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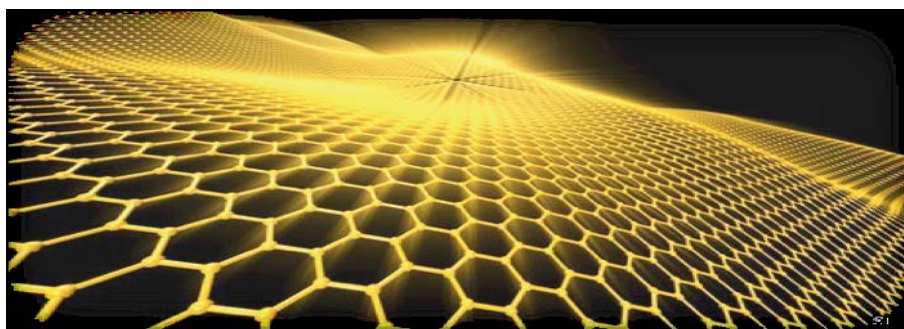
SCI Technological Workshop: Chemistry of graphene and applications in catalysis and polymer composites

Technological Workshop
Promoted by Commissione Rapporti con l'Industria
Società Chimica Italiana

**Chemistry of graphene
and
applications in catalysis and polymer composites**

Politecnico di Milano, Piazza Leonardo da Vinci 32 - Building 6, Aula G. Natta
Milan (I), 13 June 2019

BOOK OF ABSTRACT



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SCI Technological Workshop: Chemistry of graphene and applications in catalysis and polymer composites



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Gea Prioglio (Politecnico di Milano).

Program and Oral Presentations

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| 9.20 | Intercalation, functionalization, exfoliation of graphene related materials | <i>Gaetano Guerra (Università degli Studi di Salerno)</i> |
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| 10.20 | [14C]-Radiolabeling CNT and Graphene Related Materials for toxicological studies | <i>Antoine Sallustrau (CEA Saclay – Paris (F))</i> |
| 10.50 | <i>Coffee break</i> | |
| 11.10 | Selective edge functionalization for preserving sp ² carbon atoms in graphene layers | <i>Vincenzina Barbera (Politecnico di Milano)</i> |
| 11.30 | Graphene oxide coated polysulfone membranes for tap water | <i>Manuela Melucci (Isof- CNR - Bologna)</i> |
| 11.50 | Chemical sensors based on graphenic materials | <i>Fabio Di Francesco (Università degli Studi di Pisa)</i> |
| 12.10 | A molecular dynamics study of Protein adsorption on Carbon allotropes at different curvatures: from graphene to SWCNTs | <i>Giuseppina Raffaini (Politecnico di Milano)</i> |
| 12.30 | <i>Lunch and Poster Session</i> | |
| 14.00 | Supramolecular functionalization of graphene related materials for heat transfer applications | <i>Giuseppe Ferraro (Politecnico di Torino)</i> |
| 14.20 | Polyelectrolyte stabilized graphene nanoplatelets as building block for super gas barrier thin films | <i>Lorenza Maddalena (Politecnico di Torino)</i> |
| 14.40 | Can the MOF hybridization with graphene-like layers improve the CO ₂ adsorption at high pressure? | <i>Michela Alfè (IRC-CNR – Napoli)</i> |
| 15.00 | Graphene Related Materials for elastomer nanocomposites | <i>Luca Giannini (Pirelli Tyre - Milano)</i> |
| 15.20 | <i>Coffee break</i> | |
| 15.35 | G and GRM: fundamental properties and interaction with cement-based materials | <i>Marco Goisis (Italcementi Heidelberg Cement Group – Bergamo)</i> |
| 15.55 | Preliminary evaluation of nanostructured graphene for the removal of toxic trace organic pollutants from gaseous streams | <i>Stefano Cernuschi (Politecnico di Milano)</i> |
| 16.15 | A possible route to integrate eumelanin/graphene-like layers in conductive interfaces for bioelectronics applications | <i>Valentina Gargiulo (IRC- CNR - Napoli)</i> |
| 16.35 | Phosphorene: a rising star in the 2D world | <i>Maria Caporali (CNR- ICCOM - Firenze)</i> |
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| 1. | Graphene oxide promoted allylation of heteroarenes with alcohols | <i>Lorenzo Lombardi</i> (Università degli Studi di Bologna) |
| 2. | Growth of Porous MOFs on functionalized reduced graphene oxide | <i>Delia Blasi</i> (Università degli Studi di Milano) |
| 3. | Comparison between graphene and graphite silver nanoparticles nanocomposites | <i>Anna Facibeni</i> (Politecnico di Milano) |
| 4. | Assembly of pillared graphene oxide mesostructures | <i>Francesca Cardano</i> (IIT - Torino) |
| 5. | Edge functionalized graphene layers for better ultimate properties of elastomer nanocomposites | <i>Gea Prioglio</i> (Politecnico di Milano) |
| 6. | Aerogels with high strength from chitosan and exfoliated high surface area graphite | <i>Silvia Agnelli</i> (Università di Brescia) |
| 7. | Reimer-Tiemann and domino Reimer-Tiemann / Cannizzaro reactions on polyhydroxylated graphene layers | <i>Vincenzina Barbera</i> (Politecnico di Milano) |
| 8. | Overview on 3D printing techniques for graphene functionalized hydrogels | <i>Giulia Grassi</i> (Politecnico di Milano) |
| 9. | Electrically conductive inks: the role of graphitic materials | <i>Annalisa Sironi</i> (EPTATECH – Luisago (Co)) |
| 10. | Graphene for Energy Storage Applications | <i>Daniele Pontiroli</i> (Università degli Studi di Parma) |

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Intercalation, functionalization, exfoliation of graphene related materials

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The first part of the conference will describe preparation procedures and structural characterizations of graphite oxide, chemically reduced graphite oxide, exfoliated graphite oxide (often referred as graphene oxide, GO), which are the generally used precursors for bulk production of graphene materials. The main emphasis will be given to the crystalline order along different crystal directions [1].

Preparation and characterization of Graphite Oxide Intercalation Compounds (GOIC) will be also discussed [2,3]. When small ions, mainly inorganic, are intercalated, the observed crystalline structures generally exhibit a 3D long-range order, with relatively small distance between graphene sheets (< 0.6 nm), along the stacking direction. These 3-dimensional (3D) ordered GOIC generally also present order in the organization of the guest species in the interlayer space. For the intercalation of bulky ions, mainly organic, or of polar polymers, on the contrary, the crystalline order is generally limited to the distance between the graphite layers [3], which can largely increase (also up to 5 nm). By using suitable organic cations, the formation of new GOICs exhibiting a long-range order in the organization of the guest species in the interlayer space as well as a large distance between graphene sheets, can be achieved (Scheme 1) [2]. An analogous behaviour is observed for clay intercalates [4].

As for polymer nanocomposites, the relevant influence of edge-carboxylation of graphite based materials on mechanical and electrical properties of polymer composites will be also described [5]. Part of the lecture will be devoted to other kinds of 3D graphene: flexible paper and aerogels based on graphene oxide and graphene. As for graphene paper, possible routes for preparation of flexible and solvent resistant films is discussed [6]. As for aerogels, the presentation will be concentrated on *polymeric aerogels* with large amount of graphene, which can be used as catalysts or masterbatches for polymer processing [7].

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Characterization and the role of graphene nanoplatelets in origin and modified rubber matrices

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The requirements on modern elastomers used in several technical applications are increasing especially concerning heat stability, media stability, permeation behavior, electrical conductivity, strength and abrasion properties. Beside the selection of an appropriate polymer, an improved crosslinking system and other additives, the fillers play an important role. Nano-scaled materials like carbon nanotubes (CNT), nano-graphite nanoG), graphene platelets (GNP), graphenes and carbon-nanohorns (CNH) are fillers with high potential, caused by high specific surfaces and spheric porous or high aspect ratio morphologies. [1-4]. In the presented work different GNP-materials as such are characterized for their morphology, specific surfaces and adsorption properties by means of XRD, static gas adsorption and electron microscopy. Two different commercial types of GNP (xgC750 and xgM5) were used for the preparation of elastomer compounds on the base of polyisoprene (IR), nitrile-butadiene rubber (NBR), styrene-butadiene rubber (SBR) and slightly epox. (~8.8%) SBR. [6-8] The compounds were characterized for viscosity, vulcanization behavior, physicals, electrical conductivity and for the filler-polymer interaction by swelling experiments. All investigations are carried out in comparison to traditional used carbon black. The GNP xgC750 shows an extremely high specific surface of appr. 817 m²/g (N₂-adsorption). This effects a lower percolation threshold below 20 phr loading in IR or in SBR in comparison to GNP xgM5 or carbon black N 234. The GNP-compounds mixed using epoxidized-SBR show an improvement in rheological, dynamic-mechanical and thermal properties especially for xg C750. A stable filler networking using xg C750 and CB-N234 in the epoxidized rubber was demonstrated through multi-hysteresis measurements. Modification of GNP xgC50 by oxidation and esterification with dodecanol were carried out successfully, but the polymer –filler interaction in butyl rubber compounds (BIIR) could not be improved, because longer alkyl chains should be necessary. [9]

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¹⁴C-radiolabeling CNT and Graphene Related Materials for toxicological studies

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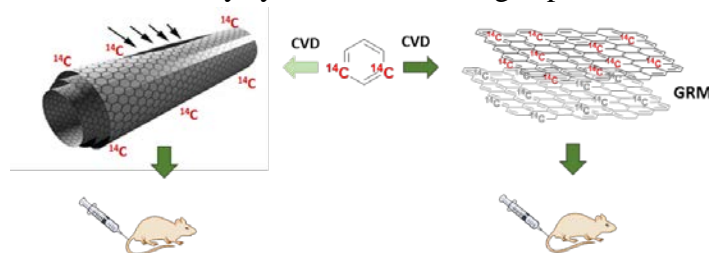
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The unique properties of Graphene Related Materials (GRM) and CNT opened the door for brand new biochemical applications and industrial perspectives. The availability of materials or dispersions of consistent quality has increased. However their commercialization process is still at a relatively early stage and the determinant question of their safety is still pending.

Radiolabeling of CNTs/GRMs with a long life radioactive nucleus, such as carbon-14, offers a unique tool to assess their biodistribution over long periods in animals and plants. Our laboratory has recently developed two straightforward and efficient ¹⁴C-radiolabeling techniques. Using a catalytic chemical vapor deposition (CCVD) method, utilizing ¹⁴C-labeled benzene as carbon source,² CNTs/GRMs were successfully synthesized with high specific activities.



Toxicological studies have then been investigated showing the ability of MWCNTs to translocate in different organs and to cross the air-blood barrier. Further investigation on GRM showed biological persistence but without any translocations. Over 12 months, MWCNTs/GRM increasingly accumulate in these organs, indicating a bio-persistence of these nanoparticles. Such preliminary results may raise safety concerns for humans in working places.

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Selective edge functionalization for preserving sp^2 carbon atoms in graphene layers

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sp^2 carbon allotropes, such as carbon black, carbon nanotubes and graphene related materials can be seen as made by graphene sheets differently assembled. The graphene sheet is the common feature in all the carbon allotropes and it is a substrate for performing chemical reactions. In the present work, functionalization reactions were performed [1-3] with the aim to introduce functional groups with heteroatoms such as oxygen and nitrogen, without altering the structure of the graphitic substrates. Functionalization was performed by using pyrrole derivatives or KOH: (i) primary amines were combined with α,δ dicarbonyl compounds and the resulting molecules were able to functionalize sp^2 carbon allotropes, with high efficiency. Indeed, the reactions, performed by simply donating either thermal or mechanical energy, were characterized by a yield up to 96% and by an atom efficiency up to 80%. The structure of the graphitic substrates remained substantially unaltered, after the reaction; [1-2] (ii) KOH was reacted with a nanosized graphite with very high surface area (HSAG), higher than 300 m^2/g . Polyhydroxylated carbon allotropes were obtained. Layers were then decorated with aldehydic groups, in ortho position with respect to the hydroxyl ones. [3]

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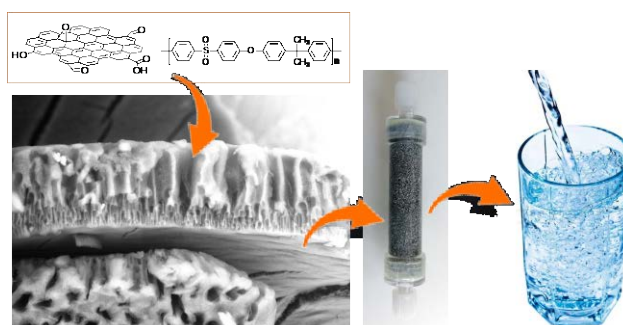
Graphene oxide coated polysulfone membranes for tap water purification

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The increase of contamination sources and the depletion of fresh water are topics of great current concern. Graphene oxide nanosheets seem promising as adsorbent for water purification. However, their processing in macroscopic filters is challenging, and their cost vs. standard polymer filters is too high. Here, we describe a simple approach to fix graphene oxide (GO) sheets on commercial polysulfone (PS) membranes [1,2] for improved removal of organic contaminants from water. This strategy requires minimal amounts of GO, deposited directly on the surface of the polymeric membrane, followed by fixation using microwaves or conventional heating.[3] The purification efficiency of the GO modified membranes is significantly improved vs. benchmark commercial PS, as demonstrated by removal of two model contaminants, Rhodamine B a textile dye and Ofloxacin a quinolone antibiotic. The adsorption of contaminants on the PSGO membranes follows the Brunauer-Emmet-Teller (BET) model, with partial swelling and intercalation of the molecules in between GO layers. The stability of the GO coating is confirmed by extensive filtration tests (100 h) by UV-vis spectroscopy.



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Chemical sensors based on graphenic materials

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In addition to fulfillment of unmet needs, cost and reliability represent major determinants for introducing new technologies in routine use. Graphene oxide and reduced graphene oxide can be produced in large quantities by the oxidation of graphite through a modified Hummer's method and consequent reduction with ascorbic acid or other reducing agents. These materials are sensitive to modifications of their chemical environment, so that they can be potentially used for the mass production of cheap chemical sensors. We report here the fabrication, testing and validation of disposable sensors based on graphene oxide and reduced graphene oxide for the potentiometric measurement of pH [1]. The combination of such pH sensor and suitable enzymes (e.g. urease) can be used to measure other chemical parameters (e.g. urea) by monitoring pH levels at the sensitive layer/sample interface [2]. It will be shown how these sensors can be used for quite different applications, like remote monitoring of marine pH levels or urea levels in blood of patients undergoing dialysis.

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A molecular dynamics study of Protein adsorption on Carbon allotropes at different curvatures: from graphene to SWCNTs

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Protein adsorption on carbon allotropes is a very important process in different fields. Using molecular dynamics (MD) simulations the adsorption of an albumin fragment, the most abundant blood protein, and of two fibronectin modules, important for cell adhesion, are studied to understand the first interaction when biomedical devices interact with biological fluids. Graphene favourably interacts with proteins, while two flat planes yield better interaction inducing larger conformational changes for the softer albumin [1], compared to fibronectin because of its stable β -sheets [2]. Interesting is the peculiar surface ordering obtained upon adsorption, as experimentally found [3].

Different topographies of carbon nanostructures influence protein adsorption. Armchair SWCNTs, similar to a graphene surface having different curvature, interact with proteins both on the external and on the internal surface. Using MD simulations it was found that increasing the curvature, increases the interaction strength. When encapsulated in the inner nanotube surface, proteins better interact maximizing the adhesion on the CNTs surface, forming non-covalent complexes with larger stability [4].

Considering finally armchair and chiral CNTs having similar curvature, the adsorption of an albumin α -helix on outer convex and on inner concave surface is studied. In the final adsorbed state, the oligopeptide maximizes its contact with the surface, displaying complexes with unlike stability. Therefore, MD simulations in this theoretical study suggest the possible separation of chiral enantiomeric nanotubes by interaction with chiral oligopeptides [5]. In addition, they suggest the possible use of aligned chiral SWCNTs as stationary phase for racemic mixtures separation, and in proteomics, because favourable protein–nanotube interaction would yield different retention times.

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Supramolecular functionalization of graphene related materials for heat transfer applications

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Graphene nano-papers fabricated from Graphite nano-Platelets (GnP) showing potential in thermal management applications because they have excellent thermal properties related to unique intrinsic thermal conductivity of individual graphene sheets [1].

The high conductivity, associated to defect-free sp² structure, drastically decrease at the interfacial thermal resistance between nano-platelets [2], so, non-covalent functionalization was performed employing a new class of organic compounds BisPyrene-based (BP) whose spacers are different chain length and the polycyclic aromatic hydrocarbons (PAHs) 7r-7r interact with graphene surface [3], building molecular junctions between GnP.

The aim of this work is to enhance the thermal conductance at the interface, aiming to fabricate higher efficiency nanopapers exploitable as heat spreader.

Supramolecular functionalized GnP (s-GnP) were characterized by fluorescence, UV-Vis and Raman spectroscopy, confirming the formation of network GnP based linked by BP molecules. The relationship between structures that use different chain length as spacer and relative thermal proprieties were investigated by Light Flash Analysis (LFA) and X-ray diffraction (XRD), showing higher thermal diffusivity for shorter BP's junctions (Figure 1).

Finally, nanopapers were validated as heat spreaders used to cool down a hotspot simulating the overheating of electronic component, evidencing better performance than Cu and Al most commonly used as spreader in electronics.

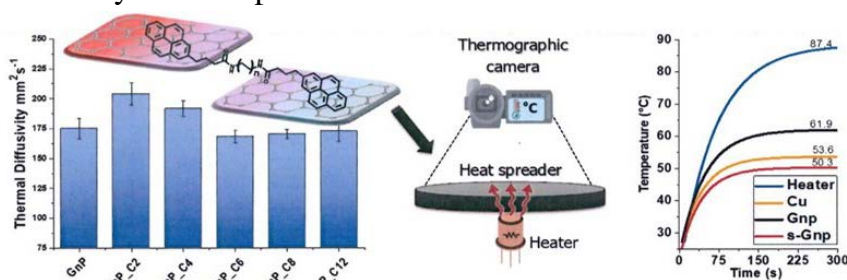


Figure 1. Schematic representation of supramolecular functionalizations of GnP and relative LFA analysis (on the left) and experimental set-up for the thermal proprieties characterization as heat spreader (on the right).

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Polyelectrolyte stabilized graphene nanoplatelets as building block for super gas barrier thin films

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Liquid exfoliation is one of the most investigated and useful technique adopted for the production of few layers graphene in large quantities [1]. However, recent stringent policies aimed at safeguarding the environment discouraged the use of organic solvents in large quantities thus promoting water as preferred dispersion medium for graphene [2]. Within this context, polyelectrolytes with high charge density have been demonstrated to be good candidate as dispersing/stabilizing agents for multilayer graphene in water [3]. In this work, graphite nanoplatelets (GnP) were ultra-sonicated in water solution of polyacrylic acid (PAA) and branched polyethylene imine (BPEI), without the presence of other additives or stabilizing agents in order to obtain water-based GnP suspensions. The prepared GnP/PAA (GP) and GnP/BPEI (GB) were used for the preparation of a layer-by-layer (LbL) assembled coating able to enhance gas barrier properties of PET films (Figure 1a). Only 5 BL GB-GP are sufficient to double the gas barrier performances in both dry and humid conditions as compared to the 5BL B-P. Surprisingly, a 10 BL GB-GP coating achieved Oxygen Transmission Rates below detection limit (<0.005 cc /m² day atm) outperforming a 10 BL coating built with just the two polyelectrolytes (Figure 1b) [4]. The good performances detected for the prepared coatings open new scenery of application for polymeric films such as electronic packaging.

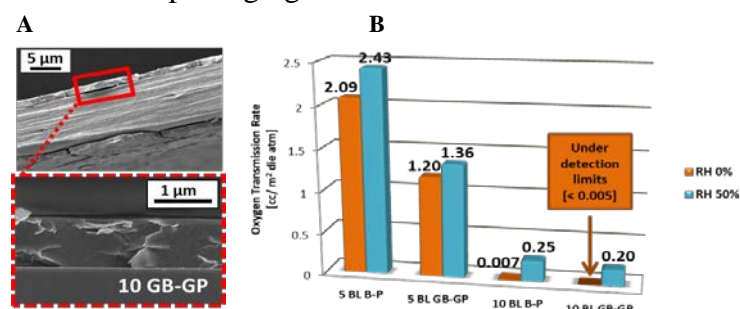


Figure 1. a) SEM micrograph of 10 BL GB-GP PET film cross-section and detail of the coating. b) Comparison of Oxygen transmission rate for 5BL B-P, 10 BL B-P, 5BL GB-GP and 10 BL GB-GP membrane.

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Can the MOF hybridization with graphene-like layers improve the CO₂ adsorption at high pressure?

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Metal-organic frameworks (MOFs) are a newly consolidated class of highly-porous coordination polymers assembled by coordination bonds between metal ions (or clusters) and organic linkers, having varied and fascinating 3D topologies, high surface areas (up to 3000 m²/g) and tunable porosity and composition. MOF are catalyzing a fast-growing interest in carbon capture and storage (CCS) technology and selective CO₂ sorption applications [1] thanks to their stability also in presence of common flue gas components such as SO₂ and NO_x. In MOFs, both metallic centres and organic ligands play a relevant role in CO₂ coordination through specific linkages and interactions. Much efforts are ongoing to boost the gas sorption and/or selectivity toward specific gases; in this context the hybridization with graphene related materials (GRM) [2, 3] leading to modifications of the MOFs moiety (generation of unpaired metallic sites, surface polarity tuning, pore size distribution tuning) is one of the currently explored options. The MOF/GRM composites are often produced adopting a one-pot strategy that allows embedding graphenic materials with functional groups able to synergistically enhance the sorption of specific analytes. The question is: how is the real gain in embedding GRM materials in MOF moiety for CCS practical applications? Trying to reply this question, we produce three 3,5-benzenetricarboxylic acid (BTC)- based MOFs embedding a GRM (namely graphene like layers, GL [4, 5]). The selected MOFs differ in metallic centre (Cu, Al, Fe), morphology, pore chemistry and textural properties exhibiting coordinatively unsaturated metal sites and high thermal stability [6]. GL layers consist of short graphenic layers with a high colloidal stability in water (particularly suitable for wet chemistry synthetic approaches), produced by a two-step oxidation/reduction wet treatment of a high surface carbon black (CB). The MOFs adsorption/desorption tests have been carried out at room temperature in the pressure range 0 ÷ 8.0 MPa for H₂, 0 ÷ 5.0 MPa for CH₄ and 0 ÷ 1.5 MPa for CO₂ respectively, using an optimized volumetric apparatus f-PcT (fast Pressure–concentration–Temperature) for accurate and reliable gas adsorption measurements [7].

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Società Chimica Italiana

SCI Technological Workshop: Chemistry of graphene and applications in catalysis and polymer composites

Graphene Related Materials for Elastomer Nanocomposites

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Elastomer are pervasive in daily life: they are the main constituent of shoe soles, tires, antivibration systems in vehicles and buildings, and are present in elastic garments, toys, etc.

In many applications, elastomers are formulated with nano-structured fillers such as Carbon Black or Silica, generating nanocomposites, to reach the desired mechanical performances.

In recent years, new (nano)materials were developed as fillers for elastomer compounds: C-based materials, in particular Graphene, nano-graphite and CNTs, are the most prominent group of such (nano)materials.

Patent and literature trends of the use of graphene and related materials in Elastomers are reviewed, with focus on tires, representing a high volume and very challenging application of Elastomer Nanocomposites.

New Materials and Technologies are a fundamental part of Pirelli's Innovation Strategy, tackled through an open Innovation Model: the contribution includes results obtained through collaborative research promoted by Pirelli on Graphene Related Materials as fillers for Rubber Nanocomposites.

G and GRM: fundamental properties and interaction with cement-based materials

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Potential of graphene and related materials is becoming increasingly clear as research proceeds (1). Cementitious materials have undergone considerable development in recent years with the use of more sophisticated admixtures and it is not surprising that research is going so far as to consider graphene and other graphene-related materials (G&GRM) as an opportunity also for this sector. Moreover the leadership of cementitious materials among man made products, as regard worldwide volumes and the indispensable role played by cement (2)(3), further justifies the investigation on possible application of G&GRM to enhance fundamental properties of the inorganic composite (4). From the chemical point of view graphene is a one-atom-thick layer of carbon atoms arranged in a hexagonal lattice. Nevertheless, the interest aroused by the potentiality of graphene has caused a proliferation of graphene producers and hence products which are based on a wider range of structures. Therefore graphene should be considered a class of materials, rather than a well-defined chemical structure, within the common meaning of the term. As a matter of fact the exfoliation of graphite generates several different products depending on number of graphene layers, average lateral size and carbon to oxygen atomic ratio (if oxidation is part of the process). Starting from this context, the presentation shows the possible interaction of graphene nanoplatelets (GNPs) and graphene oxide (GO) with cement and consequently the relevant potential applications in the cementitious composite. Questions such as dispersibility, interactions with cement hydrates, modification of cementitious matrix morphology, effect on porosity and strength are presented on the basis of the current state-of-art.

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Preliminary evaluation of nanostructured graphene for the removal of toxic trace organic pollutants from gaseous streams

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Nanotechnology and nanomaterials applications have seen a large and intensive development during recent years, with significant commercial utilizations encompassing novel materials in several advanced industrial engineering sectors: electronics, chemical and manufacturing engineering, energy conversion and storage, sensors and metrology, medicine and bioapplications. Some promising technologies involve also environmental engineering applications, with demonstrated utilizations already available in the field of electrocatalysis and oil remediation from accidental spills. Nevertheless, the potential for exploiting graphene for its utilization in the removal of gaseous compounds through adsorption processes, despite its enhanced capabilities with respect to conventional sorbent materials, it's still rather limited. The paper reports the main results of an experimental laboratory evaluation for establishing preliminary capabilities of exfoliated nanostructured graphene in the adsorption removal of trace organics from industrial gaseous streams. Investigations were performed utilizing 4-chlorophenol as a surrogate for typical chlorinated compounds present in waste to energy emissions (mainly dioxins and furans) in a laboratory adsorption bench. Tests were conducted by running in parallel the system with sorbent materials normally utilized in commercial full scale applications of the technology, constituted by granular activated carbon, in order to address comparatively the capabilities of graphene in the same operative conditions. Process performance was evaluated in terms of the main parameters utilized within adsorption technologies, namely removal efficiencies and sorption working capacities per unit mass of sorbent in the different inlet concentration ranges investigated. Results obtained clearly demonstrate highly enhanced performance of graphene with respect to conventional activated carbon in the whole ensemble of conditions evaluated, with most significant results observed for the nanostructured material supported on proper solid fiber substrates, showing very interesting potentials for its practical utilization at full scale plants.



A possible route to integrate eumelanin/graphene-like layers in conductive interfaces for bioelectronics applications

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In the manifold of available biocompatible materials to be implemented as functional bio-interfaces, the human pigment eumelanin (EU) is currently gaining increasing interest. EU is the only one, among the five kinds of natural melanin pigments, showing a weak electrical conductivity. A currently explored strategy to improve and tune its electrical properties is the integration with conductive graphene related materials (GRM) [1], opening new perspectives in the field of bioelectronics. In this context we designed and synthesized conductive interfaces by an efficient integration of EU and a newly GRM, namely graphene like (GL) layers [2-3]. GL layers were obtained by a two-step oxidation/reduction wet treatment of a carbon black [4,5]. The water stability of GL over a wide pH range and the self-assembling tendency make this material suitable for the production of hybrid materials in water suspension. At first a hybrid material (EUGL) was synthesized integrating EU and GL in a mass ratio of 1:1 by in situ polymerization of the eumelanin precursors in presence of GL. This material exhibited quite good adhesion to hydrophilic and hydrophobic surfaces, water stability, biocompatibility and improved electrical conductivity compared to the sole EU [2]. To deepen the structural relationship between the two counterparts (EU and GL) when integrated in the same material, different hybrid materials (EUGLs) were then synthesized by in situ polymerization of the eumelanin precursor DHI in presence of growing amounts of GL layers and structurally characterized also implementing advanced techniques (solid state NMR (ssNMR) and resonant photoemission spectroscopy [3]). ssNMR data indicated that structural and packing modifications occur in the hybrids with respect to EU. Such tighter packing of the constituent units was then supposed responsible for the improved electrical conductivity of the hybrids.

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Phosphorene: a rising star in the 2D world

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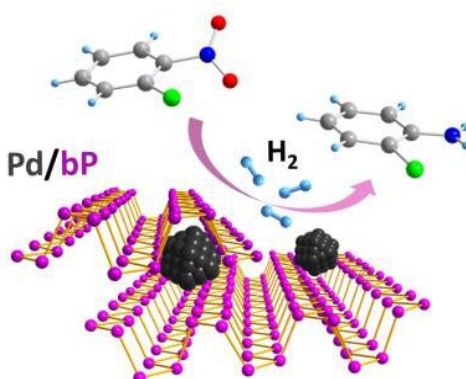
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Since its discovery in January 2014, phosphorene, the new 2D-material prepared by exfoliation of black phosphorus and formed only by P atoms, has attracted scientists for its fascinating electronic and optical properties.¹ At variance with graphene, this new single layer material has free electron pairs onto its corrugated surface that in principle can interact with metal ions, metal-ligand fragments and organic molecules.

In our labs, the surface functionalization of phosphorene with transition metal nanoparticles² was studied, and in particular for the first time EXAFS analysis was carried out to elucidate the nature of the interaction between P atoms and metal nanoclusters. Afterwards, the application of the new nanohybrids, Pd/bP and Ni/bP, in selective catalytic hydrogenation was investigated.



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Graphene oxide promoted allylation of heteroarenes with alcohols

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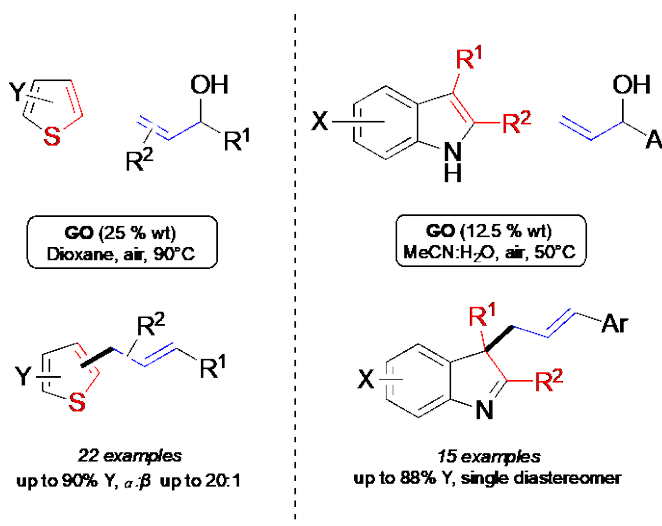
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In recent years a great research interest has been addressed to the application of graphene-based materials in organic synthesis as benign, abundant and metal free heterogeneous catalysts, leading to dramatic advantages over traditional synthetic metal-based methodologies.^[1] In this work the use of graphene oxide (GO) as a promoter for allylic Friedel-Crafts alkylation of thiophenes and dearomative allylic alkylation of indoles with alcohols will be presented.^[2]

The titled methodologies enable the functionalization of arenes in good yields under mild conditions (reagent grade solvents, air) and very low promoter loading.

Mechanistic investigations using DFT calculations and XPS analysis suggest that in both cases the “grafting” of the alcohol to the graphene surfaces by an epoxide-ring opening event, constitutes the crucial step for the process.



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Growth of Porous MOFs on functionalized reduced graphene oxide

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Metal Organic Frameworks (MOFs) are porous crystalline materials showing 1, 2 and 3 dimensional extended frameworks that are sustained by coordinative chemical bonds between organic ligands and metal cations/clusters.^[1] Their use in many different technological fields has been proposed and intensively studied.^[2] Currently, great interest is focused on the development of their composites with different materials in order to improve their properties.^[3] In this field of particular interest are the composites of MOFs with graphene where the high porosity of one component (MOFs) is combined with the high mechanical resistance and thermal and electrical conductivity of the other (graphene).

Here we present our results on the synthesis and characterization of composites of some well-known porous MOFs with reduced graphene oxide (rGO) functionalized with benzoic acid. The synthetic procedures and characterization with different analytical techniques of the obtained materials in comparison to the pure MOFs will be described and discussed.

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Comparison between graphene and graphite silver nanoparticles nanocomposites

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Polymeric nanocomposites represent a class of materials, somehow alternative to traditional composite materials. They are characterized by the presence of inorganic fillers with nanometric size (at least in one dimension) in this way generating considerable improvements of mechanical properties and performances. Metallic nanoparticles and carbon-based materials (CNT, graphite¹, graphene²...) are added to the polymer matrix to gain additional properties like magnetic, electrical, optical and antibacterial. It is well known that graphite or graphene and AgNPs (silver nanoparticles) can improve polymeric matrixes with regards to conductivity and antibacterial properties.

The aim of the present work was to compare PVA³ thin film filled with graphite or graphene decorated by AgNPs through a technique mediated by an in-house developed process.⁴ Nanocomposite synthesis included: 1) water dissolution of polymer PVA; 2) graphite or graphene suspending in the same solvent and sonication; 3) mixing of the two mixtures; 4) AgNO₃ solution adding; 5) ascorbic acid and citrate solutions adding; 6) sonicating the suspension for 15'. Silver and graphite/graphene overall concentrations were 0.04% and 0.4% w/w respectively. The obtained mixture was suitable to obtain deposited or free-standing film for characterization purposes by SEM, AFM, Raman and XRD.

By SEM investigation, graphite and graphene distribution in PVA polymer matrix turned out to be satisfactory and AgNPs growth occurred mainly on both carbon materials.

Raman spectroscopy analysis highlighted that in absence of AgNPs only confused and noisy signal could be obtained for the polymer with graphite or graphene. The presence of AgNPs enhanced the Raman peaks of graphite and graphene as well as those originated by polymer vibrational modes thus making the Raman measurement a sort of AgNPs presence indicating method. In fact, according to literature, G and 2D graphite bands change in shape, position and relative intensity with number of graphene layers⁵.

By AFM analysis we can characterize above all the nanocomposites filled with graphene⁶.

Nanocomposites were successfully obtained by in-situ synthesis of AgNPs through direct reduction of silver ions on graphite or graphene immersed in polymer solutions. With respect to the powder-based processes, the type of synthesis here described yields a greater homogeneity.

These promising results suggest possible developments of this research such as i) to evaluate the impact of carbon-based materials and AgNPs concentration in the polymer matrix on nanocomposite electrical properties; and ii) to replace dissolved polymers with natural textiles.

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Assembly of pillared graphene oxide mesostructures

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Multilayers' Graphene Oxide based mesostructures have shown appealing features for several applications, ranging from membranes' assembly to gas storage purposes.¹ In order to obtain high performing materials, the possibility to use molecular pillars, with defined shape and size, for the direct chemical functionalization of pristine Graphene Oxide (GO) substrates, represent a good tool for the achievement of these goals.² In the last years we have investigated a novel pillared material obtained by the solvothermal reaction of GO, and tetrakis(4-aminophenyl) methane (TKAm) molecules.³ The molecules, due to the presence of 4 amine groups and for their 3D conformation, easily link between the GO sheets. These porous materials have presented high stability, a good interlayer distance up to ~ 14 Å, a specific surface area (SSA) over 600 m²/g and they have been tested in their hydrogen sorption capabilities. Due to the promising obtained results, we have designed new molecules with the aim to use them for a covalent functionalization of GO to improve the performances of such hybrid structures. Indeed, we have synthesized a small library of compounds characterized by the presence of aldehyde moieties at their extremities. These functional groups are useful to achieve the formation of imine bonds with modified GO to obtain more flexible GO-based 3D materials with better performances. Moreover, we have also assembled mesostructures pillared with azobenzenes (AB) subunits presenting amine functional groups to easily link them to GO and we are now investigating their properties. We have chosen AB photo-switchable molecules, for their well-known properties and for the good results obtained by these photo-responsive materials in the last decade.⁴ The possibility to change the chemical conformation of AB entities, using simple and precise stimuli like light or heat, is a promising tool to prepare new hybrid materials with interesting and useful properties. The precise distance of the GO layers, the pores' size, the high surface area, typical of these materials, and eventually the possibility to control their properties with external stimuli, are paving the way for applications in several research fields, from energy storage purposes and membrane preparation to application in the biological realm.

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Edge functionalized graphene layers for better ultimate properties of elastomer nanocomposites

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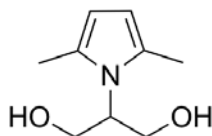
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This work considers elastomer nanocomposites based on natural rubber (NR) and high surface area graphite (HSAG), either pristine or functionalized with a biobased janus molecule, 2-(2,5-dimethyl-1H-pyrrol-1-yl)-1,3-propanediol (SP) also named as serinol pyrrole (HSAG-SP) [1-3]. SP is depicted in the picture below.



Nanocomposites based on pristine HSAG were prepared through melt blending while the ones containing HSAG-SP were prepared through latex blending.

The functionalization of HSAG with SP appears to lead to: lower viscosity, a comparable vulcanization kinetics, a lower Payne effect from shear strain sweep analyses, better tensile ultimate properties and an improved fracture behavior [4].

All these experimental findings seem to suggest that functionalization of HSAG with SP allows a better dispersion of the filler in the rubber matrix. Such better dispersion is probably due to the synergistic effect of the functionalization of HSAG with polar groups and the preparation of the composite through latex blending.

Functionalization therefore appears to be a promising tool for the reduction of the amount of filler in the composite, allowing the design of high performance, lighter and more sustainable materials for tyre applications.

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Aerogels with high strength from chitosan and exfoliated high surface area graphite

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In this work, monolithic carbon aerogels are obtained by mixing chitosan (CS) and a high surface area nanosized graphite (HSAG) in water in the presence of acetic acid. The aerogels are produced by an eco-friendly, inexpensive, simple process for producing high-quality graphene aerogels, potentially suitable for electrodes in supercapacitors [1]. Aim of this work is to optimize the mechanical strength of the aerogels by varying the composition. The HSAG/CS ratio, water content and acetic acid content were varied. Mechanical strength was measured by uniaxial unconfined compressive tests, and cyclic tests were also performed to get more information about the deformation mechanisms. All the aerogels show a dissipative behavior at any strain level. The results show that high levels of strength, up to 100 kPa at 50% compressive strain, can be obtained at a low bulk density (0.05 g/cm³) with a suitable choice of composition.

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Reimer-Tiemann and domino Reimer-Tiemann / Cannizzaro reactions on polyhydroxylated graphene layers

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Graphene layers were selectively edge-functionalized with oxygenated functional groups, maintaining their bulk structure essentially unaltered. A reaction was performed between polyhydroxylated graphene layers (G–OH) and CHCl₃/KOH/H₂O. When the reaction with KOH/H₂O was performed at 0 °C, by adding successive portions of CHCl₃, the functionalization occurred with aldehydic functional groups. When G–OH reacted with CHCl₃/KOH at room temperature, benzylic alcohol and carboxy groups were introduced. XPS, IR, Raman, and WAXD analyses indicated that the graphene layers were chemically modified with the abovementioned functional groups, without intercalated and/or absorbed molecules. It can thus be assumed that functionalization of G–OH with aldehydic groups occurred through the Reimer–Tiemann reaction and that the domino Reimer–Tiemann/Cannizzaro reaction led to aldehyde disproportionation. As further evidence and the first viable usage of the functionalization with aldehydic functional groups, chitosan was crosslinked with the graphene layers, obtaining flexible and electrically conductive carbon paper.[1]

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Overview on 3D printing techniques for graphene functionalized hydrogels

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Hydrogels represent one of the most suitable solutions for regenerative medicine, being widely employed in bio-medical engineering, especially as vehicles for drug delivery, cells encapsulation and printing of biological tissues. ^[1,2] A step toward the development of these applications is the possibility to 3D print hydrogels. As a consequence, the creation of smart micro-structures layer by layer will lead to more complex mechanical properties. However, most hydrogels do not exhibit high stretchability, toughness, stiffness and mechanical stability. ^[3,4]

To solve this issue, different strategies can be pursued, such as the addition of nanoparticles or fibers into the hydrogel.

Among the materials which can be used for the hydrogels functionalization, graphene is highly employed. Not only this material is non-toxic and bio-compatible, but also it improves the electrical properties of the films, as well as conferring mechanical stability to the 3D printed objects. ^[5,6,7]

In this overview we will focus both on 3D printing techniques available for soft-materials and on biomedical applications of hydrogel-graphene composites.

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Electrically conductive inks: the role of graphitic materials

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Electrically conductive inks are the foundations of printed electronics as they allow to print circuits on different surfaces. In wearable applications, the surface is often fabric and therefore circuits have to undergo elastic deformations, due to body movements, without losing their functional performances: in a nutshell, they have to be bendable and stretchable.

Two industrial-grade conductive, stretchable, screen-printable inks have been produced starting from some simple formulas developed at a lab scale which rely on a technology that helps the filler dispersion in the polymeric matrix. One ink is based on carbon black only and the other one is based on carbon black and graphite. Samples obtained using the so-called transfer printing technique (very common in the textile industry) have been subjected to progressive elongations and to cyclic elongations while electrical resistance data were recorded by a multimeter. The effective contribution of the graphitic portion is clear in lowering the static resistance value, in the entirety of conductivity regained after stretching to 100% and in stabilizing the cyclic elongation performance. This positive effect can be probably explained considering graphite lamellas as bridges connecting carbon black clusters and ensuring a more continuous electric path.

Graphene for Energy Storage Applications

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The progressive depletion of fossil fuels with a consequent production of electric and hydrogen vehicles and the studies on future smart-grids, open the way to an intensive research to produce more performing devices for both energy harvesting and storage. In this scenario, the development of innovative technologies exploiting novel carbon nanostructures could be the winning strategy, thanks to their low cost, unique mechanical, electronic and structural properties and to the intrinsic environment-friendly character of carbon. In this work we give an overview of the recent advances in the field of energy accumulation, conversion and storage, obtained in the “Nanocarbon Laboratory” at the University of Parma. In particular graphene-based materials demonstrated to be promising for the development of novel Li-/Na-/Mg-ion batteries [1], supercapacitors (SCs) and direct/indirect solid-state hydrogen-storage systems [2]. Graphene obtained from thermal exfoliation or laser conversion of graphite oxide, either in their pristine form, or decorated with metal oxide nanoparticles (NPs), can be efficiently used as a negative electrode in new ion batteries and high performance SCs. In fact, the replacement of the conventional anodes with graphene has shown to increase the charging capacity of the battery and can also work with ions much cheaper than Li, such as Na and Mg. Moreover, in order to further enhance performances of the electrochemical devices, one of the main successful strategies is combining graphene with transition metal oxides, which introduce pseudo-capacitive effects, allowing an improvement in specific capacities of the devices [3]. Eventually, metals nanoparticles decorated graphene can be considered a promising material for hydrogen storage, due to the possibility to modify the interaction energy with the hydrogen molecule. In particular, it is well known that the fundamental physical and chemical properties of materials can change drastically when entering the nano-size regime. Hence, one can expect significant changes in hydrogen sorption properties, such as improved kinetics and reversibility, as well as the optimization of the binding energy. For this reason, we have synthesized and optimized several graphene-based materials decorated with transition metals NPs investigating their properties for hydrogen storage applications.

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