

**AICIng**

Associazione Italiana di Chimica  
per Ingegneria



**POLITECNICO**  
MILANO 1863



Società Chimica Italiana  
Divisione di Chimica  
per le Tecnologie

# **XIII Congresso Nazionale AICIng e II Congresso Nazionale della Divisione di Chimica per le Tecnologie della SCI**



## **ATTI DEL CONVEGNO**

**25-28 giugno 2023**  
**Politecnico di Milano**

**XIII Congresso Nazionale AICIng e II Congresso Nazionale della Divisione di Chimica  
per le Tecnologie della Società Chimica Italiana**

ATTI DEL CONVEGNO

**25-28 Giugno 2023 - Milano**

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*a cura di:*

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ISBN 978 88 3623 147 8

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XIII Congresso Nazionale AICIng - Il Congresso Nazionale della Divisione di Chimica per le Tecnologie della SCI  
Politecnico di Milano, 25-28 giugno 2023

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# AICIng

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## Saluto dei Presidenti AICIng e DCT-SCI

Carissimi Colleghi,

La tredicesima edizione dell'appuntamento biennale per il Convegno Nazionale dell'AICIng presenta una novità importante, perché si svolge per la prima volta in maniera congiunta con il II Congresso Nazionale della Divisione di Chimica per le Tecnologie della Società Chimica Italiana.

A tutti i congressisti arrivati a Milano per partecipare al Convegno porgiamo il più caldo benvenuto dei Consigli Direttivi ed i nostri personali.

L'AICIng ha superato i 20 anni di attività e rimane un punto di riferimento per le attività istituzionali del nostro settore e l'edizione congiunta con la più giovane Divisione della SCI vuole sottolineare la sinergia esistente fra le due associazioni, in un momento così importante per l'Università italiana, superato il complesso periodo dovuto all'emergenza pandemica e di fronte alla sfida costituita dai progetti collegati al PNRR.

Il compito che ha sempre caratterizzato la comunità dell'AICIng è quello di guidare gli allievi ingegneri nell'apprendimento della Chimica e delle sue applicazioni all'Ingegneria ed in questo coopera con la Divisione di Chimica per le Tecnologie della Società Chimica Italiana, che raccoglie al suo interno i ricercatori che nelle Università, Enti di Ricerca ed aziende, operano nel settore della ricerca che utilizza i Fondamenti Chimici delle Tecnologie.

Esempio di tale legame è rappresentato dal premio AICIng assegnato in questa edizione al prof. Salvatore Failla, che è stato presidente dell'AICIng e ha guidato anche la costituzione della Divisione di Chimica per le Tecnologie.

Per rappresentare lo stretto legame tra la didattica, la ricerca accademica e industriale nel corso del convegno verrà svolta, come da tradizione dei nostri convegni, una Tavola Rotonda dal titolo "Dalla ricerca all'innovazione. Il ruolo del trasferimento tecnologico", organizzata dal prof. Maurizio Galimberti, a cui parteciperanno diversi relatori che rispecchiano realtà del mondo accademico ed industriale.

La qualità dei contributi scientifici dimostra chiaramente la ricchezza delle nostre tematiche di ricerca del settore, rispecchiando la sua specificità come "Fondamenti Chimici delle Tecnologie", capace di attivare la cooperazione tra numerosi gruppi del nostro settore, elementi che sono sempre stati un punto di forza dell'AICIng. Una menzione speciale va ai giovani Dottori di Ricerca a cui sono stati assegnati i Premi per le migliori Tesi di Dottorato e che rappresentano sia la vivacità che il futuro del nostro settore.

Un ringraziamento speciale va infine al Comitato Organizzatore Locale, i cui membri hanno lavorato con entusiasmo e passione per permettere lo svolgimento di questo convegno.

Il Presidente dell'AICIng Prof. Roberto Paolesse

Il Presidente DCT-SCI Prof. Piero Mastrorilli

## Saluti di Benvenuto ai Congressisti

Carissime/i colleghe/i,

come comitato organizzatore, vi porgiamo un caloroso benvenuto al XIII Congresso Nazionale dell'Associazione Italiana di Chimica per Ingegneria (AICIng) e al II Congresso Nazionale della Divisione di Chimica per le Tecnologie della Società Chimica Italiana (DCT-SCI).

Il Congresso si svolge quest'anno presso il Politecnico di Milano nella sua sede storica del Campus Leonardo, e sarà un'importante occasione di confronto tra i docenti degli Atenei italiani CHIM/07 e i loro allievi, i quali avranno l'opportunità di presentare i più recenti risultati della loro attività di ricerca scientifica orientata alla chimica di base ed applicata in ambito industriale, ambientale e biomedico, e di discutere sulla didattica chimica erogata nei corsi di Ingegneria.

I lavori del convegno, i cui atti saranno pubblicati esclusivamente in formato elettronico, sono articolati in forma di Conferenze Plenarie, Keynote, Comunicazioni Orali e conferenze da parte di giovani ricercatori a cui sono stati conferiti i premi AICIng per le migliori Tesi di Dottorato.

Una selezione di contributi al Congresso sarà anche pubblicata in una *Special Issue* della rivista *Molecules* (MDPI) intitolata "*From Molecules to Materials, Devices and Processes: The Chemical Basis of Novel Technologies*". Come da tradizione, ci sarà anche una articolata Sessione Poster che, assieme ai vari eventi sociali, consentirà la più ampia interazione tra i partecipanti.

Il Comitato Organizzatore rivolge un sentito ringraziamento ai Direttivi dell'AICIng e della Divisione di Chimica per le Tecnologie della SCI, al Politecnico di Milano e al Dipartimento di Chimica, Materiali, ed Ingegneria Chimica "G. Natta", a Fondazione Politecnico e agli Sponsor che hanno collaborato per la riuscita di questo Convegno, oltre che a tutti i partecipanti per la loro presenza.

Un ringraziamento particolare va anche ai dottorandi Stefano Elli, Lorenzo Guaita, Pietro Milesi e Simone Naddeo, che hanno contribuito alla buona riuscita del Congresso.

Infine, ai conferenzieri e a tutti i partecipanti rivolgiamo l'augurio di buon lavoro e di un piacevole soggiorno a Milano.

*il Comitato Organizzatore XIII Congresso AICIng e II Congresso DCT-SCI*

*Fabio Ganazzoli (Chair), Giuseppina Raffaini (Chair)  
Vincenzina Barbera, Maria Enrica Di Pietro, Valentina Dichiarante,  
Laura Riva, Arianna Rossetti, Alessandro Sacchetti*

## PROGRAMMA SCIENTIFICO

### XIII Congresso Nazionale AICIng - e II Congresso Nazionale della Divisione di Chimica per le Tecnologie della Società Chimica Italiana

Politecnico di Milano, 25-28 giugno 2023

**Domenica 25 giugno - Rettorato del Politecnico di Milano** - Piazza Leonardo da Vinci, 32

18:00: **REGISTRAZIONE**

19:00-21:00 **APERITIVO DI BENVENUTO**

**Lunedì 26 giugno**

8:30-9:00	<b>REGISTRAZIONE</b> Aula De Donato del Politecnico di Milano - Piazza Leonardo da Vinci, 32
9:00-9:20	<b>APERTURA LAVORI DEL CONGRESSO</b> <b>Chairs: Prof.ssa Giuseppina Raffaini e Prof. Fabio Ganazzoli</b> <b>SALUTI DI BENVENUTO:</b> <b>Prof.ssa Isabella Nova</b> – Prorettrice Delegata ( <i>Politecnico di Milano</i> ) <b>Prof. Antonio Capone</b> – Preside della Scuola di Ingegneria Industriale e dell'Informazione 3I ( <i>Politecnico di Milano</i> ) <b>Prof.ssa Marinella Levi</b> – Direttore del Dipartimento di Chimica, Materiali, e Ingegneria Chimica "G. Natta" ( <i>Politecnico di Milano</i> ) <b>Prof. Roberto Paolesse</b> – Presidente AICIng ( <i>Università degli Studi di Roma Tor Vergata</i> ) <b>Prof. Piero Mastrorilli</b> – Presidente della DCT-SCI ( <i>Politecnico di Bari</i> )
9:20-10:00	<b>Chairs: Prof. Roberto Paolesse e Prof. Piero Mastrorilli</b> <b>INVITED PLENARY LECTURE – PL1</b> <b>PREMIO AICIng per l'impegno a servizio del raggruppamento e dell'Associazione</b> <b>Prof. SALVATORE FAILLA</b> <i>Università degli Studi di Catania</i> Una fucina sotto il Vulcano: dalle molecole ai materiali

<b>Sessione 1</b>	
<b>Chairpersons: Prof.ssa Candida Milone e Prof. Giuseppe Marci</b>	
10:00-10:15	<p><b>OC1 - Claudio IMPARATO</b></p> <p><i>Università degli Studi di Napoli Federico II</i></p> <p>Synthesis of multifunctional materials by sol-gel: from mixed oxide catalysts to polymer-based hybrid nanocomposites</p>
10:15-10:30	<p><b>OC2 - Sara DALLE VACCHE</b></p> <p><i>Politecnico di Torino</i></p> <p>Composites from cellulose microfibrils and biobased latexes crosslinked via [2 + 2] photocycloaddition</p>
10:30-10:45	<p><b>OC3 - Francesca BALDASSARRE</b></p> <p><i>Università del Salento</i></p> <p>Cellulose nanocrystals-based emulsions of thyme essential oil: preparation and characterization as crop protection tools</p>
10:45-11.:00	<p><b>OC4 - Carola ROMANI</b></p> <p><i>Politecnico di Milano</i></p> <p>Synthesis of Fluorinated PAMAM-Arginine and Guanidine Conjugates as Non-Viral Vectors</p>
11:00-11:30	<i>Coffee Break</i>
<b>Sessione 2</b>	
<b>Chairpersons: Prof.ssa Roberta Bongiovanni e Dr.ssa Vincenzina Barbera</b>	
11:30-11:50	<p><b>PREMIO AICIng per Tesi di Dottorato</b></p> <p><b>Dr.ssa Emanuela MUSCOLINO</b></p> <p><i>Università degli Studi di Palermo</i></p> <p>Polysaccharide hydrogels for regenerative medicine applications</p>
11:50-12:05	<p><b>OC5 - Vincenzo VILLANI</b></p> <p><i>Università degli Studi della Basilicata</i></p> <p>Hydrogels and Bioplastics based on Agar, Gelatin and Chitosan: viscometry and kinetic models of gelling, thixotropy and crosslinking</p>
12:05-12:20	<p><b>OC6 - Emanuele LIMITI</b></p> <p><i>Università Campus Bio-Medico di Roma</i></p> <p>Tailoring the physicochemical properties of nanogels via a pneumatically driven microfluidic device</p>



12:20-12:35	<b>OC7 - Franca CASTIGLIONE</b> <i>Politecnico di Milano</i> Nanosponges-based hydrogels for drug delivery: an HR-MAS NMR investigation
12:35-12:50	<b>OC8 - Antonio D'ANGELO</b> <i>Università degli Studi della Campania "Luigi Vanvitelli"</i> Dyeing metakaolin-based geopolymers with pH indicators: a feasibility study
12:50-13:05	<b>OC9 - Michele BACK</b> <i>Università Ca' Foscari Venezia</i> Cr <sup>3+</sup> -doped Phosphors for Thermal Sensing: Advantages and Limitations
<b>13:05-14:30</b>	<b>PRANZO – accanto all'Aula De Donato del Politecnico di Milano</b>
<b>Sessione 3 Chairpersons: Prof.ssa Nadia Lotti e Dr.ssa Maria Enrica Di Pietro</b>	
14:30-14:50	<b>PREMIO AICIng per Tesi di Dottorato</b> <b>Dr.ssa Giselle DE ARAUJO LIMA E SOUZA</b> <i>Politecnico di Milano</i> Study of Structure and Dynamics of Protic Ionic Liquids (PILs) as Electrolytes and Components for Polymer Electrolytes
14:50-15:05	<b>OC10 - Francesco LANERO</b> <i>Università degli Studi di Padova</i> Microwave synthesis of new co-polypyrrole- polyketone anion exchange membranes
15:05-15:20	<b>OC11 - Serena DE SANTIS</b> <i>Università degli Studi Roma Tre</i> Nanostructured titania decorated with copper: effect of the substrate pretreatment on morphology and electrochemical performance of the electrodes
15:20-15:35	<b>OC12 - Virginia VENEZIA</b> <i>Università degli Studi di Napoli Federico II</i> Active bio-packaging produced by encapsulation of Humic Substances into electrospun PHBV films

15:35-15:50	<b>OC13 - Francesca SCARAMUZZO</b> <i>Sapienza - Università di Roma</i> Self-standing Membranes of TiO <sub>2</sub> Nanotube Arrays: Fabrication, Decoration and Use in Li-Ion Batteries
15:50-16:05	<b>OC14 - Carla BONOLA e Niccolò MANGONE</b> <i>Casa Editrice Pearson</i> Insegnare Chimica con <i>Mastering Chemistry</i>
16:05-16:30	<i>Coffee Break</i>
<b>Sessione 4 Chairpersons: Prof. Antonio Aronne e Prof.ssa Valentina Dichiarante</b>	
16:30-16:50	<b>INVITED KEY-NOTE - KN1</b> <b>Prof.ssa CRISTINA LEONELLI</b> <i>Università degli Studi di Modena e Reggio Emilia</i> Calcination of N-doped TiO <sub>2</sub> nanoparticles in a microwave oven
16:50-17:05	<b>OC15 - Alberta GENCO</b> <i>Università degli Studi di Palermo</i> Photoreforming of organics in aqueous suspension of Nb <sub>2</sub> O <sub>5</sub> /C <sub>3</sub> N <sub>4</sub> composites to obtain H <sub>2</sub>
17:05-17:20	<b>OC16 - Luigi VERTUCCIO</b> <i>Università degli Studi della Campania "Luigi Vanvitelli"</i> Development of composites with Self-responsive functions: Self-sensing, Self-heating and Self-curing
17:20-17:35	<b>OC17 - Fabrizio CAROLEO</b> <i>Università degli Studi di Roma Tor Vergata</i> Colorimetric Hg <sup>2+</sup> detection by novel cellulose-based xerogels functionalized by porphyrin receptors
17:35-17:50	<b>OC18 - Stefano ELLI</b> <i>Politecnico di Milano</i> Mechanochemical synthesis of mechanical bonds and guest-inclusion in M12L8 poly-[ <i>n</i> ]-catenanes

17:50-18:05	<b>OC19 - Elisabetta FINOCCHIO</b> <i>Università degli Studi di Genova</i> Community of Practice and Faculty Development at the Polytechnic School of Genoa University
18:05-19:00	<b><i>POSTER SESSION</i></b> <i>Si svolgerà accanto all'aula De Donato.</i>

## Martedì 27 giugno

<b>Sessione 5</b> <i>Chairpersons: Prof.ssa Isabella Chiarotto e Prof. Alessandro Sacchetti</i>	
8:30-8:45	<b>OC20 - Francesca BALDELLI BOMBELLI</b> <i>Politecnico di Milano</i> Fluorinated nanoparticles as powerful probes for bioimaging
8:45-9:00	<b>OC21 - Lucio MELONE</b> <i>Università Telematica eCampus</i> Cyclodextrin-based polynitroxides for in vivo imaging
9:00-9:15	<b>OC22 - Consuelo CELESTI</b> <i>Università degli Studi di Messina</i> Nanobiochar derived from orange peel for targeted cancer therapy
9:15-9:30	<b>OC23 - Simona SABBATINI</b> <i>Università Politecnica delle Marche</i> In vitro Cytotoxicity of asbestos: a combined FTIR and EPR study
<b>Sessione 6</b> <i>Chairpersons: Prof.ssa Silvia Licoccia e Prof. Andrea Mele</i>	
9:30-10:10	<b>INVITED PLENARY LECTURE – PL2</b> <b>Dr. FRANCESCO ROMANI</b> <i>Head of Materials Management – Pirelli Tyre Milano</i> Materiali per l'Industria dello pneumatico, la Sfida della Sostenibilità
10:10-10:30	<b>PREMIO AICIng per Tesi di Dottorato</b> <b>Dr.ssa Federica PIRAS</b> <i>Università del Salento</i> Integrated Advanced Oxidation and Biofiltration Technologies for Wastewater Reuse
<i>10:30-11:00</i>	<i>Coffee Break</i>
<b>Sessione 7</b> <i>Chairpersons: Prof.ssa Marta Feroci e Dr.ssa Arianna Rossetti</i>	
11:00-11:15	<b>OC24 - Piero MACCHI</b> <i>Politecnico di Milano</i> Coordination network for spintronic applications: the role of high pressure

11:15-11:30	<p><b>OC25 - Martina LIPPI</b>  <i>Università degli Studi di Firenze</i>  Chiral resolution via selective crystallization of diastereomeric salts: a case study involving NSAIDs</p>
11:30-11:45	<p><b>OC26 - Serena DUCOLI</b>  <i>Università degli Studi di Brescia</i>  Plastic Pollution at the micro and nanoscale: “true-to-life” test materials</p>
11:45-12:00	<p><b>OC27 - Mirko MAGNI</b>  <i>Università degli Studi di Milano</i>  Different approaches for a common scope: improving the sustainability of polymer coatings for corrosion protection</p>
<p><b>Sessione 8    Chairpersons: Prof. Pierluigi Stipa e Prof.ssa Sandra Dirè</b></p>	
12:00-12:20	<p><b>INVITED KEY-NOTE - KN2</b>  <b>Prof.ssa ALESSANDRA D'EPIFANIO</b>  <i>Università degli Studi di Roma Tor Vergata</i>  Design of hierarchical nanostructures for oxygen reduction reaction in energy conversion systems</p>
12:20-12:35	<p><b>OC28 - Emanuela MASTRONARDO</b>  <i>Università degli Studi di Messina</i>  Doping Strategies for The Enhancement of The Thermochemical Heat Storage Capacity of CaMnO<sub>3</sub></p>
12:35-12:50	<p><b>OC29 - Marialuigia RAIMONDO</b>  <i>Università degli Studi di Salerno</i>  Outperforming electrical properties of hybrid composites based on carbon nanotubes and graphene nanosheets</p>
12:50-13:05	<p><b>OC30 - Maria Chiara SPENNATO</b>  <i>Università degli Studi di Bologna</i>  Recent advances in enzyme exploitation for polymer science: recycling and upcycling</p>
13:05-14:30	<p><b>PRANZO – accanto all’Aula De Donato del Politecnico di Milano</b></p>



<b>Sessione 9</b>	
14:30-15:30	<b>Chairs: Prof. Piero Mastrorilli (President) e Prof. Salvatore Failla (Past President)</b> <b>ASSEMBLEA soci DCT-SCI</b>
15:30-16:30	<b>Chairs: Prof. Roberto Paolesse (President) e Prof.ssa Marilena Tolazzi (Past President)</b> <b>ASSEMBLEA soci AICIng</b>
16:30-17:00	<i>Coffee Break</i>
17:00-18:30	<b>TAVOLA ROTONDA</b> <b>"Dalla ricerca all'innovazione. Il ruolo del trasferimento tecnologico"</b> <b>Coordinatore: Prof. Maurizio Galimberti (Politecnico di Milano)</b> Intervengono: <b>Enrico ALBIZZATI</b> - <i>Pirelli e Università degli Studi di Milano-Bicocca</i> <b>Alessia MOLTANI</b> - <i>Comftech srl</i> <b>Chiara MARCOLIN</b> - <i>Leonardino Srl</i> <b>Roberto TIEZZI</b> - <i>Università degli Studi di Milano</i> <b>Enrico ZANOLI</b> - <i>Zanoli &amp; Giavarini S.p.A.</i>
20:00	<b>CENA SOCIALE: "Osteria del Treno" – Via S. Gregorio 46 - 20124 Milano</b>

## Mercoledì 28 giugno

<b>Sessione 10</b> <i>Chairpersons: Prof. Francesco Mauriello e Prof.ssa Isabella Natali Sora</i>	
8:30-8:45	<b>OC31 - Lorenzo VIGANÒ</b> <i>Università degli Studi di Milano-Bicocca</i> Adsorbent-photocatalytic multifunctional materials for wastewater treatment
8:45-9:00	<b>OC32 - Maria Grazia MUSOLINO</b> <i>Università Mediterranea di Reggio Calabria</i> High-entropy oxides-based electrode materials for water desalination via capacitive method
9:00-9:15	<b>OC33 - Francesca ABATEMATTEO</b> <i>Politecnico di Bari</i> Poly(vinyl alcohol) formulations as waterborne coatings to improve paper media resistance
9:15-9:30	<b>OC34 - Michelina SOCCIO</b> <i>Università degli Studi di Bologna</i> Green recycling of biobased polymeric systems
<b>Sessione 11</b> <i>Chairpersons: Prof.ssa Michelina Catauro e Prof. Giuseppe Ciccarella</i>	
9:30-9:50	<b>PREMIO AICIng per Tesi di Dottorato</b> <b>Dr.ssa Laura RIVA</b> <i>Politecnico di Milano</i> Nanocellulose: production and applications of an innovative eco sustainable resource
9:50-10:05	<b>OC35 - Alessandra ZANOLETTI</b> <i>Università degli Studi di Brescia</i> A microwave-enhanced method for the recovery of strategic metals from spent lithium-ion batteries
10:05-10:20	<b>OC36 - Biagia MUSIO</b> <i>Politecnico di Bari</i> Eco-design of innovative release agents

10:20-10:35	<b>OC37 - Dhanalakshmi VADIVEL</b> <i>Università degli Studi di Pavia</i> The investigation of LD540 behavior with albumins
10:35-11:00	<i>Coffee Break</i>
<b>Sessione 12</b> <b>Chairpersons: Prof.ssa Laura Eleonora Depero e Prof. Carlo Punta</b>	
11:00-11:15	<b>OC38 - Ivan Pietro OLIVERI</b> <i>Università degli Studi di Catania</i> Vapochromic and vapoluminescent Zn(II) Schiff- base complexes as chemosensors for volatile organic compounds
11:15-11:30	<b>OC39 - Gabriele MAGNA</b> <i>Università degli Studi di Roma Tor Vergata</i> Conductive Polycorrole Sensors for Room-Temperature Detection of Nitric Oxide
11:30-11:45	<b>OC40 - Damiano ROSSI</b> <i>Università degli Studi di Pisa</i> Doped Li <sub>4</sub> SiO <sub>4</sub> -based sorbents for CO <sub>2</sub> capture at high temperature
11:45-12:00	<b>OC41 - Nico ZAMPERLIN</b> <i>Università degli Studi di Trento</i> BaTiO <sub>3</sub> -PDMS nanocomposites for energy harvesting: enhancing the dielectric performance through ceramic particles' functionalization
12:00-12:15	<b>OC42 - Stefano FALCINELLI</b> <i>Università degli Studi di Perugia</i> Doubly Charged Species in the Upper Atmosphere of Planets and Space
12:15-12:45	<b>PREMIAZIONI e CONCLUSIONE DEI LAVORI</b>

## ***POSTER SESSION***

**18:05-19:00: Lunedì 26 giugno (accanto all'aula De Donato)**

**Non si svolgeranno *Flash Poster Presentation* in aula De Donato**

- **P1** TOLAZZI, Marilena Rare-Earth Magnet Recycling using Phosphonium based Ionic Liquids
- **P2** PUNTA, Carlo Nanocellulose-based solutions for water treatment
- **P3** DAL POGGETTO, Giovanni Inorganic polymers with waste cork powder
- **P4** CHIAROTTO, Isabella Bottom-up Synthesis and Application of Carbon Dots from Agri Food Waste
- **P5** BUGNOTTI, Daniele Effect of storage time and relative humidity in bio-nanocomposites for sustainable food packaging (BIOSTAR-PACK)
- **P6** BLANCO, Ignazio Chemical Recycling of Fully-recyclable Bio-Epoxy Matrices and Re-use strategies: a Cradle-to-Cradle approach
- **P7** CATAURO, Michelina Recycling ash from wood-fired ovens through geopolymers: synthesis and characterisation.
- **P8** ROMANO, Angela Recycling by-design of plastics through thermally protected enzymes
- **P9** BOTTARI, Alberto Chemical recycling of elastomeric and viscoelastic polyurethanes
- **P10** RUINI, Chiara Integrated approach of Life Cycle Assessment and Experimental Design in the study of an organic synthesis
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# **CONFERENZE PLENARIE**

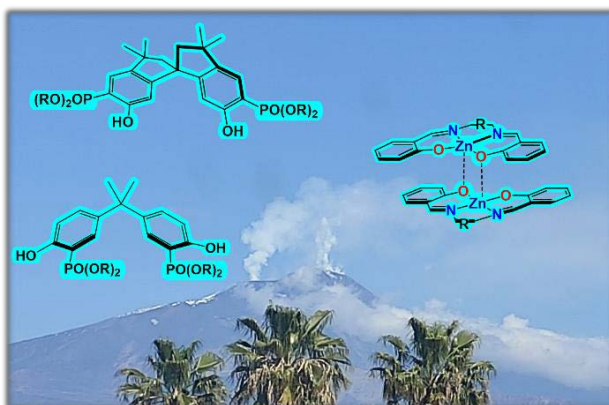
## Una fucina sotto il Vulcano: dalle molecole ai materiali

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In questa comunicazione presenterò alcune ricerche effettuate ed i risultati ottenuti sotto il vulcano. Inizialmente mi sono occupato della sintesi di una vasta gamma di derivati degli acidi alfa-amminofosfonici, i quali sono i bioisosteri degli aminoacidi naturali e che possono fungere da importanti surrogati per modificare i processi biologici, per inibire l'attività di enzimi, ed anche utili in agricoltura come erbicidi, antifungicidi ecc. Particolari molecole contenenti gruppi fosforici sono state utilizzate come recettori ciclici, achirali o chirali, ai fini del riconoscimento molecolare, rispettivamente di molecole neutre o come sensori di alcuni aminoacidi, rivelando chemoselettività ed anche enantiodiscriminazione.



Mediante la sintesi di opportuni monomeri contenenti gruppi fosforici si sono preparati poliammidi e resine epossidiche che hanno mostrato interessanti proprietà autoestinguenti. L'utilizzo di questi materiali innovativi, nell'industria aerospaziale ed elettrica, ridurrebbe l'impatto dannoso sull'ambiente in quanto il fosforo, come l'azoto ed il silicio, è considerato un ritardante di fiamma ecologico.

Ricerche più recenti riguardano la sintesi e le proprietà di aggregazione di complessi mono e binucleari di Zn(II) con basi di Schiff. La facile formazione di addotti rende questi complessi di zinco dei buoni sensori per basi di Lewis, quindi l'utilità di questi complessi è molteplice, in quanto offrono una varietà di studi di ricerca sia di base che applicativa.



## *Materiali per l'Industria dello pneumatico, la Sfida della Sostenibilità*

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Keywords: Pneumatico, Sostenibilità, Materiali

L'approccio industriale alla sostenibilità richiede interventi su diversi aspetti: riduzione del consumo di energia e risorse, impiego di materiali rinnovabili e riciclati con valutazione puntuale del Life Cycle Assessment; inoltre è fondamentale tenere in considerazione il tema recupero dei prodotti a fine vita.

Pirelli ha fissato obiettivi temporali per ridurre l'impiego di risorse da fonte fossile nel tempo, impegnandosi inoltre a conseguire la Carbon Neutrality entro il 2030.

Questo impegno ha portato Pirelli da essere la prima azienda di pneumatici a commercializzare un prodotto certificato FSC ed a comparire come una della Società "best performer" nei Ranking Internazionali di Sostenibilità Ambientale Sociale ed Economica.

Lo Pneumatico è un prodotto industriale che per molti decenni è stato progettato e costruito facendo ricorso a molti materiali ricavati da fonti fossili.

A fianco della gomma naturale, per la richiesta di prestazioni sempre più spinte, si sono affermati nel tempo vari polimeri sintetici, oltre a numerosi prodotti chimici speciali. Questi ingredienti, oltre all'impiego estensivo del Carbon Black, fino ad oggi prevalentemente prodotto a partire da derivati dal petrolio, rendono il contenuto di materiali da fonte fossile molto importate.

L'avvento della Silice negli anni '90, come filler parzialmente sostitutivo del Carbon Black, ha introdotto un materiale non ricavato direttamente dell'industria petrolchimica, ma che necessita di notevoli quantità di energia per essere prodotto, in una forma idonea all'impiego, e che richiede l'uso di compatibilizzanti specifici.

Tema importate è poi il recupero del prodotto a fine vita; la vulcanizzazione, fase conclusiva del processo produttivo, è una reazione irreversibile che rende molto difficile il recupero di materie prime seconde dagli pneumatici usati.

Le strategie per rendere lo pneumatico un prodotto sostenibile sono molteplici: ridurre i materiali da fonte fossile e sviluppare strategie per ricavare materie prime dal prodotto a fine vita, sia come processi di recupero che come design del prodotto stesso. Intermedi di origine biologica e da riciclo possono essere usati per produrre materiali con certificazione ISCC+, simili se non del tutto identici a quelli da fonte fossile, permettendo ad un tempo di preservare le prestazioni e di aumentare la percentuale di materiali sostenibili nello pneumatico.

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Materiali da fonte naturale come la lignina, in sostituzione del Carbon Black, ed il Serinol Pirrolo come attivante della silice, sono esempi di come la ricerca su materiali alternativi ed innovativi possa aiutare a ridurre l'impatto ambientale della produzione degli pneumatici.

L'avvento della Pirolisi degli pneumatici a fine vita, come processo di recupero, permette di ricavare intermedi chimici che l'industria chimica può re-impiegare e materie prime, come il Recovered Carbon Black, che possono trovare utilizzo diretto nella produzione degli pneumatici stessi.

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- [2] WO 2019162873 - Galimberti, Maurizio Stefano; Barbera, Vincenzina ADDUCT BETWEEN A PYRROLIC COMPOUND AND AN INORGANIC OXIDE HYDROXIDE.
- [3] WO 2017109672 - Luca Castellani; Thomas Hanel; Luca Zoia; Marco Orlandi; Davide Barana TYRE FOR VEHICLE WHEELS.

# ***KEYNOTE LECTURES***

## Calcination of N-doped TiO<sub>2</sub> nanoparticles in a microwave oven

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Keywords: Microwave, nanoparticle, calcination, anatase/rutile phase transition

N-doped TiO<sub>2</sub> nanoparticles are widely studied as visible-light photocatalysts [1]. An easy method for their preparation is the calcination of a TiO<sub>2</sub> precursor material containing a nitrogen source. This study is focused on the calcination under microwave irradiation of a solid mixture containing TiO<sub>2</sub> nanoparticles and a nitrogen source, namely a mixture of NH<sub>4</sub>Cl and ammonium citrate, to produce N-doped TiO<sub>2</sub> nanoparticles. Microwave irradiation triggers the combustion of the organic fraction with a decrease in weight of about 45 % in a dedicated oven (CEM Phoenix Black oven equipped with a proper scrubber system). As a result, N-doped TiO<sub>2</sub> nanoparticles are produced. Screening of the experimental conditions, including ramp and holding times, temperature, and other parameters, was performed with the aim to reproduce the results of the industrial calcination performed in a conventional oven (namely: Anatase 66 %, Brookite 29 %, Rutile 5 %), that is known to produce a material with a good photocatalytic activity for the NO<sub>x</sub> depletion [2]. Given that a very exothermic combustion of the organic materials occurs during the process, the calcination has been very difficult to control, working on a 10 g scale, and the calcination's outcome is dramatically affected by the kind of crucible used.

While we succeeded in obtaining the desired result after 3 h of calcination at 400 °C using a dense alumina crucible with a wide surface exposed to the oven atmosphere, that helped in heat loss and prevented rutile formation (Figure 1a), we obtained only rutile phase when working in a quartz fiber-made crucible at a nominal temperature as low as 250 °C (Figure 1b). This result was made possible by the kind of crucible used, i.e. the quartz fiber-made crucible favoured air exchange leading to a better combustion of organics. This combustion provides the energy required for a complete phase transition to rutile during calcination [3]. Using microwave technology, a considerable reduction of energy consumption was achieved.

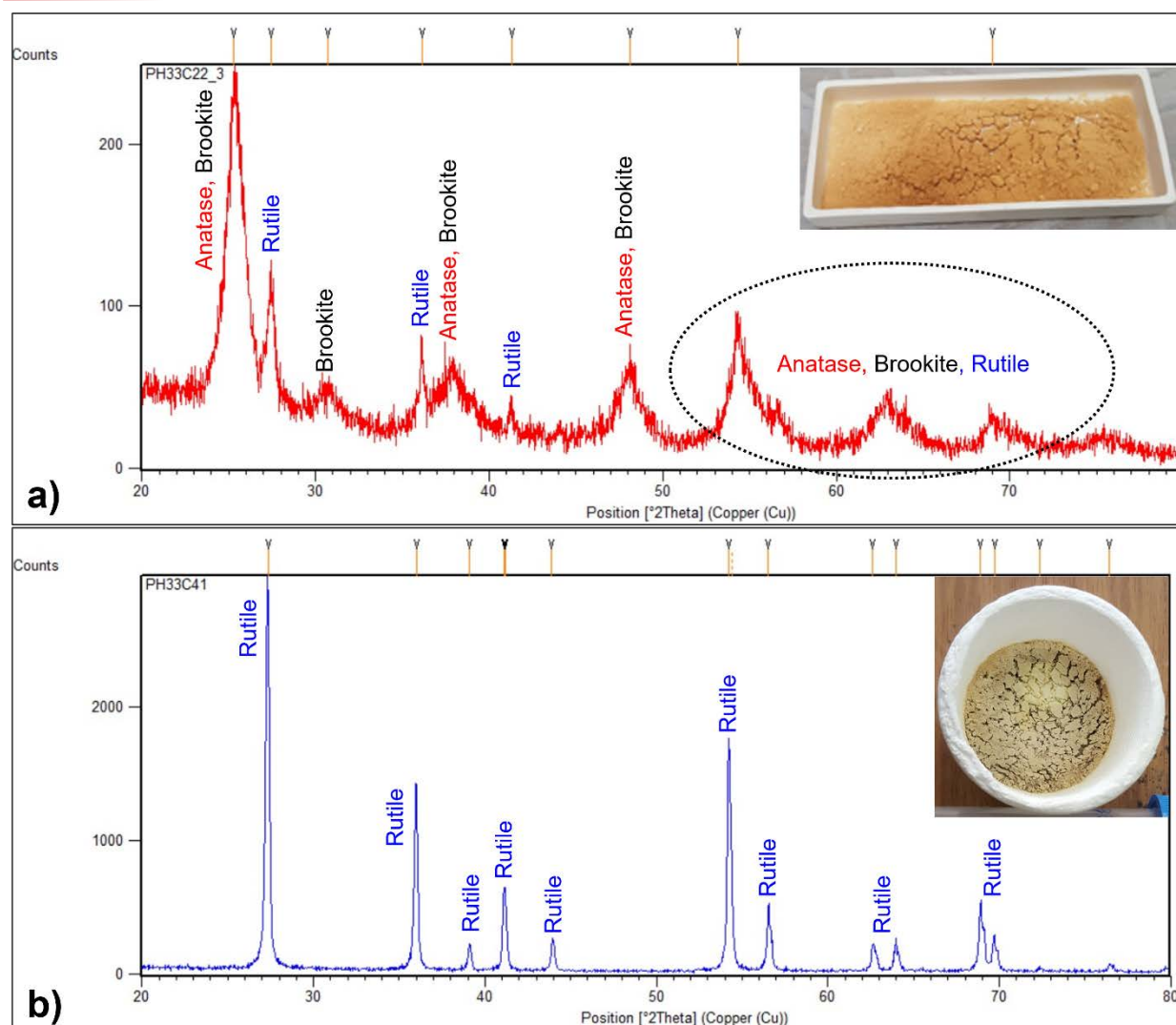


Figure 1. XRD pattern of N-doped TiO<sub>2</sub> nanoparticles after MW calcination carried out in an alumina crucible at 400 °C (a) or in a quartz fiber crucible at 250 °C (b). Mineralogic composition for a): Anatase: 53 %; Brookite: 34 %; Rutile: 13 %. Mineralogic composition for b): Rutile: 100 %.

This work was carried out in the context of a larger European project named: “Sonication and Microwave Processing of Material Feedstock (SIMPLIFY)” supported by the European Union’s Horizon 2020 research and innovation program under Grant Agreement No 820716.

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# Design of hierarchical nanostructures for oxygen reduction reaction in energy conversion systems

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Keywords: platinum group metal-free electrocatalysts, oxygen reduction reaction, Fe-C-N active sites, energy conversion, alkaline fuel cells

High-efficient electrochemical energy conversion and storage is a critical element for future energy infrastructure that is predicted to reach net-zero greenhouse gas emissions. For this purpose, H<sub>2</sub>-fed anion exchange membrane fuel cells (AEMFCs) and Zn-air batteries were found particularly suited for decarbonizing the industry sector [1,2], while alkaline direct methanol fuel cells (ADMFCs) offer advantages for portable applications [3]. The sluggish kinetics of the oxygen electrode reactions is one of the main drawbacks to spreading those technologies since they require the use of platinum-based (Pt/C for oxygen reduction reaction, ORR) or platinum group metal (PGM, e.g., RuO<sub>2</sub>, IrO<sub>2</sub> for oxygen evolution reaction, OER) catalysts to accelerate the reactions. The high cost and low durability of PGMs under operating conditions call for developing PGM-free electrocatalysts; however, the activity, density, accessibility, and durability of these cost-effective materials still need to be improved [4].

In this work, metal-organic-frameworks (MOFs) were used as self-template to obtain Co-N-C and Fe-N-C active sites. Furthermore, porous organic polymers (POPs) [5] were prepared and used as a hierarchically structured porous, soft template to modulate the materials' micro/meso/macro porosity and enhance metal functionalization. The resulting electrocatalysts showed a high content of M-N-C (M: Co or Fe) active sites, high ORR activity, methanol tolerance, and performance durability over cycling (30k), as pointed out by X-ray Photoelectron Spectroscopy, Transmission Electron Microscopy, and rotating disk electrode experiments at pH=13.

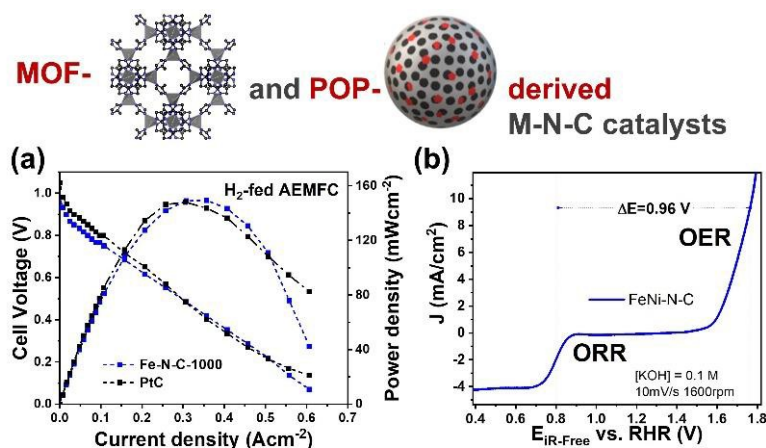


Figure 1. M-N-C catalysts performances accessed by the (a) H<sub>2</sub>-fed AEMFCs and (b) half-cell tests at pH=13.

The catalysts were assembled at the cathode side of ADMFCs and AEMFCs, demonstrating an exceptionally high power output (Figure 1a). Furthermore, POP-derived N-C supports were functionalized with Fe and Ni to evaluate their bifunctional ORR/OER activity at pH=13 (Figure 1b). The RDE experiments indicated that Fe/Ni@N-C materials could be promising candidates to replace RuO<sub>2</sub> at the cathode of Zn-air batteries.

#### Acknowledgments

This work was supported in part by the Italian Ministry of Foreign Affairs and International Cooperation", grant number CN23GR06.

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# **PREMI di TESI DI DOTTORATO**

# Polysaccharide Hydrogels for Regenerative Medicine Applications

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Keywords: polysaccharide hydrogels, 3D printing, tissue engineering

The progressive aging of global population and the constant rise of chronic-degenerative diseases are threatening the health and wellbeing of citizens in many countries [1]. Other important concerns of our times, not unrelated to the above, are about climate change and environmental degradation, causing the need for sustainable alternatives to health problems.

Polysaccharides are widely distributed in nature and their chemical behavior and interesting structural similarities with biological molecules has granted them great potential for future applications in tissue regeneration, while remaining a renewable, sustainable and carbon-neutral alternative [2].

The scope of this work is to contribute to the great efforts paid by the international scientific community in these years to develop effective and eco-sustainable ways to regenerate human tissues. Focusing on cartilage and bone regeneration, the general concept of this work lays in the harvesting of spheroids of adipose derived stem cells (SASCs) from the actual patient's adipose tissue, then in either mixing them with polysaccharides hydrogels, plating them on top of 3D printed hydrogels, or mixing and 3D printing together with the hydrogel, and ideally directly injecting or implanting at the patient's lesion site (Figure 1). Xyloglucan (XG), in the degalactosylated form (dXG), k-carrageenan (kC), and alginate (Alg) are all polysaccharides able to form hydrogels in different conditions and were here compared and tested as suitable materials for the scope.

All formulations resulted compatible with cells, but dXG gave outstanding results in terms of SASCs differentiation and proliferation demonstrating to be a perfect candidate for injectable artificial niches applications. Meanwhile, carboxylation and  $\gamma$ -

radiation of XG demonstrated to successfully functionalize and alter the XG molecular weight for further applications where these characteristics are needed. kC in blend with Polyvinyl Alcohol (PVA), a biocompatible polymer, or dXG showed a more porous morphology, preferred for cell culture, and an improved sol-gel transition in the direction of a better flowing and plasticized gel with interesting 3D printability properties. Furthermore, the utilization of Pvfp5B mussels protein demonstrated to be successful for improving PVA/kC hydrogels cell adhesion without the need to add any other chemical to the formulation.

In conclusion, these hydrogels show interesting characteristics to be used as bio-ink for 3D printing or as artificial niches with stem cells, this makes them potential candidates for tissue regeneration applications.

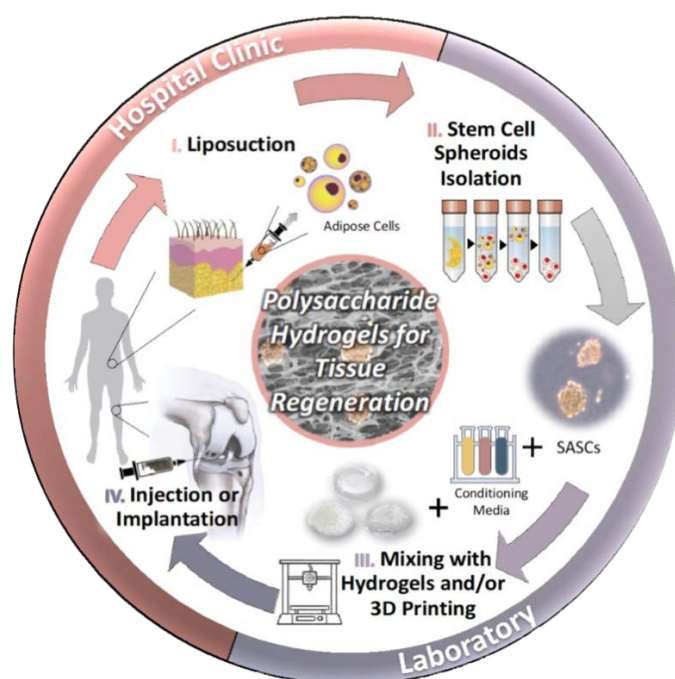


Figure 1. (I) Harvesting of adipose tissue by liposuction; (II) SASC isolation and culturing in 3D conditions; (III) mixing with polysaccharides-based hydrogels from sustainable sources and/or hydrogel 3D printing; (IV) injection or implantation of the hydrogel scaffold at the lesion site.

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## *Study of Structure and Dynamics of Protic Ionic Liquids (PILs) as Electrolytes and Components for Polymer Electrolytes*

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Keywords: Protic Ionic Liquids, Electrolytes, Polymers

The use of lithium-ions batteries (LIBs) as energy storage devices is exponentially growing. However, safety is still an issue, and some electrolyte components must be improved. In this regard, protic ionic liquids (PILs) emerged as potential electrolyte components in LIBs. When replacing flammable and volatile organic solvents, PILs are expected to improve the safety and performance of electrochemical devices. For implementing PILs as electrolyte components, a challenging task is still to understand the key factors governing their physicochemical and transport properties.

To this end, this work deeply investigated three promising PILs based on the 1,8-diazabicyclo-[5,4,0]-undec-7-ene (DBUH<sup>+</sup>) cation and the (trifluoromethanesulfonyl-nonafluorobutylsulfonyl)imide (IM14<sup>-</sup>), trifluoromethanesulfonate (TFO<sup>-</sup>) and bis(trifluoromethanesulfonyl)imide (TFSI<sup>-</sup>) anions. Here, a multidisciplinary characterization of the PILs by using multinuclear NMR methods and different physicochemical analyses provided a comprehensive understanding of the features governing the properties of the selected PILs [1].

Yet, to promote the application of the PILs as electrolyte components, an in-depth understanding of the ion mobility in the bulk system became crucial to scale their transport properties. Therefore, the translational and local dynamics in both neat PILs and PIL-based electrolytes (DBUH-IM14, DBUH-TFSI and DBUH-TFO doped with 10% molar fraction of lithium salt containing the same anion) were investigated by diffusion and relaxation NMR. Notwithstanding, the DBUH-IM14 was investigated by the innovative electrophoretic-NMR (e-NMR) measurements. This non-routine, disruptive technique

merges the NMR measurement of diffusion with the presence of an external electric field, thus mimicking the real environment experienced by the ions inside a LIB. Overall, the synergism between various NMR techniques and conductivity measurements allowed the achievement of a broad overview of the ion dynamics of these systems. Accordingly, the presence of  $\text{Li}^+$  showed a peculiar effect on the dynamics of DBUH-IM14, and from the molecular point of view, DBUH-IM14 are invaluable source of new investigation.

A step forward in designing new materials for next generation LIBs was done by preparing and testing PILs based polymer electrolytes able to further improve the safety profile and applicability of LIBs. Then, the selected PILs were confined into a polymeric matrix using poly(methyl methacrylate) (PMMA) as a host. Thermal analysis and solid-state NMR were used to probe the structural features and molecular level interactions between the ions and the PMMA backbone. The combined approach showed that DBUH-IM14 has a stronger interaction with the polymeric matrix than the other PILs.

The unpredictable behavior of DBUH-IM14-polymeric system prompted further investigations on the transport properties of DBUH-IM14-based polymer electrolytes using a much lower PMMA concentration (10% wt) in the attempt of forming a gel-like system. Then, the effect of PILs confinement onto their transport properties was probed by PFG NMR and fast field cycling NMR (FFC NMR). When blended with PMMA, a marked slowing of the overall dynamics was observed. In the case of the polymer electrolyte system,  $\text{Li}^+$  showed a minor effect on the DBUH<sup>+</sup> dynamics, whereas rotational and translational dynamics of the IM14<sup>-</sup> anion were quite sensitive to the presence of  $\text{Li}^+$ . Still, a descriptive model is currently being developed to fully explain the transport properties and relaxation profiles of these systems.

From all the achievements of this work obtained from the multifaceted experimental characterization of the molecular/atomic properties (liquid and solid-state multinuclear NMR, diffusion, relaxation and electrophoretic NMR) and the macroscopic behavior (density, viscosity, conductivity and thermal analyses), DBUH-IM14-based electrolytes emerge as promising new materials for LIB application. The fundamental knowledge on the structural features and nature of the intermolecular interactions of the IM14<sup>-</sup> anion highlighted its crucial role in driving the molecular and macroscopic properties of the electrolytes.

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## *Integrated Advanced Oxidation and Biofiltration Technologies for Wastewater Reuse*

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**Keywords:** advanced treatment, contaminants of emerging concern, wastewater reuse

Water reuse is increasingly recognized as a viable strategy in sustainable water management due to its proven capacity to counteracts water stressors associated with population growth, climate change, urbanization etc., all resulting in ever increasing water demands and consequent scarcity, especially in arid and semi-arid regions of the world.

To date, water reclamation for potable reuse is implemented in several countries in the world, with treatment trains addressing both direct and indirect potable reuse (DPR and IPR). Besides the conventional pollutants, contaminants of emerging concern (CECs) have raised great interest due to their significant increase in wastewaters at concentrations ranging from picograms to micrograms per liter, while the long-term effects on species living in aquatic environment is still unknown for the majority of substances.

In terms of available technologies, existing advanced treatments implemented in IPR and DPR trains, follow a multi-barrier approach based on the integration of different processes in order to ensure redundant, resilient and robust systems for a safe wastewater reuse. In this regard, one of the most common treatment trains employed in potable reuse applications relies on the use of membrane-based technologies, in particular of reverse osmosis (RO). However, while RO is a recognized solution for the efficient removal of a broad range of contaminants, issues related to the formation, management and disposal of highly contaminated retentates, as well as high energy consumptions, pose the necessity for new sustainable alternatives. This is driving research towards innovative technologies able to promote degradation rather than the simple separation for the elimination of CECs from wastewater.

The doctoral project described here was funded under the “Programma Operativo Nazionale Ricerca e Innovazione 2014-2020 - Azione I,1: Dottorati Innovativi con Caratterizzazione Industriale”, involving the University of Western Ontario as foreign academic partner, and Aquasoil Company as industrial partner, the latter operating a non-potable facility for agricultural reuse in the city of Fasano, Italy.

In this work, the integration of AOPs with biofiltration into granular materials has been studied as a viable alternative to membrane process-based treatment trains to achieve potable water quality standards from secondary and tertiary wastewaters.

Conventional and newly AOPs such as UV/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV and vacuum-UV (VUV) were tested at pilot and laboratory scale as pre- and/or post-treatment to biofiltration onto different granular media (activated carbon, limestone and natural zeolite), aiming at assessing and comparing the performance of the various configurations in terms of removal of both conventional pollutants and contaminants of emerging concern. LC-HRMS techniques were utilized to detect CECs in water with targeted and non-targeted approaches.

At pilot level, experimental activities were carried out in a 5m<sup>3</sup>/h plant operating in multiple parallel configurations, where a O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>-based AOP was integrated with a GAC/limestone biofiltration system in one case, or with ultrafiltration and reverse osmosis in another case.

The bioactivated carbon-based O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>-BAC-UV/H<sub>2</sub>O<sub>2</sub> treatment train was found to be a viable alternative to the membrane-based schemes involving the use O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> followed by ultrafiltration and reverse osmosis. Moreover, the integration of peroxone process with UV to carry out a O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV AOP, demonstrated to be a promising pre-treatment option for biofiltration, as it enhanced the performance in terms of CECs abatement beyond 80% of the initial load in secondary and tertiary wastewaters.

At laboratory scale, VUV was tested as pre- and post-treatment to biofiltration onto GAC and natural zeolite, demonstrating that it was possible to achieve removal efficiency higher than 90% of the initial load of CECs when integrating VUV with GAC, while 80% removal was reached even when implementing VUV as pre- and post-treatment to biofiltration onto a non-adsorbing natural zeolite.



# Nanocellulose: production and applications of an innovative eco-sustainable resource

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Keywords: nanocellulose, cellulose-based xerogels, LCA

Nanocellulose and nanocellulose-based materials are attracting an increasing interest for the positive role they could play in sustainable development, being originated from renewable resources [1]. Moreover, cellulose has a high potential of recycling from both post-consumer waste and industrial waste. These factors result extremely favorable also in the perspective of circular economy.

Given these premises, the main objectives of this Ph.D. thesis are: the first is certainly the production of cellulose nanofibers using combinations of enzymatic and chemical pre-treatments with different mechanical treatments. The choice of these processes is the result of the combination of a careful analysis of the literature, the skills concerning oxidative systems and polysaccharides of the research group where I did my Ph.D., the O<sup>SCM</sup>Lab, and the chemical-mechanical competences in the field of paper industry of Innovhub SSI - Area Carta e Cartone, the other institution supporting my Ph.D.

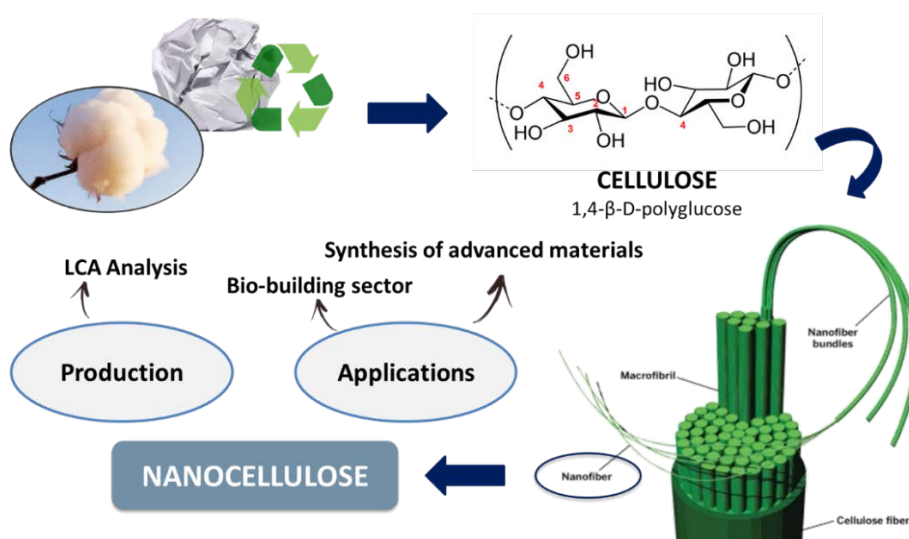


Figure 1. Summary of the Ph.D. project.



After a careful characterization of the produced nanofibers from the point of view of environmental impact through a Life Cycle Assessment (LCA) in collaboration with Mat4En2 group of Politecnico di Milano [2], the second objective of the project was to use the produced nanofibers in the most virtuous way possible in different applications. The areas in which we tried to develop the use of the fibers were the field of green building, in which cellulose nanofibers were used as an additive in non-renewable matrices such as cements and blast furnace slag [3] and in renewable building materials such as raw earth [4], and the synthesis of nanostructured materials in which nanocellulose played a key role as a building block. Regarding this last application, the aim has been to reproduce the synthesis of these xerogels, exploiting their already well-known mechanical, morphological and metal adsorption properties and then exploring different fields. Among these, the environmental decontamination from organic contaminants [5], the production of sensors for specific anions [6] and the heterogeneous catalysis [7-9] of specific organic reactions have been explored.

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# **COMUNICAZIONI ORALI**

## *Synthesis of multifunctional materials by sol-gel: from mixed oxide catalysts to polymer-based hybrid nanocomposites*

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**Keywords:** sol-gel technique, phosphorus-based acid solids, epoxy composites

Nanostructured materials based on phosphorus and silicon can play multiple roles in the challenges for a sustainable development. In biorefinery processes for the transformation of biomass into value-added chemicals and biofuels, several acid-catalysed reactions represent fundamental steps, requiring water-resistant and tuneable solid acid catalysts [1]. Transition metal (oxo)phosphates have a useful combination of Brønsted and Lewis acid sites and sufficient stability to hydrolysis and these properties can benefit from the dispersion over a porous support, such as silica. With this aim, we synthesized by sol-gel method Nb-P-Si mixed oxides, which showed remarkable catalytic performances in different biomass valorization reactions, namely the hydrolysis of inulin, the dehydration of fructose to 5-hydroxymethylfurfural and the esterification of fatty acids, even with a low content of active phase (2.5 mol% P<sub>2</sub>O<sub>5</sub> and 2.5 or 5.0 mol% Nb<sub>2</sub>O<sub>5</sub>) [2].

To better fulfil the principles of green chemistry, we have recently proposed a new sol-gel route for the synthesis of these ternary oxides. The one-pot procedure occurs in water at room temperature, with safe, available and inexpensive precursors (i.e. phosphoric acid and ammonium niobium oxalate), and does not require any catalyst, additive or organic solvent [3]. After annealing at 500 °C in air, a highly cross-linked amorphous porous structure is obtained, with Nb-O-P bonds anchoring phosphorus to the silicate matrix, as depicted by solid state NMR spectroscopy [3]. The medium-strong Brønsted and Lewis acidity, revealed by the surface characterization, results in an interesting catalytic activity in the gas-phase conversion of ethanol to ethylene (Figure 1), with unusually low yield of diethylether, a common by-product of the reaction [4].

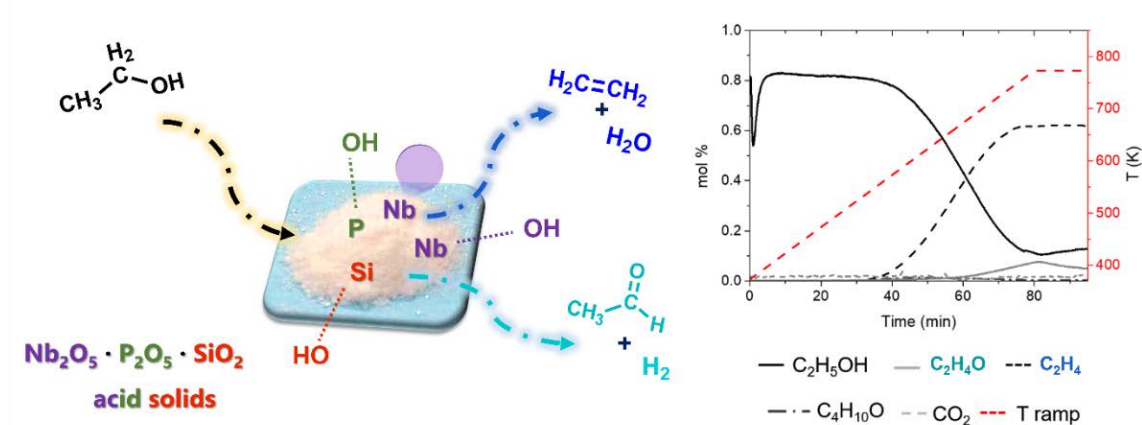


Figure 1. Representation of the conversion pathways of ethanol to ethylene or acetaldehyde over a Nb-P-Si mixed oxide acid catalyst (left) and relative temperature-programmed surface reaction profiles (right) [4].

In a ternary oxide, the introduction of a transition metal with a different acidity than niobium may allow modulating the distribution and strength of acid sites and thus the catalytic performances. Therefore, we have developed an adapted sol-gel route for the synthesis of Ti-P-Si and Zr-P-Si mixed oxides, and we are currently investigating their catalytic activity and stability in the hydrolysis of oligosaccharides.

On the other side, controlling the growth of Si-P nanostructures by sol-gel chemistry also allows their incorporation in a polymer matrix, such as epoxy resin. The fine dispersion of nanometric Si-P phases in an epoxy matrix may have significant effects on the properties of the so-obtained inorganic-organic hybrid nanocomposites. In particular, it represents a sustainable strategy to improve their thermal and fire behavior avoiding the use of toxic flame retardants.

We demonstrated the viability of such approach by modifying in-situ an epoxy resin with small amounts of Si and P (up to 1-2 wt%) through hydrolytic sol-gel [5]. The peculiar morphology of the network, containing P-modified silica lamellar nanocrystals interconnected with the polymer chains through chemical bonds, accounts for promising flame retardant features, suggesting a prevalently condensed phase mechanism, owing to the Si-O-P structures produced in the char [5]. These results open further perspectives in the design of hybrid nanocomposites with accurately tailored structure and functional properties.

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## Composites from cellulose microfibrils and biobased latexes crosslinked via [2 + 2] photocycloaddition

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Keywords: nanocellulose, biobased composites, photocrosslinking

In the quest for more sustainable thermoset composite materials, the use of biobased precursors and fillers and of greener crosslinking processes have emerged as hot research topics. Nanocellulose, considered an eco-friendly replacement for synthetic fillers, can be obtained from several kinds of vegetal biomass, including agricultural residues, agri-food industry waste or algae, and may display different morphologies and physico-chemical properties, depending on the source and the preparation method. Nanocellulose is usually produced as aqueous suspension, and is only stable at relatively low concentrations, commercial products having usually less than 30 wt% solids content. Thus, preparing thermoset composites through standard mixing and curing procedures is challenging, due to the incompatibility of most polymeric precursors with water, and the tendency of cellulose fibrils to aggregate when dried or mixed with apolar materials. To overcome these issues, complex solvent exchange procedures [1], or surface modification of the cellulose fibrils are often employed. A convenient and environmentally advantageous alternative encompasses the use of latexes as the polymeric matrix, allowing for easy mixing of apolar polymers and hydrophilic nanocellulose in an aqueous medium; crosslinking may then be induced after mixing, to improve chemical resistance and other functional properties. In this work we present novel acrylic latexes based on ethoxy dihydroeugenyl methacrylate (EDMA) and coumarin methacrylate (CMA) prepared by redox initiated polymerization in emulsion [2,3]; the pendant coumarin moieties upon irradiation with UVA light undergo a [2 + 2] photocycloaddition reaction, which can be exploited for obtaining a crosslinked polymer network (Figure 1a,b). Copolymers containing 1 wt% and 5 wt% of CMA were prepared, and their [2 + 2] photocycloaddition upon irradiation with UVA light at 365 nm was studied by UV-visible spectroscopy monitoring of the decrease of absorbance at 319 nm (Figure 1 c). Successful crosslinking was also confirmed by measuring the insoluble fraction before and after UVA irradiation.

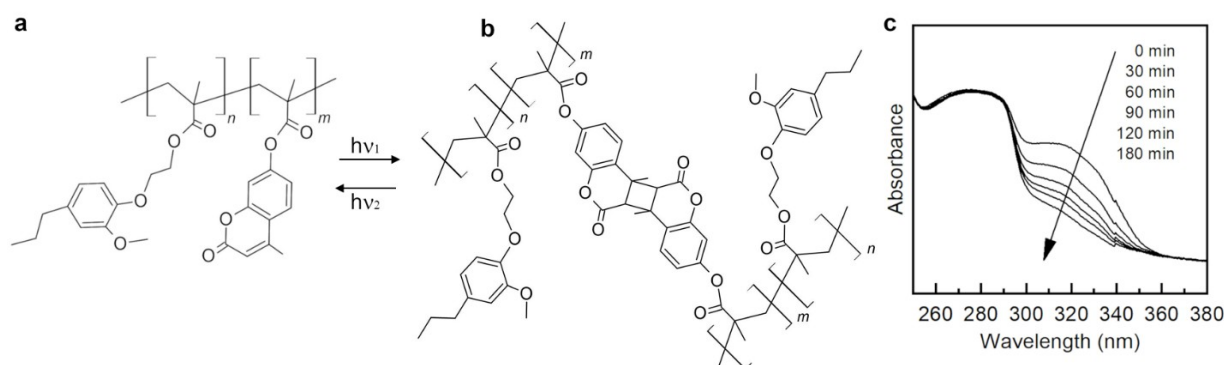


Figure 1. (a) Structure of poly(EDMA-co-CMA), (b) crosslinked poly(EDMA-co-CMA), and (c) evolution of the UV-vis absorption spectrum of poly(EDMA-co-CMA) latex film upon irradiation with UV light at 365 nm.

Composites in the form of films (Figure 2 a,d) were prepared with the poly(EDMA-co-CMA) latexes using two types of cellulosic fillers, i.e. a commercial wood-derived microfibrillated cellulose (MFC) and a nanocellulose obtained from hemp waste (HNC) [4], and crosslinked by [2 + 2] photocycloaddition upon irradiation with UVA light. The advancement of the reaction was followed by UV-visible spectroscopy and confirmed by insoluble fraction measurements. The viscoelastic behavior and thermal stability of the composites, as well as their permeability to oxygen and water vapor was assessed (Figure 2 e) and will be here discussed with respect to the effect of filler content and of crosslinking.

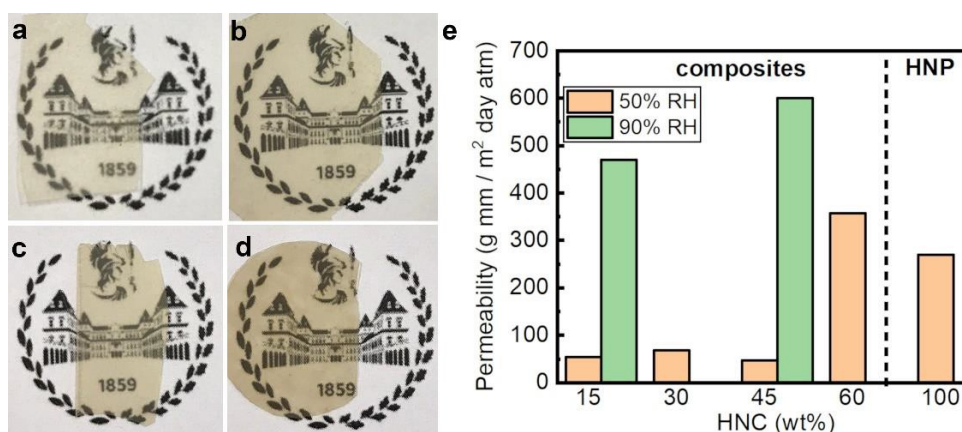


Figure 2. Photos of composite films containing (a) 15 wt%, (b) 30 wt%, (c) 45 wt%, and (d) 60 wt% of HNC, and (e) water vapor permeability of HNC nanopaper and crosslinked composite films containing HNC (at T = 38 °C).

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## *Cellulose nanocrystals-based emulsions of thyme essential oil: preparation and characterization as crop protection tools*

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Keywords: cellulose nanocrystals, plants essential oils, nanoemulsions

Essential oil based biopesticides are topic of interest for agrochemicals field because of growing attention to sustainable practices. These plants extracts are rich of many antimicrobial and antioxidant molecules, such as phenols. These bioactive compounds have some important critical issues, such as high volatility, poor solubility in water and bioavailability [1]. Nanoencapsulation allows to overcome these limits related to their physicochemical properties, enhancing stability and bioactivity [2]. Micro and nanoemulsions are easy encapsulation processes to prepare stable and scalable formulations. Different green emulsions were investigated to control pests, vectors of human or plants diseases [3].

In the present study, oil in water nanoemulsions of thyme essential oil were formulated by high-speed homogenization using tween-80 as surfactant, calcium chloride as crosslinker and cellulose nanocrystals as stabilizers. Thyme essential oil was kindly provided by Licofarma s.r.l., that is a society in the field of natural bioactives application and extraction technology through carbon dioxide in supercritical state. The procedure was investigated tuning cellulose nanocrystals/essential oil ratio and calcium chloride concentration. Thyme essential oil was characterized by GC-MS indicating the main presence of thymol. The formulated nanoemulsion resulted homogeneous after 30 days of storage at ambient temperature, even after centrifugation and dilution showing no phase separation. This good stability was confirmed by Dynamic Light Scattering and Turbiscan analysis. Microscopic analysis detected a nanometric dispersed phase into very small droplets (radius < 20 nm).



Nanoemulsions and free essential oil were investigated at different concentrations to evaluate antimicrobial activity. Samples were evaluated on *Pseudomonas savastanoi* pv. *savastanoi* (Psav, strain PvBa206), the causal agent of olive knot disease [4]. Firstly, the nanoformulation was in vitro tested by a microdilution and a disk diffusion assay: the first test revealed the capability of fully inhibiting the bacterial growth after 48 h starting from the concentration of 0.5%, while the second one showed an inhibition halo of 8-10 mm at the concentrations of 0.5 and 1% respectively. Olive seedlings were then spray-inoculated with a  $10^6$  CFU/mL Psav suspension 24 hours after being treated with the nanoemulsion at 1%. After 7- and 14-days post treatment the level of recovered epiphytic colonies was reduced up to one log unit in comparison with the untreated control, showing similar values to the copper treatment.

The current results highlight the possibility of exploiting cellulose nanocrystals-based emulsion to enhance thyme essential oil antimicrobial activity providing a new plants protection tool.

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## Synthesis of Fluorinated PAMAM-Arginine and Guanidine Conjugates as Non-Viral Vectors

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Keywords: gene delivery, fluorine, transfection

The development of novel non-viral vectors for gene delivery has gained great attention in the last years, to overcome the cytotoxicity and transfection efficiency (TE) obstacles of the cationic polymers nowadays present in literature (*i.e.*, 25kDa polyethylenimine (PEI) and high generation polyamidoamine dendrimers (PAMAM)[1][2]. The achievement of an ideal gene delivery vector still seems a long way off, due to the high manufacturing costs and the severe cytotoxicity of both high generation dendrimers and high molecular weight cationic polymers, whereas low generation and low molecular weight polymers present low TE [3]. In this scenario, functionalization strategies could be exploited to add biocompatible moieties, such as amino acids as arginine, characterized by having a guanidinium group, and to introduce fluorine atoms to decrease cytotoxicity while maintaining or enhance TE [4][5].

In this work [5], we have explored and designed combined synthetic strategies to obtain fluorinated PAMAM-arginine and guanidine polymeric conjugates as safe and efficient vectors for gene delivery with an improved TE as compared to the unfunctionalized polymers and to the golden standard nowadays used as positive controls (25kDa bPEI). Our attention was focused on the functionalization in mild reactions condition of low generation PAMAM and low molecular weight PEI, through the development of fluorinated arginine(or guanidine)-based Michael acceptors. Furthermore, the presence of fluorinated moieties not only for gene transfection improvement but also for a possible future application in the <sup>19</sup>F magnetic resonance imagining is underlined [5].

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## *Hydrogels and Bioplastics based on Agar, Gelatin and Chitosan: viscometry and kinetic models of gelling, thixotropy and crosslinking*

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Keywords: hydrogels; bioplastics; kinetic models of gelling

Hydrogels and Bioplastics based on natural polymers have great applicative and scientific importance<sup>1</sup>. The realization of a biodegradable, biocompatible and thermally stable product remains a hot topic in tissue engineering and bioprinting<sup>2</sup>. From the rheological point of view there are many open problems, such as the optimization of the formulation, the control of the aggregation kinetics, the crosslinking of the polymer material<sup>3</sup>.

Our goal is the study of gelation, thixotropy and crosslinking kinetics by means of viscometry of homogeneous dispersions; the understanding of the molecular mechanisms underlying the solution-sol and sol-gel transitions; obtaining of viscoelastic products by solvent casting; obtaining of mimetic biomaterials of the extracellular matrix of the connective tissue.

Agar, gelatin and chitosan were used as gelling agents, and we have experimented with bifunctional carbonyl cross-linkers. By means of rotational viscometry, the curves of viscosity as a function of time, shear-rate, temperature and concentration made it possible to follow the gelation, thixotropy and crosslinking kinetics (Figure 1). By solvent casting we obtained viscoelastic films suitable for dynamic-mechanical analysis. The observed behaviors were modeled by means of autocatalytic kinetics and the nonlinear Verhulst and Fischer reaction-diffusion equations.

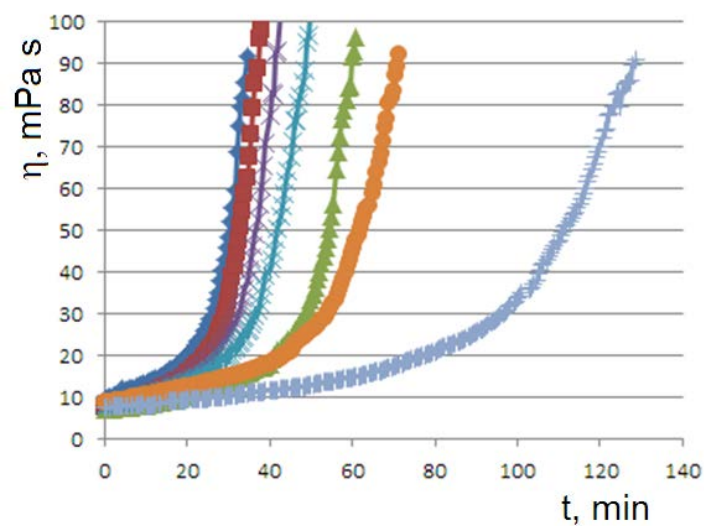


Figure 1. Viscosity curves versus flow time for gelation kinetics of gelatin with increasing crosslinking agent concentration (from left to right).

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## Tailoring the physicochemical properties of nanogels via a pneumatically driven microfluidic device

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Keywords: nanogels, droplet-based microfluidics, drug delivery

Recently, the increasing demand for novel and personalized therapeutic strategies in different diseases has posed new challenges to the scientific community. The peculiar characteristics of nanoscale drug delivery systems (DDS) and the advantages of their use in clinical practice candidate the field of nanomedicine as a guide for providing adequate answers to these problems<sup>1</sup>. Among the many DDS, nanogels (NGs) represent a promising class of nanomaterial for drug and gene delivery thanks to their unique physicochemical features. Indeed, the combination of different polymers through physical or chemical cross-linking has led to the formulation of smart materials eligible for targeting therapies in a variety of cancer scenarios<sup>2</sup>.

However, traditional synthetic routes have several drawbacks that limit the clinical application of NGs, such as poor control over reaction parameters, high polydispersity of NGs, limited batch-to-batch reproducibility, difficulty in modulating the physicochemical properties of nanocarriers, and the use of large amounts of chemicals and therapeutics. In this scenario, microfluidics has emerged as a promising approach to overcome the limitations associated with conventional batch synthesis and has great potential for controlling reaction parameters, making it an ideal platform for the production of nanomaterials<sup>3,4</sup>.

Here, we propose a droplet-based microfluidic device endowed with a pressure-actuated flow focusing junction (FFJ) for the synthesis of hyaluronan/polyethyleneimine (HA-PEI) NGs (Figure 1a). The generated water-in-oil emulsion, in which the aqueous polymers solution is the dispersed phase, utilizes

microdroplets as reaction chambers wherein nanocarrier formation occurs through chemical cross-linking between polymers. In addition, pneumatic actuation of the FFJ in the range of 0-2 bar allows real-time modulation of the orifice width, thereby controlling the microdroplet diameter and consequently the NG size (Figure 1b). By controlling the process parameters, the hydrodynamic diameter of NGs could be tuned in the range 92-190 nm while maintaining an extremely low polydispersity (0.015).

Subsequently, we validated our HA-PEI NGs as drug delivery systems in an ovarian cancer model (Figure 1c). Doxorubicin was used as the chemotherapeutic agent and results showed that *in vitro* NG-mediated delivery of sublethal drug doses resulted in enhanced therapeutic effect compared to free drug administration (Figure 1d).

Finally, these results highlight the good performances of our device for the continuous flow synthesis of polymer NGs and its capability to manipulate their physicochemical properties. Moreover, the *in vitro* validation revealed the potential applicability of the synthesized nanocarriers in different cancer scenarios.

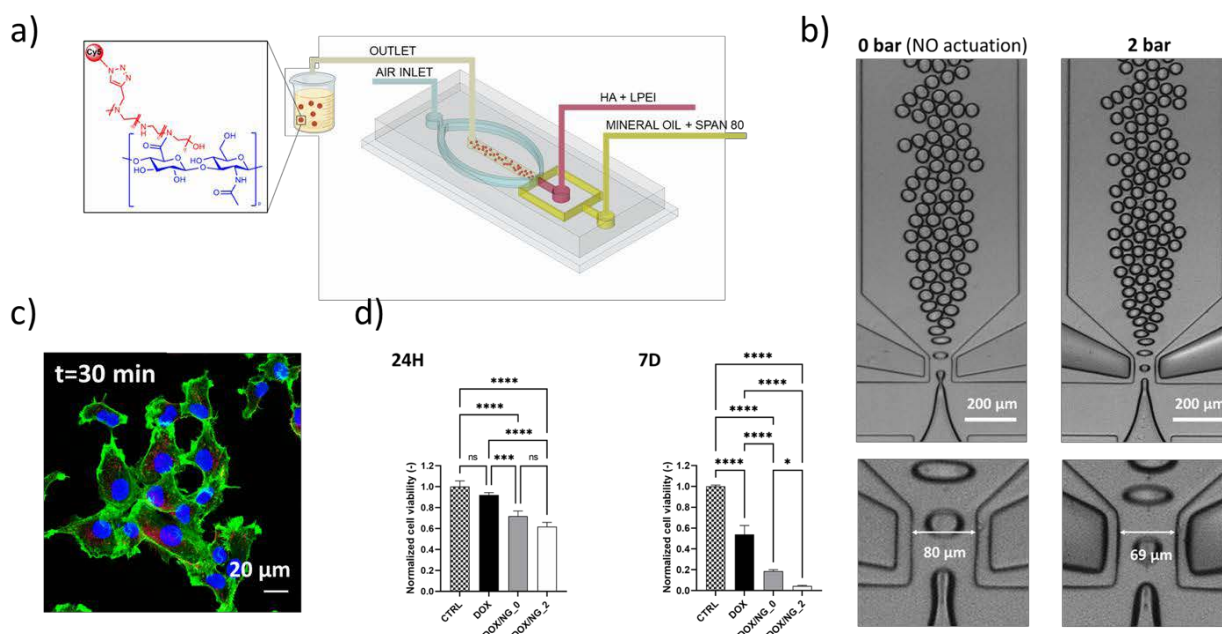


Figure 1. a) schematic representation of the experimental setup; b) effect of pneumatic actuation on droplet diameter and FFJ; c) representative image of NGs cellular uptake after 30 min of incubation in ovarian cancer cells (i.e. OVCA433); d) *in vitro* evaluation of therapeutic effect of NG-mediated drug delivery vs. free drug administration at 24h and 7 days.

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## Nanosponges-based hydrogels for drug delivery: an HR-MAS NMR investigation

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Keywords: nanosponges, diffusion-NMR, drug release

Nanosponge hydrogels are cross-linked polymeric nanoscale matrices, characterized by the ability to absorb and retain large amount of water (Figure 1a). Nowadays nanosponges [1], due to their peculiar sponge-like porous structure, are experiencing increasing use in the biomedical field, as devices for the controlled release of both lipophilic and hydrophilic drugs of various sizes. Interestingly, by adjusting the amount and type of cross-linkers or monomers used in the polymerization, it is possible to tailor the structure and porosity of the 3D network to load and transport pharmaceuticals to specific targets. In designing novel hydrogel-based systems for controlled drug delivery, optimizing the release kinetics remains a challenging step and requires a deep understanding of the mechanisms driving molecular transport within the gel matrix. In particular, the contributions of solute-solute and polymer-solute interactions on the diffusion motion of the drug, related to the polymer network pores size, play an important role. In the present work, two different kinds of nanosponges based on  $\beta$ -cyclodextrin ( $\beta$ -CD) and cyclic nigerosyl-1,6-nigerose (CNN) [2] as monomers cross-linked with pyromellitic dianhydride have been investigated.

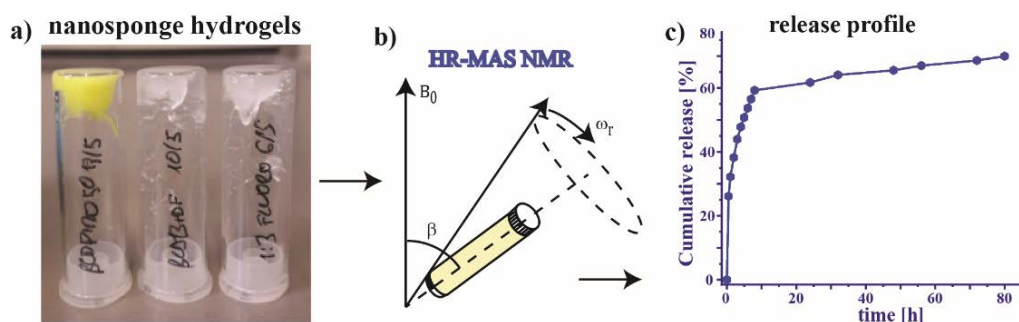


Figure 1. a) Picture of nanosponge hydrogels, b) HR-MAS NMR set-up, c) release profile of  $\beta$ -CD nanosponge loaded with piroxicam drug.

Different pharmaceutical products such as ethosuximide, piroxicam, 5-fluorouracil and dimethyl fumarate have been loaded on these nanosponges. The influence of the polymeric matrices on the drug dynamics have been studied by high resolution magic angle spinning (HR-MAS) NMR Spectroscopy (Figure 1b) which provide information on the particle mean square displacement. The experimental data, acquired at different diffusion time  $\Delta$ , indicate that the majority of the drugs experience a Gaussian diffusion motion in particular, 5-fluorouracil loaded in nanosponge polymers shows a decreased diffusion coefficient compared with water solution. Conversely, piroxicam molecules exhibit a faster diffusion in the gel phase and this is more relevant for  $\beta$ -CD nanosponges. These findings suggest that a double mechanism of solute-to-polymer adsorption on the outer surface and  $\beta$ -CD encapsulation [3] takes place in the hydrogel leading to a reduced concentration of free drug in solution. The set of complex interactions lead to slow and sustained multi-step release kinetics of piroxicam (Figure 1c) [4].

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## *Dyeing metakaolin-based geopolymers with pH indicators: a feasibility study*

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Keywords: coloured geopolymers, pH indicators, CIELAB Colour Space

Over time, a large amount of coloured materials has been used in the construction of structures, paintings, pottery, and mosaic restoration. Because of their strong mechanical and chemical resilience, geopolymers have recently received a lot of attention and have been employed in numerous fields, especially in restoration [1,2]. This study aims to synthesise coloured geopolymers by using white metakaolin and four dyed alkaline activator solutions (flowchart procedure is reported in Figure 1), which contain pH indicators (bromothymol blue, cresol red, phenolphthalein, and methyl orange). The geopolymer fresh pastes are cured at 25 or 40 °C and aged at different times at room temperature. A complete physico-chemical characterisation on white samples is performed over time by using FT-IR, ionic conductivity (IC) and pH measurements, as well as integrity and weight loss tests, while the coloured geopolymers are characterised after 56 days of ageing time. The colour hues are assessed in the CIELAB colour space before and after soaking the coloured specimens in deionized water for 1 h. FT-IR analyses confirmed the geopolymerisation occurrence, whereas pH and IC measurements and integrity and weight loss tests confirmed the stability of the synthesised materials. Finally, CIELAB space colour analysis revealed a possible application of the dyed geopolymers for indoor environments.



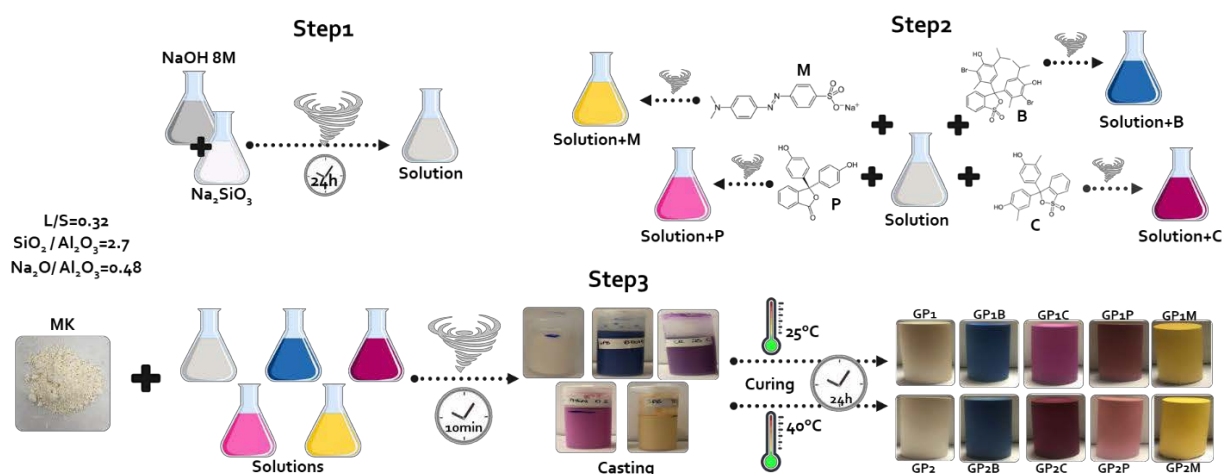


Figure 1. Scheme of geopolymer synthesis.

### Acknowledgements

This work was supported in part by “SCAVENGE” financed by Università degli Studi della Campania Luigi Vanvitelli in the framework of “Piano Strategico di Ateneo 2021-2023—Azione strategica R1.S2”. The authors would also like to thank Prochin Italia Prodotti Chimici Industriali Srl (Italy) for donating the sodium silicate used in this work.

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## *Cr<sup>3+</sup>-doped Phosphors for Thermal Sensing: Advantages and Limitations*

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Keywords: luminescence, thermometers, Cr<sup>3+</sup>

Temperature and pressure are two of the thermodynamic properties defining the state of a system. Therefore, the ability to precisely measure them is critical to get insight into materials properties.

The use of Cr<sup>3+</sup> luminescence to probe the temperature and pressure was demonstrated to be particularly effective since the early studies on ruby ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>:Cr<sup>3+</sup>) [1,2] and, nowadays, ruby is still one of the reference materials used in the worldwide laboratories. Recently, Cr<sup>3+</sup>-activated thermometers based on the ratio between <sup>4</sup>T<sub>2</sub>→<sup>4</sup>A<sub>2</sub> and <sup>2</sup>E→<sup>4</sup>A<sub>2</sub> transitions have been demonstrated to be particularly promising in terms of sensitivity, reliability, and flexibility, with better performance with respect to *R*-lines based thermometers such as ruby [3-6]. The energy gap between the <sup>2</sup>E and <sup>4</sup>T<sub>2</sub> excited states can be controlled by playing on the octahedral site of the host embedding Cr<sup>3+</sup> ions to design a class of thermometers for specific temperature ranges. The different nature of the transitions involved is the key point to understand the promising thermometric performances and the hosts for Cr<sup>3+</sup> ions can be selected by considering a suitable range of average metal-oxygen bond lengths of the octahedral site.

By considering the mullite-type Bi<sub>2</sub>M<sub>4</sub>O<sub>9</sub>:Cr<sup>3+</sup> (M=Ga, Al) systems as a case study, strengths and weaknesses of Cr<sup>3+</sup>-based thermometers will be discussed. The crystal field strength *10Dq* and the Racah parameters *B* and *C* are calculated and exploited in the framework of Tanabe-Sugano diagram to describe the effect of the structure on the electronic levels of Cr<sup>3+</sup>. Moreover, in the Bi<sub>2</sub>M<sub>4</sub>O<sub>9</sub>:Cr<sup>3+</sup> (M=Ga, Al) systems, the <sup>2</sup>E is split into two *R*-lines (called *R*<sub>1</sub> and *R*<sub>2</sub>) allowing to simultaneously define two thermometric parameters (based on <sup>4</sup>T<sub>2</sub>-<sup>2</sup>E and *R*<sub>1</sub>-*R*<sub>2</sub> couples) working into two different temperature ranges in the same compound. The thermometric performances

of the systems are compared with the literature discussing parameters such as the relative sensitivity ( $S_r$ ), the temperature uncertainty ( $\delta T$ ) and the reproducibility ( $R$ ). The absolute sensitivity of Boltzmann distribution-based systems is theoretically investigated demonstrating the potential of  $\text{Cr}^{3+}$ -activated phosphors as luminescent thermometers. Finally, the flexibility of this class of thermometers will be discussed and an example of real application will be introduced, showing the possibility of this family of thermometers to locally probe the temperature of a metallic catalyst during the catalytic reaction of  $\text{C}_2\text{H}_4$  hydrogenation [7].

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## Microwave synthesis of new co-polypyrrole-polyketone anion exchange membranes

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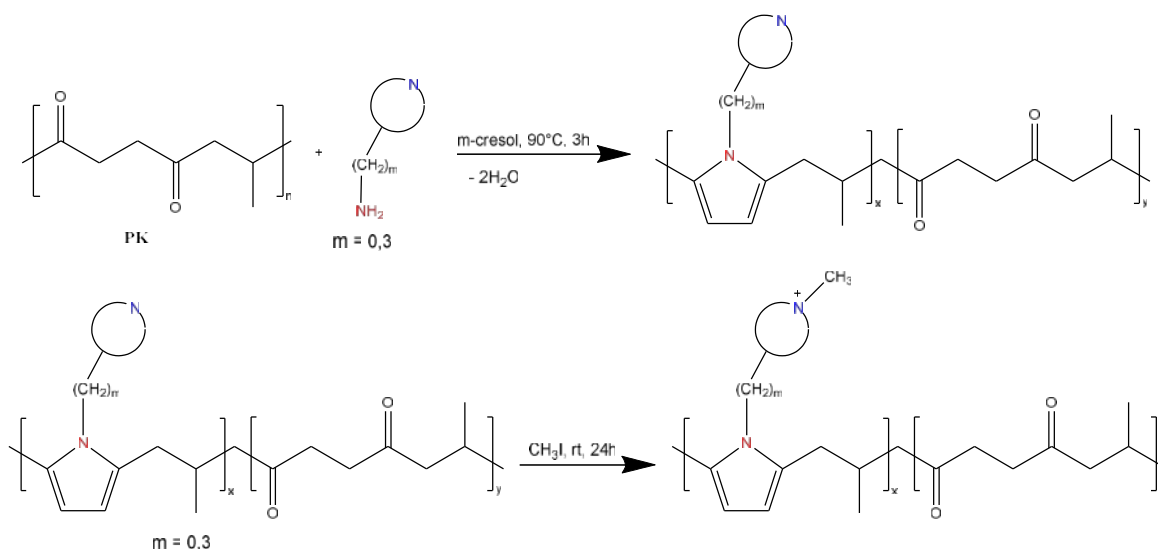
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Keywords: Anion-exchange polymers, Functionalized polyketone, Microwave assisted synthesis

Polyketones (PKs) are a class of semicrystalline, thermoplastic, and easily available polymers which have attracted attention as inexpensive precursors for the production of anion-exchange ionomers [1-4].

In this work a terpolymer PK is reacted with two different cycloaliphatic primary amines. The synthesis has been performed in a microwave reactor, allowing a significant reduction of the reaction time and some interesting effects in the properties of the membranes obtained by solvent casting.

Two degrees of functionalization of the polyketone backbone for each amine have been obtained operating in the corresponding amine/PK molar ratio. The anion exchange version of the membranes has been obtained by simple reaction with methyl iodide and subsequent ion exchange in potassium hydroxide solution. The molecular structure, thermal and ion conduction properties of the membranes are evaluated in relation to their electrical behaviour as determined by Broadband Electric Spectroscopy.



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## Nanostructured titania decorated with copper: effect of the substrate pretreatment on morphology and electrochemical performance of the electrodes

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Keywords: micro-structured surfaces, copper electrodeposition, electro-reduction

The production of materials with micro-structured surfaces, such as for example vertically aligned nanotubes (NT), involves the possibility of obtaining large surface areas and therefore enhanced electrocatalytic and photo-electrocatalytic capacities. Pristine titania NTs are generally used as photoanodes in water splitting. Much more often NTs arrays are coated with organic substances or metal oxides or even mixed metal oxides [1][2]. Only a limited effort has been so far devoted to the fabrication of NTs coated or decorated with metals in the elementary state.

On the other hand, some metals such as copper, for example, have shown interesting electrochemical properties in the environmental field, particularly in the electroreduction of  $\text{NO}_x$  or in the conversion of  $\text{CO}_2$  to organic molecules.

This work investigates the possibility to develop cathode materials by galvanostatic electrodeposition of copper micro-particles on differently treated titanium-based surfaces.

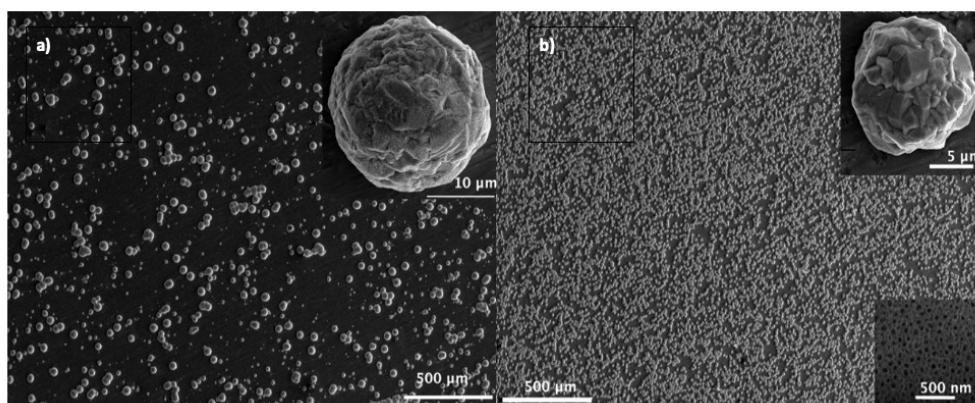


Figure 1. SEM images of electrodeposited Cu on Ti (a) and  $\text{TiO}_2$  nanotubes (b).

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The surface modifications will include etching with hydrogen fluoride and anodization in a glycerol-containing electrolyte to promote the growth of an ordered titania nanotube array. The effect of an intermediate thermal treatment before deposition will be also evaluated.

The morphology, structure, and electrochemical properties of the cathodes will be characterized by SEM imaging, XRD spectra, corrosion tests, EIS spectra, and cyclic voltammetry before and after use.

Finally, the materials will be tested in the reduction of aqueous solutions containing nitrate or chlorate.

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## *Active bio-packaging produced by encapsulation of Humic Substances into electrospun PHBV films*

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Keywords: humic substances, electrospinning, antioxidant and antimicrobial films

The development of active and sustainable food packaging materials is crucial to reduce the use of the conventional plastics and prolong food quality, thus minimizing the environmental footprint of packaged food. Therefore, the combination of a bio-based and biodegradable polymer with natural additives, is the most coherent technological route to meet sustainability issues.

In this context, waste to wealth approach can cope with these major challenges by providing for bioavailable active compounds from waste residues. Among these, humic substances (HS), the alkali soluble fraction of organic matter, usually found in water, soil and sediments, provide an important bio-source for redox-active compounds since they are rich in quinones, phenols, carboxyl, and hydroxyl moieties. Accordingly, HS can generate or scavenge reactive oxygen species (ROS), exhibiting antioxidant, antibacterial and anti-inflammatory features, which make HS extremely promising as sustainable additives for polymer matrixes. Furthermore, these properties can significantly be enhanced by the combination of these biomolecules with an organic or inorganic matrix that can template HS supramolecular structure.

Herein, the electrospinning technology has been exploited to design composite films made of electrospun biodegradable and bioderived polymers in the presence of HS [1,2]. To this purpose, electrospun composites made by incorporating different amounts of HS into poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) matrix were produced and converted into homogeneous and continuous films. These were characterised to assess the morphology, thermal, crystallinity, optical, mechanical, antioxidant and barrier properties of the resultant PHBV-based films as well as antifungal activity against *Aspergillus flavus* and *Candida Albicans* and antimicrobial



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properties against *Staphylococcus aureus*, *Escherichia coli*, *Bacillus cereus*, *Enterococcus faecalis*, *Salmonella typhi* and *Listeria monocitogenes*.

The obtained results suggest that the electrospinning methodology is a promising and sustainable approach to give biowaste a new value through the development of multifunctional materials for active packaging applications.

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## *Self-standing Membranes of TiO<sub>2</sub> Nanotube Arrays: Fabrication, Decoration and Use in Li-Ion Batteries*

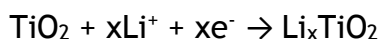
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Keywords: TiO<sub>2</sub> nanotube arrays, energy storage

Lithium-ion batteries (LIBs) are among the most common devices for energy storage. In this kind of devices, the anode is normally based on graphite, capable of intercalating/deintercalating Li<sup>+</sup> between its planes with high safety and long-lasting life cycle. However, graphite suffers from a reduced Li-ion cyclability and low energy density, and its specific capacity is nowadays considered insufficient for increasing market needs [1]. Among the possible alternative to graphite, TiO<sub>2</sub> is undoubtedly an excellent candidate, since it exhibits a low/negligible volume variation over cycling, good durability, and high lithiation/de-lithiation potential. The ion intercalation occurs during the electrochemical reduction of the species Ti(IV) to Ti(III), according to the following reaction:



Within this context, the use of TiO<sub>2</sub> based nanostructures is highly convenient, since they provide larger specific surface area and a shorter diffusion path for the ions [2]. Electrochemically synthesized TiO<sub>2</sub> nanotube arrays have already been used for fabrication of microanodes; however, when using the arrays anchored to the metallic layer underneath it is impossible to determine the actual electrode active mass, thus preventing from the determination of the actual specific capacity of the material [3-4]. To overcome this issue, we developed an efficient method for the fabrication of TiO<sub>2</sub> nanotube arrays self-standing membranes, which were subsequently successfully used as anodes for LIBs.

Two layers of TiO<sub>2</sub> nanotube arrays with different crystalline phases were synthesized by mean of electrochemical oxidation of Ti [5-6]. Subsequently, we induced the detachment of the array from the metal by selectively destroying with HF just the layer at the bottom (i.e. at the metal/oxide interphase). Moreover, we decorated the TiO<sub>2</sub> nanotube arrays with Ag nanostructures by photoreduction of Ag<sup>+</sup>, using a green and cheap procedure. Besides a full morphological and structural characterization by mean of SEM and XRPD, both pristine and Ag-decorated self-standing membranes were successfully tested as anodes for T-shaped LIBs assembled in half-cell configuration.

The pristine membranes exhibit a capacity of around 100 mAh/g, being the theoretical TiO<sub>2</sub> specific capacity equal to 185 mAh/g. Upon comparing the electrochemical properties in terms of areal capacity (mAh/cm<sup>2</sup>), our materials show higher values than analogous arrays attached to Ti. Specific capacity rises up to almost 150 mAh/g in the case of the Ag-decorated membranes. This experimental evidence is probably due to the formation of a protective layer over the nanotube surface and an additional alloying/dealloying of lithium in silver.

The highly encouraging results obtained so far pave the way (i) to the synthesis of a broad range of composites with a fine tuning of their electrochemical properties, and (ii) to their use in “beyond lithium” devices, such as Na-ion batteries.

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## *Insegnare Chimica con Mastering Chemistry*

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La chimica è una disciplina complessa che richiede un approccio integrato per essere compresa e padroneggiata appieno. Mastering Chemistry, sviluppato dall'MIT, è un innovativo programma educativo progettato specificamente per l'insegnamento della chimica a livello universitario.

Mastering Chemistry offre una serie di risorse interattive e personalizzabili che coinvolgono gli studenti in attività pratiche, esercizi e simulazioni che favoriscono l'apprendimento attivo. Gli strumenti di valutazione integrati consentono agli studenti di verificare immediatamente la comprensione dei concetti chiave e di ricevere feedback istantaneo per il miglioramento continuo. I docenti possono monitorare il progresso degli studenti, identificare le aree di difficoltà e adattare il proprio insegnamento di conseguenza.

Un aspetto unico di Mastering Chemistry è la sua capacità di adattarsi alle esigenze individuali degli studenti. Attraverso l'utilizzo di algoritmi di apprendimento automatico, il programma analizza il percorso di apprendimento di ogni studente e fornisce raccomandazioni personalizzate per potenziare la comprensione dei concetti e colmare eventuali lacune di conoscenza.

Il programma include anche una vasta libreria di risorse didattiche, come video esplicativi, simulazioni interattive e materiale di studio aggiuntivo, che consentono agli studenti di approfondire i loro studi e di applicare i concetti appresi in modo più concreto.

Grazie alle sue caratteristiche interattive, personalizzabili e di valutazione, questo programma offre agli studenti un ambiente di apprendimento coinvolgente e favorisce il raggiungimento di una solida comprensione dei principi chimici fondamentali. I docenti possono sfruttare le sue potenti funzionalità per migliorare l'insegnamento e monitorare il progresso degli studenti in modo efficiente.

## Photoreforming of organics in aqueous suspension of Nb<sub>2</sub>O<sub>5</sub>/C<sub>3</sub>N<sub>4</sub> composites to obtain H<sub>2</sub>

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Keywords: hydrogen, composite materials, photo-reforming

Photocatalysis based on the use of semiconductors has gained, during the recent years, increased attention as promising sustainable process for H<sub>2</sub> and fine chemicals production, given the possibility of activating such photocatalysts by visible light radiation [1]. We have observed, by using TiO<sub>2</sub> as photocatalysts, that the generated H<sub>2</sub> comes both from water-splitting and from organic substrate dehydrogenation [2]. Unfortunately, the most active photocatalysts are active under UV irradiation, so further studies are necessary to improve the solar light absorption ability of the semiconductors. In this work, bare and composite materials based on C<sub>3</sub>N<sub>4</sub> and Nb<sub>2</sub>O<sub>5</sub> have been used as photocatalysts for the photo-reforming of aqueous solutions of oxygenated compounds containing alcohol groups as sacrificial reagent, i.e. playing the hole scavenger role in the mechanism of heterogeneous photocatalysis [3]. The photo-reforming activity in this work has been measured under both UV-LED irradiation and natural sunlight illumination. Moreover, the presence of metallic Pt as co-catalysts has been studied. Carbon nitride (C<sub>3</sub>N<sub>4</sub>) based materials are good candidates for solar energy conversions. The choice of C<sub>3</sub>N<sub>4</sub> and Nb<sub>2</sub>O<sub>5</sub> arises from the fact that their heterojunction can lead to lower recombination between the photo-generated electrons and holes by forming four possible heterojunction schemes: type II, Z-scheme, S-scheme and Schottky junction [4]. Both Nb<sub>2</sub>O<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub>/C<sub>3</sub>N<sub>4</sub> composites have been prepared by hydrothermal synthesis and all of them were physical-chemically characterized. C<sub>3</sub>N<sub>4</sub> has been prepared using melamine as precursor. The catalysts reported in this work have been prepared in different ways: some catalyst have been calcinated at 200 °C or 500 °C and also heterostructures have been prepared using different ratios in weight between Nb<sub>2</sub>O<sub>5</sub> and C<sub>3</sub>N<sub>4</sub>. According to this, SSA and energy gap of catalysts changes. Photo-reforming tests were performed at room conditions in a 50 mL cylindrical Pyrex photoreactor with 0.32·g·L<sup>-1</sup> of solid dispersed

in 35 mL of 4% w/w (0.27 M) triethanolamine (TEOA) aqueous solution. Selected runs were carried out by using aqueous solutions of methanol, ethanol, glycerol or 5-hydroxymethylfurfural (5-HMF) as hole scavengers. The photoreactor was externally illuminated by two UV LED IRIS 40 with an irradiation peak centered at 365 nm. The irradiance of the two LED, measured in the range 315-400 nm by a UVX Digital radiometer, resulted  $1450 \text{ W}\cdot\text{m}^{-2}$ . In the absence of Pt the activity of the photocatalysts was very low and consequently, here are reported only the results obtained in the presence of Pt (1 % with respect to the photocatalyst). Figure 1 reports the productivity results obtained under UV-LED irradiation.

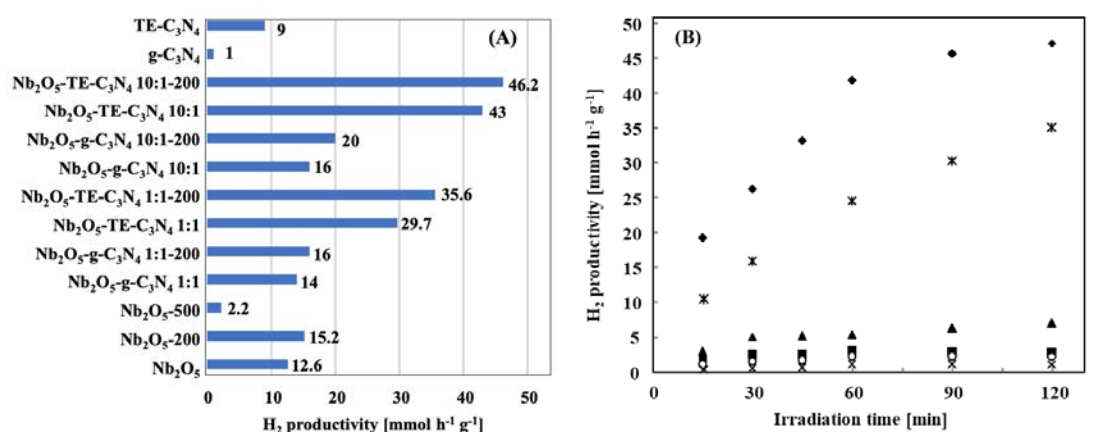


Figure 1. (A) Productivity observed for the various photocatalysts used for the 0.27 M triethanolamine aqueous solution photo-reforming and (B) productivity observed for runs carried out by using Nb<sub>2</sub>O<sub>5</sub>/TE-C<sub>3</sub>N<sub>4</sub> 10:1-200 as photocatalyst and different hole scavengers: (◆) TEOA 0.27 M; (\*) Ethanol 0.27 M; (▲) Methanol 0.27 M; (■) Glycerol 0.27 M; (x) Glucose 0.27 M; (O) 5-hydroxymethylfurfural 0.5 mM.

Heterojunction Nb<sub>2</sub>O<sub>5</sub>/TE-C<sub>3</sub>N<sub>4</sub> 10:1-200, is the best photocatalyst tested in this work, giving rise a productivity of ca.  $46 \text{ mmol h}^{-1} \text{ g}^{-1}$  that was 4 or 5 times those obtained in the presence of pristine Nb<sub>2</sub>O<sub>5</sub> or TE-C<sub>3</sub>N<sub>4</sub>, respectively. Interestingly, the apparent quantum efficiency of the optimal material reached a value of 14 % under UV LED irradiation. Selected runs were performed under natural sunlight illumination by using a cylindrical Pyrex 125 mL photoreactor irradiated by the top and containing 100 mL of an aqueous suspension of  $0.32 \text{ g}\cdot\text{L}^{-1}$  or  $0.60 \text{ g}\cdot\text{L}^{-1}$  of photocatalyst in 4% w/w aqueous solution of TEOA. The photon flux impinging the photoreactor was measured in the range 315-400 nm by the radiometer every 10 min throughout the photocatalytic tests in order to estimate the cumulative energy entering the system. Nb<sub>2</sub>O<sub>5</sub>-TE-C<sub>3</sub>N<sub>4</sub> 10:1-200 was the most performant photocatalysts also under this condition giving a hydrogen productivity of  $810 \text{ }\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$  or  $630 \text{ }\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$  when using  $0.32 \text{ g}\cdot\text{L}^{-1}$  or  $0.6 \text{ g}\cdot\text{L}^{-1}$ , respectively.

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## Development of composites with Self-responsive functions: Self-sensing, Self-heating and Self-curing

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Keywords: self-responsive function, carbon filler, epoxy resin

This work concerns the design of composites having integrated self-responsive functionalities based on nanostructured forms of carbon, such as multi-wall carbon nanotubes and expanded graphite. In particular, the study focuses on three different smart functions strongly desired in the field of aeronautical materials: self-sensing, self-curing and smart thermal management. The above-mentioned functions are based on two physical phenomena: the “piezoresistivity” (changes in the electrical resistivity of the composites resulting from mechanically applied strains) [1-3] and the Joule effect (heat generated by the current flow through the composite) [3-5]. In the first case, the adopted approach allows the detection of micro-damages in the materials that a visual inspection is unable to detect. In the second case, the heat generated through the joule effect, on the one hand, allows avoiding the ice growth on the most vulnerable parts of the aircraft, on the other can be exploited to promote polymerization reactions of the uncured filled resin (electro-curing) [6]. The results evidence that this last methodology can be really very effective, highlighting different advantages, ranging from a save-energy process to a higher curing degree and as a consequence to a better mechanical performance, with respect to traditional curing processes in an oven or autoclave.

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## Colorimetric $\text{Hg}^{2+}$ detection by novel cellulose-based xerogels functionalized by porphyrin receptors

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Keywords: xerogels, optical sensors, nanocellulose

Access to drinking water is an important issue today, and among inorganic pollutants heavy metal ions play an important role in their harmful effects on the environment and human health [1]. Among the different heavy metals, mercury has been one of the most studied as its extensive use in different fields of application has led to its spread in the environment, resulting in accumulation in humans with highly toxic effects [2]. Most techniques for the detection of mercury ions in water require the use of complex and expensive laboratory instrumentation, with long measurement times that make them useless for real-time contaminant level monitoring. In this scenario, the development of low-cost, transportable and easy-to-use colorimetric sensors for monitoring  $\text{Hg}^{2+}$  is a great alternative [3].

Tetra (4-carboxyphenyl)porphyrin TCPPH<sub>2</sub> coordinates  $\text{Hg}^{2+}$  ions in its central core by the inner nitrogen atoms. This phenomenon causes the color change of the receptor, from pink to green. The intensity of colorimetric variation is proportional to the concentration of mercury ions present in the aqueous sample. To use the porphyrin receptor by the CSPT-like optical instrument setup, it is necessary to anchor the TCPPH<sub>2</sub> on a solid support suitable for optical measurements in water. To reach this goal, cellulose-based nanosponges (CNS) functionalized with the porphyrin receptor have been used as solid supports.

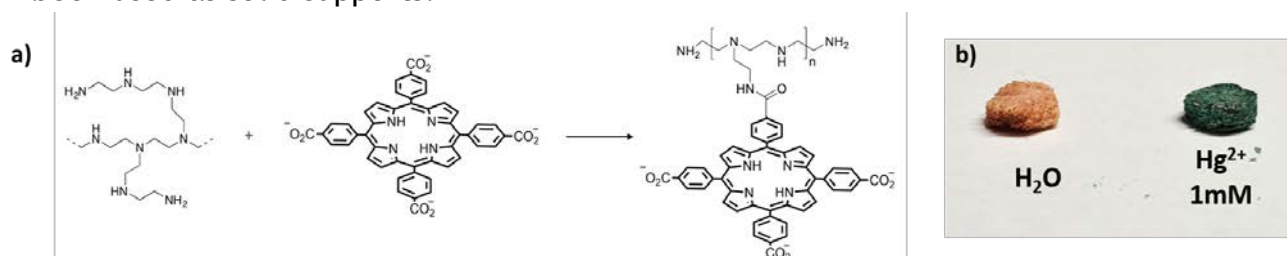


Figure 1. a) Functionalization of bPEI with the porphyrin receptor TCPPH<sub>2</sub>; b) Colorimetric variation of CNS@TCPPH<sub>2</sub> after the immersion in  $\text{Hg}^{2+}$  1mM water solution.

CNS can be obtained by combining TEMPO-oxidized cellulose nanofibers (TOCNF) and branched polyethyleneimine (bPEI) as building-blocks [4]. In order to link covalently the receptor to the solid support, bPEI was functionalized with the porphyrin TPPCH<sub>2</sub> (Figure 1a), and the functionalized polymer was then combined with TOCNF to obtain a homogeneous mixture. This latter was freeze-dried and thermally treated in order to get functionalized cellulose-based nanosponges, CNS@TCPPh<sub>2</sub>, a material able to detect mercury ions by a naked-eye colorimetric variation after immersion in Hg<sup>2+</sup> aqueous solutions (Figure 1b).

To make a practical use of the novel solid sensors, a new instrumental setup for optical analysis has been developed, using for its realization low-cost and familiar electronic devices such as LEDs and PC Web-Cam. The measuring chamber has been realized by a 3D printer, the CNS@TCPPh<sub>2</sub> have been cut into slices and placed inside a transparent PMMA holder, which is connected through tubes to the peristaltic pump that flows the sample solution to be analyzed (Figure 2a and 2b). The web-cam records the video of the colorimetric change during the measurement and then converts it digitally to obtain the value of the ion concentration Hg<sup>2+</sup> (Figure 2c). Optical analyses have shown good results in terms of selectivity and sensitivity for mercury detection. The use of porphyrins as receptors enables synthetic modulation of the molecular structure of the sensing materials, thus allowing future development of sensors for the detection of different pollutants by exploiting the same cellulose-based xerogels as solid supports.

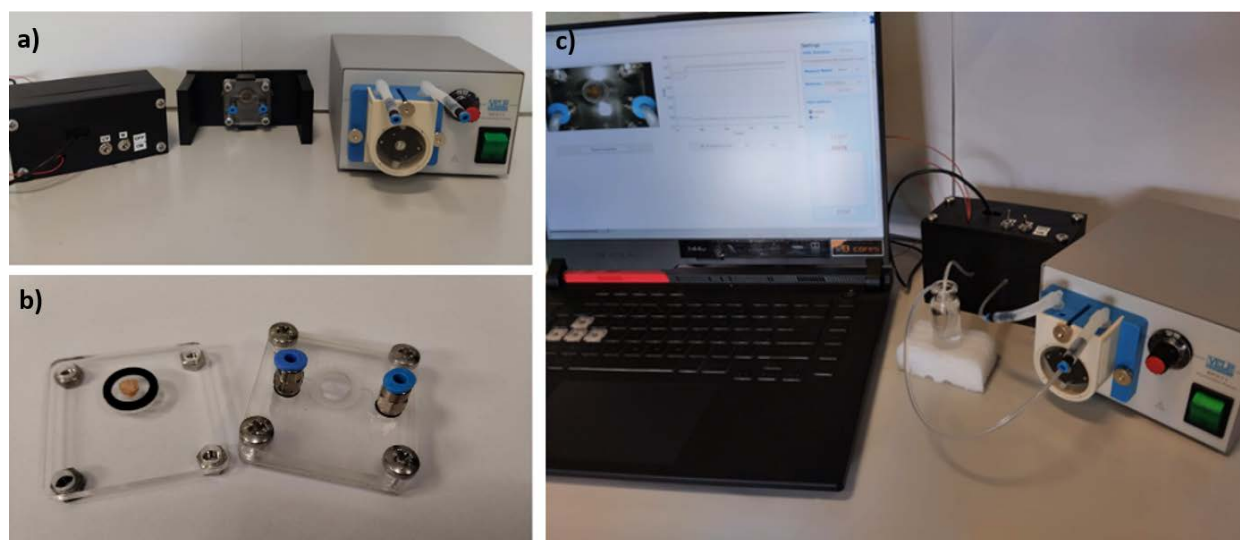


Figure 2. a) The CSPT-like instrument setup: the measuring chamber made by 3D printer (with LEDs and PC-Webcam) and the peristaltic pump. b) The transparent PMMA holder through which the sample flows and the CNS@TCPPh<sub>2</sub> are placed. c) A photo during the optical analysis. The PC-Webcam records the colorimetric variation of CNS@TCPPh<sub>2</sub> while the peristaltic pump flows a Hg<sup>2+</sup> sample.

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## Mechanochemical synthesis of mechanical bonds and guest-inclusion in $M_{12}L_8$ poly-[ $n$ ]-catenanes

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Keywords: Mechanochemistry, Catenanes, Guest-Inclusion X-Ray Diffraction.

Mechanically interlocked molecules (MIMs) have captured the interest of researchers not only for the original topology and challenging synthesis but also for their potential applications<sup>[1]</sup>. Among all the structures, a unique class of interesting MIMs are poly-[ $n$ ]-catenanes formed by interpenetrated large  $M_{12}L_8$  icosahedral nanocages (*i.e.*, internal cage volumes ca. 2600 Å<sup>3</sup>)<sup>[2]</sup>.

This self-assembled material is reported to be synthesized by means of instant synthesis and slow crystallization making kinetic or thermodynamic control possible for product formation<sup>[2]</sup>. The target of this work was to follow a sustainable approach, and, inspired by the 12 principles of the green chemistry, work toward the removal of the solvent in the synthesis. By mechanochemical means, we grinded the exo-tridentate ligand tris-pyridylbenzene (TPB) and ZnBr<sub>2</sub>, to obtain an amorphous homogeneous powder in short time (15 min) and high yields (~80%). The characterization of the material was carried out by means of powder XRD, SEM, ATR-FT-IR, EA, TGA confirming the selective formation of the [(ZnBr<sub>2</sub>)<sub>12</sub>(TPB)<sub>8</sub>]<sub>*n*</sub>  $M_{12}L_8$  poly-[ $n$ ]-catenane (1) (Figure 1). High-resolution solid-state NMR was exploited to study the dynamic behavior and mobility of the moieties of the structure.

The concatenated structure revealed to work as a dynamic reversible system<sup>[3]</sup>, making the material very versatile, with potential to be used in a wide range of applications such as guest inclusion, isomer recognition, gas adsorption, catalytic activity, etc.... Furthermore, we found that when the catenane is immersed in water, the structure is destroyed giving the possibility to recycle the organic TPB ligand, supporting the sustainable potential for using the material also on an industrial scale.

Despite the successful solvent-free synthesis of this mechanically interlocked material, there is still work to do on its properties and, especially, on its broad range of applications. For example, the in-water behaviour of 1, with the release of the guest in the aqueous environment, suggests the study of pharmaceutical active principles as trapped molecules. Paracetamol is being studied by including it in the amorphous catenane and evaluating the encapsulated amount to be released. We are evaluating the

possibility of using 1 as a drug-delivery system, exploiting the dynamic behaviour of this  $M_{12}L_8$  poly- $[n]$ -catenane.

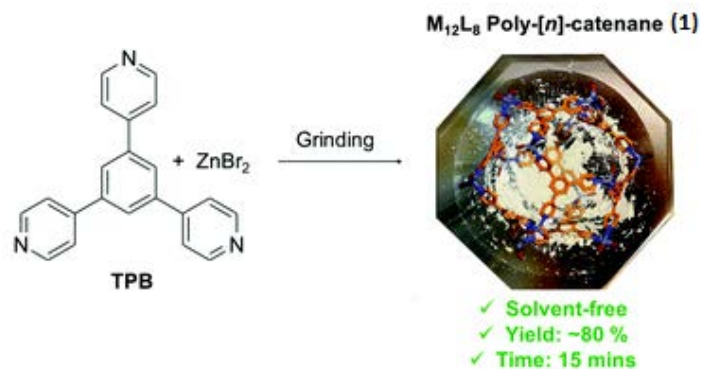


Figure 1. Synthesis of  $[(ZnBr_2)_{12}(TPB)_8]_n$  (1) poly- $[n]$ -catenane<sup>[4]</sup>.

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## *Community of Practice and Faculty Development at the Polytechnic School of Genoa University*

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Keywords: Community of Practice, Faculty Development, Chemistry

At the University of Genova, the first organized experiences of teaching innovation started with the formation in 2016 of the G.L.I.A. group (Gruppo di Lavoro di Ateneo sulle Tecniche di Insegnamento e Apprendimento) established with the aim of promoting ideas on teaching practices among teachers of the University and to develop the sensibility towards a new kind of educational experiences [1]. Since then, several activities of Faculty Development have been organized and presented to the academic community, giving rise to a fruitful network of interactions.

Nowadays, Faculty Developments activities are centered on:

Teachers formation: through Seminars and Workshops, focused on specific topics and methodologies and open to everyone in the academic community upon reservation, and through the FOR.I.U. course, which is a partially residential course organized in several meetings and addressed to teachers who intend to develop their didactic approach, mainly focusing on the participation of young researchers.

Projects: addressed to course degrees and based on the activation of projects for teaching innovation to support teachers in introducing innovative methodologies and approaches.

Research: since 2019 the Congress on Faculty Development is organized yearly at Genova University, with national and international speakers from Universities and Teaching centers, publishing an exhaustive open-access abstract book; the Quaderni del GLIA publication, a journal on Faculty Development innovative teaching and the participation to the national Special Interest Groups (with ASDUNI), focusing on specific academic topics. The Unige Teaching and Learning Center (U.T.L.C.) recently set up at our University coordinates these activities together with GLIA [2].

Within these activities, the Communities of Practice (CoP), set up in 2017, play an important role. Communities of Practice are one of the main approaches to Faculty Development by helping academics to share teaching experiences and innovations in a kind of informal group of professors who meet to develop their teaching skills. In these communities, people aim for continuous learning through sharing with all the participants positive results as well as difficulties in the experience of teaching [3,4]. Communities of practice are active for each School of the University of Genova, led by two or more facilitators (figure 1). In spite of a small number of participants, the CoP

at the Polytechnic School met more than 30 times in different locations, either in presence, either on line during the COVID quarantine period. The scheduled meetings, every one/two months, are carried out at lunchtime, as informal moments to listen and report one's experiences. Some meetings are focused on specific topics, for instance by inviting speakers and experts from other Schools or colleagues involved in innovative teaching experiences. All meetings are indeed open to topics suggested spontaneously by the participants, to share resources, tools, and recurring problems. A number of participants in the CoP belong to the Department of Civil, Chemical and Environmental Engineering, namely to the Chemistry and Chemical Engineering area, thus active learning experiences are spread and tested in several courses of bachelor and Master degrees at the Engineering School. Activities of Classroom Response Systems (i.e. Socrative, Wooclap) have been applied in large classes, for instance during Chemistry lectures (CHIM07) delivered to the 1<sup>st</sup> year of the Bachelor's degree in Biomedical Engineering and to the 1<sup>st</sup> year of Master degree in Bioengineering, and in small classes, for instance Chemistry of Environmental Processes (CHIM/07) for the 1<sup>st</sup> year Master degree in Environmental Engineering, Chemical Thermodynamics in Ideal Systems for the 2<sup>nd</sup> year of the Bachelor's degree in Chemical and Process Engineering and the module of Chemical Thermodynamics in Non-Ideal Systems (ING-IND/24) for the 1<sup>st</sup> year of the Master degree in Chemical and Process Engineering.



Figure 1.  
Faculty Development Initiatives at Genova University.

The activity “Podcast in Chemical and Process Engineering” was introduced in the academic year 2020/2021 (course Multiscale Analysis and

Computer Simulation of Chemical Processes, Master degree in Chemical and Process Engineering) as a result of sharing examples of best practices between participants of the CoP of the Polytechnic School. This approach has been chosen to encourage the engagement of the students while discussing topics related to chemical and process engineering and provide an innovative communication format [5]. These experiences have been monitored by the analysis of the “Teaching evaluation questionnaires” (Questionario di Valutazione della didattica) obtaining good results. Therefore, in our experience, a significant impact of CoP has proven to be the sharing of good practices, as exemplified by the application of the specific methodologies here presented.

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## Fluorinated nanoparticles as powerful probes for bioimaging

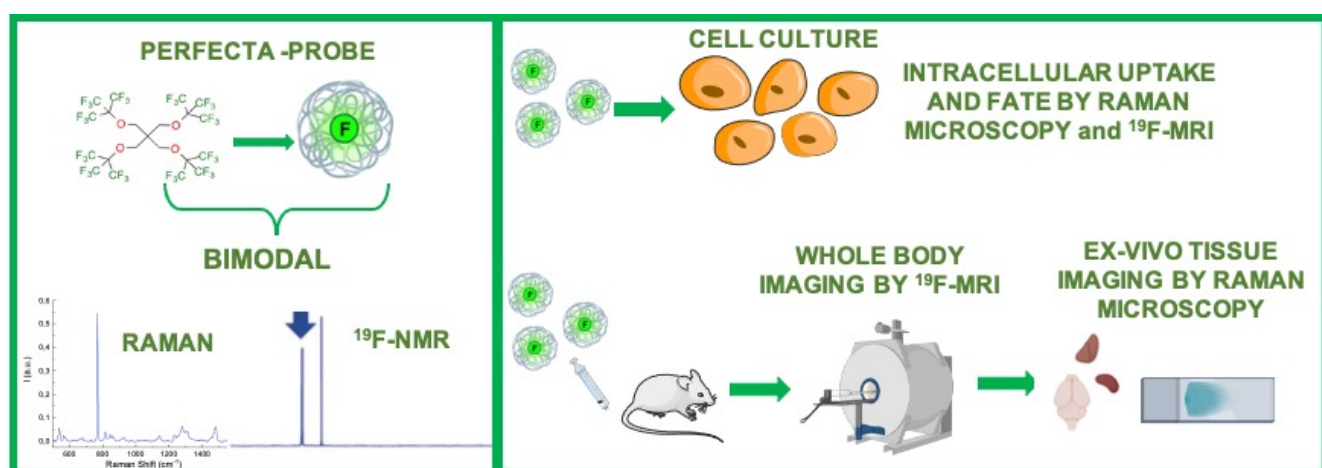
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Keywords: nanoparticles, cell labelling, imaging

This work addresses the current need for novel sensitive, robust, and selective diagnostic tools for non-invasive *in vivo* imaging, which are able to improve the medical practice through earlier diagnosis of disease, implementation of targeted therapies, and localization of diseased tissues. Our approach is based on the development of sustainable fluorinated probes enabling <sup>19</sup>F-MRI, as a complementary tool, to be coupled with other diagnostic imaging techniques such as <sup>1</sup>H-MRI, Raman and fluorescence imaging, in order to overcome their present shortcomings. This talk reports about a unique fluorinated imaging agent (PERFECTA) bearing 36 equivalent <sup>19</sup>F atoms and therefore showing a single, intense <sup>19</sup>F-NMR signal. Biocompatible nanoformulations of PERFECTA demonstrated excellent cellular compatibility and spectral properties (relaxation times and sensitivity) adequate for *in vivo* <sup>19</sup>F-MRI use (Figure 1) [1-2]. In this presentation PERFECTA ability to work as multiscale and multimodal probe will be shown [3]. Moreover, effects of fluorination on self-assembly of PERFECTA amphiphilic derivatives [4] will be also presented as well as their biological interactions and response.



**Figure 1.** (Left) Molecular structure of PERFECTA and schematic drawing of a representative nanoparticle (F-NP) containing it. Typical Raman and <sup>19</sup>F-NMR spectra of PERFECTA NP dispersions. (Right) Representative scheme of F-NP applications in medicine as diagnostic tool for ex-vivo and *in vivo* cell labelling.

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## Cyclodextrin-based polynitroxide for *in vivo* imaging

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Keywords: cyclodextrin, nitroxide, MRI imaging

Cyclodextrins (CDs), a class of cyclic oligosaccharides formed by  $\alpha$ -(1,4) linked glucopyranose units, can be used for the synthesis contrast agents (CAs) based on nitroxide radicals as a less toxic alternative to gadolinium-based CAs.<sup>[1]</sup> Water soluble supramolecular organic radical contrast agents (ORCAs) obtained from CDs functionalized with (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) radicals have been proposed recently for the *in vivo* detection of glioma tumor in animal models (Figure 1).<sup>[2]</sup> A first set of molecules (CD<sub>n</sub>1, n=6,7,8 is the number of both TEMPO and glucopyranose units) was investigated by superconducting quantum interference devices (SQUID) magnetometry in order to define the role of the CD macrocycle on the effective magnetic moment ( $\mu_{\text{eff}}$ ). The  $\mu_{\text{eff}}$  value increased from 3.982  $\mu_{\text{B}}$  (CD61) to 4.522  $\mu_{\text{B}}$  (CD81) but was limited by intramolecular antiferromagnetic interactions. A set of water-soluble ORCAs (CD<sub>n</sub>8, n=6,7,8) was prepared by a sequence of thiol-ene and Cu(I)-catalyzed alkyne-azide "click" reactions. The <sup>1</sup>H water relaxivities  $r_1$  of these ORCAs had values comprised between 0.739  $\text{mM}^{-1} \text{s}^{-1}$  (CD68) to 1.047  $\text{mM}^{-1} \text{s}^{-1}$  (CD88) in D<sub>2</sub>O/H<sub>2</sub>O 9 : 1 (v : v) at 300 K. The compound CD78 was tested on glioma-bearing rats with reduced side effects and good relaxivity *in vivo*.

A new version of these molecules with nitroxides different from TEMPO has been developed recently with the aim to increase the persistence of the radical in presence of a reducing environment after the *in vivo* administration.<sup>[3]</sup>

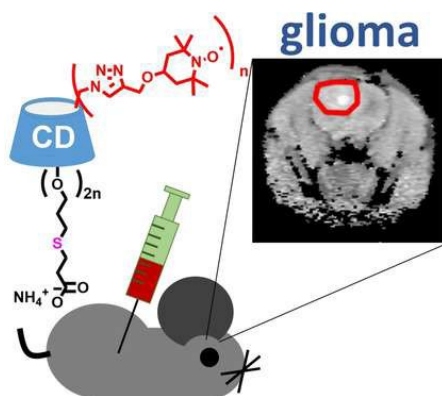


Figure 1. (n=6, 7, 8; ref. [2])

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## Nanobiochar derived from orange peel for targeted cancer therapy

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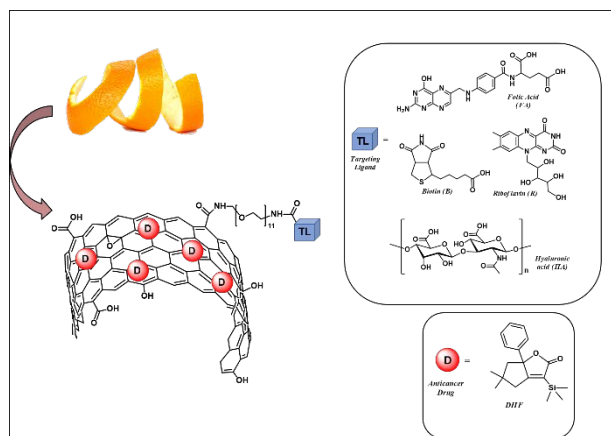
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Keywords: carbon-based nanomaterials, targeting ligands, anticancer activity

Graphene based nanomaterials (GBM) have opened up extraordinary avenues in cancer therapy, allowing the development of cancer targeted drug delivery systems (DDSs) able to improve the efficacy of conventional anticancer drugs [1,2]. New green routes for GBMs synthesis have been recently exploited, starting from renewable resources, such as lignocellulosic biomass waste, affording the GBM, nanobiochar (NBC)



[3]. Fluorescent NBC with graphene structure have been synthesized by hydrothermal carbonization method (HTC) and exfoliation procedures from orange peel waste and investigated as smart nanocarrier for targeted cancer drug delivery. Four different targeting ligands (TLs), namely riboflavin (vitamin B2), biotin (vitamin B7), folic acid (vitamin B9) and hyaluronic acid, have been covalently

conjugated to the graphene surface of NBCs by means of a cleavable PEG linker. The nanosystems have been characterized by FTIR, Raman, TGA, DLS, PL and HRTEM analyses and loaded with the anti-cancer drug DHF [4]. The results of the *in vitro* biological tests demonstrated the high biocompatibility of the NBC-based systems and the best results in terms of adsorption capacity for the samples conjugated with biotin and riboflavin, which elicited antitumour activity in all cell lines studied. The high water dispersibility of NBC-based systems showed the potential to overcome some critical limitations of currently used anticancer drugs.

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## *In vitro Cytotoxicity of asbestos: a combined FTIR and EPR study*

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Keywords: asbestiform minerals, ROS, citotoxicity

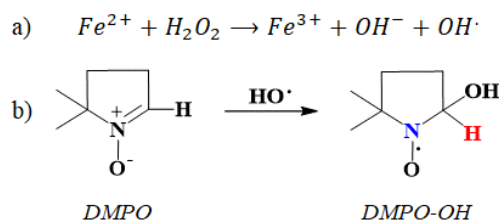
Asbestos is known to represent a severe hazard for human health, being listed as the third most abundant pollutant on a global scale [1]. The internalization of respirable micro- to nano-sized asbestos fibres can lead to their gradual accumulation, particularly in lungs, where they drive different pathogenic effects such as chronic inflammation, asbestosis, pleural effusion, and, as later manifestations, lung carcinoma or pleural mesothelioma [2]. Although the epidemiological association between asbestos exposure and malignant lung diseases is well established, the mechanisms linking asbestos exposure and inhalation to the development of Asbestos-related diseases (ARDs) are still not fully understood. However, the role of several elements such as Al, Fe, Mn, Mg, Ca, Si, Zn and Na ions released from asbestos fibres is a subject of intensive multidisciplinary investigations [3].

The present study examined in vitro the biological effects of two different natural non-commercial asbestos fibres from natural outcrops: Chrysotile from Valmalenco (Chr-VM) and Fibrous Erionite from Jersey Nevada (Eri-JN), compared to standard asbestiform minerals Chrysotile (Chr-UICC) and Crocidolite (Cro-UICC) into two epithelial human cells (MeT5A and A549) mimicking respiratory environment.

Fibres biological effects were investigated in terms of morphological and ultrastructural cellular changes, cell viability, ROS production and depletion of intracellular glutathione.

SEM-EDAX microanalysis and Infrared Spectroscopy were performed to assess the chemical composition of the fibres and to evaluate their different capacity to influence the microenvironment through the release of several toxic metal ions.

Iron ions were considered to play a key role in asbestos toxicity because of their ability to induce ROS generation. For this reason, free radical release was investigated by means of electron paramagnetic resonance (EPR) spin trapping technique (Fig.1) in order to clarify the relationship between Fe ions surface occurrence and asbestos reactivity [4]. In particular, the Fenton reaction has been considered, which is one of the most biologically relevant reactions known to occur in vivo between H<sub>2</sub>O<sub>2</sub> and Fe (II) ions present in asbestos surface, producing hydroxyl radicals (HO•) rapidly trapped by 5,5-dimethyl-3,4-dihydro-2H-pyrrole N-oxide (DMPO), which likely represents the most used water-soluble Spin Trap.



Scheme 1. Reactions involved: a) Fenton; b) Spin Trapping.

In order to evaluate a possible connection between fibre-associated superficial elements loss, free radical activity and glutathione pathway, we considered the superficial iron and magnesium release from fibres in cultures, reputed as element loss from the native mineral. Despite our data indicated that all types of fibres used were able to reduce cell viability, different oxidative stress levels into the cell were observed on the basis of asbestos fibres characteristic.

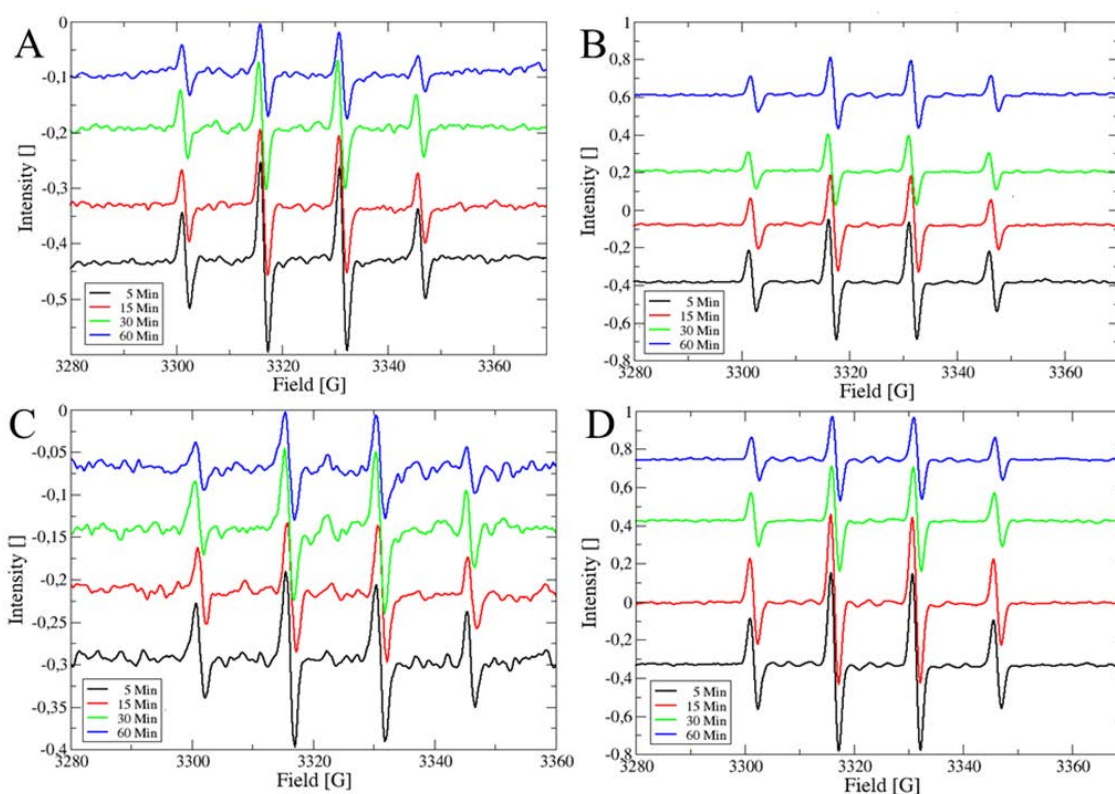


Figure 1. EPR spectra of [DMPO-OH]• adduct obtained from (A) Chr-UICC, (B) Chr-VM, (C) Cro-UICC, and (D) Eri-JN fibres.

Globally the results obtained reflect the cytotoxic effects exerted in vitro by both Chr-VM and Eri-JN fibres and evidence the different toxicity pathways prompted by these fibres species due to their different crystal assemblages and properties.

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## Coordination network for spintronic applications: the role of high pressure

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Keywords: spintronics, high-pressure crystallography, X-ray diffraction

The recent progresses in quantum information theory [1] have fostered the rapid development of new, disruptive computational methods.

These unprecedented opportunities have become possible thanks to the research on known quantum magnets and the discovery of new compounds, with the purpose to extend the current portfolio of materials for spintronics devices.

Spintronics differs from charge electronics in that the information carrier is the electrons' angular momentum itself (the spin), instead of the electron charge.

In this context, together with “traditional” ceramic and intermetallic materials, hybrid organic-inorganic materials have recently attracted attention because of their larger tuneability.

For example, coordination networks, based on spin active transition metal ions interconnected by organic nucleophilic linkers, offer many opportunities.

In fact, these materials can guarantee 1D, 2D and 3D magnetic networks, sometimes interconvertible by external stimuli like temperature or pressure.

Moreover, by selecting the proper organic linkers, one could fine tune the magnitude of the magnetic exchange.

Our research focuses on antiferromagnetic (AFM) coordination networks. AFM spintronics is of interest because energy efficiencies are outstanding compared to ferromagnets and the spin dynamics is faster by orders of magnitude.

Upon application of pressure, different phenomena could occur like the *orbital reordering* (a change of the energy of the various d-orbitals of the metal ion in the ground state) [2-4].

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This has strong implications on the magnetic network that can increase/decrease its dimensionality or switch the directions of privileged magnetic susceptibility of the material [5].

A survey of these effects will be presented, based on experimental observations and theoretical simulations.

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## Chiral resolution via selective crystallization of diastereomeric salts: a case study involving NSAIDs

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Keywords: NSAIDs, enantioselective crystallization, solid-state characterization

About 60% of the drugs on the market are chiral, exerting their therapeutic effect through one of the two enantiomers. For a long time, such drugs have been commercialized in their racemic mixture but now, due to the constant demand from the regulatory authorities, about 50% of them are sold in their pure enantiomeric form. The need to obtain enantiopure APIs (Active Pharmaceutical Ingredients) in an efficient (and possibly economical) manner is of fundamental importance in pharmaceutical industry and has prompted a search for new methods to separate racemic mixtures. Chiral resolution can be achieved in two ways: by the so-called asymmetric synthesis or by racemic separation.<sup>1</sup> As asymmetric synthesis usually has low overall yields, racemic separation, which may be achieved employing different methods like for example chromatography or selective crystallization, is the procedure most commonly used in industry. By crystallization the two enantiomers are separated due to the different solubility and crystallization propensity of the corresponding diastereomeric salts. The choice of the, optically active, resolving agent is of great importance to promote preferential crystallization of the enantiopure compound in high yield and is typically time-consuming and largely empirical. Hence the use of X-ray diffraction can be very helpful in understanding the forces and interactions involved in the chiral recognition process.<sup>2</sup>

Among all the chiral APIs, non-steroidal anti-inflammatory drugs (NSAIDs) possess a therapeutic effect mostly dependent on their absolute configuration. Naproxen, for example, is only administered in the form of S-(+)-naproxen (eutomer), whereas its enantiomer (distomer) is hepatotoxic. Inspired by the promising use of aminoindanols as basic resolving agents for the diastereomeric resolution of racemic acids<sup>3</sup>, we report here the preliminary results of experimental and *in silico* investigations of a series of

diastereomeric salts of APIs belonging to the NSAID arylpropionic family performed in order to better understand the chiral discrimination mechanism and obtain useful information to design the most preferred enantioselective crystallization procedure.

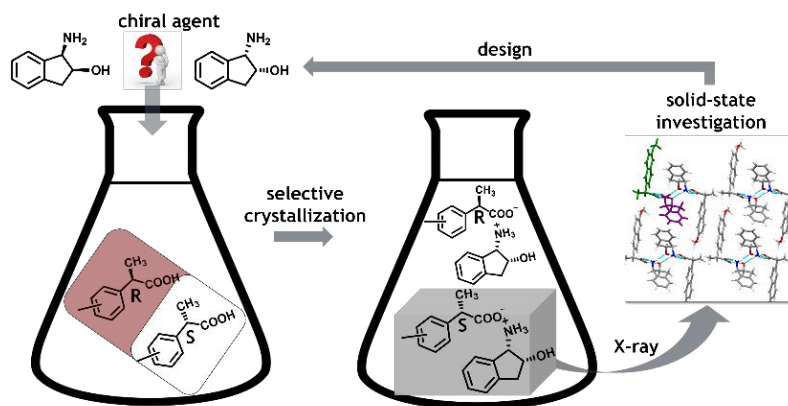


Figure 1. Schematic representation of enantioselective crystallization.

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## *Plastic Pollution at the micro and nanoscale: “true-to-life” test materials*

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Keywords: micro/nanoplastics, test materials, biological interface

Plastic pollution is globally recognized as an environmental challenge for ecosystems and human health. Most plastic waste flows from land to oceans, strongly impacting marine life and organisms. More recently, small fragments at the micro and nanoscale originating from the breakdown process of bigger pieces of plastic litter have become of increasing concern, driving the research efforts toward the understanding of sources, distribution, fate, and impact of these particles [1]. However, their limitation in size contributes to the lack of adequate methods for qualitative and quantitative studies [2]. In this framework, there is also a strong need to create good reference materials for laboratory studies, optimization of protocols, and construction of databases, mimicking as closely as possible the real particles [3]. In this contribution a study of micro and nanoplastics through the preparation of more realistic reference materials, named here “true-to-life” materials, will be presented. In case of fragments at the microscale, “true-to-life” microplastics generated by mechanical fragmentation of daily used plastic items were used to develop a novel approach for direct microplastics quantification, based on a handheld portable near-infrared spectrometer coupled with chemometrics [4]. The results are poised to impact for a fast, reliable, and in-situ environmental microplastics quantification. In case of fragments at the nanoscale, “true-to-life” nanoplastics separated from the bigger pieces at the microscale were challenged to investigate the nanoscale behaviour of the interactions with biological system. In particular, the formation of a protein corona from human plasma was investigated, showing that a different protein corona cloaked “true-to-life” nanoplastics with respect to synthetic polystyrene nanobeads [5]. These findings highlight the need to integrate field and laboratory data and test more environmentally relevant conditions, proposing true-to-life nanoplastics as a more truthful material for environmental nanoplastics and opening the possibility to new and unexpected results

in biological interactions. This research was funded by PON “R&I” 2014-2020: SIRIMAP—Sistemi di Rilevamento dell’Inquinamento MARino da Plastiche e successivo recupero-riciclo and by COMET program executed by the Austrian Research Promotion Agency

(FFG): microONE “Microplastic Particles: A Hazard for Human Health?”, in the frame of COST Action CA20101: PRIORITY - Plastics monitoring detection Remediation recovery.

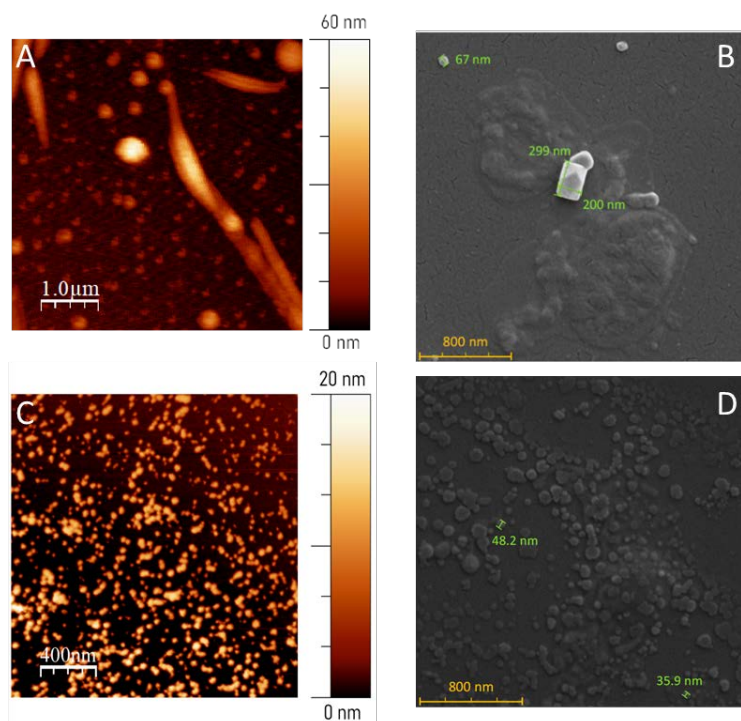


Figure 1. Representative true-to-life nanoplastics images. A: AFM of polyamide nanoplastics; B: SEM of PET nanoplastics; C and D: AFM and SEM of PS nanoplastics.

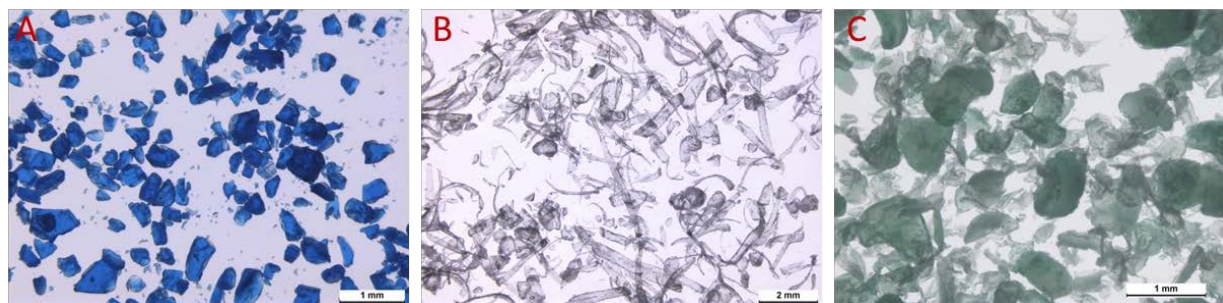


Figure 2. Representative true-to-life microplastics images by optical microscope. A: PS microplastics; B: PP microplastics; C: HDPE microplastics.

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## *Different approaches for a common scope: improving the sustainability of polymer coatings for corrosion protection*

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Keywords: circular economy, recyclable coatings, biowaste

The ever-growing demand for raw materials necessary to satisfy the "hunger" of modern society is one of the biggest issues that global policies have to face and solve in the near future. The corrosion protection is one of the areas in which our expertise can contribute to this worldwide challenge. Among the available technological solutions, polymeric organic coatings represent a strategic sector for the applied research, not only for its market value (10.7 billion US dollars in 2022), but also for its need of very high amount of raw materials, primarily deriving from petrochemical industry that is expected to be restricted in the next future by environmental laws. In this context, our research team is pursuing two parallel paths, both aimed at improving the sustainability of polymer coatings by implementing a circular economy approach. The common goal of reducing the need for raw materials is achieved through two complementary aspects:

- i) implementing compounds derived from bio-waste;
- ii) making recyclable the polymer coating itself.

Here we present the rationale and the main results of these two research lines.

### *i) Polymer coatings from tomato peel waste*

The project aims at the valorization of tomato peels, an abundant agricultural waste in Italy that is currently exploited only in few low added-value chains (animal feed, waste-to-energy). In this work, the attention will be focused on the utilization of the cutin monomer, derived from the depolymerization of tomato peels, as curing agent of some naturally-derived epoxydized prepolymers for the preparation of corrosion protection coatings for carbon steel (Figure 1, left). First, the innovation will be discussed with respect to the few analogous examples in literature, then the focus will



be shifted on the electrochemical assessment of the protective features of the coatings under natural and accelerated aging conditions, and on the correlation with their thermal, physical and mechanical properties. The performance of the fully naturally derived coatings will be compared with that i) of control coatings (partially natural ones), with the pre-polymer or the hardener being petrol-based, and ii) of a benchmark coating, made of bisphenol A diglycidyl ether and phthalic anhydride (fully petrol-derived).

#### ii) Towards recyclable polymer coatings

The second project aims at developing recyclable anticorrosion coatings endowed with hydrophobicity, fluorescence and self-healing properties (Figure 1, right) [1-3]. The starting point was poly(phenylene methylene) (PPM), a thermoplastic polymer with high chemical and thermal stability but that suffers from poor processability and high brittleness. We have overcome these disadvantages by developing PPM-based copolymers (co-PPMs) obtained by side chain engineering [4]. In this way, the physical properties and workability of the material can be systematically modified. Notwithstanding the multidisciplinary study, the present talk will be focused on the electrochemical investigation. Through testing protocols specifically developed, we have assessed the corrosion protection performance of a series of co-PPM-based coatings, improving step by step their protection capability. Among the most intriguing results, we can mention: i) crack-free and low porosity coating; ii) high protection performance with a coating thickness ten times lower than that of the products available on market; iii) self-healing capability; iv) optical features exploitable for the inspection of the coatings integrity. Proof of a lab-scale solvent-based recycling, allowing the selective recovery of both metal and polymer, will also be discussed.

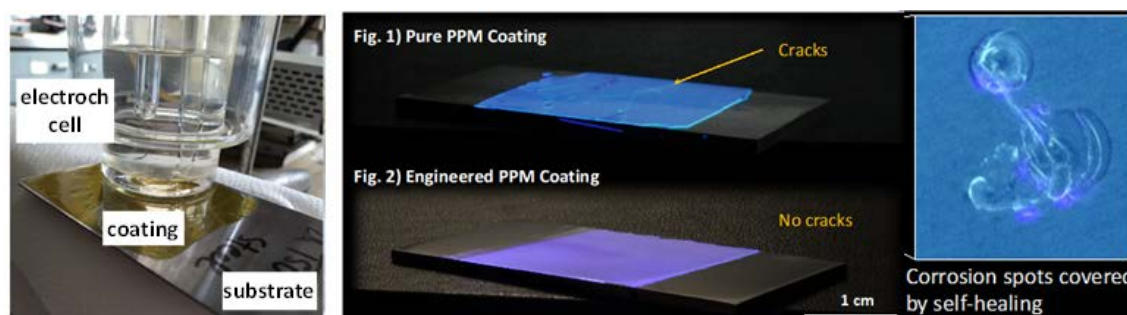


Figure 1. Left: electrochemical setup for the study of tomato peels derived epoxy coatings. Right: snapshots (386 nm UV light) of PPM-based coatings together with a magnification of a small area of an engineered PPM coating after an accelerated electrochemical test.

#### Acknowledgments

Mirko Magni thanks FSE-REACT-EU PON “RICERCA E INNOVAZIONE” 2014-2020 and Engitec Technologies SpA for co-funding his current researcher position. Fondazione Cariplo is also thanked for the financial support to the tomato-derived coatings project named “CutToPro” (grant No. 2021-0651).

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# Doping Strategies for The Enhancement of The Thermochemical Heat Storage Capacity of $\text{CaMnO}_3$

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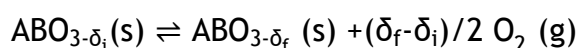
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Keywords: thermochemical heat storage, perovskite oxides, doping

Successful commercialization of concentrating solar power (CSP) plants requires effective energy storage for the supply of power on demand during solar transients. High temperature thermal energy storage ( $\geq 700$  °C up to 1200 °C) has the potential to address not only the storage needs but also the power capacity due to the efficiency gains from high temperature operation. Perovskites ( $\text{ABO}_3$ ) have been considered promising candidate for high temperature ThermoChemical heat storage (TCS) applications through oxygen exchange reactions [1]:



The amount of chemical heat stored per mole of material, or chemical heat storage capacity, is given as:

$$Q^M \left( \frac{\text{kJ}}{\text{kg}_{\text{ABO}_3}} \right) = \frac{1}{M_{\text{ABO}_3}} \int_{\delta_i}^{\delta_f} \Delta_{\text{red}}h \left( \frac{\text{kJ}}{\text{mol}_\text{O}} \right) d\delta$$

where  $\Delta_{\text{red}}h$  is the enthalpy of reduction associated with the redox-reaction,  $\delta_i$  is the initial oxygen non-stoichiometry (at  $T = T_{\text{discharge}}$ ) and  $\delta_f$  is the non-stoichiometry at a final condition of interest. Despite it is intuitive that the larger the reaction enthalpy ( $\Delta_{\text{red}}h$ ) and extent ( $\Delta\delta = \delta_f - \delta_i$ ) are, the larger would be the heat storage capacity. In reality, since the reaction enthalpy corresponds to the energy associated to the generation of oxygen vacancies, the higher is the reaction enthalpy (the more difficult is the material to be reduced/oxidized), the smaller is the reaction extent. Entropy is not a metric usually considered when estimating the thermochemical storage capacity of a material, but it is an essential property because the reaction extent depends monotonically on this term. Accordingly, materials with large entropy of reduction and intermediate enthalpy of reduction are desirable for chemical heat storage applications. We aim here at tuning the  $\text{CaMnO}_3$  heat storage temperature window and

enhancing the heat storage properties by co-doping with equal amounts of La and Fe on the A and B sites, respectively  $((La_xCa_{1-x})(Fe_xMn_{1-x})O_3)$ . X-ray absorption spectroscopy and diffraction studies revealed that Fe and Mn adopt, respectively, the 3+ and 4+ oxidation states under ambient conditions, and that the dopants are incorporated into the intended octahedral B sites. Interestingly, the chemical heat storage capacity depends on both reaction enthalpy and reaction extent, and the  $La_{0.05}Ca_{0.95}Fe_{0.05}Mn_{0.95}O_{3-\delta}$  composition offers a more attractive combination of these factors than the 10% La doped composition, despite a lower reaction enthalpy in the former. This result is a consequence of the substantially larger extent of reduction enabled by the higher entropy than that of  $La_{0.1}Ca_{0.9}Fe_{0.1}Mn_{0.9}O_3$ . Under technologically relevant conditions, operating over a temperature window of 700 to 1200 °C and under an oxygen partial pressure of about  $10^{-3}$  atm, the thermochemical heat storage capacities of  $La_{0.05}Ca_{0.95}Fe_{0.05}Mn_{0.95}O_3$  and  $La_{0.1}Ca_{0.9}Fe_{0.1}Mn_{0.9}O_3$  are  $378.5 \pm 1.0$  kJ/kg<sub>ABO<sub>3</sub></sub> and  $282.3 \pm 1.5$  kJ/kg<sub>ABO<sub>3</sub></sub>, respectively, and exceed the values not only of the undoped material, but for the first material also of different singly doped analogs (Figure 1) [2,3]. Furthermore, with respect to the singly Fe-doped CaMnO<sub>3</sub> we narrowed the operating temperature range from 400-1200 °C to 700-1200 °C, that is the target one for the CSP plants. Hence, we demonstrated that by co-doping it is possible to tailor reduction enthalpy and extent, together with the operating temperature range.

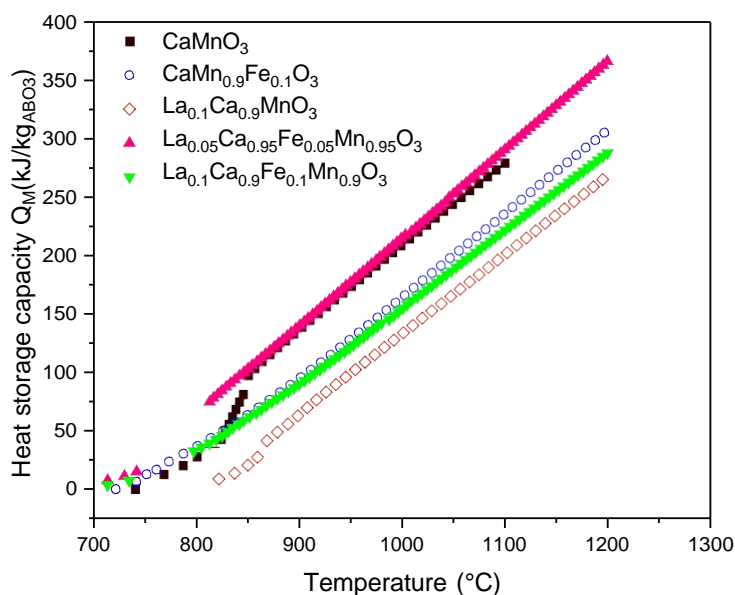


Figure 1. Comparison  $La_{0.05}Ca_{0.95}Fe_{0.05}Mn_{0.95}O_3$  and  $La_{0.1}Ca_{0.9}Fe_{0.1}Mn_{0.9}O_3$  with previously investigated compositions CM, CMF10 and LCM10 under similar operating conditions ( $p_{O_2}=10^{-3}$  atm,  $T_{dis}=700^\circ\text{C}$ ,  $T_{ch}=1200^\circ\text{C}$ ).

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## *Outperforming electrical properties of hybrid composites based on carbon nanotubes and graphene nanosheets*

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Keywords: Tunneling Atomic Force Microscopy (TUNA), Electrical Properties, Carbon Nanostructures

The electrical properties of epoxy hybrids filled with Graphene Nanosheets (GNs) and Multi-Wall Carbon Nanotubes (MWCNTs) were investigated by Tunneling Atomic Force Microscopy (TUNA). In this work, through TUNA technique, which is able to detect ultra-low currents ranging from 80 fA to 120 pA [1-2], it was possible to understand the correlation between electrical conductivity, on a micro/nano space scale, and the arrangement of the electrically conductive paths through the sample. Two different amounts of mixed fillers, namely below 0.1 wt% and above 0.5 wt%, were dispersed by ultrasonication into a tetrafunctional epoxy matrix at five different MWCNTs:GNs mix ratios. At a low amount of nanoparticles, 0.1 wt%, the hybrid nanofiller concentration allows for detecting a very interesting synergy toward an increase in the electrical conductivity of several orders of magnitude, and a lowering of the Electrical Percolation Threshold (EPT). Both the computational and experimental results highlight that, owing to the hybrid MWCNT/GNs network formation, the hybrid nanocomposites outperform their single-nanofiller counterparts [3]. Therefore, we demonstrated the synergistic effect of the two conductive nanofillers, MWCNTs and GNs, on the electrical properties of nanohybrid systems by a combined computational and experimental approach. The first, allowing to characterize these materials at nanoscale, and the second by direct current (DC) measurements and investigation by TUNA of the electrical mapping of nanometric domains characterized by high current density with the formation of a conductive network. In this work, we found that at 0.1 wt% (below the EPT for the two binary polymer composites based only on MWCNTs or GNs nanofillers), the addition of the graphene nanosheets (GNs) to the material filled with MWCNT only, determines for the hybrid ternary samples, an increase in the electrical conductivity of many orders of magnitude compared to that recorded for the resin loaded with MWCNTs alone. In this regard, the specimen with the MWCNTs:GNs ratio of 1:1 showed

an electrical conductivity of  $3.73 \times 10^{-4}$  S/m while for the sample filled only with MWCNTs a value equal to  $1.06 \times 10^{-13}$  S/m was recorded. It is worth noting that higher electrical conductivity values were also recorded for the other MWCNTs:GNs combination ratios, leading to the conclusion that graphene nanosheets play a key role in increasing the electrical performance of the epoxy nanohybrids. Through TUNA analysis of the conductive nanodomains of hybrid systems, it was possible to detect the presence of a conductive network responsible for the good electrical properties imparted by the carbon-based nanofillers uniformly dispersed in the matrix and able to improve the composite interfacial properties synergistically. From TUNA images, MWCNTs connecting the epoxy matrix and GNs and  $\pi$ - $\pi$  interactions between MWCNTs and GNs were clearly visible. Furthermore, computational analysis showed that MWCNTs aggregated at the GN interface, in agreement with experimental data (see Figure 1). This assembly, not observed in the graphene nanosheet-free composite system, seemed to make the hybrid system more conductive at the MWCNT concentration below the EPT, compared to the binary one based on MWCNTs alone. We hypothesized that this behavior derived from the specific morphology assumed by the MWCNTs at the interface with GNs.

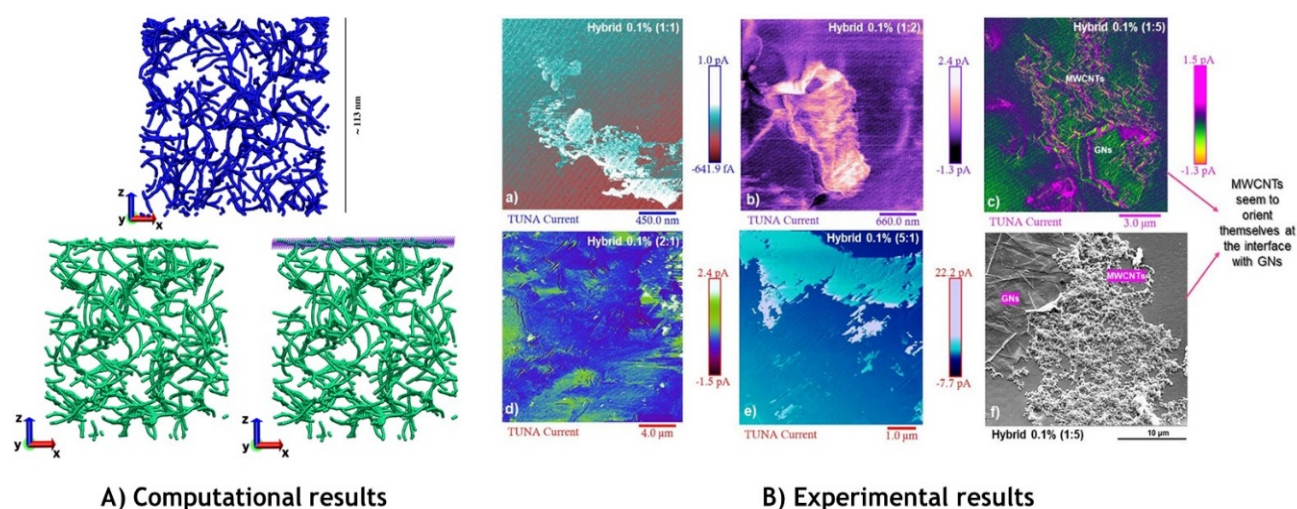


Figure 1. A) Schematic picture of simulated MWCNTs. Top panel: MWCNTs shown in blue for the simulated composite system including MWCNTs only. Bottom panels: MWCNTs in the simulated system including GNs are shown in green (left panel) to appreciate their aggregation at interface with GN. MWCNTs and GNs for the same simulation are shown in the right panel (GNs shown as violet points); B) (a-e) TUNA Current pictures of Hybrid 0.1% (MWCNTs:GNs) samples at different filler mix ratios (1:1; 1:2; 1:5; 2:1; 5:1); (f) FESEM picture of Hybrid 0.1% (1:5) sample.

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## *Recent advances in enzyme exploitation for polymer science: recycling and upcycling*

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Keywords: upcycling, biocatalysis, multi-layer delamination

Introduction. The activities here described aim to contribute to the “greening” of chemistry in the field of polymer science, in particular in plastic recycling. Plastic recycling represents an opportunity for upgrading waste management practices and improving a circular economic development. In this context, the use of plastic-degrading enzymes and, thus, the use of biodegradable polymers have gained growing attention in the last decades, in different fields, including packaging and agriculture.[1] The main advantages of biocatalysts are that they are biodegradable and non-toxic for humans and the environment, their usage enables working in a reasonable range of pressure and temperature conditions, and the use of metals and organic solvents can be avoided. The strategy of an enzymatic depolymerization of plastic waste can be re-interpreted in terms of re-polymerization of the obtained oligomers to new high-performance polymers (upcycling) that can have properties suitable for specific applications, for example in the adhesives, packaging and/or textile sectors. To improve the sustainability of these processes the use of enzymes immobilized or not, can be studied. On the other hand, enzymes can be exploited to develop innovative strategies for the recycling of non-recyclable multi-layer materials. Indeed, protection systems to allow the enzyme embedment in a multi-layer material formulation can be developed. At the end-of-life of the packaging, after deprotection, the enzymes can exert their degrading activity with consequent delamination and recycling of layers. Then, the development of enzymatic approaches for polymer recycling/upcycling allows to contribute to the construction of a bioeconomy paradigm using biocatalysis. [2]

Research Strategy. The first approach of this research is focused on the use of lipases: they can hydrolyse in aqueous media and reverse the reaction in non-aqueous media. [3] The experimental activities were carried out by performing i) chemical and

enzymatic depolymerization of PLA monitored at different reaction times, ii) the obtained oligomers were functionalized for the synthesis of new polymers by esterification. Preliminary results show that by enzymatic depolymerization it is possible to modulate the length of the oligomers (OLAs) obtained in an easier way than by a chemical approach. The obtained OLAs can be functionalized to obtain polyesters for different applications. [4] Azelaic acid (AZA) has proved to be a valuable bio-based monomer for the synthesis of biodegradable and sustainable polymers: the insertion of AzA units contributes to the flexibility, elasticity and hydrophobicity of the formed products [5]. In the second part of the study, cutinase from *Humicola Insolens*, selected as a highly degrading polyester hydrolytic enzyme [6], is immobilized in Mg/Al layered double hydroxide structures. The immobilization efficiency results are high. After a specific trigger in an appropriate medium, the enzyme is released with no loss of activity. Moreover, its thermal stability strongly improves after immobilization, since its half-life at 90 °C increases by 6 times. The immobilized cutinase is finally embedded in poly(butylene succinate-co-adipate) by melt blending and after triggering is able to completely degrade the polymer within 24 h.

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The study was carried out within the framework of the PRESERVE project, funded by the European Union under Horizon 2020. Grant Agreement: 952983 and TERMINUS project, funded by the European Union under Horizon 2020. Call: H2020-NMBP-ST-IND-2018. Grant Agreement: 814400.

## *Adsorbent-photocatalytic multifunctional materials for wastewater treatment*

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Keywords: multifunctional materials, sustainability, wastewater

Water resource pollution due to heavy metal ions and organic molecules, such as pesticides, is a global issue which has not been resolved yet. As for now, several water purification treatments have been considered, solvent extraction and precipitation being some examples, but each treatment presents its limitations due to its cost, efficiency, environmental impact, and the formation of toxic by-products. Alternative emerging treatment techniques, such as advanced oxidation processes, have come under heavy research. In this context, it is well-known the efficacy of TiO<sub>2</sub> nanoparticles (NPs) in the photodegradation of a wide range of organic molecules due to the oxygen radical generated under UV irradiation. However, the agglomeration and the necessity to recover the TiO<sub>2</sub> NPs from the slurry stream impede a large-scale application of this method. Moreover, a technological development of this treatment is required for a real application on a large scale.

To improve TiO<sub>2</sub> dispersion and recovery, the immobilization of NPs on a supporting system is strategic.[1] In particular, adsorbents are promising materials for the development of multifunctional nanocomposite, having both adsorbent and photocatalytic properties, for the removal of contaminants from industrial wastewater. Furthermore, a synergic combination is also beneficial for catalytic performances: adsorbent centres bring organic pollutants close to TiO<sub>2</sub> photoactive sites, improving the degradation efficiency and capacity of the system. [2] Notably, silica-based materials are well-known adsorbents able to entrap both pollutants and heavy metal cations.

In this scenario, the present work aims to obtain a multifunctional composite membrane, with adsorbent and photocatalytic properties, based on the efficient combination of SiO<sub>2</sub> or silicates with TiO<sub>2</sub> to remove both organic and inorganic water pollutants, also employing recycled waste materials.

In detail, we evaluated both synthetic and natural silica materials, having different shapes, such as spherical SiO<sub>2</sub> NPs, prepared by sol-gel method, as well as anisotropic sepiolite (Sep) and halloysite (Hall) phyllosilicates, consisting of fibrous magnesium silicate and aluminosilicate nanotubes, respectively. [3] Silica-titania hybrid materials were efficiently synthesised by adding an acidic solution of titanium isopropoxide in



ethanol to a water suspension of SiO<sub>2</sub> NPs or aluminosilicate clay. Then, thermal treatment of the product is crucial to obtain anatase titania. An exhaustive multi-technique characterization of the multifunctional materials demonstrated the efficient decoration of each support with dispersed and uniform spherical anatase NPs with a mean diameter of 7 nm (Figure 1).

Considering the rising interest towards a circular economy, the step forward considered was the employment of unconventional waste materials, such as tionite. Tionite is a by-product of TiO<sub>2</sub> manufacture from titaniferous minerals (ilmenite, FeTiO<sub>3</sub>), which are treated with concentrated H<sub>2</sub>SO<sub>4</sub> at 100 °C. The residual mud is then recovered and neutralized. Unspent 0.14 tons of tionite are averagely obtained from 1 ton of titaniferous mineral.

Tionite obtained using Ca(OH)<sub>2</sub> as a neutralizing agent was firstly evaluated, showing that the material consists of mesoporous NPs with various shapes made of a combination of TiO<sub>2</sub>, with the prevalence of the rutile phase, aluminosilicates, and a significant amount of CaSO<sub>4</sub>·2H<sub>2</sub>O. Since the preliminary photocatalytic tests conducted on tionite showed no significant photodegradation yields, an alternative treatment based on NaOH neutralization was carried out in order to simplify tionite composition and improve its photoactivity.

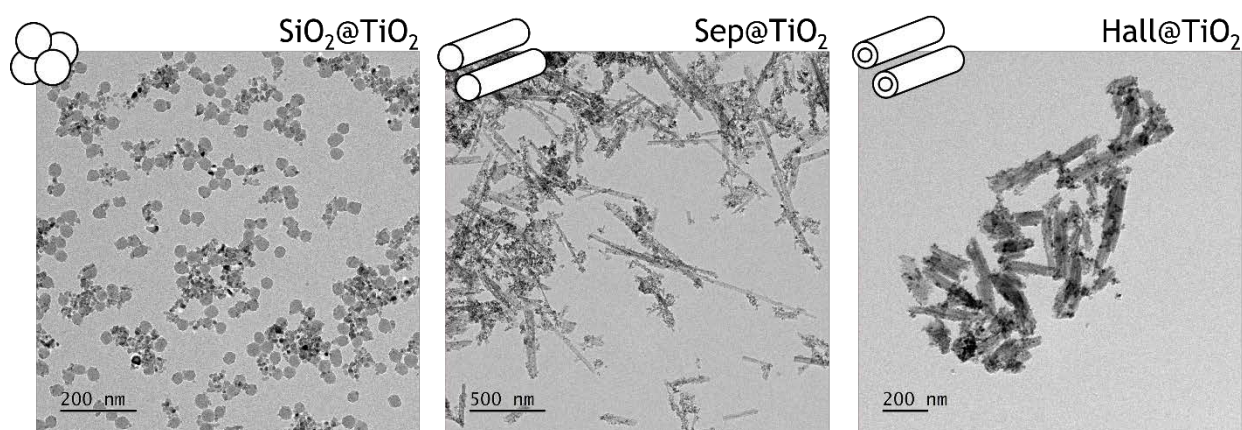


Figure 1. a) TEM micrographs of TiO<sub>2</sub> NPs anchored to different silica/silicates support.

Photocatalytic and adsorbent properties of all the synthesized materials are under evaluation.

To sum up, the effective combination of TiO<sub>2</sub> with silica-based materials provided a promising multifunctional material with both photocatalytic and adsorbent properties. Tionite composition and morphology suggest its feasibility as a substitute for the aforementioned materials in wastewater treatment.

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## *High-entropy oxides-based electrode materials for water desalination via capacitive method*

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Keywords: high-entropy oxides, carbon/high-entropy oxides composites, capacitive deionization

Water pollution and scarcity have become serious world-wide issues for sustainable development during the past decades, due to rapid population growth, climate change and industrial development. Seawater and/or brackish water desalination is one of the most promising and practical solution for many societies to tackle global water scarcity. In contrast to conventional water desalination processes, like thermal distillation, reverse osmosis, electrodialysis, capacitive deionization (CDI) is emerging as promising and the most sustainable technology thanks to its environmental friendliness, high efficiency, low energy consumption, easy regeneration of the electrodes and low operating potential [1]. CDI is an electrochemical method, able to remove salt ions from salty solutions, based on the formation of an electrical double-layer (EDL) on the porous electrode/solution interface when a low voltage (0.8-2.0 V) is applied to the electrodes. The structure and properties of the electrode materials play a decisive role on the electrosorption performance and removal rate [2]. Therefore, the development of highly performing advanced materials is crucial for the commercial application of the CDI technology. Recently, high-entropy oxides (HEOs), a new oxides system, consisting in a single-phase multi-component solid solutions, stabilized by high configuration entropy, with amazing functional properties, have attracted considerable interest for their great potential in a wide range of applications.

This contribution reports the synthesis and characterization of HEOs and carbon/HEO composites and the evaluation of their specific capacitance in view of their possible use as active electrode materials for water CDI. To investigate the effect of the material size and morphology HEOs were prepared by using two different methods.

CrMnFeCoNi-HEO with spinel structure (sHEO) and MgCoNiCuZn-HEO with rock-salt structure (rHEO) in form of nanoparticles (NPs) or nanofibers (NFs) are synthesized via sol-gel and electrospinning, respectively, followed by heating treatment at lower temperatures than the standard solid-state techniques, thus reducing the environmental impact [3]. C/CrMnFeCoNi-HEO (C/sHEO) and C/MgCoNiCuZn-HEO (C/rHEO) composite NFs are obtained from the same spinnable solution and electrospinning conditions as HEOs NFs by a different thermal treatment, namely stabilization in air at 225 °C for 2 h and subsequent carbonization in N<sub>2</sub> atmosphere at 700 °C for 2 h and 900 °C for 2 h. The formation of the electrical double layer and electrochemical capacitive performance are evaluated by cyclic voltammetry (CV) technique.

In the scan rates range investigated (5-100 mV s<sup>-1</sup>), the specific capacitance improves in the order C/rHEO NFs  $\cong$  sHEO NPs < sHEO NFs < C/sHEO NFs (Fig. 1).

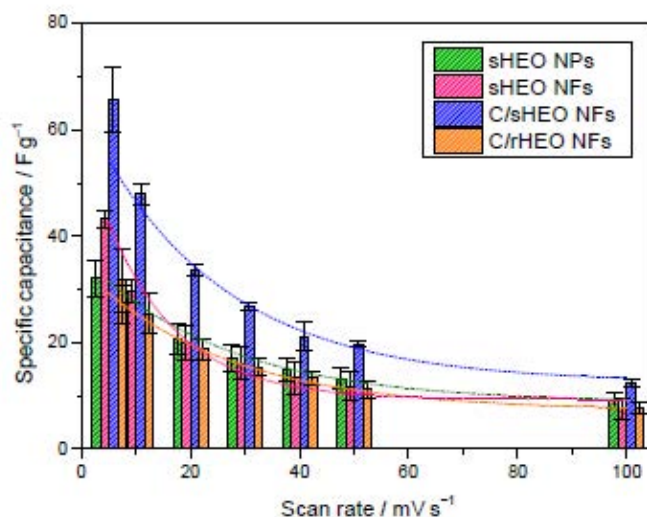


Figure 1. Specific capacitance of HEOs and C/HEO composites as a function of potential scan rate.

The results of the physicochemical and electrochemical analyses suggest that the size of the HEO grains is an important parameter: the smaller the grains, the larger the surface available for the adsorption and the higher specific capacity. In pure HEOs, the fibrous morphology favors the formation of smaller-sized HEO grains. The best capacitive performance is obtained when the beneficial contributions of the carbon matrix and smaller-sized HEO grains are synergistically coupled.

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## *Poly(vinyl alcohol) formulations as waterborne coatings to improve paper media resistance*

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Keywords: Poly(vinyl alcohol), nanocellulose, polyurethanes

Paper media is a highly used material in many applications due to its biodegradability, recyclability and compostability. However, deterioration of paper encouraged the development of coating treatments to improve its resistance properties.

Among all, water-based poly(vinyl alcohol) (PVA) solutions are often used not only for their eco-friendly composition, but also for an improvement in the paper resistance [1]. In this contribution three different kinds of PVA-based formulations were developed adding nanocellulose (NC) derivatives or a polyurethane derivative (PU).

In fact, NC is gaining more and more interest [2] because of its unique properties (i.e., high surface area, colloidal stability, low toxicity, chirality and mechanical strength). Moreover, hydroxyl groups on its surface can be functionalized [3], allowing the tuning of mechanical and physico-chemical properties and providing the possibility to develop new eco-sustainable materials. Both siloxane and epoxy NC derivatives were successfully produced. Siloxane nanocellulose derivatives were prepared having a polymerizable methacrylic moiety, curable by UV light; while epoxy nanocellulose derivatives were prepared with the aim to crosslink PVA hydroxy groups under thermal heating.

On the other hand, PUs have been often used in industrial coatings for their weatherability, solvent resistance and anticorrosion properties [4], thus acrylate oligomers can be used on paper as surface treatments able to improve flexibility and chemical resistance. Consequently, a polymerizable PU prepolymer containing methacrylic moieties was prepared and added to PVA obtaining a waterborne formulation, which was deposited on paper media and cured by UV light.

NMR, FT-IR, DSC and TGA techniques have been used to evaluate the chemical properties of treated paper and mechanical tests (i.e., traction, double folds) provided the possibility to evaluate paper resistance.

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## Green recycling of biobased polymeric systems

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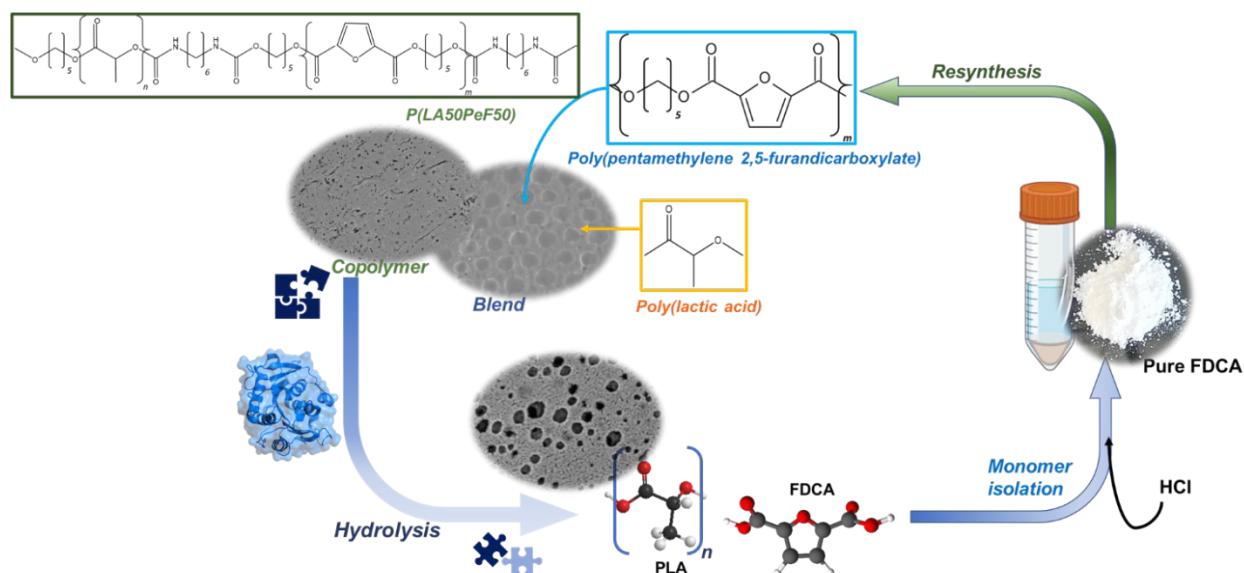
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Keywords: chemical design, biopolyesters, green recycling

Notwithstanding the prevalence of terephthalic acid-based polyesters, novel monomers are settling as competitive alternatives. A fascinating example is 2,5-furandicarboxylic acid (FDCA), successfully derived from renewable resources. Among furan-based polyesters, poly(pentamethylene 2,5-furandicarboxylate) (PPeF) is one of the most interesting, showing outstanding gas barrier properties and high flexibility [1]. PPeF blending/copolymerization with another well-known biobased polymer, poly(lactic acid) (PLA), leads to considerably better mechanical and gas barrier properties of this latter, making it suitable for flexible food packaging applications, overcoming PLA intrinsic limitations, such as brittleness and poor thermal stability. By playing with composition and chemical architecture, new biopolymers were obtained. Although presenting numerous advantages, polymer blends and copolymers entail a big challenge when they come to recycling. In this view, enzymatic hydrolysis constitutes an outstandingly valuable solution, due to its substrate specificity, allowing separation and recovering of the single components and monomers.

The aim of this work was the application of *Thermobifida cellulositilytica* cutinase [2] to preferentially hydrolyse PPeF from PLA/PPeF blends and PLA-PPeF copolymer. The FDCA monomer was successfully recovered from the hydrolysate, with a high purity level, and reused for PPeF re-synthesis. The results confirmed the fully circularity of bioplastics, from production to after-life recycling and finally re-synthesis (Scheme 1).



Scheme 1.

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## Acknowledgment

M.S., M.M., N.L. acknowledge the Italian Ministry of University and Research. The contribution is based upon work from COST Action FUR4Sustain, CA18220, supported by COST (European Cooperation in Science and Technology).

## *A microwave-enhanced method for the recovery of strategic metals from spent lithium-ion batteries*

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Keywords: Spent-Lithium-ion batteries, circular economy, microwave heating

This work proposes a new microwave (MW) treatment of spent lithium-ion batteries (LIBs), for strategic metal recovery by carbothermic reduction, involving short treatment times, without requiring the addition of either external additives or an inert atmosphere. This new technology, recently patented (Italian patent pending n. 102022000002351), won the EIT RAW Materials competition, as a promising idea of the sustainable management of raw materials [1]. This treatment can be achieved by a synergistic combination of a graphite-based MW absorber with a patented MW susceptor, which allowed to boost the overall efficiency of the carbothermal treatment. Finally, malic acid was utilised as a green leaching agent, decreasing the process's chemical footprint [2]. The choice of L-Malic acid relied on the sustainable management of this chemical after the treatment (recoverable) and for its neglecting secondary emissions (compared to the inorganic acids), making it suitable for future environmentally friendly applications.

Compared with conventional carbothermal treatments, the possibility to recover raw materials by reactions occurring in an air atmosphere allows reaching simplified environmental conditions for the extraction of metals, thereby increasing the sustainability of the recycling process. In addition, the required treatment times are very short (only a few minutes). Another advantage of the proposed technology is the possibility to avoid the separation of the anode and cathode materials in the pre-treatment process. Finally, it is very important to highlight that the proposed method allows the treatment of a combination of various discarded LIBs materials, which represents the real situation in industrial recycling plants, where spent battery typologies are generally not separated.

Figure 1 reports the layout of the proposed recycling process based on the black mass (BM) leaching with water and L-malic acid, after the MW treatment. The finer BM fraction (< 0.5 mm), obtained after sieving, was used.

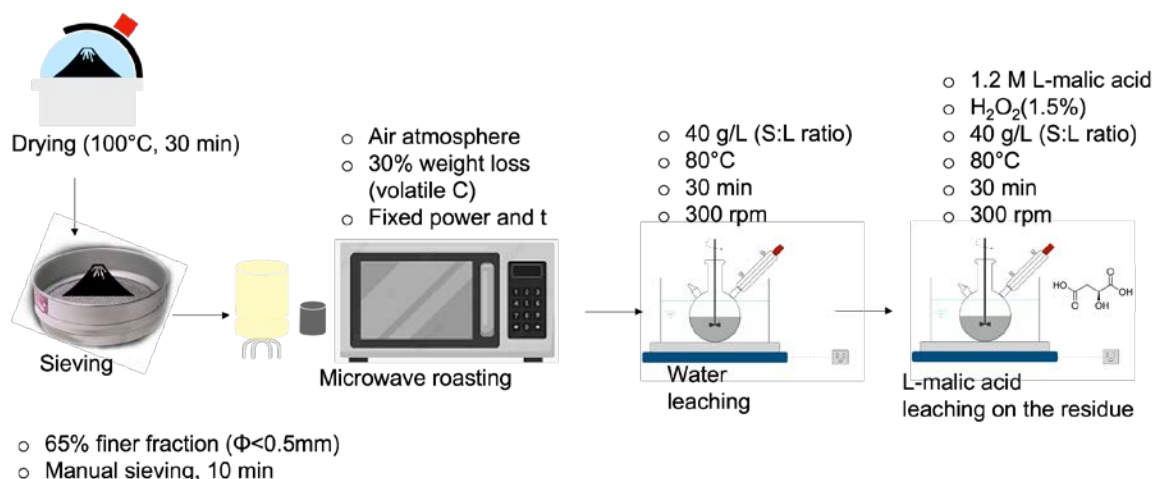


Figure 1. Layout of the whole procedure for metals recovery: it is based on MW followed by leaching with water and environmentally friendly organic acid (L-malic acid) for the simultaneous extraction of Li (mainly in water), Ni, Co, and Mn.

Considering that cathodic material Li(Ni-Co-Mn) oxide, having oxidation property and graphite, having reduction property, are both present in the cathode a typical carbothermic reaction can occur, with lower temperatures in comparison to the material expected decomposition, due to coupling reactions [3], as widely discussed by thermo-kinetic studies. The thermal process is followed by leaching in water (to recover lithium) and L-malic acid (to recover the other metals as Co, Mn, and Ni) and obtaining a recovery process resulting to be competitive with metals extraction from respective ores. The next goal will be to exploit food waste to produce organic acids and test them to recover the metals from BM treated by MW.

This work was supported by Fondazione Cariplo with the project Tech4Lib “Low-energy technologies for circular economy of spent lithium-ions batteries based on enhanced microwave effects”.

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## *Eco-design of innovative release agents*

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Keywords: release agent, bio-based polymer, composite material

The growing attention towards sustainability and circularity in chemical technologies has led to the need to design new materials characterized by better chemical-physical properties together with a lower impact on human health and the environment.

To achieve this goal, it is essential to direct research towards the development of new synthetic strategies for the production of materials widely used in industrial contexts. A project is underway in our laboratory focused on the development of synthetic processes characterized by greater sustainability both for the operators who work on the production line and for the substances emitted into the atmosphere during the production phases. The project aims to develop innovative materials to be included in composite products. During the research activity, particular attention is paid to the principles of eco-design and green chemistry, looking at the ecological and toxicity profile of the reagents and solvents used.

In particular, the research project aims to achieve two main objectives: 1. the development of alternative formulations to those more commonly used in the composite products industry in compliance with Health, Safety and Environment (HSE) requirements; 2. the generation of new bio-based release materials originating from natural building blocks.

In this context, the formulation based on a mixture of carnauba wax in aromatic solvents (toluene, xylene) commonly used on an industrial scale for the production of release agents has been revised. A particular focus was on the principles of eco-design and green chemistry, looking at the ecological and toxicity profile of the reagents and solvents used. This aspect is of paramount importance during the large-scale production process in order to control and possibly reduce contamination from internal and external VOCs and to meet HSE requirements for operators on the production line.

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The second objective set by this research work concerned the development of new polymeric materials to be used as release agents characterized by improved environmental and toxicological sustainability during the different phases of their life cycle (production, use, and end of life). Thus, great attention was devoted to the potential use of natural building blocks for the synthesis of bio-based release agents and their application for the production of composite products on industrial scale was explored.

The adoption of several analytical techniques (spectroscopic analysis such as Infrared Spectroscopy and Nuclear Magnetic Resonance, morphological observations with optical and Scanning Electron Microscopy, and thermal analysis) was fundamental to obtaining a complete characterization of the prepared materials.

In the present communication, the objectives and the main milestones of the conducted research activities will be described.

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## The investigation of LD540 behavior with albumins

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Keywords: HSA, BSA, absorption

HSA (Human Serum Albumin) is the enlightenment of serum albumin originating in the blood serum of humans which is the largely bounteous protein in human blood. The potential immunologic reaction in biological applications in humans believed that HSA binding and reaction is in the highest necessity. To compare we done in the BSA (Bovine Serum Albumin) also. LD540 (4,4-difluoro-2.3,5.6-bis-tetramethylene-4-bora-3a,4a-diaza-s-indacene) has been disclosed by Morgan and Boyer merely as one specific member of a large generic group of bodipy dyes reported to be useful for dye laser systems and photochemical agents in the treatment of diseased tissues using photodynamic therapy techniques. We use UV-vis absorption and emission spectroscopies to study the interaction of LD540 with both HSA and BSA. LD540 was efficiently bound with Human Serum Albumin and Bovine Serum Albumin. The docking studies further confirm the binding of LD540 with preferred amino acids in serum albumins. The binding constant values support the statement of interactions.

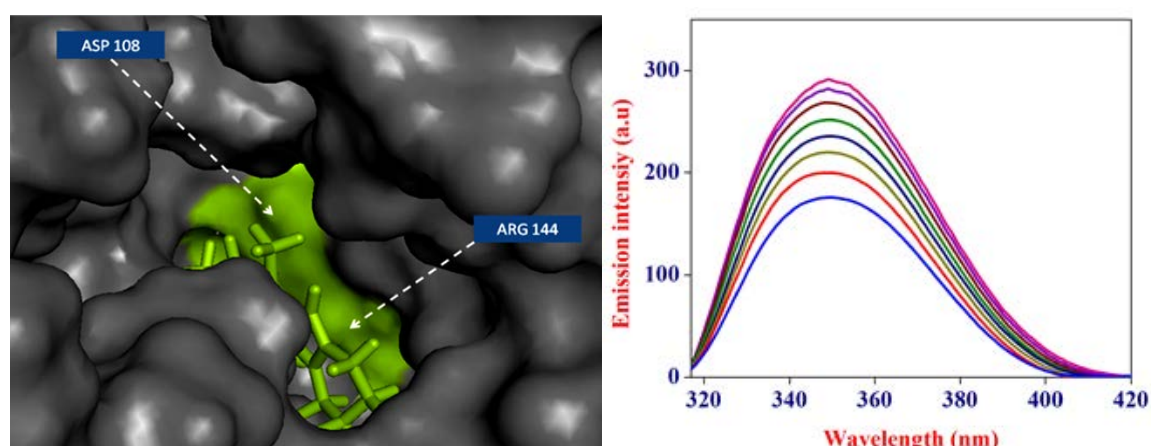


Figure 1. The interaction of LD540 with BSA.

**Table 1. Binding parameters**

System	$K_{sv}(\text{dm}^3 \text{mol}^{-1})$	$K_a(\text{dm}^3 \text{mol}^{-1})$	$K(\text{dm}^3 \text{mol}^{-1})$
LD540-HSA	$1.69 \times 10^9$	$0.25 \times 10^7$	$0.24 \times 10^7$
LD540-BSA	$1.58 \times 10^9$	$0.17 \times 10^6$	$0.2 \times 10^6$



# Vapochromic and vapoluminescent Zn(II) Schiff- base complexes as chemosensors for volatile organic compounds

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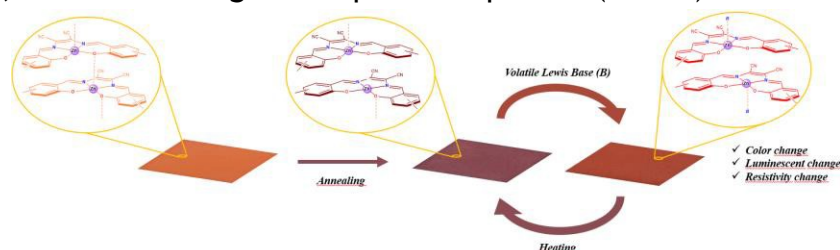
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Keywords: Zn(II) Schiff base complexes; Paper-based sensors; VOCs

Volatile organic compounds (VOCs) play a crucial role in the climate changes because they represent one of the principal atmosphere pollutants.<sup>1</sup> For this reason, the fast, selective and quantitative detection of VOCs represents a pivotal asset for preserving the environmental healthiness.

Zn(II) Schiff-base complexes are Lewis acidic species having photophysical, vapochromic, vapoluminescent and chemiresistive properties, tuneable through the structure of N<sub>2</sub>O<sub>2</sub> ligand and upon interaction with Lewis bases.<sup>2-4</sup>

Here, we present a study on the vapochromic and vapoluminescent properties of Zn(II) Schiff-base complexes having different substituents in the salicylidene rings, to develop arrays of chromogenic and fluorogenic chemosensors tailored for the detection of VOCs with Lewis basicity, such as oxygenated VOCs (OVOCs or oxVOCs), nitrogen-containing VOCs (NVOCs), and volatile organic sulphur compounds (VOSCs).



In order to develop disposable and low-cost chemosensors, Zn(II) Schiff-base complexes deposited on paper strips were explored. The exposure to VOCs implies different and reversible color and luminescent changes of these paper-based sensors. Therefore, they can be involved for the fabrication of disposable arrays of chromogenic and fluorogenic chemosensors for in-situ detection of VOCs.

This research is funded by the University of Catania, PIACERI 2020/2022, Linee di Intervento 2 e 3 and by European Union (NextGeneration EU), through the MUR-PNRR project SAMOTHRACE (ECS00000022).

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## Conductive Polycorrole Sensors for Room-Temperature Detection of Nitric Oxide

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Keywords: resistive sensors, nitrogen oxide, polycorrole

A novel class of conductive polymers based on polycorroles, an organic semiconductor, is introduced. Corroles are sensitive molecules well-known for their optical and catalytical properties [1]. Recently, we investigated the properties of polycorroles firstly in combination with other conductive molecular materials to form heterojunction devices sensitive to ammonia [2]. This contribution illustrates the application of polycorrole films of different formulations as resistive room-temperature gas sensors. Results indicate a large sensitivity and selectivity to NO. This finding is of great interest since nitric oxide is an environmental pollutant recently gaining interest for its pathological and physiological roles, such as vascular, inflammatory, and neurological regulation functions. Besides the sensitivity to NO, the sensors show a residual but not negligible cross-sensitivity to other gases, such as CO, CO<sub>2</sub>, and H<sub>2</sub>. This property enables the formation of sensor arrays implementing the combinatorial selectivity of electronic noses.

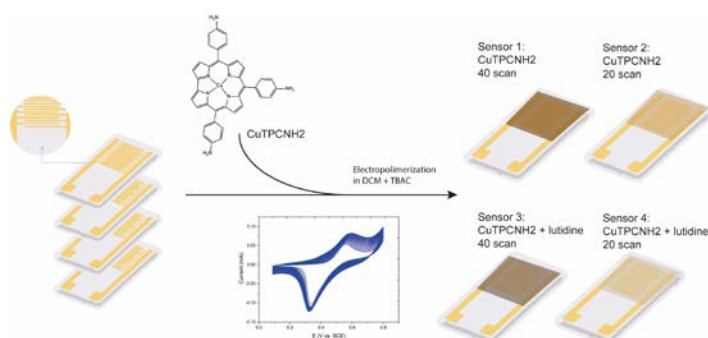


Figure 1. Sensor array fabrication via cyclic voltammetry.

Briefly, four sensors were prepared by electro-polymerizing 5,10,15-(4-aminophenyl)corrolato]copper(III) (CuTPCNH<sub>2</sub>) [2] (see Figure 1) onto a couple of interdigitated electrodes. Sensor 1 (S1) and sensor 2 (S2) were obtained by 40 and 20 voltammetric cycles, whereas sensor 3 (S3) and sensor 4 (S4) were polymerized, again

at different cycles, but in the presence of 2,6-lutidine (5% v). The sensors were allocated in an air-tight chamber connected to mass flow controllers to settle the gas dilution in synthetic air, and resistances were measured at various concentrations of NO, CO, H<sub>2</sub>, and CO<sub>2</sub>. The relative change of resistance has been considered as the sensor response. In S1 and S2, the polycorrole chain is expected to undergo protonation during the polymerization process, giving rise to a p-type conductive polymer. As a result, sensor resistances increase in the presence of reducing species such as NO (see S1 characteristic curves in Figure 2). This reaction can be prevented by a proton scavenger, such as lutidine, whose presence in the polymer changes the majority of charge carriers turning the p-type character into n-type, thus reverting the sign of the sensor response (see S3 in Figure 2a).

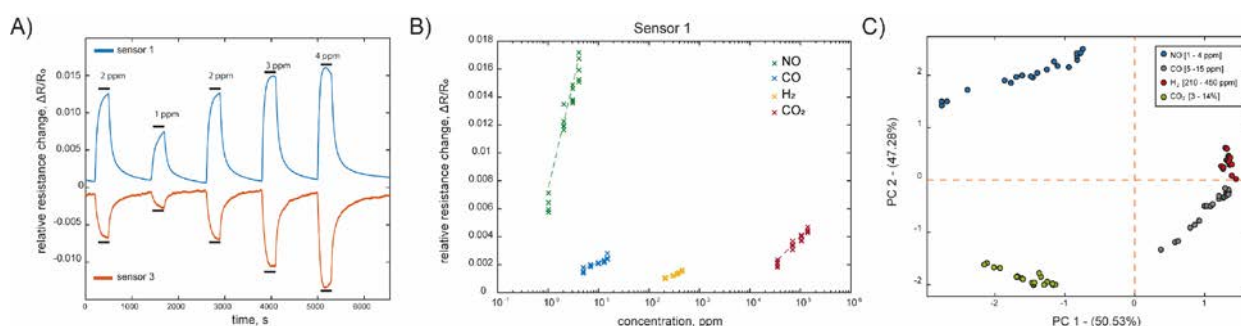


Figure 2. (a) Relative resistance changes of S1 and S3 different NO concentrations. (b) Scores projection onto the first two Principal Components after data normalization.

Regardless of the p-type and n-type nature of polymers, all sensors show a marked sensitivity towards NO, with sub-ppm detection limits (estimated LODs, S1: 18 ppb, S2: 12 ppb, S3: 90 ppb, S4: 16 ppb). The sensitivity to the other gasers is about one or two orders of magnitude smaller (see, for example, S1 and S3 characteristic curves in Figure 2b). Albeit these differences, the sensitivities with respect to CO, H<sub>2</sub>, and CO<sub>2</sub> are large enough to allow for detection limits compatible with the operating range in many applications; e.g., the estimated LOD of CO of S2 and S3 is 230 and 160 ppb, respectively. Finally, the little disparity in sensor formulation differentiates the sensitivity patterns of sensors enabling the application of the combinatorial selectivity principle of electronic noses. This property is manifested by the Principal Component Analysis shown in Figure 3c. The tested gases are pertinent to a manifold of practical applications, not least medical diagnosis. Moreover, previous results established that the sensitivity of corroles based sensors is strongly affected by the metal ion coordinated at the center of the macrocycle [1]. This property, combined with the affordable protocol for tuning the p-type or n-type conductivity, will be exploited to develop large sensor arrays.

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## Doped $\text{Li}_4\text{SiO}_4$ -based sorbents for $\text{CO}_2$ capture at high temperature

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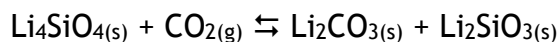
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Keywords: Lithium orthosilicate,  $\text{CO}_2$  capture, sorbent

Introduction. One of the most effective methods to lower power plant carbon dioxide emissions is post-combustion  $\text{CO}_2$  capture based on regenerable solid sorbents [1]. Lithium-based ceramics, such lithium orthosilicate ( $\text{Li}_4\text{SiO}_4$ ), were discovered to be among these sorbents that could capture  $\text{CO}_2$  at high temperatures and low concentration.  $\text{Li}_4\text{SiO}_4$  shows significant  $\text{CO}_2$  sorption capacity (up to 367 mg/g sorbent), good cyclability and lower regeneration temperatures compared to other sorbents as  $\text{CaO}$ , zeolites, metal-organic frameworks, and activated carbons [2].  $\text{Li}_4\text{SiO}_4$  exhibits the following sorption/desorption reaction:



$\text{CO}_2$  adsorption is generally carried out at 500-700 °C, depending on the  $\text{CO}_2$  partial pressure. Firstly, the reaction between  $\text{Li}_4\text{SiO}_4$  and  $\text{CO}_2$  occurs leading to the formation of a solid product shell on the particle surface consisting of lithium carbonate,  $\text{Li}_2\text{CO}_3$ , and lithium metasilicate,  $\text{Li}_2\text{SiO}_3$ ; then,  $\text{CO}_2$ ,  $\text{Li}^+$  and  $\text{O}^{2-}$  diffuse through the formed solid shell. It is assumed that  $\text{CO}_2$  diffusion resistance plays a dominant role, particularly under low  $\text{CO}_2$  partial pressures. For this reason, various doping methods have been proposed to improve  $\text{Li}_4\text{SiO}_4$  activity such as the addition of alkali carbonates ( $\text{K}_2\text{CO}_3$  or  $\text{Na}_2\text{CO}_3$ ) [2] that form molten eutectic carbonate mixtures with the product  $\text{Li}_2\text{CO}_3$  at high sorption temperatures (about 500 °C). The resultant molten carbonate shell greatly improves  $\text{CO}_2$  diffusion throughout the liquid layer.

Materials and methods.  $\text{Li}_4\text{SiO}_4$  powders were synthesized by solid-state reaction mixing  $\text{Li}_2\text{CO}_3:\text{SiO}_2$  with a molar ratio of 2:1 in a ceramic mortar with distilled water (2 mL/g of reagents). The suspension was dried at 105 °C for 2 h and calcined in a muffle furnace increasing the temperature up to 900 °C at 5 °C/min and maintaining this temperature for 6 h. After calcination, the pure  $\text{Li}_4\text{SiO}_4$  powders were grounded and sieved below 75  $\mu\text{m}$  and mixed with  $\text{K}_2\text{CO}_3$  (10-30 wt.% on the total weight) to obtain K-doped  $\text{Li}_4\text{SiO}_4$  powders.  $\text{CO}_2$  sorption performance of the produced sorbents was preliminarily investigated by a Thermogravimetric Analyser at 580 °C for 120 min,

under a 150 mL/min of N<sub>2</sub>/CO<sub>2</sub> at 4 vol.% of CO<sub>2</sub> (P<sub>CO<sub>2</sub></sub> = 0.04 atm). During the sorption, the weight increase due to CO<sub>2</sub> sorption was recorded as a function of time. Then, the sorbent was regenerated by switching the feed gas stream to 100 % N<sub>2</sub> and raising the temperature to 620 °C to increase the desorption rate. Further, the best performing doped powders were used to produce porous cylindrical pellets by gel-casting processes mixing the powders with gelatine and foaming agent used as binder and pore former, followed by drying and calcination at 850 °C for removing the gelatine and sintering the material.

**Results and discussion.** The sorption performance of the K-doped Li<sub>4</sub>SiO<sub>4</sub> powders is reported in Fig.1a. The sorption capacity of the powders containing 10, 20, and 30 wt.% of K<sub>2</sub>CO<sub>3</sub> after 120 min was about 134, 201, and 216 mg CO<sub>2</sub> for g of total sorbent, respectively. The best result for the powders was achieved with the highest K<sub>2</sub>CO<sub>3</sub> content, corresponding to a conversion X<sub>Li<sub>4</sub>SiO<sub>4</sub></sub> of about 83 %. The produced K-doped 30 wt.% Li<sub>4</sub>SiO<sub>4</sub> pellets (Fig.1b) showed a porous structure (Fig.1c) and good compression resistance (1.8 MPa (ASTM C1424)). However, its sorption performance (Fig.1a) is lower than the starting doped powder due to lower surface area (BET area 1.2 vs 1.8 m<sup>2</sup>/g), as expected. Thus, the gel casting method must be perfected in terms of ratio powder/foaming agent/gelatine to increase the microporosity of the resultant pellets and therefore their sorption capacity while maintaining good mechanical resistance in view of their use in a full-scale fixed bed adsorber.

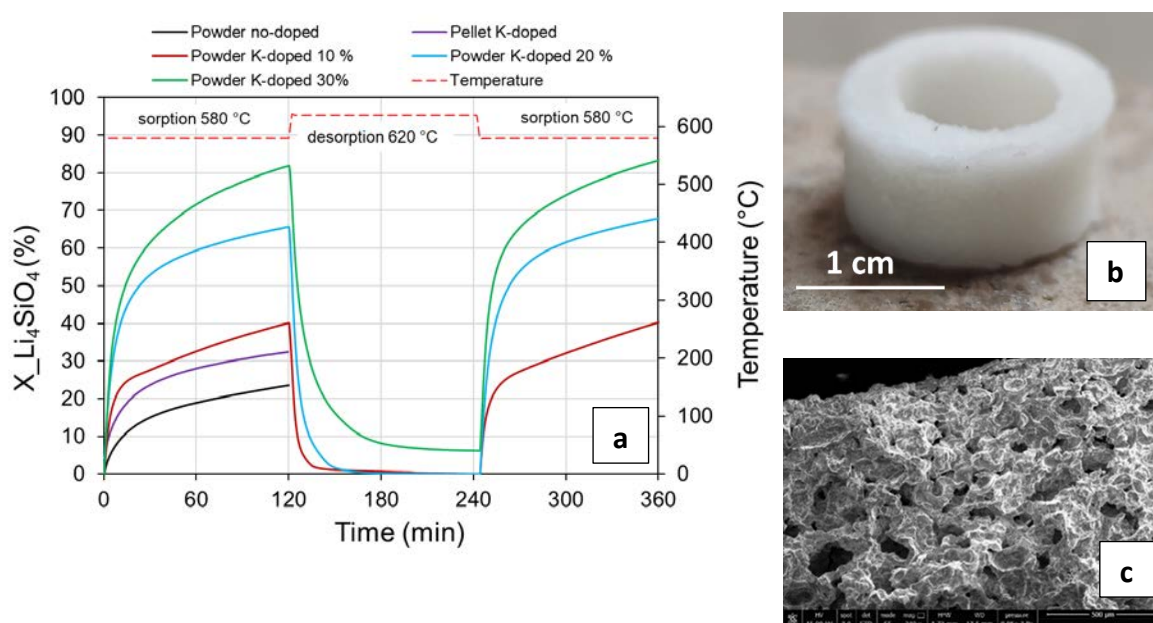


Figure 1. a) CO<sub>2</sub> sorption/desorption profile of K-doped Li<sub>4</sub>SiO<sub>4</sub> powders and pellet; b) K-doped Li<sub>4</sub>SiO<sub>4</sub> pellet; c) SEM image of cross section of K-doped Li<sub>4</sub>SiO<sub>4</sub> pellet.

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## *BaTiO<sub>3</sub>-PDMS nanocomposites for energy harvesting: enhancing the dielectric performance through ceramic particles' functionalization*

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Keywords: nanocomposites, functionalization, dielectric properties

The growing need for wireless and portable electronic devices has made energy harvesting and piezoelectric materials essential in decreasing reliance on non-renewable energy sources. Piezoelectric materials have become noteworthy due to their capacity to convert mechanical stress or strain into electrical energy, which renders them encouraging for diverse applications. Nonetheless, their inherent properties such as low electromechanical coupling coefficient and mechanical strength usually curtail their performance. Likewise, dielectric elastomers (DEs) also encounter natural restrictions like low dielectric properties, electromechanical coupling coefficient, and mechanical strength. To tackle these obstacles, nanocomposites have emerged as a valuable solution. Different types of nanocomposites consisting of a polymer matrix combined with a high-performance dielectric/piezoelectric phase were devised, which showed improved piezoelectric features, such as enhanced piezoelectric coefficients, superior thermal stability, and more efficient energy conversion [1].

The interface between the polymer matrix and the ceramic filler in polymer-ceramic nanocomposites plays a crucial role in achieving the desired properties and performance of the composite material. Methods like surface modification of the ceramic filler, polymer functionalization, and the use of coupling agents or compatibilizers can tune the interface [2-3].

The present work focuses on the functionalization with different organotrialkoxysilanes of BaTiO<sub>3</sub> nanoparticles (NPs) synthesized via wet-chemical methods, [4] and the evaluation of organosilanes' impact on the dielectric performance of PDMS-based nanocomposites. Both bare and functionalized NPs were dispersed in PDMS in a production process involving the simultaneous application of heat and an electric field to produce 100 um thick film composite.

Particles' functionalization was studied by FTIR (Fourier Transform Infrared spectroscopy), EDXS (Energy Dispersive X-Ray Spectroscopy), and solid-state NMR (Nuclear Magnetic Resonance), and the yield of functionalization was obtained by TGA (thermogravimetric Analysis). Functionalization was proven to be successful with all the employed organosilanes, with high degrees of functionalization [5].

The impact of surface functionalization on particles dispersibility was evaluated by SEM and EDXS spectroscopy. Finally, PDMS-based film composites were extensively characterized through dielectric spectroscopy in a wide range of frequencies and temperatures, and their dielectric breakdown strength was measured to calculate the energy density and evaluate the suitability of obtained films for energy harvesting applications. It was found that the presence of functionalizing agents linked to the nanofillers' surface is beneficial for the dielectric performance of PDMS-based film nanocomposites. The functionalization is responsible for an increased value of dielectric constant thanks to the activation of different polarization mechanisms and for an improved value of dielectric breakdown, possibly because of charge trapping effects due to the intrinsic chemical structure of the functionalizing agents. Furthermore, the large improvement of the dielectric properties was achieved with lower filler content with respect to similar works reported in the literature, resulting in higher values of energy density that can be stored in the materials, and consequently valuable energy harvesting performance.

In summary, advances in energy harvesting and piezoelectric materials can transform the way electronic devices are powered, leading to a better quality of life. However, It is crucial to deeply investigate the interface effects to enhance the performance of piezoelectric and dielectric materials, and functionalization with organosilanes seems to be a promising approach to achieve this goal.

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## *Doubly Charged Species in the Upper Atmosphere of Planets and Space*

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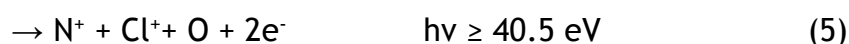
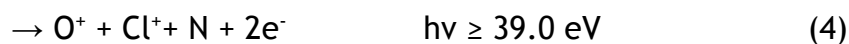
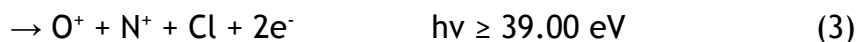
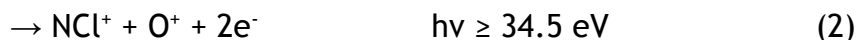
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Keywords: molecular dications, double photoionization, synchrotron radiation

Doubly positive charged atomic or molecular ions, also named atomic/molecular dications, are formed whenever a chemical system has a high amount of energy available, as for example in flames. We can find these species in low concentrations in many natural plasmas such as planetary ionospheres, interstellar clouds and comet tails [1,2]. Astronomers found ionized gas containing  $\text{H}_2\text{O}^+$ ,  $\text{CO}^+$ ,  $\text{CN}^+$ , and  $\text{CO}_2^+$  molecular dication in the tail of Hyakutake comet in 1996. In the early 2000s,  $\text{N}_2^{2+}$  and  $\text{CO}_2^{2+}$  were predicted to exist in the ionosphere of Mars, Venus and Titan (the largest moon of Saturn) where they have been detected with significant densities [3]. The role of molecular dications in the upper atmosphere of planets has been investigated by our and other groups, pointing out the possibility for such ionic species to be involved in the escape processes by Coulomb explosion [4]. Our group since 2001 is able to generate molecular dications in double photoionization experiments by using tunable UV and EUV photon source at the Synchrotron Facility of Elettra, Basovizza (Trieste). Many molecular dications were produced and characterized during the last decade:  $\text{N}_2\text{O}^{2+}$ ,  $\text{C}_6\text{H}_6^{2+}$ ,  $\text{C}_2\text{H}_2^{2+}$ ,  $\text{CO}_2^{2+}$ . More recently, the double photoionization of propylene oxide ( $\text{CH}_3\text{CHCH}_2\text{O}$ ), nitrosyl chloride ( $\text{ClNO}$ ) and allene ( $\text{CH}_2\text{CCH}_2$ ) has been investigated. They are molecular species very interesting for atmospheric chemistry and astrochemistry whose characterization was done at the beamlines “GasPhase” and “CircularPolarization” using the ARPES (Angle Resolved PhotoEmission Spectroscopy) end station exploiting the PEPIICO (Photoelectron-Photoion-Photoion) coincidence technique coupled with the TOF (time-of-flight) mass spectrometry [5].

Results, obtained in the double photoionization of  $\text{ClNO}$  molecules, recording data from 24.0 up to 70.0 eV of photon energy, will be showed and discussed at the conference, highlighting the fragmentation microscopic dynamics of the intermediate  $\text{ClNO}^{2+}$  dication. In this regard, it was possible to extract the energy thresholds for several

fragmentation channels produced by double photoionization of ClNO (see Figure 1). They are the following:



The measured threshold energies reported above were obtained by accumulating 2-4 hours at each investigated photon energy with a 200 meV energy step.

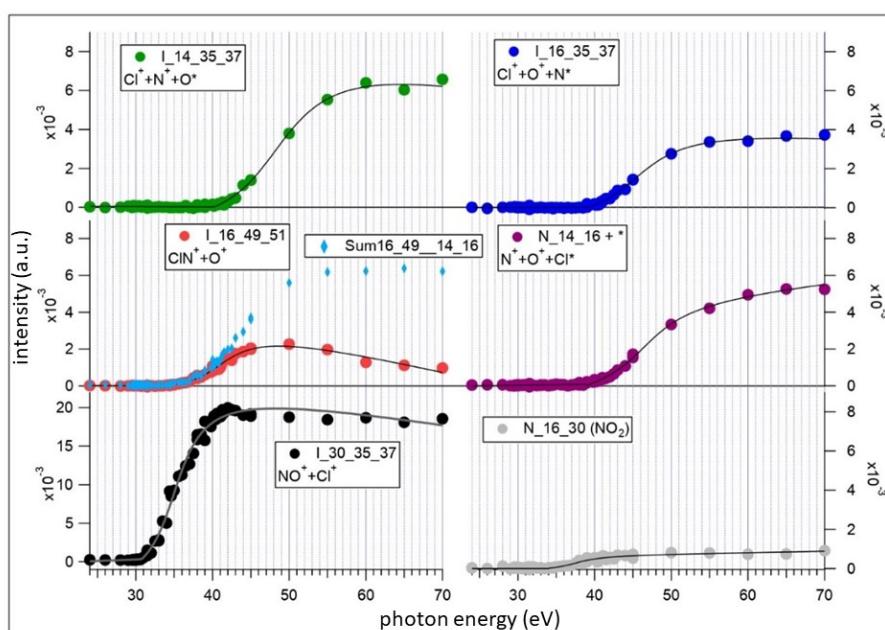


Figure 1: Measured relative cross sections and threshold energies of the fragmentation channels recorded in the double photoionization of ClNO (24.0-70.0 eV photon energy range). The channel producing  $\text{NO}^+ + \text{Cl}^{2+}$  (reaction (6)) is not reported because, due to its very low intensity, it needs a more careful analysis which is in progress. In the left and lowest panel is reported the measured fragmentation channel leading to  $\text{NO}^+ + \text{O}^+$  coming out from the double photoionization of  $\text{NO}_2$  molecules being an impurity of the ClNO sample: its abundance is at least of a factor 4 lower respect to the others.

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# **SESSIONE POSTER**

## Rare-Earth Magnet Recycling using Phosphonium based Ionic Liquids

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Keywords: ionic liquids, metal recovery, REEs

Due to the limited availability of primary ore deposits and supply risk, research attention is being drawn towards the recovery of Rare Earth Elements (REEs) from secondary sources [1-2]. Raw materials play a fundamental role in the current and future technologies necessary for achieving sustainable development goals as outlined in the UN 2030 Agenda. Notably NdFeB and SmCo magnets, as secondary solid wastes, are significantly rich in REEs such as Nd, Sm, and Dy [3]. Current hydrometallurgical processes for the recovery of the REEs from aqueous solutions have some interesting advantages but require the use of significant amounts of toxic volatile organic compounds [4]. Ionic liquids (ILs) have many potential applications since they present many advantages such as negligible vapor pressure, reusability and high thermal stability [5].

In this work, we assess the performance of phosphonium based ILs ([P<sub>66614</sub>][Dec] and [P<sub>66614</sub>][Cl]) for separation of REEs from other metals from magnets (Figure 1). The versatility of more environmentally friendly IL with decanoate anion at different pH was studied. Moreover, in the acid leaching step, the effects of acid concentration and leaching time were investigated. To complete the recovery process, further separation was proposed using two phosphonium based ILs consecutively, resulting in a high yielding procedure. It was found that bivalent ions are extracted from highly acidic media, while REEs prefers different acid concentrations in both ILs. After extraction, the water phase was measured by ICP-OES to quantitatively determine metal concentrations and magnet composition.

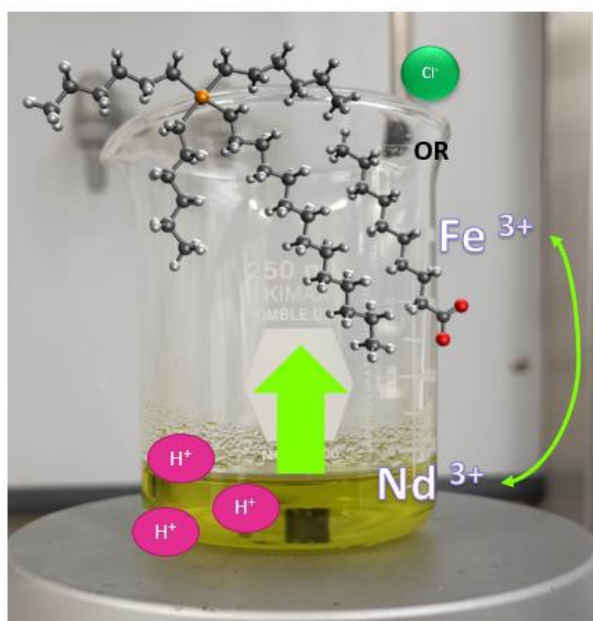


Figure 1. Graphical representation of selective extraction of metals by [P<sub>66614</sub>][Dec] from acidic media.

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## Nanocellulose-based solutions for water treatment

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Keywords: Nanocellulose, eco-design, wastewater decontamination

The growing and urgent demand for water and wastewater decontamination from a wide range of pollutants asks for the development of more effective and safe technologies. In this context, the design of manufactured nanomaterials (MNM) for an efficient water treatment is attracting more and more interest due to their promising adsorption performances. At the same time, MNM also raise concerns due to their potential (eco)toxicity and the uncertainty related to their final fate. For this reason, a safer-by design strategy is recommended in developing new MNM, which should combine a high decontamination efficiency with verified eco-safety [1,2]. A first step in this route consists into the proper choice of starting material for the production of MNM [3].

Herein we report an overview of our recent findings on how nanocellulose, simply derived from biomass as renewable source, could represent a sustainable and eco-safe solution for developing new MNM with high sorption performances for water treatment [4]. 2,2,6,6-Tetramethylpiperidinyloxyl (TEMPO)-oxidized cellulose nanofibers (TOCNF), bearing carboxylic groups on the C6 position of some glucopyranose units, have been produced from different sources [5] and their eco-safety has been verified by an in vivo acute study with marine mussels *Mytilus galloprovincialis* [6]. TOCNF have been successfully used both as building blocks for the design of nanostructured sorbent materials for water treatment, by thermal cross-linking with polyamine derivatives [7,8], and as suitable supports for silver nanoparticles (AgNPs), providing nano-composites with enhanced sorption performances towards heavy metals [9].

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## *Inorganic polymers with waste cork powder*

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Keywords: cork waste, metakaolin, aluminosilicate network, alkali activation

Cork powdery waste (CW) from agglomerated cork caps manufacturing is usually exploited for its energy content in waste-to-energy plants. In this contribution, we propose its exploitation as additive for inorganic polymers consolidated via alkali activation. In particular, amounts of 2.4, 4.8 and 9.1 wt% (percentage calculated upon dry metakaolin) of the as-received cork powdery waste were added to a MK-based geopolymer formulation and then activated with NaOH and Na silicate solutions [1]. The inorganic polymer paste was opportunely shaped for the production of solid blocks that were chemically tested. To improve the sustainability of the final solid material, no pre-treatments were performed on the CW nor thermal curing was conducted during the solidification stage of the inorganic polymer paste. The solidified materials presented an apparent density in the range  $1.521\text{-}0.990 \pm 0.001 \text{ g/cm}^3$ , combined with a total porosity in the range  $35.61\text{-}56.22 \pm 0.003 \text{ vol\%}$  passing from 2.4 to 9.1 wt% of CW, respectively. These physical properties were dependent upon ageing time as well as the compressive strength that ranged from 2.5 to 1.5 MPa at 28 and 90 days of curing time. Microstructural investigations completed the study evidencing the homogenous dispersion of the cork particles within the MK-based inorganic polymer when proper mechanical stirring of the fresh paste was operated.

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## Bottom-up Synthesis and Application of Carbon Dots from Agri Food Waste

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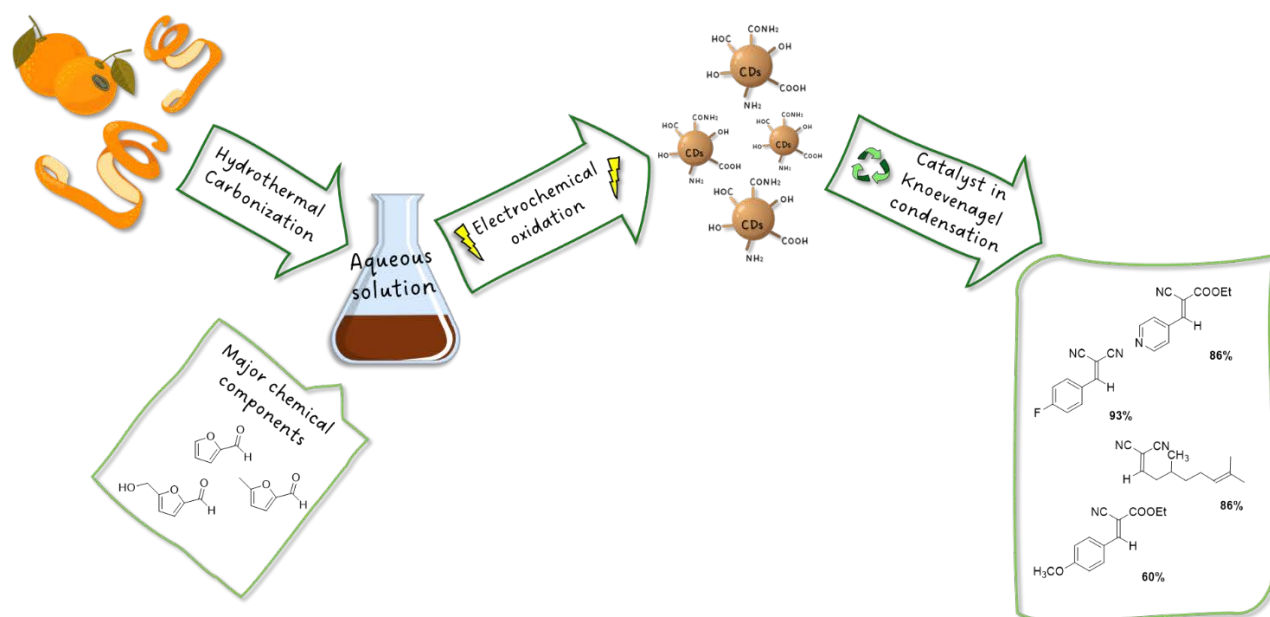
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Keywords: carbon nanodots, reusable nano catalyst, electrochemical synthesis

Waste disposal is a main topic especially for agricultural and food ones nowadays. These side products of our industries are abundant and still full of relevant organic substances that can be translate in a large quantity of carbons, so it's important find a way to fully exploit them, in fact we present the synthesis of new useful carbon nanoparticles, Carbon Dots (CDs) derived from orange peel waste. Our innovative starting material is represented by the aqueous phase (AQS) obtained after the hydrothermal carbonization of the industrial orange peels themselves. The AQS is demonstrated by GC-MS analysis is rich of interesting furfural derivates (61.82 % of 5-hydroxymethylfurfural and 16.69 % of furfural) [1] and following a reproducible oxidative electrochemical *bottom-up* procedure we isolated the CDs as a brown powder with more than 30% of yield (w/w%). The nanoparticles have been plenty characterized (SEM, TEM, DLS, FTIR, TGA, UV and fluorescence emission).[2] It is demonstrated that our CDs are efficient heterogeneous catalyst in Knoevenagel condensation reusable for five times without significant activity loss. The reaction has been performed in mild condition stirring the reagents and catalyst free of any organic solvents. The studies were carried out on different carbonyl compounds (aromatic and aliphatic aldehydes and ketones) and activated methylene compounds. Moreover, a comparison with 5HMF derived-CDs, from pure 5-hydroxymethylfurfural major component of AQS, revealed worse catalytic activity than the biowaste ones. [3]



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## *Effect of storage time and relative humidity in bio-nanocomposites for sustainable food packaging (BIOSTAR-PACK)*

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Keywords: food-packaging, starch, ageing

In the food-packaging industry, petroleum-based materials represent a considerable source of pollution since they usually are non-degradable and single use. The environmental impact is even worsened by the food waste issue. As a matter of fact, Italians waste about 100 kg of food per person every year, 27 kg of which is still edible. In this frame, the BIOSTARPACK project aims to decrease the food waste impact by developing new packaging materials from organic wastes able to ensure longer shelf-life to food and to be recyclable. [1] Starch is a natural polysaccharide which can be easily extracted from food waste and used in form of film after gelatinization; it is usually employed with the addition of filler and plasticizers to improve gas barrier and mechanical properties. In this project, bio-nanocomposites films made of starch as a matrix and sepiolite clay as a filler are produced. A first characterisation of the films pointed out the complete loss of starch crystallinity during the film processing, even after the addition of glycerol and sepiolite. [2] However, starch may undergo retrogradation, i.e. the capability to re-crystallize over time (ageing). This process depends on several parameters such as temperature, relative humidity (RH), time, water content, plasticizer and filler addition [3].

In this study, the evolution of starch microstructure during the retrogradation of bio-nanocomposite films aged at different conditions is presented (Figure 1). For this purpose, multinuclear solid-state nuclear magnetic resonance (ss-NMR) and X-ray diffraction (XRD) techniques were used at different time points. Moreover, the capability of the films to reversibly change from amorphous to crystalline structure at different RH will be presented.

At the highest RH (90%), the retrogradation started immediately: the crystallinity of starch increased over time showing the formation of a B-type polymorph, but the presence of sepiolite clearly hindered the process. On the contrary, at 50% RH all films remained amorphous.

Starch nanocomposite films also showed the capability to recover the amorphous state after storage in dessiccator at 0% RH, suggesting the possibility to control their microstructure by controlling RH during storage.

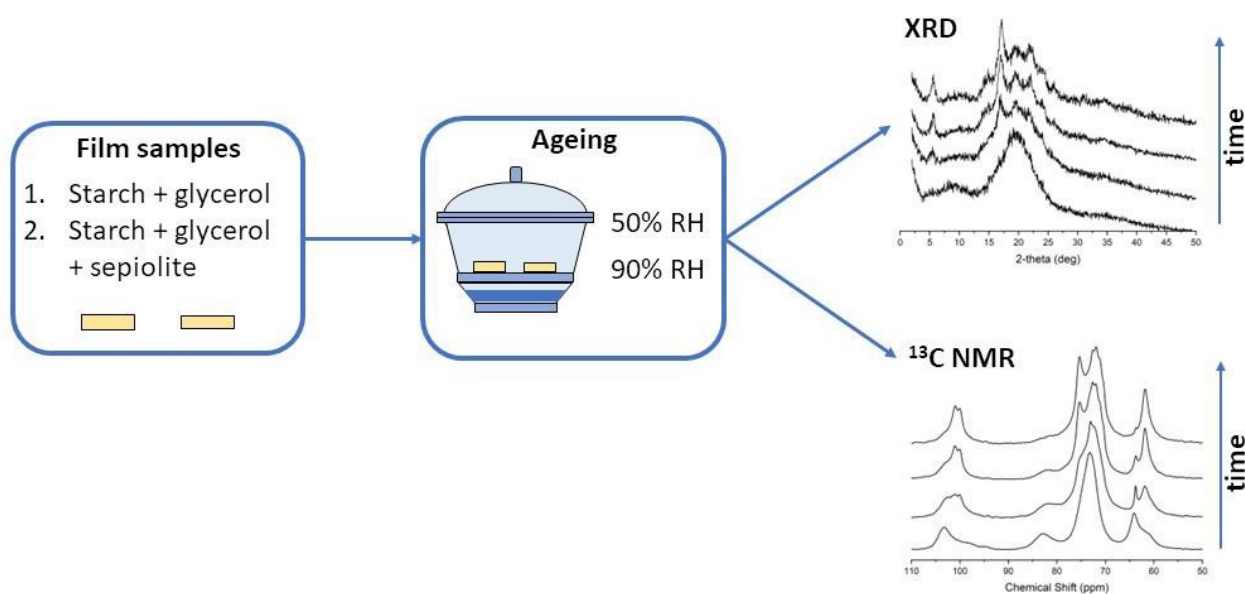


Figure 1. Scheme of the experiment and evolution of XRD patterns and <sup>13</sup>C CPMAS NMR spectra of starch+glycerol films with ageing time at 90% RH.

This study points out that monitoring the ageing effect at different conditions is of paramount importance to highlight possible microstructural variations that could have an impact on the performance of packaging materials based on starch nanocomposites.

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## Chemical Recycling of Fully-recyclable Bio-Epoxy Matrices and Re-use strategies: a Cradle-to-Cradle approach

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Keywords: Bio-epoxy, recycling, Epoxy resins

Epoxy resins are among the most used and commercialized thermosets due to their outstanding peculiarities, such as their easy processing, cost-effective processability, chemical resistance, high durability, insulating property, adhesive property, low thermal expansion, in addition to good thermal and mechanical properties [1]. Due to their interesting properties epoxy resins find different applications in several industrial fields, such as paints and coatings, adhesives and sealants, matrices for fibers reinforced composites, electrical and electronic components, marine, wind turbines, and so on. Epoxy market was estimated at USD 22.9 billion in 2021 and it is expected to expand at a compound annual growth rate (CAGR) of 7.3% from 2022 to 2030 [2]. Despite their application is becoming predominant in many application areas, a huge concern is growing more and more about epoxy's resins widespread use, because of their non-recyclability once they have reached their End-of-Life (EoL).

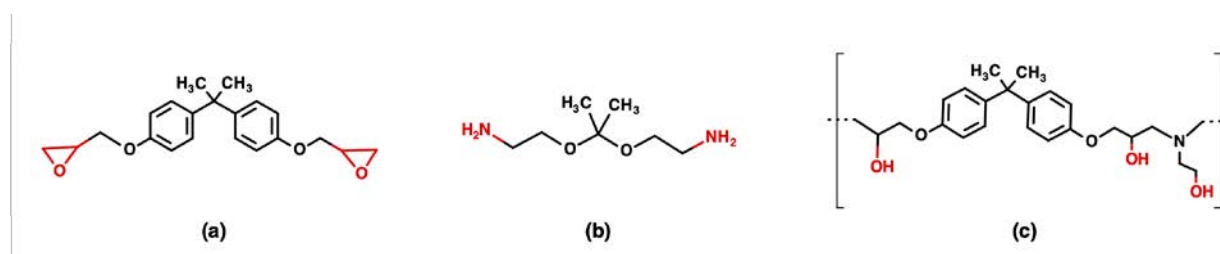


Figure. Chemical structures of (a) Polar Bear (part A), (b) Recyclamine™ R\*101 (b), and (c) recycled thermoplastic deriving from the chemical recycling process of the epoxy resin matrix (Polar Bear and Recyclamine™ R\*101).

Industries and academia are looking for more environmentally friendly recycling routes to reduce the environmental impact of epoxy resins [3]. In this work, we propose an alternative re-use strategy that starting from the produced recycled polymer (rTP)

encompasses a truly circular economy (CE) approach relying on the Cradle-to-Cradle (C2C) concept.

C2C philosophy was developed for the first time by McDonough and Braungart [4], and this approach aims to remodeling and reshape the productive cycle of consumer products to make sure that they can be infinitely reused rather than just being recycled with a downgrading of their properties or uses [5]. Starting from the bio-based epoxy prepolymers and the recycled polymer (rTP) different formulations with rTP contents varying from 15 to 27 wt% were processed with different cure cycles. All the systems were thoroughly characterized by thermo-mechanical testing. All the collected data by the run tests were statistically analyzed as replicated general factorial design. In the end, the best formulation, was identified using an optimization process relying on the desirability functions approach.

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# Recycling ash from wood-fired ovens through geopolymers: synthesis and characterization

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Keywords: wood ashes; geopolymers; waste; recycling

In recent years, geopolymers (GP) have been used as alternatives for recycling different types of waste [1]. In Italy, pizza making, which traditionally utilizes wood-fired ovens, results in a large quantity of wood ash (WA) that is often unused. Given their characteristics, including composition and fine granulometry, wood ashes are scraps that lend themselves well to being incorporated into geopolymeric matrices.

In this study, geopolymers with different percentages of wood ash used as filler are synthesized and evaluated. The synthesis process involves the use of WA, metakaolin, sodium silicate and sodium hydroxide. The characterization concerns the assessment of the structure and chemical stability of the materials as well as the mechanical strength, and the evaluation from the biological point of view. The results highlight the stability of the geopolymers. The mechanical strength achieved the best result with 20% of WA. Eventually, biological assays give an idea about the durability of these materials.

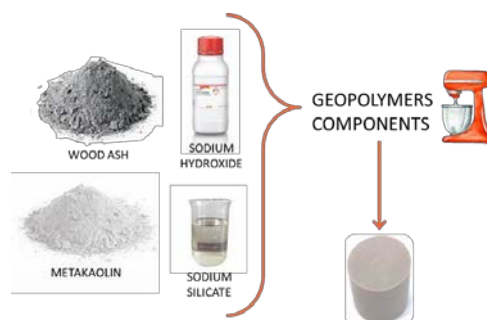


Figure 1. Procedure of geopolymers synthesis.

## Acknowledgments

This work was partly supported by "SCAVENGE" financed by Università degli Studi della Campania "Luigi Vanvitelli" in the framework of "Piano Strategico di Ateneo 2021-2023 - Azione strategica R1.S2". The authors would also like to thank Prochin Italia Prodotti Chimici Industriali Srl (Italy) for donating the sodium silicate used in this work.

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## Recycling by-design of plastics through thermally protected enzymes

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Keywords: enzyme immobilization, thermal resistance, polymer formulation

Packaging accounts for more than 40% of all plastics produced every year and plastic accumulation in the environment has become a serious problem, thus the improvement of its circularity from origin to subsequent life cycles is now a priority. An effective and eco-friendly approach to solve such problem is the use of biodegradable materials, whose global production capacities are set to increase from around 1.1 million tonnes in 2022 to approximately 3.5 million tonnes in 2027 [1]. In particular, a new strategy for the management of plastics is based on the design of polymers that contain degrading enzymes in their formulation: the enzymes should be activated only at the end-of-life of the material. However, the harsh conditions used in most industrial plastic processes cause denaturation and loss of activity of enzymes, thus efficient protection strategies are necessary. In this way, thermally protected enzymes could be embedded in plastic formulation, obtaining novel “degradable on-demand” materials.

In the present study, cutinase from *Humicola Insolens*, selected as a highly degrading polyester hydrolytic enzyme [2], is immobilized in Mg/Al layered double hydroxide structures. The immobilization efficiency results high and the enzyme thermal stability strongly improves after immobilization, since its half-life at 90 °C increases by 6 times.

Then the immobilized cutinase is embedded in a poly(butylene succinate-co-adipate) matrix by melt blending. After a specific trigger in an appropriate medium, the enzyme is released with no loss of activity and results to be able to completely degrade the polymer within 24 h.

These novel enzyme-containing polymers could be used as adhesives in multilayer plastic materials for packaging applications: at the end of the packaging life, enzymes can cause the biodegradation of the adhesives, then the delamination of the product and the recovery of the separated layers (Figure 1).

The novel strategy here proposed suggests a solution to improve plastic circularity from origin to subsequent life cycles and could help to reach the ambitious targets pursued by recent European policies [3].

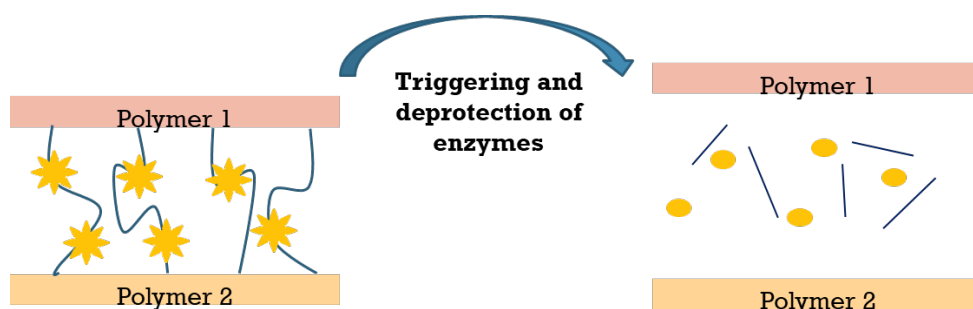


Figure 1. Degradation of the adhesive in multi-layer materials using thermally protected enzymes.

The study was carried out within the framework of the TERMINUS project, funded by the European Union under Horizon 2020. Call: H2020-NMBP-ST-IND-2018. Grant Agreement: 814400. This report reflects only the views of the authors. European Commission and Research Executive Agency are not responsible for any use that may be made of the information it contains, see §29.5 of H2020 General Model Grant Agreement for details.

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# Chemical recycling of elastomeric and viscoelastic polyurethanes

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Keywords: Glycolysis, split phase, reformulation

Polyurethanes (PUs) are a very versatile class of polymers with widespread applications. Polyurethanes are polymers with increasing market penetration, and their worldwide demand is estimated to be 18 million tons per year in 2014 [1]. At the end of their life, PUs are mainly landfilled and recycling at the end of their life is fundamental in the frame of a circular economy approach.

Glycolysis chemical recycling, a process based on a transesterification reaction [2], seems to receive more interest for its mild experimental conditions and the higher purity of the recovered products [3]. Different glycols can be used for the depolymerization process, as a function of the type of PU and the experimental conditions. The output of the reaction could be a single phase product or a split phase system.

In this work, a complete process for the chemical recycling of the PUs was performed, from the synthesis of the polymers with virgin ingredients to reformulation and synthesis of PUs with partially replaced building blocks, through glycolysis chemical recycling, as resumed in Figure 1.

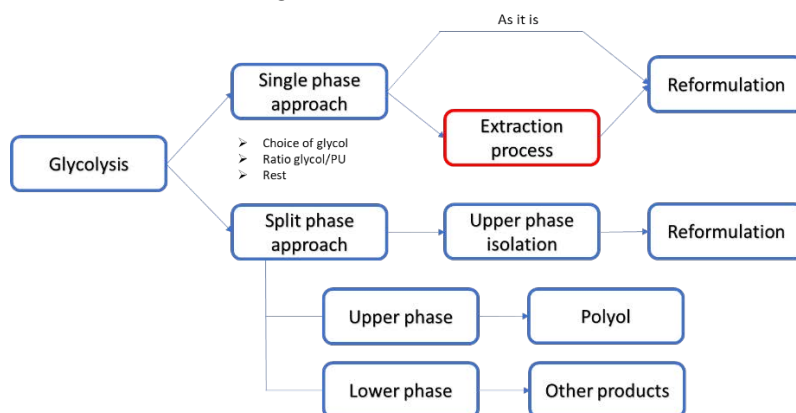


Figure 1. Block diagram of the present work.

Mechanical, thermo-mechanical, and chemical recycling of PU were carried out. The PUs used were an elastomeric flexible PU, an elastomeric rigid PU, and a viscoelastic PU. The glycols used were: ethylene glycol; 1,4-butanediol; serinol pirrole (SP) [4], and

glycerol. Two approaches were used to recover the polyol fraction: the first was a single phase process, and the second was a split phase process. In the single phase approach, an extraction process was applied in order to obtain the polyol fractions free of diamines and of the glycol used for the depolymerization and with the highest purity possible to increase the possible percentage usable in reformulation. The progress of the depolymerization reaction was checked by using  $^1\text{H-NMR}$  technique. To our knowledge, a new system for monitoring the reaction process was being developed. Preparation and characterization of different types of PUs were made, using the products obtained from the depolymerization in place of virgin material.

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## Integrated approach of Life Cycle Assessment and Experimental Design in the study of an organic synthesis

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Keywords: Organic Synthesis, Life Cycle Assessment, Design of Experiment

The purpose of the following work is to determine the environmental impacts associated with a basic organic synthesis carried out in different conditions as planned by an experimental design approach. The Nucleophilic Substitution reaction (SN<sub>2</sub>), in Figure 1, between the phenolic group of Vanillin and 1-bromobutane (BrBu) as alkylating agent was selected as a model reaction and performed in a basic environment in presence of potassium iodide (KI) and potassium carbonate (K<sub>2</sub>CO<sub>3</sub>). The product, 4-butoxy-3-methoxybenzaldehyde is a viscous oil.

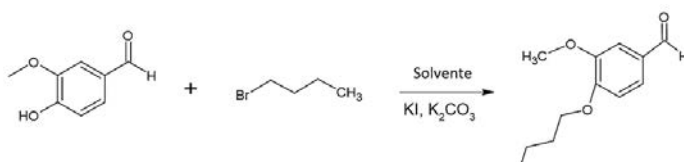


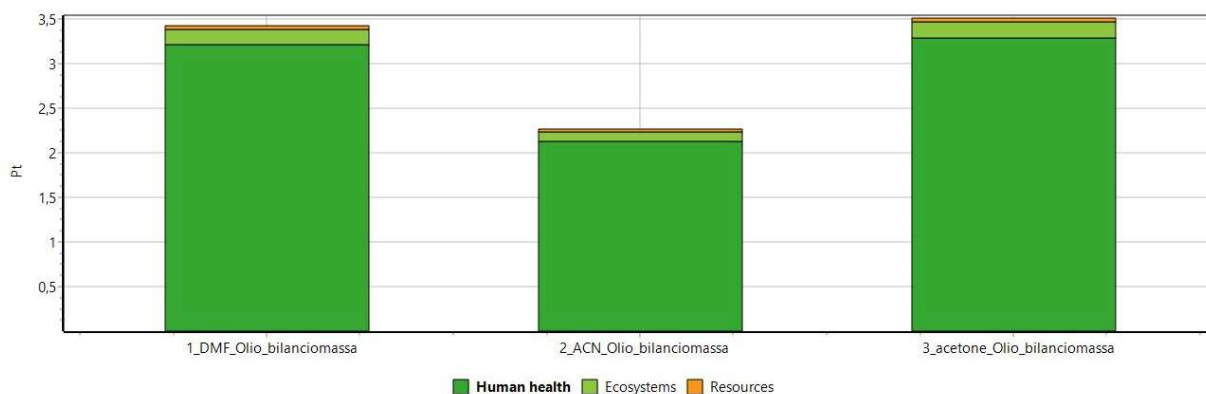
Figure 1: Nucleophilic substitution reaction.

Three different solvents were chosen to carry out the reaction, each associated with a different reaction temperature: dimethylformamide (80 °C), acetone (55 °C) and acetonitrile (80 °C). The possible influencing factors in the Nucleophilic Substitution reaction were investigated using the Experimental Design technique (DoE). The selected parameters are: the solvent (dimethylformamide, acetone, acetonitrile) reaction time (h), KI/Vanillin molar ratio, K<sub>2</sub>CO<sub>3</sub>/Vanillin molar ratio, BrBu/Vanillin molar ratio. Due to the huge number of factors and their different typology, i.e. qualitative and quantitative factors, a D-Optimal design approach was used. In particular, with a D-optimal design it has been possible to obtain a balanced spread of the experiments, keeping a low number of runs. Table 1 shows the planned experiments, conditions and yields. Nineteen (19) runs were performed randomly. Using the Life Cycle Assessment methodology (LCA) for each solvents the best run

(highest yield) was analysed, to determine the respective environmental impacts. The LCA study was performed using the SimaPro calculation tool and primary data were used together with secondary ones from the Ecoinvent database (v3.8) for modelling the background processes (transports and electric energy). A comparison between the three different solvents was made, the functional unit being a mass equal to 1 gram of the final reaction product. The reaction carried out in acetonitrile has the lowest potential environmental impact, as shown in Figure 2, probably because of the higher yield in comparison to the other solvents which allows to use less resources (chemicals and energy) to obtain the final product. This study allowed a comparison between three different solvents used for the same synthesis, optimizing the reaction conditions thanks to the experimental design, and allowing a study of the related environmental impacts to be carried out on the reactions with the best yield. Moreover, when the LCA results were used as additional responses in the experimental design, it was possible to identify regions within the experimental space that represented the best compromise between high yield and the low environmental impact.

Table 1: Table planned using the D-Optimal approach.

Run number	Reaction	Solvent	Time (h)	V/Br	KI	K <sub>2</sub> CO <sub>3</sub>	Yield (%)
1	6	ACETONE	8	2	0	1	20
2	17	ACETONE	8	2	2	1	46
3	3	ACETONE	24	1	2	1	50
4	10	ACETONE	8	1	0	2	2
5	12	ACETONE	24	1	2	2	21
6	18	ACN	8	1	0	1	14
7	2	ACN	24	2	2	1	78
8	13	ACN	24	2	0	2	54
9	11	ACN	8	1	2	2	50
10	15	DMF	24	1	0	1	49
11	1	DMF	8	1	2	1	76
12	9	DMF	24	2	0	2	51
13	19	DMF	8	2	2	2	61
14	4	DMF	16	1,5	1	1,5	73
15	5	DMF	16	1,5	1	1,5	71
16	7	ACETONE	16	1,5	1	1,5	38
17	8	ACETONE	16	1,5	1	1,5	34
18	16	ACN	16	1,5	1	1,5	18
19	14	ACN	16	1,5	1	1,5	17



Confronto di 1 g '1\_DMF\_Olio\_bilanciomassa', 1 g '2\_ACN\_Olio\_bilanciomassa' e 1 g '3\_acetone\_Olio\_bilanciomassa'; Metodo: ReCiPe 2016 Endpoint (H) V1.06 / World (2010) H/A / Punteggio singolo

Figure 2: Single Score results of the comparison between the runs of the reactions with the highest yields.

## *Sustainability analysis of lithium-ion batteries recycling processes developed at low TRL*

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**Keywords:** lithium-ion batteries, embodied energy, carbon footprint

The lithium-ion batteries (LiBs) recycling processes generally start with the discharging of the batteries to reduce their hazard level resulting from residual stored energy, which could otherwise activate further reactions and overheating. The following steps are generally based on mechanical, pyrometallurgical, and hydrometallurgical treatments. These treatments aim to recover economically strategic materials from the electrodes of the LiBs cells.

As part of the European Green Deal, in 2020 a new legislative framework was proposed by the European Commission to replace the 2006 Battery Directive. The targets for recycling efficiencies were settled to 65% for LiBs and 75% for Pb-acid batteries by 2025. Moreover, the target material recovery rates of 95% for Co, Cu, Pb, Ni, and 70% for Li by 2030 have been proposed.

Highlighting the critical raw materials recovery potential can enhance productivity and increase the recyclability of these strategic materials. These activities require the establishment of suitable procedures able to account for the sustainability of a new process, aiming to maximize the recycling potential and support strategic choices in terms of selected technologies. However, some already existing instruments, devoted to evaluating the environmental impacts of technologies, such as life cycle assessment (LCA), have some disadvantages related to their complexity, multiple indicators use, and the need to set preliminary decisions, also with insufficient inventory data. They are often not applicable to emerging technologies, developed at low technology readiness levels.

In this frame, a simplified tool to evaluate the sustainability of raw materials substitution has been recently developed, with the aim to propose suitable resource-saving alternatives. This is the ESCAPE approach “Evaluation of Sustainability of material substitution using CARbon footPrint by a simplifiEd approach” (Bontempi, E., 2017).

The method is based on the calculation of EE<sub>raw</sub> (the embodied energy of the raw material in MJ/kg), EE<sub>sub</sub> (the embodied energy of the newly proposed material in MJ/kg), CF<sub>raw</sub> (the CO<sub>2</sub> footprint of the raw material in kgCO<sub>2</sub>/kg), and CF<sub>sub</sub> (the CO<sub>2</sub> footprint of the newly proposed material in kgCO<sub>2</sub>/kg).



The embodied energy is defined as the energy required to produce materials from ores and feedstock. This parameter includes the direct and indirect energy consumed during the process of producing 1 kg of a specific material. The CO<sub>2</sub> footprint represents the equivalent mass in kg of greenhouse gasses (kg CO<sub>2</sub> equivalent) produced and released into the atmosphere during the production of 1 kg of the material (Ashby, M.F. 2012). A sustainability index (see Figure 1) quantifies the environmental benefits of a raw material recovery and/or substitution (ESCAPE index) and it can be defined using EE and CF parameters (Fahimi, A., 2022).

In the present work, different hydrometallurgical processes for the recovery of metals from discarded lithium batteries are compared to evaluate their sustainability. For this aim, the ESCAPE approach is used and its potentialities are demonstrated. All calculations referred to 1 kg of BM material and in the final calculation, EE and CF referred to 1 kg of a strategic metal (the choice is Co).

The results show that the choice of leaching processes based on inorganic acids is currently the most suitable possibility for the recovery of metals from LIBs. It is desirable, however, in the future to invest more in developing technologies based on the use of organic acids, because the ESCAPE index, used to compare different processes, is always very close to zero, indicating that a slight process improvement may increase its sustainability. This may be achieved, for example, through the recovery and reuse of organic leaching solutions. In conclusion, it was shown that considering their low material and management costs, the recycling processes could be less impactful in comparison to extracting metals from the corresponding ores. In addition, the location to carry out the LIBs recovery processes is not indifferent, because the embodied energy and carbon footprint values vary from country to country depending on the national energy mix. Finally, the evaluation based on eco-costs reveals that the use of organic acids in hydrometallurgical methods to recycle critical metals from spent LIBs could be more costly (approximately fivefold) than the average use of inorganic acid.

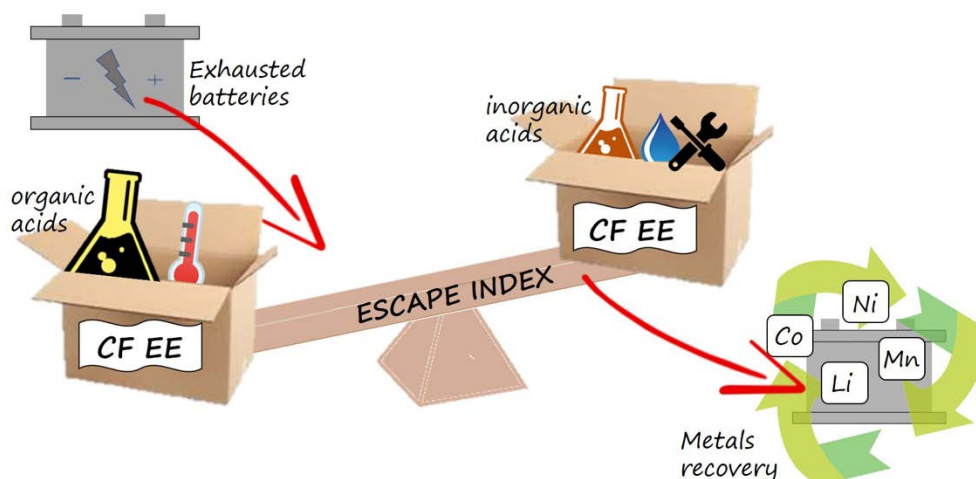


Figure 1. Basics of ESCAPE approach.

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# *Organosolv Treatment of Bagasse Beer for Enhanced Biomass Valorization and Microwave-Assisted Conversion of Hemicellulose to Furfural as a Platform Chemical*

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Keywords: Aqueous/ethanol organosolv, biomass valorization, microwave-assisted conversion

Organosolv treatment is an effective green method for the extraction of valuable components from lignocellulosic biomass. This process uses an organic solvent under specific conditions to break down the lignin and hemicellulose content in the biomass, resulting in a cellulose-rich material [1]. Bagasse is a by-product of the brewing industry, composed of cellulose (40%), hemicellulose (30%), and lignin (20%), which contain hydroxyl and phenolic groups that can be modified to generate materials with interesting chemical properties [2]. In this study, we aimed to separate the lignin, cellulose, and hemicellulose fractions of bagasse through organosolv pretreatment in water and ethanol mixture. The fractions were recovered by separating the cellulose from the other two polymers through hydrothermal treatment, and the effects of temperature, reaction time, and ethanol concentration on the amount and quality of fractions were investigated. Hemicellulose, a significant component of lignocellulosic biomass, is a complex mixture of polysaccharides, therefore its conversion into value-added chemicals, such as furfural, has attracted significant attention due to the abundance and low cost of such a raw material in biomass [3-4]. One of the most interesting platform chemical that can be produced by the dehydration of hemicellulose using acid catalysts is the Furfural. Indeed, this work reports the results obtained investigating the conversion of hemicellulose extracted from beer bagasse into furfural using microwave irradiation under optimized conditions, achieving a molar yield more than 70%. This work provides an alternative route for the utilization of beer bagasse, mitigating its environmental impact while improving the economics of a brewery

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## *Sustainable aliphatic/aromatic furan-based films for food packaging applications*

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Keywords: Poly(trimethylene 2,5-furanoate), biobased copolyesters, gas barrier properties

To address the requirements of the so called “circular economy”, reuse of natural sources and recycling should be maximized, and a drastic reduction of wastes should be achieved. This is particularly true for plastic products, whose production was of about 390.7 million tonnes in 2021 [1]. Interestingly, about 44% of the total plastic produced is used for packaging applications [1]. For this reason, from the packaging point of view, the main objective is to find solutions effective in preserving or even prolonging the shelf-life of the packaged products. This could also avoid the massive waste of food products, which is one of the main plague of our century. Moreover, if the volumes of plastics are considered, flexible packaging should be preferred to rigid one, in order to minimize the consumption of both sources and energy during production and transport [2]. Another challenge is related to the use of renewable sources to produce bio-based building blocks, which can be used, in turn, for the eco-design of sustainable polymers, characterized by the same properties as their fossil-based counterparts. In recent years, 2,5-furandicarboxylic acid (FDCA) is being attracting considerable attention among bio-based building blocks, being one of 12 high value-added chemicals obtained from sugars according to the US Department of Energy. Moreover, it can be derived from second and third generation cellulosic feedstocks, such as non-food crops and wastes, thus avoiding the exploitation of both food and lands cultivated for food production. According to this, furan-based polyesters started being investigated as sustainable alternatives to conventional fossil-based ones, such as poly(ethylene terephthalate) (PET) and poly(trimethylene terephthalate) (PTT). In the present contribution, we realized aromatic/aliphatic random copolymers poly(trimethylene 2,5-furandicarboxylate-co-trimethylene sebacate) (PTFcoPTSeb) for

potential applications in food packaging (Figure 1). In detail, the parent homopolymer poly(trimethylene 2,5-furandicarboxylate), PTF, has been chosen thanks to its bio-based nature, high thermal stability, chemical resistance and good barrier properties. As to its main drawback, i.e. the high mechanical stiffness, which results in high fragility and poor elongation at break, it can be overcome by copolymerization, an efficient strategy used to tune and improve unsatisfactory features of a homopolymer. In detail, aliphatic sebacic acid was chosen as co-unit, mimicking the chemical structure of Ecoflex® polymer, commercialized by BASF [4]. High molecular weight copolymers containing 5, 15 and 25 mol % of poly(trimethylene sebacate) (PTSeb) co-units were synthesized by solvent-free two-step melt polycondensation. Polymeric films were obtained by compression moulding, and chemical, thermal, tensile and gas barrier properties were then investigated.

As expected, the introduction of TSeb aliphatic co-units allowed to improve the flexibility of the materials, maintaining or even improving the already good barrier properties. Impressively, the copolymer containing 15 mol% of TSeb co-units is characterized by a shape memory behaviour, together with barrier performances comparable to those of EVOH, commonly used in multilayer packaging films. Composting experiments have been also carried out, demonstrating the presence of at least 15 mol% of TSeb co-units in PTF main chain renders the final material compostable. Thus, copolymerization of PTF with PTSub allowed to obtain very performing materials, with high potential in flexible food packaging field.

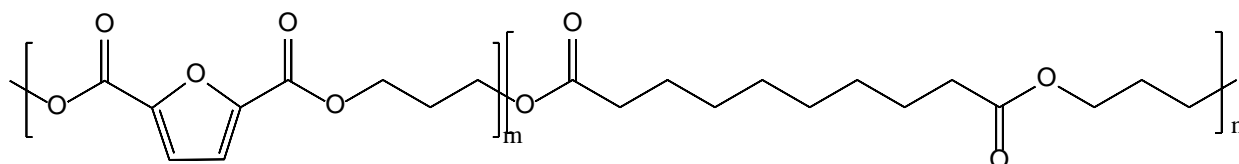


Figure 1. Chemical structure of (PTFcoPTSeb) copolymers.

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## Food analysis by Community-Built NMR Analytical Systems

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NMR spectroscopy is gaining ever-growing importance in analytical chemistry. In the last decade, quantitative NMR (qNMR) and non-targeted approaches allowed for great improvements in both quantification of molecules in complex mixtures and identification of product features in suitable sample pools. Metrological traceability of products can be successfully achieved by qNMR even when no certified reference materials are commercially available. Along with quantification and purity assessment of molecules, NMR is emerging also as a powerful tool in food chemistry, especially when searching for product features such as cultivar, geographical origin, typicality of the production process, etc.

The great application potential of NMR spectroscopy derives from the fact that, based on theory, the ratio between a signal generated by the molecule under investigation and the signal of a reference molecule depends exclusively on the corresponding mole ratio. In other words, when a given sample is analyzed by different spectrometers, the same output is obtained in terms of signal ratios independently of the hardware configuration. This offers the unique opportunity to develop community-built analytical systems capable of identifying sample features and quantifying a number of molecules.

In this presentation, based on our previous [1-3] and recent studies, the first examples of community-built analytical systems will be shown. In particular, the case study of both the identification of wheat and pasta samples and the quantification of betaine will be presented. The advantages and the limitations of using non-targeted NMR analyses performed at different magnetic fields will be also discussed.

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## The full valorization of anchovy fillet leftovers: a prospective life cycle assessment

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Keywords: Circular Economy, Life Cycle Assessment, Fish-waste Valorization

The reuse and valorization of the fish waste is a key stone within the circular “blue economy”. In this context, in recent years, the LimoFish process used for producing fish oil, organic fertilizer or biogas starting from anchovy fillet leftovers (AnLeft) with agro-solvent *d*-limonene was proposed [1-3].

Aiming to assess the environmental impacts of the LimoFish process, a prospective life cycle assessment model was developed and implemented at both laboratory and industrial scales with the aim to estimate impacts on climate change and freshwater eutrophication. At the laboratory scale, the potential impacts were estimated at 29.1 kg CO<sub>2</sub> eq/kg AnLeft and 1.7E-07 kg PO<sub>4</sub> eq/kg AnLeft, whereas at the industrial scale, the impacts were estimated at 1.5 kg CO<sub>2</sub> eq/kg AnLeft and 2.2E-07 kg PO<sub>4</sub> eq/kg AnLeft. The major contributor to the environmental impact was electricity consumption, with a significant role played in the production of *d*-limonene. However, cold pressing extraction could reduce the impacts by approximately 70%. Furthermore, using the solid by-product as organic fertilizer or input to anaerobic digestion could provide additional environmental benefits to the process. Thus, the LimoFish process represents a low-impact strategy that aims to reduce the demand for natural resources and promote the circular economy principles in the fishing industry.

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## *Biostar-Pack: preparation of starch nanocomposites towards the valorization of organic food waste for sustainable packaging*

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Keywords: starch, sepiolite, food-packaging

The BIOSTAR-PACK project [1] addresses the challenge of the valorisation of organic wastes in the development of composite films for sustainable food packaging applications. In this scenario, starch is an attractive material due to its high availability, low cost, good biocompatibility and high biodegradability, combined with a moderate oxygen permeability. However, starch film-forming ability, transparency and flexibility can be negatively affected by its crystallinity, and the resulting films perform poorly in terms of mechanical and water barrier properties. To overcome these drawbacks, natural fillers can be added to starch; among these, sepiolite is of particular interest due to its low cost, high availability, remarkable chemical and mechanical stability. Moreover, the structural characteristics of this clay (scheme in Figure 1b) provide good adsorption properties, thus offering the opportunity to achieve both reinforcing and water barrier effect in starch nanocomposites.

Starch nanocomposites were produced by i) yuca starch gelatinization, ii) homogeneous dispersion of sepiolite by mechanical mixing in water and iii) addition of glycerol [2]. Solid state nuclear magnetic resonance (ss-NMR) and X ray diffraction (XRD) analyses were employed in order to study the effect of both processing and introduction of sepiolite on the structure of starch-based films. The processing method allowed to disrupt the rigid lattice structure of semicrystalline starch (Figure 1a), thus obtaining amorphous flexible films, with high transparency and good resistance, respectively

evaluated by UV-Vis spectroscopy and thermogravimetric (TG) analyses, even at high sepiolite loading (15 wt.%).

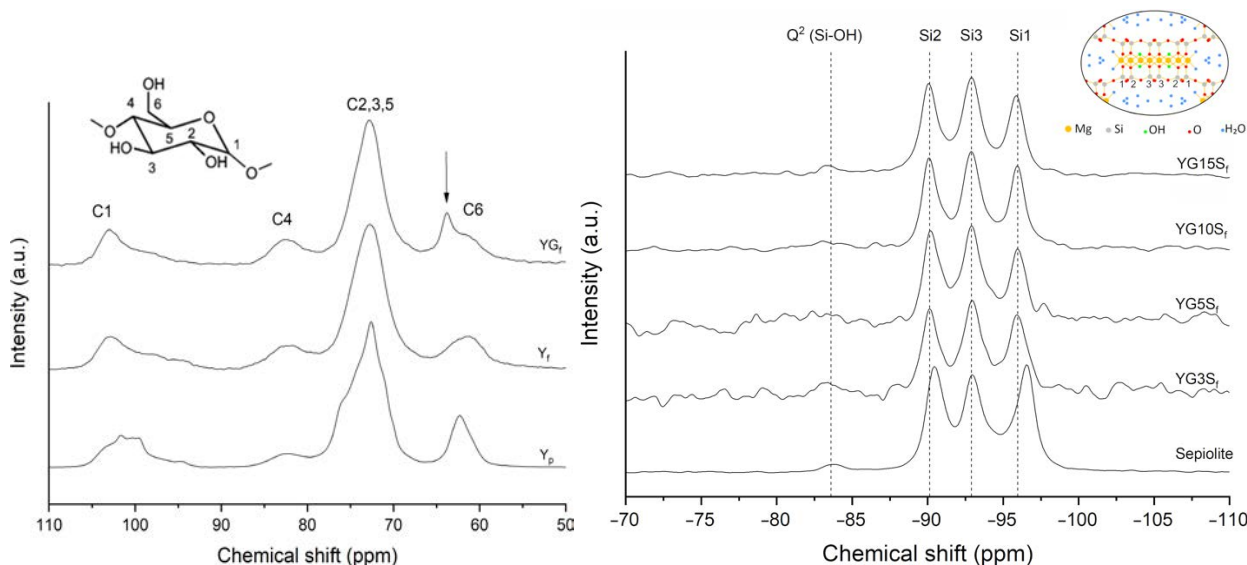


Figure 1. a) <sup>13</sup>C CPMAS NMR spectra of yuca starch powder (Y<sub>p</sub>), and starch films without (Y<sub>f</sub>) and with glycerol (YG<sub>f</sub>). The arrow indicates the glycerol methylene peak. b) <sup>29</sup>Si CPMAS NMR spectra of pristine sepiolite (Si1, Si2, Si3 refer to Si atoms shown in the scheme) and starch nanocomposites containing glycerol, with sepiolite loadings from 3 to 15 wt.% [2].

The properties of the bio-nanocomposites apparently depend on complex interactions among sepiolite, glycerol and starch chains. In particular, the polysaccharide interacts with sepiolite, inducing a preferential filler orientation along crystallographic planes {0k0}, as suggested by XRD analyses. According to <sup>29</sup>Si CPMAS NMR results (Figure 2), also glycerol interacts with sepiolite by partially substituting water present in the sepiolite's channels [2].

Interactions between starch chains and inorganic fillers can be exploited to fine-tune the final properties of biocomposites and to improve the recyclability of the resulting packaging materials. This can be pursued through the design of particle-matrix interfaces based on appropriate functionalization strategies. Accordingly, we recently reported on the possibility of modifying both silica and sepiolite surfaces by reaction with an alkoxysilane bearing photoreversible cinnamic side groups [3]. The results pointed out the efficacy of this route in providing tailored silicate nanoparticles with photoreversible tails, which can be potentially used as building blocks for innovative organic-inorganic hybrid nanomaterials with peculiar recyclability properties.

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## *CO<sub>2</sub> sequestration and storage in seawater: experimental and modelling approaches*

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Keywords: Ocean alkalinization, marine chemistry, carbon dioxide

It is well-known that carbon dioxide levels in the atmosphere have grown drastically in the past century. This has led to an increase in the global mean surface temperature and affects many environmental compartments.[1] Several “negative emission technologies” have been proposed, that are expected to work alongside a drastic reduction in CO<sub>2</sub> emissions so as to limit the worst effects of climate change. Some of these try to exploit and accelerate the natural CO<sub>2</sub> sequestration by the oceans.[2] Any method based on this idea should properly calibrated since, if pursued on a massive scale, it will affect the ocean’s carbonate system, represented by the chemical equilibria:[3]



Note that the increase in atmospheric carbon dioxide concentration has already shifted this equilibrium and decreased the ocean’s average pH from 8.2 to 8.1, a shift that is unprecedented in the last 65 million years [1].

We are currently investigating two approaches to marine CO<sub>2</sub> capture and storage:

- Ocean Liming (OL) by dispersion of calcium hydroxide on the ocean’s surface, with the aim of enhancing the natural absorption of CO<sub>2</sub> from the atmosphere;[2,4]
- Buffered Accelerated Weathering of Limestone (BAWL) for storing carbon dioxide from industrial processes as aqueous hydrogen carbonate, by reacting it with calcium carbonate suspensions and calcium hydroxide in specially designed reactors.[5]

Although conceptually different, these approaches have several problems in common, that need to be understood and addressed. For example: avoiding abrupt changes in the seawater’s pH that would be harmful for the marine environment, ensuring the stability of the treated seawater against precipitation of mineral phases and the release of CO<sub>2</sub> back in the atmosphere, assessing the overall efficiency and economic

viability of the processes. We will briefly describe our approach to these problems and technologies, combining laboratory scale experiments, chemical and fluid dynamic modelling, field tests on small-scale plants, economic and life cycle analyses, and the assessment of impacts on sea life through a collaboration with marine biologists.

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## Cyclopentadienyl-phenylenediamino-cobalt complexes as homogeneous selective electrocatalysts for CO<sub>2</sub> reduction

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**Keywords:** CO<sub>2</sub> reduction, cobalt complexes, cyclic voltammetry

Carbon dioxide (CO<sub>2</sub>), derived from both nature and human activities, is the largest contributor among greenhouse gases to the well-known problem of global warming. From another point of view, CO<sub>2</sub> is also considered as one of the most accessible and plentiful carbon sources for the preparation of more complex derivatives and intermediates [1], even at lower costs than those on the current market [2]. Thus, catalysts able to reduce CO<sub>2</sub> selectively and efficiently are highly desired and electrocatalysts based on metal complexes represent a good option because of the versatility and tunability of their properties [3]. Among the metal complexes proposed as electrocatalysts for CO<sub>2</sub> reduction, those formed with “non-innocent” ligands received great attention because, in addition to the metal, the ligand moiety also contributes to the redox activity of the catalyst. This characteristic allows redox processes involving multiple electrons also in compounds of metals which typically present one-electron redox activity, avoiding the use of catalysts based on expensive noble metals [4]. Furthermore, the presence of “non-innocent” ligands in the catalyst increases the selectivity toward CO<sub>2</sub> reduction vs hydrogen evolution reaction (HER) [5]. In this contribution we report a study on the electrochemical reduction of CO<sub>2</sub> achieved by using the heteroleptic cobalt complexes [CpCo(R<sub>n</sub>L<sub>n</sub>X)] (see Figure 1) which bear two “non-innocent” ligands: cyclopentadienyl (Cp) and *o*-phenylenediamine (R<sub>n</sub>L<sub>NN</sub>, 1-4) or 2-aminothiophenol (R<sub>n</sub>L<sub>NS</sub>, 5) [6,7]. The electrocatalytic properties of these complexes have been investigated by electrochemical techniques (in anhydrous DMSO and in the presence of water), DFT calculations and condensed Fukui function analysis, with the aim to investigate the electronic structure of these compounds and to highlight the structure-properties relationship. Moreover, the effects due to the presence of different kinds of electron-withdrawing substituents on the phenylenediamine ring, and the those induced by the replacement of one of the two

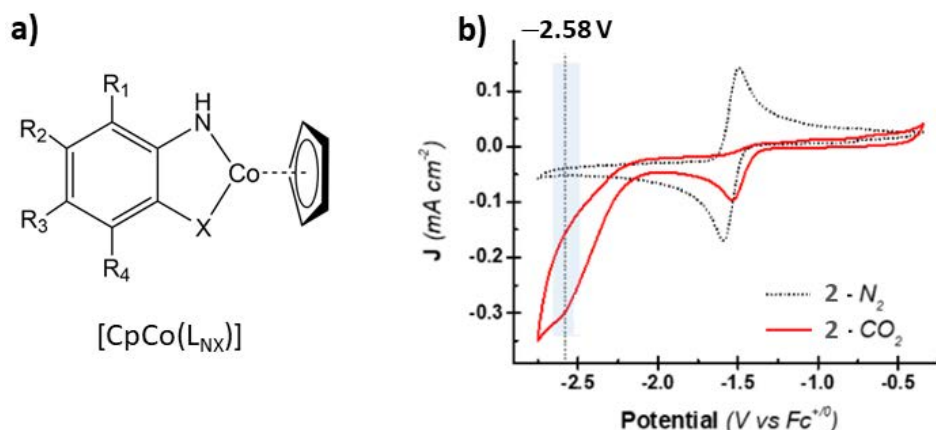


Figure 1. a) Structural formula of complex  $[\text{CoCp}(\text{L}_{\text{NX}})]$  X = NH,  $\text{R}_1\text{-R}_4 = \text{H}$ : 1; X = NH,  $\text{R}_1\text{-R}_4 = \text{F}$ : 2; X = NH,  $\text{R}_1 = \text{R}_2 = \text{R}_4 = \text{H}$ ,  $\text{R}_3 = \text{NO}_2$ : 3; X = NH,  $\text{R}_1 = \text{R}_2 = \text{R}_4 = \text{H}$ ,  $\text{R}_3 = \text{COOH}$ : 4; ) X = S,  $\text{R}_1\text{-R}_4 = \text{H}$ : 5. b) Cyclic voltammograms of complex 2 recorded under nitrogen (black line) and carbon dioxide (red line) atmosphere in anhydrous DMSO solution; scan rate =  $100 \text{ mV s}^{-1}$ .

amino groups of the phenylenediamine ligand with a sulfur atom, have been investigated. Electrochemical investigations showed that all the studied compounds present good electrocatalytic capability (see Table 1). Moreover, they exhibited a high selectivity toward  $\text{CO}_2$  reduction vs HER. The effect of the sulfur atom instead of a -NH group causes a positive shift of the reduction potential and an increase of the molecular stability. Under anhydrous conditions, complex 5 showed the highest current enhancement in the presence of  $\text{CO}_2$ . The presence of only one -NH group in 5 explains the different trend in the catalytic activity observed in the presence of water. DFT calculations and condensed Fukui function analysis are in agreement with the observed experimental results.

Table 1. Peak analysis of anhydrous complexes 1-5 under  $\text{CO}_2$  atmosphere, and corresponding current enhancements in anhydrous and wet conditions.

	1	2	3	4	5
E (V)	-2.54	-2.58	-1.97	-2.19	-2.54
$I_{\text{CO}_2}/I_{\text{N}_2}$	4.12	5.59	4.52	2.78	9.41
$I_{\text{CO}_2}/I_{\text{N}_2}$ with $\text{H}_2\text{O}^a$	24.40	31.07	4.09	9.97	22.73

<sup>a</sup> 9.09 % V/V  $\text{H}_2\text{O}/\text{DMSO}$

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## Exploring the Circular Economy's Potential for Foundry Sands

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Keywords: Foundry sand, circular economy

Sand, gravel, and crushed stone are crucial components of the global economy, especially in the development of urban infrastructure through concrete production [1]. Sand and gravel extraction, the second most exploited natural resource in the world after water, amounts to 50 billion tonnes annually [2,3]. Until recently, waste foundry sand (WFS) was mostly disposed of through landfilling, which was not only environmentally harmful but also increased production costs due to the shortage of landfills [4,5]. Recycling of WFS was limited due to high investment costs, insufficient nurturing measures, deficient regulations, and a lack of consumer interest in products produced using recycled aggregates [6,7]. Exhausted foundry sand has great potential for reuse [6,7,8], but several factors contribute to its low level of reuse, including the lack of normative regulations for environmental protection and promoting appropriate reuse, and the absence of an established process for evaluating and permitting reuses. In addition, prospective stakeholders may be unaware of the potential uses of waste foundry sand or may assume that it will not perform adequately from an engineering perspective, or that it may contain unacceptable concentrations of toxic constituents even after treatment. Foundries themselves may not be aware of the potential of the sand or may not have considered simple operational changes that could dramatically improve the characteristics of waste foundry sand and facilitate finding alternatives to landfill disposal.

ASSOFOND, the Italian Association of Foundries, conducted a research project funded by the CARIPO Foundation in collaboration with IUSS Pavia, the University of Brescia,

and the Consortium INSTM. The project focused on analysing foundry sands and furnace slags, specifically those from 38 foundries situated in the Lombardy Region. The findings of the study showed that WFS exhibit high levels of heterogeneity, making it impractical to establish a universal protocol for their recycling.

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## *Targeting phenolics through supercritical CO<sub>2</sub> technology: valorization of coffee silverskin for functional extracts production*

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Keywords: Supercritical CO<sub>2</sub>, Silverskin, Biomass valorization

Waste management and valorization are nowadays at the centre of world's most discussed concerns when dealing with sustainable development, the common goal of the current concepts of bioeconomy and circular economy. The principal aim is to ensure zero-waste strategies since all side-stream products are granted a second life, providing new higher-value products with a concomitant solution to waste accumulation issues.

Within circular models, the agri-food value chain represents the sector in which there is the highest production of waste biomass with a direct strong potential to be further exploited to research bioactive molecules from these side-streams [1].

The exploitation of by-products towards the generation of added-value compounds should meet and merge the need to develop alternative and innovative extraction techniques that are able to guarantee the sustainability of the entire process, from biomass selection to the technological methods, to final added-value generation. Among unconventional extraction techniques, supercritical CO<sub>2</sub> technology is characterized by low environmental impacts since the use of organic solvents can be avoided or minimized, ensuring safer and selective processes directly on the biomass without any pre-treatment, with the possibility of recycling the employed CO<sub>2</sub> in industrial plants [2].

In this context, this work presents, for the first time, the valorization of coffee silverskin's polar compounds by means of supercritical CO<sub>2</sub> [3]. A schematic of the project is displayed in Figure 1a.

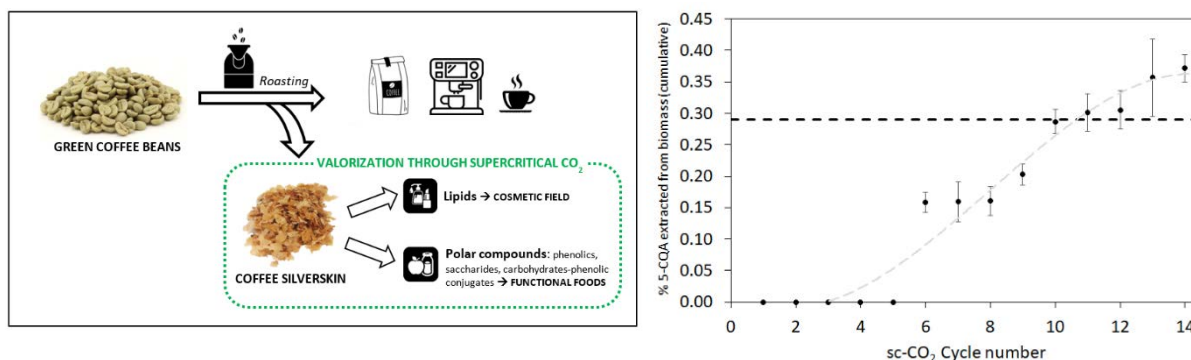


Figure 1. a) Schematic overview of the project; b) extraction kinetics of chlorogenic acid (5-CQA) from silverskin through sc-CO<sub>2</sub>

Silverskin, the thin layer directly in contact with the coffee bean removed during the roasting process, was selected as an interesting case study. It represents about 4.2% (w/w) of coffee beans and accounts for a production of 2400 tons of waste produced per year only in Italy. Despite its promising applications, silverskin is still underutilized and nowadays is discarded by the roasters as solid waste in landfill.

The extraction with supercritical CO<sub>2</sub> in the presence of a co-solvent was able to efficiently target polar phenolic compounds (Figure 1b), such as 5-caffeoylquinic acid (one of the most abundant chlorogenic acids), providing extracts enriched up to 40% in this class of compounds. Moreover, other beneficial co-extracted products were identified, such as other simple phenolics and carbohydrate-phenolic conjugates, dealing mainly with antioxidant and prebiotic properties. The strategy minimized the excessive use of organic solvents while avoiding any presence of inorganic or organic acids conventionally employed when solvent-based methods are used.

Overall, silverskin was confirmed to represent a potential raw material for the production of chlorogenic acid-enriched extracts by means of a green technique such as supercritical CO<sub>2</sub>. A very interesting application could be related to prebiotics in food products such as yogurt and derivatives since coffee chlorogenic acids have already been demonstrated to increase the growth of total bacteria to a similar magnitude to fructooligosaccharides, which are the positive prebiotic control [4]. Upcoming studies are desirable to assess the nutraceutical and antioxidant profiles of these extracts in order to confirm the potential commercial interest in this ambitious and virtuous “waste-to-products” valorization chain.

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## Squalane: a test case for computational rheology of molecular and complex fluids

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**Keywords:** Molecular dynamics, viscosity, lubricants

The thermal and transport properties of fluids and their mixtures are of interest for several technological applications, such as lubricants. In particular, the viscosity behaviour of medium-sized molecular fluids is still an open topic. With experiments is possible to obtain results at relatively low shear rates, while molecular dynamics simulations provide information over short times or at high shear rates.[1,2] It is important to validate and optimize the cost/benefits ratio of the simulations, so as to extend them to situations where experiments would be difficult (e.g., high shear rates and pressures, of interest for elastohydrodynamic lubrication [3]) or time consuming (e.g., systematic exploration of complex mixtures).

In this work, we aim to extend a previous computational study of hexadecane [4] to more complex molecular liquids. Squalane (C<sub>30</sub>H<sub>62</sub>) has been chosen because it has already been extensively characterized, being used as a standard for viscosity measurements thanks to its purity. [5,6] In addition, it has a complexity that allows to test the performance of the force fields, that are used as an input to the simulations. There are several approaches for the calculation of viscosity, including both equilibrium methods (for the linear, zero-shear response) and non-equilibrium methods (for the non-linear, shear-rate-dependent response). These will also be tested, with respect their reliability and computational cost.

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# Study on Perampanel for drug sensing by DFT and Raman spectroscopy

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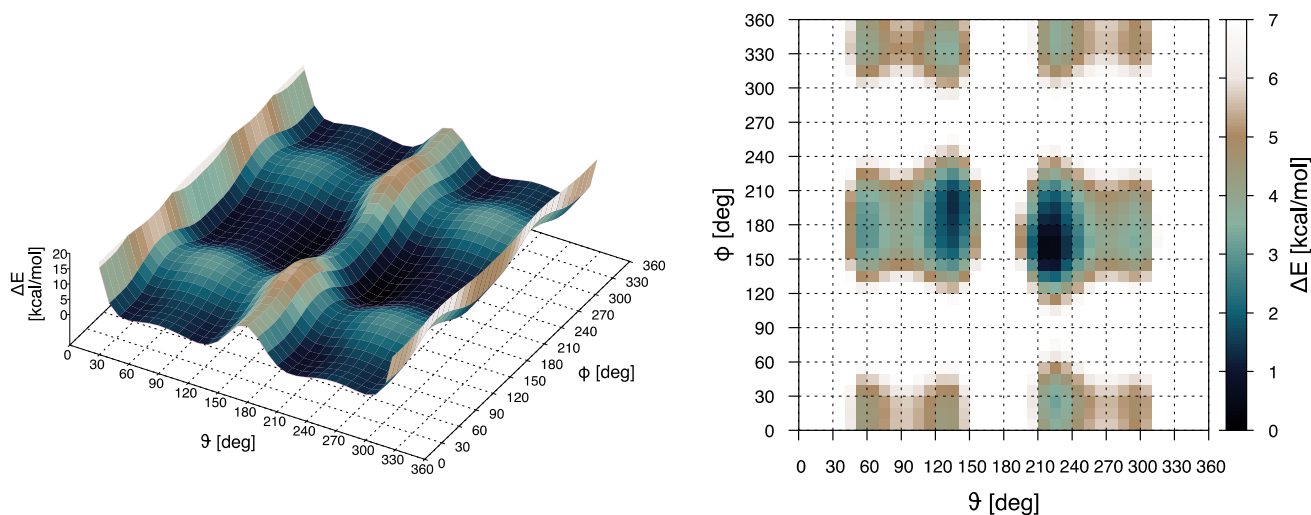
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Keywords: Perampanel, Raman spectroscopy, Density Functional Theory

Perampanel (PER) is an anti-epilepsy drug used to treat and prevent the onset of seizures. Given the seriousness of the treating disease and the potential collateral effects of PER, only a narrow dosage range can effectively treat the patients [1]. Therapeutic Drug Monitoring (TDM) is thus used to control the presence of PER in the patients' biological fluids, e.g., blood plasma [2].

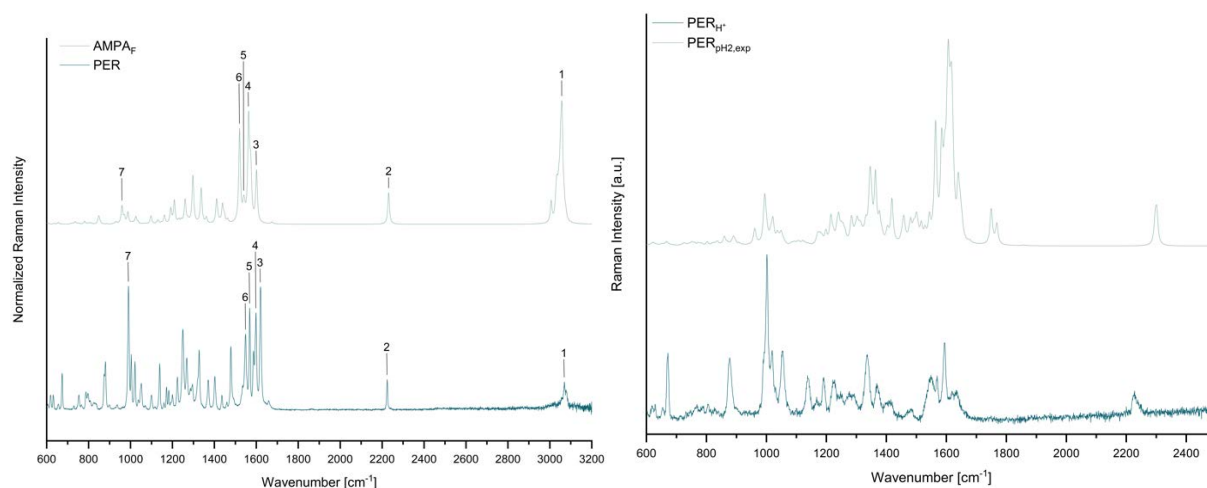
In recent years, to improve the patient's quality of life, non-invasive alternative techniques have been investigated to accompany and complement TDM. Specifically, Raman spectroscopy and SERS can detect Perampanel in its protonated forms [3][4]. But a detailed theoretical model of both the molecular and vibrational structure of PER is still lacking.

In such context, the work presented here is the computational effort aimed to produce a thorough model of the chemical and vibrational structure of PER. Using the B3LYP/6-31G(d,p) method, the Potential Energy Surface (PES) of PER was systematically investigated. The exploration of the PES brought up the equilibrium PER conformers, among which one matches the structure of PER within its target receptor as reported in the Protein Data Bank [5].



PES (left) and PES map (right) of PER.

From the equilibrium structures of PER, we could simulate the theoretical Raman spectra. Furthermore, since SERS analyses are performed in acidic conditions, by protonating such structures also the theoretical SERS spectrum could be determined. Comparing the theoretical Raman and SERS spectra with the experimental data [4] gave a promisingly good match, which validates this model as a benchmark for future vibrational spectroscopy studies on PER.



Comparison between theoretical (top) and experimental (bottom) Raman (left) and SERS (right) spectra.

A conformational study based on Molecular Mechanics (MM) and Molecular Dynamics (MD) simulations of PER in vacuo and in explicit water is ongoing [6]. The adsorption process on the gold surface will be investigated for comparison with experimental data [7].

#### Acknowledgements

C.P., G.F., and M.T. have been partially funded by European Union - Next Generation EU.

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## *A close look at the catalyst surface: Oxygenated and Chlorinated VOCs conversion over Fe-Ceria catalyst through FT IR spectroscopy.*

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Keywords: FT-IR spectroscopy, VOC conversion, Ceria catalyst

A series of Ceria supported catalysts containing Cobalt, Nickel, Copper or Iron has been prepared by incipient wetness impregnation over a commercial CeO<sub>2</sub> support, both in form of powders and deposited onto open-cell ceramic foams, following the procedure previously reported [1]. The formulation containing 7% wt Fe on high surface area Ceria in the form of nanopowder (FeCe-HS, s.a.  $\approx 90$  m<sup>2</sup>/g) has been fully characterized by FT-IR spectroscopy, DR-UV Vis.NIR spectroscopy, XRD, and SEM techniques. Characterization results point out the formation of highly dispersed Fe<sub>2</sub>O<sub>3</sub> particles weakly interacting with Cerium oxide support and tuning surface properties such as basicity, which is decreased by Iron oxide addition, as detected by the decreased amount of surface carbonate species. Moreover, new exposed hydroxy groups appear, related to the Fe oxide phase. SEM micrographs evidence that the impregnation procedure leads to some changes in the morphology of nanoparticles, which become more irregular. Considering the reported good oxidation activity of Ceria catalysts [2], the conversion of methanol, ethanol and 2-chloropropane has been carried out on these surfaces directly by the use of FT IR spectroscopy in static conditions and without oxygen in gas phase. As a matter of fact, Oxygen-containing VOC are often emitted in industrial waste streams, thus their catalytic combustion has been studied over several materials. On the other side, the combustion of chlorinated VOC requires specific attention due to their toxicity and stability [2]. In our experimental set-up, self-supporting disks of catalytic pure powders are activated in vacuum up to 400 °C, directly in the IR cell connected to a gas manipulation apparatus, then vapors of reactants are put in contact with the surface at room temperature and at increasing temperatures, monitoring both adsorbed and gas phase species. In this approach, the catalyst oxidation activity is due only to the lattice oxygen. Methanol and ethanol reactive adsorption at room temperature mainly leads to the formation of alkoxy species strongly bound to exposed coordinatively unsaturated ions. In spite of the very

low Iron content, over FeCe-HS sample IR results evidenced new alkoxy groups likely coordinated at the Iron oxide surface or at the Ceria-Iron oxide interface. Increasing temperature by step of 50° from room temperature to 150°C leads to the detection of typical C-O stretching bands in the low frequency region, whose wavenumbers depend on the chemical nature of the exposed ions. Already at 150°C carboxylate species are forming, characterized by strong and complex bands in the region 1600-1400 cm<sup>-1</sup>, that reach the maximum intensity at 300°C (figure 1). At higher temperatures carboxylate are decomposed and also carbonate are formed likely due to the formation and subsequent adsorption of CO<sub>2</sub> from organic combustion suggesting that lattice oxygen is sufficient to oxidize adsorbed organic species.

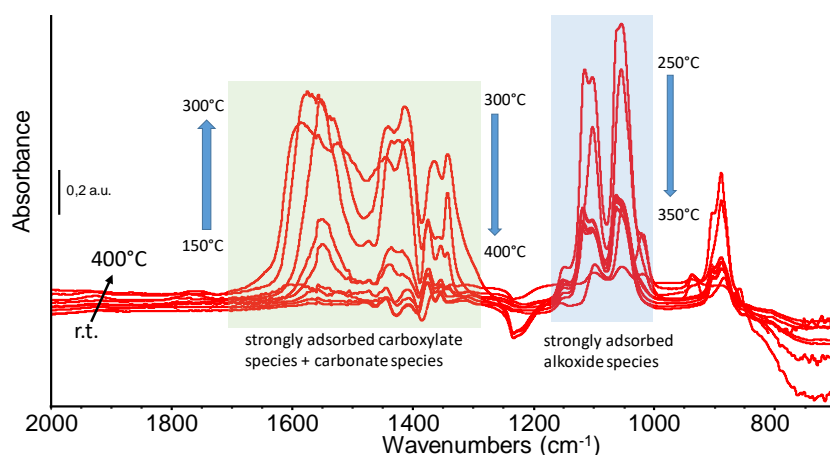


Figure 1. FT IR subtraction spectra of surface species arising from ethanol adsorption and thermal evolution over FeCe-HS catalyst. The activated surface spectrum has been subtracted.

The comparison with pure ceria surface shows that, although the catalytic activity is not so different, in our conditions carboxylate species are more stable at the ceria surface, possibly decomposing to carbonate at higher temperatures. Moreover, some partial oxidation products are detected (carbonyl stretching band at about 1700 cm<sup>-1</sup>). A similar reaction pathway can be detected for methanol oxidation, although shifted to higher temperatures. Formates are indeed the main species arising from methanol oxidation over both Ceria and Fe-Ceria surfaces. Adsorption of 2-chloropropane as Cl-VOC model molecule has also been carried out over FeCe-HS and a nucleophilic substitution of the Cl atom readily occurs at the catalyst surface at room temperature, leading to the formation of adsorbed alkoxy species that can undergo oxidation at higher temperature, following the previously reported pathway.

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## Unusual properties of $M_{12}L_8$ poly-[ $n$ ]-catenanes: a QM/X-ray study

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Keywords: poly-[ $n$ ]-catenanes, dynamic  $M_{12}L_8$  cages, solid state DFT simulation

In this contribution, the properties of poly-[ $n$ ]-catenanes composed of interlocked  $M_{12}L_8$  icosahedral nanometric cages are investigated by a combination of QM calculations and X-ray diffraction experiments. TPB (exotridentate trispyridyl benzene) ligand and  $ZnX_2$  ( $X=Cl, Br, I$ ), in the presence of appropriate templating molecules, form metal-organic cages as microcrystalline materials. Synchrotron single-crystal X-ray data collected at 100K allowed to solve the first structure and to detect guest molecules at the internal walls of the cages [1]. The processes involved in guest absorption, release and exchange are studied by QM calculations [2] providing a rationalization of the experimental outcomes. Packing energies in terms of monomeric and dimeric cages and host-guest interactions has been determined. As a results, a plausible mechanism of “closed-open” dynamic channels is discussed [3].

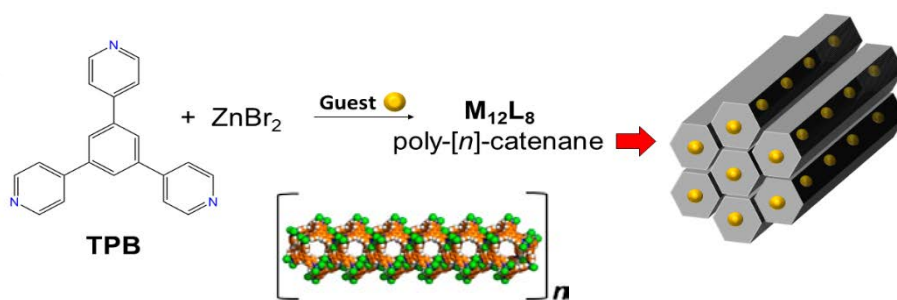


Figure 1. Scheme of synthesis of poly-[ $n$ ]-catenane by TPB and  $ZnBr_2$ . The hexagonal prisms represent 1D chains packed in a crystalline phase.

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## *Waste oil/water emulsions as absorbents for volatile organic solvents abatement*

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Keywords: oil/water emulsions, VOS abatement, absorption

**Introduction.** The global VOSs emissions due to tanneries are about 62'000 tons/year of which around 21'000 tons/year are produced by the Italian districts (LIFE00 ENV/IT/000184, ARPAT, 2009). The emissions include both hydrophilic and hydrophobic solvents. Grassi et al. estimated that n-butyl acetate constitutes 77 % of the water-insoluble organic compounds produced by Santa Croce district [2]. Several techniques can be adopted for the VOSs abatement such as thermal incineration, catalytic oxidation, biological degradation, absorption, adsorption, condensation, and membrane separation [3]. The proper VOSs abatement system is selected considering the industrial process, the specie and the concentration of VOSs, and the feasibility of recovery and reuse of the solvents. At the state of the art, tanning industries use absorption towers to treat the air stream using water as sorbent. These systems show high performance to capture powders, pigments, and water-soluble compounds but have low efficiency in the removal of hydrophobic VOSs. The choice of a sorbent suitable for both hydrophilic and hydrophobic VOSs will increase the abatement efficiency of the system. Many studies were carried out testing organic compounds, such as silicon oil and vegetable oil, and their emulsions with water as an alternative to water. In this study, vegetable oil/water emulsions were investigated as absorbents in a bubbler to remove n-butyl acetate (BA) from an air stream.

**Materials and methods.** Two vegetable oils were selected: commercial corn oil (O) and waste cooking oil (WO). BA was chosen because is the most common hydrophobic solvent in the leather paints. Emulsions with a volume percentage of oil between 0 to 5 % were prepared. The use of a surfactant (S) was also investigated. Henry's volatility constant of BA in the pure oils was determined by static absorption tests. Dynamic absorption experiments were carried out to evaluate the absorption behaviour of the investigated sorbents. The tests were performed by flowing an air stream with a flow rate of 3.0 L/min and a BA concentration of 500 ppmv (corresponding to 2.6 g/m<sup>3</sup>) into a bubbler filled with 400 mL of sorbent. A VOSs sensor was used to measure the inlet and the outlet BA concentrations in the gas stream during the test.

**Results and discussion.** Henry's constant of BA in the oils and in the emulsions were smaller than water thus suggesting a greater solubility of BA in the organic compounds

(Tab. 1). As can be observed in Fig. 1 and Tab.1, emulsions showed higher efficiency and absorption capacity than water. The higher the oil volume fraction, the greater the absorption performance. The surfactant did not have significant influence on the absorption process. Emulsions with WO showed similar absorption performance to the ones with O thus suggesting that the waste oil could be used. The use of a waste has the advantage to reduce the environmental impact and costs.

Table 1. Henry's law constant, H, and absorption capacity, Q, of water, oils, and emulsions.

Sorbent	H (atm)	Q (g/L)
Water	15.91	0.20
Corn oil (O)	0.0057	14.7
Waste oil (WO)	0.0061	11.6
<b>Emulsions</b>		
O-2%	7.61	0.39
O-2%-S-0.2%	6.48	0.50
O-2%-S-0.5%	6.66	0.47
O-5%	3.65	0.84
O-5%-S-0.5%	3.33	0.84
WO-2%	6.41	0.48
WO-2%-S-0.2%	6.26	0.48
WO-5%	4.07	0.75
WO-5%-S-0.8%	3.62	0.83

$$H(\text{atm}) = \frac{P_{VOC}}{x}$$

$P_{VOC}$ : BA partial pressure in the gas phase (atm)

$x$ : BA molar fraction in the liquid phase

$$Q(\text{g/L}) = \frac{F_G \int_0^t (C_{in} - C_{out}) dt}{V_L}$$

$C_{in}, C_{out}$ : BA inlet and outlet concentration (g/L)

$F_G$ : gas flowrate (L/s)

$t$ : time (s)

$V_L$ : absorbent's volume (L)

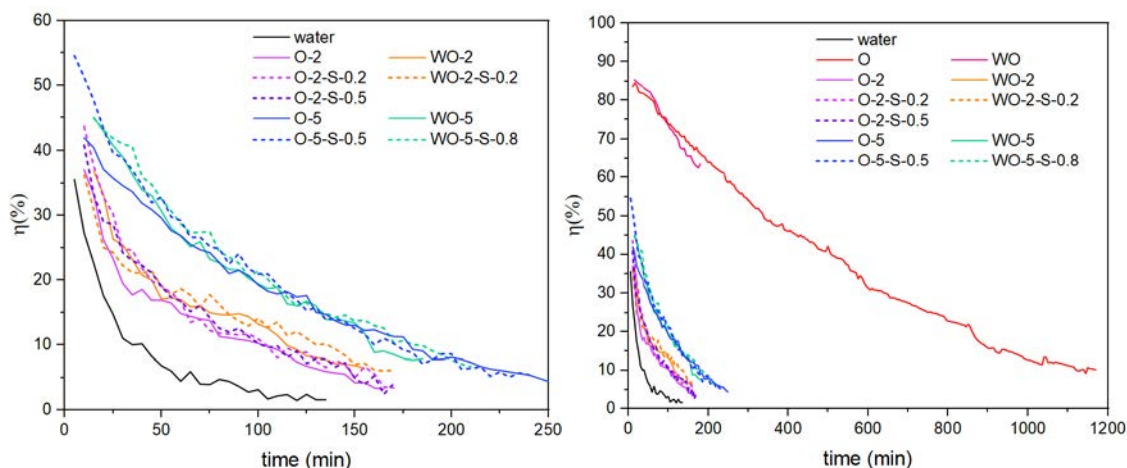


Figure 1. Instant efficiency as a function of the time for water, oils, and emulsions.

**Acknowledgment.** The authors would like to thank the European Union for the financial support of the present study in the project ReVoc4LIFE under the LIFE 2020 research programme (Grant number LIFE20 ENV/IT/000688).

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## Blood-Brain Barrier (BBB) permeability of new miconazole-like scaffold compounds by HPLC-ESI-MS/MS

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Keywords: MRM, amoebic meningoencephalitis, *Naegleria fowleri* new inhibitors

### Introduction

Primary amoebic meningoencephalitis (PAM) due to *Naegleria fowleri* (*N.F.*) is a fulminating brain infection, with a fatality rate over 97% [1], also due to the lack of effective treatments [2]. Therefore, the development of efficacious and safe drugs for the PAM treatment remains an unmet medical need. Miconazole (MIC), used topically for the treatment of fungal or yeast infections, presents medium anti-*N.F.* potency and medium brain permeability [3,4]. In the present research, among a certain number of synthesized compounds tested *in silico* towards *N.F.*, two miconazole-like scaffold molecules (1, 2, structures in the Table) were selected due to their best activity ( $EC_{50} < 2.5 \mu\text{M}$ ) and tested *in vivo* on mice for BBB permeability. The distribution of MIC, 1 and 2 between blood and brain was analyzed by an optimized HPLC-ESI-MS/MS method, by using the MRM technique.

### Experimental

Samples were analysed by a Waters 1525 $\mu$  HPLC-ESI-MS/MS, using a Supelco Ascentis® Express C18 (15 cm  $\times$  2.1 mm) 2.7  $\mu\text{m}$  column, Milli-Q water/formic acid 05 mM (A) and acetonitrile/formic acid 5 mM (B) as mobile phase, flowing at 0.20 mL/min. Data acquisition, data handling and instruments control were performed by MassLynx Software 4.1 v (Data Handling System for Windows, Micromass, UK).

Stock solutions of 1, 2 and MIC (1 mg/mL in methanol) were appropriately diluted with the mobile phase (A:B, 70:30, v:v) and used to optimize the chromatographic separation, the ESI source parameters and the MRM method. Elution program: 0-1 min, 30% B; 1-16 min, 45% B; 16-17 min, 45% B; 17-18 min, 30% B; 18-38 min, 30% B. MRM method in positive ionization (ES<sup>+</sup>): MIC, 417 $\rightarrow$ 159 (*m/z*) and 417 $\rightarrow$ 161 (*m/z*); 1, 415 $\rightarrow$ 159 (*m/z*); 2, 365 $\rightarrow$ 159 (*m/z*); dwell cell, 0.200 s. Source parameters: CV 2700



V, CV 22 V, ST 150 °C, DT 350 °C, CG flow 30 L h<sup>-1</sup>, DG flow 400 L h<sup>-1</sup>.

The calibration curves of 1, 2 and MIC were calculated analysing the MRM peak area against the standard nominal concentrations 2.5, 5.0, 10.0, 25.0, 35.0 and 50.0 ng/mL. Matrix effect (ME) in brain and plasma was evaluated [5].

Diluted plasma and brain extracts of mice treated with compounds 1, 2 (experiments *in vivo* in triplicate) and MIC (in duplicate) were used as received but appropriate dilution with the mobile phase, filtered at 0.22 µm and analysed in triplicate.

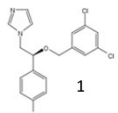
### Results

Very good quality parameters were found in term of linearity, LOD and LOQ for 1, 2 and MIC in the analysed range, and a generally weak ME [5] was found in both plasma and brain (see Table). All compounds MIC, 1 and 2 were detected in brain: plasma (P) and brain (B) concentrations of 1 was found similar to MIC, while 2 demonstrated a brain permeability better than both MIC and 1, with a B/P distribution coefficient ~1.

### Conclusions

The MRM technique was successfully applied for the analysis of very low amount (ng/mL) of analyte in complex biological sample, providing the *in vivo* assessment of BBB permeability of newly synthesized compounds well acting towards the amoeboid form of *N.F.* The EC<sub>50</sub> value of 1.5 µM and the B/P distribution coefficient ~1 (suggesting free distribution to the brain) of compound 2 make it a promise for further optimization into a drug candidate for PAM.

Table. Chromatographic data, mass spectral data (ES+) and quality parameters for compounds 1, 2 and miconazole MIC. B=brain, P=plasma.

Compound	t <sub>R</sub> (min)	MRM (m/z)	R <sup>2</sup>	LOD (ng/mL)	LOQ (ng/mL)	ME (%) (B)	ME (%) (P)
 1	6.66	365→159	0.9994	2.52	8.39	-7.75	-20.31
	8.89	415→159	0.9942	7.69	30.34	18.34	0.15
MIC	10.30	417→159 417→161	0.9980	4.50	14.99	15.02	8.23

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## Hydrogel-like PBS-based thermoplastic copolymer for biomedical applications

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Keywords: poly(butylene succinate), poly(triethylene diglycolate), hydrogel-like behaviour

As known, biomedicine is a multidisciplinary branch of medical science, which incorporates skills in chemistry, material science, biology, engineering and medicine, and aims to improve human health. To reach this goal, it involves the development of many different devices, such as, just to name a few, artificial supports, called scaffolds, for the regeneration, *in vitro*, of new functional tissues, or micro- and nano-carriers for the controlled release of drugs, therapies and active substances [1]. Many of these applications, including the abovementioned ones, require the use of polymers, which are often preferred to other classes of materials due to their high availability, easy processing, a wide range of properties, and their stability in physiologic conditions. Aliphatic polyesters represent an interesting sub-category inside the broader world of polymers, thanks to their biocompatibility and biodegradability. Moreover, they can be *ad-hoc* designed simply by varying their chemical structure, composition and molecular architecture, to make their properties suitable for the intended applications.

In the present work, we started from poly(butylene succinate) PBS, a biocompatible commercialized aliphatic polyester widely investigated in the literature also for biomedical purposes [2]. As in most cases, a polymer cannot satisfy all the requirements for a peculiar application. Thus, copolymerization revealed to be an effective tool to tune and improve the properties of a material without altering the already good ones. In the case of PBS, its main limitations in biomedicine are related to the high crystallinity of the homopolymer, which implies high mechanical stiffness. To overcome this drawback, we copolymerized PBS with another aliphatic polyester, poly(triethylene diglycolate) (PTED), characterized by the presence, in its macromolecular chain, of ether oxygen atoms, to obtain a new high molecular weight copolyester, poly(butylene succinate/triethylene diglycolate) P(BS50TED50). In detail,

PBS and PTED were first synthesized by two-step melt polycondensation, and P(BS50TED50) was then obtained by reactive blending equal weight amounts of the two parent homopolymers. The reaction was carried out for 35 minutes, in order to reach a multiblock architecture, consisting of long blocks of PBS, which confer to the material a semicrystalline nature and ensure its processability, and long blocks of PTED, these last characterized by high hydrophilicity, due to the presence of ether oxygen atoms. The chemical structure of the copolymer was then analyzed and confirmed by proton nuclear magnetic resonance and gel permeation chromatography. Furthermore, the so-obtained copolymer was processed in both compression molded film and microparticles. The thermal and structural properties, the surface hydrophilicity, as well as its mechanical response were also investigated by means of calorimetric measurements, X-Ray diffractometric analysis, water contact angle and stress-strain measurements, respectively. As a result, the introduction, in PBS macromolecular chain, of the same weight amount of PTED blocks, is responsible for improved hydrophilicity, which is necessary, for example, for all the applications in which cell adhesion is involved. Surprisingly, in P(BS50TED50) copolymer, the peculiar behavior typical of hydrogels was also observed, opening new possibilities for the application of PBS-based copolymers in cell culture, medical surgery and biosensing, due to its similarity to extracellular matrix (ECM) components [3].

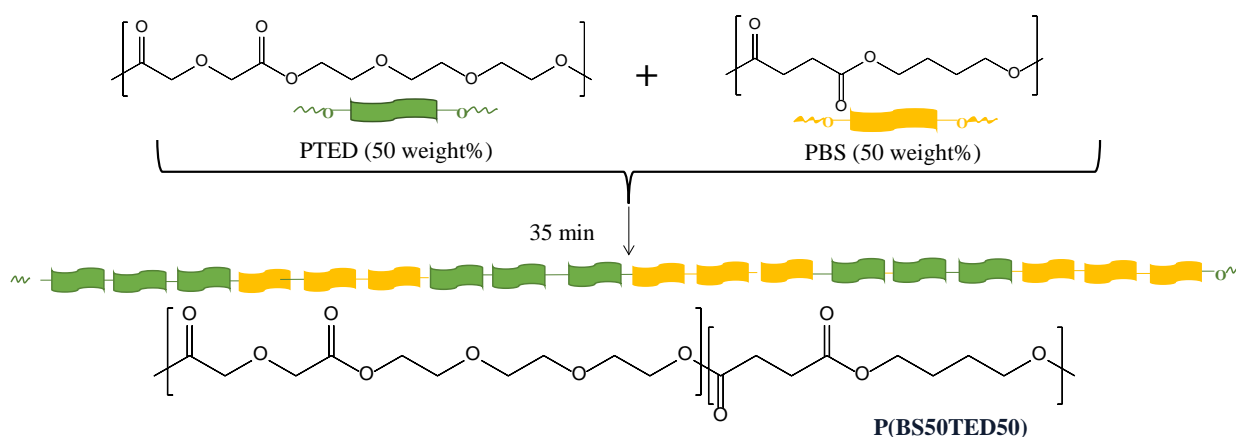


Figure1. Chemical structure of PBS, PTED and P(BS50TED50) block copolymer.

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## Printability assessment of a thermosensitive photocurable biomaterial ink

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Keywords: Hydrogel, Microextrusion bioprinting, Printability assessment.

**Introduction:** As one of the most extensively applied additive manufacturing technologies, microextrusion bioprinting manages to bioprint high-viscosity fluids, forcing the bioink to flow through the nozzle and producing a continuous stream of material [1]. In this work, a novel semi-synthetic hydrogel, consisting of gelatin methacrylate and Pluronic F127 (PF127), has been specifically formulated to match the requirements of microextrusion bioprinting process [2]. A complete printability assessment was carried out to find the optimal processing parameters ensuring high shape fidelity and stability of the printed construct.

**Materials and methods**

**Ink preparation:** Gelatin methacrylate was synthesized starting from gelatin (type A, from porcine skin) and methacrylic anhydride (MA, 0.8 mL/g of gelatin) [3], and dissolved at 5% w/v in diluted DMEM (Dulbecco's Modified Eagle Medium, 1:5 dilution) at 45 °C. Then, Pluronic F127 was slowly added to the solution reaching the final concentration of 20% w/v. Finally, Irgacure 2959 (2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone) was added (1 mg/mL) as a photocatalyst.

**Printability assessment:** Bioprinting of GelMA-PF127 ink was performed by a pressure-assisted bioprinting process using a custom-designed equipment [4]. A three-step printability assessment was adopted to determine whether the microextrusion process could be used to print GelMA-PF127 hydrogel into 3D constructs, and to derive the optimal printing parameters. First, a complete rheological evaluation was carried out to characterize the ink in terms of viscoelastic properties, temperature-dependence and shear thinning behaviour. Then, an initial screening was performed to identify the fiber-formation regime, coupled to the analysis of the deposited filament as an input

for an empirical predictive model based on Response Surface Methodology (RSM). Finally, the deposition of a 3D pattern was investigated to establish whether a layer-by-layer stacking occurs without merging.

**Biocompatibility assessment:** To evaluate the cytocompatibility of both the bioink and the 3D printing process, human dermal fibroblasts were used as a cell model, and their viability was assessed after printing. A fluorescent staining was also performed to investigate cell distribution within the bioprinted constructs.

### Results and discussion

As a result of the preliminary assessment of the fiber formation during extrusion and the fiber deposition on a substrate, the window of printability of the formulated ink was obtained (Figure 1 a,b). The contour plot of the RSM empirical models, reporting the percentage difference between the measured filament diameter and the nominal needle diameter are shown in Figure 1 (c,d). According to the results of the printability assessment, a 27G needle, a working pressure of 800 mbar and 5 mm/s printing speed were selected to ensure the formation of consistent fibers under stable extrusion conditions, maximizing printing resolution. The bioprinted 3D constructs displayed high levels of cell viability and proliferation, providing the basis for the development of *in vitro* models mimicking the architectural complexity of native tissues.

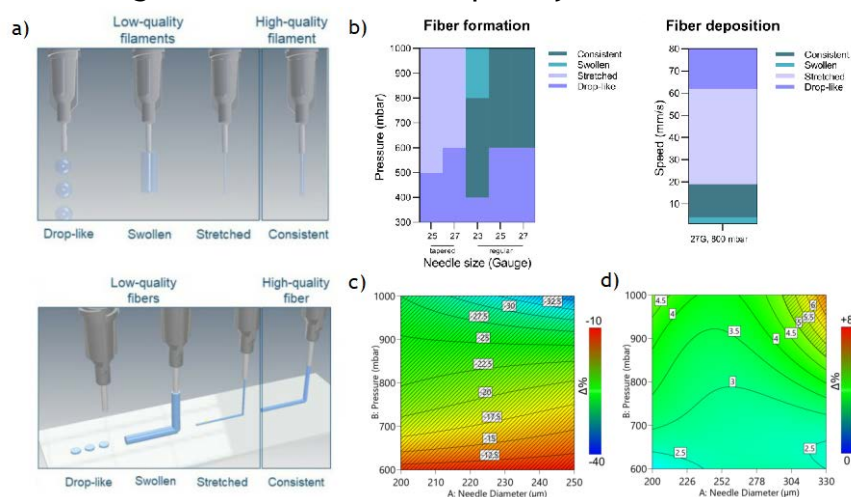


Figure 1. Quality criteria for the selection of optimal printing parameters (a) and window of printability (b). Contour plots of RSM empirical models for tapered (c) and regular (d) needles. Adapted from [2].

### Conclusions

The present work reports the formulation and characterization of a novel hydrogel with both thermosensitive and photocurable features for application as a bioink. By merging the thermosensitive characteristics of Pluronic with the cross-linking features of GelMA, the formulation showed a printability window characterized by good shape retention and chemical stability following photo-crosslinking, as demonstrated by a thorough printability assessment, performed employing empirical predictive models.

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## Development of MEK and AURKA drug inhibitors delivery systems for the treatment of metastatic melanoma tumour

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Keywords: Alisertib, Trametinib, Nanoformulations

Although melanoma treatment strategies have been significantly improved over the last decade leading to increased patient survival, unresolved issues are still present even in current gold-standard therapies. One of the main problems is the presence of non-responsive or relapsing patients, and new drug combinations could be a solution to increase the effectiveness of therapy targeting a larger portion of patients. In particular, kinases are nowadays established therapeutic targets in the design of novel drugs against cancer<sup>1</sup>. A recent *in vivo* screening performed at European Institute of Oncology (IEO, Milan) demonstrated that the dual targeting of Aurora kinase A (AURKA) and MEK by using the combination of drug inhibitors alisertib and trametinib is highly effective against patient derived xenograft metastatic melanoma tumors<sup>2</sup>. This synergy has already outperformed the gold-standard therapy both in *in vitro* and *in vivo* models. Nevertheless, aiming at clinical trials, improved drug bioavailability, cellular uptake and tumour accumulation are needed. Better strategies to increase drug solubility are looked for in this work. A systematic study at the molecular level, from a chemical and crystallographic point of view, is performed with the aim of unravelling the internal interaction profile of alisertib and trametinib. This information is fundamental to design novel pharmaceutical co-crystals and salts of studied inhibitors, thus increasing their solubility in biological media. Finally, to overcome toxicity and efficacy issues and to better accumulate drug inhibitors at the tumour site, novel drug loaded nanoformulations are designed, with functionalized surfaces suitable for *in vivo* applications.

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## *Multifunctional uses of furan derivatives: from fine chemicals to bio-based materials*

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Keywords: bio-based feedstocks, thermoset resins, pyrrole compounds

Climate change is one of the most crucial topics of recent decades. The synthesis and overconsumption of oil-based materials and their critical end-life are the worst aspects in terms of recycling. Recently, the scientific community established four key-parameters to promote the development of sustainable materials [1]. The use of bio-based and renewable feedstocks is surely a stable starting point to realize a circular material. Terpenes, lignocellulosic feedstocks, proteins, and carbohydrates are considered excellent candidates for obtaining multifunctional and highly reactive molecules. In particular, lignocellulosic moieties represent a huge source of chemical platforms. These raw materials could lead to the preparation of useful bio-based feedstocks after several chemical treatments, in particular furans [2-4]. A variety of furan derivatives can be obtained. 2,5-dimethylfuran (DMF) is surely one of the most attractive furan molecules due to its high chemical reactivity for the synthesis of 2,5-hexanedione (HD). The ring-opening reaction of DMF to HD is a process strictly dependent on the presence of acidic media [5,6]. The presence of catalysts could catalyze the entire process [7]. However, chemical purification steps are needed to obtain pure HD.

On the other hand, furfuryl alcohol is the only example of a furan molecule that leads to the formation of bio-based thermoset resins. In particular, the reaction in acidic aqueous media under mild conditions guarantees the propagation of furfuryl alcohol to the respective oligomers. A cured thermoset resin is successfully obtained via Diels-Alder cycloaddition between two or more oligomer chains by increasing the reaction temperature [8,9]. However, furfuryl alcohol could not be used in some applications due to its critical safety data. A novel synthetic procedure for obtaining furan resins has to be developed.

In this work, the multifunctional uses of furan derivatives for the synthesis of different molecules or materials will be shown. The reactions and the experimental conditions used have been inspired by the general principles of Green Chemistry [10,11].

In particular:

- a. Pyrrole compounds were successfully synthesized via one pot - two step synthesis in which DMF was the starting material. The reactions were performed in neat conditions. The obtained HD was used as a starting



material in reaction with primary amines for the synthesis of pyrroles. No purification was needed for each step (Figure 1);

- b. 2-furoic acid and 2,5-furandicarboxylic acid led to the formation of bio-based thermoset resins when reactions were performed in the presence of alternative methylene donors. The hypothesis of the work has been confirmed by performing DSC analysis.

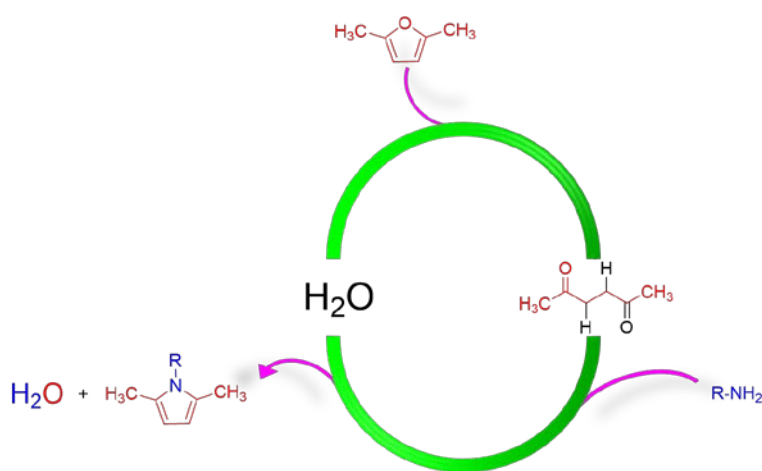


Figure 1

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## Macrostructure control of bio-derived elastomeric polyesters

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Keywords: polyesters, elastomers, macrostructure

Rubber compounds acquire great dynamic-mechanical properties and the intriguing entropic elasticity only after crosslinking, nonetheless at the expense of degradability and recyclability. The average amount of microplastics released in the environment was estimated to be about 3.3 million tons and the primary sources of these are textiles and TRWP (“namely tire-road wear particles”) [1].

One way to make thermoset rubbers circular materials is to adopt polymers which could undergo depolymerization, by applying selective degradation reactions. The essential feature of these polymeric materials should be the presence of reversible bonds linking the repeating units: ester bond is a suitable one. Elastomeric polyesters can be obtained starting from biobased diacids and dialcohols. They were already present in the report from US Department of energy [2] and are available on the market.

In this work, amorphous polyesters, suitable for the preparation of elastomeric composites, were synthesized by step growth condensation polymerization, following the inspiring work by L. Zhang [3]. Their macrostructure can be controlled by means of the reaction with chain extenders such as mellophanic dianhydride, a derivative of bio-C6 building blocks, and an isomer of the commercially available pyromellitic dianhydride. The impact of this treatment on the polymers properties was studied and composites with polar fillers such as silica and functionalized carbon black were prepared and characterized.

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## *Novel functional biomaterials from egg white protein irradiation*

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**Keywords:** wound dressings, egg proteins, radiation processing

Wound management, including acute and chronic wounds, has a significant economic impact on health care, the outcome of many medical interventions and the quality of life of patients. The development of new dressings that can prevent infection and promote wound healing is critical to effective wound management. Egg white proteins have been shown to promote wound healing and tissue regeneration. It has also been reported that egg white components can kill or inhibit various pathogens. Whole egg white and their fractions, rather than individual components, appear to be more effective but there is no clear understanding of the mechanism of action. [1] In this study, three proteins derived from egg white, such as lysozyme, ovotransferrin and ovalbumin, are incorporated into new hydrogel dressing formulations based on mixtures of a polysaccharide, xyloglucan, known for its inherent antioxidant properties and a synthetic biocompatible polymer, PVA, which can be chemically cross-linked with ionising radiation. The mixture of the two polymers results in a porous structure, capable of incorporating water and absorbing exudates, which is also partially adhesive to the skin. High-energy irradiation induces cross-linking of the synthetic polymer, without the addition of cross-linkers and catalysts, and thus providing mechanical strength and, at the same time, sterility. The influence of irradiation on the properties of the films and the proteins incorporated therein is discussed.

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### Acknowledgments

Horizon Europe Project EURATOM-IA titled "RADiation harvesting of bioactive peptides from egg prOteins and their integration in adVanced functional products – RADOV" Project n. 101061694.

# Adsorption of Cisplatin and Its Derivatives on Graphene

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Keywords: graphene, cisplatin, molecular dynamics

## Introduction

Cisplatin is widely regarded as a key discovery in the field of anticancer drugs, playing an important role as the basis of combination therapy for a variety of solid tumors. The main mechanism of action of cisplatin involves intracellular activation by hydration of one of the two chloride leaving groups, followed by covalent binding to DNA to form a DNA adduct. This process triggers a series of biochemical events which lead to the cell death [1]. However, it is well-known that, after administration, the platinum complexes are excreted either in their original form or as metabolites, which eventually enter the effluent streams of hospitals and homes, thus entering the water cycle. These compounds are poorly biodegradable, and several advanced water treatment methods have been proposed for their removal [2].

Carbon-based adsorbent materials have proven attractive for the treatment of water contaminated with pharmaceutical compounds[3], due to their high loading capacity, affinity for organic compounds, and possibility to be regenerated. Such adsorbent materials can be combined with advanced oxidation processes (AOP) to increase their efficiency. Indeed, pharmaceutical compounds, i.e. cisplatin derivatives, which are usually present in liquid samples at low concentrations (< 1ppm) can be concentrated by adsorption and removed by AOP.

Graphene is a carbon-based material in two-dimensional (2D) sheets[4] which has been previously tested in water treatment applications as drug adsorbent [5]. Platinum complexes were previously shown to be able to be adsorbed by this material through non-covalent interactions [3]. In this study we employ molecular dynamics (MD) simulations to investigate the adsorption of cisplatin (cpt) and of its mono- (wcpt) and di-aqua (w2cpt) derivatives on graphene surfaces to obtain insights on the adsorption mode and thermodynamics.

## Computational methods

MD simulations were carried out for cpt, wcpt, and w2cpt (1-5 molecules) immersed in a tetragonal box with sides  $x = y = 5.1$  and  $z = 11.0$  nm. Graphene surface (5x5nm) was generated by the GOPY application and the topology was obtained as described previously [5,6]. For the Pt-complexes an in-house flexible force field was used [7].

The box was filled with a specific number of SPC/E water molecules that replicates the density of water. The particle-mesh Ewald method is used to calculate long-range electrostatic interactions [8] and a cut-off of 1.2 nm was employed for the short-range interactions. After energy minimization, the system was equilibrated for 5 ns in the NVT ensemble and in the NPT ensemble at 1 bar and 300 K. Production simulations were run for 50ns. The potential of mean force profiles were obtained using the umbrella sampling technique [9]. The setup of the configurations was done as described previously [10]. All simulations are done with GROMACS 2021.3 [11].

## Results

Platinum complexes are spontaneously adsorbed on surfaces by assuming an orientation parallel to the surface (Figure 1) and no aggregation of the adsorbed molecules is observed during the simulation.

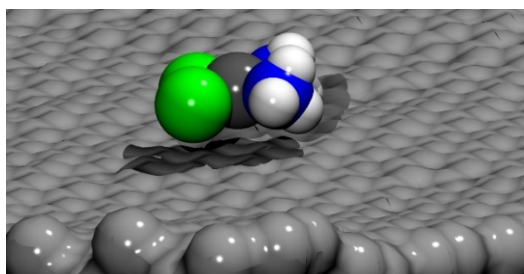


Figure 1. Cisplatin adsorbed on graphene

Only in the case of the system containing 5 w2cpt, the escape of one molecule from surface is observed during the simulation time. This is likely due to the weaker adsorption on the neutral surface of the doubly charged compound, which, on the other hand, presents a strong interaction with water.

The adsorption free energy ( $\Delta G_{\text{ads}}$ ) obtained from PMF (-5.2, -4.6 and -2.5 kcal mol<sup>-1</sup> for cpt, wcpt and w2cpt respectively) thus showing a higher affinity for the parent compound. This trend can be explained by the hydration free energies ( $\Delta G_{\text{hyd}} = -62.9, -83.9, -218.0$  kcal mol<sup>-1</sup> for cpt, wcpt and w2cpt) as, upon adsorption, one side of the platinum compound is completely de-solvated. Since w2cpt presents the most negative  $\Delta G_{\text{hyd}}$  it is expected that the adsorption process be less favored than the other species.

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## Intermolecular interactions between quercetin and amorphous SiO<sub>2</sub> surface for drug delivery in biomedical applications

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Keywords: biomaterial, drug delivery, molecular dynamics simulations

The new generation of biomaterials able to incorporate drugs for in situ release after implantation is important in many pharmaceutical and biomedical applications. Several drugs show problems of diffusion through biological barriers [1] and the control of local administration is crucial to avoid cytotoxic effects.

Molecular Mechanics (MM) and Molecular Dynamics (MD) simulations are a useful tool to investigate drug and biomaterial surface interactions at atomistic level [2,3]. In this work the interaction between quercetin molecule, a flavonoid drug studied for its antioxidant and anticancer properties, and the amorphous SiO<sub>2</sub> surface terminated with silanol groups is studied using a simulation protocol proposed in previous work [3]. This protocol provides *i*) the initial energy minimization, *ii*) MD runs until the equilibrium state was achieved *iii*) final geometry optimizations of the final configuration assumed by the system at the end of MD run. These simulations are performed using the Consistent Valence Force Field (CVFF) [4] and Materials Studio packages [5]. At first the conformational study of quercetin single molecule was performed. The optimized geometry after MM and MD simulations lasting 2 ns at room temperature is reported in Figure 1.

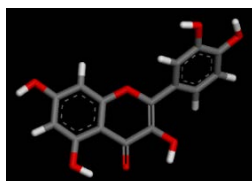


Figure 1. Optimized geometry of quercetin molecule after MD run. Color code: carbon atoms are in grey, oxygens in red, hydrogen atoms in white.

Afterwards, the adsorption process of quercetin molecule on the amorphous SiO<sub>2</sub> surface was studied starting from four different initial arrangements near the solid



surface in a simulation box of size equal to  $(85.53 \times 85.53 \times 250.0)$  Å considering the periodic boundary conditions. After the energy minimization of four different initial geometries and then four MD simulations at room temperature lasting 1 ns, quercetin molecules display favorable intermolecular interactions in the adsorption process during MD run due to H-bonds between drug and SiO<sub>2</sub> surface. These intermolecular interactions are weak. During the MD run, the adsorption and desorption process takes place, as reported in Figure 2, where the distance of the center of mass (c.o.m.) of the quercetin molecule and the best-fit plane of the SiO<sub>2</sub> surface, always fixed during MD run, is reported.

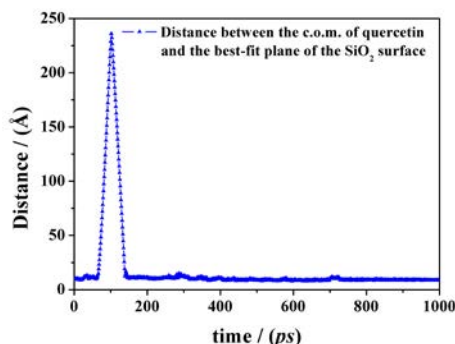


Figure 2. Distance between the c.o.m. of quercetin molecule and the best-fit plane of the silica surface calculated during a MD run lasting 1 ns.

The H-bonds between quercetin drug molecule and silica surface stabilize the adhesion on this solid surface. The H-bonds between the C–O and –OH quercetin groups with the hydroxyl groups and oxygen atoms exposed by silica surface stabilize the interactions drug-biomaterial, as in an optimized geometry after MD run reported in Figure 3 (see dashed blue lines). These preliminary theoretical results and the ongoing study at higher drug concentration will be compared to the experimental data from Fourier-Transform Infrared Spectroscopy (FT-IR) of quercetin molecules entrapped in a silica matrix obtained via the Sol-Gel methods studied by M. Catauro *et al.* [6].

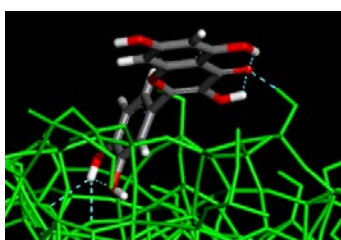


Figure 3. Optimized geometry of quercetin drug adsorbed on the amorphous SiO<sub>2</sub> surface terminated with silanol groups. Color code is the same of Figure 1, all silica surface atoms are in green for clarity. The H-bonds are in dashed blue lines.

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## *In Situ Modification of Hybrid Silica-Epoxy Flame Retardant Nanocomposites by Phosphorus via a Green Hydrolytic Sol-Gel Route*

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Keywords: sol-gel synthesis, hybrid nanocomposites, flame retardance

The most serious restriction to the widespread application of epoxy resins is their low fire resistance, including the generation of toxic smoke and flammable gases during combustion [1]. Flame retardance of epoxy resins is usually imparted using suitable additives and/or properly modified curing agents [2]. Herein, via a two-step green synthetic procedure, the chemical modification of the epoxy matrix with reactive silicon and phosphorus precursors is explored to obtain nanocomposites with intrinsic flame-retardant features [3]. Nanoscale phase separation occurs in the first step, forming an inverse micelle system in which polar nanodomains act as nanoreactors for the hydrolysis of silanes (Si precursors) [4], giving rise to silica lamellar nanocrystals (SLNCs). In the second step, inside the silica nanodomains, the formation of stable Si-O-P bonds occurs despite the usually low stability of such linkages [5], because the reactivity of phosphoric acid (P precursor) with the oxirane rings of the polymer chain is balanced by its tendency to diffuse into polar nanodomains (Figure 1, left). Intriguingly, the use of phosphoric acid alone in epoxy composite manufacturing leads to a wormlike morphology of the network, whereas its addition in the presence of silanes results in the formation of SLNCs with a thinner interlayer distance [3].

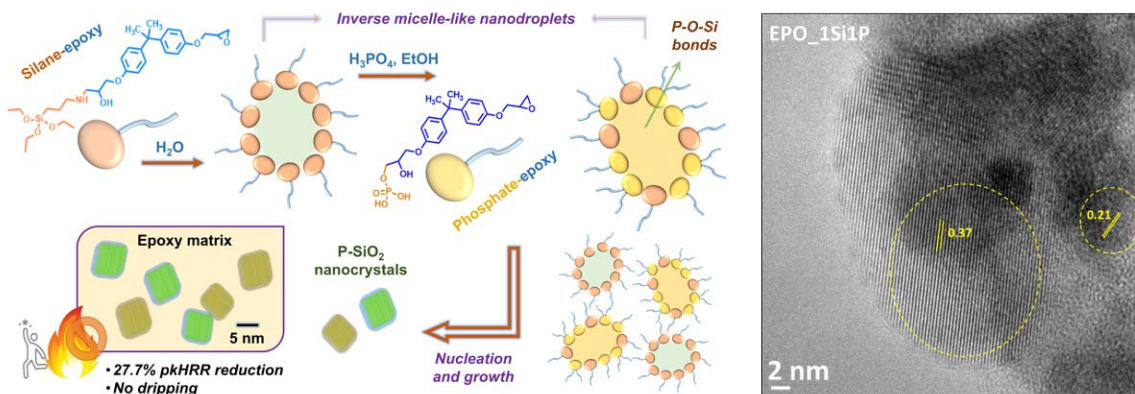


Figure 1. Schematic representation of synthetic route (left). HRTEM image of a Si-P-epoxy nanocomposite showing nanocrystals with lamellar morphology and two different sheet thicknesses (right).

The special morphology of these hybrid Si/P nanocomposites (Figure 1, right), formed by two co-continuous phases, accounts for interesting flame retardant features: no dripping phenomena during UL94 tests (though the materials were all not classifiable), a remarkable reduction (up to 27.7%) in the peak of heat release rate, the formation of a large amount of coherent and continuous char both in nitrogen and air atmosphere. Moreover, the low CO/CO<sub>2</sub> ratio in the smokes obtained by the cone calorimeter tests suggests that a prevalent condensed phase mechanism occurs in which the silanol groups of Si-O-Si polymeric species, belonging to the organic-inorganic co-continuous network, condense with the decomposition products of mono- and di-phosphate groups (i.e. polyphosphoric acids) leading to the formation of P-O-Si polymeric substructures on a very abundant char. This latter can provide an effective ceramic thermal shield, limiting the heat exchange and the transfer of oxygen between the gas phase and the polymer matrix [3].

The above findings suggest considering these hybrid epoxy systems as suitable matrices for the design of composites with enhanced flame retardant features, in the presence of very low flame retardant loadings and therefore with a limited detrimental impact on the mechanical performances of the final products. The intrinsic fire resistance of these materials opens some interesting perspectives for their development and application in several industrial areas, for example in flame retardant coatings, sealants, components of electronic circuit board substrates or fiber-reinforced structural composites.

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## Azahelicenes as inherently chiral selectors for electrochemical enantiodiscrimination of biomolecules

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Keywords: azahelicenes, cyclic voltammetry, chiral selection

Aza[n]helicenes (Fig. 1) are a class of chiral multinuclear molecules possessing peculiar electronic and chiroptical characteristics due to their extended conjugated aromatic system associated with a central distortion from planarity.<sup>1</sup> They are configurationally stable only when the number of fused six-membered rings is  $\geq 6$

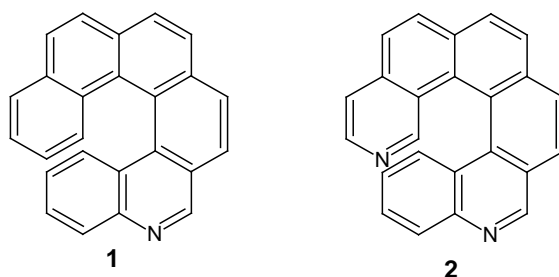


Figure 1. 5-aza[6]helicene (1) and 2,12-diaza[6]helicene (2).

Helicenes are intrinsically chiral compounds, in which the stereogenic scaffold responsible for chirality and the molecular group responsible for their specific properties coincide.<sup>2</sup> Configurationally stable mono- and diaza[6]helicenes 1 and 2 were synthesized, separated into enantiomers, quaternarized by reaction with alkyl iodides and used as additives in achiral ionic liquids to act as selectors in electrochemical enantiodifferentiation experiments on different chiral probes.

The synthesis of azahelicene 1 was obtained by the use of a Wittig condensation; it was necessary to choose an appropriate synthetic strategy in order to avoid substantial formation of a non-helical byproduct.<sup>1</sup> On the other hand, product 2 was obtained by Heck condensation, since by using the Wittig procedure it proved impossible to separate the product from  $\text{Ph}_3\text{PO}$ .<sup>2</sup> Once obtained, the two azahelicenes were

separated into their enantiomers by chiral preparative HPLC.<sup>1-3</sup> The enantiomers were reacted with 1-iodooctane in order to obtain their quaternary salts; the iodide counteranion was then exchanged with bis (trifluoromethanesulfonyl)imidate (bis-triflimidate, NTf<sub>2</sub>), since it would not be stable during electrochemical experiments. Compound 2, having two non-equivalent nitrogen atoms, could in principle yield three different quaternary salts; however, it was ascertained that the first nitrogen to react is always the one in position 2; when this position is alkylated, due to strong inductive effects the second nitrogen can only be alkylated under much harsher conditions. Therefore products 3 and 4 were obtained and electrochemically characterized.

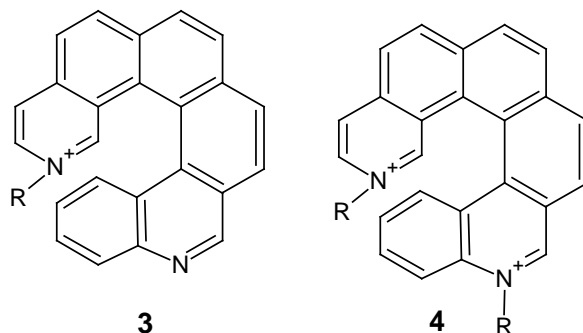


Figure 2. N-ethyl-2,12-diaza[6]helicene-2-ium (3) and N,N'-diethyl-2,12-diaza[6]helicene-2,12-dium (4) cations).

The quaternary compounds were electrochemically characterized by cyclic voltammetry (CV) and then introduced as 0.01 M additives in the achiral ionic liquid (BMIM)NTf<sub>2</sub>. The resulting chiral medium was used as solvent to record the CV patterns of the (R)-(+)- and (S)-(-)-N,N'-dimethyl-1-ferrocenylethylamine chiral probe enantiomers on screen-printed electrode (SPE) cells with an Au working electrode. Different chiral probes were used to test the enantiodiscrimination ability of these selectors in CV experiments; among these the benchmark electroactive enantiomer probes (R)-(+)- or (S)-(-)- N,N' -dimethyl- 1-ferrocenylethylamine and the aminoacids Tyrosine and Tryptophane. In all cases enantiodiscrimination was very good compared to the one obtained with asymmetric ionic liquids not inherently chiral. Enantioselection is higher in the case of compound 4, with two quaternary nitrogens, than with compound 3, while this latter is more effective than the parent azahelicene 2.

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## Preparation and characterization of a new hybrid heterohelicene

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Keywords: helicenes

Due to their remarkable electronic features and intrinsic chirality, carbo- [1] and heterohelicenes [2] [3] have been the subject of extensive research in recent years, as concerns both their synthesis and their possible applications. Among heterohelicenes, the most frequently encountered are azahelicenes (1) and thiahelicenes (2) (Fig.1).

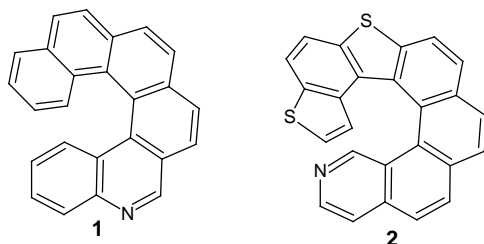


Figure 1. a) 5-aza[6]helicene (1); b) -2-aza-11,14-dithia[7]helicene (2).

While azahelicenes contain one or more electron-poor six-membered azine rings, in thiahelicenes electron-rich five-membered thiophene rings alternate with benzene rings. Hence, we thought of coupling these two features in order to obtain a hybrid structure, to explore its electronic and optoelectronic behaviour.

We followed a convergent synthetic strategy, preparing a three-ring azahelicene moiety (3) and a three-ring thiahelicene one (4), and then coupling them via a Wittig condensation (Fig.2).

N

Figure 2

The final disubstituted ethene (5), as a mixture of *cis* and *trans* isomers, was then photocyclized under UV light irradiation in acetonitrile to obtain mainly the desired product (6), together with a very small quantity of byproduct (7) [4]. We hypothesized

that interaction between the nitrogen and sulfur atoms of the terminal rings helps precursor (5) to maintain the correct conformation for ring closure to (6). The product was characterized with respect to its optical properties and calculations are underway concerning its electronic features.

N

Figure 3. Fotocyclization with the two products 6 e 7.

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## Ad-hoc designed aliphatic random copolymers for cardiac differentiation of pluripotent stem cells

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**Keywords:** poly(butylene succinate)-based scaffolds, human induced pluripotent stem cells, cardiac differentiation

Tissue engineering is a branch of biomedicine aiming to replace injured or missing tissue with a new functional one. As to cardiovascular diseases, which are the leading cause of death worldwide, this means to substitute irreversibly damaged cardiomyocytes and restore contractile functionality, overcoming the limitations of conventional treatments, such as drug-supported transplantation [1]. In order to recreate artificially a new functional tissue, cells must be seeded and cultured on proper 3D porous scaffolds. The peculiar morphology of these supports allows cells to grow, proliferate and develop their extracellular matrix (ECM). It has been also demonstrated that mechanical properties of scaffolds, in particular their rigidity, can influence cells' differentiation in a phenotype, whose mechanical characteristics are like those of the artificial support [2]. As to the materials used for the fabrication of scaffolds, polymers, and in particular aliphatic polyesters, are for sure the most interesting, thanks to their versatility, a wide range of properties, tuneable in relation to the intended use, biodegradability and, most important, biocompatibility.

Considering this scenario, in the present work two aliphatic random copolymers of poly(butylene succinate) (PBS), poly(butylene succinate/Pripol), P(BSBPripol), and poly(butylene/neopentyl glycol succinate), P(BSNS), containing two different subunits, neopentyl glycol and Pripol 1009, were successfully synthesized (Figure 1). PBS was chosen as starting homopolymer, due to its high thermal stability, wide processing window and biocompatibility [3]. Copolymerization with the two different co-units has



been necessary to decrease the high crystallinity and mechanical rigidity of PBS, which limit its applications in soft tissue engineering. The two copolymers have been subjected to electrospinning, to obtain 3D fibrous scaffolds, and then their solid-state properties have been deeply investigated. First, the different chemical structure of the copolymers is responsible for a different thermal and mechanical behaviour. In particular, it was possible to reach values of elastic modulus close to those of soft tissues. After that, biocompatibility was evaluated using human induced Pluripotent Stem Cells (hiPSCs), which were first seeded and successfully let grow on both the scaffolds. Moreover, the cells maintained their stemness during culture. After the application of a proper differentiation protocol towards cardiomyocytes lineage, on the P(BSBPripol) scaffold a significant upregulation of cardiac markers involved in both early and mesoderm differentiation was also observed (Figure 1).

All these results confirm that a proper *ad-hoc* chemical design and, in turn, the solid-state properties and morphology of the 3D substrate, play a key role in regulating the fate of hiPSCs. Thus, the materials investigated can be considered as effective supports for regeneration of functional cardiac tissue.

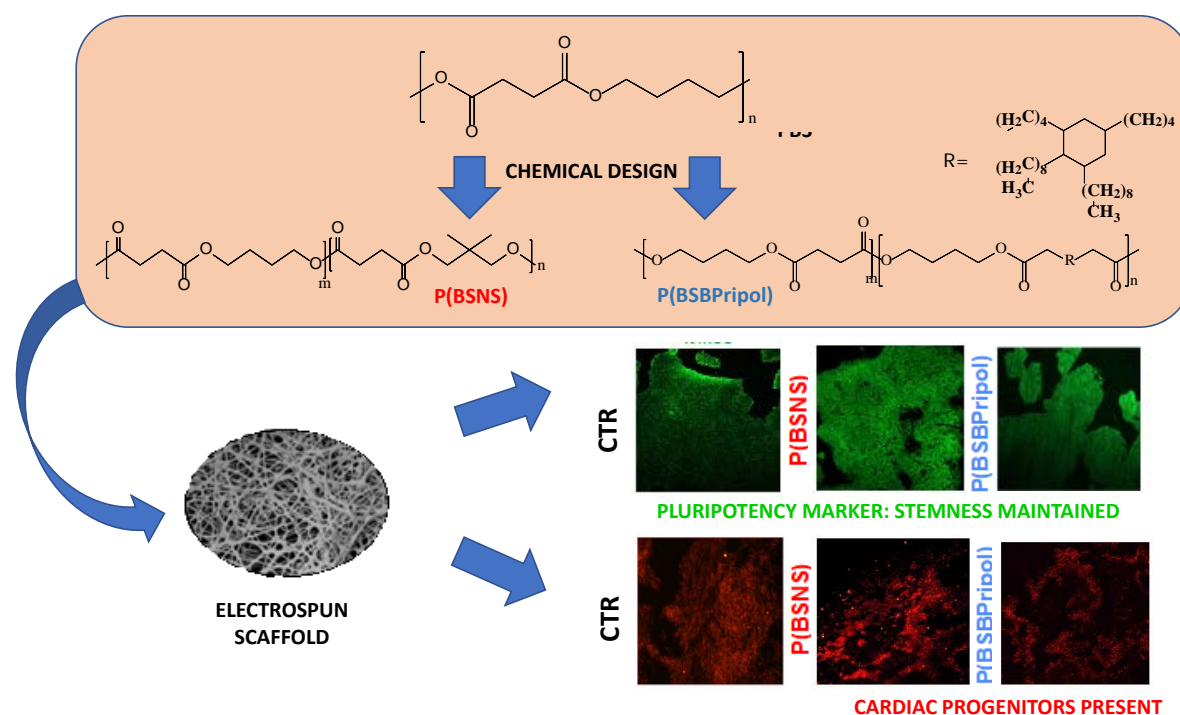


Figure 1. Schematic representation of the experimental plan.

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## Halogen-bonded metal-organic frameworks

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In the past year great attentions have been paid to the exploration of crystalline porous materials for their fascinating structures and wide applications. Both covalent and non-covalent interactions have been used to build crystalline porous materials with open frameworks, giving diversity of structures and functions.

In particular, the use of metals in crystal engineering has developed entirely new classes of materials such as coordination polymers (CPs) and Metal Organic Frameworks (MOFs). The interest in these materials is related to their easy structural and functional tunability that allows for a plethora of applications in quite different fields, such as gas adsorption and separation, catalysis and molecular recognition. Decorating the structure of ligands compounding CPs and MOFs with tailored functionalities is a pivotal strategy to control and tune their functional properties. Ligands bearing hydrogen bonding (HB) functionalities have widely used in this field, while structures with halogen bonding (XB) donor/acceptor groups have been poorly investigated.

In this communication, we report the exploitation of a cooperative approach between halogen bond, hydrogen bond and coordination bond for the assembly of hybrid metal organic materials. Specifically, three new hybrid systems and their properties will be discussed: (I) a new XB donor-fluorinated-MOF containing unsaturated metal centres which shows a selective and reversible solvent absorption accompanied by solvatochromic effect, (II) a coordination polymer having a XB donor and an azobenzene unit and (III) a fully organic framework sustained by XB and HB which shows a reversible uptake of guest molecules.

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## *Bionanocomposites based on a covalent network of chitosan and edge functionalized graphene layers*

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Keywords: Bionanocomposites, chitosan, edge functionalized graphene layers

Bionanocomposites are a class of materials that combine biobased polymers with nanoparticles or nanofibers to enhance their properties. These materials have gained significant attention due to their potential to replace traditional synthetic materials with sustainable and biodegradable alternatives. As a biopolymer, chitosan (CS), poly (N-acetyl-D-glucosamine), a copolymer of linked 2-acetamido-2-deoxy-D-glucopyranose and 2-amino-2-deoxy-D-glucopyranose, is of great interest.

Graphene and graphene-related materials have outstanding thermal, mechanical, and electronic properties. They are increasingly used for the preparation of bionanocomposites.

Carbon papers and aerogels were prepared from chitosan and graphene layers with aldehydic edge functional groups (G-CHO). CS and G-CHO were mixed with a mortar and pestle, and carbon papers and aerogels were obtained from a stable acidic water suspension through casting and liophilization, respectively [2]. The obtained graphitic materials were characterized with elemental analysis, titration, X-ray analysis, FT-IR, and Raman spectroscopies. It was demonstrated that CS and G-CHO are able to form chemical bonds, thus forming a crosslinked network. This work demonstrates that carbon papers and aerogels can be prepared without adopting the traditional oxidation-reduction procedure, avoiding harsh reaction conditions and dangerous and toxic reagents, solvents, and catalysts. It also paves the way for selective modification of graphene layers by exploiting the reactivity of aromatic rings.

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## Low temperature synthesis of bismuth-halogen perovskites for photoelectrochemical applications

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Keywords: lead-free perovskites, solar cells, photocatalytic tests

During the last decades, the demand for renewable energy became much stronger; as an example, in the European Union, in 2022, renewable energies are nearing 40% of total electricity generation. Since solar energy is one of the widely available, and low environmental impact renewable resources, the search for low-cost components of the final device for its conversion is strongly oriented. Several novel materials have been developed and continuously improved for this application and metal halide perovskites are one of those. Metal halide perovskites are materials having a general stoichiometry of  $ABX_3$ , adopting the structure of perovskite mineral, calcium titanate ( $CaTiO_3$ ). The crystal structure consists of metal cations that are situated at the B-site octahedrally coordinated with halide anions at the X-site. At the center of the unit cell A-site atom is located; usually, alkali-metal cations or small polyatomic cations are located in this site, with the goal of filling and charge-balancing the structure [1]. Moreover, metal halide perovskites can be either all-inorganic (when the A-site cation is an inorganic cation such as  $Cs^+$ ,  $Rb^+$ ), or hybrid organic-inorganic when the A-site cation is an organic polyatomic cation such as methylammonium or formamidinium.

These classes of semiconductor materials have been widely used in optoelectronic applications, and recently also in the energy sector. In fact, it is classified as part of emerging photovoltaic (PV) technologies; moreover, the development of perovskite-based photocatalysts, active towards visible light, have been studied [2]. In this work the search for a versatile, all-inorganic, lead-free halide perovskite material using simple solution processing methods, and exploiting its performance in photo-based applications is pursued. To this aim, bismuth-halogen based powders were produced according to the literature [2], using the low-temperature reaction between cesium iodide (CsI) and bismuth chloride ( $BiCl_3$ ) or iodide ( $BiI_3$ ). Different solvents (N,N-dimethylformamide, dimethyl sulfoxide) and relative reactant-to-solvent ratios were investigated in order to find out the optimized conditions. Obtained powders were characterized by means X-ray diffraction (XRD) analysis; optical characterization of the samples was taken out and evaluated from Diffuse Reflectance UV spectra. Perovskite-based powders were used as starting materials for the realization of Grätzel-like solar cells, where perovskites represented the active layers; at the same time, the sol-gel method was used in order to deposit thin films of Electron Transport Layer (ETL,  $TiO_2$ , ZnO) [3] and Hole Transport Layer (HTL, NiO) [4]; graphite was also employed as HTL. Photovoltaic efficiency tests were performed in controlled conditions using a 50 W

halogen lamp. Results showed that all the geometry of the cells and the features of different components of the device strongly affect their overall efficiency. At the same time, prepared powders were tested as visible light active photocatalysts; aqueous solutions of organic dyes were used as molecular probes with the aim to evaluate the efficiency of the perovskites. Experimental data highlighted that the onset of the perovskitic structure strongly affect both the photovoltaic and photocatalytic performances: in fact, pure iodide sample displayed the stoichiometric crystalline phase  $\text{Cs}_3\text{Bi}_2\text{I}_9$ , leading to the best results, whereas the mixed chloride-iodide sample, namely a solid solution between the two pure compounds,  $\text{Cs}_3\text{Bi}_2\text{I}_9$  and  $\text{Cs}_3\text{Bi}_2\text{Cl}_9$  [5], did not give a stable solid phase. Therefore, some degradation reactions took place during photoelectrochemical tests affecting the stability of the overall device.

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## *X-Ray diffraction analysis of historic mortars of the Bergamo Walls*

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### Introduction

Characterization of historic mortars is becoming increasingly important for factors related to the preservation, restoration and maintenance of historic buildings. Various techniques are available, from chemical to microstructural. These techniques are often used in combination, to gain an understanding of the microstructure and chemical and physical properties of materials [1]. This paper presents the results obtained from the X-ray diffraction analysis of samples taken from the Venetian walls of Bergamo, in the part of Baluardo di Valverde. Composite historical mortars consist of an aerial (air hardening) or hydraulic (water hardening) binder, such as gypsum or lime, and an aggregate fraction made up of sand-to-gravel sized mineral grains, rock, or fossil fragments, often sourced from nearby beach or fluvial sand deposits. However, alternative materials such as crushed pottery, tiles, or bricks have also been utilized. To ensure proper restoration, it is crucial to gather data on the textural, chemical, and mineralogical characteristics of the mortars, aiding restorers in selecting and producing compatible replacement or repair mortars that align with the original mortars from both physical and chemical perspectives.

### Experimental

The samples analysed were taken from 9 cores, 2 to 4 meters in length, containing parts of mortar, rocks and other fill materials used in the construction. Small portions of mortar were extracted from different locations on each core. Each of them was ground and analyzed individually, for a total of about 40 samples. Moreover, for three cores (cores B, D and H), a large amount of sample (about 250g of mortar) was collected and ground, and five different measurements were performed, to gain information on the average mortar composition. X-Ray diffraction patterns were collected with a Bruker D8 Advance diffractometer (DaVinci Design) in Bragg-Brentano geometry. Measurements were performed in the  $\theta/2\theta$  configuration using Cu radiation  $K\alpha = 1.5418 \text{ \AA}$ . The diffracted signal was collected with a 24-channel LYNXEYE XE-T detector in 0-D mode. The angular range collected was from 2 to 70  $^{\circ}2\theta$  in steps of 0.01  $^{\circ}2\theta$  with a



measurement time of 0.1 s per step. For the identification of the phases, the patterns were analysed using DIFFRACPLUS EVA<sup>®</sup> version 5.1.0.5 software associated with the ICDD-PDF (International Centre for Diffraction Data - Powder Diffraction Files) database (2021). Semi-quantitative analysis was carried out on the basis of phases reflection intensities using the RIR (Reference Intensity Ratio) method as implemented within the EVA<sup>®</sup> software.

## Results

In Figure 1 the semi-quantitative analysis of the large samples is reported. In order of abundance, were detected calcium carbonate ( $\text{CaCO}_3$ , in red) in the crystalline forms of calcite (mainly) and aragonite, quartz ( $\text{SiO}_2$ , in blue), micas and clay minerals (mainly muscovite, in green), magnesium hydroxide ( $\text{Mg}(\text{OH})_2$  in the brucite form, in purple), and other phases (mainly feldspars, in orange).

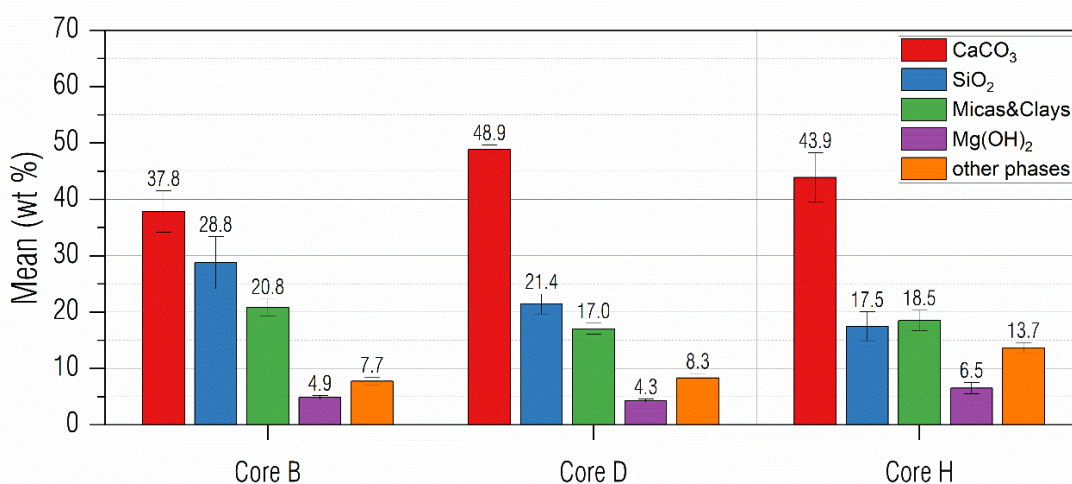


Figure 1: semi-quantitative analysis of cores B, D and H.

The high abundance of  $\text{CaCO}_3$ , knowing that usually the percentage of aggregates (sands) added to the mix generally can be 2 to 3 times higher than the binder portion, suggests a good portion of calcium carbonate was also present in the aggregate fraction. Measurements on a selected fraction of black aggregates confirms that they are mainly constituted by  $\text{CaCO}_3$ . The revealed  $\text{Mg}(\text{OH})_2$  is mainly found in the matrix as big white lumps, suggesting that a Mg rich lime, probably obtained from a dolomite-like mineral, was used in the mortar preparation, and the magnesian component was segregated and not reacted due to its very low solubility in water ( $K_{\text{sp}} = 5.02 \times 10^{-6}$ ) compared to that of  $\text{Ca}(\text{OH})_2$  ( $K_{\text{sp}} = 5.61 \times 10^{-1}$ ) [2].

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## Co-Crystal Strategy for Tuning the Properties of Amino Acid-based Hydrogels

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Keywords: Supramolecular Hydrogels, Crystal Engineering, Self-assembly

Low molecular weight hydrogelators (LMWH) are opening up a plethora of applications in chemistry and engineering (e.g., catalysis, optical devices), biology (e.g., cell cultures), and medicine (e.g., drug delivery), thanks to their good biocompatibility.<sup>[1]</sup> Among them, *N*-Fmoc-pentafluoro-phenylalanine (F<sub>5</sub>-Phe) showed an interesting hydrogelation behaviour, deriving from the peculiar packing of its Fmoc moiety and perfluorinated phenyl ring.<sup>[2]</sup> In the challenging attempt to tune the properties of its hydrogels, we confirmed that crystal engineering could be a useful tool.

Starting from structural studies on the 1:1 cocrystal formed by F<sub>5</sub>-Phe and benzamide (Fig. 1), we were able to demonstrate that the packing perturbation induced by the presence of benzamide in the solid state was consistent with the behaviour of the corresponding mixed hydrogel. This design approach could thus offer a valid method for predicting and tuning the strength and release properties of amino acid-based hydrogels, given the possibility of encapsulating molecules of pharmaceutical interest.



Figure 1. X-ray crystal structure of the 1:1 cocrystal of F<sub>5</sub>-Phe and benzamide.

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## A deep dive into structure and dynamics of hydrophobic eutectics and eutectogels

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Keywords: Non-ionic Deep Eutectic Solvents, Supramolecular gel, NMR spectroscopy

Hydrophobic non-ionic eutectic solvents (HES) are recently standing out from the crowd of (deep) eutectic solvents, (D)ES [1]. Compared to conventional type III hydrophilic (D)ES, non-ionic HES typically display lower viscosities, are chloride-free, and can be used in applications where even low water contents represent an issue [2].

If considerable progress has been achieved in the understanding of intermolecular interactions and mobility within traditional hydrophilic (D)ES, very little is known for HES [3]. An in-depth study of the HES composed of L-menthol with three phenol analogues with a different degree of steric hindrance around the hydroxyl group (Fig.1) highlights the concurrence of electronic and steric factors –next to the H-bond– in driving the formation of a type V DES and ruling its peculiar properties [4].

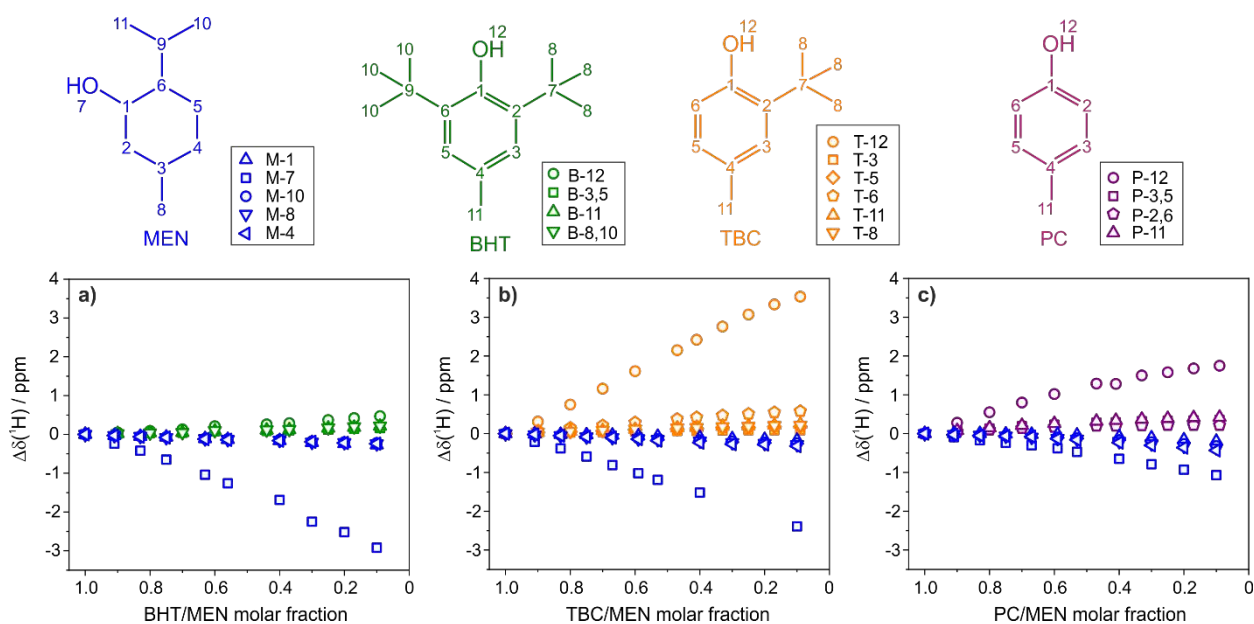


Figure 1. Change in <sup>1</sup>H NMR chemical shift of selected protons of BHT (green), TBC (orange), PC (purple), and MEN (blue) in the HES systems BHT/MEN (a), TBC/MEN (b), and PC/MEN (c), as a function of composition at 343 K. A molar fraction of 1.0 corresponds then to the pure individual component.

As a further step, hydrophobic non-ionic eutectogels (HEG) can be prepared from the immobilization of HES in a solid-like scaffold. We recently demonstrated that stable and homogeneous gels can be obtained in a matter of minutes using a low-cost low molecular weight gelator at a very low loading, with a simple one-pot preparation process ranked as “excellent” in the EcoScale metrics (Fig. 2) [5].

A multidisciplinary approach is applied combining liquid-state and HRMAS NMR methods with FTIR, thermal and rheological measurements, to shed light into structure and dynamics of the semi-solid samples. Noteworthy, the liquid-like nature of the hydrophobic mixture is retained upon gelation, and an unexpected increase of the diffusive motion of the HES components is observed under confinement compared to pure HES

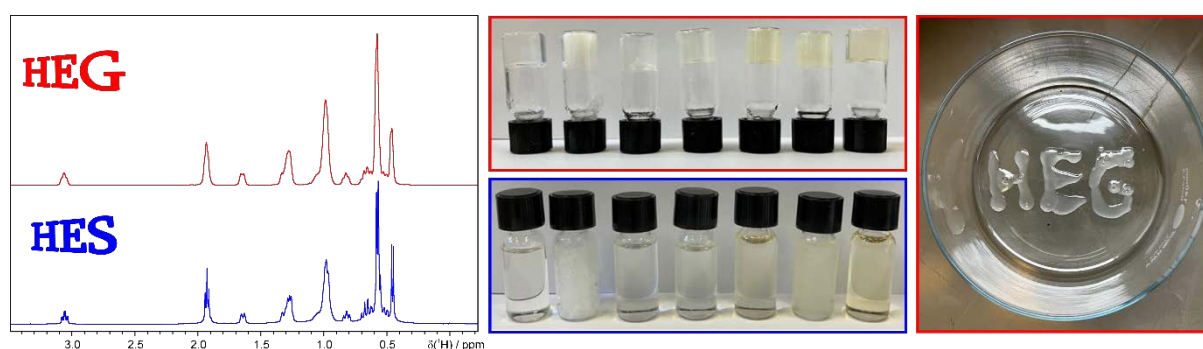


Figure 2. (a) Liquid-state and HRMAS  $^1\text{H}$  spectra of a representative HES and HEG, (b) pictures of the full set of developed HES (bottom) and HEG (top) and (c) photograph of a representative HEG.

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## Starch films plasticised by novel dicationic imidazolium-based ionic liquids

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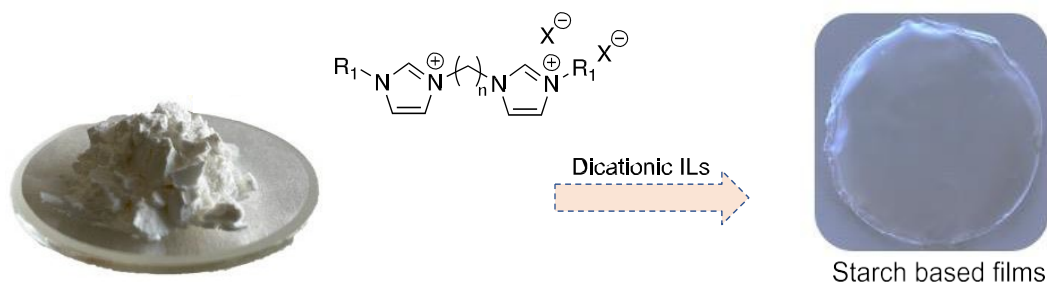
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Keywords: Bioplastics, Starch, Dicationic Ionic Liquids

Over the years the use of petrol-based plastics has increased about 20 times in the last 50 years<sup>1</sup> and their usage in many sectors has resulted in environmental problems. Natural polymers have been considered a replacement for common plastics due to their degradability, relative abundance, non-toxicity, and low cost. In this sense, starch is one of the most abundant polysaccharides found in plant storage organs and it is readily available. Nevertheless, starch is a brittleness material due to strong interactions among chains which confine their mobility<sup>2</sup>. To obtain effective starch films some plasticizers may be introduced that can improve the polymeric segmental mobility.



Many compounds, such as polyols, urea, and citric acid, have been studied to be effective in the plasticization of starch<sup>3</sup>. However, these small molecules can diffuse out of the polymer matrix after some time, causing changes in the material properties. Recently, imidazolium-based ionic liquids (ILs)<sup>4</sup> have been studied as new plasticizers due to their unique properties. In addition, ionic liquids, besides acting as plasticizers, can impart several useful properties to prepared films due to their antioxidant, antibacterial and conductive activities<sup>5</sup>. Lately, dicationic ionic liquids (DILs), a new category of ILs family, attracted great concern as it represents an interesting variation of the cationic partner. Dicationic liquids are more tunable in comparison to

monocationic ILs because of large number of possible combinations of various anions, cations, and linker.

In this work, the influence of the type and the length of the linkage chain on film properties will be discussed through different techniques, such as the Fourier Transform Infrared Spectroscopy (FT-IR), X-ray diffraction analysis (XRD), Electrochemical Impedance Spectroscopy (EIS) and performing mechanical and antimicrobial activity tests.

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## *Chemical and technological solutions for the management of WEEE: the PINECOR project*

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Keywords: WEEE, recycling, PINECOR project

The growing marketing of Electrical and Electronic Equipment (EEE) and their increasingly short life cycle dramatically increase the production of waste derived from them (WEEE, Waste electrical and electronic equipment). Out of the total WEEE collected, the largest quantity, 117,472 tons, is represented by large whites (R2, for example washing machines), followed by cold and air conditioning with 98,937 tons (R1, for example refrigerators), by small appliances and photovoltaic panels with 71,494 tons (R4), by devices with screens with 71,035 tons (R3) and, rather distant, by the light sources with 2,444 tons (R5) [1].

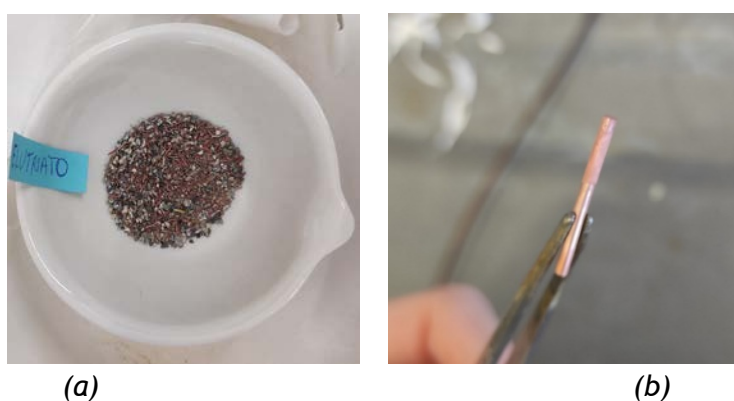
The recycling of WEEE if combined with an improved approach for the recovery of secondary raw materials could generate important implications both from an environmental point of view (correct disposal and reduction of waste volumes, adequate disposal of dangerous substances, decarbonisation) and from an economic point of view, i.e. recovery of valuable materials and their relocation in the value chain.

The PINECOR (ECO-efficient and Integrated Process for WEEE Recovery) project is co-financed by the Italian Ministry of the Environment and Energy Security (MASE) which aims to develop innovative solutions to optimize the recovery of glass and of siliceous and (basic and precious) metal fractions deriving from the recycling of WEEE. PINECOR intends to enhance the recovery of Secondary Raw Materials from "dry mechanical treatments" of WEEE rich in glass free of toxic metal oxides, with high reuse potential, intercepted in groupings R1, R2, R4. The applied process is integrated and eco-efficient and combines synergistic approaches, encouraging the reuse not only of the main fractions, but also of the residues which are currently sent for disposal and represent an additional cost. Regarding to grouping R4, in particular referring to mixed small household appliances, two processes were attempted for the separation of the product fractions (mainly metals and plastics): separation by means of dense homogeneous liquids and by means of the elutriation process. In both cases, the plastics and metals were separated by difference in specific weight. In the second case, we obtained the mix of plastic materials separated into three fractions (corresponding to three holes located on the back of the elutriator tube which, from top to bottom, allow the gradual

outflow of plastics of density growing. Elutriation works both on absolute density and apparent density, i.e., dependent on particle size). The main types identified by Step are shown below:

Step 1 – Lightweight plastic	Step 2 – Medium weight plastic	Step 3 – Heavy weight plastic
POLYSTYRENE	POLYPROPYLENE (PP)	POLYCARBONATE (PC)
POLYPROPYLENE (PP)	ACRYLONITRILE BUTADIENE STYRENE (ABS)	POLYOXYMETHYLENE (ACETAL) (POM)
STYRENE ACRYLONITRILE (SAN)		POLYAMIDE (PA 6)
BLEND OF POLYPROPYLENE AND ETHYLENE / PROPYLENE (PP+EPDM).		POLYCARBONATE / ACRYLONITRILE BUTADIENE STYRENE BLEND (PC + ABS)

Even the recovery of the metal fraction present in the mixture of small household appliances was considered (Figure 1(a)). The focus was the recovery of Cu, which not only constitutes the preponderant fraction, but also the one with the greatest value, in consideration of the current market price and its demand. The chemical process applied consists of a first phase of chemical leaching followed by galvanic electrodeposition and starting either from the ground waste as it is or from the same after physical separation of the different product fractions with an elutriator. This step allowed us to work with small quantities of solution, thanks to the reduced volume of incoming sample. In both strategies an acid solution based on chlorides and containing  $\text{Cu}^{2+}$  was used, maintaining the same solution both for the leaching phase and for the subsequent phase of galvanic electrodeposition. The composition of the leaching solution has been optimized in order to guarantee both a rapid solubilization of the metallic fraction and a galvanic deposition of the copper with high efficiency; the metallic copper obtained with this process is extremely pure (Figure 1(b)), as confirmed by the semi-quantitative analysis carried out by SEM-EDS.



**Figure 1.** (a) metallic fraction separated by elutriation; (b) copper electrode after electroplating.

## References

[1] 2022, Rapporto RAEE, Centro di Coordinamento RAEE.

## Acknowledgments

This research was co-financed by MASE/PINECOR project. Authors are thankful the other two industrial partners, TREEE Srl (Treatment and Recycling of Electrical and Electronic Equipment) and TRE EFFE Industrial Hydraulic Supplies srl, and SICER Spa - Raw materials and semi-finished products for the ceramic industry, which showed interest in the PINECOR project.



## Noble metal free Cu<sub>2</sub>O/TiO<sub>2</sub> catalysts for glycerol photoreforming

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### Introduction

The depletion of fossil fuels and the increasing of environmental pollution raised the interest of the scientific community towards renewable energy sources. Among the various energy sources, H<sub>2</sub> is considered the most promising clean energy carrier of the future [1]. The photocatalytic conversion of biomass into fuels and high value chemicals with the contemporary H<sub>2</sub> production is an ideal and sustainable alternative to the use of fossil resources [2,3]. In this context, glycerol is an interesting biomass derivative as it is obtained in large quantities as a waste product of the biodiesel production industry. Among the used photocatalysts, TiO<sub>2</sub> has aroused great interest as an anodic material for substrate oxidation because it is abundant, cheap and stable. As cathodic material, responsible for H<sub>2</sub> evolution, a noble metal like platinum has been often used [2] and today few cheap alternatives can be found in literature.

This contribute reports the results of anaerobic heterogeneous photocatalytic solar/UV light glycerol reforming in aqueous solution, using commercial TiO<sub>2</sub> loaded with platinum and/or coupled with copper oxide to verify the efficacy of Cu<sub>2</sub>O in replacing Pt for the formation of H<sub>2</sub>.

### Materials and method

The coupled samples were obtained by a simple and inexpensive ball grinding approach by mixing different amount of commercial TiO<sub>2</sub> Aeroxide P25 and Cu<sub>2</sub>O [4]. Samples containing Pt (0.5 wt%) were prepared, for the sake of comparison, by a photodeposition method [2]. The samples were characterized by X-Ray Diffraction, Raman spectroscopy, specific surface area measurements, Scanning Electron Microscopy, UV-Vis diffuse reflectance spectroscopy, Photoluminescence, Temperature programmed reduction and photoelectrochemical measurements. The photocatalytic activity was studied in a 250 mL cylinder-shaped Pyrex reactor by using a 125 W medium pressure Hg lamp (main emission peak at ca. 365 nm) or a 150 W halogen lamp (simulating the solar spectrum) as irradiation sources. During each run glycerol conversion, hydrogen and CO<sub>2</sub> formed in the gas phase and 1,3-dihydroxyacetone (DHA) and glyceraldehyde (GA) in the liquid phase were determined.

### Results and discussion

Commercial P25 displays a band-gap values typical of the anatase-rutile mixture; the deposition of Pt does not modify the value but increases the absorption in the visible

region (Table 1). The composites samples containing Cu<sub>2</sub>O present two absorption edges corresponding to the two oxides (at ca. 3.10 eV for TiO<sub>2</sub> and ca. 2.00 eV for Cu<sub>2</sub>O) that confirm the formation of a heterostructure. The addition of little amount of Cu<sub>2</sub>O did not influence the specific surface area of TiO<sub>2</sub>.

Pt-P25 was effective in the oxidation of glycerol with a conversion of 40.6 % after 5 h of irradiation and DHA selectivity of 11.4 %, and no GA was formed in the liquid phase. The maximum H<sub>2</sub> amount was 0.99 mM with an average production rate of 0.17 mmol h<sup>-1</sup>g<sup>-1</sup>. As far as the coupled systems are concerned, the best results were obtained with 3% Cu<sub>2</sub>O P25 and approximately, the same amounts of CO<sub>2</sub> and H<sub>2</sub> as those obtained with Pt-P25 were produced with a glycerol conversion of ca. 33%. In the presence of Cu<sub>2</sub>O also GA was formed due probably to the different surface properties with respect to pristine P25. By coupling P25 with 3%Pt-Cu<sub>2</sub>O a decrease in the photoactivity with respect to 3% Cu<sub>2</sub>O P25 was observed probably due to the Cu<sup>+</sup> photocorrosion under irradiation when it is in close contact with Pt. In the presence of the sample obtained after photodeposition of Pt onto the 3% Cu<sub>2</sub>O P25 composite, the same photoactivity of this latter was obtained confirming that Pt Cu<sub>2</sub>O plays the same role as Pt. The obtained results show the effectiveness of Cu<sub>2</sub>O in replacing Pt for H<sub>2</sub> production from glycerol photoreforming in water solution.

Table 1 Results obtained after 5 h of UV irradiation. X = glycerol conversion, S = selectivity. DHA = 1,3-dihydroxyacetone, GA = glyceraldehyde. \*Run carried out in pure water.

Sample	Eg (eV)	S.S.A. (m <sup>2</sup> g <sup>-1</sup> )	X [%]	S <sub>DHA</sub> [%]	S <sub>GA</sub> [%]	CO <sub>2</sub> [mM]	H <sub>2</sub> [mM]	H <sub>2</sub> [mmolh <sup>-1</sup> g <sup>-1</sup> ]
Pt-P25	3.12	48	40.6	11.4	-	0.15	0.99	0.17
2% Cu <sub>2</sub> O P25	3.08	51	22.3	9.55	13.5	0.08	0.35	0.06
	2.02							
3% Cu <sub>2</sub> O P25	3.10	48	32.9	10.3	5.39	0.16	1.01	0.17
	2.00							
4% Cu <sub>2</sub> O P25	3.09	48	21.3	9.94	11.2	0.08	0.45	0.07
	2.00							
3%(Pt Cu <sub>2</sub> O) P25	3.06	48	27.5	8.23	7.9	0.10	0.58	0.09
Pt (3% Cu <sub>2</sub> O P25)	3.20	48	35.2	9.19	7.89	0.19	1.10	0.18
3% CuO P25	3.06	47	11.5	16.1	11.2	0.05	0.33	0.05
3% Cu <sub>2</sub> O P25*	3.10	48	-	-	-	-	0.04	0.007
	2.00							

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## Magnetic nanocomposite aerogels in catalysis

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Keywords: nanocomposite, ferrite, aerogel

A strategy towards materials for heterogeneous catalysis is based on the use of sol-gel processes leading to well-defined features. These include controlled texture and porosity, as through the sol-gel method materials with tuneable surface area, pore size and pore architecture can be obtained. In particular, sol-gel processes including either conventional or supercritical gel drying procedures can be used to produce xerogels or aerogels. Although strategies for the production of aerogels are usually more challenging, materials with unique textural features such as extended and open porosity and large pore volumes can be obtained. For such reason, aerogels have been proposed both as catalysts and as supports for catalytically active nanophases.[1,2]

In this work, we report the investigation of magnetic nanocomposites based on magnetic ferrites dispersed on highly porous silica for the catalytic synthesis of a bis-heterocyclic compound. In particular, the synthesis of a bis-indolyl methane (BIM) has been studied, as these compounds represent promising substrates for pharmaceutical and chemical products.[3] The outcome of the reaction was assessed by <sup>1</sup>H NMR analysis of the crude mixture and it was found that the nanocomposite aerogels enable room temperature production of the investigated BIM compound. In addition, the magnetic properties inferred to the nanocomposite by the dispersed ferrite were exploited to recover the catalyst, enabling therefore optimization of the separation steps and prospective reuse of the catalyst. The results offer the possibility to investigate the potential and limitations of porous silica-based magnetic nanocomposites such as aerogels in catalytic organic synthesis.

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## Steel Slags based catalyst for partial hydrogenation of Fatty Acid Methyl Esters from Waste Cooking Oil

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Wastes offer an opportunity in terms of catalysis. The growing interest in their direct application as active materials is mainly driven by a combination of economic and environmental reasons. In this context, steel slags<sup>1</sup> can play a significant role in catalysis and their use is of great economic importance and could contribute to the reduction of solid waste. Herein, we report on the synthesis and characterization of a new catalyst based on steel slags with magnetic properties able to facilitate its recovery and reuse after the catalytic cycle. This new material was constituted of a nanocomposite of nickel nanoparticles and iron oxides deposited onto steel slags as support with basic features, and it was used as catalyst for the partial hydrogenation of FAMEs (Fatty Acid Methyl Esters)<sup>2</sup> coming from waste cooking oil. The partial hydrogenation reaction aimed at selectively converting all C18 polyunsaturated esters into C18:1 monounsaturated product, thus turning a waste into a feedstock for valuable biofuel (Figure 1).

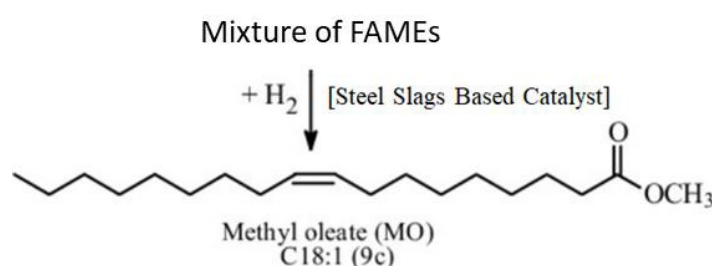


Figure 1: Hydrogenation reaction of FAMEs.

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## Catalytic valorisation of *Chlorella sp.* algae to obtain 5-Hydroxymethylfurfural in the presence of $Nb_2O_5$ or $NbOPO_4$

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Microalgae are interesting biomass able to growth in not-arable lands, in wastewaters or seawaters. There are plenty of species of microalgae and several of them find application in various industrial sectors because they are source of several products in an integrated biorefinery view [1]. In fact, after the solvent extraction of microalgal biomass, usually employed in biodiesel production, the remaining biomass which contains the carbohydrate fraction may be used for its sugar content. As proof of concept, the valorisation of the whole biomass from the recalcitrant *Chlorella sp.* microalga has been carried out in two-steps: i) the extraction of the sugar content and ii) its conversion into 5-hydroxymethylfurfural (5-HMF). Firstly, the pre-treatment of the lyophilised algae was optimized to obtain the maximum release of carbohydrate monomers and then a heterogeneous catalytic isomerisation/dehydration reaction was performed in order to convert the monosaccharides (essentially glucose and fructose) released from algae to yield 5-HMF. For this aim, two acidic heterogeneous catalysts, namely  $Nb_2O_5$  and  $NbOPO_4$  have been used. Both are commercial products provided by CBMM and they have been physico-chemically characterised. The isomerisation/dehydration reactions proceed through a tandem pathway involving the Lewis and Brønsted acid sites provided by the surface of the acidic solids giving rise to the isomerization of glucose to fructose, followed by dehydration of fructose to 5-HMF, as schematised in Figure 1.

Microalgae *Chlorella sp.* Pozzillo, isolated from Sicilian littoral, has been cultivated and molecularly characterized [2]. The biomass was harvested, frozen and freeze-dried. An acidic hydrolysis was performed for the quantification of total monosaccharides content. In order to valorise the biomass, a preliminary treatment is mandatory to break the membrane of the algae cells for the releasing of the carbohydrates to obtain C6 and C5 sugars in solution. For this aim, the *Chlorella sp.* was subjected to various pre-treatments, pursuing the best conditions to yield the greatest quantity of sugars in solution (avoiding the use of concentrated HCl).

Different experimental settings, such as sonication, hydrothermal treatment, acidic hydrolysis with aqueous diluted acetic acid were tested in combination or alone. The further presence of SiO<sub>2</sub> pellets (10 g·L<sup>-1</sup>; 0.2÷0.5 mm) was also tested. After the treatments, the suspensions were filtered and the concentration of sugars analysed by HPLC. The use of ultrasonication and successive hydrothermal treatment in acetic acid solution in the presence of the SiO<sub>2</sub> pellets gave the best results yielding in solution to a 35 % of the total sugars present in the algae.

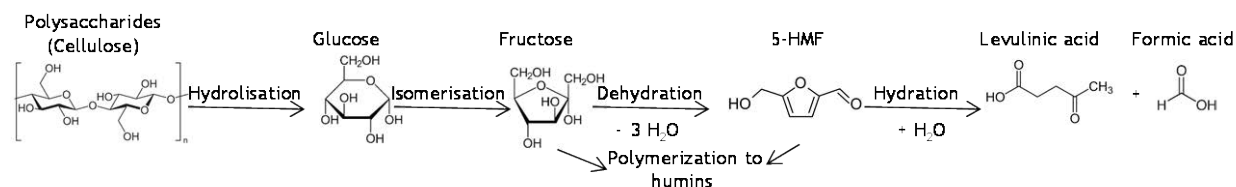


Figure 1. Scheme of the reaction for 5-HMF production from the cellulose provided by the algae by different steps involving acidic catalysis.

The successive isomerisation and dehydration of the carbohydrates extracted from the algae to obtain 5-HMF, was performed by heterogeneous catalysis in hydrothermal conditions. Nb<sub>2</sub>O<sub>5</sub>, was used to identify, through a DoE approach, the best reaction conditions, that were 4.45 h of reaction at 210 °C with 200 % in mass of catalyst with respect to the lyophilized alga. A yield to 5-HMF of about 18 % of the total sugars contained in the algae was obtained. A further optimisation has been achieved in the presence of NbOPO<sub>4</sub>, which resulted more acidic than Nb<sub>2</sub>O<sub>5</sub> and which led to 21 % yield to 5-HMF on the total sugars.

The higher number of Brønsted acidic sites (BASs) on the NbOPO<sub>4</sub> catalyst surface with respect to Nb<sub>2</sub>O<sub>5</sub> has been claimed to justify its better performance [3]. Indeed, both hydrolysis of polysaccharides to monosaccharides and dehydration of fructose to 5-HMF are mainly catalysed by BASs, the increased yield to 5-HMF in the presence of NbOPO<sub>4</sub> can be attributed to the improvement in both these two steps of the overall process. These results were furtherly optimised through the use of NbOPO<sub>4</sub> as catalyst in a biphasic system, using an H<sub>2</sub>O/MIBK (50/50 v/v). A reactive extraction was performed, obtaining a yield to 5-HMF of 29 % on total sugars.

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## Selective photocatalytic degradation in the presence of amine-stabilized boronate groups grafted at the surface of TiO<sub>2</sub>

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Heterogeneous photocatalysis (HP) has been mainly applied to environmental remediation due to the capability of unselectively degrading most of the organic pollutants present in the reaction medium. However, recent literature demonstrated the possibility of selectively performing reactions of industrial interest as greener alternatives to existing processes. [1] The selective protection and recovery of valuable compounds present in waste streams together with other useless or noxious species is the challenge of a more actual environmental approach, combining waste remediation and reuse of valuable resources. For instance, industrially relevant catecholic compounds are often present along with other organic compounds in agricultural and food industrial waste streams which need to be treated. [2] The objective of this work is to provide a proof of concept of the possibility displayed by HP to selectively bind and protect from degradation a model 1,2 diol compound (Alizarin red, AR), while simultaneously performing the degradation of a second model pollutant (Methylene blue, MB). To this aim, the surface of a commercial TiO<sub>2</sub> (Evonik P25) has been functionalized with 3-aminopropyltrimethoxy silane (APTMS) and 4-carboxyphenylboronic acid (CPBA) and the catalysts has been used to carry out photocatalytic tests in aqueous solution containing both the model compounds (AR and MB) under visible light irradiation.



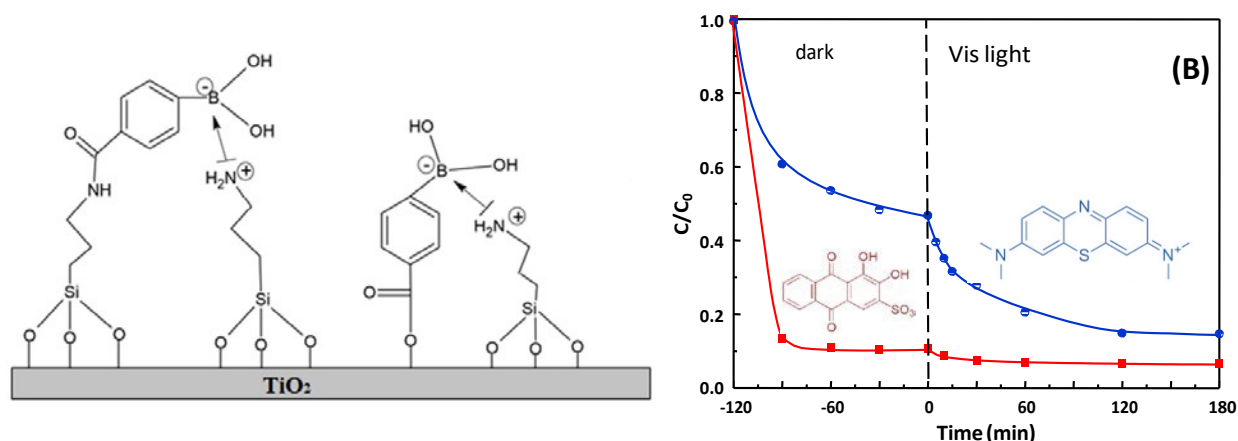


Figure 1. Scheme of the amine-stabilized boronate at the surface of TiO<sub>2</sub> (A). Normalized concentration of MB (blue) and AR (red) versus visible light irradiation time in the presence of surface modified TiO<sub>2</sub>.

A thorough solid state NMR characterization indicated that ca. 50% of the amino groups did not react with the carboxylic group of CPBA, but stabilized vicinal boronate groups as shown in Figure 1A. The amino-stabilized tetracoordinated boronate groups can bind selectively AR through reversible covalent interactions, but not MB molecules. Accordingly, oxidation of both model compounds was observed in the presence of bare TiO<sub>2</sub> (data not shown) as expected. Instead, the presence of amino-stabilized boronate groups at the surface of TiO<sub>2</sub> hindered the photocatalytic degradation of AR, while simultaneously allowing oxidation of MB (Figure 1B). In fact, electron transfer from the excited dye to the conduction band of TiO<sub>2</sub> is possible for MB, but not for AR molecules interacting with the boronate groups. The presence of the amino groups enables the existence of these interactions, generally taking place at pH > 8.8, also at natural pH values. This is a remarkable advantage for practical applications. Results envisage the possibility of designing processes for the recovery of valuable compounds while simultaneously degrading other noxious and/or useless species present in the same stream.

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# Degradation of oxytetracycline in water using photocatalyst powder immobilized on mullite ceramic foam

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Keywords: Heterogeneous photocatalysis, Lanthanum ferrite, Oxytetracycline

## Introduction

The immobilization of a photocatalyst on a solid support is essential for practical environmental applications, as the photocatalyst is then not dispersed in the solution with contaminants and can be recycled numerous times. LaFeO<sub>3</sub> powder and LaFeO<sub>3</sub> supported on a mullite-based ceramic foam are promising materials in the photocatalytic degradation of oxytetracycline (OTC) under visible light irradiation and in the presence of H<sub>2</sub>O<sub>2</sub> [1].

## Experimental

Oxytetracycline dyhydrate ( $\geq 97\%$ ) is used as model pollutant. LaFeO<sub>3</sub> nanopowder was prepared by citrate auto-combustion method as described in our previous work [2]. Synthetic mullite is a ceramic with chemical formula Al<sub>4+2x</sub>Si<sub>2-2x</sub>O<sub>10-x</sub> (x=0.4). The foam was prepared from ceramic slurries by the replication process with an open polyurethane sponge as the template. The macropores of the mullite foam were 0.5-5.0 mm in diameter. The photocatalyst powder covering the outer surfaces was placed layer by layer through dropping repeatedly an alcohol slurry of LaFeO<sub>3</sub> powder and then thermal treated in air at moderate temperature. With this procedure, the catalyst particles remain nanometric. Degradation of OTC was evaluated in buffered solutions (phosphate buffer, pH=5.0) since at pH=5.0 OTC is poorly photolyzed due to the scarce visible light absorption. An OTC solution ( $5.0 \times 10^{-6}$  M) was prepared with distilled water (phosphate buffer) and the oxidising agent (0.003 M H<sub>2</sub>O<sub>2</sub>) was added at the time of the experiment. Parallel tests were carried out, one with the LaFeO<sub>3</sub> supported on the mullite foam, the other with the mullite foam without catalyst. The initial OTC solution was divided into the two glass reactors. A volume of 400 mL of OTC was poured into each reactor and the foam was then inserted. The mixtures were stirred in the dark for 20 minutes in order to allow adsorption/desorption equilibrium on the mullite foam

and catalyst surface. Then, two fluorescent lamps (daylight, 8W each) emitting in the 380-780 nm region were turned on for 4 h. All degradation tests were repeated twice.

## Results

Photocatalytic removal of OTC in water is presented in Figure 1. After 240 min of irradiation, the mullite foam without catalyst and LaFeO<sub>3</sub> supported on the mullite foam degraded 34% and 50% of OTC, respectively. The addition of H<sub>2</sub>O<sub>2</sub> increases the photodegradation rate of organic pollutants by removing the surface-trapped electrons, thereby lowering the electron-hole recombination rate and increasing the efficiency of hole utilization for reactions, such as  $\text{OH}^- + \text{h}^+ \rightarrow \bullet\text{OH}$ .

Generally, preliminary adsorption of substrate molecules on the surface of the catalyst is necessary for highly efficient photocatalytic degradation. The adsorption of molecules on metal-oxide surface is influenced by the acid-base properties of the surface. The point of zero charge (PZC) for LaFeO<sub>3</sub> is at pH= 8.9 suggesting that the surface charge of catalyst is positive in our tests. OTC exists predominantly as a zwitterion between pH 3.6 and 7.5 resulting from the loss of proton from the phenolic diketone moiety. In this study the OTC solution is buffered at pH = 5.0, so OTC is in its zwitterionic form. Physisorption of OTC molecules on mullite foam promotes photodegradation of the contaminant by their surface diffusion to the photocatalytic sites.

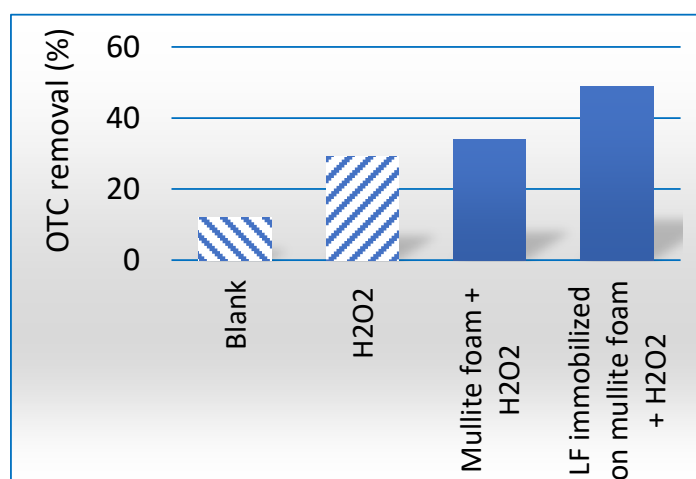


Figure 1. (A) Photocatalytic degradation of OTC after 240 min of visible light irradiation. LF = LaFeO<sub>3</sub>, C<sub>0</sub>=5·10<sup>-6</sup> M, the OTC solution is phosphate buffered at pH = 5.0.

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## *ABO<sub>3</sub> perovskite oxides as candidate materials for hydrogen storage*

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Finding an alternative energy source to fossil fuels is a priority among the goals of our society. In fact, fossil fuels provide over 80% of all energy consumed globally and, in particular, the transport sector accounts for almost 60% of the world energy consumption. [1] Among the most sustainable sources hydrogen is the favourite because it has high energy storage capacity, equal to 120 MJ/kg (= 33.33 kWh), and its only reaction product is H<sub>2</sub>O. However, hydrogen has an extremely low density (0.089 kg/m<sup>3</sup>), hence for its storage the solid state would be the most effective solution. [2] Metal hydrides have been widely investigated to this aim due to their high hydrogen storage densities, but they are also characterized by slow kinetics and are unable to release hydrogen at low temperatures, as the applications require. [3] As candidate materials for hydrogen storage we are evaluating ABO<sub>3</sub> perovskite oxides because these materials have a high thermal stability, they are relatively active, they allow the exploitation of a great variety of elements in the composition while maintaining the basic structure unchanged and, to improve its efficiency, it is also possible to easily vary the stoichiometry.[4] Among the different materials investigated CaMnO<sub>3</sub> (CM) seems to be the most promising. This material was synthesized by Pechini method and characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) microscopy analyses. Moreover, to determine the theoretical maximum hydrogen amount that can be stored in the structure of CM structural evaluations were applied. Due to orthorhombic structure of this compound and considering the presence of octahedral voids (whose dimension is 2.82 Å<sup>3</sup>), we evaluated the fitting of both molecular hydrogen and hydride ion. So, approximating the species to a sphere, we can observe that hydrogen as H<sup>-</sup>, with an ionic radius of 1.34 Å cannot fit into the material structure considered, while molecular hydrogen, with a radius of 0.74 Å, can theoretically fit into an octahedral void. Then the H<sub>2</sub> adsorption/desorption measurements as a function of pressure (till 40 bar of H<sub>2</sub>) were carried out with a High Pressure Gas Sorption Analyzer (i-Sorb Anton Paar), a volumetric system, at different temperatures. The achieved results have shown that the non-stoichiometric amount of oxygen affects the hydrogen storage capacity. In particular, the structures with an excess of oxygen exhibit a higher H<sub>2</sub> absorption capacity: at 100

°C, CM absorbs 0.44 kg/m<sup>3</sup> of H<sub>2</sub> while the uptake of H<sub>2</sub> for CaMnO<sub>3±δ</sub> is 0.98 kg/m<sup>3</sup> (Figure 1).

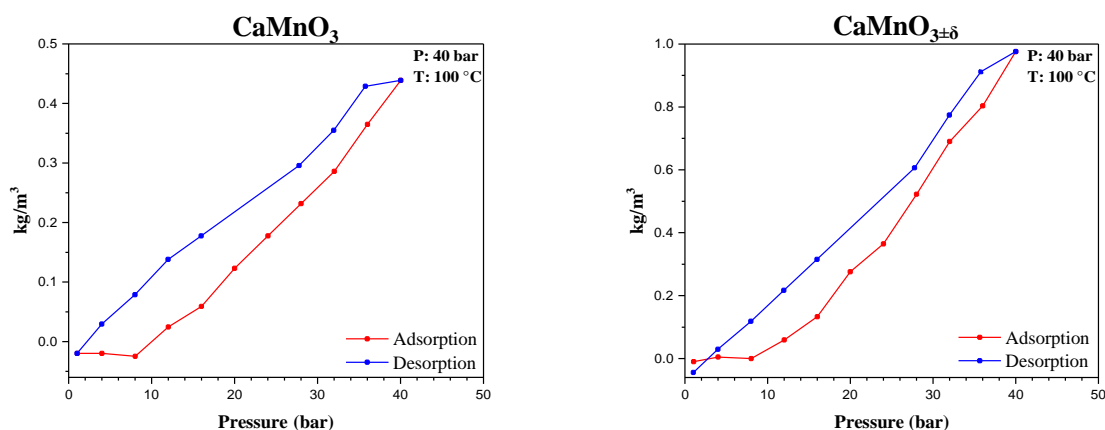


Figure 1. Adsorption/desorption of H<sub>2</sub> at 40 bar e 100 °C for CaMnO<sub>3</sub> and CaMnO<sub>3±δ</sub>.

In order to enhance the storage capacity of these oxides, we are also investing the addition of 1% wt. Pd<sup>0</sup>, which should promote the dissociation of hydrogen and, therefore, improve the ad/desorption kinetics of this gas. As a result, we observed that, at the same experimental conditions, the materials in presence of Pd<sup>0</sup> absorbs a significantly larger amount of H<sub>2</sub> 12.88 kg/m<sup>3</sup> and 44.95 kg/m<sup>3</sup> respectively (Figure 2). What is more, they are able to retain it for future utilization.

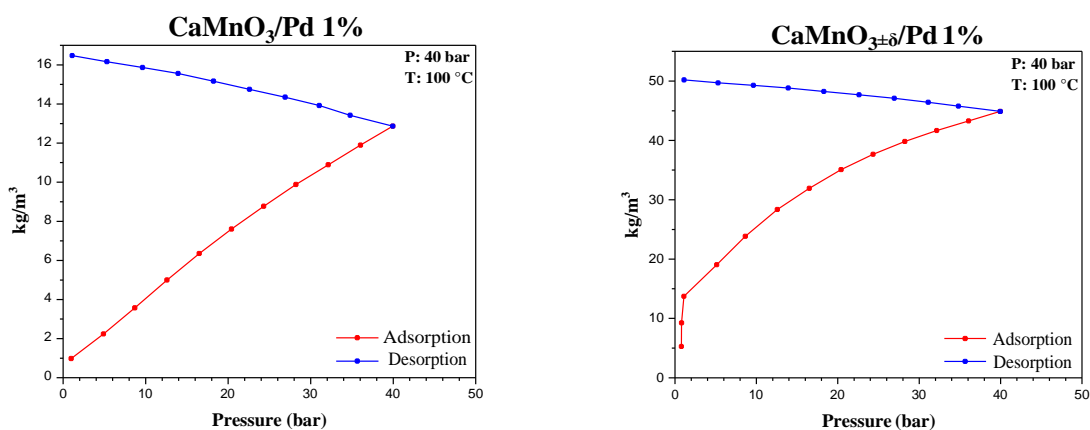


Figure 2. Adsorption/desorption of H<sub>2</sub> at 40 bar e 100 °C for CaMnO<sub>3</sub>/Pd 1% and CaMnO<sub>3±δ</sub>/Pd 1%.

Further studies are ongoing to investigate the gas release conditions and eventual structural modifications to better understand the mechanism by which hydrogen is stored and consequently improve the storage efficiency.

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## *Towards the recovery of metals from spent lithium-ion batteries: an academy-industry joint venture to face the several challenges*

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Keywords: hydrometallurgy, metal recovery, circular economy

Lithium-Ion Batteries (LIBs) are electrochemical devices almost ubiquitous today, from portable electronics to electric vehicles. The presence of some critical materials (e.g., Co, Ni and, from 2020, Li) is forcing the scientific and industrial community to find out effective strategies to recover such materials from the constantly increasing spent LIBs. This is a critical target for the reduction of the EU's socio-economic dependence on foreign Countries for this strategic technology. Today, pyrometallurgical technologies for spent LIBs treatment are available, however the stringent recovery rate defined by EU for the coming years can only be achieved by developing efficient hydrometallurgical recovery processes.

Despite the relatively simple working principle, LIBs are very complex devices in which many different materials are tightly compressed, stacked or rolled together to craft objects with the plenty of combination of chemistry, shape and dimension available on market. This great variety entails challenges for the recycling processes. Firstly, an automatic opening/disassembling step of spent LIB cells aimed at removing the two electrodes (and the separator) intact from the protective case is a very hard task especially when thinking about industrial volumes. At the moment, the only industrially acceptable way for treating spent LIBs is to shatter them, originating heterogeneous mixtures of strips (or, in worst conditions, agglomerates) of metallic case, plastic separator and shielding, and current collectors on which the electroactive materials is attached (metal oxides on the cathode and graphite on the anode). After a step deputed to detach as much active material as possible, this black mass is sent to the chemical stages of a hydrometallurgical process aimed at dissolving the metal compounds.

Secondly, to overcome the difficulty in sorting the incoming spent LIBs by their chemistry, and considering the need to recycle all of them, the development of a robust

process capable of treating any type of battery is required. In the scientific literature, there are many different hydrometallurgical strategies aimed at recovering critical metals from LIBs but they mainly act on single chemistries, being either pristine metal oxides or real samples often obtained by a manual detachment of the metal oxide powder from the thin sheets of the aluminium collector.

In the present research project, part of the *European Battery Innovation* project (IPCEI Batterie 2), we try to fill this experimental gap, providing effective clues on the efficacy and efficiency of leaching performed on black mass samples from “industrial grade” grinded spent LIBs. The first issue of working with such real samples, which are heterogeneous mixtures and in the scale of kilograms, has been the determination of a reliable average composition in terms of metal contents. Then, leaching efficiency was evaluated for a series of low cost and commonly available organic acids and complexing agents (Figure 1, top) identified as alternatives potentially more environmentally friendly than strong mineral acids. An *in operando* tri-parametric protocol for the on-line monitoring of the leaching was developed. Eventually, clues revealing the differences in the interaction between metal ions and the two most promising leaching agents will be disclosed (Figure 1, bottom).

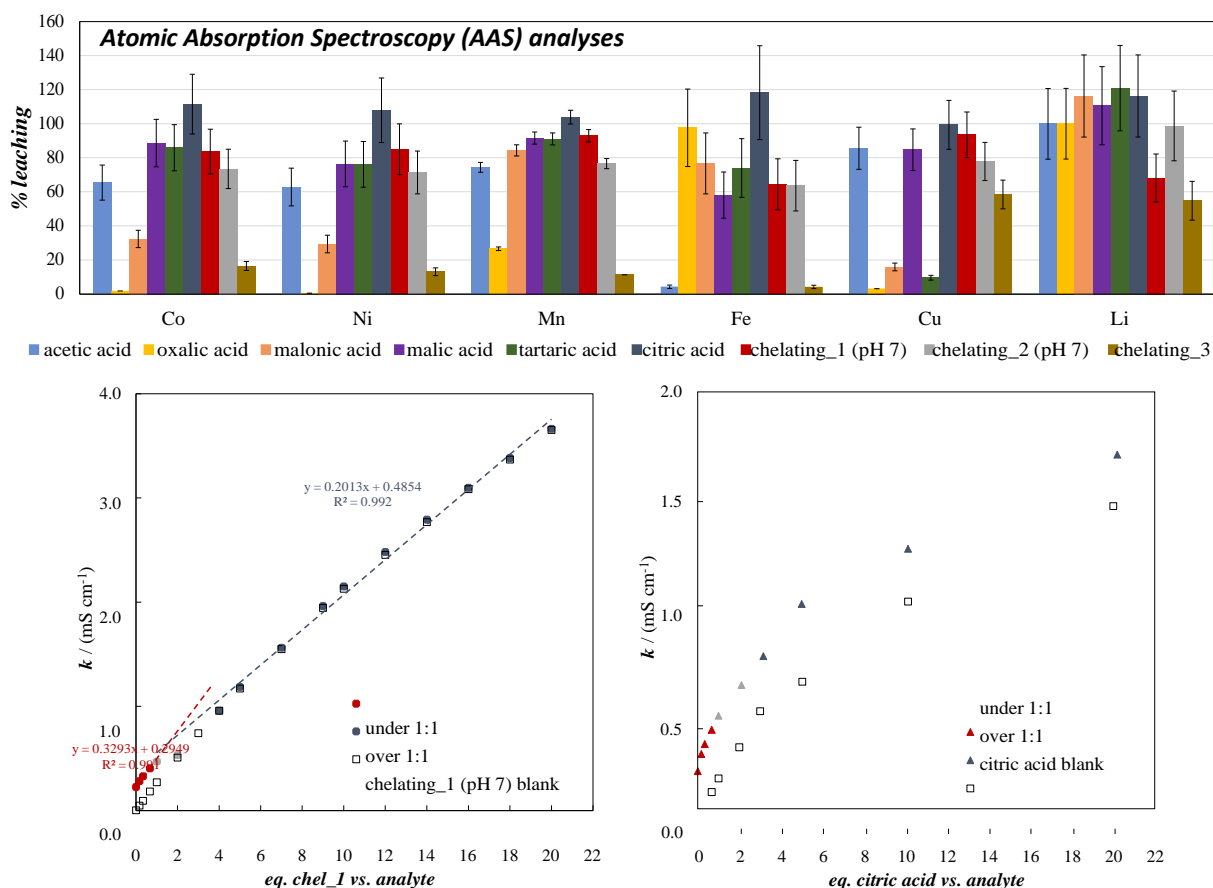


Figure 1. Top: leaching efficiency of the organic agents. Bottom: variation of conductivity as a function of the amount of the leaching agent vs. metal ion. Here the case of a solution with 1 mM  $\text{Co}^{2+}$  ions.

### Acknowledgments

Mirko Magni thanks FSE-REACT-EU PON “RICERCA E INNOVAZIONE” 2014-2020 and Engitec Technologies SpA for co-funding his current researcher position. Engitec Technologies is also thanked for supporting the participation to the present congress.



## *Oxidative cleavage of C=C double bond through nitrate radicals generated in photocatalytic TiO<sub>2</sub> suspensions*

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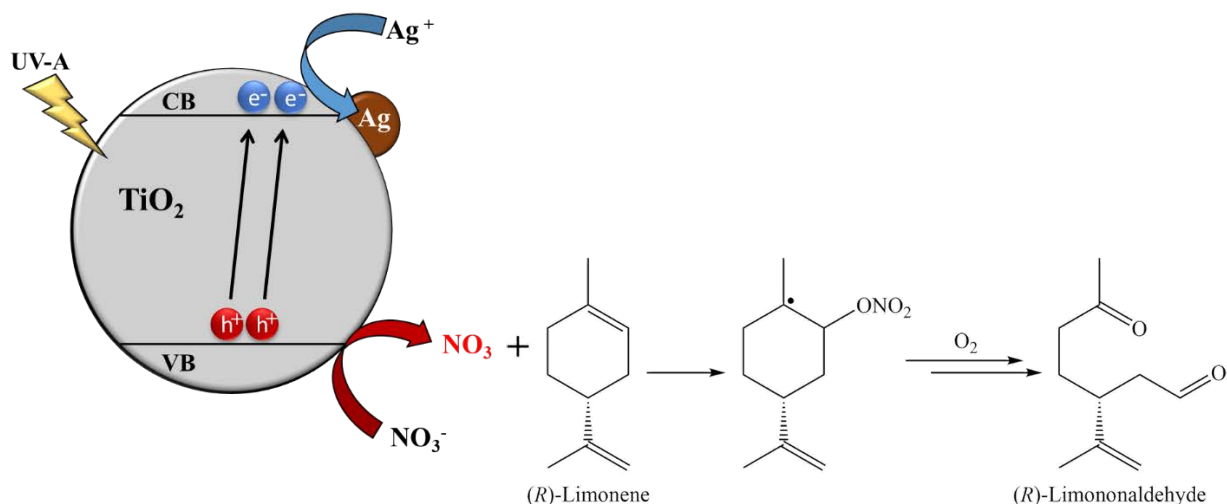
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Keywords: Nitrate radicals, TiO<sub>2</sub> photocatalysis, C=C oxidative cleavage

Alkenes are highly important compounds in modern industrial chemistry due to their versatility as starting materials for a wide range of reactions, including electrophilic addition/substitution, hydrogenation, and oxidation [1]. When exposed to strong oxidizing agents, alkenes can be oxidatively cleaved, yielding valuable carbonyl compounds [2-3]. Additionally, the oxidative cleavage of cyclic olefins is particularly intriguing because it can lead to the production of bi-functionalized  $\alpha,\omega$ -compounds, which can serve as precursors for various polymers, resins, and plasticizers, such as polyamides and polyurethanes [4]. Although several methods have been proposed so far for the oxidative cleavage, many of those involve the use of stoichiometric unfriendly oxidizing agents or harsh reaction conditions, which go in contrast with green chemistry principles making these methods inappropriate for industrial application. On the other hand, the main industrially implemented process (hydroformylation), requires drastic conditions (200 °C and 100 atm) and occurs in the presence of homogenous catalysts [5], thus alternatives based on heterogeneous catalytic systems which take place under mild conditions are required.

Nitrate radicals have been extensively researched for their interactions with natural and anthropogenic volatile emissions in the atmosphere [6]. These radicals can specifically react with unsaturated bonds, leading to the formation of carbon-centered radicals and, consequently, a broad scope of organic oxidized compounds [7]. Although

nitrate radicals have industrial potential, their production has been challenging, hindering practical applications. Recently, a new method has been proposed for the photocatalytic generation of nitrate radicals using titanium dioxide under mild and greener conditions [8]. Building on this method and the chemistry of nitrate radicals in the presence of olefinic compounds, we developed a novel photocatalytic synthesis method for carbonyl compounds using commercially cheap and robust  $\text{TiO}_2$  as photocatalyst. *R*-Limonene has been utilized as a prototypical olefinic compound for the purpose of elucidating its potential industrial applications as a fundamental building block for novel materials. Moreover, given its characteristic structural feature of possessing two double bonds, limonene serves as a valuable model for the study of the selectivity of reaction mechanisms. Upon careful optimization of the experimental conditions, we achieved selectivity values towards limononaldehyde up to 60% within 60 min of irradiation with UV-A with an overall yield of 36% in a batch reactor using bare  $\text{TiO}_2$  P25. Nonetheless, this method is general and can be extended to other olefinic compounds, potentially enabling the production of other industrially important compounds. On top of that, the addition of nitrate radicals to unsaturated bonds offers a practical and convenient approach for the synthesis of carbonyl compounds from olefins, as well as a promising alternative to traditional methods for producing fine chemicals.



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## Carbon Dots: Electrochemical Synthesis and Applications

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Keywords: carbon dots, electrochemical synthesis, heterogeneous catalysis

Carbon dots (CDs) are quasi-spherical fluorescent carbon-based nanomaterials, with a diameter usually equal to or less than 10 nm. These nanoparticles are characterized by a carbon core and a surface functionalized with different chemical groups. Since their discovery in 2004, several synthetic procedures have been developed over the years, with the aim of modulating their size, the chemical groups present on the surface and therefore their physicochemical properties. Overall, the synthetic approaches for CDs preparation can be divided into two groups: top-down and bottom-up. In the top-down processes large carbon-based materials (such as nanotubes, graphite, graphene) are fragmented by physical or chemical methods to form nanoparticles; on the other hand, in the bottom-up processes CDs are obtained by oxidation, polymerization and carbonization of small molecules [1]. Due to their peculiar and interesting features, such as chemical stability, water solubility, low toxicity, excellent biocompatibility, in combination with photoelectric properties, CDs have generated considerable interest in different scientific areas. Indeed, they have been employed in many fields, such as in chemical and electrochemical sensors, in photovoltaics, as well as in nanomedicine, applied in bioimaging, as drug carriers or for the detection and inactivation of different microorganisms.

In light of these considerations, we developed an electrochemical synthesis of CDs by bottom-up method, using different molecules as carbon sources, in order to obtain nanoparticles with variable surface functionalization. Galvanostatic or potentiostatic conditions were employed and evaluated to modular the physicochemical properties of CDs. The obtained nanoparticles were characterized by SEM, FT-IR, UV-Vis and fluorescent excitation and emission spectra [2]. The variable surface functionalization and the consequent effects on their physicochemical properties can pave the way for advance applications of these CDs in organic chemistry, nanomedicine, and photovoltaics devices.

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## *Enhancing thermal conductivity of polymer nanocomposites through filler functionalization*

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Keywords: nanocomposites, silsesquioxanes, thermal conductivity

In advanced electronic applications, it is necessary to choose and adopt materials that primarily own high thermal conductivity and electrical insulation, but also good processing ability, flexibility and corrosion resistance in order to design small, flexible and portable devices. Polymers are widely employed in industrial applications, from electronics to biomedical applications, due to their remarkable features, such as light weight, structural compactness, resistance against corrosion, ease of processing, low cost and good chemical stability. However, the limited thermal conductivity (TC) of polymers is one of the main technological obstacles for specific applications, such as electronic packaging. The production of innovative polymer composites with improved thermal conductivity is necessary to overcome this issue [1].

In this sense the present study explores the development of hybrid nanocomposites (NCs) made of bare or functionalized Al<sub>2</sub>O<sub>3</sub> nanoparticles (NPs) and ladder-like polysilsesquioxanes (LPSQ), investigating the effect of particles functionalization. Ceramic NPs are chosen since they provide high TC and electrically insulating properties [1], whereas the LPSQ are exploited since they provide improved mechanical, thermal, dielectric properties and supply excellent compatibility with polymeric matrices [2].

In detail, the NPs are functionalized with the same organosilane used for the preparation of the ladder-like structured poly(methacryloxypropyl) silsesquioxanes (LPMASQ), i.e. methacryloxypropyltrimethoxysilane (MPTMS) (Figure 1). Having the same functional group promotes an improved compatibility and a homogeneous distribution of the filler (i.e. alumina NPs) in the silsesquioxane matrix even at high filler concentrations.

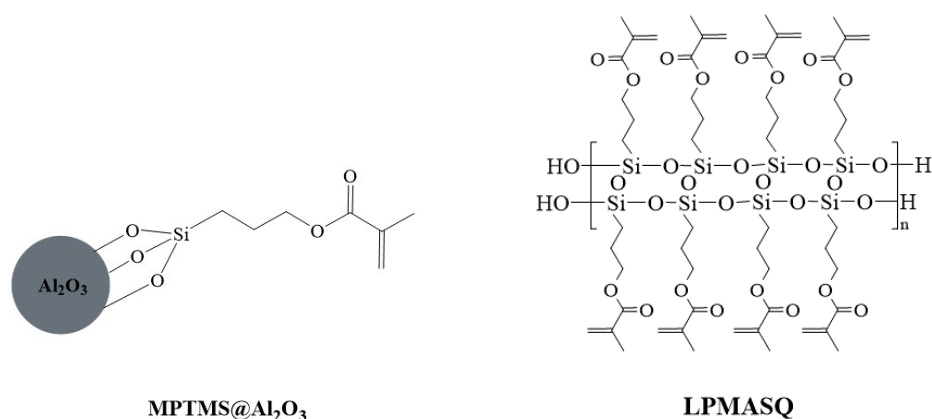


Figure 1: Alumina nanoparticles functionalized with methacryloxypropyltrimethoxysilane (left), ladder-like structured poly(methacryloxypropyl) silsesquioxanes (right).

Different loadings of bare and functionalized alumina NPs (MPTMS@Al<sub>2</sub>O<sub>3</sub>) are dispersed in the LPMASQ solution and a variable amount of photoinitiator is added to the mixture. Nanocomposites films are prepared by a simple solvent-casting technique followed by UV curing. Photoinduced crosslinking is monitored using Attenuated Total Reflection Fourier Transform Infrared (ATR FTIR) spectroscopy and solid-state Nuclear Magnetic Resonance (NMR). The thermal evolution of the nanocomposites is evaluated by thermogravimetric analysis (TGA). Thermal conductivity ( $k$ ) of NCs is calculated from the values of samples density ( $\rho$ ), specific heat capacity ( $c_p$ ) and thermal diffusivity ( $\alpha$ ), exploiting the equation:

$$k = \rho \cdot c_p \cdot \alpha \quad \left[ \frac{W}{m \cdot K} \right]$$

SEM images show a high homogeneity in the dispersion of fillers in the composites with functionalized NPs, as well as a strong interface between the particles and the LPMASQ. On the other hand, the composites prepared with bare nanoparticles show the presence of aggregates. It is worth noting that functionalization of the NPs allows higher amounts of filler to be added to LPMASQ due to their enhanced suspending ability, thus improving the degree of crosslinking in the final composites and producing a significant increase in thermal conductivity. In fact, the TC of composites filled with bare alumina NPs increases linearly with filler concentration up to an increase of 77.4% (at the maximum possible loading equal to 17.1 vol%) with respect to LPMASQ, while composites with functionalized NPs show a remarkable increase in thermal conductivity up to 107.2%, with a filler content of 40.1 vol%.

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## Low-Cost Metal-Free Electrodes for the Oxygen Reduction Reaction

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Keywords: Electrocatalysts, Carbon Quantum Dots, Ionomer

The oxygen reduction reaction (ORR) is of fundamental importance for the performance of many electrochemical devices such as solid electrolyte fuel cells (PEFC). The large energy required to break the O=O double bond ( $\approx 500$  kJ/mol), especially under acidic conditions, requires the use of expensive catalysts such as platinum group compounds. Under alkaline conditions, the ORR is faster, so catalysts based on alternative materials that do not contain noble metals can be employed.

In this work, nanomaterials based on carbon quantum dots (CQDs) were synthesised and their use as catalysts for anion-exchange membrane fuel cells (AEMFCs) was investigated.

Starting from low-cost, non-toxic precursors and employing a not expensive synthesis technique such as hydrothermal methods, CQDs with different functional groups were synthesised. The CQDs obtained were used to make electrodes whose catalytic capabilities were tested.

To develop an electrode, a polymeric binder is required in addition to the catalyst, whose task is to avoid aggregation of the catalyst, oxygen permeability and ensure the transport of the hydroxide from the catalyst to the anion exchange membrane (AEM).

In this study, we will show the results obtained in our laboratories with electrodes developed using activated carbon paper, CQDs as catalysts and different binders. This contribution will show the results obtained so far.

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## *Nanobiochar wasted-derived from orange peel for the detection of nitrites and sulfites by electrochemical sensor*

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Keywords: Nanobiochar, orange peels waste, nitrites and sulfites

Nitrites and sulphites are preservatives found in many beverages and foods, but their use can cause considerable pathologies in humans such as intestinal tumours [1], allergic reactions, nausea, etc. [2,3]. The use of these substances in daily life increases the need for the development of a method for monitoring these compounds on real samples to safeguard human health and the development of sensors capable of simultaneously detecting these contaminants [4]. In the literature we find various sensors for monitoring nitrites and sulfites, but few examples have been reported for the simultaneous detection of these [5].

Carbon nanomaterials are of great interest because of their excellent electrochemical properties, particularly those derived from green sources [6]. Among the carbon nanomaterials, nanobiochar (NBC), derived from natural sources is highly studied for the development of sensors [7] and its good properties (high porosity, large surface area, presence of functional groups, etc.) [8] can be further improved through activation techniques. The dimensions of this material are less than <100 nm [9], and the most used synthesis method for its production is a top-down approach.

The work we present aims to develop a sensor for the simultaneous detection of nitrites and sulfites from orange peel by the synthesis of biochar by hydrothermal carbonization (HTC). The biomass used and the synthesis parameters, such as temperature, time, etc, can generate different hydrochar (HTC) with different properties. The resulting HTC was activated by basic treatment and subsequent filtration on 100 nm Millipore to extract only the smallest particles. In this way, after a subsequent purification with dialysis bags, the nanobiochar obtained was characterized and used for the development of the electrochemical sensor (NBC/SPCE). The NBC/SPCE response showed the ability of this sensor to detect the presence of nitrites and sulfites both in separate solutions and simultaneously showing a detection limit (LOD) of 2.08 and 43  $\mu\text{M}$  respectively, also showing good stability and repeatability of the analysis. The

excellent sensor capabilities also showed the possibility of using this device for detection in real samples such as commercial mineral water and white wine (Fig.1).

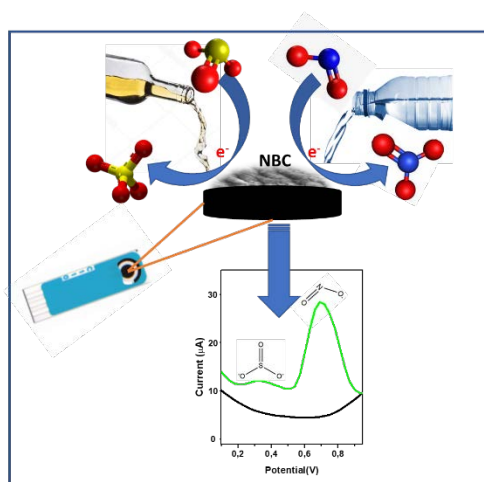


Figure 1. Representation of the simultaneous response of nitrites and sulfites with the NBC/SPCE sensor.

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## Different Strategies to Increase the Stability of Anion Exchange Membranes

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Keywords: fuel cells, anion exchange membranes, stability

The ever-growing energy demand with the simultaneous need to drastically reduce polluting emissions leads to consider increasingly efficient energy conversion systems; among these, polymer electrolyte fuel cells are extremely promising.

In the International Laboratory Ionomer Materials for Energy (LIME) research has focused in recent years on anion exchange membrane fuel cells (AEMFC). Unlike the more common proton conduction cells, AEMFCs have the advantage of not using noble metal catalysts for the oxygen reduction reaction (ORR).

Unfortunately, the low durability of anion exchange membranes (AEMs) in basic conditions limits their use on a large scale [1]. Durability can be discussed in terms of the stability of cationic groups (usually ammonium groups) responsible for the ion conduction, and the stability of the backbone responsible for the mechanical properties. Quaternary ammonium groups exhibit several degradation mechanisms: second order nucleophilic substitution  $S_N2$ , Hoffman elimination (E2) and Ylide formation. The backbone, when functionalized, becomes sensitive to attack by  $OH^-$ , which degrades its structure. As a result, the conductivity is lower and the polymer becomes brittle.

Various strategies have been explored to mitigate the degradation of AEMs due to alkaline media: charge delocalization [2], introduction of a long chain to separate the charge and the backbone [3], introduction of a second phase [4], synthesis from monomers to obtain a backbone without ether groups.

In this contribution, after a short overview of the progress made on anion exchange membranes based on commercial polymers, such as polysulfone (PSU) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [5], we will focus on the synthesis of two new ionomers with a backbone devoid of alkaline-labile ether bonds: poly(alkylene biphenyl

butyltrimethyl ammonium) (ABBA) [6], and poly (vinylbenzylchloride-co-hexene) copolymer grafted with N,N-dimethylhexylammonium groups [7].

ABBA was obtained via polycondensation of a specific long side chain precursor, followed by quaternization with trimethylamine (TMA). The reaction was efficient, easy to modulate and reach a high IEC values such as 2.5 meq/g. The crosslinked poly(vinylbenzylchloride-co-hexene) copolymer grafted with N,N-dimethylhexylammonium groups was obtained by copolymerization with Ziegler-Natta method, employing the complex  $ZrCl_4 (THF)_2$  as a catalyst. The resulting aliphatic ionomer showed good alkaline stability and after 72 h of treatment in 2M KOH at 80°C the remaining IEC was 76%, confirming that ionomers without ether bonds are less sensitive to  $S_N2$  attack.

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# Synthesis and characterization of tailored PBS-PCL cross-linked systems as potential shape-memory material

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Keywords: semicrystalline networks, shape-memory properties, smart materials

Polycaprolactone (PCL) and polybutylene succinate (PBS) are biodegradable semicrystalline polyesters with low  $T_g$  (-60 and -40 °C, respectively) and quite different melting temperatures around 60 and 110 °C, respectively. Here the preparation and thermal characterization of tailored semicrystalline cross-linked networks through the photopolymerization of methacrylated PCL and PBS<sup>1</sup> is described (*figure 1*).

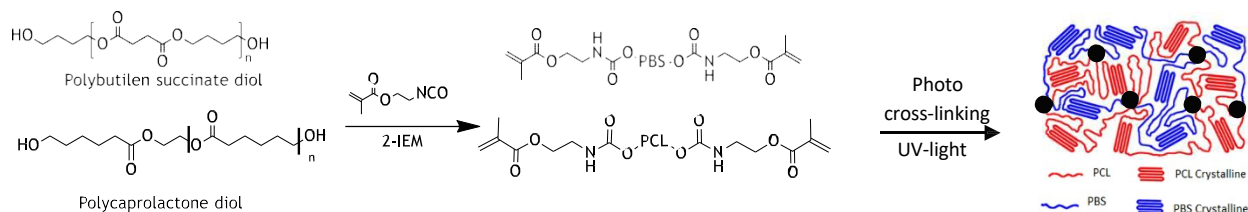


Figure 1. Functionalization of polyesters diols and preparation of semicrystalline PBS-PCL networks.

The final properties of the semicrystalline network depend on the molecular weight of the prepolymers, the blend's composition and cross-linking degree. PCL diol with  $M_n=10k$  Da and PBS diol with  $M_n$  around 10,5k Da have been functionalized with a methacrylate isocyanate and subsequently photo-cross-linked in order to obtain a network with tailored structure and properties. In *table 1*, compositions and properties of the prepared networks are reported.

Table 1. Codes, compositions and properties of PBS-PCL networks.

Code <sup>a</sup>	G <sup>b</sup>	$T_c$ PBS; $T_c$ PCL	$T_m$ PBS; $T_m$ PCL	$X_c$ PBS <sup>c</sup> ; $X_c$ PCL <sup>c</sup>
PBS_PCL 60:40	93 %	70 °C; 21 °C	109 °C; 50 °C	29%; 38%
PBS_PCL 40:60	86 %	58 °C; 19 °C	108 °C; 50 °C	29%; 38%
PBS_PCL 25:75	82 %	/ ; 19 °C	108 °C; 50 °C	31%; 36%
PBS_PCL 15:85	82 %	/ ; 21 °C	107 °C; 49 °C	36%; 41%

a) The code refers to the wt % compositions; b) Gel Content; c) Crystallinity content calculated from the melting enthalpy<sup>2</sup> normalized over polymer weight fraction.

As it is possible to see from the data reported in *table 1* and *figure 2*, the photo-crosslinked PBS\_PCL networks exhibit two different and well-separated crystallization and melting regions, close to those of the two homopolymers and also in agreement with those observed for linear PBS-PCL multiblock copolymers<sup>2</sup>.

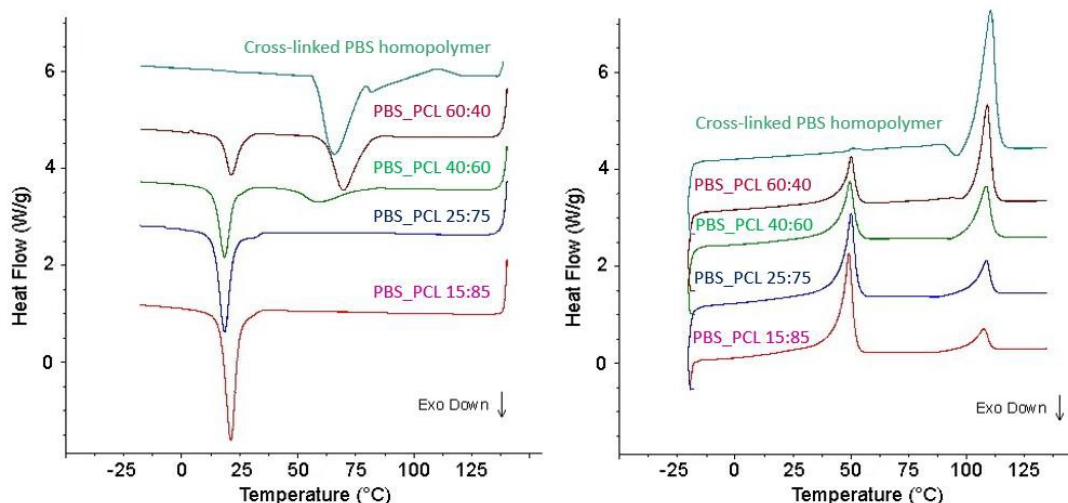


Figure 2. DSC thermograms of PBS\_PCL networks at 20 °C/min with different wt% compositions (on the left the first cooling scans, on the right the subsequent heating scans).

DSC thermograms of PBS\_PCL networks recorded at 20 °C/min are reported in figure 2. In the left figure, it can be seen a clear crystallization of PCL for every blend composition (around 20 °C), while a neat crystallization peak of PBS is detectable only for compositions with a percentage of PBS higher than 40%. Despite that, in the subsequent heating scan (figure right), in addition to the melting peak of PCL (around 50 °C), an endothermic melting peak (around 110 °C) attributable to the melting of a PBS crystalline phase is detected for all the compositions, even when PBS is present only at 15%. This effect is probably due to the slow crystallization rate of PBS chains. Stating on the presence of netpoints and two well-separated crystalline domains, these materials should be characterized by some unusual and interesting shape memory properties (SMP). After some preliminary tests, both irreversible triple shape effect, induced by the melting and crystallization of the two crystalline phases, and reversible two-way effect were detected. In *figure 3*, it's possible to observe the reversible two-way shape memory effect performed by cycling the sample between 65 and 0 °C.

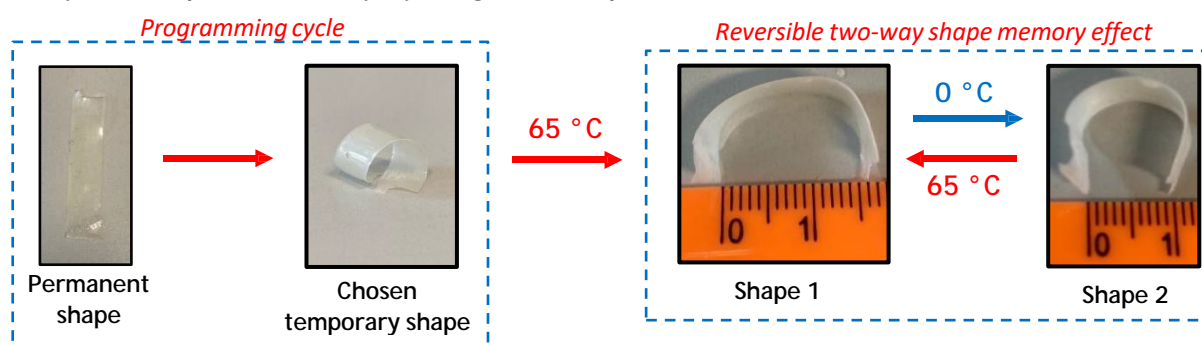


Figure 3. Reversible two-way shape memory effect of PBS\_PCL 25:75.

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## *Droplet-based synthesis of nanogels: a Design of Experiments approach*

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### Abstract

In recent years, the combination of nano and personalised medicine has emphasised the possibility of using nanotechnology to design innovative diagnostic and therapeutic strategies<sup>1</sup>. Among the variety of smart nanomaterials, polymeric nanogels (NGs) represent a promising drug delivery system for the treatment of different healthcare scenarios. Due to their versatility, obtained *via* chemical or physical cross-linking of different polymers, and their peculiar physico-chemical characteristics, NGs meet biocompatibility criteria, promote high drug encapsulation efficiency and sustained release over time, preserving the optimal drug concentration for therapeutic aims<sup>2</sup>. To date, conventional NGs syntheses hinder the potential transposition of nanocarriers into clinical applications and affect drug release, preventing the treatment from reaching optimal performance. Therefore, microfluidic approach represents a powerful tool to solve these shortcomings, ensuring high batch-to-batch reproducibility and scalability of NGs production and precise control of reaction parameters over time<sup>3,4</sup>. In particular, droplet-based microfluidic devices provide the in-flow generation of micro-droplets, conceived as a self-contained reaction chamber to form NGs, for the synthesis of nanocarriers with highly reproducible characteristics, in terms of composition, physico-chemical features and size, with extremely low polydispersity<sup>5</sup>. However, microfluidic devices offer the possibility of modulating a wide range of process parameters, both compositional and fluid-dynamic. This leads to a large number of different experimental conditions that need to be investigated in order to identify the optimal conditions according to needs and therapeutic applications.



We propose a Design of Experiments (DoE) study for the droplet-based synthesis of hyaluronan-polyethylenimine (HA-PEI) NGs obtained *via* water-in-oil emulsion through a flow focusing junction (FFJ) (Figure 1(a)).

Three different molar ratios between the two polymers ( $MR_{PEI/HA} = 3, 6, 9$ ) and three different flow rates ratios between the dispersed phase (aqueous polymers solution) and continuous phase ( $Q_D/Q_C = 0.1, 0.2, 0.4$ ) were chosen for a three-level, two-factor study ( $3^2$  full-factorial) (Figure 1(b)). For each condition, the resulting NGs were characterised in terms of size (Figure 1(c)), polydispersity index (PDI) (Figure 1(d)), final NG composition, biocompatibility (Figure 1(e)), drug release profile, cellular uptake and therapeutic effect (using cisplatin as a model drug). The experimental results were used to design a system of empirical models (Figure 1(f)) able to identify the correct set of process parameters leading to NGs matching the desired set of application-specific performance indicators.

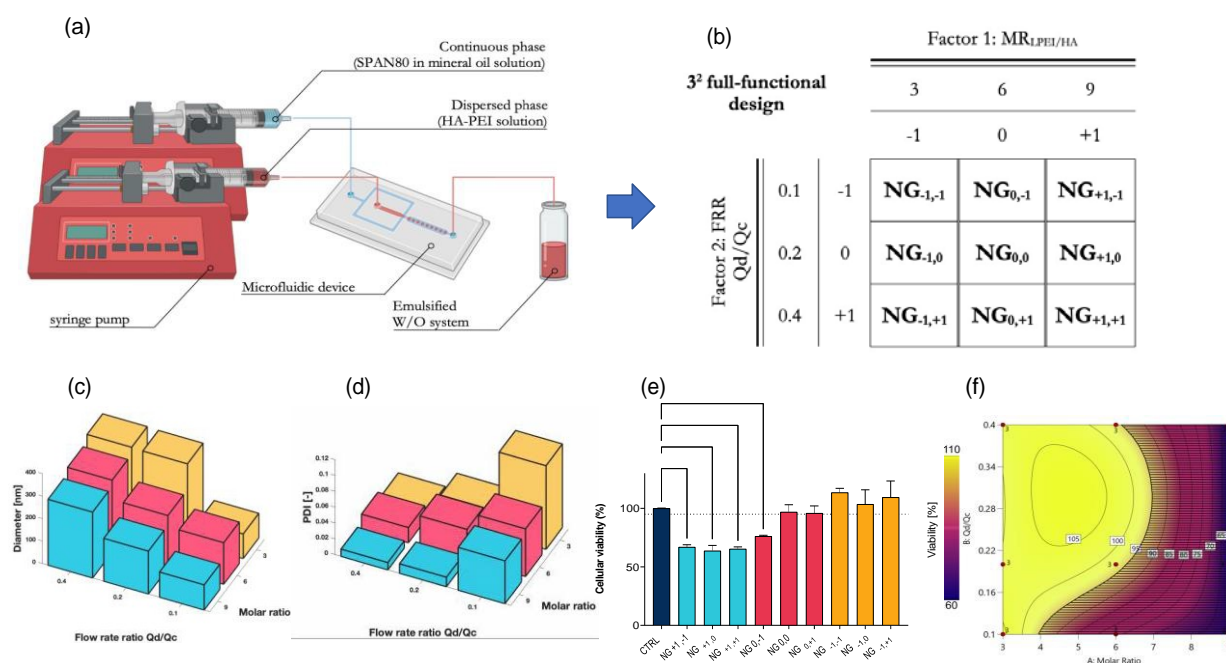


Figure 1. (a) Experimental set-up of NGs microfluidic synthesis; (b) Experimental conditions of NGs syntheses chosen for the parameter study; (c) 3D graph of resulting NGs diameters; (d) 3D graph of resulting NGs PDI; (e) Cell viability performed by MTT assay, following the NGs incubation for 24h on OVCA433 cells; (f) Representative contour plot of biocompatibility empirical model.

Hence, optimization of the synthesis process by the combination of droplet-based microfluidic approach and DoE strategies enables the design of nanomaterials with on-demand characteristics as drug delivery systems, improving NGs performances in a variety of clinical applications.

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## *Butlerov reaction: a detailed LC-MS characterization*

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**Keywords:** prebiotic chemistry, complex reaction systems, high resolution mass spectroscopy

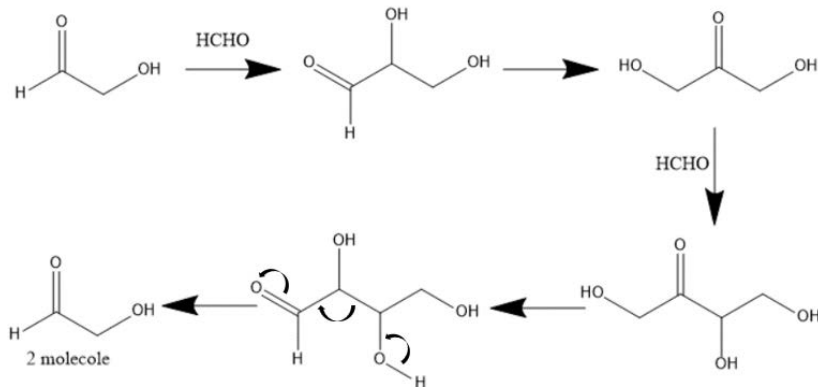
The Butlerov reaction is an autocatalytic system in which an aqueous formaldehyde solution yields a complex mixture of sugars. This process is also known as formose reaction.

It was first identified by Alexander Michailovich Butlerov in 1861, when he performed the oligomerization of an aqueous formaldehyde solution in the presence of calcium and barium hydroxides. The resulting solution was a mixture of monosaccharides, featuring a distinct sweet smell<sup>1, 2</sup>. The formose reaction is still highly regarded as one of the main possible processes that occurred on primordial Earth.

The formose reaction mechanism hasn't been completely understood yet. This system is composed of 5 distinct reactions: enolate formation and protonation, aldol addition, retro aldol reaction and Cannizzaro reaction<sup>3</sup>.

Since its discovery, a lot of hypotheses have been made pertaining to the reaction mechanism. What scientists agree on is the autocatalytic mechanism which starts from formaldehyde (C1, HCHO). It then dimerizes to glycolaldehyde (C2, C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>) in the slow step of the reaction, the trigger phase of the whole process which needs an activated metal catalyst in basic media (usually Ca(OH)<sub>2</sub>).

Ronald Breslow's hypothesis stands out as one of the most plausible. The first molecule of glycolaldehyde forms through an unfavorable mechanism in the slow step of the reaction, but subsequent C<sub>2</sub> molecules react faster generating an autocatalytic cycle involving glycolaldehyde itself. Triose, tetrose, pentose and homologous sugars are then produced, but they are still subjected to retro-aldolization and aldolization to produce branched, shorter, or longer sugar chains<sup>4</sup>.



To our knowledge, all the studies present in literature perform derivatization before analyzing sugars. In our opinion, the derivatization reaction can interfere with the large amount of chemical equilibrium present, leading to artifacts. For this reason, in this work, all analysis has been performed using a UHPLC-HRMS (Ultra High-Performance Liquid Chromatography-High Resolution Mass Spectrometry) without any derivatization. Thanks to the high-resolution mass spectrometer, it is possible to detect the exact mass of the products of the reaction, allowing for a focus on the actual profiles of the formation and degradation of the formed sugars.

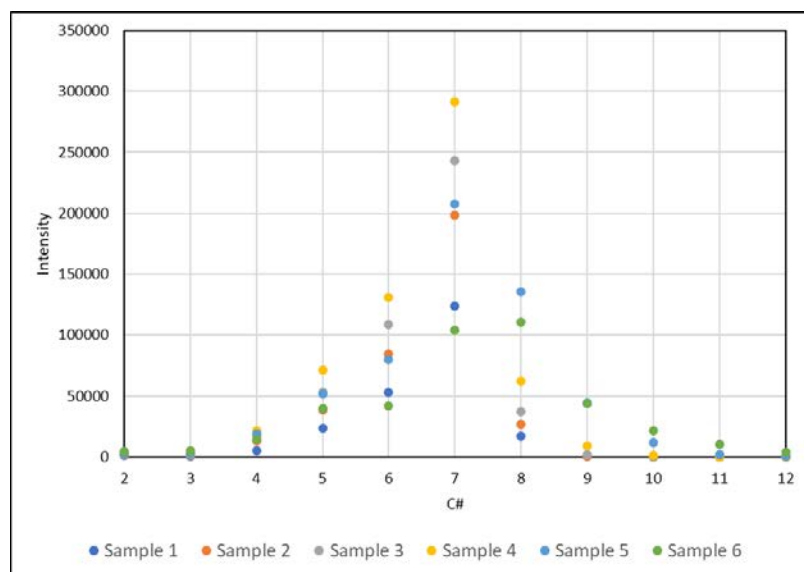


Figure1. Comparison of sugar intensities by carbon number.

From a preliminary result, a large amount of sugars having 7 carbon atoms have been detected (Figure1).

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## Microwave-assisted multicomponent cascade for the synthesis of novel thiophene[3,2-d]pyrimidine derivatives

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Keywords: multicomponent reactions, antimicrobials, thiophene-based scaffolds

The worldwide increase of multidrug resistant (MDR) and extensively drug resistant (XDR) strains of microorganisms, such as *Staphylococcus aureus* and *Mycobacterium Tuberculosis*, together with the lack of new effective drugs in the last decades, suggested the urgent need for the identification of innovative antimicrobial targets and inhibitors. [1] A fast and easy synthetic pathway can surely enhance the drug discovery process, and that was one of our project's cornerstone.

Referring to SAR previously reported in recent works [2,3], the *Gewald* and the *Groebke-Blackburn-Bienaymé* multicomponent reactions [4] were here applied in a microwave-assisted cascade to synthesize a library of new thiophenes derivatives as potential antimicrobial agents. Starting from commercially available materials, in just three steps we were able to introduce three different sites of diversification and afford the respective products with yields ranging from moderate to very good.

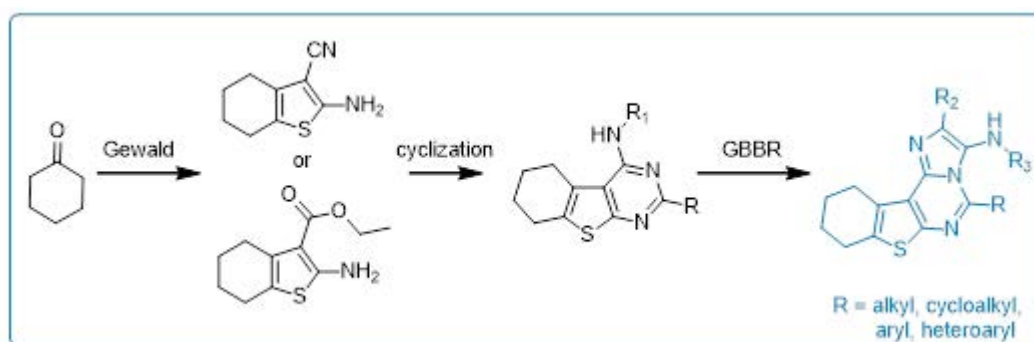


Figure. General scheme for the designed thiophene[3,2-d]pyrimidine derivatives.

Desired aromatic and aliphatic substituents were thus inserted into the scaffolds, in order to modulate their hydrophobicity, water solubility, and exploring the steric hindrance around the main core.

A library of hit compounds was therefore developed, and subsequently evaluated for *in vitro* screening tests against the most common MDR strains.

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## Pyrolyzed tannery sludge as sorbent of volatile organic compounds from tannery emissions

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**Introduction.** The Italian tanning industry is the leading European producer of high-quality leathers, with a value equal to 63 % of the continental turnover contributing to 23 % of the global value produced worldwide [1]. However, it has a great impact on the environment, due to its large water consumption with a huge amount of biological and chemical waste generated, and the high emissions of volatile organic compounds, VOCs, from leather finishing cabins. It is estimated that, from every ton of raw hide/skin, between 4 and 50 kg of VOCs are emitted into the air [1]. The wastewater streams produced by the leather industry are commonly conveyed to centralised wastewater treatment plants where the typical treatments comprise physical-chemical processes followed by activated sludge-based biological treatment to eliminate the organic matter. In Italy, also a tertiary treatment must be often included such as the Fenton process (oxidation) to meet the COD limit of 160 mg/L set by the Italian law for discharge into surface water bodies. The resultant tannery sludge (TS) is a solid waste with high S content and heavy metals due to basic chromium salts, syntans, pigments, dyes, retanning agents, etc. used in the tanning process. In Italy, these sludges are classified as special non-hazardous waste, and their current destination is in controlled landfill. The putrescible organic material and the presence of heavy metals as Cr<sup>3+</sup> leads to the need to stabilize the TS before being disposed of or, preferably, recovered. Thermal treatment as pyrolysis permits to stabilise, preventing the Cr<sup>3+</sup> oxidation, and reduce the volume/mass of waste to be disposed of. In addition, the carbonaceous residue obtained from pyrolysis of TS (PTS) could be used as sorbent depending upon its properties finding a valuable alternative to landfill. In the present work the use of PTS coming from an Italian tannery sludge pyrolysis plant was investigated, after further pyrolysis carried at controlled temperature and time, as adsorbent for the removal of n-butyl acetate, a typical solvent used in the finishing leather formulations, from air emissions.

**Materials and methods.** The PTS used in this study was produced in the tannery sludge treatment plant located in Santa Croce sull'Arno, Pisa (Italy). The PTS (particle size 1.2-3.0 mm) was furtherly pyrolyzed (PPTS) at controlled temperature and residence time in a pilot scale continuous tubular pyrolyzer for the adsorption tests. n-butyl acetate (Sigma, Aldrich, ACS reagent  $\geq 99.5$  %) was selected in this study being the



most commonly solvents used in the leather finishing formulations. Fixed bed adsorption experiments were performed to determine the breakthrough curves at room temperature using an air stream containing n-butyl acetate. Sorption tests were performed in a lab scale fixed-bed column using air streams containing various concentrations of n-butyl acetate, at various superficial velocities and bed heights.

Results and discussion. Tab. 2 shows the results of the pyrolysis tests carried out on PTS at different temperatures. As shown, further pyrolysis increases the BET area of the PTS. The adsorption breakthrough curves of PTS and PPTS samples and their sorption capacity are reported in Fig. 1a, b, respectively. Breakthrough curves were successfully fitted by Bohart-Adams (B-A) model. By pyrolysis at 850 °C for 20 min the BET of PTS increased from 72 to 142 m<sup>2</sup>/g, improving its sorption capacity. Preliminary sorbent desorption tests, carried out by hot nitrogen in the temperature range 120-150 °C, demonstrating the feasibility of thermal regeneration of this material.

Table 2. Pyrolysis yields and textural characteristics of the PPTS samples obtained by pyrolysis at different temperatures and times.

Pyrolysis temperature (°C)	600	750	800	850	850	850
Residence time (min)	120	60	20	6	20	60
Solid residue yield (% dry basis)	82.1	85.2	80.0	80.1	77.3	75.2
BET (m <sup>2</sup> /g)	97.9	127.2	113.9	126.5	141.9	113.1
Total pore volume (cm <sup>3</sup> /g)	0.103	0.133	0.125	0.127	0.155	0.114
Micropore volume (cm <sup>3</sup> /g)*	0.044	0.057	0.051	0.057	0.066	0.050
Average pore radius (Å)	21.1	20.92	21.90	20.1	21.83	20.11

\* Horváth-Kawazoe (HK) method.

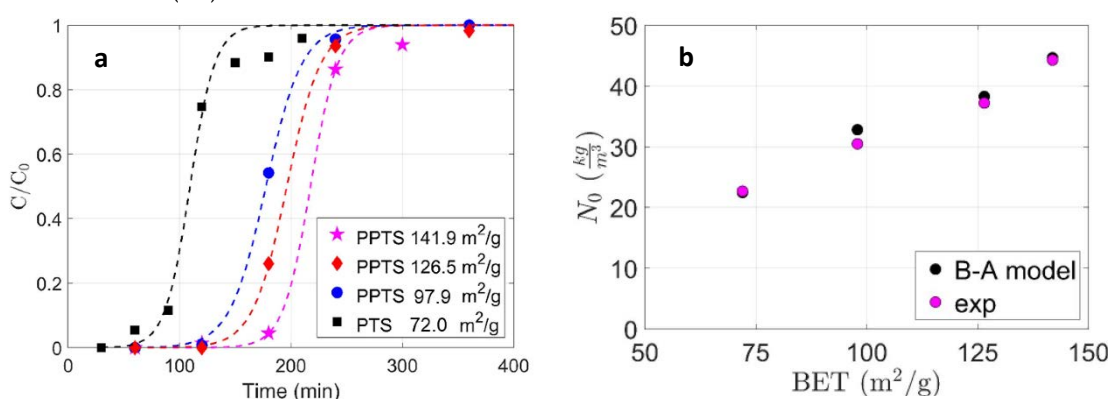


Figure 1. a) Breakthrough curves of PTS and different PPTS samples under the same sorption conditions ( $v_s = 0.034$  m/s,  $C_0 = 20.0$  g/m<sup>3</sup>,  $L = 20$  cm,  $T = 22$  °C) and b) sorption capacity of pyrolyzed tannery sludge as a function of the BET surface area (fitting by the Bohart-Adams model) expressed as  $kg_{BA}/m^3$  (bulk density of PPTS of 600 kg/m<sup>3</sup>).

Acknowledgements. The authors thank the Tuscany Region for the financial support of the project VOC TAN through the fund POR FESR 2014 - 2020 (Grant number: 3553.04032020); and the European Union for the financial support of the project ReVoc4LIFE under the LIFE 2020 research programme (Grant number LIFE20 ENV/IT/000688).

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## Pt(II) and Au(I) complexes with ionic- and hydrophobic-groups functionalized TPA derivatives

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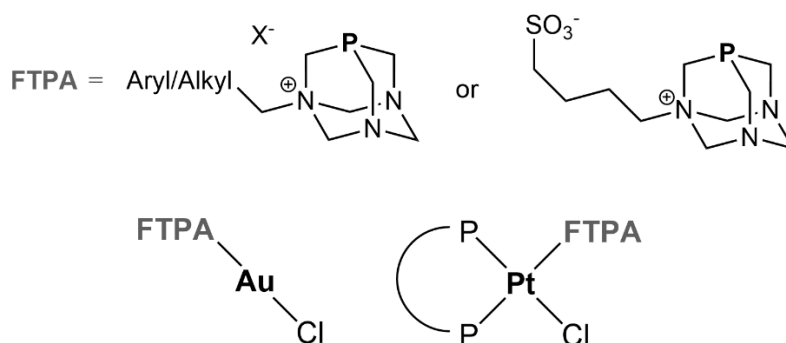
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Keywords: platinum(II), gold(I), functionalized 1,3,5-triaza-7-phosphaadamantane

TPA (1,3,5-triaza-7-phosphaadamantane) is water soluble monophosphine ligand characterized by a small cone angle and nitrogen atoms in a cage-like structure. Its peculiar stability, even in the presence of mild oxidant, and multiple nucleophilic sites, make it extremely interesting as a ligand in organometallic chemistry and prone to further functionalization [1]. Considering the huge variety of reactions catalysed by platinum(II) and gold(I) phosphine complexes [2], but also the possibility to make use of TPA's easy functionalization, we decided to synthesize some Pt(II) and Au(I) complexes with N-functionalized TPA derivatives (FTPA) bearing either a long alkyl hydrophobic or a ionic hydrophilic side chain. The FTPA ligand could be used for supramolecular interactions in confined systems such as micelles or capsules. The complexes are characterized and studied as pre-catalysts in model reactions, such as the hydration of alkynes and oxidation of ketones.



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Acknowledgements: the authors wish to thank Fondazione CaRiPaRo for funding the project Ricerca Scientifica di Eccellenza 2018 "Selective catalysis in supramolecular confined spaces (SELECT)".

## Cu based catalysts on Steel Slags for the reduction of nitroarenes in aqueous medium

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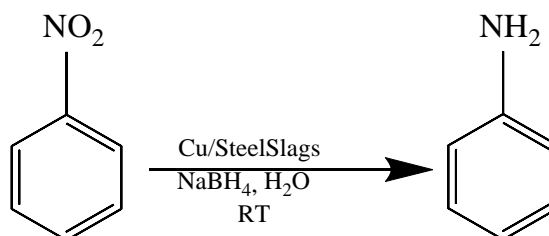
Keywords: Steel slags, copper catalyst, nitrobenzene reduction

Copper catalysts are widely used for the reduction of nitroarenes to anilines <sup>[1]</sup>, which are important building blocks for the synthesis of various drugs, dyes, and materials <sup>[2]</sup>. The reduction of nitroarenes involves the removal of the nitro group (NO<sub>2</sub>) and the addition of hydrogen (H<sub>2</sub>) to form anilines. The relevance of using copper catalysts for this reaction is due to their ability to activate hydrogen molecules and facilitate their addition to the nitro group.

On the other hand, steel slags are by-product of the steelmaking process, which contain various metals such as iron, calcium, silicon, magnesium, and aluminium, and they have basic features <sup>[3]</sup>. Both properties can catalyse some chemical reactions.

Thus, the use of copper catalyst supported on steel slags matrix for the nitroarene reaction could be promising in the development of new and more efficient synthetic methods for the synthesis of anilines and other nitrogen-containing compounds.

The present study investigates the catalyst precursor CuO/SteelSlags obtained by mixing copper sulphate pentahydrate (CuSO<sub>4</sub>·5H<sub>2</sub>O) and steel slags for 2 hours, followed by separation of the solid fraction by centrifugation and drying. The transformation of copper oxide into an active metal form occurred under reaction reductive conditions. In fact, the nitroarene reduction was carried out at room temperature in an aqueous medium with sodium borohydride (NaBH<sub>4</sub>) as the reducing agent (scheme 1).

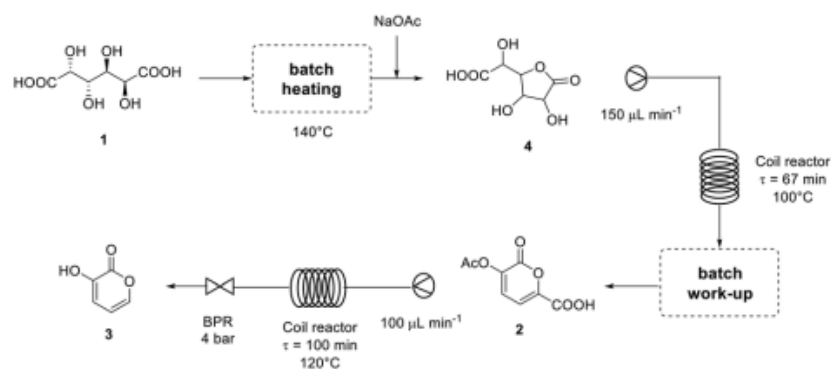


Scheme 1. Reaction conditions.

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Scheme 2. Flow process developed for the synthesis pyrones 2 and 3.

The batch conditions were optimized by keeping into account the insolubility of 1 in most solvents. For this reason this latter was reacted firstly to give the corresponding lactone form (4)[8] that was then converted to pyrone 2 (68-85% yield). Heating of 2 in water brings to the formation of 3-hydroxy-2-pyrone (3) by decarboxylation reaction (99% yield).

Overall, the optimized reactions were efficiently transferred to a continuous flow reactor obtaining the desired 2-pyrones in high yields (90-99%) and shorter times (66 minutes vs 3 hours for pyrone 2 and 33 minutes vs 6/24 hours for pyrone 3).

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## Advanced Oxidation Processes (AOPs) for the Efficient Removal of Organic Pollutants: Link Bench to Pilot Scale

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Keywords: AOPs, Hydrogen Peroxide, Ozone, Sulfamethoxazole

The primary focus of recent years is to develop simple, safe and efficient technologies for the treatment of wastewater which is increasingly rich in organic pollutants and, therefore, alarming about their impact on public and environmental health.

Part of the studies carried out in the framework of the PANIWATER project consists in the validation of advanced oxidation processes (AOPs) on a laboratory scale to be transferred to a pilot scale and aimed at the removal of probe organic micropollutants from aqueous [1].

In continuity with our interest in studying the abatement of emerging contaminants in real water matrices [2], we have investigated the removal of sulfamethoxazole (SMX). Bench-scale collimated beam experiments allowed to demonstrate that SMX can be a candidate probe pollutant from water matrices. Different parameters such as the initial probe concentration, UV, O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> doses, were used to estimate the most promising experimental conditions for SMX removal in simulated wastewater, allowing to study the potential synergies between experimental approaches performed at different scales. AOPs have been carried out by using a pilot prototype based on the MITO3X® technology according with the layout shown in Figure 1.

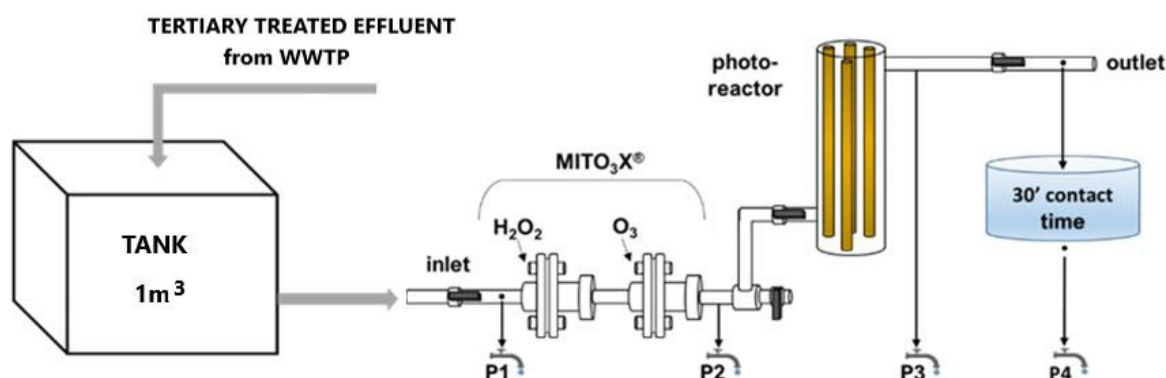


Figure 1. Pilot prototype layout integrating MITO<sub>3</sub>X technology with the UV photoreactor and schematic representation of sampling points.

The pilot system was installed and operated downstream the municipal wastewater treatment plant (WWTP) of the city of Fasano (Brindisi).

The MITO3X® technology allows the simultaneous dosage of liquid H<sub>2</sub>O<sub>2</sub> (30% w/w) and gaseous O<sub>3</sub> under high- mixing-gradient and high-pressure conditions. MITO3X® was coupled with a conventional UV photoreactor equipped with 4 low pressure mercury lamps emitting at 254 nm (each lamp of 100 W electrical power, with UV emission efficiency of 30-35% relative to electrical energy input, see Figure 1). SMX was spiked in 1 m<sup>3</sup> of tertiary treated wastewater effluent to obtain the initial stock aqueous solutions with concentrations ( C<sub>0</sub> ) ranging within 355-240 µg/L. These solutions were used to test SMX removal at four different flow rates (Q1, Q2, Q3, Q4) and sampling points (P1, P2, P3, P4). Four operating conditions, obtained by changing flowrates while keeping the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> ratio constant to 1:1 and constant UV power, were tested and the trend of SMX removal has been summarized in Figure 2.

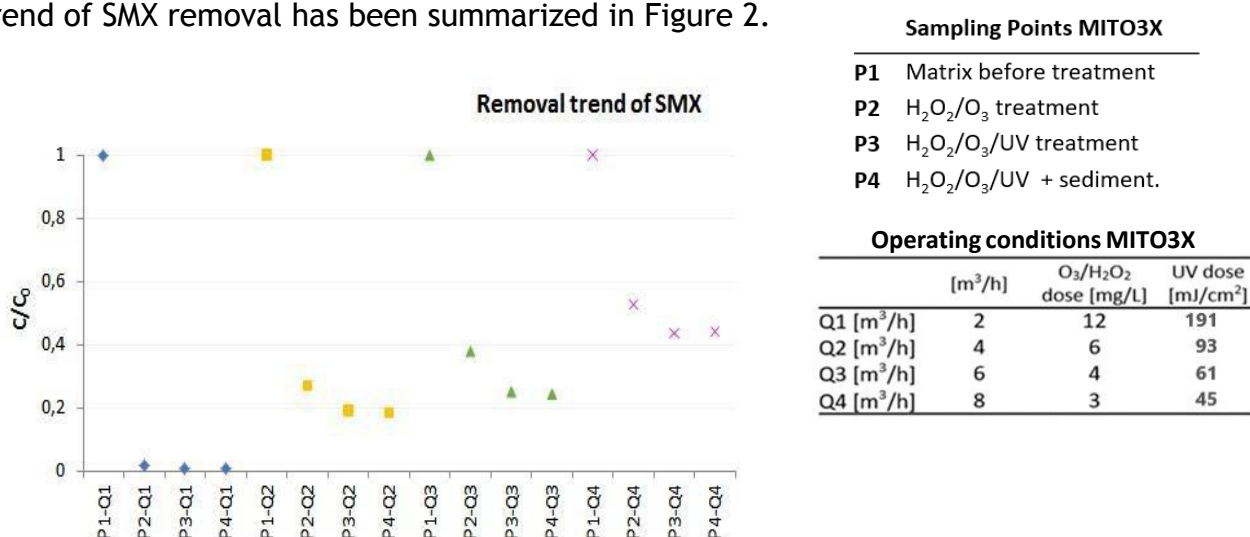


Figure 2. SMX removal from tertiary treated wastewater.

On the basis of the pilot scale trials, it was possible to observe that the removal of SMX improved as the UV-dose increased. The UV irradiation combined with the increasing amount of oxidizing agents such as ozone or hydrogen peroxide enhanced the generation of hydroxyl radicals responsible of the improved removal efficiency of SMX. Interestingly, analogous trend of removal of SMX and the emerging contaminants in real water matrices from secondary and tertiary treatment have been observed. This findings as well as the future challenges and perspectives in catalytic advanced oxidation processes designed to improve the removal of different classes of pollutants in water [3], will be here summarized in view of the possible scale up from bench to pilot scale.

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## Synthesis of new water-soluble electroactive species for sustainable Redox Flow Batteries (RFB)

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Keywords: redox flow battery, electroactive species, energy storage

Redox flow batteries (RFBs) are a promising technology as a grid-level energy storage system and have attracted growing attention because of their unique advantages such as long lifetime, simple structure, and decoupled power and energy [1]. In these devices, the electrochemical storage is carried out through reduction and oxidation reactions of chemical species. The peculiarity of RFBs is that active species are dissolved in liquid electrolytes, with the reaction occurring at the solid-liquid interface. Figure 1 shows a general scheme of an RFB consisting of a cell, a flow system (electrolyte tanks, pumps, pipes), and electrical controls. The active species are dissolved in a liquid and separated by an ion-exchange membrane, and both half-cells are connected by chemically inert conducting electrodes.

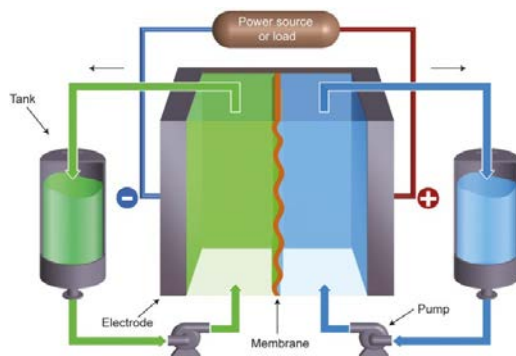


Figure 1. Schematic representation of a redox flow battery (RFB).

The chemical properties of the electroactive species are fundamental for developing the device as it can obtain a different energy capacity depending on the compound's solubility. Moreover, they have to be stable to the electrochemical process as if not the device's functioning would be compromised. The possibility of using liquid solutions aimed this work to develop a new sustainable battery exploiting an aqueous medium in which to dissolve the electroactive compound. Aqueous organic redox flow batteries (AORFBs) have recently raised great interest because water-soluble organic molecules combine the advantages of high flexibility in molecular engineering of the organic species with low costs [2-4]. Since high water solubility should be associated with the capability to undergo redox processes within the range of the stability potential of water porphyrins, phthalocyanines, and quinones were identified as promising candidates.



Porphyrins and related macrocycles play essential roles in nature and key features of these "pigments of life" are their redox-active behavior, coordination abilities, and light-harvesting properties. In this regard, Zn-tetraphenylporphinesulfonate (ZnTPPS) was synthesized (Figure 2) and characterized electrochemically, and its application in RFBs was evaluated.

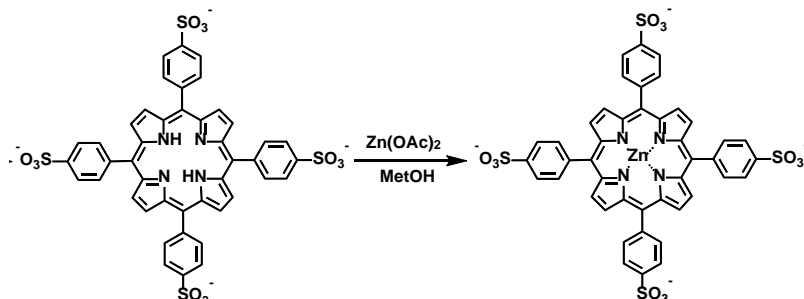


Figure 2. Synthetic routes for the synthesis of Zn-tetra phenyl porphinesulfonate (ZnTPPS).

Quinones are a class of compounds that, thanks to the possibility of rearranging the double and single bonds of their structure, are able to present the form of fully conjugated cyclic diketones [5]. With the purpose of increasing the energy storage of the system, compounds characterized by a great conjugation and high symmetry of the carboxylic groups were taken into consideration, to improve the energy transfer. Attention was focused on dipotassium 2,9-disulfonyl-5,6,12,13-tetrahydroquinolino (2,3-b)acridine-7,14-dione (QNC-S) which is a structural analog of quinacridone, a p-type photoelectrocatalyst used for H<sub>2</sub>O<sub>2</sub>-generating photocathodes.

Since quinacridone is only soluble in sulfuric acid, water solubility was achieved via the disulfonation reaction shown in Figure 3.

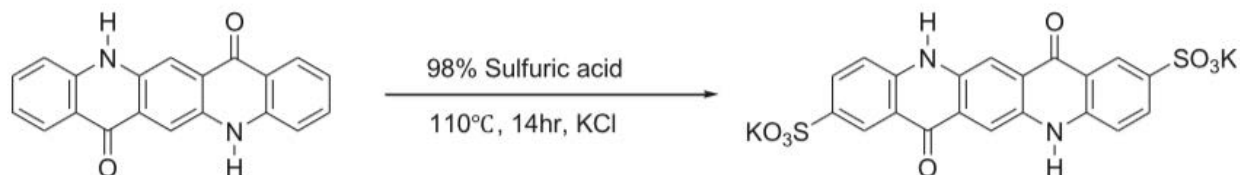


Figure 3. Synthetic routes for the synthesis of Dipotassium 2,9-disulfonyl-5,6,12,13-tetrahydroquinolino [2,3-b] acridine-7,14-dione (QNC-S).

Several techniques have performed the electrochemical characterization of the prepared electrolytes; the reversibility of the redox couples in terms of peak-to-peak separation has been evaluated by CV analysis, while the diffusion coefficient and the kinetic rate constants have been estimated by LSV-RDE experiments. A 5 cm<sup>2</sup> AORFB has been assembled using the selected electrolyte. The battery performance has been evaluated by electrochemical parameters measurements such as Energy and Voltage Efficiency and coulomb efficiency.

#### Acknowledgments

This project has received funding the Regione Lazio through the project POR FESR LAZIO 2014-2020, N° A0375-2020-36492

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## *Gamma-radiation induced modifications on polysaccharides to increase their 3D printability for tissue engineering applications*

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Keywords: gamma-radiation, 3D printing, hydrogels

3D printing is a versatile, layer-by-layer fabrication technology of 3D structures through progressive deposition of materials directly guided by predefined digital models.[1] The availability of biocompatible materials as inks opens to the possibility of printing scaffolds for tissue engineering, that incorporate cells and/or other bioactive molecules, such as adhesion proteins or peptides, growth factors, miRNA, DNA, etc. Temperature-responsive hydrogels derived from polysaccharides are interesting bio-ink candidates because they are biocompatible and biodegradable and gelation can be fast and does not require crosslinking agents. However, it is important that the sol-to-gel transition can occur at temperatures that are not harmful to the biological material that is incorporated. Furthermore, the physicochemical properties of the cell-laden hydrogel have to be harmonized with the viscoelastic behavior of the formulation during and after the extrusion from the printing nozzle. To this aim, gamma irradiation on polysaccharides can be used to affect and tailor the viscosity of the hydrogel to reach the best printability conditions as it causes a reduction in polymer weight [2]. Furthermore, algal polysaccharides have also been demonstrated to play an important role as free-radical scavengers in vitro and antioxidants for the prevention of oxidative damage in living organisms. The activity of algal polysaccharides is dependent on their

structure such as the degree of sulfation, the molecular weight, the sulfation position, type of sugar and glycosidic branching. Algal oligomers, obtained by gamma irradiation on algal polysaccharides, exhibit antioxidant properties attributed mainly to depolymerization with corresponding increase in reducing sugar [5].

In this context, the radiation-induced chemical modification of polysaccharides is studied as a mean of modifying their molecular weight and chemical structure and optimizing the properties of the networks formed upon extrusion from the ink nozzle for 3D printing. The rheological behavior was investigated for its impact on both processing and product properties. The typical advantages of high energy irradiation treatments of not requiring chemicals or catalysts and providing for sterilization, when the absorbed doses are with the sterilization dose range, are particularly important in the prospect use of these polymers in tissue engineering.

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# Correlation Between Structure, Coordination, and Ion Conductivity of POE-Based Polymer Electrolytes for Calcium Secondary Batteries

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Keywords: Electrolytes, polymer, secondary battery

The world energy economy is facing a global transition, and batteries based on novel chemistries are required in order to support this phenomenon. Polyoxoethylene-based (POE) materials are one of the most investigated systems to obtain flexible ion-conducting polymer electrolytes (PEs) for the next generation secondary batteries.

In the present study, novel Ca<sup>2+</sup>-conducting PE membranes are proposed based on CaTf<sub>2</sub>-doped POE, and the impact of the Ca<sup>2+</sup> doping and chain length on the microstructure and on the ion conductivity mechanism is investigated. Upon CaTf<sub>2</sub> doping, the vibrational spectroscopies, MDSC and BES reveal the presence of a mesoscale heterogeneity and of an interaction between the Ca<sup>2+</sup> and the polymer hosting matrix. In particular, two domains are formed, which are attributed to the “free” POE chains and the POE chains coordinating Ca<sup>2+</sup> cations. The latter are responsible for the formation of a weak “dynamic cross-link” network. BES studies confirm that the long-range charge migration mechanism of Ca<sup>2+</sup> is mediated by the exchange of Ca-based species between different POE chains. By comparing PC400/CaTf<sub>2</sub> and PC1000/CaTf<sub>2</sub> PEs, it is observed that the interchain hopping of Ca<sup>2+</sup> is assisted by the dynamic polymer chains in the order PC1000 > PC400. Finally, Tf<sup>-</sup> anions act as plasticizers inducing an improvement of the host polymer matrix dynamics, whose effect is more intense in the case of PC1000/CaTf<sub>2</sub>. In conclusion, a family of PEs is obtained, endowed with an Ca<sup>2+</sup> conductivity value up to *ca.* 10<sup>-4</sup> S·cm<sup>-1</sup> at 80 °C. This conductivity value is compatible with the implementation of the proposed electrolytes into a calcium prototype battery device.

## Acknowledgments

This research was funded by European Union’s Horizon 2020 research and innovation programme, grant number No 928145 (FETOPEN-VIDICAT).

# High-Temperature “Ex-Situ” Cyclic Voltammetry to Study the Oxygen Reduction Reaction on Electrocatalysts in Conditions Mimicking Fuel Cell Operation

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Keywords: Cyclic voltammetry, electrocatalysts, oxygen reduction reaction

The massive efforts dedicated over the last decades to the development of improved electrocatalysts (ECs) and membrane-electrode assemblies (MEAs) have already yielded a significant reduction of the loading of platinum needed to devise low-temperature fuel cells (LT-FCs) achieving the performance and durability level that is required for applications. However, more research is still needed to further curtail the amount of Pt in a LT-FC; this is particularly relevant to prevent supply bottlenecks in the perspective of a large-scale rollout of this technology.

In a conventional LT-FC running on direct hydrogen most of the Pt loading is concentrated on the cathode electrode, where it is needed to promote the sluggish oxygen reduction reaction (ORR). It is often very time-consuming to optimize the features of a MEA to maximize its performance in a LT-FC running in operating conditions. This is especially the case if the MEA mounts innovative ORR ECs exhibiting features that are very different from benchmark ECs in terms of chemical composition of the active sites and morphology. Thus, the general practice is to screen developmental ORR ECs through “ex-situ” techniques before focusing MEA optimization only on the most promising systems.

The most widespread “ex-situ” approach to screen developmental ORR ECs involves the use of a rotating (ring) disk electrode (R(R)DE) setup. Though very practical and accurate, conventional R(R)DE experiments are able to study the ORR features of an EC only in quite a narrow set of operating conditions ( $T = 30-60^{\circ}\text{C}$ ;  $P = 1$  bar). These latter are different from those that are most commonly adopted at the cathode of a LT-FC ( $T = 80-100^{\circ}\text{C}$ ;  $P = 2 - 3$  bar). As a result, the information obtained on the ORR

features of an EC by means of conventional R(R)DE studies may not be fully representative of the behavior of the EC in an operating LT-FC.

To address this shortcoming herein we present an innovative setup able to elucidate the ORR features of both benchmark and innovative ECs in experimental conditions that are very close to those found in operating low-temperature FCs. Specifically, the setup consists of a homemade channel flow electrode (CFE) cell operated in a rather simple closed system with a controlled oxygen concentration and maintaining a high level of cleanliness.

The modeling, materials selection, design, and testing of a versatile CFE cell developed from scratch is presented. The cell is compatible with commercially-available RDE components and special care is devoted to ease the overall assembly of the experimental setup. The cell is characterized by a well-defined hydrodynamics, a low dead volume, a high mass-transfer rate and a high signal/noise ratio. The cell also allows to measure accurately the pressure and the temperature in close proximity of the working electrode. It is demonstrated the possibility to study the ORR features of ECs up to a temperature of 80°C and a pressure of 3 bar. Both benchmark and innovative ECs are taken into consideration. The latter exhibit features that are very different in comparison with the conventional Pt/C ECs, especially in terms of: (i) chemical composition of the active sites, that typically includes more than one element; and (ii) morphology of the support, that is based on different carbon nanostructures. The proposed setup is implemented to determine crucial ORR features of the ECs, including the kinetically-controlled current, the activation energy and the accessibility of O<sub>2</sub> to the active sites.

#### **Acknowledgements**

This research has received funding from: (a) the European Union's Horizon 2020 research and innovation program under grant agreement 881603; (b) the project 'Advanced Low-Platinum hierarchical Electrocatalysts for low-T fuel cells' funded by EIT Raw Materials; (c) Alkaline membranes and (platinum group metals)-free catalysts enabling innovative, open electrochemical devices for energy storage and conversion - AMPERE, FISR 2019 project funded by the Italian Ministry of University and Research; and (d) the German Federal Ministry of Education and Research (BMBF) under grant agreement number 03SF0585.

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Dichiarante Valentina  
Dirè Sandra  
Dispenza Clelia  
Dondi Daniele  
Ducoli Serena  
Elli Stefano  
Espro Claudia  
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ISBN 978-88-3623-147-8



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