiations at room temperature. The latter process allowed us to produce high quality AZO thin films deposited on plastic substrates (polyethylene naphthalate, PEN), without any thermal process, with electro-optical performance comparable to those of AZO films deposited on glass and annealed at 400 °C. By changing the ion species, energy and dose of irradiation, we showed that the improvement of the electrical properties does not simply depend on the strain or polycrystalline domain size, as often stated in the literature. The O^+ beam at this low energy is stopped inside the AZO film, likely inducing the compensation of O vacancies, which are electron donors. The implantation of Ar^+, atlow energy and room temperature,has been applied tosamples deposited on thin flexible PEN. Our results set Ar^+ ion beam processing as a good way to get highly conductive AZO thin films in the case of plastic or organic substrates, which cannot be processed at high temperatures.

#P140 - GOLD NANOPARTICLES PRODUCED BY LASER FOR MEDICAL APPLICATIONS

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Gold nanoparticles produced using a high intensity Nd:Yag pulsed laser ablating a gold target wer prepared in biocompatible liquids at different concentrations and size distribution.

The produced solution was characterized using optical absorption from the near UV, to visible, up ti the near IR wavelength region. At concentration range between 1 mg/ml up to 2.5 mg/ml the solution can be employed to be injected in live biological evironments, as mice and rats, without collateral effects.

Low energy (45 KeV) X-rays 2D imaging was employed to monitor the gold nanoparticles vehiculation as a contrast medium, inside the organs as a fuction oh the tme. Imaging demostrate that some organs absorb mre than others. Measyrements of gold nanoparticles up-take and decay in some organs were performed, as will be presented.

The introduction of gold in biological tissues, and microscopically in cells, permits to enhance the effective atomic number of sick tissues.

The increase of the local electron density enhance the absorption coefficient values to X-ray and the electron and nuclear stopping powers of particles. Thus, the released dose of ionizing radiations to the tissue can be significantly increased.

The application of the gold nanoparticles to the imaging contrast improvement with respect to traditional solutions and the possibility to prepare tumoral tissue for the radio-therapeutic treatments will be presented and discussed.

#P141 - Nanostructured materials as template for porphyrin J- aggregates

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The widespread interest into organic- inorganic hybrid nanocomposites takes advantage by the emergence of new optical properties and chemical behavior, both in solution and on solid surface, coming from the conjunction of chemically different building blocks. This class of materials have been extensively exploited in several scientific fields, as imaging, catalysis, photonics and optoelectronics. In this framework, due to their interesting spectroscopic properties and their ability to form self-assembled structures, porphyrins represent interesting candidates as organic building blocks to realize hybrids nanocomposite materials. In particular, tetrakis (4- sulphonatophenyl) porphyrin ($TPPS_4$) is an intriguing compound due to its ability to form self- assembled J-aggregates with different shape and size extremely dependent on the experimental conditions as, pH medium, reactant concentrations, addition of salt and templating agents [1-2]. Here, wefocus on the $TPPS_4$ aggregation process assisted and/or catalyzed by the presence of inorganic nanostructured materials such as gold nanostructures and carbon nanotubes (CNTs). Our goal is to build up new hybrids nanocomposites, whose properties merge the optical and photophysical properties of organic and inorganic nanostructures. Exploiting the class of metallic nanosized materials, we have chosen gold nanorods (Au NRs) and clusters composed of ten atoms (Au_{10}). The presence of Au NRs prompts the formation of highly ordered structures of porphyrins in solution whereas J-aggregates trigger the interaction among Au NRs leading to the formation of a J-aggregates/ Au NRs nanohybrid material [3]. Self- assembled structures can be also formed in the presence of Au_{10} clusters, obtaining nanohybrid materials composed of nanostructured gold and the aggregated porphyrin both in solution and on glass surface. Experimental findings have shown the growth of Au_{10} clusters forming a metallic layer on the glass surface whose properties are strictly related to experimental conditions. The optical and photophysical properties of these components make them interesting candidates for a range of potential applications. Moreover, the aggregation process has also been examined in the presence of amine functionalized CNTs showing the importance of the alkyl chain length and the number of amine groups in promoting the porphyrin aggregation process. All the investigated nanocomposites have been examined by a detailed spectroscopic and morphologic characterization in solution and on solid state.

1. N. Micali, V. Villari, M. A. Castriciano, A. Romeo, L. Monsu` Scolaro , J. Phys. Chem. B 2006, 110, 8289;

2. I. Occhiuto, G. De Luca, M. Trapani, L. Monsù Scolaro, R. F. Pasternack, Inorg. Chem., 2012, 51, 10074;

3. M. Trapani, G. De Luca, A. Romeo, M. A. Castriciano, L. Monsù Scolaro, Spectrochim. Acta Mol. Biomol. Spectrosc. 2016, accepted for pubblication.

#P142 - Black Diamond: a surface-nanostructured material for high temperature

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Black diamond, a novel material developed in the framework of the European FET project ProME^{3}THE^{2}US^2 (www.prometheus-energy.eu, GA 308975), is obtained by a controlled nanoscale periodic texturing of CVD diamond surface, performed by means of ultra-short pulse lasers. Such a process represents a technologically easy process to fabricate ripples with a periodicity of about 170 nm on diamond surface, able to drastically modify the interaction with solar radiation from typical optical transparency up to solar absorptance values even higher than 90%. Here we demonstrate that surface texturing gives rise to a strong enhancement of photo-responsivity in the visible range (up two orders of magnitude larger than the starting transparent diamond film). The operating mechanisms of black diamond is discussed and explained by disentangling the optical enhancement from an electronic increased density of states within the diamond bandgap corresponding to an actual intermediate band able to support an efficient photoelectronic conversion of sub-bandgap photons (<5.47 eV) [1]. The introduction of an intermediate band results in an enhanced external quantum efficiency up to 800 nm wavelengths, without affecting the film transport capabilities. Here, we further discuss recent results of process development and optimization, such as a reduced periodicity of the ripples and fabrication of 2D periodic structures [2]. The achieved optical and photoelectronic outstanding results open the path for future application of black diamond as a photon-enhanced thermionic emission cathode for solar concentrating systems, with advantages owing to the excellent electronic properties combined with a potentially very low work function and high thermal stability, as well as for solar sensors.

[1] P. Calvani, A. Bellucci, M. Girolami, S. Orlando, V. Valentini, R. Polini, and D. M. Trucchi, “Black Diamond for Solar Energy Conversion”, Carbon 105 (2016) 401-407.

[2] A. Bellucci, P. Calvani, M. Girolami, S. Orlando, R. Polini, and D. M. Trucchi, “Optimization of Black Diamond Films for Solar Energy Conversion”, Applied Surface Science 380 (2016) 8-11.

#P143 - Memory-Driven Order-Disorder Transition of 3D-Supramolecular Architecture Based on Calix[5]arene and Porphyrin Derivatives in Solid Polymeric Matrix

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Here we report the relocation at the solid matrix of a well-characterized 3D supramolecular structure, pre-formed in solution through the iterative association of a polymer based on calix[5]arene tethered poly(*p*-phenyleneethynylene) with a complementary synthetic porphyrin, endowed with alkanediyldiammonium functions at the distal meso-positions, to generate a 3D supramolecular network. Such a highly-ordered supramolecular assembly was hosted in a solid matrix based on polydimethylsiloxane (PDMS). Although the supramolecular 3D-ordered system was initially disrupted after mixing with PDMS, macroscopically forming a dispersion of de-phasing porphyrin aggregates, we found that a short (120 s) thermal shock (up to 250 °C) induces the de-aggregation of the porphyrin aggregates and the partial restoration of the original 3D-supramolecular structure. The reassembled 3D supramolecular system has been found to be stable only at high temperature, decaying again, in a long time, with temperature lowering, to dispersed porphyrin aggregates. The whole process behaves as a cyclically reversible order-disorder transition. This phenomenon is described, for the first time, and it is accounted for in terms of memory recovery system as definitely the novel material appears to partially remember its past supramolecular organization, being able to restore the former molecular architecture.

#P144 - Colloidal Synthesis of Plasmonic Bipolar Ga2FeO4 Spinel-type Nanocrystals

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Conductive oxides nanocrystals (NCs) are particularly promising materials since they can be integrated in solar cells, lighting devices, optoelectronic devices, etc. [1] These materials are characterized by the presence of free carriers which leads to conductivity and, in some cases, to a localized surface plasmon resonance (LSPR). Free charges in these materials are typically associated to doping species or to intrinsic defects. [2] Fine modulation of doping level, hence of the plasmon resonance, has been successfully demonstrated for many n-type systems, but the same level of performances has not been achieved yet for p-type systems. [3] A new class of materials that has shown great potentialities for both n and, especially, p-type doping has been recently emerged: A_2BO_4 spinel oxides. [4] At 0K, these materials can be characterized by a fcc oxygen sublattice where B^{2+} cations occupy octahedral sites while A^{3+} cations are equally distributed between octahedral and tetrahedral sites. At temperature higher than 0K, an intrinsic disorder in the crystal structure exists, driven by the cross-substitution between A and B cations (*i.e.* some A^{3+} cations can substitute B^{2+} ions on tetrahedral position and, in turn, B^{2+} ions can substitute A^{3+} cations on octahedral sites). This process creates intra bandgap states that, in some of these materials, can generate free carriers. A possible way to induce disorder in those structures is to synthesize off-stoichiometric spinel oxide crystals.

Here we present the synthesis of interesting unexplored Ga_2FeO_4 spinel-type (GFO) NCs *via* a colloidal approach that allows for the control over their size distribution, crystallinity and composition. We show that, while stoichiometric GFO NCs are intrinsic semiconductors, off-stoichiometric NCs, produced under either Fe-rich or Ga-rich conditions, behave as degenerately doped semiconductors. In such system we calculated the presence of Ga^{3+} cations in tetrahedral positions creates electron-donor levels close the conduction band, while Fe^{2+} cations in octahedral sites create hole-acceptor levels close the valence band. As expected, off-stoichiometric spinel oxide NCs show both a NIR absorption peak that, through pump and probe measurements, was attributed to a LSPR. The control over the composition of such NCs resulted also in the modulation of their LSPR response. Moreover, as elucidated by electrical measurements, Ga-rich GFO NCs exhibited a n-type electrical behavior, while Fe-rich GFO NCs exhibited p-type conductivity.

[1] Rao C. N. R. *et al.*, The Chemistry of Nanomaterials: synthesis, properties and applications, Wiley-VCH (**2004**); Aricò A. S. *et al.*, *Nature Materials,* (**2005**), 4, 366. [2] Smyth D. M., *Sol. State Ionics*, (**2000**), 129, 5. [3] Ye, X. et al., *J. Am. Chem. Soc.* (**2014**), 136, 11680; Wang, Z. et al. *Adv. Mater.* (**2016**), 28, 3831. [4] Pauder T. R. et al., *Adv. Funct. Mater*., (**2011**), 21, 4493.

#P145 - L10 FePt-based exchange coupled composite thin films for next generation perpendicular magnetic recording media

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$L1_0$ ordered FePt alloy is currently considered as the most promising candidate for next generation ultra-high density magnetic recording media (> 1 Tbit/in^2) for hard disk drives, due to its high magnetocrystalline anisotropy (5 – 10 MJ/m^3), which ensures room temperature thermal stability of grains with size down to 3 nm [1,2]. However, due to the large switching field of this material, the writability issue must be solved to comply with conventional recording heads. Exchange coupled composites (ECC) consisting of high- and low-anisotropy ferromagnetic phases sharing a common interface have been proposed as an efficient way to reduce the switching field without compromising the thermal stability. High- and low-anisotropy magnetic phases can be separated either by a sharp interface (exchange-spring media), with or without a non-magnetic layer, or by a region where the anisotropy gradually varies from high to low values (graded media), the latter structure being proposed to yield a larger reduction of the switching field for similar values of the thermal stability. Moreover, while in conventional ECC systems the cross sectional shape is identical for the hard and soft phases, in the ledge-type composites the soft region is more extended in the recording direction.

This contribution reports on the results of our recent studies on the magnetic behavior and its correlation to the morpho-structural properties of different $L1_0$-FePt-based exchange coupled composite films including A1/$L1_0$-FePt graded films on MgO (100) [3] and glass substrates [4] and Co/$L1_0$-FePt ledge type structures [5], all of them being promising for future ultra-high densities magnetic recording (≥ 1 Tbit/in^2).

[1] “Ultrahigh-Density Magnetic Recording”,G. Varvaro and F. Casoli Eds., Pan Stanford Publishing Pte. Ltd., 2016

[2] G. Varvaro et al., J. Magn. Magn. Mat. 415, 368 2014

[3] V. Alexandrakis et al., J. Appl. Phys. 109, 07B729 2011

[4] G. Barucca et al., in preparation

[5] Th. Speliotis et al., J. Appl. Phys.119, 233904 2016

#P146 - SYNTHESIS OF CALCIUM CARBONATE NANOCRYSTALS AND THEIR POTENTIAL APPLICATION AS VESSELS FOR DRUG DELIVERY

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The development of drug carriers for the cellular uptake of drugs, therapeutic proteins and nucleic acids is of particular interest. Because nucleic acids, proteins, and peptides are not taken up into cells via passive diffusion, their intracellular uptake by nanocarriers is a key to targeting the delivery of these compounds at the cellular or organelle level. Specifically, the incorporation of these compounds into nanocarriers will improve the efficiency of their intracellular uptake or delivery to specific organelle, thereby ensuring their therapeutic effects. Furthermore, clarifying the intracellular trafficking mechanisms may also facilitate the discovery of new drug delivery strategies, such as targeting to specific cell organelles.

A large variety of nano/microparticles has been described in literature and optimised to increase efficacy and sustain the targeting into cancer cells. Among such novel and intriguing nanostructured materials, calcium carbonate ($CaCO_3$) is an extremely important material, both in the fundamental research and industry, determined by their defined proprieties, such as morphology, structure, size, specific surface area and chemical purity. In our previous work we demonstrated that calcium carbonate microparticles are considered as the ideal drug carriers due to their excellent biocompatibility and ability to readily penetrate cancer cells[1-3]. After an extensive characterization of $CaCO_3$ nanoparticles synthesized by spray drying technique, we exploited the features of this nanomaterial to use it in biological application as vessels in drug delivery systems. The goal of this study was to define the cellular trafficking and transport of these nanoparticles using confocal microscopy combined with ultrastructural examination to provide an overview of particle trafficking, such as mobility, as well as cellular localization of particles. Pure $CaCO_3$ nanoparticles were used both as a substrate to build layer by layer (LbL) self-assembled polyelectrolyte nanocapsules, and as drug carrier, in order to obtain a delivery system for the sustained release of two promising anti cancer molecules (*cisplatin* and BEZ-235). The efficiency of these systems was assessed on a panel of four human tumour cell lines

#P147 - Rare-earth doped silica optical fibres for ionizing radiation detection

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Scintillating silica optical fibre sensors have shown interesting results for ionizing radiation monitoring and therefore can be useful for dosimetry applications in medical field. In fact, they enable a remote, punctual and real-time dose assessment (Mones et al., 2008). In addition, the high radiation hardness that characterizes silica optical fibers, makes these systems promising for radiation detection in high energy physics experiments (Chiodini et al., 2014).

This work aims to review the recent progresses in the development and characterization of rare-earth doped silica fibres. The radioluminescent and dosimetric properties of Ce, Eu, Yb and Pr-doped silica matrices are described and the advantages and challenges in the use of these materials for dosimetry in medical and technical applications are shown.

In radiation therapy, an effective approach to deal with the stem effect, that is a spurious luminescent signal in the UV-VIS region due to the irradiation of the passive fibre (i.e. Cerenkov light and intrinsic fluorescence) must be considered. The opportunity to use Yb as dopant and to exploit its near infrared emission for the stem effect optical discrimination is presented (Veronese et al., 2014).

In the field of high energy physics, radioluminescent optical fibres could find applications in future detectors and calorimeters. The possible choice of Pr as dopant, in view of its fast scintillation time is described and discussed.

REFERENCE

E. Mone set al., *Ce-doped optical fibre as radioluminescent dosimeter in radiotherapy*, Radiation Measurements, Volume 43, Issues 2–6, February–June 2008, Pages 888–892.

N. Chiodini, I. Veronese, A. Vedda, *Rare Earth Doped Silica Optical Fibre Sensors for Dosimetry in Medical and Technical Applications*, Advances in Optics Volume 2014 (2014), http://dx.doi.org/10.1155/2014/974584

I. Veronese et al., *Infrared luminescence for real time ionizing radiation detection,* Appl. Phys. Lett. 105, 061103 (2014), http://dx.doi.org/10.1063/1.4892880.

#P148 - Electrophoretic deposition of dispersion ZrB2 and SiC powder on woven carbon fiber for the processing of novel UHTCMCs

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Electrophoretic deposition of dispersion ZrB_2 and SiC powder on woven carbon fiber for the processing of novel UHTCMCs

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Abstract

In the present work, the deposition of Zirconium diboride (ZrB_2) or/and Silicon carbide (SiC), on carbon fibers via electrophoretic (EPD) is studied. The final purpose is the fabrication of novel UHTCMCs for aerospace, with optimized fiber/matrix interface Ceramic coatings are indeed necessary for optimization of the fiber/matrix bonding, oxidation protection and prevention of fiber-matrix interfacial degradation at elevated temperatures. Ethanol–based Ceramic suspensions of ZrB_2 or/and SiC powders have been studied in order to find the suitable solid concentration and dispersant amount, poly(ethyleneimmine) (PEI), for the deposition. PEI was found to be effective for the dispersion of both ZrB_2 and SiC powders in ethanol solution. The d.d.p. (Volt) applied to the electrophoretic cell was varied from 5 to 30 Volt with holding times between 5 and 180 minutes. An incremental approach was adopted starting from deposition on to individual bundles, and then unidirectional carbon fabrics, to end with 2D carbon fabrics. The unidirectional coated woven carbon fibers were further infiltrated with a ceramic slurry, overlapped and treated by hot pressing for densification. The microstructure of the polished sections of carbon fibers and unidirectional fabrics coated was examined by scanning electron microscopy and optical microscopy. The structure obtained by the combination of these techniques is typical of a new generation of materials defined ultra high temperature ceramics matrix composites (UHTCMC), which can potentially couple the high oxidation resistance of UHTCs to the damage tolerance of CMCs, provided that a suitable matrix/fiber interface is tailored.

#P149 - Keratin film for active packaging plasticized with citric acid

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Innovative packaging materials have been the focus of extensive efforts extending the shelf-life of food, enhancing consumer safety, reducing wastes to the production sector, and being environmental friendly. Particularly, biopolymers such as lipids, proteins, polysaccharides and mixtures thereof, have been investigated to enhance the properties of films for packaging. Active packaging with antibacterial property is a concept in food technology based on incorporating an antimicrobial compound inside the packaging material or using a packaging material with inherent antimicrobial properties to reduce or inhibit microbial growth. In the present work, keratin and citric acid were mixed in water in order to produce a stretchable film with antibacterial properties for application in active packaging. Keratin is a natural protein that can be extracted from wool or other natural resources. Unfortunately, keratin alone has poor mechanical properties. Citric acid was employed as compatibilizer and plasticizer to improve the mechanical properties of films; it forms strong hydrogen bonds with hydroxyl groups and enhances interactions between macromolecules. In addition, citric acid has antibacterial properties and it is used in many different food products as preservative. The films obtained by blending keratin and citric acid showed excellent biocidal effect and high elongation value (600 %). Probably, the capability of citric acid to form hydrogen bonds is responsible for this great improvement of extensibility. On the other hand, the study of FT-IR spectrum allows to understand that the presence of citric acid in aqueous solution enhance the content of alpha helix structure in the film, with a reduction in the amount of side chain and disorder in the structure. Consequently, the high grade of the film elongation is possible because molecular structures are able to move freely in the film.

#P150 - Polypyrrole-coated textiles with antibacterial properties

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This work is focused on the development and the evaluation of antibacterial and electrical properties of fabrics produced by polypyrrole functionalisation. PPy was applied to textile materials by chemical oxidative in situ polymerisation from aqueous solutions of pyrrole. The textile materials were selected among those manufactured by the industrial partners. Process conditions (monomer, oxidant and dopant concentrations, oxidant/monomer molar ratio, liquor ratio, weight uptake, kind of dopant) were studied to improve antibacterial properties, as the first goal. Antibacterial activity against Escherichia coli, Staphylococcus aureus and Klebsiella pneumoniae of treated textile materials was evaluated following international standard test method ASTM E 2149. The antibacterial efficiency was assessed after fastness tests simulating stresses to which the textiles are subjected during processing, maintenance and final use. Fastness was evaluated following international standard test methods, namely laundering (with anionic and non-ionic detergents), dry-washing and fastness to acid and alkaline perspiration. The second goal of the project was the development of electro-conductive coating for EMI shielding. High-conducting (doped) PPy coatings were applied to textiles keeping the track of the findings related to the development of antibacterial PPy-based finishing. Before laundering, fabrics treated with PPy showed 100% of bacterial reduction, while untreated cotton fabric had practically no antimicrobial activity. After dry-cleaning, PPy fabrics showed high bacterial reductions (99%). Antimicrobial properties resulted depleted after non-ionic and anionic launderings. For the production of EMI shielding textiles, it was found that 4 g/l of pyrrole concentration is enough for obtaining significant attenuation of microwaves.

#P151 - Fabrics based on Cyclodextrin/Photosensitiser systems for Photodynamic Antimicrobial Therapy

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In the development of new antibacterial therapeutic approaches to fight multidrug-resistant bacteria, photodynamic antimicrobial therapy (PAT) represents a well-known alternative to treat local infections caused by different microorganisms.[1-3] Here we present a polypropylene (PP) fabric finished with citrate-hydroxypropyl-βCD polymer (PP-CD)[4] entrapping the tetra-anionic 5,10,15,20-tetrakis(4-sulfonatophenyl)-21H,23H-porphine (TPPS) as photosensitizer eluiting fabric for PAT. The concept is based on host–guest complexation of porphyrin in the cavities of CDs immobilized on the PP fibers, followed by its sustained and controlled delivery in release medium and simultaneous photo-inactivation of microorganisms. Morphology of fabric was characterized by optical (OM) and scanning electron microscopies (SEM). Optical properties were investigated by UV-vis absorption, steady- and time-resolved fluorescence emission spectroscopy. X-ray Photoelectron Spectroscopy (XPS) and FT-IR revealed the surface chemical composition and the distribution map of the molecular components on the fabric, respectively. Direct $^1O_2$ determination allowed to assess the potential photodynamic activity of the fabric. Release kinetics of TPPS in physiological conditions pointed out to the role of the CD cavity to control the TPPS elution. Transfer of TPPS from textile to colonies of Gram (+) S. aureus ATCC 29213 was ascertained by both microscopy and UV-vis extinction and fluorescence spectra which were acquired on bacterial cells microscopic images. Finally, photodynamic antimicrobial efficacy and anti-adhesive properties were established on porphyrin- treated cells after irradiation.

1. Hanakovaa, A.; Bogdanovab, K.; Tomankovaa, K.; Pizovaa, K.; Malohlavaa, J.; Bindera, S.; Bajgara, R.; Langovaa, K.; Kolarb, M.; Mosingerc, J.; Kolarovaa, H. *Microbiological Research* **2014**,169, 163–170.

2. *Nanobiomaterials in Antimicrobial Therapy: Applications of Nanobiomaterials*. Elsevier: Cambridge, USA, 2016.

3. Dai, T.; Huang, Y.-Y.; Hamblin, M. R., Photodynamic Therapy for Localized Infections—State of the Art. *Photodiagnosis Photodyn Ther* **2009,** *6*, 170-188.

4. Laurent, T.; Kacem, I.; Blanchemain, N.; Cazaux, F.; Neut, C.; Hildebrand, H. F.; Martel, B.. *Acta Biomateralia* **2011**, *7*, 3141-3149.

#P152 - IMIDAZOLIUM IONIC LIQUIDS AS ANTIMICROBIAL ADDITIVES OF BIOMEDICAL PVC

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In the last years ionic liquids (ILs) have attracted research interest for their thermal stability, non-inflammability, negligible vapour pressure, solvation ability, biocompatibility, low toxicity, etc [1]. ILs based on imidazolium salts have been used in a wide range of biological and material science applications as scaffold for biomimetic applications, oxygen transport membranes, surfactants, plasticizers, antimicrobial and anti-inflamatory agents[2]. It was reported that imidazolium ILs showed strong antimicrobial activity, comparable to that of commercial antimicrobial compounds such as Triclosan and that ILs biocidal activity is mainly due to the alkyl chain length in the cation[3].

The aim of this study was the development of antimicrobial PVC compounds loaded with 1-10% (w/w) of 1,3-dimethyl5-sulfoisophthalate 1-hexadecyl-3-methyl imidazolium salt (PC4). PC4 was synthesised according to Colonna et al.[4] and characterized by NMR and TGA. PVC-PC4 compounds were obtained by mixing, at 150 °C for 3 minutes, PVC pellets and PC4 powder (1-10% w/w) in a Brabender mixer. Films of compounds were realized by compression moulding. Thermal and mechanical properties (elastic modulus E, tensile stress TS and elongation at break EB) of compounds were measured. Results demonstrated that the presence of PC4 in PVC formulation did not affect thermal and mechanical properties of compounds. The antimicrobial activity of PVC-PC4 compound films was determined by disk diffusion method. The inhibition zone (mm) surrounding the films, on TSA plates seeded with inocula of *Escherichia coli* and *Staphylococcus epidermidis* at an initial concentration of 10^3CFU/mL, was measured after 24 h of incubation at 37°C. Plates seeded with *S. epidermidis* showed an inhibition zone (6 mm) around PVC film containing 10% (w/w) of PC4, whereas no inhibition zone was observed against *E. coli* growth, confirming a higher antimicrobial action against gram positive bacteria[4]. In all cases there was no growth of these strains on the PVC-PC4 compound films.

1 Mahaian S., Sharma R., Mahajan R.K. *Langmuir* 2012, 28, 17238-17246

2 Anderson E.B., Long T.E. *Polymer*, 2010, 51, 2447-2454

3 Luczak J., Jungnickel C., Łącka I., Stolte S., Hupka J. *Green Chem.* 2010, 12, 593-601

4 Colonna M., Berti C., Binassi E., Fiorini M., Sullalti S., Acquasanta F., Vannini M., Di Gioia D., Aloisio I. *Polymer*, 2012, 53, 1823-1830

#P153 - Antimicrobial PVC silver zeolite composites: plasticizers influence

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Polyvinyl chloride (PVC) is a polymer widely used in medical field to produce equipments for blood transfusion, medical devices, etc. The replacement of di-2-ethyl hexyl phthalate (DEHP) from PVC processing, reducing or eliminating the health risk caused by its release into environment together with the achievementof antimicrobial properties are undoubtedly important for the development of new PVC products relevant for health care applications.

In this study we used PVC plasticized with DEHP, di-isononyl phthalate (DINP) and tris-2-ethyhexyl trimellitate (TOTM) to test the influence of plasticizers on silver release from PVC silver composites. Polymer composites were prepared by mixing PVC pellets with a silver zeolite (SZ) in the amount of 10-20 wt%. The antibacterial activity of PVC SZ composites was tested on *Escherichia coli*and *Staphylococcus epidermidis*in culture broth, on agar plate and in sterile urine seeded with these strains for simulation purposes. The results indicate that the addition of large amount of SZ did not influence the processability and the formability of the composites as well as their thermal and mechanical properties, if compared to neat plasticized PVC. Composites showed antibacterial activity against *S. epidermidis* and *E. coli* in culture broth, direct inhibition on agar plate and in urine supplemented with bacteria. PVC-DEHP SZ composites exhibited a good antimicrobial activity at 10% wt of silver zeolite, while the best performance of composites of PVC plasticized with DINP and TOTM was at 20% wt of silver zeolite.In sterile urine, composites induced a significant reduction of viability of both strains already at 24 h, inhibiting *E. coli*growth up to 20 days, whereas their antimicrobial action against *S. epidermidis*vanished within 5 days. Data on silver release suggest that the different steric hindrance of plasticizers influence the migration and release of the antimicrobial agent from polymeric matrix to the environment.

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Bigongiari Alessandra	**#138**	**Smart surfaces and functionalization**	**13 Tue**
Bodrenko Igor	**#132**	**Energy storage and water splitting**	**13 Tue**
Bollani Monica	**#160**	**Wide band gap semiconductors for power electronics and sensor applications**	**13 Tue**
Bolognini Gabriele	**#363**	**Optical fiber materials and devices**	**16 Fri**
Bonadies Irene	**#078**	**Stimuli responsive: bio-organic materials**	**13 Tue**
Bondavalli Paolo	**#092**	**Energy storage and water splitting**	**13 Tue**

Bonfa' Pietro	**#326**	**Magnetism and spintronics**	**15 Thu**
Boninelli Simona	**#045**	**Solid state lighting and LEDs**	**12 Mon**
Borbone Fabio	**#044**	**Solid state lighting and LEDs**	**12 Mon**
Borzenkov Mykola	**#202**	**Smart surfaces and functionalization**	**14 Wed**
Bosi Matteo	**#313**	**Chemistry and functionalization of 2D materials**	**15 Thu**
Bossi Alberto	**#043**	**Solid state lighting and LEDs**	**12 Mon**
Bottari Cettina	**#072**	**Materials and processes for environmental protection and sustainability**	**12 Mon**
Bottari Cettina	**#113**	**Stimuli responsive: organic-inorganic materials**	**13 Tue**
Boucheham Abdelghani	**#212**	**Photovoltaics**	**14 Wed**
Brancolini Giorgia	**#136**	**Smart surfaces and functionalization**	**13 Tue**
Buccheri Maria Antonietta	**#067**	**Materials and processes for environmental protection and sustainability**	**12 Mon**
Buonocore Francesco	**#165**	**Growth and synthesis of 2D materials**	**13 Tue**
Buonocore Giovanna Giuliana	**#368**	**Active packaging materials**	**16 Fri**
Buzio Renato	**#061**	**Mechanical properties of 2D materials composites**	**12 Mon**
Buzio Renato	**#304**	**Organic electronics**	**15 Thu**
Caccamo Sebastiano	**#213**	**Photovoltaics**	**14 Wed**
Cacialli Franco	**#037**	**Solid state lighting and LEDs**	**12 Mon**
Caddeo Claudia	**#012**	**Composites, Light weight materials and sustainability**	**12 Mon**
Caironi Mario	**#114**	**Printed electronics**	**13 Tue**
Calvi Sabrina	**#115**	**Printed electronics**	**13 Tue**
Camarda Pietro	**#157**	**Wide band gap semiconductors for power electronics and sensor applications**	**13 Tue**
Cannavò Antonino	**#193**	**Wide band gap semiconductors for power electronics and sensor applications**	**14 Wed**
Cantarella Maria	**#030**	**Materials and processes for environmental protection and sustainability**	**12 Mon**
Capobianchi Aldo	**#316**	**Chemistry and functionalization of 2D materials**	**15 Thu**
Capodilupo Agostina Lina	**#300**	**Organic electronics**	**15 Thu**
Caporali Stefano	**#011**	**Composites, Light weight materials and sustainability**	**12 Mon**
Carbone Alessandra	**#356**	**Fuel cells**	**16 Fri**
Carbone Carlo	**#221**	**Electronic/optical/magnetic/quantum properties of 2D materials**	**14 Wed**
Carella Antonio	**#308**	**Photovoltaics**	**15 Thu**
Carlomagno Ilaria	**#168**	**Growth and synthesis of 2D materials**	**13 Tue**
Carnevali Virginia	**#163**	**Growth and synthesis of 2D materials**	**13 Tue**
Carravetta Vincenzo	**#071**	**Materials and processes for environmental protection and sustainability**	**12 Mon**
Carrega Matteo	**#223**	**Electronic/optical/magnetic/quantum properties of 2D materials**	**14 Wed**
Caschera Daniela	**#140**	**Smart surfaces and functionalization**	**13 Tue**
Cassone Giuseppe	**#328**	**Materials under extreme conditions and ultra–fast transitions**	**15 Thu**
Castaldo Rachele	**#036**	**Materials and processes for environmental protection and sustainability**	**12 Mon**
Castellero Alberto	**#337**	**Thermoelectrics**	**15 Thu**

Castellini Alessia	**#205**	**Smart surfaces and functionalization**	**14 Wed**
Castriciano Maria Angela	**#074**	**Stimuli responsive: bio-organic materials**	**13 Tue**
Cataldi Pietro	**#060**	**Mechanical properties of 2D materials composites**	**12 Mon**
Catone Daniele	**#231**	**Materials under extreme conditions and ultra–fast transitions**	**14 Wed**
Cattarin Sandro	**#102**	**Materials and processes for environmental protection and sustainability**	**13 Tue**
Cavalli Silvia	**#075**	**Stimuli responsive: bio-organic materials**	**13 Tue**
Cavallini Massimiliano	**#204**	**Smart surfaces and functionalization**	**14 Wed**
Cecchi Stefano	**#087**	**Oxide and nanomaterials for non-volatile memories**	**13 Tue**
Cecchini Raimondo	**#086**	**Oxide and nanomaterials for non-volatile memories**	**13 Tue**
Cedola Alessia	**#016**	**Materials and methods for Conservation of Cultural Heritage**	**12 Mon**
Cedola Alessia	**#050**	**Biomimetic materials triggering cell phenotype and tissues regeneration**	**12 Mon**
Cerruti Pierfrancesco	**#003**	**Stimuli responsive materials**	**12 Mon**
Chiasera Alessandro	**#364**	**Optical fiber materials and devices**	**16 Fri**
Christian Meganne	**#025**	**2D materials for energy applications**	**12 Mon**
Ciccarella Giuseppe	**#183**	**Nanobiocomposites for in–vitro diagnostics and targeted drug**	**14 Wed**
Cicco Nunzia	**#252**	**Biological applications of 2D materials**	**15 Thu**
Cola Adriano	**#159**	**Wide band gap semiconductors for power electronics and sensor applications**	**13 Tue**
Colella Silvia	**#207**	**Photovoltaics**	**14 Wed**
Colombelli Adriano	**#139**	**Smart surfaces and functionalization**	**13 Tue**
Colonna Stefano	**#280**	**Chemistry and functionalization of 2D materials**	**15 Thu**
Comoretto Davide	**#301**	**Organic electronics**	**15 Thu**
Conoci Sabrina	**#319**	**Chemistry and functionalization of 2D materials**	**15 Thu**
Convertino Annalisa	**#216**	**Nanobiocomposites for in–vitro diagnostics and targeted drug**	**14 Wed**
Cortese Barbara	**#248**	**Biological applications of 2D materials**	**15 Thu**
Covi Erika	**#052**	**Oxide and nanomaterials for non-volatile memories**	**12 Mon**
Cramer Tobias	**#271**	**Organic electronics**	**15 Thu**
Cramer Tobias	**#294**	**Materials under extreme conditions and ultra–fast transitions**	**15 Thu**
Cricenti Antonio	**#217**	**Nanobiocomposites for in–vitro diagnostics and targeted drug**	**14 Wed**
Cristiano Fuccio	**#297**	**Materials under extreme conditions and ultra–fast transitions**	**15 Thu**
Cucini Riccardo	**#230**	**Materials under extreme conditions and ultra–fast transitions**	**14 Wed**
Cusano Andrea	**#361**	**Optical fiber materials and devices**	**16 Fri**
D'Amora Ugo	**#262**	**3D printing materials in biomedical research**	**15 Thu**
D'Angelo Daniele	**#279**	**Chemistry and functionalization of 2D materials**	**15 Thu**
D'Arrigo Giuseppe	**#088**	**Oxide and nanomaterials for non-volatile memories**	**13 Tue**
Dacapito Francesco	**#164**	**Growth and synthesis of 2D materials**	**13 Tue**
Dacapito Francesco	**#054**	**Oxide and nanomaterials for non-volatile memories**	**12 Mon**
Dal Poggetto Giovanni	**#220**	**Nanobiocomposites for in–vitro diagnostics and targeted drug**	**14 Wed**
Dapporto Massimiliano	**#201**	**Smart surfaces and functionalization**	**14 Wed**
de Caro Tilde	**#018**	**Materials and methods for Conservation of Cultural Heritage**	**12 Mon**
De Falco Francesca	**#068**	**Materials and processes for environmental protection and sustainability**	**12 Mon**

De Falco Gianluigi	**#142**	**Materials and processes for environmental protection and sustainability**	**13 Tue**
de Julian Fernandez César	**#344**	**Magnetic materials for medicine**	**16 Fri**
De Luca Giovanna	**#256**	**Electronic/optical/magnetic/quantum properties of 2D materials**	**15 Thu**
De Luca Ilenia	**#187**	**Nanobiocomposites for in–vitro diagnostics and targeted drug**	**14 Wed**
De Luca Oreste	**#318**	**Chemistry and functionalization of 2D materials**	**15 Thu**
De Luise Adriana	**#083**	**Biomimetic materials triggering cell phenotype and tissues regeneration**	**13 Tue**
De Renzi Valentina	**#199**	**Growth and synthesis of 2D materials**	**14 Wed**
De Santis Roberto	**#241**	**Magnetic materials for medicine**	**15 Thu**
De Stefano Luca	**#100**	**Materials and processes for environmental protection and sustainability**	**13 Tue**
de Weerd Chris	**#181**	**Photovoltaics**	**14 Wed**
Deambrosis Silvia	**#330**	**Materials under extreme conditions and ultra–fast transitions**	**15 Thu**
Dediu Valentin Alek	**#240**	**Magnetic materials for medicine**	**15 Thu**
Del Rio Castillo Antonio Esau	**#197**	**Growth and synthesis of 2D materials**	**14 Wed**
Dell'Angela Martina	**#228**	**Materials under extreme conditions and ultra–fast transitions**	**14 Wed**
Depalo Nicoletta	**#219**	**Nanobiocomposites for in–vitro diagnostics and targeted drug**	**14 Wed**
Deretzis Ioannis	**#210**	**Photovoltaics**	**14 Wed**
Destri Silvia	**#272**	**Organic electronics**	**15 Thu**
Di Benedetto Francesca	**#111**	**Stimuli responsive: organic-inorganic materials**	**13 Tue**
Di Carlo Gabriella	**#017**	**Materials and methods for Conservation of Cultural Heritage**	**12 Mon**
Di Fonzo Fabio	**#133**	**Energy storage and water splitting**	**13 Tue**
Distefano Dario Luigi	**#014**	**Composites, Light weight materials and sustainability**	**12 Mon**
Doebelin Nicola	**#200**	**Smart surfaces and functionalization**	**14 Wed**
Dozio Samuele	**#343**	**Magnetic materials for medicine**	**16 Fri**
Faggio Giuliana	**#167**	**Growth and synthesis of 2D materials**	**13 Tue**
Fanciulli Carlo	**#342**	**Thermoelectrics**	**15 Thu**
Fanciulli Carlo	**#340**	**Thermoelectrics**	**15 Thu**
Fasolino Ines	**#080**	**Biomimetic materials triggering cell phenotype and tissues regeneration**	**13 Tue**
Fazio Enza	**#161**	**Wide band gap semiconductors for power electronics and sensor applications**	**13 Tue**
Ferdeghini carlo	**#096**	**Energy storage and water splitting**	**13 Tue**
Fernandes Patricio Tatiana Marisa	**#347**	**Magnetic materials for medicine**	**16 Fri**
Fieramosca Antonio	**#259**	**Electronic/optical/magnetic/quantum properties of 2D materials**	**15 Thu**
Filice Simona	**#131**	**Energy storage and water splitting**	**13 Tue**
Fiorentini Vincenzo	**#324**	**Magnetism and spintronics**	**15 Thu**
Fiorenza Patrick	**#122**	**Wide band gap semiconductors for power electronics and sensor applications**	**13 Tue**
Fisichella Gabriele	**#258**	**Electronic/optical/magnetic/quantum properties of 2D materials**	**15 Thu**
Flammini Roberto	**#166**	**Growth and synthesis of 2D materials**	**13 Tue**
Foti Antonino	**#019**	**Materials and methods for Conservation of Cultural Heritage**	**12 Mon**
Fraboni Beatrice	**#268**	**Organic electronics**	**15 Thu**
Frascaroli Jacopo	**#055**	**Oxide and nanomaterials for non-volatile memories**	**12 Mon**

Fratesi Guido	**#270**	**Organic electronics**	**15 Thu**
Frigerio Jacopo	**#365**	**Optical fiber materials and devices**	**16 Fri**
Fujii Jun	**#222**	**Electronic/optical/magnetic/quantum properties of 2D materials**	**14 Wed**
Fumagalli Francesco	**#023**	**2D materials for energy applications**	**12 Mon**
Galeotti Francesco	**#362**	**Optical fiber materials and devices**	**16 Fri**
Galinetto Pietro	**#174**	**Smart surfaces and functionalization**	**13 Tue**
Galizia Pietro	**#290**	**Magnetism and spintronics**	**15 Thu**
Gandini Alessandro	**#008**	**Composites, Light weight materials and sustainability**	**12 Mon**
Garcia Ferre Francisco	**#333**	**Materials under extreme conditions and ultra–fast transitions**	**15 Thu**
Garroni Sebastiano	**#108**	**Stimuli responsive: organic-inorganic materials**	**13 Tue**
Gasperi Gabriele	**#106**	**Materials and processes for environmental protection and sustainability**	**13 Tue**
Genco Armando	**#306**	**Organic electronics**	**15 Thu**
Gennari Oriella	**#249**	**Biological applications of 2D materials**	**15 Thu**
Gentiluomo Silvia	**#317**	**Chemistry and functionalization of 2D materials**	**15 Thu**
Gerbi Andrea	**#057**	**Oxide and nanomaterials for non-volatile memories**	**12 Mon**
Giamberini Marta	**#001**	**Stimuli responsive materials**	**12 Mon**
Giangregorio Maria Michela	**#315**	**Chemistry and functionalization of 2D materials**	**15 Thu**
Giannazzo Filippo	**#224**	**Electronic/optical/magnetic/quantum properties of 2D materials**	**14 Wed**
Giannazzo Filippo	**#188**	**Wide band gap semiconductors for power electronics and sensor applications**	**14 Wed**
Giansante Carlo	**#307**	**Photovoltaics**	**15 Thu**
Gilioli Edmondo	**#234**	**Materials under extreme conditions and ultra–fast transitions**	**14 Wed**
Girolami Marco	**#191**	**Wide band gap semiconductors for power electronics and sensor applications**	**14 Wed**
Girolami Marco	**#190**	**Wide band gap semiconductors for power electronics and sensor applications**	**14 Wed**
Grande Marco	**#349**	**Novel 2D materials based devices**	**16 Fri**
Grassano Davide	**#226**	**Electronic/optical/magnetic/quantum properties of 2D materials**	**14 Wed**
Greco Francesco	**#116**	**Printed electronics**	**13 Tue**
Greco Giuseppe	**#123**	**Wide band gap semiconductors for power electronics and sensor applications**	**13 Tue**
Grimaldi Gaia	**#292**	**Materials under extreme conditions and ultra–fast transitions**	**15 Thu**
Grimaudo Roberto	**#286**	**Magnetism and spintronics**	**15 Thu**
Gucciardi Pietro Giuseppe	**#215**	**Nanobiocomposites for in–vitro diagnostics and targeted drug**	**14 Wed**
Günther Sebastian	**#162**	**Growth and synthesis of 2D materials**	**13 Tue**
Heun Stefan	**#350**	**Novel 2D materials based devices**	**16 Fri**
Hostaša Jan	**#367**	**Optical fiber materials and devices**	**16 Fri**
Iacobellis Rosabianca	**#180**	**Photovoltaics**	**14 Wed**
Iacobucci Stefano	**#189**	**Wide band gap semiconductors for power electronics and sensor applications**	**14 Wed**
Iafisco Michele	**#182**	**Nanobiocomposites for in–vitro diagnostics and targeted drug**	**14 Wed**

Impellizzeri Giuliana	**#146**	**Materials and processes for environmental protection and sustainability**	**13 Tue**
Invernizzi Marta	**#266**	**3D printing materials in biomedical research**	**15 Thu**
Irrera Alessia	**#041**	**Solid state lighting and LEDs**	**12 Mon**
Jedrkiewicz Ottavia	**#295**	**Materials under extreme conditions and ultra–fast transitions**	**15 Thu**
Kakhiani Khatuna	**#282**	**Chemistry and functionalization of 2D materials**	**15 Thu**
Khouzami Khaoula	**#013**	**Composites, Light weight materials and sustainability**	**12 Mon**
Kovtun Alessandro	**#206**	**Smart surfaces and functionalization**	**14 Wed**
Krahne Roman	**#038**	**Solid state lighting and LEDs**	**12 Mon**
La Notte Luca	**#238**	**Printed electronics**	**14 Wed**
La Via Francesco	**#120**	**Wide band gap semiconductors for power electronics and sensor applications**	**13 Tue**
Lama Giuseppe Cesare	**#006**	**Stimuli responsive materials**	**12 Mon**
Lamperti Alessio	**#195**	**Growth and synthesis of 2D materials**	**14 Wed**
Laureti Sara	**#320**	**Magnetism and spintronics**	**15 Thu**
Lavorgna Marino	**#059**	**Mechanical properties of 2D materials composites**	**12 Mon**
Lazzarini Laura	**#225**	**Electronic/optical/magnetic/quantum properties of 2D materials**	**14 Wed**
Leo Angelo	**#323**	**Magnetism and spintronics**	**15 Thu**
Leporatti Stefano	**#214**	**Nanobiocomposites for in–vitro diagnostics and targeted drug**	**14 Wed**
Liscio Fabiola	**#305**	**Organic electronics**	**15 Thu**
Lo Nigro Raffaella	**#124**	**Wide band gap semiconductors for power electronics and sensor applications**	**13 Tue**
Loffredo Fausta	**#237**	**Printed electronics**	**14 Wed**
Lombardo Domenico	**#151**	**Nanobiocomposites for in–vitro diagnostics and targeted drug**	**13 Tue**
Lombardo Salvatore	**#277**	**Photovoltaics**	**15 Thu**
Lombardo Salvatore Francesco	**#293**	**Materials under extreme conditions and ultra–fast transitions**	**15 Thu**
Longo Massimo	**#085**	**Oxide and nanomaterials for non-volatile memories**	**13 Tue**
Lufrano Francesco	**#094**	**Energy storage and water splitting**	**13 Tue**
Maggi Claudio	**#007**	**Stimuli responsive materials**	**12 Mon**
Malagoli Andrea	**#291**	**Materials under extreme conditions and ultra–fast transitions**	**15 Thu**
Malandrino Graziella	**#056**	**Oxide and nanomaterials for non-volatile memories**	**12 Mon**
Manet Ilse	**#154**	**Nanobiocomposites for in–vitro diagnostics and targeted drug**	**13 Tue**
Mannino Giovanni	**#177**	**Photovoltaics**	**14 Wed**
Mariano Fabrizio	**#040**	**Solid state lighting and LEDs**	**12 Mon**
Mas-Torrent Marta	**#267**	**Organic electronics**	**15 Thu**
Masi Sofia	**#209**	**Photovoltaics**	**14 Wed**
Mattoli Virgilio	**#346**	**Magnetic materials for medicine**	**16 Fri**
Mattoni Alessandro	**#176**	**Photovoltaics**	**14 Wed**
Maya-Vetencourt José Fernando	**#246**	**Biological applications of 2D materials**	**15 Thu**
Mazzaglia Antonino	**#185**	**Nanobiocomposites for in–vitro diagnostics and targeted drug**	**14 Wed**
Mazzaro Raffaello	**#273**	**Photovoltaics**	**15 Thu**
Mecozzi Laura	**#250**	**Biological applications of 2D materials**	**15 Thu**

Meduri Angelo	**#032**	**Materials and processes for environmental protection and sustainability**	**12 Mon**
Melucci Manuela	**#145**	**Materials and processes for environmental protection and sustainability**	**13 Tue**
Mengucci Paolo	**#261**	**3D printing materials in biomedical research**	**15 Thu**
Messina Elena	**#064**	**Mechanical properties of 2D materials composites**	**12 Mon**
Messina Grazia M. L.	**#076**	**Stimuli responsive: bio-organic materials**	**13 Tue**
Mikolajick Thomas	**#051**	**Oxide and nanomaterials for non-volatile memories**	**12 Mon**
Milazzo Rachela Gabriella	**#194**	**Wide band gap semiconductors for power electronics and sensor applications**	**14 Wed**
Milazzo Ruggero	**#296**	**Materials under extreme conditions and ultra–fast transitions**	**15 Thu**
Militello Valeria	**#251**	**Biological applications of 2D materials**	**15 Thu**
Minuto Francesco Demetrio	**#127**	**Energy storage and water splitting**	**13 Tue**
Mirabella Salvo	**#155**	**Wide band gap semiconductors for power electronics and sensor applications**	**13 Tue**
Mirabella Salvo	**#158**	**Wide band gap semiconductors for power electronics and sensor applications**	**13 Tue**
Mirabile Gattia Daniele	**#130**	**Energy storage and water splitting**	**13 Tue**
Miritello Maria	**#042**	**Solid state lighting and LEDs**	**12 Mon**
Miscuglio Mario	**#352**	**Novel 2D materials based devices**	**16 Fri**
Mohajeri Soha	**#147**	**Materials and processes for environmental protection and sustainability**	**13 Tue**
Molle Alessandro	**#253**	**Electronic/optical/magnetic/quantum properties of 2D materials**	**15 Thu**
Mollica Nardo Viviana	**#021**	**Materials and methods for Conservation of Cultural Heritage**	**12 Mon**
Molteni Elena	**#303**	**Organic electronics**	**15 Thu**
Montaleone Daniel	**#103**	**Materials and processes for environmental protection and sustainability**	**13 Tue**
Montanino Maria	**#235**	**Printed electronics**	**14 Wed**
Morales Piero	**#203**	**Smart surfaces and functionalization**	**14 Wed**
Morandi Vittorio	**#198**	**Growth and synthesis of 2D materials**	**14 Wed**
Moras Paolo	**#287**	**Magnetism and spintronics**	**15 Thu**
Moroni Lorenzo	**#260**	**3D printing materials in biomedical research**	**15 Thu**
Moros Maria	**#110**	**Stimuli responsive: organic-inorganic materials**	**13 Tue**
Morvillo Pasquale	**#239**	**Printed electronics**	**14 Wed**
Munaò Gianmarco	**#233**	**Materials under extreme conditions and ultra–fast transitions**	**14 Wed**
Munaò Gianmarco	**#077**	**Stimuli responsive: bio-organic materials**	**13 Tue**
Nappini Silvia	**#257**	**Electronic/optical/magnetic/quantum properties of 2D materials**	**15 Thu**
Nava Giorgio	**#093**	**Energy storage and water splitting**	**13 Tue**
Netti Paolo A.	**#149**	**Nanobiocomposites for in–vitro diagnostics and targeted drug**	**13 Tue**
Nicotra Francesco	**#134**	**Smart surfaces and functionalization**	**13 Tue**
Nicotra Giuseppe	**#353**	**Novel 2D materials based devices**	**16 Fri**
Nipoti Roberta	**#121**	**Wide band gap semiconductors for power electronics and sensor applications**	**13 Tue**
Oliveri Ivan Pietro	**#104**	**Materials and processes for environmental protection and sustainability**	**13 Tue**
Orgiani Pasquale	**#288**	**Magnetism and spintronics**	**15 Thu**

Pagliusi Pasquale	**#171**	**Smart surfaces and functionalization**	**13 Tue**
Palermo Vincenzo	**#058**	**Mechanical properties of 2D materials composites**	**12 Mon**
Papa Elettra	**#035**	**Materials and processes for environmental protection and sustainability**	**12 Mon**
Pasini Mariacecilia	**#299**	**Organic electronics**	**15 Thu**
Passeri Daniele	**#289**	**Magnetism and spintronics**	**15 Thu**
Patrucco Alessia	**#047**	**Biomimetic materials triggering cell phenotype and tissues regeneration**	**12 Mon**
Pedicini Rolando	**#129**	**Energy storage and water splitting**	**13 Tue**
Pedrielli Andrea	**#063**	**Mechanical properties of 2D materials composites**	**12 Mon**
Pellegrino Luca	**#091**	**Oxide and nanomaterials for non-volatile memories**	**13 Tue**
Perego Andrea	**#359**	**Fuel cells**	**16 Fri**
Perego Andrea	**#357**	**Fuel cells**	**16 Fri**
Petralia Salvatore	**#172**	**Smart surfaces and functionalization**	**13 Tue**
Pezzella Alessandro	**#073**	**Stimuli responsive: bio-organic materials**	**13 Tue**
Piacentini Emma	**#069**	**Materials and processes for environmental protection and sustainability**	**12 Mon**
Piazza Aurora	**#314**	**Chemistry and functionalization of 2D materials**	**15 Thu**
Pietralunga Silvia Maria	**#126**	**Energy storage and water splitting**	**13 Tue**
Pignatelli Daniela	**#135**	**Smart surfaces and functionalization**	**13 Tue**
Pittaccio Simone	**#173**	**Smart surfaces and functionalization**	**13 Tue**
Pittori Martina	**#247**	**Biological applications of 2D materials**	**15 Thu**
Poghosyan Sergey	**#327**	**Magnetism and spintronics**	**15 Thu**
Politano Antonio	**#348**	**Novel 2D materials based devices**	**16 Fri**
Ponsiglione Alfonso Maria	**#345**	**Magnetic materials for medicine**	**16 Fri**
Prestipino Santi	**#152**	**Nanobiocomposites for in–vitro diagnostics and targeted drug**	**13 Tue**
Privitera Stefania	**#089**	**Oxide and nanomaterials for non-volatile memories**	**13 Tue**
Puglisi Concetto	**#371**	**Active packaging materials**	**16 Fri**
Pulci Olivia	**#254**	**Electronic/optical/magnetic/quantum properties of 2D materials**	**15 Thu**
Pulci Olivia	**#255**	**Electronic/optical/magnetic/quantum properties of 2D materials**	**15 Thu**
Ramirez Rodriguez Gloria Belen	**#049**	**Biomimetic materials triggering cell phenotype and tissues regeneration**	**12 Mon**
Rampino Stefano	**#276**	**Photovoltaics**	**15 Thu**
Raucci Maria Grazia	**#184**	**Nanobiocomposites for in–vitro diagnostics and targeted drug**	**14 Wed**
Ravera Francesca	**#010**	**Composites, Light weight materials and sustainability**	**12 Mon**
Rea Ilaria	**#153**	**Nanobiocomposites for in–vitro diagnostics and targeted drug**	**13 Tue**
Ricci Davide	**#169**	**Smart surfaces and functionalization**	**13 Tue**
Ricci Davide	**#186**	**Nanobiocomposites for in–vitro diagnostics and targeted drug**	**14 Wed**
Righetti Maria Cristina	**#033**	**Materials and processes for environmental protection and sustainability**	**12 Mon**
Righetti Maria Cristina	**#034**	**Materials and processes for environmental protection and sustainability**	**12 Mon**
Righi M. Clelia	**#062**	**Mechanical properties of 2D materials composites**	**12 Mon**
Ritacco Tiziana	**#264**	**3D printing materials in biomedical research**	**15 Thu**

Rizzato Silvia	**#285**	**Magnetism and spintronics**	**15 Thu**
Rizzo Antonella	**#332**	**Materials under extreme conditions and ultra–fast transitions**	**15 Thu**
Rizzo Aurora	**#027**	**2D materials for energy applications**	**12 Mon**
Rizzoli Rita	**#274**	**Photovoltaics**	**15 Thu**
Roccaforte Fabrizio	**#119**	**Wide band gap semiconductors for power electronics and sensor applications**	**13 Tue**
Roddaro Stefano	**#335**	**Thermoelectrics**	**15 Thu**
Ronca Alfredo	**#263**	**3D printing materials in biomedical research**	**15 Thu**
Roncaglia Alberto	**#338**	**Thermoelectrics**	**15 Thu**
Rosato Roberta	**#275**	**Photovoltaics**	**15 Thu**
Rossi Giacomo	**#098**	**Energy storage and water splitting**	**13 Tue**
Rovera Eugenio	**#097**	**Energy storage and water splitting**	**13 Tue**
Ruani Giampiero	**#179**	**Photovoltaics**	**14 Wed**
Ruffini Andrea	**#084**	**Biomimetic materials triggering cell phenotype and tissues regeneration**	**13 Tue**
Ruggeri Rosa	**#360**	**Fuel cells**	**16 Fri**
Ruiz Franco Jose Manuel	**#112**	**Stimuli responsive: organic-inorganic materials**	**13 Tue**
Russo Pietro	**#009**	**Composites, Light weight materials and sustainability**	**12 Mon**
Salerno Simona	**#081**	**Biomimetic materials triggering cell phenotype and tissues regeneration**	**13 Tue**
Samperi Filippo	**#370**	**Active packaging materials**	**16 Fri**
Sandri Monica	**#082**	**Biomimetic materials triggering cell phenotype and tissues regeneration**	**13 Tue**
Sangiorgi Nicola	**#309**	**Photovoltaics**	**15 Thu**
Sangregorio Claudio	**#245**	**Magnetic materials for medicine**	**15 Thu**
Sannino Alessandro	**#046**	**Biomimetic materials triggering cell phenotype and tissues regeneration**	**12 Mon**
Santangelo Saveria	**#028**	**2D materials for energy applications**	**12 Mon**
Sanvito Stefano	**#284**	**Magnetism and spintronics**	**15 Thu**
Scarfiello Riccardo	**#024**	**2D materials for energy applications**	**12 Mon**
Schilirò Emanuela	**#125**	**Wide band gap semiconductors for power electronics and sensor applications**	**13 Tue**
Scidà Alessandra	**#351**	**Novel 2D materials based devices**	**16 Fri**
Sciuto Antonella	**#192**	**Wide band gap semiconductors for power electronics and sensor applications**	**14 Wed**
Sciuto Emanuele Luigi	**#170**	**Smart surfaces and functionalization**	**13 Tue**
Scuderi Viviana	**#070**	**Materials and processes for environmental protection and sustainability**	**12 Mon**
Sementa Luca	**#053**	**Oxide and nanomaterials for non-volatile memories**	**12 Mon**
Sennato Simona	**#218**	**Nanobiocomposites for in–vitro diagnostics and targeted drug**	**14 Wed**
Simonutti Roberto	**#150**	**Nanobiocomposites for in–vitro diagnostics and targeted drug**	**13 Tue**
Siracusano Stefania	**#128**	**Energy storage and water splitting**	**13 Tue**
Smecca Emanuele	**#178**	**Photovoltaics**	**14 Wed**
Sotillo Belén	**#229**	**Materials under extreme conditions and ultra–fast transitions**	**14 Wed**
Sprio Simone	**#079**	**Biomimetic materials triggering cell phenotype and tissues regeneration**	**13 Tue**
Stepien Grazyna	**#244**	**Magnetic materials for medicine**	**15 Thu**

Stingelin Natalie	**#029**	**Materials and processes for environmental protection and sustainability**	**12 Mon**
Strano Vincenzina	**#354**	**Novel 2D materials based devices**	**16 Fri**
Strano Vincenzina	**#156**	**Wide band gap semiconductors for power electronics and sensor applications**	**13 Tue**
Suárez Daniel G.	**#227**	**Electronic/optical/magnetic/quantum properties of 2D materials**	**14 Wed**
Taccola Silvia	**#004**	**Stimuli responsive materials**	**12 Mon**
Taddei Fabio	**#339**	**Thermoelectrics**	**15 Thu**
Tammaro Loredana	**#369**	**Active packaging materials**	**16 Fri**
Tampieri Anna	**#242**	**Magnetic materials for medicine**	**15 Thu**
Telesio Francesca	**#196**	**Growth and synthesis of 2D materials**	**14 Wed**
Todisco Francesco	**#175**	**Smart surfaces and functionalization**	**13 Tue**
Toro Roberta G.	**#144**	**Materials and processes for environmental protection and sustainability**	**13 Tue**
Torrisi Giacomo	**#211**	**Photovoltaics**	**14 Wed**
Tortiglione Claudia	**#048**	**Biomimetic materials triggering cell phenotype and tissues regeneration**	**12 Mon**
Tozzini Valentina	**#022**	**2D materials for energy applications**	**12 Mon**
Trucchi Daniele M.	**#143**	**Materials and processes for environmental protection and sustainability**	**13 Tue**
Tuccitto Nunzio	**#269**	**Organic electronics**	**15 Thu**
Valentini Gianluca	**#099**	**Energy storage and water splitting**	**13 Tue**
Vanazzi Matteo	**#334**	**Materials under extreme conditions and ultra–fast transitions**	**15 Thu**
Varesano Alessio	**#105**	**Materials and processes for environmental protection and sustainability**	**13 Tue**
Varvaro Gaspare	**#322**	**Magnetism and spintronics**	**15 Thu**
Verdini Alberto	**#310**	**Photovoltaics**	**15 Thu**
Vikulov Sergey	**#117**	**Printed electronics**	**13 Tue**
Villa Elena	**#109**	**Stimuli responsive: organic-inorganic materials**	**13 Tue**
Villani Fulvia	**#236**	**Printed electronics**	**14 Wed**
Vinci Antonio	**#331**	**Materials under extreme conditions and ultra–fast transitions**	**15 Thu**
Xia Zhenyuan	**#065**	**Mechanical properties of 2D materials composites**	**12 Mon**
Yahya Mohamed Fatema	**#141**	**Materials and processes for environmental protection and sustainability**	**13 Tue**
Zappia Stefania	**#031**	**Materials and processes for environmental protection and sustainability**	**12 Mon**
Zhang Qiaoming	**#118**	**Printed electronics**	**13 Tue**
Zimbone Massimo	**#101**	**Materials and processes for environmental protection and sustainability**	**13 Tue**
Zizzari Alessandra	**#005**	**Stimuli responsive materials**	**12 Mon**
Zontone Federico	**#312**	**Photovoltaics**	**15 Thu**
Zur Lidia	**#366**	**Optical fiber materials and devices**	**16 Fri**