Società Chimica Italiana
Divisione di Chimica
per le Tecnologie

Napoli
4-7 settembre 2022

ATTI

1° Congresso Nazionale della Divisione di Chimica per le Tecnologie della Società Chimica Italiana

Napoli, 4-7 settembre 2022

A cura del Comitato Organizzatore

PREFAZIONE

Il 1° Congresso Nazionale della Divisione Chimica per le Tecnologie della Società Chimica Italiana si svolgerà a Napoli nei giorni 4-7 settembre 2022 presso l'Aula Magna del Centro Congressi dell'Università di Napoli Federico II.

Il Congresso è organizzato dai ricercatori afferenti al settore scientifico disciplinare CHIM/07 dei seguenti Atenei: Università di Napoli Federico II, Università della Campania Luigi Vanvitelli, Università di Napoli Parthenope e Università di Salerno.

Le tematiche scientifiche oggetto del Convegno riguardano principalmente i fondamenti chimici e chimico-fisici dei diversi settori delle tecnologie, con particolare riguardo a quelli che si riferiscono ai materiali, alle loro proprietà e alla loro interazione con l'ambiente. Esse comprendono tutti i temi attinenti ai fondamenti chimici delle tecnologie e alle relative applicazioni.

Il Congresso si pone l'obiettivo di fornire spunti di riflessione e di confronto ai partecipanti e facilitare lo scambio di idee, conoscenze ed esperienze tra l'Accademia ed il mondo industriale.

ORGANIZZATO DA:

DI C Ma PI
Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale
Università degli Studi di Napoli Federico II

Università degli Studi della Campania *Luigi Vanvitelli*
Dipartimento di Ingegneria

Dipartimento di Ingegneria

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SALUTI ISTITUZIONALI

Carissime Colleghe e Colleghi,

a tutti voi che siete convenuti a Napoli per partecipare alla I edizione del Convegno Nazionale della Divisione porgo il più caloroso benvenuto a nome del Consiglio Direttivo e mio personale.

La Divisione nasce a seguito dell'assemblea, convocata dal Decano Prof. Attilio Citterio su richiesta del Direttivo AICIng, dei professori ordinari del SSD CHIM/07 tenutasi il 12-04-2019 presso il Politecnico di Milano. Successivamente il 29-11-2019 si è tenuto a Roma La Sapienza l'Assemblea Costitutiva dei Soci proponenti per l'approvazione dello Statuto.

Questo incontro viene in un momento molto complesso per l'Università italiana in cui il CUN sta lavorando sul riordino degli SSD del nostro sistema universitario, proponendo un nuovo modello che verosimilmente porterà ad una riduzione degli attuali settori concorsuali e l'eliminazione degli SSD. La Divisione mediante il suo Presidente o suoi delegati è presente nei Tavoli Istituzionali e in questo caso specifico, cioè il riordino dei settori concorsuali e dei corsi di studio, partecipa attivamente al tavolo di lavoro SCI-CUN evidenziando la specificità didattica dei "Fondamenti Chimici delle Tecnologie" all'interno di tutti i Corsi di Studio in Ingegneria.

La pandemia ha rallentato gli eventi organizzativi, ma adesso ci troviamo qui in presenza tra le bellezze della città di Napoli e della Campania tutta, in questa splendida Aula Magna dell'Università degli Studi di Napoli Federico II situata sul lungomare, nel cuore del centro storico della città.

Il Convegno registra un ottimo successo nel numero dei contributi scientifici inviati, tutti di elevata caratura, mostrando chiaramente la ricchezza delle nostre linee di ricerca, la loro specificità come "Fondamenti Chimici delle Tecnologie" e la capacità di cooperazione tra gruppi del nostro settore.

Un ringraziamento va ai relatori e, in particolare, al Gruppo Giovani della Divisione che con il loro entusiasmo ci fanno ben sperare sul futuro sia del nostro SSD, sia del sistema di ricerca italiano. Un ringraziamento speciale va alle giovani Dottoresse e Dottori under 35 premiati con l'assegnazione di una Borsa di partecipazione, ma anche a tutti coloro che hanno partecipato alla selezione.

Un sentito ringraziamento va al Comitato Organizzatore, i cui membri si sono fortemente impegnati per rendere questo nostro incontro non solo interessante, ma anche piacevole.

A tutti voi i miei migliori auguri di buon lavoro.

Il Presidente della Divisione
Prof. Salvatore Failla

Salvatore Failla

Cari Colleghe e Colleghi,

a nome del Comitato Organizzatore vorrei rivolgere a tutti voi un caloroso saluto di benvenuto a Napoli.

Consapevoli dell'importanza dell'impegno che ci è stato attribuito, ci auguriamo che il Congresso possa adeguatamente riflettere la ricchezza delle tematiche di ricerca che contraddistinguono e caratterizzano l'attività scientifica delle ricercatrici e dei ricercatori che aderiscono alla Divisione di Chimica per le Tecnologie e che possa soddisfare appieno le vostre aspettative.

Ci auguriamo che possiate trascorrere una piacevole permanenza a Napoli e che possiate ammirare e fruire delle bellezze e dei tesori artistici della nostra millenaria città.

Il Presidente del Comitato Organizzatore
Prof. Antonio Aronne

Con il patrocinio di:

- *Scuola Politecnica e delle Scienze di Base dell'Università di Napoli Federico II*
- *Università degli Studi di Salerno*
- *Università della Campania Luigi Vanvitelli*
- *Università di Napoli Parthenope*
- *Associazione Italiana Chimica per l'Ingegneria (AICIng)*
- *Associazione Italiana di Calorimetria e Analisi Termica (AICAT)*

Si ringraziano gli Sponsor per il loro supporto a questa iniziativa:

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LA SEDE

Il Centro Congressi dell'Università degli Studi di Napoli Federico II nasce dalla crescente richiesta, da parte di soggetti interni ed esterni all'Ateneo, di utilizzare alcune sedi storiche per l'organizzazione di eventi.

Importanti strutture quali l'Aula Magna storica, l'Aula Magna di Via Partenope e il Complesso dei SS. Marcellino e Festo, grazie a considerevoli lavori di restauro, sono state recuperate al loro antico splendore.

Queste sale, insieme con l'Aula Carlo Ciliberto e la Sala Blu di Monte Sant'Angelo e la magnifica Villa Orlandi di Anacapri, offrono un alto livello di comfort ed innovative attrezzature tecniche tali da assicurare la funzionalità in ciascuna fase congressuale.

Per maggiori informazioni consultare il sito web del Centro Congressi: www.centrocongressi.unina.it

Via Partenope, 36, 80121 Napoli NA

PROGRAMMA SCIENTIFICO

Domenica 4 Settembre

18:30 – 19:30 **Accredito partecipanti**
18:30 – 20:30 **Aperitivo di benvenuto**
(Terrazza 10° piano, **Hotel Royal Continental**, Via Partenope 38, Napoli)

Lunedì 5 Settembre

8:30 – 9:00 **Accredito partecipanti**

9:00 – 9:15 **Saluti di benvenuto**: Gioconda Moscariello (Presidente della Scuola Politecnica e delle Scienze di Base, Università di Napoli Federico II), Salvatore Failla (Presidente del Comitato Scientifico, Università di Catania) e Antonio Aronne (Presidente del Comitato Organizzatore, Università di Napoli Federico II)

9:15 – 9:55 PL1: **Angela Agostiano** Università di Bari **- *Chairperson: Salvatore Failla***
Soft Chemistry Tool Box For New Functions: Original Bottom-up Opportunities for Engineering Multifunctional Hybrid Architectures

Materiali per applicazioni biomedicali

I sessione comunicazioni orali - Chairperson: Roberta Bongiovanni e Roberto Paolesse

9:55 – 10:10 O1: **Greta Bergamaschi** SCITEC-CNR (Milano)
Hybrid Peptide-Agarose Hydrogels for 3D Bioassays
10:10 – 10:25 O2: **Francesca Baldassarre** Università del Salento
Synthesis and chemical modifications of cellulose nanocrystals hybrids systems as potential theranostic platforms
10:25 – 10:40 O3: **Monica La Milia** Università di Palermo
Rare cell capture platforms based on antibody-conjugated electrospun nanofibre mats for noninvasive prenatal diagnostics
10:40 – 10:55 O4: **Pasqualina Scala** Università di Salerno
Advanced biopolymer filtration system for Peripheral Blood Mononuclear Cells collection: a study on filter composition and in vitro filtrate composition

10:55 - 11:15 **Coffee break**

11:15 – 11:45 KN1: **Santo Di Bella** Università di Catania
Lewis acidic Zinc(II) salen-type complexes as multifunctional molecular materials

II sessione comunicazioni orali

11:45 – 12:00 O5: **Raffaele Longo** Università di Salerno
Design of electrospun membranes loaded with functionalized Fe_3O_4 nanoparticles for anticancer application
12:00 – 12:15 O6: **Emanuela Muscolino** Università di Palermo
Design, synthesis and characterization of a theranostic nanoplatform for tumor site-specific delivery of doxorubicin
12:15 – 12:30 O7: **Michela Pisani** Università Politecnica delle Marche
Glycolipid based Lyotropic Crystalline mesophases for targeted delivery of dexamethasone
12:30 – 12:45 O8: **Consuelo Celesti** Università di Messina
Functionalized titanium surfaces with anti-bacterial adhesion properties
12:45 – 13:00 O9: **Fabiana Pandolfi** CNR Roma
Liposomes as drug delivery system for Antarctic fish-derived antimicrobial peptides (AMPs)

13:00 – 14:30	**Pranzo libero**

Materiali derivati da risorse rinnovabili e scarti

III sessione comunicazioni orali ***- Chairperson: Elza Bontempi e Gian Paolo Suranna***

14:30 – 14:45	O10: **Maria Michela Dell'Anna** Politecnico di Bari ***Chemical valorisation of wastes from different sources***
14.45 – 15:00	O11: **Francesco Mauriello** Università Mediterranea di Reggio Calabria ***Conversion of lignin-derived aromatic ethers under reductive catalytic fractionation conditions***
15:00 – 15:15	O12: **Chiara Ruini** Università di Modena e Reggio Emilia ***Life Cycle Assessment study for the obtainment of Levulinic Acid from Cynara Cardunculus L. biomass for the synthesis of innovative bioplasticizer***
15:15 – 15:30	O13: **Sara Dalle Vacche** Politecnico di Torino ***Photocuring of biobased polymer – nanocellulose composites***
15:30 – 15:45	O14: **Emilia Paone** Università Mediterranea di Reggio Calabria ***From Waste to an Efficient Heterogeneous Catalyst: Spent Lithium-Ion Batteries for the Reductive Upgrading of Biomass-Derived Furfural***

Presentazioni flash ***- Chairperson: Consuelo Celesti***

15:45 – 15:50	FP1: **Daniele Bugnotti** Università di Trento ***NMR and XRD study of starch-based nanocomposite reinforced with natural fillers for bio-packaging applications (BIOSTAR-PACK)***
15.50 – 15:55	FP2: **Francesco Lanero** Università di Padova ***Microwave assisted Paal-Knorr reaction on polyketones***
15:55 – 16:00	FP3: **Valentina Petrelli** Università di Bari ***Combination of analytical tools for identifying microplastics in Apulia seawater***
16:00 – 16:05	FP4: **Lorenzo Viganò** Università di Milano Bicocca ***Sustainable design of composite materials for wastewater treatment***
16:05 – 16:10	FP5: **Elisa Manzini** Università di Milano Bicocca ***Study of Nanoparticles Effect on Technologically Relevant Rubber Blends***
16:10 – 16:15	FP6: **Larisa Lvova** Università degli Studi di Roma Tor Vergata ***Seeking Sustainable Solutions for Energy and Environment at Tor Vergata***
16:15 – 16:20	FP7: **Vincenzo Arconati** Università della Campania L. Vanvitelli ***Synthesis via Sol-Gel process of Hybrids materials: Biological and chemical characterization***
16:20 – 16:25	FP8: **Veronica Viola** Università della Campania L. Vanvitelli ***Sustainable metakaolin-based geopolymers using oak ashes filler***

16:25 – 17:15	**Coffee Break** + **I sessione poster**

IV sessione comunicazioni orali ***- Chairperson: Maurizia Seggiani e Ignazio Blanco***

17:15 – 17:30	O15: **Sara Filippi** Università di Pisa ***Recycling of waste oils as rejuvenators for aged bitumen in RAP***
17:30 – 17:45	O16: **Isabella Lancellotti** Università di Modena e Reggio Emilia ***Chemical resistance in acids of alkaline activated materials from volcanic materials and metallurgical slags***
17:45 – 18:00	O17: **Alessio Occhicone** Università di Napoli Parthenope ***Red Mud-Blast Furnace Slag Based Alkali-Activated Materials***
18:00 – 18:15	O18: **Ernestino Lufrano** Università della Calabria ***Solid State Polymer Electrolytes for Lithium Sulfur batteries (Li-S)***

Martedì 6 Settembre

9:00 – 9:40 PL2: **Vito Di Noto** Università di Padova **- *Chairperson: Antonio Aronne***
Interplay between Synthesis, Mechanisms and Performance of Ionomers and Electrocatalysts for Ion-Exchange Membrane Fuel Cells

Materiali per applicazioni energetiche

V sessione comunicazioni orali **- *Chairperson: Candida Milone e Pierluigi Stipa***

9:40 – 9:55 O19: **Giuseppe Marcì** Università di Palermo
C_3N_4/reduced graphene oxide photocatalysts for H_2 evolution from photoreforming of aqueous solutions of organic molecules
9:55 – 10:10 O20: **Giulia Calabrese** Università di Messina
Hydrogen storage through $ABO_{3\pm\delta}$ perovskite oxides
10:10 – 10:25 O21: **Emanuele Previti** Università di Messina
Coatings of Calcium Lactate for Thermal Energy Storage Applications
10:25 – 10:40 O22: **Paolo Sgarbossa** Università di Padova
New functionalized polyketones for anion exchange membranes
10:40 – 10:55 O23: **Francesca Lorandi** Università di Padova
Interplay between Physicochemical Features, Oxygen Reduction Reaction Mechanism and Fuel Cell Performance of "PGM-free" Hierarchical Electrocatalysts Comprising Fe-Sn Active Sites

10:55 – 11:15 **Coffee Break**

- *Chairperson: Cristina Leonelli e Fabio Ganazzoli*
11:15 – 11:45 KN2: **Antonella Gervasini** Università di Milano
Bare and functionalized hydroxyapatite, multifunctional materials for controlling air and water pollution

Materiali per usi speciali

VI sessione comunicazioni orali

11:45 – 12:00 O24: **Manuela Stefanelli** Università di Roma Tor Vergata
The bride side of merging prolinated porphyrins and ZnO nanoparticles for chiral sensor development
12:00 – 12:15 O25: **Barbara Di Credico** Università Milano Bicocca
Self-assembled silica-based nanoparticles in advanced materials for tyre application
12:15 – 12:30 O26: **Anita Ceccucci** Università di Roma Tre
Functionalization of metallic and semiconductive surfaces for multifunctional coatings
12:30 – 12:45 O27: **Giuseppina Anna Corrente** Università della Calabria
π-conjugated organic mixed valence materials for multi-responsive, smart and versatile devices
12:45 – 13:00 O28: **Manfredi Caruso** Politecnico di Milano
Engineered polyethylenimine-based materials: novel heterogeneous catalysts for sustainable organic transformations

13:00 – 14:30 **Pranzo libero**

Metodi di sintesi ed analisi

VII sessione comunicazioni orali **- *Chairperson: Marilena Tolazzi e Piero Mastrorilli***

14:30 – 14:45 O29: **Cristina Leonelli** Università di Modena e Reggio Emilia
Calcination of N-doped TiO_2 nanoparticles in microwave oven

14:45 – 15:00	O30: **Valentina Dichiarante** Politecnico di Milano *Perfluoro-tert-butoxyl-substituted scaffolds: from bioimaging to the functionalization of surfaces and nanomaterials*
15:00 – 15:15	O31: **Roberto Grisorio** Politecnico di Bari *In-Situ Formation of Zwitterionic Ligands: Changing the Passivation Paradigms of $CsPbBr_3$ Nanocrystals*

Presentazioni flash - *Chairperson: Valentina Petrelli*

15:15 – 15:20	FP9: **Cinzia Michenzi** Università di Roma La Sapienza *Carbon dots from Orange Peel Waste by an Integrated Hydrothermal and Electrochemical Process: A Contribute to the Circular Chemistry*
15:20 – 15:25	FP10: **Giovanni Crivellaro** Università di Padova *Additives to improve the performance of ambipolar zinc-polyiodide redox flow batteries*
15:25 – 15:30	FP11: **Gioele Pagot** Università di Padova *Coordination and Conductivity Mechanism in Ionic Liquid-based Electrolytes for Advanced Multivalent Metal Batteries*
15:30 – 15:35	FP12: **Yannick Herve Bang** Università di Padova *Hierarchical “Core-Shell” Carbon Nitride Pt-alloy ORR Electrocatalysts: Correlation between the Porosimetric Features, Morphology, “Ex-Situ” and “In-Situ” Electrochemical Performance*
15:35 – 15:40	FP13: **Federico Brombin** Università di Padova *Structure, Coordination and Conductivity Studies in POE-Based Polymer Electrolytes for Calcium Secondary Batteries*
15:40 – 15:45	FP14: **Giulio Pota** Università di Napoli Federico II *Efficient and easy co-immobilization of Cellulase and β-glucosidase on Mesoporous Silica Nanoparticles for the hydrolysis of cellulose derived from agricultural biomass*
15:45 – 15:50	FP15: **Virginia Venezia** Università di Napoli Federico II *Antibacterial electrospun hybrid TiO_2/Humic Acid PHBV fibers for active packaging*
15:50 – 15:55	FP16: **Paola Amato** Università di Napoli Federico II *Eco-sustainable design of hybrid redox-active materials for the degradation of LLDPE*
15:55 – 16:45	**Coffee Break + II sessione poster**

VIII sessione comunicazioni orali - Chairperson: Marilena Tolazzi e Piero Mastrorilli

16:45 – 17:00	O32: **Silvia Mazzotta** IIT Torino *Green synthetic approach for direct functionalization of graphene with Dimethyl acetylenedicarboxylate*
17:00 – 17:15	O33: **Vito Gallo** Politecnico di Bari *Community-built analytical systems for food authenticity assessment and metabolite quantification*
17:15 – 17:30	O34: **Marica Antonicelli** Politecnico di Bari *Non-targeted NMR method to assess the authenticity of autochthonous lentils*
17:30 – 18:30	**Assemblea dei Soci**
20:30	**Cena Sociale** (**Cenacolo Belvedere Carafa**, Via Aniello Falcone 122, Napoli)

Mercoledì 7 Settembre

9:00 – 9:40	PL3: **Paolo Di Petta** MBDA S.p.A. ***- Chairperson: Veronica Ambrogi*** ***Circularity through replacement of treatments and materials***

Materiali per applicazioni in ambito ambientale

IX sessione comunicazioni orali ***- Chairperson: Maurizia Seggiani e Gian Paolo Suranna***

9:40 – 9:55	O35: **Olimpia Tammaro** Politecnico di Torino ***Reverse micelles synthesis of mesoporous Fe-doped CeO_2 as UV/Visible photocatalyst for Ibuprofen degradation***
9:55 – 10:10	O36: **Serena Regina** CNR Rende ***Use of natural polymers to develop stable and durable performing membranes***
10:10 – 10:25	O37: **Viviana Bressi** Università di Messina ***Electrochemical detection of Pb^{2+}, Cd^{2+} and Hg^{2+} in sea water by sPEEK/TPyP-sensor***
10:25 – 10:40	O38: **Angelo Ferlazzo** Università di Messina ***From waste FFP2 masks to the development of a Hg-selective fluorescence sensor***
10:40 – 10:55	O39: **Ivan Pietro Oliveri** Università di Catania ***Transmetalation properties of Zn(II) salen-type complexes as chemosensors for recognition of Cu^{2+} ions in water***
10:55 – 11:15	**Coffee Break**

X sessione comunicazioni orali ***- Chairperson: Elza Bontempi e Ignazio Blanco***

11:15 – 11:30	O40: **Lidietta Giorno** CRN Rende ***Highly Selective Biofunctionalized Nanocomposite Membranes for Molecular Recognition and Bioconversion***
11:30 – 11:45	O41: **Luisa Barbieri** Università di Modena e Reggio Emilia ***A sustainable technological system for fertilization and cultivation box***
11:45 – 12:00	O42: **Maria Laura Santarelli** Università di Roma La Sapienza ***Analytical approach by Raman spectroscopy for the evaluation of microplastics in the marine environment (Marine Litter)***
12:00 – 12:15	O43: **Miriam Cappello** Università di Pisa ***Tannery sludge as a sorbent of VOCs in tannery air emissions***
12:15 – 12:30	O44: **Cataldo Simari** Università della Calabria ***Quaternized polyepichlorohydrin-based membrane as high-selective CO_2 sorbent for cost-effective carbon capture***
12:30 – 12:45	O45: **Sergio Santoro** Università della Calabria ***Photothermal Assisted Evaporation (PhAEV) system for brine treatment***
12:45 – 13:00	O46: **Luigi Ciani** TA Instruments - Divisione di Waters Spa ***Caratterizzazione tramite analisi termica di materiali utilizzati nelle batterie a ioni di litio***
13:00	**Premiazioni** e **Chiusura Congresso**

POSTER

- *I sessione: lunedì 5 settembre*

P1. Electro-Curing: New strategy for the curing of epoxy-nanocomposites
Luigi Vertuccio
Università della Campania "Luigi Vanvitelli"

P2. Current conduction mechanisms in structural resins loaded with non-covalently functionalized graphene nanosheets
Marialuigia Raimondo
Università di Salerno

P3. Hemp fibers modified with graphite oxide as green and efficient solution for water remediation
Gianluca Viscusi
Università di Salerno

P4. A Formalism for the Comparison of Electrocatalysts for the Oxygen Reduction Reaction (ORR) based on Thin-Film Rotating Ring-Disk Electrode studies
Enrico Negro
Università di Padova

P5. A New Frontier in Membranes for Redox Flow Batteries: The Polyketone-Based Membranes
Keti Vezzù
Università di Padova

P6. Self-healing biodegradable polymers
Elisa Calabrese
Università di Salerno

P7. Molecular Dynamics study of Silica-Ketoprofen hybrid materials synthesized by Sol-Gel: Interaction study for drug delivery
Michelina Catauro
Università della Campania "Luigi Vanvitelli"

P8. Natural Methylxanthines: electrochemical oxidation methods and MS techniques as synergic tools to evidence intermediates
Rita Petrucci
Università di Roma La Sapienza

P9. Free N-heterocyclic Carbenes from Bronsted Acidic Ionic Liquids: Direct Detection by Electrospray Ionization Mass Spectrometry and Study of their Speciation
Isabella Chiarotto
Università di Roma La Sapienza

P10. Interactions for drug delivery: a Molecular Dynamics study of inclusion complexes between anticancer 5-fluorouracil and β-cyclodextrin
Giuseppina Raffaini
Politecnico di Milano

P11. MgAl-CO_3 layered double hydroxide (LDH) nanoscopic crystallites: Physico-chemical and biological characterization
Antonio D'Angelo
Università della Campania "Luigi Vanvitelli"

P12. Production of Monolayer and Bilayer Nanofibers via Electrospinning Process
Raffaele Longo
Università di Salerno

P13. Modified POSS nanoparticles for the stabilization of styrene-isoprene-styrene triblock copolymer
Ignazio Blanco
Università di Catania

P14. Metakaolin(MK)-based geopolymers filled with volcanic fly ashes: spectroscopic and thermo-mechanical characterizations
Ignazio Blanco
Università di Catania

P15. Effect of formulation of physico-chemical properties of MK-based geopolymers added with waste corundum powder
Giovanni Dal Poggetto
Università di Modena e Reggio Emilia

P16. Multivariate statistical analysis applied to UV-Vis/NIR spectra for Determination of Diisocyanate Group Content in Polyurethanes
Alessandra Ciampa
Politecnico di Bari

P17. Microwave effect on silane functionalized cellulose nanofibrils: a ^{13}C and ^{29}Si solid state NMR investigation
Francesca Serena Abatematteo
Politecnico di Bari

P18. Sulfonated Poly(ether ether ketone) membrane optimization for the set-up of an in-house built small-sized Vanadium Redox-Flow Battery
Antonino Rizzuti
Politecnico di Bari

- ***II sessione: martedì 6 settembre***

P19. The use of PLGA-Encapsulated Epigallocatechin 3-Gallate nanoparticles as a new potential biomedical system: a combined computational experimental approach
Simona Sabbatini
Università Politecnica delle Marche

P20. Steel slags-based materials as catalysts for transesterification and reduction reactions
Maria Stella Leone
Università di Bari

P21. Vapor explosive detection through PbS colloidal quantum dots-based optical sensors
Monica Orsini
Università di Roma Tre

P22. Tacticity of functional polymers studied by solution and solid state NMR spectroscopy
Vito Gallo
Politecnico di Bari

P23. Innovative approach for the synthesis of carbon dots by conversion of beer bagasse via Hydrothermal Carbonization Processes
Viviana Bressi
Università degli Studi di Messina

P24. Attribution of Pollution Source in Apulian Ports by means of Multivariate Statistical Analysis
Rosa Ragone
Politecnico di Bari

P25. TiO_2 nanotube arrays decorated with metallic nanoparticles: a versatile tool for a wide range of applications
Francesca A. Scaramuzzo
Università di Roma La Sapienza

P26. Waste wood biomass valorisation by using Deep Eutectic Solvents (DESs)
Darya Nefedova
Politecnico di Bari

P27. Evaluation of the sustainability for Lithium-Ion batteries recycling technologies
Elza Bontempi
Università di Brescia

P28. Non-isothermal kinetic study of pyrolysis of multi-layered plastic food packaging. Effect of zeolite catalyst
Stefano Vecchio Ciprioti
Università di Roma La Sapienza

P29. Cobalt(II) complex formation in $[C_4mim][Tf_2N]$
Andrea Melchior
Università di Udine

P30. Photothermal responsive core-shell nanosystem based on C dots functionalized with poly(N-isopropylacrylamide) for light-triggered drug release
Giuseppe Consiglio
Università di Catania

P31. Adsorption of cisplatin by dithiocarbamate-functionalized silica
Marilena Tolazzi
Università di Udine

P32. Synthesis and photophysical characterization of Donor-Acceptor molecular architectures with potential Thermally Activated Delayed Fluorescence (TADF) behaviour
Claudia Carlucci
CNR-NANOTEC - Lecce

P33. Versatile Indanone/Indandione-based Thermally Activated Delayed Fluorescence Organic Materials with Diversified Emissive Behaviors of AIE and RTP
Daniele Conelli
Politecnico di Bari

P34. Perspectives and challenges of micro/nanoplastics issues
Laura Eleonora Depero
Università degli Studi di Brescia, INSTM

P35. Synthetic and formulation studies for the development of innovative releasing agents
Giuseppe D'Orazio
Politecnico di Bari

P36. Synergistic effects of combined UVA light and atmospheric plasma for efficient chemical decontamination and microbial inactivation of packaged fish products
Daniele Bugnotti
Università di Trento

P37. Characterization and treatment of non-recyclable plastics fraction in municipal solid waste streams - RECOVER project
Patrizia Cinelli
Università di Pisa

P38. Toward greener productions of amphiphilic nanostructures based on Cashew Nut Shell Liquid (CNSL) components
Ermelinda Bloise
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COMUNICAZIONI ORALI

PL1 • SOFT CHEMISTRY TOOL BOX FOR NEW FUNCTIONS: ORIGINAL BOTTOM- UP OPPORTUNITIES FOR ENGINEERING MULTIFUNCTIONAL HYBRID ARCHITECTURES

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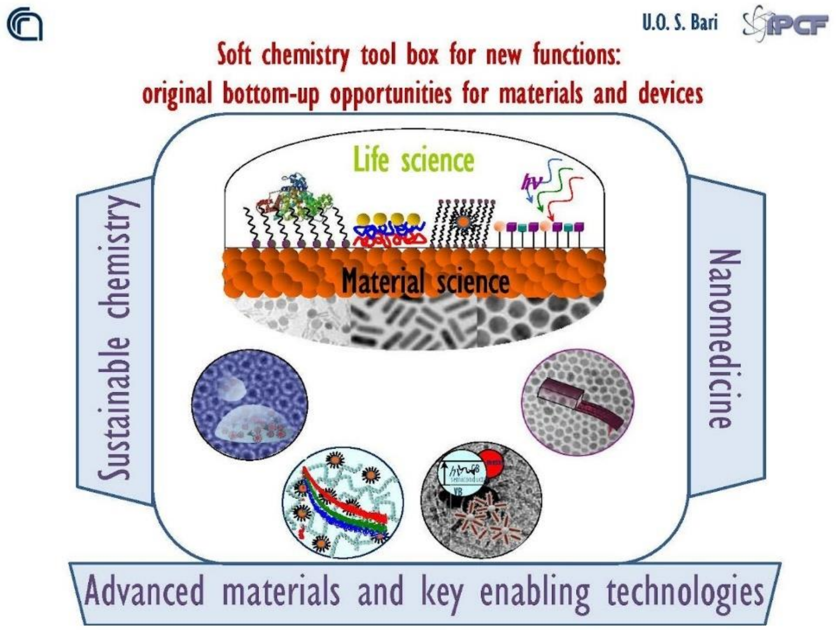
One of the most important challenges of the last years is represented by the synthesis of (bio)organic/inorganic hybrid structures with properties opportunely designed and changed by manipulating the organization of single components contributing to the realization of novel multifunctional and composite nanostructures that reflecting the synergy among the components, have the potential to overcome the functionality of traditional materials and address specific applications.

In this perspective, “bottom-up” approaches, taking advantages of different driving forces involved in the assembling process, such as electrostatic interaction, covalent bonding, coordination and supramolecular interactions, allow to arrange NPs and to manipulate the inter-particle distance.

This presentation will report the most recent results in the design and fabrication of specialized systems involving properly functionalized nanoparticles and nanostructures with highly controlled physical and chemical properties and a careful surface engineering.



Soft chemistry tool box for new functions:
original bottom-up opportunities for materials and devices

In particular will be examined

1) New multifunctional and multi-targeting nanomaterials for environmental and biomedical application.

2) Liposome systems to realize new hybrid biocompatible materials, such as mucus-penetrating liposomes, vesicle-encapsulated nanocrystals (NCs), and biomimetic functionalized surfaces.

3) Inclusion complexes between variously functionalized cyclodextrines (as host systems) and natural or synthesized porphyrins (as guest systems) for both biomedical (photodynamic therapy, PDT) and biotechnological applications.

4) Functional bio-organic hybrid complex for light harvesting and conversion ability.

PL2 • Interplay between Synthesis, Mechanisms and Performance of Ionomers and Electrocatalysts for Ion-Exchange Membrane Fuel Cells

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Ion-exchange membrane fuel cells (IEMFCs) are a family of electrochemical energy conversion and storage devices characterized by several attractive features, including outstanding energy conversion efficiency and a clean operation. IEMFCs are a cornerstone of the *"hydrogen economy"*, one of the most promising avenues to decarbonize the energy sector, with the ultimate purpose to curtail the emissions of greenhouse gases and mitigate global warming. Therefore, a goal of great practical relevance is to devise highly performing, durable and inexpensive IEMFCs.

IEMFCs consist of an electrolyte membrane sandwiched between two electrodes. At the membrane-electrode interfaces are located electrocatalytic layers (EC layers) comprising suitable electrocatalysts (ECs) able to promote the redox processes exploited by the IEMFC operation. The IEMFC sub-families are distinguished by the attributes of the membrane, especially in terms of: (i) chemical features (*e.g.*, polymeric backbone); (ii) mobile ion(s) (*e.g.*, protons for proton-exchange membrane fuel cells, PEMFCs, OH^- anions for anion-exchange membrane fuel cells, AEMFCs); and (iii) operation temperature. In the environment modulated by the ionomer, the properties of the ECs, with particular reference to the chemical composition of the active sites and support morphology, are correlated to their performance. Hence, to obtain an IEMFC exhibiting a high performance and durability is imperative to rationally design membranes and ECs that are: (i) highly compatible with one another; and (ii) able to express their best performance and durability in the same set of operating conditions.

This contribution overviews our research activities aimed at the development of ECs and membranes for application in PEMFCs, high-temperature PEMFCs and AEMFCs. The topics include: (i) the innovative approaches for the synthesis of the functional components; (ii) the aspects of their physicochemical characterization, together with the unique and comprehensive frameworks contrived for the integration and interpretation of the experimental outcomes; and (iii) the steps to integrate the functional components in high-performing IEMFC prototypes.

The ECs considered here are meant to promote the oxygen reduction reaction (ORR), a sluggish electrochemical process that is a major bottleneck in the operation of IEMFCs fueled with hydrogen. State-of-the-art ORR ECs are based on Pt nanoparticles supported on carbon (*"Pt/C"* ECs). Pt/C ECs warrant a sufficient performance, but suffer from a poor durability and require a high loading of platinum, a strategic element that is prone to trigger supply bottlenecks especially in the event of a large-scale rollout of IEMFCs. The ECs devised in our research laboratory are aimed at addressing all of these issues with materials exhibiting a number of unique features, as follows. (i) Active sites with either an intrinsic ORR kinetics much improved above the Pt baseline or completely *"Pt-free"*, consisting of an *"active metal"* (*e.g.*, Pt, Fe) whose performance is boosted by one or more *"co-*

catalyst” (*e.g.*, Co, Ni, Cu, Sn). (ii) Strong, covalent interactions between the active sites and the C-/N- ligands of the *“coordination nests”* on the surface of the EC support, warranting a high durability. (iii) A support featuring a *“core-shell”* morphology, wherein a *“core”* consisting of suitable carbon system(s) is covered by a carbon nitride (CN) *“shell”*, bestowing facile charge and mass transport features (**Figure 1(a)**). The resulting ECs bestow the IEMFC a high performance with a minimized loading of Pt. Specifically, the PEMFC prototypes mounting the ECs here described yielded more than 20 $kW\cdot g_{Pt}^{-1}$.

The second main topic of this overview is the development and the study of the conductivity mechanism of separator membranes for IEMFCs. The latter consist mainly of ionomer matrices (*e.g.*, perfluorinated systems such as Nafion™, SPEEK and developmental anion-exchange block copolymers), both pristine and doped with suitable nanofillers (*e.g.*, conventional ceramic oxoclusters, *“core-shell”* oxocluters, among many others). The matrix-nanofiller interactions modulate the physicochemical features of the resulting hybrid inorganic-organic membrane, allowing to improve crucial features for applications in IEMFCs such as: (i) mechanical stability; and (ii) conductivity in dry conditions and high temperature. Other separator membranes are overviewed, including: (i) anion-exchange ionomers based on polyketone matrices (**Figure 1(b)**); (ii) hybrid inorganic-organic membranes for HT-PEMFCs based on oxocluster nanofillers and polybenzimidazole-like matrices; and (iii) membranes swollen with proton-conducting ionic liquids. These membranes underwent a thorough characterization elucidating their morphology, structure, thermal properties, thermomechanical relaxations and electric response (**Figure 1(c)**). The integration of all the above knowledge yielded a unique, comprehensive and general framework which proved crucial to elucidate the interplay between the physicochemical properties of the different phases within each membrane and their overall conductivity mechanism. This allowed to trigger the development of new high-performing separator membranes for application in IEMFCs.

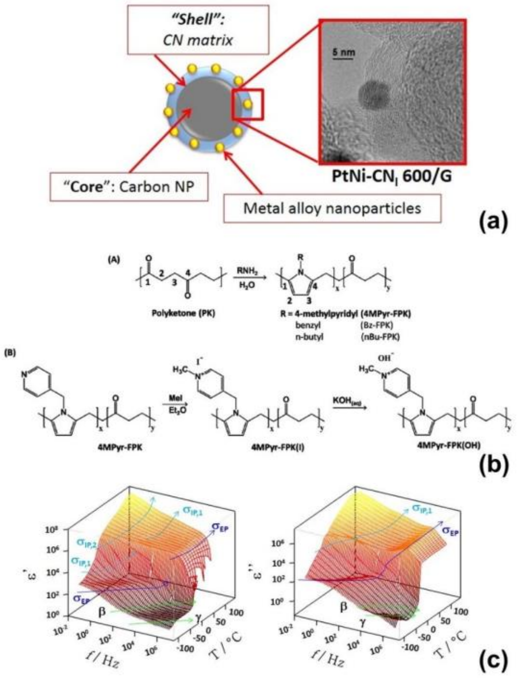

Figure 1. (a) Morphology of a selected electrocatalyst. (b) Synthesis approach for the preparation of polyketone-based membranes for anion-exchange membrane fuel cells. (c) Real (ε’) and imaginary (ε”) permittivity of wet Nafion ionomer.

Figure 1. (a) Morphology of a selected electrocatalyst. (b) Synthesis approach for the preparation of polyketone-based membranes for anion-exchange membrane fuel cells. (c) Real (ε’) and imaginary (ε’’) permittivity of wet Nafion ionomer.

PL3 • Circularity through replacement of treatments and materials

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Nowadays, REACH constrains are greatly impacting defence industry. In the context of replacement of hazardous materials, the theme of circularity is of fundamental importance. New technologies in the domain of surface treatments, 3D printing and ceramic materials should provide efficiency in recycling and quantity reduction, including the introduction of green alternatives. Several replacement processes are being developed and implemented, but a much higher level of attention is needed to ensure that all REACH regulations could be timely respected introducing eco-friendly substances and treatments.

KN1 • Lewis acidic Zinc(II) salen-type complexes as multifunctional molecular materials

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The most recent results on the sensing properties and responsive supramolecular nanostructures of the Lewis acidic Zn(II) salen-type complexes, are presented.[1,2] The Lewis acidic character of these complexes is consequence of the structure of the tetradentate N_2O_2 ligand, which constrains the metal center to a pseudo-planar coordination. In the absence of Lewis bases, stabilization is accomplished by mutual intermolecular Zn···O interactions with formation of dimeric/oligomeric aggregates, while in the presence of Lewis bases monomeric adducts are formed through an axial coordination. The sensing properties of these mononuclear or dinuclear complexes can be related to the optical absorption changes and fluorescence emission enhancement associated with the formation of the adducts upon addition of a monotopic or ditopic Lewis base, either by deaggregation of the aggregate species or displacement of the solvent coordinated to the metal center. A recent issue associated with Zn(salen)-type complexes is their capability to transmetalate with divalent ions of the first transition series. It can be related to the stability of the starting adducts and nature of the counteranion. Therefore, transmetalation in Zn(salen)-type complexes can be governed by the appropriate choice of the solvent and counteranion, with potential applications for the synthesis of new M(salen)-type complexes and for sensing specific cations. These complexes are also involved in the formation of responsive nanostructures with vapochromic, mechanochromic, and thermochromic characteristics is driven by non-mutual intermolecular Zn···O interactions, further stabilized by π–π stacking interactions and/or interdigitation of the alkyl side groups.

The Lewis acidic character is not a prerogative of Zn(salen)-type complexes of tetradentate Schiff-bases. Many other classes of Zn(II) complexes can possess this property, depending on the structure of the ligand pocket. Therefore, the study of the properties of other families of Zn(II) complexes deserves further investigations with many potential developments.

Acknowledgements
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KN2 • Bare and functionalized hydroxyapatite, multifunctional materials for controlling air and water pollution

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Hydroxyapatite (HAP) is a particular kind of calcium phosphate that may be used as a promising ecological material for remediation treatments of air and waters, besides its established use for decades in biomedical applications. Interestingly, HAP can be extracted from various bio-wastes or synthesized from cheap precursors. The particular structure and surface properties of HAP, such as amphotericity, adsorption capacity, and ion exchange with cations/anions of various metals, determine its success as an adsorbent material for water remediation[1] and as a heterogeneous catalyst[2] in reactions of the air quality protection.

The HAP structure (Figure 1) is highly flexible with possibility of varying the composition without altering its structural properties. The amphoteric properties of HAP are closely related to the Ca/P ratio, therefore the ratio of acidic to basic sites can be changed with syntheses aimed at obtaining HAP with different Ca/P ratios. For example, when the Ca/P is 1.50, HAP behaves like an acid material, while when the Ca/P ratio is 1.67, HAP exhibits basic properties, and Ca/P ratios between 1.50 and 1.67 impart amphoteric properties to the materials.

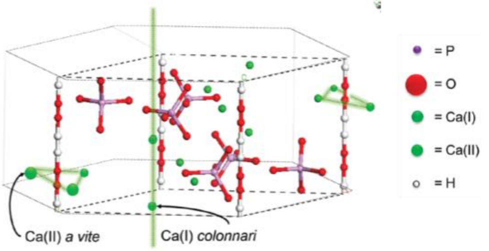

Figure 1. Detail of the hydroxyapatite structure

Concerning the ion exchange property typical of apatites, the Ca^{2+} ion can be replaced by other metal ions allowing easy introduction into the structure of cations of catalytic interest and giving rise to solids with acidic (for example Cu^{2+} or Fe^{3+}, typical Lewis acids) and/or redox characteristics (e.g., transition ions, Cu^{2+}, Co^{2+}, Mn^{2+}, etc.). Then, through an easy surface functionalization of HAP with targeted addition of metal species with catalytic property, promising catalysts for some environmental reactions can be obtained: total oxidation of volatile organic compounds (VOCs), reduction/decomposition of NO_x (NH_3-SCR, N_2O-dec) and selective ammonia oxidation (NH_3-SCO).

Potentiality and limits of materials based on hydroxyapatite for environmental applications in water remediation and air-quality protection will be presented and discussed.

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O1 • Hybrid Peptide-Agarose Hydrogels for 3D Bioassays

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Hydrogels represent ideal environments to locally confine biomolecular probes onto analytical surfaces under solution mimetic conditions. Yet, severe limitations still exist in matching unimpaired analytes diffusion with stable probe entrapment. Herein, we report on a hybrid hydrogel obtained by combining a self-assembling peptide with low-temperature gelling agarose that proved of simple and robust application towards the fabrication of microdroplet arrays.[1]

The two distinct hydrogel components favorably combine to provide a novel material entailing unique features towards 3D assays, as here demonstrated in microdroplet arrays fabrication. The hydrogel microstructural and functional properties are easily tunable, resulting in a unique combination of favorable features which include: 1) spontaneous and rapid formation; 2) direct use in microarrays fabrication due to favorable viscoelastic properties; 3) self-adhesiveness on hydrophobic surfaces.

Most importantly, the 3D assay format showed greatly superior performances with respect to conventional planar 2D assays, as here demonstrated both in model antibody-epitope recognition and in real case scenario IgG immunoreactivity. Overall, the developed material overcomes many of the limitations that currently plague hydrogel for immunoassays limiting their widespread applications (limited mass transport, complex fabrication, poor versatility of use), while being user-friendly, robust and cost-effective.

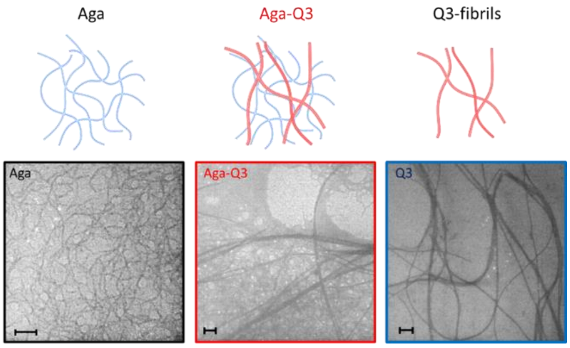

Figure 1. TEM images of Aga 0.05% w/v as mono-component, Aga-Q3 0.05% w/v-25µM mixture and Q3 25µM as mono-component. Scalebars correspond to 200 nm.

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O2 • Synthesis and chemical modifications of cellulose nanocrystals hybrids systems as potential theranostic platforms

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Nanocellulose is one of the most promising nanomaterials thanks to its renewable and biodegradable nature. In particular, the interest in cellulose nanocrystals (CNCs) for drug delivery is due to their unique physical-chemical properties, biocompatibility as well as their large surface area-to-volume that offer opportunity for positive molecular interactions with poorly-soluble drugs, stabilization of drugs nanocrystals and smart chemical modifications [1, 2]. In the recent years, there have been studied different nanocellulose-based products exploiting chemical modifications and producing both single systems, hybrids, and composites [3]. We have experimented new synthetic approaches for cellulose nanocrystals hybrids systems exploiting two types of CNCs. The complexation with other biopolymers has been investigated using chitosan, arabic gum and maltodextrin, producing nanoaggregates, nanoparticles and nanocapsules. These systems have been used to encapsulate potential anticancer substances which come from nature, carvacrol and oregano essential oil (OEO). Finally, CNCs chemical modifications have been studied to tune chemical and biological features. Fluorescent probe anchoring has been applicated to obtain a potential imaging system for a future theranostic application.

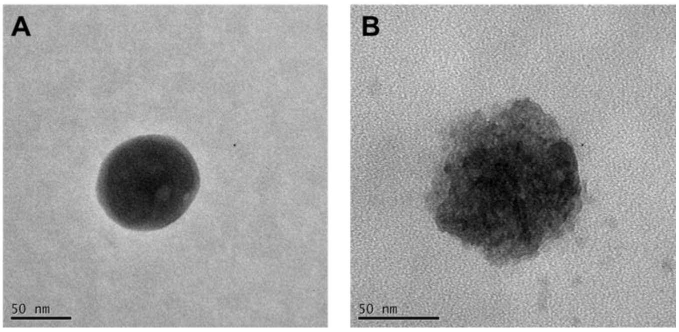

Figure 1. TEM images of OEO (A) and carvacrol-loaded (B) CNCs hybrids systems

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03 • Rare cell capture platforms based on antibody-conjugated electrospun nanofibre mats for noninvasive prenatal diagnostics

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The chance of surviving to a disease often depends on early diagnosis and effective therapy. In the field of early prenatal diagnosis, micromanipulation is a reliable technique for manual selection and isolation of rare fetal cells in maternal biological fluids for molecular or cytogenetic analysis. This technique allows obtaining pure cell populations for analysis, but it is expensive and time consuming, as it requires qualified and experienced staff and specific equipment [1].

The aim of this study is to make the prenatal diagnosis more economical and reproducible in the hospital environment, by creating a device that allows selecting rare cells from biological samples in a semi-automated way. The device consists in electrospun nanofiber mats with surface functional groups conjugated to antibodies capable of selectively binding to the antigens present on the surface of target cells.

Nanofiber mats were produced from polymer mixtures of Nylon 6.6 and Polyacrylic Acid (PAA) in a suitable solvent, with or without the addition of a third polymer, synthetized in house, that should prevent non-specific cell binding. The first phase of the work was devoted to the determination of the operating parameters for electrospinning to optimize the morphology of the mats, their mechanical resistance and handling characteristics. Bioconjugation protocols, based on EDC/NHS (1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride)/(Sulfo-(N-hydroxysulfosuccinimide) chemistry were developed to provide the electrospun mats with specific cell capture abilities. In order to facilitate the recognition of the antibody by the receptors expressed by the target cells, the functional groups of the mat were previously reacted to a linker that acts as a spacer arm. Antibodies labelled with fluorescent probe were used to be able to assess the success of the conjugation reactions by fluorimetry and spectrofluorimetry analyses.

Protocols for cell capture tests on antibody-decorated mats were devised using different cell suspensions: fetal cells (CF), mesenchymal stem cells (MSC) and lymphocytes (WBCs, White Blood Cells). The results of the capture tests were obtained by observing the mats under the optical and electron microscopes (SEM).

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04 • Advanced biopolymer filtration system for Peripheral Blood Mononuclear Cells collection: a study on filter composition and *in vitro* filtrate composition

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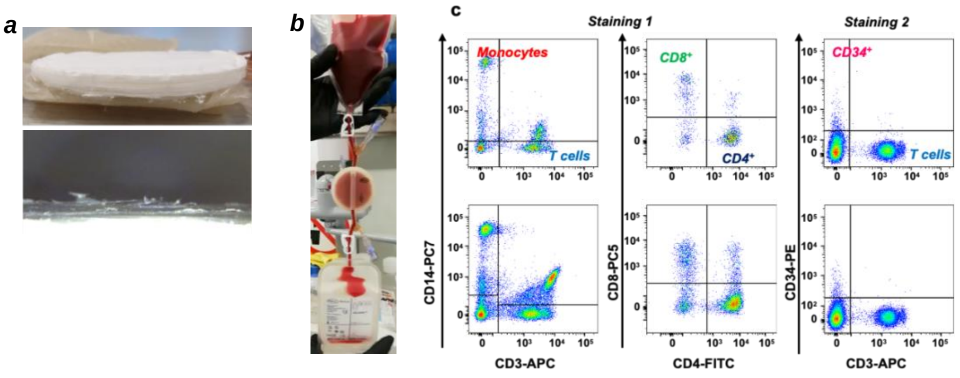
Abstract

Blood filtration systems aim to concentrate peripheral blood mononuclear cells (PBMCs), involved in regeneration processes, from whole blood [1]. These cells are adopted in clinical practice for autologous transplantation in critical limb ischemia with successful limb rescue [2]. In this work, a commercial blood filter was studied in its structure and functions, and filtered PBMCs were characterized by flow cytometry. The percentage of positive cells pre- and post-filtration was preserved, confirming filter efficiency to concentrate cells in a collecting smaller volume (from 120mL to 10mL 0.9% saline solution). No differences were observed in percentage of larger size cells (monocytes, $p = 0.6490$), T cells (CD3+ T cells, $p = 0.3762$; CD4+ T cells, $p = 0.5062$; and CD8+ T cells, $p = 0.4891$), and rare circulating cell populations in healthy conditions (CD34+ hematopoietic stem cells, $p = 0.2875$). These data confirmed filter efficiency and open perspectives to further investigation of filtered PBMC role in regeneration processes, such as in a myogenic *in-vitro* model [3].

Figure 1. Opened filter structure assembled with 12 slices of 50 mm with 3.2 mm of height and of an extremely high hydrophilic polymer filtration membrane **(a)**. Blood passage through assembled slices **(b)**. Flow cytometry blood composition pre- and post-filtration (**c**).



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O5 • Design of electrospun membranes loaded with functionalized Fe_3O_4 nanoparticles for anticancer application

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The electrospinning process allows producing nanofibrous membranes that mimic well the human tissue. [1] For this reason, it is now widely exploited to produce biocompatible membranes for biomedical applications. Thus, they are now deeply studied for their potentialities to treat topically various types of diseases, limiting so the side-effects with non-invasive therapies. [2]

In the current research, electrospun membranes made of Polycaprolactone (PCL) loaded from 2% to 10% of Fe_3O_4 nanoparticles, functionalized with citric acid, are produced, according to a procedure already reported in literature [3]. The functionalization has been done to improve the compatibility between PCL and magnetite nanoparticles. The morphology of the membranes has been studied by FESEM-EDX, proving that the fiber diameters are between 500 nm and 3 µm for all the systems, and the distribution of nanoparticles is homogeneous over all the samples, as reported in Figure 1. The membranes have been tested against melanoma cell lines, proving their cytotoxic activity against tumoral cells. Promising results have been obtained in light of membrane application as a topical treatment of skin cancer.

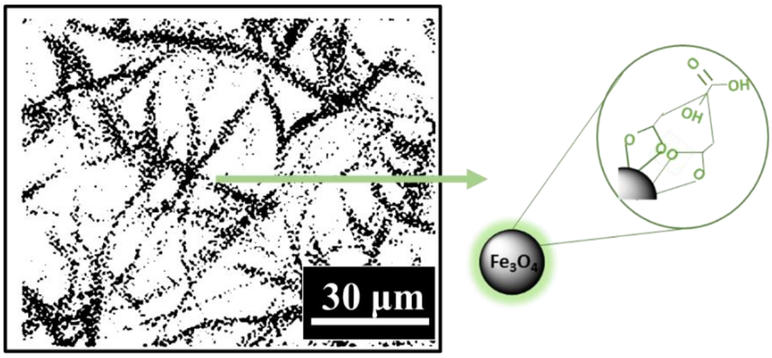

Figure 1. FESEM-EDX of the electrospun membranes loaded with Fe_3O_4 functionalized nanoparticles

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O6 • Design, synthesis and characterization of a theranostic nanoplatform for tumor site-specific delivery of doxorubicin

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Cancer is the second most common cause of death worldwide, accounting for nearly 10 million deaths in 2020, or nearly one in six deaths, but also the highest clinical, social, and economic burden in terms of cause-specific Disability-Adjusted Life Years (DALYs) among all human diseases [1]. Although the number of therapeutic options has increased over the years, there are still drawbacks related poor drug bioavailability and non-specific targeting, responsible for interpersonal variability of the therapeutic effects and severe adverse side effects. In the last two decades, different type of nanovectors of chemical and biological nature that can incorporate and deliver anticancer molecules for chemotherapy, radiotherapy, nucleic acid-based therapy, modulation of the tumor microenvironment and immunotherapy have been proposed.

The distribution of nano-scale drug delivery platforms is primarily controlled by the passive diffusion facilitated by the enhanced-permeability-retention (EPR) effect, which is present in some solid tumors. Hence optimization of the particle size and circulation time of nanovectors is of paramount importance for the success of treatment. However, there are additional biological delivery barriers in solid tumors, such as the desmoplastic tumor microenvironment and increased interstitial pressure due to dysfunctional lymphatics. Imaging can help to evaluate the uniformity of delivery but, to achieve high efficacy, specific retention and cell delivery is typically controlled by active targeting of theranostic to specific molecular targets present on cancer cells using high-affinity molecules, such as antibodies, antibody fragments, peptides, etc. [2].

Our work aims at designing, synthetizing and evaluating nanogels decorated with bombesin (BBN), a peptide belonging to the family of gastrin-releasing peptide receptors (GRPR). Primary breast tumors overexpress GRPR and high GRPR expression is also found in metastatic lymph nodes in 94.6% of cases, hence distant metastases can also be targeted. Poly(N-vinylpyrrolidone)-co-acrylic acid nanogels (P0.5AA50) were used as nanoplatform. The nanogel has been decorated with the BBN peptide modified with DOTA (Lys1Lys3 (DOTA) Bombesin1-14 (BBN_DOTA), a chelating agent that allows the incorporation of radioactive ions in order to track the delivery and image the distribution prior to the administration of the therapeutic dose. The same nanoplatform (P0.5AA50_BNN_DOTA) was used to conjugate a chemotherapeutic drug, doxorubicin (DOXO), via a redox-cleavable linker that can enable intracellular glutathione-triggered release in tumor cells. The nanoplatform has been characterized in terms of particle size distribution, surface charge density, degree of conjugation of BBN_DOTA, and DOXO. Biodistribution of P0.5AA50_BNN_DOTA labelled with radioactive ions was also investigated.

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O7 • Glycolipd based Lyotropic Crystalline mesophases for targeted delivery of dexamethasone

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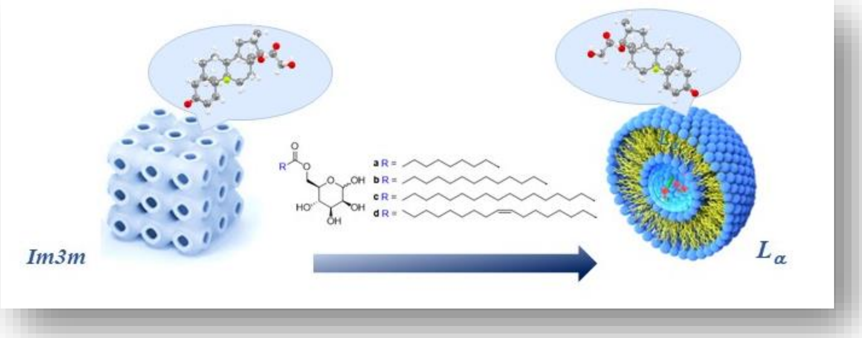
The role of glycolipids in more innovative formulations such as cubosomes and hexosomes is currently under investigation since the development of these self-assembled structures as drug carriers is relatively new and expanding.[1-3] In particular, sugar-functionalized lyotropic liquid crystals (LLC) can be highly specific towards certain cells and tissues and be involved in molecular recognition mechanisms at the surface of cells thus enhancing their drug delivery capacity. The aim of this work was to carry out a systematic study on the structure and mesomorphic behaviour of GMO/glycolipids mixtures as a function of the nature of the glycolipids, mannose-based esters with hydrocarbon chains of different lengths, and of their concentration. At the same time, the physiochemical interaction between Dexamethasone, a potent anti-inflammatory agent, and the lipid matrix were also studied. To achieve this aim, SAXS, ATR-FTIR spectroscopy and Dynamic Light Scattering (DLS) were used. The encapsulation efficiency and drug release were also evaluated.

The results show a phase transition from a bicontinuous cubic phase, *Im3m*, to lamellar phase, L_α, by increasing the concentration of glycolipids in the lipid matrix. The successful encapsulation of dexamethasone has only a small effect on the lipid phase structure determining an increase of lattice parameters in the cubic phases and not in the lamellar ones.



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O8 • Functionalized titanium surfaces with anti-bacterial adhesion properties

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Pure titanium and titanium alloys are the most used in dentistry and orthopedics because of their unique mechanical properties, corrosion resistance in biological media, and their good biocompatibility and osseointegration ability [1]. However, despite the outstanding mechanical and biological properties of titanium-based devices, the implant failure, mainly due to postoperative infection and/or immune responses, still remains a significant concern, leading to adverse clinical outcomes [2]. Among the different antibacterial compounds, quaternary ammonium salts (QASs) exert a strong antimicrobial activity against a wide class of microorganisms including bacteria, fungi, and viruses [3]. In this study, we investigated the possibility to develop inherent anti-bacterial medical devices by covalently inserting bioactive ammonium salts onto the surface of titanium metal substrates. Titanium discs have been modified by silane chemistry and functionalized with quaternary ammonium salts (QASs) and with oleic acid (OA). The samples have been characterized by ATR-FTIR and SEM-EDX analyses and investigated for the roughness and hydrophilic behaviour. The bacterial adhesion inhibition tests performed against the Gram-negative *Escherichia Coli* and Gram-positive *Staphylococcus aureus*, showed a clear anti-adhesion activity for the samples containing a long alkyl chain between the silicon atom and the ammonium functionality. The results of biological preliminary tests highlight the importance of chemical functionalization in addressing the antimicrobial activity of metal surfaces and open new perspectives in the development of antimicrobial implantable titanium medical devices.

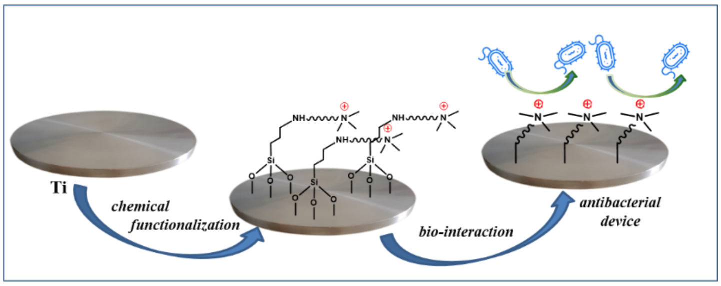

Figure 1. Schematic diagram illustrating titanium surface modification with anti-bacterial adhesion properties.

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O9 • Liposomes as drug delivery system for Antarctic fish-derived antimicrobial peptides (AMPs)

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Antimicrobial peptides (AMPs) are among the most promising biomolecules for the development of new drugs to fight multidrug-resistant (MDR) bacteria and biofilm-associated infections. Although many natural and synthetic AMPs have good antimicrobial activity against MDR bacteria, their use is still limited by low cell permeability and oral bioavailability, limited stability, and some toxicity. The inclusion of AMPs in liposomes could protect them from degradation, increasing their bioavailability and reducing their toxicity [1,2]. This research was focused on some AMPs derived from a peptide isolated in an Antarctic fish [3] whose activity against ESKAPE (*E. faecium, S. aureus, K. pneumoniae, A. baumannii, P. aeruginosa*, and *Enterobacter* sp.) pathogenic bacteria [4] and different *Candida* species [5] had already been shown. For each AMP, depending on its physico-chemical properties and its antibacterial mechanism of action, the optimal liposome formulation was developed, by exploring anionic, cationic and neutral liposomal formulations, consisting of saturated and unsaturated lipids, also in presence of cholesterol. The lipid composition and the lipid/AMP molar ratio were varied and different preparation protocols were investigated in order to obtain stable and monodisperse formulations with the highest AMP entrapment efficiency, as determined by UV measurements. The colloidal stability of liposomes over time was evaluated by Dynamic Light Scattering (DLS) and ζ potential measurements; the morphological characterization was carried out by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Finally, the ability of the selected liposomal formulations to interact with liposomes mimicking the bacterial cell membrane was assessed by fluorescence resonance energy transfer (FRET) experiments. The most promising candidates will be tested in *in vitro* and *in vivo* models for toxicity, pharmacokinetics and antibacterial efficacy.

This work was carried out in the frame of the project NANOPEPTOBAT (Project n° A0375-2020-36557) funded by Regione Lazio within the call "Progetti Gruppi di Ricerca 2020" POR FESR Lazio 2014-2020.

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010 • CHEMICAL VALORISATION OF WASTES FROM DIFFERENT SOURCES

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Bioeconomy has been defined by the European Commission as the economy using renewable natural resources to produce goods and energy. Therefore, it potentially could support economic growth with job creation in both agricultural and industrial areas, reduce dependence on fossil fuels, and improve environmental sustainability of the economic system. Circular Economy aims at extending the life of products and resources through processes such as reuse and recycling, thus closing the cycle of resources. The symbiosis between Bioeconomy and Circular Economy is the key for a sustainable development of the modern economy. In this framework, herein we report on some chemical processes developed in our labs for waste valorisation (Figure 1), such as:

- Synthesis and upgrading of biodiesel obtained from waste cooking oil (WCO)[1]
- Use of steel slags-based materials as catalysts for transesterification and reduction reaction
- Innovative and sustainable procedures for preparation of nanocellulose from waste wood flours[2]

Figure 1. chemical valorisation of waste cooking oil, waste wood flour and steel slags

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O11 • Conversion of lignin-derived aromatic ethers under reductive catalytic fractionation conditions

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Owing to the improvement of reductive catalytic fractionalization (RCF) processes (also known as lignin-first biorefinery) [1], a complete valorization of lignocellulosic biomasses into value-added chemicals, renewable energy and biofuels is firmly established today.

The basic catalysis beyond the depolymerization of lignin in RCF processes involves the lysis of C–O and C–C bonds in the presence or in the absence of added molecular hydrogen by using simple C1-C3 alcoholic H-donor solvents (methanol, ethanol and 2-propanol) as such or in mixture with water in the temperature range of 120–240 °C.

The cleavage of the etheric C–O bond in diphenyl ether (DPE), phenethyl phenyl ether (PPE) and benzyl-phenyl ether (BPE) has been investigated by using Ru/C (5% wt) and Pd/C (5% wt), as heterogeneous catalysts, under reaction conditions generally adopted for the reductive catalytic fractionalization of lignocellulosic biomasses (lignin-first approach) [2].

Ru/C was found to be a better catalytic system, with respect to Pd/C, in the production of aromatic compounds from lignin model diphenyl ether (DPE) that was studied as model molecule to investigate the complex hydrogenolysis-hydrogenation-hydrolysis reactions that occur in the cleavage of the etheric 4–O–5 C–O bond.

The direct C–O bond breaking (hydrogenolysis-hydrogenation route) is preferred in the presence of 2-propanol (that provides best results both in terms of DPE conversion as well as in the production of aromatic compounds), whereas the hydrogenation-hydrogenolysis pathway is favored by using molecular hydrogen. At the same time, by adding water as co-solvent, the impact of the reductive hydrolysis-hydrogenation route becomes more significant allowing the preferential formation of hydrogenated phenolic compounds.

Noteworthy, a very high selectivity to the hydrogenolysis was observed in the case BPE and PPE as a consequence of both their higher steric hindrance, with respect to DPE, that limits the adsorption of their aromatic rings onto the Ru metal surface as well as to the lower tendency of phenol to undergo a hydrogenation process when toluene or ethyl benzene are present in the reaction medium.

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O12 • Life Cycle Assessment study for the obtainment of Levulinic Acid from *Cynara Cardunculus L*. biomass for the synthesis of innovative bioplasticizer.

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This work was carried out within the VISION 2017 project, an acronym for "Development and promotion of levulinc acid and carboxylate platforms through the formulation of new and advanced PHA-based biomaterials and their exploitation for 3D printed green-electronic applications", financed by the Italian Ministry of Universities and research under the PRIN 2017 project. The VISION project aims at, partially, contributing to overcome the environmental issues related to the production and disposal of fossil-based polymers and additives by developing fully bio-based nanocomposites to be employed for the fabrication of piezoelectric, as well as chemical, sensors through additive manufacturing techniques, to be integrated with electronics leading to bio-based fully integrated systems[1]. Different types of lignocellulosic biomasses are studied in the VISION project (e.g. grape pomace and residual *Cynara Cardunculus* L. biomass) as renewable resources to obtain high-value molecules. However, since bio-based plastics and additives are not devoid of environmental impacts, to trustworthy and reliably assess the environmental benefits of the VISION project, all of its actions need to be assessed by applying the Life Cycle Assessment (LCA) methodology. Particularly, this work is focused on the obtainment of levulinic acid from residual *Cynara Cardunculus* L. biomass, through an acid catalyzed hydrolysis assisted by microwave heating, as recently optimized by some of the authors[2]. The as-obtained levulinic acid was then used to synthesize ketal-diester additives to be used as bioplasticizers, making possible to potentially produce completely ecological bioplastics, counteracting the issue related to the non-biodegradability nature of conventional additives, such as phthalates. Particularly, a three steps selective synthesis was recently optimized by some of the authors[3], in order to obtain five different molecules with different side chains that demonstrated remarkable plasticizing effectiveness when added to both Poly(Vinyl chloride)[3] and Poly(3-hydroxybutyrate) (PHB)[4]. The LCA results, in conjunction with those from the experimental activities, made it possible to find the optimal compromise (among the different modelled bioplasticizers) between environmental impacts and mechanical and thermal properties, highlighting the most impacting phases of each process, thus proposing alternative scenarios and possible meliorative interventions.

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O13 • Photocuring of biobased polymer – nanocellulose composites

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Biobased materials and sustainable processes are attracting a steadily growing interest due to environmental concerns. Photopolymerization is considered a green process, due to low energy input, high reaction rates, and low VOC emissions, it is therefore of interest for the preparation of fully biobased composites.[1] In this work we demonstrate the feasibility of the UV-induced curing of epoxidized [2] and (meth)acrylate biobased monomers, neat and in the presence of a nanocellulosic reinforcement. Monomers derived from cardanol, an alkylphenolic compound extracted from cashew nutshell liquid, a sustainable raw material derived from cashew nutshells, and from soybean oil, were studied.

For the photocured composites, wood-derived microfibrillated cellulose (MFC) or hemp-derived nanocellulose (HNC) wet templates were prepared by filtration, impregnated with the monomer and photoinitiator, and eventually irradiated with UV light. Fourier Transform InfraRed (FTIR) spectroscopy was used to investigate the extent and the kinetics of the photocuring, both for the unfilled monomers and for the composites, monitoring the disappearance of the peaks at 910 cm^{-1} related to the epoxy ring or at ca. 1640 cm^{-1} related to the (meth)acrylic C=C bonds (Figure 1). All the monomers could be successfully cured within seconds or minutes. It appeared however that for the epoxidized monomer the curing reaction in the presence of nanocellulose was hindered and a high amount of photoinitiator was needed to complete the cure. The thermogravimetric analysis indicated also a decreased thermal stability of the nanocellulose in the composite, compared with neat nanocellulose. On the other hand, employing a (meth)acrylic resin, curing was quantitative even in the presence of nanocellulose, and the degradation of nanocellulose was not observed. By a thorough analysis of the two systems, the reason for the inhibition of the crosslinking of the epoxy matrix and for the nanocellulose degradation was identified.

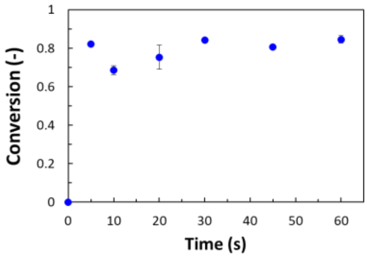

Figure 1. Conversion of acrylated epoxidized soybean oil vs UV irradiation time.

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O14 • From Waste to an Efficient Heterogeneous Catalyst: Spent Lithium-Ion Batteries for the Reductive Upgrading of Biomass-Derived Furfural

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The global warming and the climate change can be mitigated by an effective and aware use of recyclables in the light of the circular economy model. In the last years, we have witnessed a lot of research efforts from both academia and industry players in the recycling of electronic wastes (e-wastes) also considering that, at global scale, they already exceed more than 54 Mt in 2019 with an average of 7.3 kg per capita [1]. The management, the disposal and the recycling of e-waste are foremost crucial since, if not correctly conducted, can generate serious problems for the environment and the human health. Spent Li-ion batteries (LIBs) are widely present in most of electronic devices including mobile phones, personal computers, electric vehicles and already represent an important secondary resource for the recovery of important metals such as lithium, cobalt and nickel. The mixture of anodic and cathodic materials arising from the mechanical shredding of spent Li-ion batteries (LIBs), also known as "Black Mass" (BM), can be easily converted into an efficient heterogeneous Co-Ni catalyst for the selective hydrogenation of biobased furfural and other biomass-derived aldehydes and ketones. Yet, the approach is general and can be applied to a variety of substrates under widely different conditions. The production of the new catalyst involves simple calcination of the e-waste material followed by reduction with H_2 at 500 °C (Figure 1). The so-obtained BM catalyst was then tested in the conversion of furfural (FUR) into furfuryl alcohol (FAL), a precious building block widely used in the chemical and pharmaceutical industry, both in the presence as well as in the absence of added hydrogen. Complete conversion of furfural into furfuryl alcohol is achieved after 90 min at 120°C under 10 bar H_2 in 2-propanol. High furfural conversion can also be obtained under transfer hydrogenation conditions by using 2-propanol as solvent/H-donor. The study opens the route to the use and recycle of spent LIBs as valued raw material of precious catalytic materials suitable for use in fine chemicals production [2].

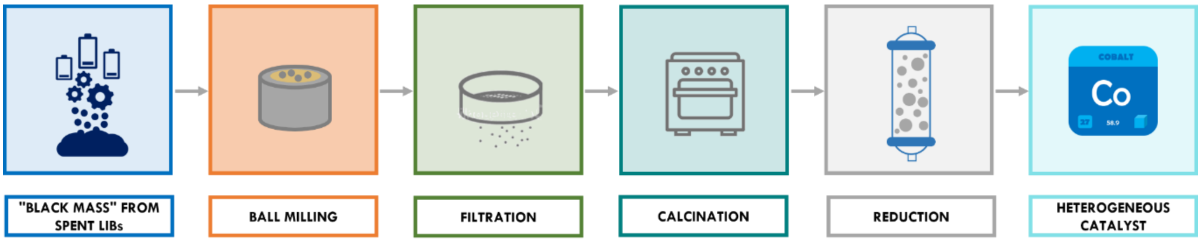

Figure 1. Schematic representation of the mechano-thermal treatment of spent LIBs "black mass" for the preparation of Co-based heterogenous catalysts.

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O15 • Recycling of waste oils as rejuvenators for aged bitumen in RAP

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The recycling of materials considered "waste" is an important goal for developing low environmental impact processes, even in pavement constructions. Therefore, the use of reclaimed asphalt pavement (RAP) is an important strategy in the preparation of new roads [1-2]. Anyway, the bituminous binder in RAP has been subjected to oxidative aging, that determines a physical hardening and limits its workability and performances like the cracking susceptibility. For this reason, quite expensive additives, acting as rejuvenators, must be used together with RAP to restore the binder original viscosity and properties, thus allowing an increase in the percentage of RAP in the new formulations. In this study the recyclability of a waste mineral oil (MO) from the automotive industry and a waste domestic cooking vegetable oil (VO) as rejuvenators for aged bitumen in RAP was tested (Figure 1). The oxidized bituminous binder in RAP was simulated using a 50/70 base bitumen that was artificially aged in laboratory. Several mixtures were prepared by adding different percentage of recycled oils to restore the desired properties. Waste oils were compared measuring compatibility, diffusivity, and rejuvenating efficiency. The domestic cooking vegetable oil resulted the best rejuvenating agent and about 4.0 wt.% of this additive is enough to restore binder viscosity and stiffness.

Figure 1. Schematic approch to realize a sustainable road pavement using RAP rejuvenated using waste oils.

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O16 • Chemical resistance in acids of alkaline activated materials from volcanic materials and metallurgical slags

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Volcanic materials, such as volcanic ash and paleo-soils and metallurgical slags have been tested to be used in alkali activated materials production due to their high aluminosilicate and amorphous content. Compositional optimization is important for the obtainment of a reticulated network responsible for chemical and mechanical resistance, therefore percentages of metakaolin to be added to the alkali activated paste were considered in the mix design.

The geopolymeric samples were characterized in terms of integrity in water, which provides indirect information on the geopolymerization process. The degree of geopolymerization was analyzed by measuring pH and ionic conductivity of the eluates after 24h of immersion of the sample in distilled water- Additionally, it was tested the reactivity of the geopolymers in Hydrochloric acid solution to determine the percentage of material that has been converted to "cement" and the portion that has not reacted with the alkaline solution.

The deteriorating effect of acids on cementitious materials has become a worrying problem over the world. The durability at acid attack is a desirable property for structural materials because the phenomenon of acid rains is a widespread, serious and real problem. Samples were tested on the resistance to acid attack in terms of weight loss, appearance analysis and porosity change. The acids that have been analyzed are weak and strong; as weak acid there is Acetic acid 0,5 N that evaluates the behavior of a material to the action of meteoric waters. Among strong acids there are Sulfuric acid at different concentrations, Nitric acid and Hydrochloric acid. The results obtained are compared with those resulting from the attack of geopolymers containing 100% metakaolin which are considered as reference. Results showed that the carbonatic phases are strongly dissolved in any type of acid and the geopolymeric gel modifies its composition with dissolution of Al. The attack of the acid onto the gel is firstly due to Al leaching out. So Al-rich geopolymer networks are dissolved more evidently and shift the amorphous halo to lower 2θ in the XRD patterns.

O17 • Red Mud-Blast Furnace Slag Based Alkali-Activated Materials

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Bayer process is widely diffused in the world for alumina/aluminium production, but it creates a large amount of alkaline waste material known as red mud (RM). The aluminosilicate nature of the RM makes it potentially suitable as a precursor for the production of alkali-activated materials. In this work, RM was mixed with different percentages of blast furnace slag (BFS) and then activated by sodium silicate solution at different SiO_2/Na_2O ratios. Obtained samples were characterized by chemical-physical analyses and compressive strength determination. Very high values of compressive strength, up to 50 MPa, even for the higher percentage of RM in the raw mixture (70 wt.% of RM in powder mixture), were obtained. In particular, the higher compressive strength was measured for cubic samples containing 50 wt.% of RM, which showed a value above 70 MPa [1]. The use of RM as a precursor of alkali-activated materials is one of the best opportunities for both the ecosystem and the economy. In fact, starting from the results obtained with the pastes, mortar samples have been prepared by alkali activation of RM with various percentages of BFS and inert construction and demolition aggregates. Mortar samples were characterized by compressive strength determination showing very interesting values. Such material can be used to manufacture solid bricks for structural use and concrete tiles for road paving or for other purposes in the construction field. The environmental impact of the studied samples was evaluated by a LCA “cradle-to-gate” approach and the results have been compared with traditional materials currently marketed (figure 1) [2]. The LCA results show that obtained samples are characterized by a lower environmental impact compared to commercial products and that can be used as an eco-sustainable alternative in the construction industry.

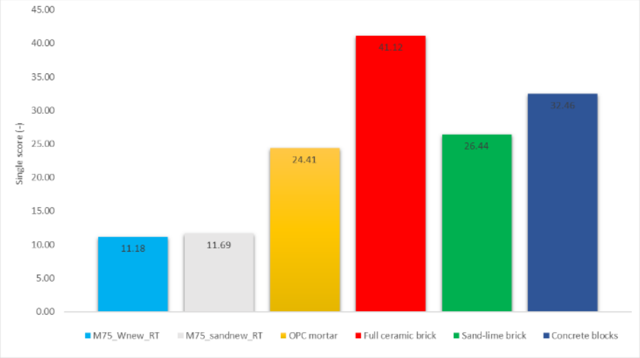

Figure 1. LCA analysis performed on mortars and compared with commercial products.

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O18 • Solid State Polymer Electrolytes for Lithium Sulfur batteries (Li-S)

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The solid-state polymer electrolytes (SPEs) have attracted great interest because they might improve lithium-battery technology by replacing the liquid electrolyte currently in use and thereby enabling the fabrication of flexible, compact, laminated solid-state structures, free from leaks and available in variety of geometries. SPEs are typically dual-ion conductor systems, obtained by dissolving a lithium salt in a polymer matrix, therefore, both cations and anions are mobile and will cause a concentration polarization leading to poor performances of batteries. A compromise between the characteristics of a solid-state polymer electrolyte and a gel-like polymer electrolyte could be a solution to these issues. Gel polymer electrolytes (GPEs) are a promising and concrete concept of electrolytes for lithium-battery technology [1]. Recently, single lithium-ion conducting solid polymer electrolytes (SLIC-SPEs) have been proposed as an innovative concept of polymer electrolytes, where anions are covalently bonded to the polymer, inorganic backbone, or immobilized by anion acceptors, and only the Li^+ cation will contribute to a permanent flow of charge [2]. Also, it is of great interest the free-radical photopolymerization, which turns out to be a low-cost, solvent-free and energy-saving technique very well established for many applications. This technique, can be suitably adapted to the preparation of solid-state polymer electrolytes. They are considered as the next generation safe electrolytes, and generally accepted to have advantages over conventional SPEs such as unity transference number, absence of harmful effect of anion polarization, extremely low rate of Li dendrite growth and immobilization of the lithium polysulfides in the lithium-sulfur (Li-S) batteries [3].

For this purpose, solid state electrolytes were synthesized by dispersion of nano-additives bearing suitable functional groups [4]. Besides, a thorough and systematic study of the lithium-ion transport was conducted by pulsed-field gradient nuclear magnetic resonance (PFG-NMR) and electrochemical impedance spectroscopy (EIS), while the mechanical properties of the film electrolytes have been tested by dynamic mechanical analysis (DMA) in a wide temperature range.

The electrochemical studies have been conducted both in Li/Li symmetric cell and in secondary Li-S cells.

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019 • C_3N_4/reduced graphene oxide photocatalysts for H_2 evolution from photoreforming of aqueous solutions of organic molecules

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The photo-reforming of aqueous solutions containing oxygenated organic molecules combines photocatalytic water splitting and oxidation of organic in a single process at ambient conditions coproducing clean H_2 and high-value chemicals in the presence of a semiconductor. The photocatalytic H_2 evolution mediated by TiO_2 concluded that H_2 would come either from water-splitting and from the organic substrate [1]. Graphitic carbon nitride (g-C_3N_4) have been recently used as photocatalyst for solar energy conversions; however, their practical application is limited by the slow charge transfer dynamics. In this work we have explored the fabrication of a heterojunction between C_3N_4 and reduced graphene oxide (rGO) which has been recognized to boost electrical conductivity and improve carriers' separation [2]. In the composites, g-C_3N_4 plays the role of the photocatalyst whereas rGO can store and transport electrons to reaction sites so improving the activity as electron transfer medium [3]. Ag was also added as co-catalyst. The prepared composites were used as photocatalysts for the photo-reforming of triethanolamine and ethanol in water.

C_3N_4 was obtained by a double calcination using melamine as the precursor [4], whereas the rGO was prepared by a modified Hummers' method. Ag was deposited using $AgNO_3$ and the metal was reduced by $NaBH_4$. The photocatalysts are labelled as rGO x/CN y/Ag z, where the x, y and z indicate the corresponding nominal weight percentage of the components in the solid composite. The amount of rGO was in the range 20 to 25 % whereas the Ag in the range 1 to 5%, carbon nitride being the remaining percentage. The resulting samples were fully physico-chemically characterized. The photoreforming tests were performed under UV-LED (365 nm) or natural solar light irradiation using triethanolamine or ethanol as organic substances to be oxidized. The effect of Pt (1% in weight) as further co-catalyst deposited in-situ on the composites during selected photocatalytic experiments was also studied. The amount of H_2 greatly increased when Ag and Pt were present, indicating a synergistic effect between the two metals.

The H_2 formation rate achieved 1,415 $\mu mol \cdot g^{-1} \cdot h^{-1}$ in the absence of Pt and 87,871 $\mu mol \cdot g^{-1} \cdot h^{-1}$ in the presence of Pt under UV LED irradiation. This last value was better than that obtained in the same conditions in the presence of the benchmark photocatalyst, TiO_2 Evonik P25. The apparent quantum efficiency of the best material (rGO 24/CN 75/Ag 1) was ca. 9 % by using both UV LED or natural sunlight irradiation.

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O20 • Hydrogen storage through ABO$_{3\pm\delta}$ perovskite oxides

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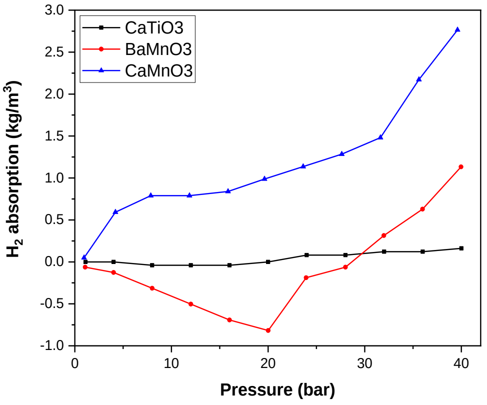
Today, fossil fuels such as oil, natural gas, and coal provide over 80% of all energy consumed globally. However, the need to exploit sustainable energy resources is becoming increasingly urgent. In fact, fossil fuels are not sustainable due to the release of greenhouse gases and other pollutants, which are mainly responsible for global warming.[1] Therefore, among the potential candidates, hydrogen is considered the most viable choice due to its high energy storage capacity of 120 MJ/kg (= 33.33 kWh), which is more than double the energy density of the most conventional fuels.[2] Furthermore, hydrogen-powered systems emit no harmful substances, only water (H_2O) and warm air. Given the extremely low density of this gas, solid-state storage systems are one of the most viable solutions. Generally, the most exploited materials are metal hydrides which, however, are characterized by slow kinetics and are unable to release hydrogen at low temperatures. It is here investigated perovskite oxides as an alternative for H_2 storage. These materials are thermally stable and relatively active and also allow the exploitation of a great variety of elements in the composition while maintaining the basic structure unchanged, and it is also possible to vary the stoichiometry in order to improve its efficiency.[3] Specifically, $BaMnO_3$ (BM), $CaMnO_3$ (CM), and $CaTiO_3$ (CT) were explored. These materials were synthesized by solid-state synthesis (CT) and Pechini method (BM and CM) 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. The as prepared materials were single-phase and showed high thermochemical stability. The H_2 absorption and desorption analysis as a function of pressure, and at different temperatures, were carried out with a High Pressure Gas Sorption Analyzer (i-Sorb Anton Paar). According to the investigations carried out, among the investigated materials, $CaMnO_3$ is able to absorb and release a larger amount of H_2 than BM, and CT (2.76 kg/m^3, 1.13 kg/m^{3,} and 0.16 kg/m^3, respectively) at very mild temperatures and pressures, namely, 308.15 K and 40 bar, that can be considered realistic conditions for applications such as storage in mobile systems (e.g., vehicles). As further advancement, it will be explored the addition of small amounts of transition metal nanoparticles (e.g., Pd), which should promote the dissociation of hydrogen and, therefore, it is expected to improve the ab/desorption kinetics of this gas.



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O21 • Coatings of Calcium Lactate for Thermal Energy Storage Applications

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The increasing cost of energy, as well as concerns about environmental pollution due to its production, are pushing the international community to promote measures to decrease energy consumption by reducing waste. Thermal energy storage (TES) systems are used, particularly in buildings and in industrial processes, to stock thermal energy for later usage applications. Among TES technologies, hydrated salts, employed as thermochemical materials, are largely studied because of their high energy storage density. These systems are based on a reversible chemical reaction to store (release) heat during the dehydration (hydration) process, according to the following equation:

$$A\cdot xH_2O(s) + \text{heat} \leftrightarrow A(s) + xH_2O(g).^1$$

As a new thermochemical material, we propose here an organic hydrated salt that could be easily obtained by a neutralization reaction between lactic acid and $CaCO_3$ or $Ca(OH)_2$: Calcium Lactate Pentahydrate (CLP). The obtained results demonstrate that CLP works under typical operating conditions of low-temperature heat storage systems (dehydration temperature 80°C and hydration temperature between 20-65°C) and shows a dehydration heat of 1021 kJ/kg. In addition, CLP does not undergo deliquescence even under high relative humidity (100%), in contrast with commonly used hydrated salt. What is more, CLP is a non-toxic, non-corrosive, non-flammable, and non-explosive reactant similar to the products of dehydration reaction, that combined with low cost and high heat of reaction, promote this salt as a promising material for thermal energy storage, opening new paths for the material selection and engineering in this application field. In order to improve the diffusion of vapour during the hydration process and to increase the heat transfer efficiency with the heat exchanger, coatings of CLP with different polymeric matrices were prepared. The three different involved binders are polymers with a great water vapour permeability[2], in particular (i) silane, (ii) polysiloxane and (iii) SPEEK (sulfonate polyether ether ketone) were investigated. Specifically, in the case of silane, the silanol binder was obtained through an acid-catalyzed sol-gel process; while for polysiloxane a dehydrogenative coupling reaction, catalyzed by an organo-tin, was carried out. For i and ii, the salt is preliminary mixed with EtOH and added to the polymeric solution. With regard of SPEEK, it was preventively dissolved in DMF and then mixed with salt. As far as the composition of the coating mixture is concerned, it consists of 50% in weight of filler (CLP) and 50% in weight of binder, for each matrix used. The coatings have been deposited on aluminium strips using drop test technique. The hydration tests have shown that the best kinetics is found for coatings with SPEEK, furthermore, this binder is the most flexible among those investigated and therefore better resists the process of volume shrinkage/expansion of the salt caused by the cyclic dehydration/hydration reactions. Finally, different binder based composite coatings were investigated demonstrating the applicability of CLP in coating technology. The results also promote this engineering as a new area of investigation capable of closely linking an improvement in terms of heat exchange performance, widening, meanwhile, the industrialization of the manufacturing process.

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O22 • New functionalized polyketones for anion exchange membranes

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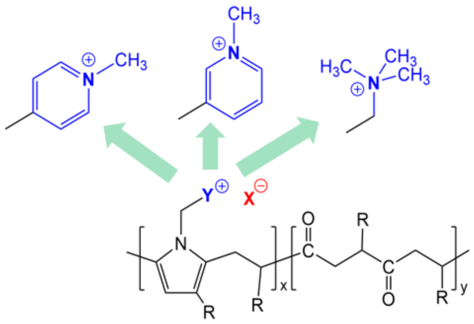
We present new anion exchange membranes (AEMs) based on the polypyrrole-polyketone backbone for electrochemical application, obtained from polyketones (ethylene, propylene, and carbon monoxide copolymer). Polyketones show 1,4-dicarbonyl repeating units that allow the grafting of different side chains and functionalities through Paal-Knorr cyclization reaction with a primary amine bearing the desired functional group.

In this work, some of the most recent results obtained using 3-picolylamine and dimethylaminoethylamine will be presented and compared with those previously reported by some of us [1-2]. The functionalization degree was tuned by changing the amount of amine and/or the reaction conditions like temperature and time. The obtained polymers were solvent cast to produce the membranes that were then quaternized and characterized to investigate their structure, functionalization degree, thermal stability, and ion conductivity for the possible application in electrochemical devices.



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O23 • Interplay between Physicochemical Features, Oxygen Reduction Reaction Mechanism and Fuel Cell Performance of *"PGM-free"* Hierarchical Electrocatalysts Comprising Fe-Sn Active Sites

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The development of advanced electrocatalysts (ECs) for the oxygen reduction reaction (ORR) is a very active active research area in the field of electrochemical energy conversion and storage devices. In the operation of ion-exchange membrane fuel cells (IEMFCs), the ORR is a major bottleneck as it introduces very large overpotentials. Furthermore, ORR ECs for the acidic environment typically comprise a significant loading of platinum-group metals (PGMs) to meet practical performance requirements,[1] raising concerns due to the low abundance of PGMs.

This work reports a new family of hierarchical ORR ECs (H-ECs) that: (i) are *"PGM-free"* and based on bimetallic Fe-Sn active sites; (ii) comprise a support *"core"* consisting of a blend of nanostructured carbon species covered by a carbon-nitride *"shell"* stabilizing the active sites in C- and N- *"coordination nests"*. The H-ECs are obtained by means of a unique synthetic protocol that allows for modulating: (i) the active site composition; (ii) the EC structure; and (iii) the morphology and porosity features, which are critical to control the transport of reactants and products in the final device.[2],[3] The interplay between the synthetic parameters, physicochemical properties and electrochemical performance is elucidated, emphasizing: (i) the impact of the metals on the ORR performance and mechanism, both in acidic and alkaline environment; and (ii) the effect of the nanostructured carbon species in the *"core"* on the porosimetric features of the H-ECs and, in turn, on the mass transport properties of the fuel cell prototypes.

The composition, morphology, porosimetric features and structure of the *"PGM-free"* H-ECs are determined by inductively-coupled plasma atomic emission spectroscopy, CHNS microanalysis, near-ambient pressure X-ray photoelectron spectroscopy, ultra-high resolution scanning electron microscopy and transmission electron microscopy, nitrogen physisorption, and wide-angle X-ray diffraction. The ORR is studied via the cyclic voltammetry with the thin-film rotating ring-disk electrode (CV-TF-RRDE) technique. Finally, the H-ECs are adopted to fabricate FC prototypes tested under operating conditions.

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O24 • The bride side of merging prolinated porphyrins and ZnO nanoparticles for chiral sensor development

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Chiral discrimination is one of the most arduous challenges in chemical sensor development, since most of the chiral systems work efficiently in solution but lose their stereoselective properties when used at solid state. Porphyrins are diffusely assembled to give organized materials expressing elements of chirality at the supramolecular level, commonly resulting from the amplification of the chiral information stored by the porphyrin monomers. For instance, we have very recently reported that toluene solutions of Zn prolinated porphyrin derivatives give easily chiral films when drop casted on glass slides.[1] A valuable alternative for preparing chiral solid films is based on the use of hybrid materials combining inorganic nanoparticles with organic sensing elements. Indeed the increasing of the surface area of sensing layers following the merging could greatly extend the range of detection of volatile chiral compounds or even enrich porphyrinic materials of chemoresistive properties when semiconductors are employed. We previously reported that chiral porphyrin derivatives grafted onto ZnO nanoparticles were able to discriminate limonene enantiomer vapors when tested in QMB sensors[2]. The present contribution will illustrate recent results with these systems, whose preparation was optimized and focused on novel porphyrin derivatives by varying metal ions inserted and chiral center configuration (Figure 1). The potentialities of these hybrid materials have been also tested in chemoresistive sensors by depositing them on interdigitated electrodes and evaluating the light activation of the chemical sensitivity along with conductivity, as just observed for other achiral porphyrinoid-capped ZnO nanoparticles[3].

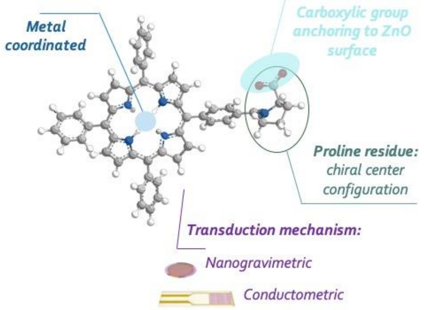

Figure 1. Options offered by prolinated porhyrin derivatives to develop chiral sensors

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O25 • Self-assembled silica-based nanoparticles in advanced materials for tyre application

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SiO_2-based nanoparticles (NPs) are commonly used to produce high-performance rubber nanocomposites (RNCs) with enhanced properties critically depending on i) the NPs geometrical characteristics; ii) the interfacial interactions between polymer and NPs and iii) the control of the morphology of the aggregates at the local scale within the NC. Recently, the dramatic improvements in polymer composites properties have been mainly attributed to the ability of filler NPs to self-assemble into highly anisotropic structures.

In this contest, during the last decade, we have systematically studied the influence of different parameters, such as NPs size, chemical structure, and surface chemistry, and also NP-NP and NP-polymer interactions at interface, with the aim to develop strategies for the NPs self-assembly in RNCs and thus to improve their mechanical and energy-saving properties for tyre applications. Firstly, we explored the anisotropic silica-based NPs, both synthetizing rod-like silica particles having different aspect ratio and modifying naturally occurring silicate fibers[1] with specific size. Successively, we also considered the spherical silica NPs, decorated with polymeric coating, the so-called "hairy" NPs. In any case, silica-based fillers, opportunely synthesized or modified, when embedded in a rubber polymer, self-assembled into highly anisotropic structures repeated in a continuous manner throughout the whole matrix. A detailed investigation at the macro and nanoscale of the self-assembled structures was performed in terms of organization and networking of NPs, nature of the interactions and impact of these features to the improved reinforcement and reduced dissipative phenomena.

The results of this study indicate that the macroscopic mechanical properties of silica-based RNCs can be remarkably enhanced by self-assembled filler domains, whose formation and structure can be controlled by manipulating the chemistry at hybrid interface between the particles and the polymers. In particular, rod-like silica NPs obtained by a controlled acid treatment of pristine sepiolite fibers have given rise to new elastomeric tyre compositions,[2] industrially developed in Pirelli Tyre laboratories, giving rise to the SmartNET ™ Silica technology.[3] This technology allows to create a strong, long-lasting tyre with high rolling efficiency, thanks to the filler capability to form self-assembled domains that connects the nanometric structure of the particle to the macroscopic characteristics of the compound.

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O26 • Functionalization of metallic and semiconductive surfaces for multifunctional coatings

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The bulk properties of a material play an important role in determining the overall suitability for a certain application but it is the surface to have the most critical influence on how a material interacts with its surrounding environment. Coatings significantly improve material properties besides adding new features such as antibacterial properties, corrosion resistance, conductivity and are therefore employed in several fields comprising biomedicine and biosensors. Here, a functionalization method is proposed, which allows for the covalent surface insertion of different organic linkers to be used as anchors for the attachment of biopolymers or bioactive molecules (Figure 1b). This strategy allowed to obtain surfaces uniformly functionalized with three different organic linkers, using green solvents and non-aggressive conditions. thus offering The results obtained constitute a good starting point for the realization of stable polymeric coatings permanently bonded to the surface and offer an interesting alternative to the classic synthesis methods that use organic solvents.[1].

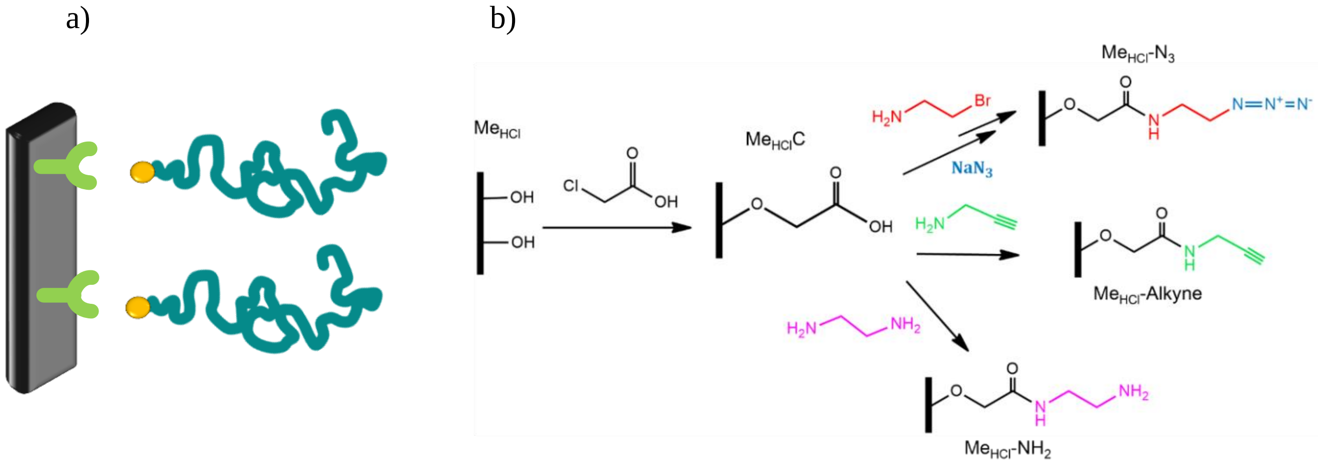

Figure 1. (b) A schematic representation of covalent anchoring: «grafting to» approach and (a) reaction schemes for the metal functionalization with organic linkers.

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O27 • π-conjugated organic mixed valence materials for multi-responsive, smart and versatile devices

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Materials with tunable absorption and emission, sensitive to various stimuli (e.g. heat, light, electric) have aroused considerable attention in the fields of lighting, sensing, display, and optoelectronics.[1] To date, there is a significant focus on organic π-conjugated materials because of their high contrast, fast response, processability, and cost-efficiency.[2] In this context, an open issue is the stability of the electroactive molecules subject to several electrochemical redox cycles. A valid strategy to overcome this issue is the use of organic mixed-valence compounds (MVs), which are being investigated due to their excellent reversible redox switching cyclability from the neutral state to the highly stable, oxidised radical-cation mixed-valence state.[3] MV systems were build up using a π-conjugated bridging unit and two or more redox centers, which both play a crucial role. These systems are crucial materials in electrochromic (EC) and electrochrofluorochromic (EFC) devices, allowing the modulation of both coloration and emission, respectively, by rapid, reversible and locally focused electrical stimuli. Herein, we provide an overview on organic MVs with different bridging units (fluorine, dibenzofulvene and benzothiadiazole) and a different number of arylamino redox centres,[4-5] highlighting the importance of the molecular design and of the structure-properties relationships that results in a fine-tuning of devices response, in terms of different colorations, contrast ratio, response time, quantum yield, etc.[4-5]

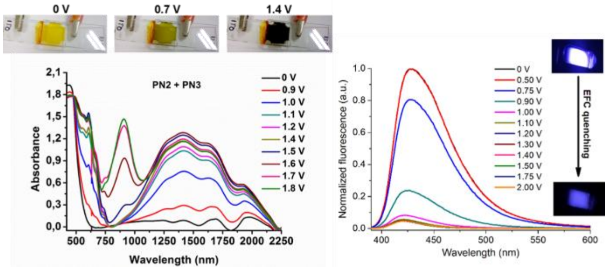

Figure 1. Examples of reversible EC and EFC devices.

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O28 • Engineered polyethylenimine-based materials: novel heterogeneous catalysts for sustainable organic transformations

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Being one of the twelve principles of "Green Chemistry", catalysis represents a key tool for designing increasingly sustainable transformations for bulk and fine chemicals production.

Particularly, there is a growing interest in the transition from homogeneous catalytic systems to "greener" heterogeneous ones. Indeed, heterogeneous conditions ensure an easy recovery and reuse of the catalyst, resulting in the overall reduction of process waste.[1] Polyethyleneimine (PEI) is known to be a suitable material for the synthesis of heterogeneous catalysts. However, in most cases, PEI is used as a grafting agent or as a support for catalytically active metal species.[2,3] Surprisingly, only a few works reported the direct heterogenization of PEI and its use in amine-catalyzed reactions. According to our previous experience in the field,[4] the aim of the present work has been the synthesis of a library of different PEI-based materials to be used as heterogeneous catalysts in widely applied amine-catalyzed reactions (*viz.* Knoevenagel and Henry reactions). Starting from both branched and linear PEI with different molecular weights, their reactivity toward different crosslinkers like epoxides, isocyanate, dianhydrides, and acyl chlorides was tested. The performance of the resulting catalysts toward model reactions was evaluated at room temperature, or by applying thermal or MW heating under different conditions. In designing sustainable and scalable processes, great attention has been given to the minimization of reaction times as well as to the possibility of switching from organic solvents to water medium. Interesting results in terms of conversion and selectivity of the reactions were obtained also in the case of important pharmaceutical intermediates.

The last goal of this study has been the loading of these materials with different metals (*viz.* Cu, Co, Pd, Mn) and their employment as heterogeneous catalysts in industrially-relevant coupling reactions (*viz.* Suzuki and Heck reactions). The unquestioned advantage of heterogeneous catalysis over homogeneous systems, the easy synthetic pathway we have designed, and the effectiveness of these systems toward different amine- and metal-catalyzed reactions also in aqueous medium represent promising starting points for a wider application of these systems.

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O29 • Calcination of N-doped TiO_2 nanoparticles in microwave oven

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N-doped TiO_2 nanoparticles (ND-TiO_2 NPS) are widely studied as visible-light photocatalysts. An easy method for their preparation is the calcination of a precursor TiO_2 material containing a nitrogen source. This study is focused on the calcination under microwave irradiation of a solid mixture containing TiO_2 nanoparticles and a nitrogen source, namely a mixture of NH_4Cl and ammonium citrate, to produce ND-TiO_2 NPS. Microwave irradiation triggers the combustion of the organic fraction with a decrease in weight of about 45% in a CEM Phoenix Black oven equipped with a proper scrubber system. 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 calcination performed in a conventional oven (Anatase 66%, Brookite 29%, Rutile 5%), which previously showed to produce a good photocatalytic material for the NOx depletion[1]. Given that a very exothermic combustion of the organic materials occurs during the process, the calcination has been very difficult to control, yet we succeeded in reproducing the doped powder in a MW oven in 3 h calcination at 375°C using a dense alumina crucible with a wide surface exposed to the oven atmosphere, that helped in heat loss, thus preventing rutile formation (Figure 1, left). The final product showed a comparable photocatalytic activity with respect to the one obtained in a conventional oven (Figure 1, right). Using microwave technology, a considerable reduction of energy consumption was achieved.

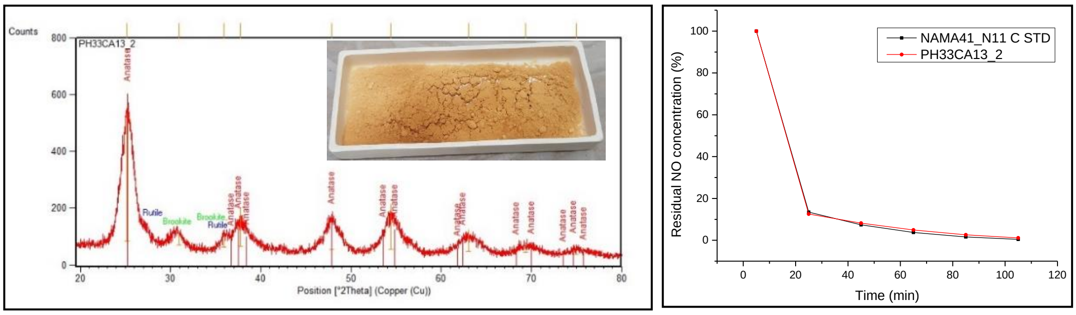

Figure 1. Left: XRD pattern of ND-TiO2 NPS after MW calcination. **Right**: photocatalytic activity of the MW calcined nanomaterial (red line) in comparison with a conventionally calcined sample (black line).

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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O30 • Perfluoro-*tert*-butoxyl-substituted scaffolds: from bioimaging to the functionalization of surfaces and nanomaterials

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The constantly increasing role of fluorinated compounds in materials science, medicine, industry and technology has to deal with severe environmental and toxicological concerns regarding the bioaccumulation tendency of perfluoroalkanes with linear chains longer than six carbon atoms. In search of more sustainable alternatives, promising results were reported using a short-chain multibranched fluorinated compound with 36 equivalent ^{19}F atoms, called PERFECTA (Figure 1a), which was initially formulated into stable and biocompatible aqueous emulsions for ^{19}F Magnetic Resonance Imaging.[1] Taking inspiration from PERFECTA's structure, a series of derivatives were obtained by selective replacement of one of its four fluorinated arms with a different reactive group (X in Figure 1b). This synthetic approach afforded several compounds, bearing 27 equivalent fluorine atoms each, that are useful building blocks for further functionalization and conjugation steps.

In particular, this dendron-like moiety has been linked to different functional groups, including thiols, alcohols, carboxylic acids or esters, azido- or amino- functionalities, leading to a variety of possible applications, including stabilization of noble metal nanoclusters, (super)hydrophobic surface coatings, and functionalization of biopolymers.[2-5] Further studies are currently ongoing for introducing other functional groups, and thus broadening the range of possible applications.

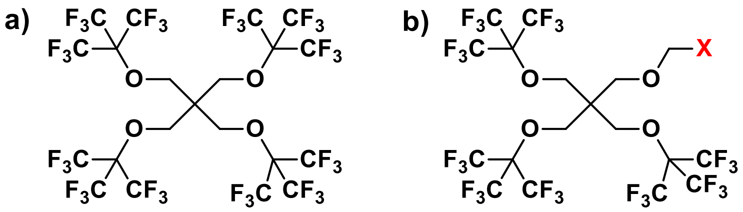

Figure 1. Molecular structures of: (a) PERFECTA; (b) F_{27}-derivatives.

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O31 • In-Situ Formation of Zwitterionic Ligands: Changing the Passivation Paradigms of $CsPbBr_3$ Nanocrystals

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Cesium lead-halide perovskites nanocrystals are at the forefront of research on emissive materials for optoelectronic applications. However, $CsPbBr_3$ nanocrystals (NCs) protected by traditional lipophilic capping ligands suffer from colloidal and optical instability under ambient conditions, due to the surface rearrangements induced by the polar solvents used for the NC purification stages.[1] To avoid post-synthetic approaches, thus far ascertained as the only viable stability-improvement strategy, the surface passivation paradigms of as-prepared $CsPbBr_3$ NCs should be revisited. In this communication, we disclose that the addition of an extra halide source (8-bromooctanoic acid) to the typical $CsPbBr_3$ synthesis precursors and surfactants leads to the *in-situ* formation of a zwitterionic ligand already before Cs^+ injection. As a result, $CsPbBr_3$ NCs become insoluble in nonpolar hexane, with which they can be washed and purified, and form stable colloidal solutions in the relatively polar dichloromethane, even after prolonged exposure to ambient conditions. The improved NCs stability stems from the effective bidentate adsorption of the zwitterionic ligand on the perovskite surfaces, as supported by theoretical investigations. Furthermore, this bidentate functionalization enables the obtainment of blue-emitting NCs with high PLQYs by UV-irradiation in CH_2Cl_2, acting as photo-induced chlorine source.[2] Therefore, the *in-situ* generation of zwitterionic ligands can change the surface passivation mode of $CsPbBr_3$ NCs, allowing the production of pure and stable nanomaterials.

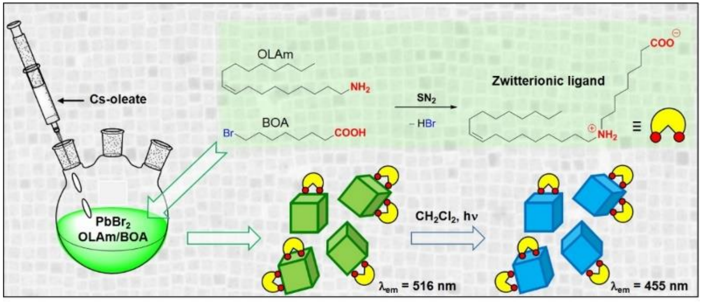

Figure 1. Schematic representation of the in-situ formation of the zwitterionic ligands and photo-induced post-synthetic transformations of the corresponding passivated NCs.

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032 • Green synthetic approach for direct functionalization of graphene with Dimethyl acetylenedicarboxylate

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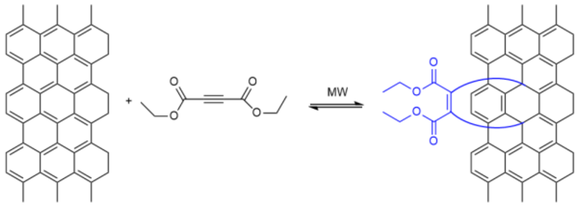
A wide range methods for surface modification of graphene were developed thanks to its ability to works as a diene or dienophile in Diels-Alder (DA) reactions.[1-4] In 2011, Sarkar et al.[5,6] first carried out the DA reaction using graphene as the diene. In 2020, Zhang and colleagues[7] on studied covalent bonding of N-(4-hydroxyl phenyl) maleimide (4-HPM, as dienophile) on the surface of graphene (as diene) via the DA reaction.

In the present work we have investigate one facile DA reaction. The reaction occurs between the defective graphene as a source of diene and Dimethyl Acetylenedicarboxylate (DMAD) as a dienophile under different experimental conditions, introducing the use of microwave technology and minimizing the time required for synthesis. The samples were characterized by thermogravimetry (TGA) coupled with FT-IR spectrophotometer, Raman and Uv-Vis and the most promising procedure was selected.

This reaction provides fundamental information for understanding the experimental condition, for future applications. The covalent functionalization of graphene via Diels-Alder reactions on defective graphene is a simple and elegant efficient approach for electronic and optical applications.



Scheme 1 Graphene reaction (diene) with diethyl (dienophile) with Diels-Alder reaction mechanism

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O33 • COMMUNITY-BUILT ANALYTICAL SYSTEMS FOR FOOD AUTHENTICITY ASSESSMENT AND METABOLITE QUANTIFICATION

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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 our previous studies carried out with different NMR spectrometers (300 to 700 MHz),[1,2] the first examples of community-built analytical systems will be shown. In particular, the case study of a data-driven grape juice identification system will be presented along with the advantages and the limitations of using non-targeted NMR analyses performed at different magnetic fields. Moreover, quantification of metabolites in grape juices by using a community-built calibration tool will be also shown.[3] The feasibility of NMR spectroscopy to generate statistically equivalent NMR signal ratios from a number of different spectrometers will be demonstrated also for other complex mixtures such as aqueous extracts of wheat and flour.[4] Finally, potential use of benchtop NMR in both quantification of standard molecules and valorization of food biodiversity will be introduced.

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034 • NON-TARGETED NMR METHOD TO ASSESS THE AUTHENTICITY OF AUTOCHTHONOUS LENTILS

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Lentils (*Lens culinaris*), a high-protein plant food, are cultivated and consumed worldwide. Among the main producers of this food product, Canada is the leading one and the largest exporter of lentils in the world. The drastic decline of lentils cultivation recorded in Italy has made the country one of the largest importers of this foodstuff, mainly from Canada. Nevertheless, in Italy lentils are still cultivated in restricted geographical areas and to ensure their high-quality value, national trademarks have been introduced. Altamura Lentil has recently received the denomination of Protected Geographical Indication (IGP). This product is cultivated in a distinctive land between Apulia and Basilicata and its qualitative attributes are correlated to the environmental conditions typical of the original land. Therefore, the development of rapid and robust analytical methods capable of establishing the authenticity of lentils and, thus, preserving the cultivation of local varieties is becoming an urgent task. In this context, the non-targeted nuclear magnetic resonance (NMR) approach is receiving increasing attention as a rapid tool for assessing the authenticity of foods, due to its ability to unveil specific product features[1-2] that can be used by data driven classifiers to establish the quality of the food[3-4]. In the present work, a non-targeted NMR approach was successfully applied to assess the authenticity of Altamura lentils and to establish its geographical origin, in a way to discriminate this class of product from the other Italian and/or imported lentils. Furthermore, the developed model was able to highlight a clear differentiation of lentil samples according to harvest year. The results demonstrate the beneficial application of non-targeted NMR in assessing and preserving the authenticity of local food products.

Figure 1. Scheme of the proposed non-targeted NMR approach to assess the authenticity of Altamura Lentil.

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035 • Reverse micelles synthesis of mesoporous Fe-doped CeO_2 as UV/Visible photocatalyst for Ibuprofen degradation

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The massive presence of compounds, called emerging organic pollutants (EOCs), in the environment, causes damage to the ecosystem and human health. Pharmaceutical and personal care products (PPCPs) are used in daily life, with a continuous increase in their concentration in water. The presence of ibuprofen -the third most prescribed and sold drug in the world- in both surface and wastewater has shown that the current purification methods of urban and pharmaceutical industry waste are inadequate. Among several chemical and physical methods proposed for the removal of ibuprofen, photodegradation is considered one of the most promising green chemistry technologies to address the environmental issue in water purification, due to its low-cost, versatility, and environmental friendliness [1]. This research aims to design cost-effective and high-performance catalysts that enhance the degradation of ibuprofen under visible light irradiation. Cerium oxide is a promising candidate for this purpose. This material shows a better response in the visible region of the solar spectrum and a long lifetime of charge separation, compared to the benchmark TiO_2 counterparts. Furthermore, doping with other metals can increase the ceria photoactivity. Among the heteroatom dopants, transition metals are regarded to be the most promising candidates, as they can create defect states in the band gap or introduce energy levels in it. We use a controlled precipitation approach to produce mesoporous Fe-doped Ceria nanoparticles (NPs). Ceria and doped-Ceria NPs were synthesized via a reverse microemulsion at room temperature and using BrijC10 as a surfactant [2]. Fe/CeO_2 catalysts were prepared by a one-pot reverse micelle strategy (nominal molar percentage of 0.5, 1, 2.5, 5, 10). The use of the reverse micelles approach provides an aqueous core that acts as a nanoreactor for the controlled nanoprecipitation of CeO_2 and simultaneously allows the dispersion of Fe species on the formed CeO_2 supports. The obtained samples have been calcinated at relatively low temperature and then the physico-chemical properties have been characterized by several techniques (XRD, N_2 physisorption, FESEM, UV-Vis, Raman and photocatalytic test). The obtained results prove that the reverse micelle precipitation allowed the synthesis of highly crystalline materials, with high surface area value (SSA_{BET} up to $180m^2g^{-1}$) and the presence of lattice defects. The catalytic tests show different behaviour of the samples using UV or Visible light, indicating the presence of different catalytic mechanisms still under investigation. A 60% and 70% degradation of ibuprofen after 5h is achieved for the Vis and UV light, respectively (best performance is obtained with the low Fe samples).

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O36 • Use of natural polymers to develop stable and durable performing membranes

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Humans impact the physical environment in many ways: overpopulation, pollution, burning of fossil fuels and deforestation. Climate change, soil erosion, poor air quality and undrinkable water result from this negative impact. Membrane processes are among the technologies that remedy many of these problems (e.g., water treatment, gas separation, etc.), but at the same time it can be a polluting technology. Indeed, most membranes are developed starting from petrochemical derived materials. The attempt to replace these materials with those of natural derivation finds some obstacles as the membranes based on these renewable materials lack of chemical and mechanical stability. In this research work, biopolymers were selected on the basis of their chemical properties. The functional groups of pectin (PEC) and alkaline lignin (AL) were considered suitable for successfully carrying out the chemical reactions chosen as a strategy to develop eco-sustainable membranes. PEC, with its carboxyl groups, successfully performed the esterification reaction on the hydroxyl groups of polyvinyl alcohol (PVA). A highly water stable PVA/PEC crosslinked membrane, with an unprecedented mechanical resistance, and with long-term unchanged water vapor barrier properties has been developed [1]. On the other hand, the hydrophobic/hydrophilic character of the AL was exploited to guarantee a good interaction with the hydrophobic polyvinylidene fluoride (PVDF). This strategy allowed to develop a membrane with high separation performance of oil from oily wastewater. Besides, a membrane with a minimized quantity of non-biodegradable polymer, and with high affinity for water, thanks to the AL-hydroxyl groups, was obtained. The potential of these membranes for biofunctionalized hybrid systems will be also discussed.

Acknowledgements

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O37 • Electrochemical detection of Pb^{2+}, Cd^{2+} and Hg^{2+} in sea water by sPEEK/TPyP-sensor

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Heavy metals have been the subject of numerous scientific researches for years as they often represent pollutants of the soil and the marine ecosystem which, if not properly monitored, become risk factors for dangerous human diseases[1]. Some of these metals such as zinc, copper and manganese are considered as trace elements that are required by living organisms. However, when their presence reaches higher concentrations it can lead to toxic effects[2]. These undesired effects are also present for heavy metals such as cadmium, lead and mercury, even with trace amounts[3]. The first causes of heavy metal pollution of natural water sources are the agricultural and industrial activities that are complete by less common sources such as cosmetic products, cars and waste disposal. The constant, rapid and highly sensitive monitoring until trace amounts of heavy metals concentrations that accumulate in water and environment is therefore essential. In this discussion, we will present the preliminary results relating to the development of electrochemical sensors for monitoring heavy metals. For the electrochemical measurements, screen-printed sensors (SPCE) of DropSens, were modified by depositing a previously solubilized sulfonated poly(ether ether ketone) (sPEEK) in DMAc (1 wt%) on a carbon electrode. To improve the conductivity and electronic stability, the polymer matrix was modified by incorporating *meso*-substituted phenyl porphyrin (TPyP). This allow the percentage modulation of the different porphyrin species present in the proton-conducting channels of the polymer in the range 0.2 wt%-12.8 wt% (porphyrin/polymer). The electrochemical capability of the sensor sPEEK/TPyP-SPCE was studied from Linear Sweep Voltammetric and Square Wave Anodic Stripping Voltammetry techniques in the presence of three metal ions such as Pb^{2+}, Cd^{2+} and Hg^{2+}.

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O38 • From waste FFP2 masks to the development of a Hg-selective fluorescence sensor

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Heavy metals are among the most dangerous pollutants and are highly hazardous for the environment and humans. In particular, mercury (Hg) can be found into water, air and soil polluting the environment [1], and creating health problems for living beings [2]. Thus, the development of highly sensitive sensors for Hg detection is highly demanded.

In recent years, the COVID-19 emergency has led the global population to the use of masks to counteract the viral infection. Their disposal has in turn become a major problem because of the pollution they have generated [3].

Based on above considerations, we have tried to exploit a waste product such as FFP2 masks for COVID-19 as a raw material to prepare a nanomaterial to be used in the development of a fluorescent sensor for the sensitive and selective determination of mercury.

FFP2 masks were treated with a mixture of H_2SO_4 and HNO_3, the solution neutralized and separated from the salts produced a water-soluble extract of nanometer size. The photoluminescent performance of the as prepared extract was evaluated to study the sensitivity to Hg in the concentration range of 1 to 1000 μM and its selectivity with respect to other heavy metals.

The results of this study showed that the fluorescence behavior of nanomaterials derived by FFP2 masks has promising applications for the development of simple, fast, and sensitive optical sensors for the detection of mercury at low concentrations.

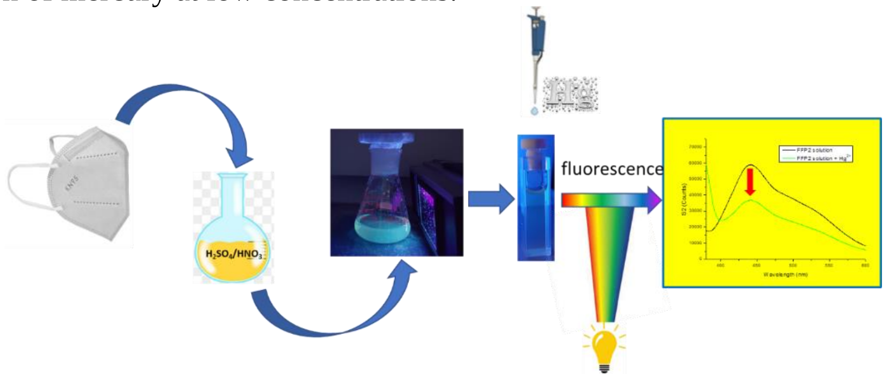

Figure 1. Scheme for reuse of FFP2 mask as sensitive material for mercury detection.

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039 • Transmetalation properties of Zn(II) salen-type complexes as chemosensors for recognition of Cu^{2+} ions in water

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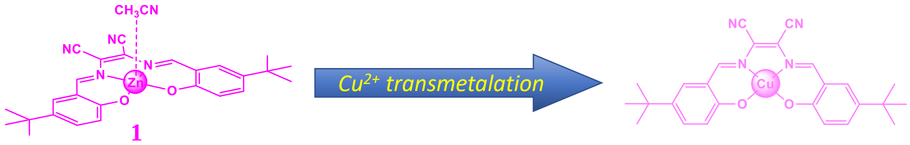
Copper(II) ions play a pivotal role in chemical, biological and environmental systems, therefore a deficit or an excess of this metal ion could compromise the health of plants, animals, and humans.[1] In this contest, the detection of Cu^{2+} ions, especially in aqueous phase, is fundamental in terms of environmental and life concern. Chromogenic and fluorogenic chemosensors represent ideal tools for a simple, fast and highly sensitive detection of this important metal ion.[2]

Zn(II) salen-type complexes are Lewis acidic species able to form aggregates or monomeric adducts in non-coordinating or coordinating solvents, respectively.[3] Moreover, they are versatile chemosensors because allow the chromogenic/fluorogenic detection of neutral and anionic Lewis bases,[4-5] through the disaggregation of aggregate species and of metal ions by transmetalation of the monomeric adducts. Regarding the latter issue, we have recently demonstrated that transmetalation properties of Zn(II) salen-type complexes can be tuned in relation to the Lewis basicity of solvent and nature of metal salts.[6]

Here, we present the selective and sensitive detection of Cu^{2+} ions in water involving the transmetalation ability of the Lewis acidic Zn(II) Schiff-base complex, **1**.



1

Solutions of **1** in CH_3CN show a selective and fast transmetalation of aqueous solutions of Cu^{2+}, involving a naked-eye color change and a complete quenching of fluorescence. The limit of detection of **1** with Cu^{2+} is 0.6 μM, lower than the limit of the World Health Organization (WHO) and US Environmental Protection Agency (EPA) for Cu^{2+} in drinking water. Therefore **1** represents a useful chromogenic and fluorogenic chemosensor for the recognition of Cu^{2+} ions in water.

This research was supported by the University of Catania, PIACERI 2020/2022, Linee di Intervento 2 e 3.

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O40 • Highly Selective Biofunctionalized Nanocomposite Membranes for Molecular Recognition and Bioconversion

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Biofunctionalized polymeric frameworks with high selectivity are needed in many areas, including biocatalytic systems (e.g., for water and air treatment and purification) and biorecognition devices (e.g., for detection of micropollutants). Imparting biological functions to artificial membranes (e.g., through immobilization of biomacromolecules, such as enzymes and antibodies on polymeric membranes) is a strategy obtain biohybrid systems with high selectivity and robustness. Wet chemistry methods to attach biomacromolecules to porous membranes by covalent bond in mild conditions able to preserve biomacromolecular conformation and selectivity will be illustrated. The materials chemistry, physical-chemical properties, membrane structure and topography at nanoscale play crucial role in influencing enzyme activity/selectivity acting on both enzyme conformation and transport of substrate to the immobilized enzyme. Strategies to improve the membrane microenvironment where the enzyme is immobilized, by using functionalized nanoparticles have been explored and will be discussed. The use of biohybrid systems for case studies in biocatalysis and biosensors will be presented.

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O41 • A sustainable technological system for fertilization and cultivation box

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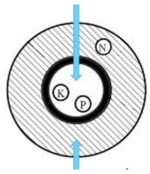
A new integrated system for house and vertical gardens cultures is proposed in this study by synergic application of innovative fertilizer and led lighting [1]. Residues of different production sectors, considered by-products or EoW, have been used as pouring or vitrifying or nutrients or growth substrate agents, depending on their chemical and mineralogical characteristics. Light and porous granules with a core-shell structure in which an aluminosilicate and/or silicate matrix is coated with organic matter have been produced. Both the pH values around neutrality, and the electrical conductivity below 2 dS/m, have allowed them to be used inside the soil for lettuce cultivation tests. Rational approach such as DoE has been used to set up tests and analyze results leading to robust models correlating fertilizer quantity, compositions, led light with finals plant growth parameters [2]. Controlled environment in terms of temperature and humidity (climatic chamber) has been used. A controlled released of nutrient system has been obtained with the follower characteristics:
i) P and K release extended over time and micro-pollutants release absent;
ii) synergic positive interaction between the new materials and the LED modules which lead to improved plant growth [3].



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Acknowledgments

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O42 • Analytical approach by Raman spectroscopy for the evaluation of microplastics in the marine environment (Marine Litter)

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Microplastic pollution is a widespread problem in the planet's oceans and seas. Identified over time in different areas, they immediately interested the scientific world both for the definition of their origin and their removal.

Microplastics are classified as foreign material to the composition of the waters in which they are found, having dimensions less than 5 mm. These are plastic materials of various origins (from fishing nets to lighters and flip-flops) that end up in the sea or rivers and can even reach groundwater either through negligence or lack of proper infrastructure.

Their identification in water is not easy, given their size and the ability to distribute themselves in depth (stratification in the water column).

The analytical systems used for their identification, based on different techniques from spectroscopy to thermal analysis, require separation before identification and therefore water filtration actions, separation by size and shape.

In order to obtain a simplification in the analytical procedure, the recognition in water would be required, but this type of analysis is made complicated precisely by the possible interactions that water can create with plastic materials, furthermore the presence of microorganisms and biofilms on the plastic fragments makes them complicated the identification in water. Considering also their diffusion in large areas both in horizontal and vertical extension (water column), the definition of their distribution and nature represents an element of difficulty that the experts are trying to evaluate and overcome through the application of spectroscopic analytical techniques with wide-ranging analysis action.

In this work, we describe the experience of evaluating microplastics through Raman spectroscopy as a characterization technique, potentially applicable also in situ, taking into account the presence of water and biofilms. In particular, the work reports the need to evaluate the characteristics of the instrumentation for the identification of microplastics, considering how the latter can change with aging in water and with the growth of biofilm on their surface.

The work is supported by ESA project “*BLUE - Brillouin – backscatter - fluorescence LIDAR research for Underwater Exploration of marine litter*”.

O43 • Tannery sludge as a sorbent of VOCs in tannery air emissions

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The tanning industry have a great impact on the environment, for the large consumption of water, the huge amount of waste generated and high emissions of volatile organic compounds (VOCs). A possible solution to reduce the VOCs emissions is to use the sludge, derived from the wastewater treatment, as sorbent. The production of carbon adsorbent from waste sludge has been investigated by several authors[1,2]. The studies focused on the sorption capacity of the obtained adsorbent for adsorption in aqueous solution showing promising results. However, to our knowledge, use of tannery sludge as absorbent for the removal of organic gases has not been reported so far. In the present study, we investigate the use of a granulate deriving from an Italian full-scale pyrolysis plant of tannery sludge as sorbent for the removal of VOCs from air emissions (TTS). A further pyrolysis treatment was carried out to increase specific surface area (BET) and, consequently, its VOC sorption capacity. Different operating conditions were investigated to evaluate their effect on the sorption capacity. Sorption/desorption tests were performed on lab scale sorbent fixed-bed using air streams containing various concentrations of n-butyl acetate, a typical solvent used in the finishing leather formulations (Figure 1). A commercial activated carbon was used as reference sample.

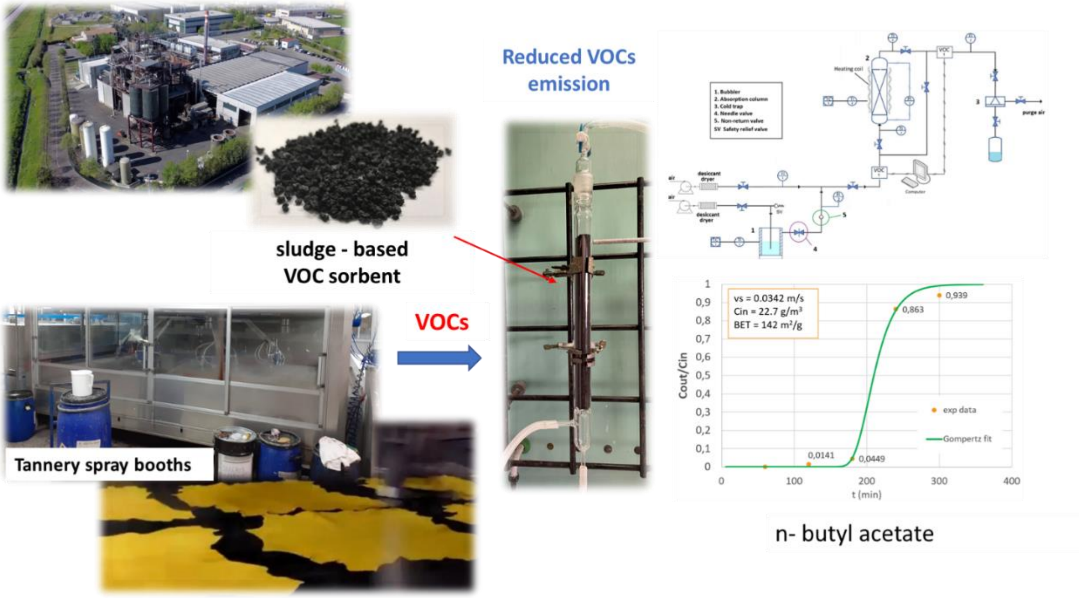

Figure 1. Tannery pyrolysed sludge and the set-up to evaluate its VOC sorption capacity.

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O44 • Quaternized polyepichlorohydrin-based membrane as high-selective CO_2 sorbent for cost-effective carbon capture

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Membrane-based carbon capture has been rapidly emerging as promising technique for effectively cutting anthropogenic CO_2 emissions and mitigating global warming in the future[1]. De facto, membrane technology offers a series of competitive advantages over conventional capture technologies (e.g., amine scrubbing[2] and solid porous sorbents[3]), such as the absence of dangerous emissions or need of harmful chemicals, lower footprint, modular design, low energy consumption, environmental friendliness, no solvent volatilization, and easy scale-up[4].

To date, most studies have concentrated on non-reactive polymers such as ether oxygen-rich polymers, thermally rearranged polymers, etc.[5], which typically operate according to physical processes, such as solution–diffusion mechanism or molecular sieving. Unfortunately, these membranes are generally affected by low selectivity, with the results that current polymeric sorbents did not surpass the cost efficiency of conventional carbon capture technologies[6].

Now, in the case of porous sorbents, the chemical grafting of amino groups on the surface represents a general strategy to improve their CO_2 capture and the selectivity performance. Contrariwise, the same approach was rarely replied in the field of polymeric sorbents.

Here, our goal is to extend the approach beyond solid-supported amines to tackle the typical selectivity issue of the polymeric solvent. Accordingly, a trimethylammonium-functionalized polyepichlorohydrin (PECH) membrane was synthesized using inexpensive and environmentally friendly raw materials and easy synthetic steps. Thereafter, the capture performance of the sorbent was assessed by both termogravimetric analysis (TGA) and Sievert type (volumetric) apparatus under various temperature, humidity and loading pressure conditions. Differential Scanning Calorimetry (DSC) was used to investigate heat evolution during CO_2 adsorption/desorption processes. The proposed membranes hold great potential as CO_2 sorbent because can potentially provide the high capture ability, high selectivity and scalability of liquid amine while making the process less expensive, reversible and eco-friendly.

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O45 • Photothermal Assisted Evaporation (PhAEV) system for brine treatment

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Discharged brine is a serious environmental question caused by the low water recovery factor (40-50%) of widespread Seawater Reverse Osmosis (SWRO) plants [1]. In fact, undesirable ecological and toxicological effects of hypersaline discharged SWRO brines on soil and groundwater, sediment infauna, seagrass and epifauna, planktons etc were observed [1].

Nevertheless, desalination brine has been recently recognized an unlimited and potentially exploitable source of minerals under the impulse of the Circular Economy. Literature studies demonstrated the opportunity to concentrate desalination brine up to supersaturation, thus implementing the pioneering concept of Membrane Crystallization (MCr). Nevertheless, the energy input (higher than100kWh/m^3, also in presence of heat recovery systems) hampers the feasibility of MCr at industrial scale [2].

With the aim to by-pass the bottleneck of the technology, the vaporization of the water from brine on membrane surface was assisted by inexpensive photothermal coatings based on Poly(vinyl alcohol) load with carbon black nanoparticles (NPs). The NPs acted under the solar light as hot-spots securing a light-to-heat conversion on membrane surface (temperature improvement form 30°C to 49.4 °C as shown in Figure 1.a) utilized for facilitating the water vaporization. The enhanced vaporization of the water (1.05 kg m^{-2} h^{-1}) secured a progressive concentration of desalination brine up to the supersaturation provoking the crystallization of NaCl crystals (Figure 1.b) obtaining a Mg-rich brine. To demonstrate the scalability of the developed technology, the SWRO retentate was fed through a prototype (Photothermal Assisted Evaporation system-PhAEV) equipped with 4 m^2 of photothermal surface (Figure 1.c).

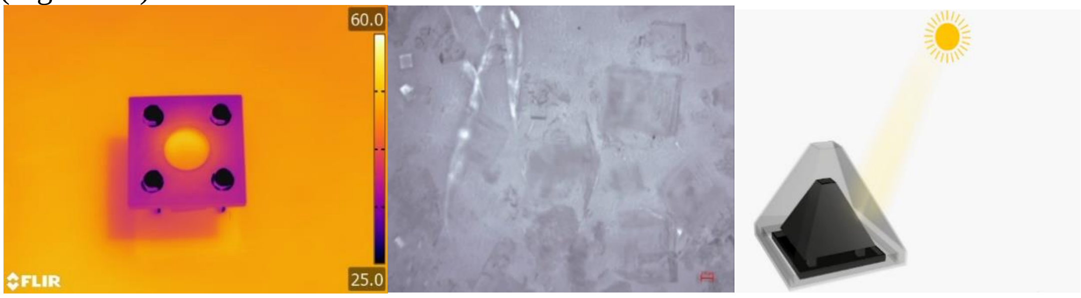

Figure 1. a) Infrared picture of phototehrmal coating, b) NaCl crystals obtained from the brine, c) PhAEV prototype.

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046 • Characterization of Li-Ion battery components via Thermal Analysis

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The market of Li-Ion batteries is growing exponentially [1], and the applications are becoming more and more various: from smartphones, to laptops, to cars, to houses and solar/wind farms. That calls for more efficiency during charging and discharging, more reliability, and more power capacity.

New materials are being developed to address those requests and they must be carefully characterized under several points of view.

TGA, DSC, TMA, DMA and other techniques can give a full overview of the behaviour of innovative materials, as well as give deep insight in the fabrication process [2].

In this work we present a small collection of case studies where Thermal Analysis proves to be a critical tool to characterize various aspects of materials employed in the fabrication and development of Li-Ion batteries: composition of anode materials, melting and degradation of LiCO3, stability of electrolytes.

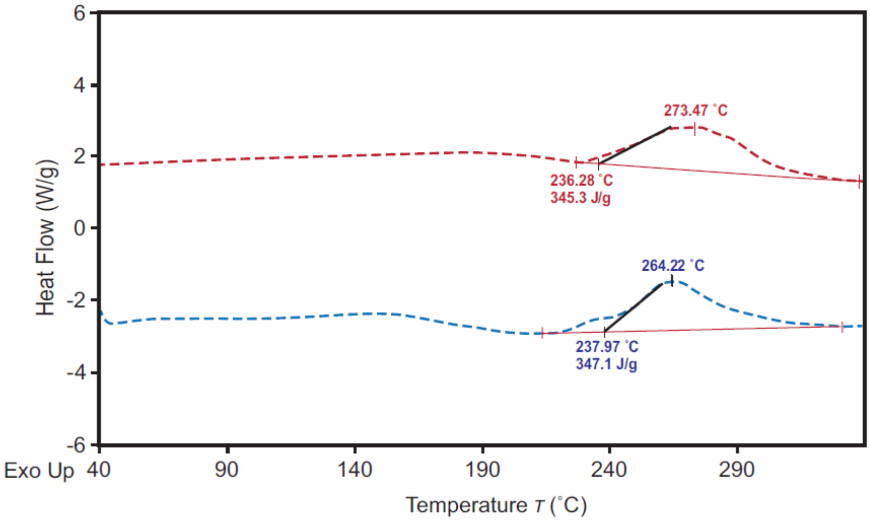

Figure 1. Runaway heat of an Electrolyte measured by a DSC

References

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PRESENTAZIONI FLASH

FP1 • NMR and XRD study of starch-based nanocomposite reinforced with natural fillers for bio-packaging applications (BIOSTAR-PACK)

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Food wastes from Italian consumers count on average over 100 kg per year, of which 27 kg is still edible. Moreover, packaging materials are produced and consumed in an unsustainable manner, leading to bioaccumulation into our food chain (e.g. plastic debris in fish and birds), water pollution and greenhouse gas emissions.

The BIOSTAR-PACK[1] project aims to reduce the impact of food waste by promoting the reuse and valorization of organic wastes in the development of a new packaging material, recyclable and able to ensure a longer shelf life to food.

Figure 1. The BIOSTAR-PACK logo.

In this study the structural characterization, mainly through multinuclear solid-state nuclear magnetic resonance spectroscopy (NMR) and X-ray diffraction (XRD) techniques of nanocomposite films made of starch and silica-based fillers, such as silica nanoparticles or natural clays, is presented. Starch is a natural polysaccharide that can be easily extracted from food wastes and whose properties may change or have an impact on the resulting composite film. As a matter of facts, the botanic origin of raw starch influences relevant properties such as crystallinity degree and crystalline structures, which change also according to the processing. For this purpose, the implementation of different models[2,3] based on NMR and XRD analyses for the elucidation of starch structural properties will be shown. Moreover, the impact in terms of structure modification and molecular dynamics of different type and amounts of filler as well as of the plasticizer will be presented, aiming to elucidate the starch-filler-additives interactions.

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FP2 • Microwave assisted Paal-Knorr reaction on polyketones

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The Paal-Knorr reaction is a well-known cyclization reaction of γ-diketones. This reaction performed on polyketones (PKs) has attracted attention for the possible production of anionic exchange membranes (AEMs). The presence of γ-diketonic repeating units allows the grafting of different side chains. The main problems related to this kind of reaction are the statistically random and less then complete conversion of diketonic units; in particular, the functionalization degree is significantly dependent to reaction time and temperature. The literature reports good conversion of diketonic units to polypyrrole ones (Figure 1) using primary amines after several days (3-9 days) of reaction at the boiling T of the amine. [1-3]

In this work, reaction time was extremely reduced by moving from traditional conduction heating to microwave heating. Several tests were conducted using 3-(aminomethyl)pyridine as the primary amine. Functionalized polymers obtained from the microwave assisted Paal-Knorr reaction were used to prepare anion exchange membranes in iodide form. Molecular structure, thermal and conductive properties of these membranes were evaluated in order to compare the results to the analogue membrane obtained from the traditional Paal-Knorr reaction and to consider their application in electrochemical devices.

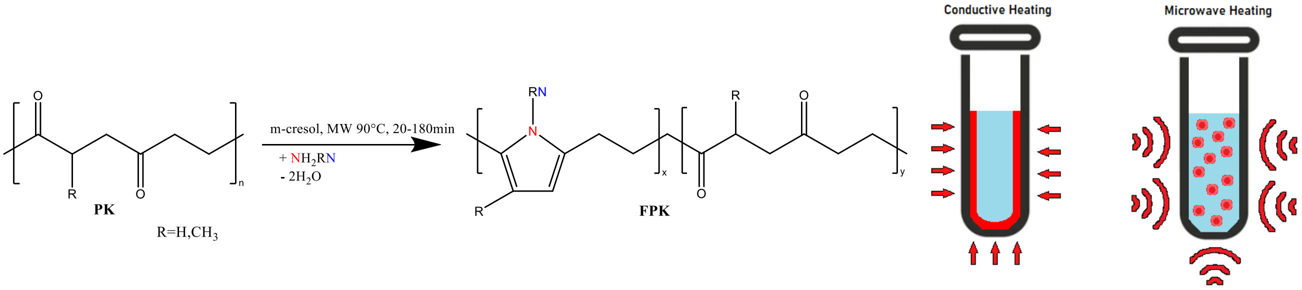

Figure 1. Paal-Knorr reaction on PK (on the left); effect of different heating methods (on the right)

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FP3 • Combination of analytical tools for identifying microplastics in Apulia seawater

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Marine microplastic pollution has become a global environmental concern and is a growing issue due to the possible interaction with the marine biota and the potential risks to human health.[1]
Depending on their emission source, microplastics can be classified as primary, that are directly released into the environment as small plastic particles, or secondary deriving from the deterioration of larger plastics during their utilization or after discarding.
In order to evaluate the environmental quality of seawater, these studies aim to quantify and identify the types and origins of microplastic in coastal zones near to four different ports in the Apulia region located in the towns of Bari, Barletta, Manfredonia and Vieste.
To monitor the spatial distribution and season trends of marine microplastic litter, the performed analysis combines morphological observation by microscopic analysis with infrared spectroscopy [2] to gain insight into the correlation between the nature of plastic and the accumulation in seawater.

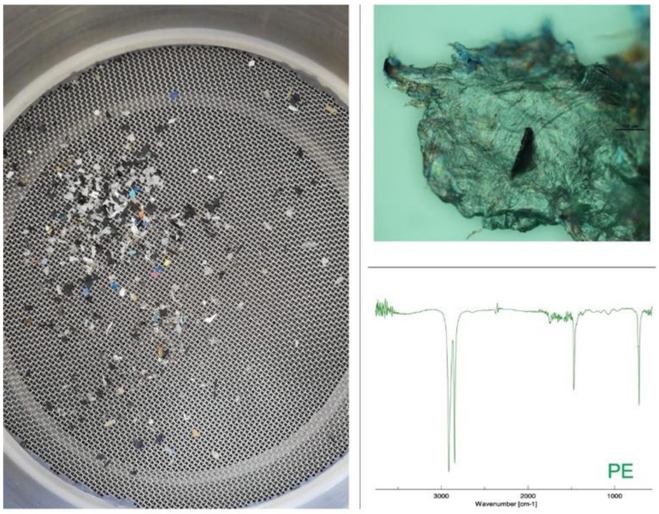

Figure 1. Picture of microplastics recovered on sieve. Microscope image of plastic fragment. FT-IR spectrum of polyethylene.

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FP4 • Sustainable design of composite materials for wastewater treatment

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Over the last decades, the reduction of water contamination has become a crucial issue both at academic and industrial level. Herein, we refer to inorganic species, namely heavy metal ions (Fe^{3+}, Cu^{2+}, Mn^{2+}, Ni^{2+}), and organic molecules such as pesticides, both representing a threat to human health and the ecosystem. Among the several materials available, reduced graphene oxide (rGO) provides remarkable results in removing inorganic pollutants because the oxygen-bearing functional groups allow the self-assembly of the material in self-standing membranes with an optimal capture efficiency of different metal ions.[1] On the other hand, it is well known the efficacy of titanium dioxide (TiO_2) nanoparticles (NPs) in the photodegradation of organic pollutants due to the reactive oxygen species generated under UV irradiation.[2] In this scenario, the present work aims to obtain a composite membrane with adsorbent and photocatalytic properties based on the efficient combination of rGO and TiO_2 to remove organic and inorganic water pollutants. We expect that photodegradation in the presence of an effective connection between rGO and TiO_2 takes advantages in different ways: i) by holding contaminants close to the photocatalyst surface and ii) by extending the absorption range of TiO_2 to the visible range, thanks to the formation of Ti-O-C or Ti-C bonds at the titania/graphene interface. To achieve this, TiO_2 NPs were functionalized with an amino-group-bearing coupling agent, i.e. 3-aminopropyltriethoxysilane (APTES), that can efficiently interact with rGO carboxyl groups. Structural and morphological characterisations of rGO-TiO_2 were performed by an exhaustive multi-technique approach. A feasibility study about contaminants capture and degradation performance was conducted on slurries containing rGO-TiO_2. The purpose is to optimize the combination of rGO and TiO_2 in hybrid adsorbent and photocatalytic composites to ensure high accessibility and uptake of pollutants, the enrichment of their density at the photocatalytic active sites and to preserve from annihilation the short-living radical intermediates involved in the photodegradation mechanism. At the same time, with particular attention to circular economy, considering the rising interest in the employment of unconventional waste byproducts, the applicability as photocatalyst of the tionite is currently under evaluation. Tionite is a by-product of TiO_2 manufacture from titaniferous minerals, which are treated with concentrated sulphuric acid. Usually, tionite is disposed directly to landfills causing serious environmental issues, hence its valorisation would bring indisputable advantages to both economy and ecosystem.

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FP5 • Study of Nanoparticles Effect on Technologically Relevant Rubber Blends

Elisa Manzini,[1,*] Massimiliano D'Arienzo,[1] Luca Giannini,[2] Silvia Guerra,[2] Silvia Mostoni,[1] Roberto Scotti,[1] Luciano Tadiello,[2] and Barbara Di Credico[1]

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Tyre materials are complex multiphase rubber systems containing different polymers and additives. The compatibility of the polymers and the diffusion of compound ingredients are recognized as important factors to define the structure and morphology of rubber nanocomposites (NCs) as well as the overall materials properties. However, the natural incompatibility of most rubbers often produces phase-separated morphologies with poor interfacial adhesion, downgrading the mechanical and thermal properties of the NCs. In this context, some studies[1,2] reported that filler nanoparticles (NPs) choice has a great influence in preventing domain coarsening or stabilizing suitable morphologies. However, most of the proposed investigations for the physical mechanisms which control the NPs-induced morphological modifications are mainly related to a specific polymer system.

The present work aims to study the influence of isotropic and anisotropic nanofillers on the behaviour of different rubber blends and to gain information on their potential effect on structural and morphological modifications of multiphase rubber systems. Technologically relevant polymer blends such as styrene butadiene rubber (SBR)/butadiene rubber (BR) were considered by changing the styrene and vinyl content of the SBR copolymer as well as the polymers viscosity. Rubber blends were prepared by solvent-swelling and melt-mixing, considering step by step the introduction of additional additives, such as oils and vulcanizing agents, and finally the reinforcing NPs, such as silica and sepiolite fillers, in order to: i) test the blend morphological modifications and thus ii) evaluate the impact on mechanical properties. For this, an extensive investigation by optical and atomic force microscopy, thermal and thermomechanical analysis was performed.

In both preparation approaches, the SBR/BR blend shows incompatibility at increasing styrene content, at the selected vulcanization temperatures, in agreement between thermomechanical and morphological analyses. Furthermore, the addition of the filler affects the blend compatibility by changing the thermal and thermomechanical parameters. The role of relevant parameters, such as the NPs surface chemistry and morphology, compounding method and vulcanization temperature, is currently under investigation with the aim to establish a rational correlation between the filler effect and polymer blends properties.

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FP6 • Seeking Sustainable Solutions for Energy and Environment at Tor Vergata

Simonetta Antonaroli, Fabrizio Caroleo, Alessandra D'Epifanio, Cadia D'Ottavi, Silvia Licoccia, Larisa Lvova, Gabriele Magna, Federica Mandoj, Barbara Mecheri, Sara Nardis, Roberto Paolesse, Manuela Stefanelli

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Sustainable development should combine the current needs without compromising the possibility of future generations to meet their own needs. Action can be taken at different levels to ensure sustainable solutions for different ambitious challenges. Chemistry takes charge of providing access to inexpensive and sustainable energies for everyone and minimizing effects of human activities for environmental protection. Research activities carried out at Tor Vergata aim at reaching such goals, being focused on the development of innovative materials for energy conversion/production/storage purposes and for environmental monitoring by chemical sensors, Figure 1. For energy applications, the research is addressed to the achievement of catalysts, polymer electrolytes, and ceramic oxides for high and low temperature fuel cells, redox flow batteries, and bioelectrochemical systems where the electrochemical properties are optimized by tailoring the interplay of morphology, microstructure, and surface chemistry. Moreover, the microalgal biomass are carefully selected and studied to obtain high lipids production with good percentage of unsaturated fatty acid extracted. Finally, the sensitive materials based on porphyrinoids combined with inorganic nanostructures are finely prepared for purposes of environmental monitoring, industrial processes control, foodstuffs quality assessment and clinical analysis. The developed chemical sensors used as single devises or in array configuration together with appropriate chemometric techniques for data treatment.

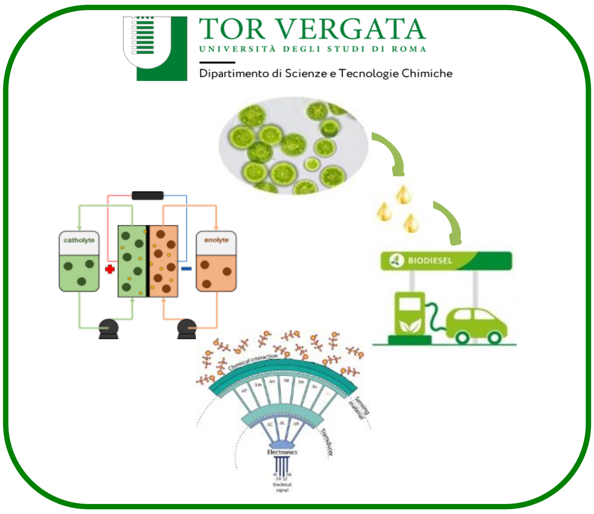

Figure 1. The sustainable solutions for energy and environment at Tor Vergata University.

FP7 • Synthesis via Sol-Gel process of Hybrids materials: Biological and chemical characterization

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This study aims to synthesize, via the Sol-Gel method, a biomaterial useful as a medical device[1]. The failure of medical devices such as bones prosthesis is mainly due to inflammatory and infection phenomena, that could be avoided by entrapping antioxidant drugs in the matrix of the biomaterial[2]. In this context, the Silica-PEG-quercetin hybrid systems with different weight percentages of PEG (0, 6, 12, 24, 50 wt%) and quercetin (0, 5, 10, 15 wt%), respectively, were synthesized (as reported in Figure 1) and characterized. The physicochemical properties were assessed by Fourier Transform-Infrared spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM), whereas the antibacterial properties were studied by Kirby–Bauer test against both Gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*) and Gram-positive (*Enterococcus faecalis and Staphylococcus aureus*) strains. FT-IR analysis detected the formation of the hybrid materials by H-bonds and the SEM images confirmed a good homogenization of the materials enclosed in the prepared composites. Independently from the composition, both Gram-positive and Gram-negative bacteria are inhibited[3].

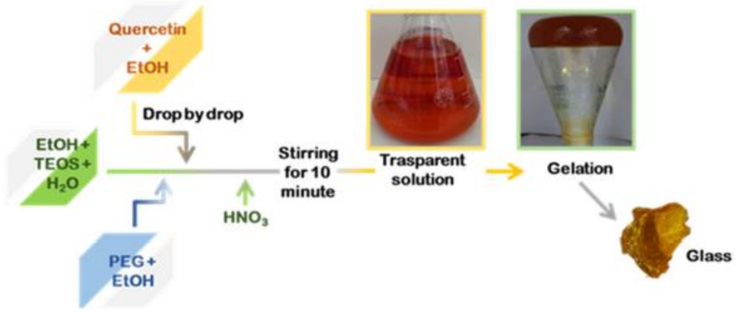

Figure 1. Flowchart procedure of the sol–gel synthesis.

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FP8 • Sustainable metakaolin-based geopolymers using oak ashes filler

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Meeting society's housing and infrastructural needs sustainably is, unquestionably, the most important challenge confronting the concrete industry today. For a variety of reasons, the concrete construction industry is still not sustainable [1].

Since the early 1980s, geopolymer materials have attracted great attention as promising materials for the substitution of Ordinary Portland Cement (OPC). This is due not only to their excellent properties, low cost, low carbon dioxide emissions, and facile synthesis but also to the possibility to add in their matrix waste materials [2, 3].

This research aims to investigate the feasibility of the inclusion of oak wood ashes as a filler material for metakaolin-based geopolymers. Geopolymers with 10% and 20% of oak wood ashes filler were synthesized, characterized, and compared. In particular different parameters and tests were realized: integrity test, weight loss test, pH, conductivity, FT-IR, antibacterial activity, and mechanical strength.

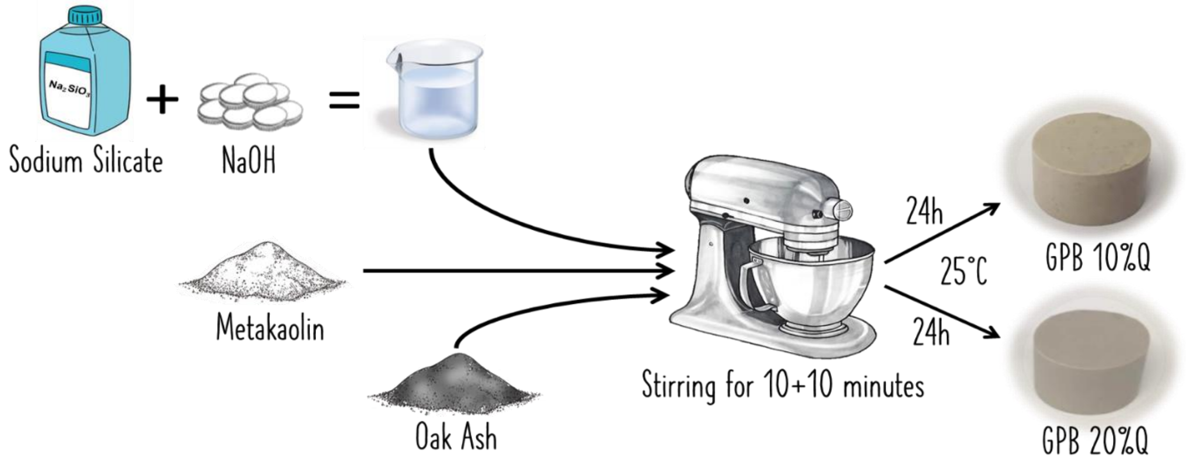

Figure 1. Picture of synthesis.

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Acknowledgement

We thank Prochin Italia S.r.l. for providing sodium silicate for the synthesis of the designed materials.

FP9 • Carbon dots from Orange Peel Waste by an Integrated Hydrothermal and Electrochemical Process: A Contribute to the Circular Chemistry

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With more than 50 million metric tons in 2021 worldwide, of which two million tons produced in Southern Italy, the orange juice industry alone generates a huge volume of orange peel waste (OPW) that requires suitable management, considering the high OPW biodegradability, that causes its fast uncontrolled fermentation. [1]Therefore, the direct disposal of this secondary product without previous proper processing, raises serious environmental issues and economic loss for the citrus industry since traditional disposal strategies, such as incineration or landfilling, are expensive and insufficient in terms of environmental protection and energy efficiency. In this contribution, the OPW waste has been transformed into carbon dots (CDs) by a simple and ecofriendly hydrothermal [2] and electrochemical approach. The prepared CDs have been characterized from the morphological, structural and optical points of view, highlighting a photoluminescence emission centered at 340 nm and a very good quantum yield (QY). The most challenging peculiar features of the so obtained CDs, were highlighted by studying their potentials as non-toxic, effective and recyclable emerging catalysts in peculiar reactions for the generation of carbon-carbon bond, under very mild conditions.

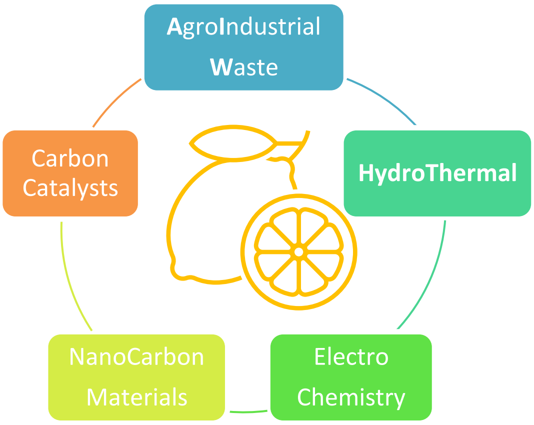

Figure 1. Circular Chemistry

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FP10 • Additives to improve the performance of ambipolar zinc-polyiodide redox flow batteries

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Zinc-polyiodide Redox Flow Batteries (RFBs) have been proposed as an alternative to Vanadium RFBs thanks to the larger availability of active species, the higher solubility in water of active species and the higher theoretical working potential [1, 2]. In this work, we propose a green and non-toxic buffer solution composed by acetic acid and sodium acetate in order to improve the quality of the zinc deposit at the anode. This aim is pursued by: (i) inhibiting the strong complexation between Zn^{2+} and I^- ions, thus reducing the energy barrier for the deposition/stripping mechanism; and (ii) stabilizing the pH at the interface to limit the formation of unreactive ZnO.

Raman spectroscopy studies on electrolytes reveal a decrease of ZnI_x^{2-x} complexes in solution owing to the hybrid monodentate coordination of Zn^{2+} by the AcO^- anion. Electrochemical investigations show a consistent enhancement of the *ex-situ* coulombic efficiency for the Zn/Zn^{2+} redox couple, and a more stable voltammogram over long-term cycling. The best performing electrolyte in *ex-situ* experiments (0.25 M of acetate buffer, 1.5 M ZnI_2) shows improved performance in a single cell device: (i) the coulombic efficiency after 100 cycles at 40 $mA \cdot cm^{-2}$ is 98.2%; and (ii) the energy efficiency is 85%. SEM analysis of the deposits formed on the electrodes shows how the devices with acetate buffer is able to produce a more homogeneous distribution of zinc on the electrode surface and also the complete suppression of ZnO deposits.

This work demonstrates the importance of: (i) the pH stabilization in order to avoid local fluctuations on the anodic electrode surface; and (ii) the reduction of the strong coordination between Zn and I ions, which is responsible for local pH variations that ultimately alter the homogeneity of the deposits.

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FP11 • Coordination and Conductivity Mechanism in Ionic Liquid-based Electrolytes for Advanced Multivalent Metal Batteries

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In the recent years, the global energy economy is experiencing a transition towards its production from more sustainable and "*green*" sources. The intrinsic characteristics of these methods, such as the intermittency and misalignment between disposability and demand, require the use of energy storage systems, such as secondary batteries. Despite the high performance of Li-ion batteries, the high cost, low abundance and toxicity of their components (*e.g.*, the Co-based cathodes) request the development of new devices based on novel chemistries. In this regard, the holy grail is the production of battery systems based on abundant multivalent metals. It has been recently demonstrated that ionic liquids (ILs) are suitable solvents in order to obtain stable and high performing electrolytes able to conduct and deposit/strip multivalent metals.[1] The outstanding electrochemical properties of these materials are ensured by the presence of a high-reactive magnesium salt (*i.e.*, the "*delta*" form of $MgCl_2$) and of a suitable metal halide (*e.g.*, $AlCl_3$, $TiCl_4$, *etc*.).[2,3] In this project we have developed a family of IL-based electrolytes for the Mg^{2+} ion conduction doped with an alkyl tin halide compound. In this way, the hybrid chemico-physical properties of Sn-based species can be exploited to improve the coordination existing between the inorganic magnesium salt and the organic IL. An advanced study on the thermal and structural properties of the proposed material will be presented, with a particular focus on the interactions established between the different chemical species and complexes composing the materials. Insights on the conductivity mechanism occurring in a wide range of temperature will be gauged and thoroughly described by means of the broadband electrical spectroscopy studies.[4]

Acknowledgments

The project "Interplay between structure, properties, relaxations and conductivity mechanism in new electrolytes for secondary Magnesium batteries" (Grant Agreement W911NF-21-1-0347-(78622-CH-INT)) of the U.S. Army Research Office. The project "VIDICAT" (Grant Agreement 829145) of the FET-Open call of Horizion 2020.

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FP12 • Hierarchical *“Core-Shell”* Carbon Nitride Pt-alloy ORR Electrocatalysts: Correlation between the Porosimetric Features, Morphology, *“Ex-Situ”* and *“In-Situ”* Electrochemical Performance

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The widespread commercialization of proton-exchange membrane fuel cells (PEMFCs) is still bottlenecked by the high loading of platinum-group elements (PGMs), typically platinum, in the cathodic electrocatalytic layer. One strategy to overcome the sluggish kinetics of the oxygen reduction reaction (ORR) taking place at the PEMFC cathode is to raise the mass activity of Pt by implementing Pt-alloy electrocatalysts (ECs) [1]. This allows to decrease the overall Pt loading in the membrane electrode assembly (MEA), the crucial functional component at the heart of the PEMFC.
This contribution discusses *“core-shell”* hierarchical ECs (H-ECs) consisting of: (i) a hierarchical *“core”* comprising a blend of nanostructured carbons, that are covered by (ii) a carbon nitride (CN) *“shell”* wherein Pt-alloy active sites are stabilized by C- and N- ligands in “*coordination nests”* [2]. The active sites are based on Pt together with Ni and Cu as *“co-catalysts”* to enhance the ORR kinetics [3]. The bulk of the support of the H-ECs is minimized to promote mass transport phenomena. The morphology of the H-ECs is probed by ultra-high resolution scanning electron microscopy (UHR-SEM) and transmission electron microscopy (TEM), and is discussed in relation to the synthetic parameters and chemical composition. In a second step, nitrogen physisorption techniques are used to evaluate the porosimetric features of the H-ECs, including the specific surface area and the size distribution of the pores. The porosimetric and morphological features are correlated with the electrochemical performance of the H-ECs as measured: (i) “*ex-situ”*, via cyclic voltammetry with the thin-film rotating ring-disk electrode method (CV-TF-RRDE); and (ii) in single PEMFC under operating conditions as a function of the partial pressure of oxygen in the cathodic feed. A new framework is finally proposed to rationalize and quantify the porosity-morphology-performance correlation for the H-ECs.

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FP13 • Structure, Coordination and Conductivity Studies in POE-Based Polymer Electrolytes for Calcium Secondary Batteries

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The world energy economy is facing a global transition, and batteries based on novel chemistries are required in order to support this phenomenon. Calcium-based electrolytes are one of the most promising materials thanks to higher and more uniform distribution of calcium on Earth's crust respect to lithium (0.002% for Li *vs.* 4.1% for Ca), volumetric capacity (2073 mAh·cm^{-3}) and working potential (-2.87 V *vs.* SHE) [1]. Poly(oxyethylene)-based (POE) materials are one of the mostly investigated systems to obtain flexible, thermal stable ion-conducting polymer electrolytes (PEs).

In the present study, Ca^{2+}-conducting PE membranes are obtained by the homogenous doping of the host polymeric matrix with a calcium-based salt. As it is observed in the literature [2], in PEs the dynamics of the hosting matrix may assist the long-range charge migration processes and thus the ionic conductivity of active mobile ions. Therefore, to develop improved electrolytes for the next generation secondary batteries it is crucial to determine the coordination existing between the mobile ions and the host polymer matrix. Broadband Electrical Spectroscopy (BES) is a powerful technique which can unravel the interplay between the microstructure and the electrical response and thus elucidating the conductivity mechanism occurring in the proposed PEs [2]. In the proposed Ca^{2+}-conducting PE membranes, BES studies reveal i) the conduction pathways (σ_{EP}, $\sigma_{IP,i}$) take place at the interface between the mesoscopic nanodomains of the microstructure; ii) two "*segmental modes"* (α_{slow} and α_{fast}) are attributed to *"segmental motions"* of the polymer hosting matrix; and iii) the long-range charge migration mechanism of Ca^{2+} is mediated by the exchange of Ca-based species between different POE chains. Finally, the anions of the calcium salt can act as plasticizers establishing weak *"dynamic crosslinks"* that further promote the interchain hopping of Ca-based species and increase the ionic conductivity value up to *ca.* 10^{-4} S·cm^{-1} at moderate temperature (*ca.* 80°C), allowing for their use into a calcium prototype battery device.

Acknowledgements

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FP14 • Efficient and easy co-immobilization of Cellulase and β-glucosidase on Mesoporous Silica Nanoparticles for the hydrolysis of cellulose derived from agricultural biomass

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The enzymatic hydrolysis of lignocellulosic biomass represents a powerful tool to produce fermentable sugars to obtain biofuels. The enzymes responsible for the hydrolysis of cellulose belong to the cellulase family, made up of Endoglucanase (EG), cellobiohydrolase (CBH) and β-glucosidase (BG) which act sequentially and synergistically. Immobilization of cellulase over insoluble supports can overcome various drawbacks of using free enzymes such as instability, high cost and difficult reusability. However, it is challenging because cellulose is water insoluble, leading to diffusion limitations. Moreover, the scarce amount of BG in the enzymatic cocktail affects the overall process efficiency since it relieves the inhibition exerted by cellobiose on cellulolytic enzymes[1]. Wrinkled silica nanoparticles (WSN) with central-radial pore structure were identified as ideal supports for BG to avoid diffusion limitations.[2] Here, we implemented an easy co-immobilization procedure of BG and cellulase by adsorption on WSN. The immobilization was carried out separately, simultaneously, and sequentially in order to optimize the synergy between cellulase and BG. The biocatalysts were used for the hydrolysis of cellulose extracted from *Eriobotrya japonica* leaves, obtaining yield in glucose as high as 85% in 24 h (Fig 1). Moreover, supported enzymes retained 83% and 72% glucose production after 9 cycles of reaction and incubation at 90°C, respectively, exhibiting remarkable improvement in both operational and thermal stability [3].

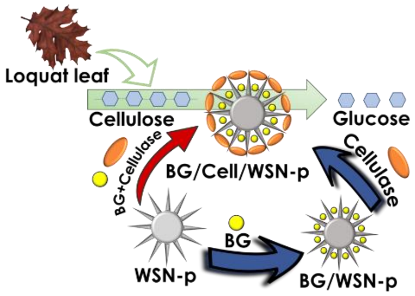

Figure 1. Whole process from cellulose extraction to glucose production.

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FP15 • Antibacterial electrospun hybrid TiO_2/Humic Acid PHBV fibers for active packaging

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The synergistic combination at the molecular scale between an organic and inorganic component into a hybrid nanostructure is a very effective strategy for enhancing the intrinsic properties of the organic phase. At the same time, the electrospinning technology enables design of high-performance active and bioactive systems based on polymer yarns of nanofibers with high surface-to-volume ratios. Exploring the synergy between these approaches, the aim of this work is the development of nanocomposite nanofibers made of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) derived from fermented fruit waste with enhanced functional performance. To this purpose, hybrid nanoparticles based on the molecular combination of titanium dioxide and humic acids from different sources (TiO_2_HA) were added to PHBV solutions and finally electrospun as woven non-woven mats. Morphology, thermal and crystallinity properties were studied through SEM, SEM-EDX, TGA/DSC and XRD analyses. The antimicrobial efficacy was assessed against different bacterial strains, highlighting that hybrid fibers showed an effective antimicrobial activity through reactive oxygen species (ROS) generation. Therefore, the combination of hybrid nanomaterials with electrospinning methodology is a promising sustainable approach to convert biowaste into active materials for food-packaging applications.

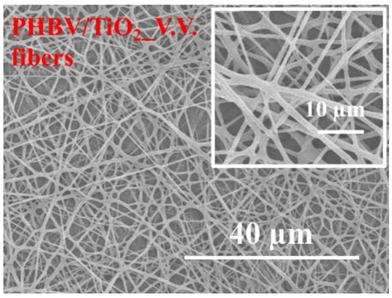

Figure 1. SEM image of PHBV/TiO_2_HA composite fibers

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FP16 • Eco-sustainable design of hybrid redox-active materials for the degradation of LLDPE

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Plastics are semi-synthetic or synthetic organic polymers with a wide variety of application due to their durability, versatility, hydrophobicity, and relatively low cost. However, despite their benefits to the daily life, plastics are associated with high levels of waste and release into the environment, in fact most of them are difficult to degrade and can persist in the environment for a century because of their degradation resistance [1]. In view of the harmfulness of plastic waste, it is necessary to take effective measures to remove them from the environment. Polyethylene (PE) stands out to be one of the most diffused commercial polymers in packaging field, due to its good mechanical properties (i.e., high strength, elongation), biochemical resistance (barrier properties against water-borne organism responsible for food spoilage), and easy processing [2,3]. In this work, hybrid materials were synthesized by combining semiconductor oxides, such as ZnO and TiO_2, with bioderived organic components. These materials have been tested in the degradation of LLDPE both under UVA/light irradiation and at ambient light. The combination of SEM/TEM, XRD, TGA/DSC, ATR/FTIR, EPR and DRUV techniques was considered to define the structure-property-function relationship for the prepared hybrid materials as well as to monitor the changes induced on the polymeric films by hybrid catalysts used in the degradation treatments. The obtained results demonstrated the validity of this eco-sustainable experimental approach to obtain hybrid catalysts with enhanced ROS-generating properties useful for the effective degradation of a LLDPE film.

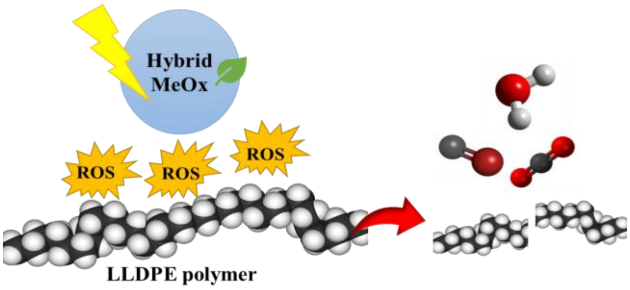

Figure 1. Schematic representation of the degradation process induced by ROS-generating hybrid materials.

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CONTRIBUTI

POSTER

P1 • Electro-Curing: New strategy for the curing of epoxy-nanocomposites

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Nanostructured forms of carbon can be incorporated into epoxy resin to confer self-sensing properties, heating ability, auto-repair function, damage monitoring function, etc.[1-3]. The curing process of epoxy composites is currently based almost exclusively on thermal curing cycles, for which an oven or an autoclave is used [4]. Alternative curing methods for composite manufacturers are of great industrial interest and can help save energy. In this paper, an alternative curing strategy, based on the application of an electric field, is proposed. The resin is obtained through the dispersion of carbon nanotubes (3% by weight), which act as nanometric heater elements in the epoxy matrix. The electro-curing is activated by applying an external electric power, which allows tunable cross-linking within the epoxy matrix entrapped between the nanotubes. The electro-curing method allows for reaching higher Curing Degrees (C.D. = 100%) with respect to the conventional process in the oven (C.D. =100%).

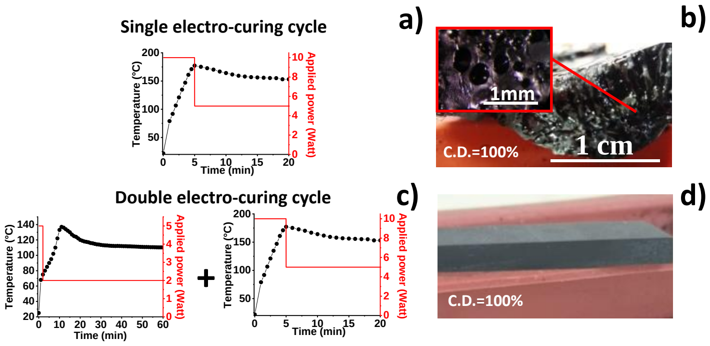

Figure 1. a) Electro-curing cycle carried out with a single step b) image of the sample cured with a single electro-curing cycle; c) electro-curing cycle carried out with a double step; d) image of the sample cured with a double electro-curing cycle

The increase of the temperature must be accurately controlled by adjusting the applied power and choosing electro-curing cycles suitable to obtain a good compromise between the material performance and the energy employed. When a single electro-curing cycle is used (see Figure 1a), although the C.D. is 100%, the sample evidences numerous trapped bubbles (see Figure 1b). Whereas, the use of a double electro-curing cycle (see Figure 1c) limits the autocatalytic nature of the cross-linking reactions, avoiding the formation of bubbles and locally degraded regions as shown in Figure 1d.

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P2 • Current conduction mechanisms in structural resins loaded with non-covalently functionalized graphene nanosheets

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This work focuses on a non-covalent π-π interaction between graphene nanosheets (G) and a pyrene-based molecule (py). The proposed modification proved successful in preserving the relevant electronic properties of graphene, while promoting a better dispersion of the nanofiller due to the reduced viscosity with consequent improvement of the rheological properties of the formulated nanocomposites [1]. Tunneling Atomic Force Microscopy (TUNA) analysis was carried out using G-py weight percentages both below (0.1wt% of G-py) and above (1wt% of G-py) the Electrical Percolation Threshold (EPT) to investigate the current conduction mechanisms of the epoxy/graphene systems. In particular, for the lowest G-py load, in most of the sample domains, no electrically conductive paths are observed, while, for the highest G-py load, the presence of a conductive network at the nanoscale level with efficient adhesion to the interface indicates that the sample is above the EPT (see Figure 1). The possibility to detect low currents also for the sample at the lowest G-py amount (0.1wt%) confirms the good electrical performance of the nanocomposites and, consequently, the successful performed functionalization. The electrical results are in perfect agreement with the rheological ones. In fact, the inclusion of a functionalized G-py amount of 0.5wt% caused the decrease in the complex viscosity of the unfilled epoxy resin, while instead, the same quantity of unfunctionalized G resulted in an increase of its viscosity. The non-covalent modification significantly improves the thermal stability of the graphene nanosheets, also determining an increase in the oxidative thermostability of the structural nanocomposites.

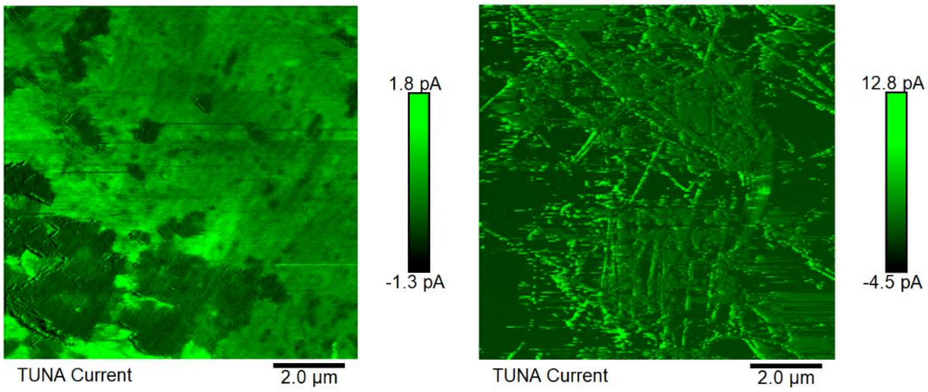

Figure 1. TUNA Current pictures of the two epoxy/graphene systems, loaded with 0.1wt% of G-py (on the left) and 1wt% of G-py (on the right).

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P3 • HEMP FIBERS MODIFIED WITH GRAPHITE OXIDE AS GREEN AND EFFICIENT SOLUTION FOR WATER REMEDIATION

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Nowadays, the presence of synthetic dyes in industrial effluents is leading to environmental concerns due to the impact of such contaminants on ecosystems and human health [1]. Dyes are substances used in many industrial fields. Among all, methylene blue is a cationic dye with high water solubility. Many methods have already been applied to remove synthetic dyes from industrial wastewaters. Adsorption process is the most used one since its technological simplicity, low cost and wide availability of adsorbents [2]. The use of common sorbents and their regeneration could noticeably increase the cost of the adsorption process. In our case, in an effort to address the need to develop more sustainable biomaterial-based sorbents, modified and engineered hemp fibers are fabricated to be a versatile class of sorbents. The use of hemp fiberboards will allow to easily handle the adsorbent facilitating the desorption and reusability processes and limiting, in this way, the operating costs.

The use of hemp fibers modified with graphite oxide for the removal of methylene blue from aqueous solutions was investigated. Parameters such as contact time, pH, temperature and initial concentration of dye were varied and their effects on the adsorption recovery were evaluated. The adsorption process attained the equilibrium within 30 minutes while the adsorption capacity was found to increase with increasing contact time. Maximum adsorption capacity slightly increases with temperature indicating that the process is slightly endothermic ($\Delta H = 3.43$ KJ/mol). A mathematical algorithm was applied to individuate the optimal set of process parameters ($pH = 9.25$, $T = 53.8°C$ and $C_0 = 13.2$ mg/L) which maximizes the removal capacity. The amount of dye was found to be highly dependent on pH regime, initial concentration of dye and slightly dependent on temperature. Regeneration studies showed 5% drop in adsorption capacity after 10 cycles. It follows that hemp fibers modified with carbons could be used as an easily available adsorbent. So, it is raising up as an alternative for costlier adsorbent materials used in waste water treatment processes.

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P4 • A Formalism for the Comparison of Electrocatalysts for the Oxygen Reduction Reaction (ORR) based on Thin-Film Rotating Ring-Disk Electrode studies

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Several families of electrochemical energy conversion and storage devices (*e.g.*, fuel cells and metal-air batteries) exploit the oxygen reduction reaction (ORR) in their operation. Very often, the ORR is the slowest electrochemical process in these systems and plays the most relevant role to degrade their energy conversion efficiency. Thus, to devise high-performing ORR electrocatalysts (ECs) is of crucial importance for practical applications. Unfortunately, to understand in detail the operating mechanism of an ORR EC is typically complex and time-consuming, requiring the implementation of a broad spectrum of advanced techniques and extensive data analysis. Consequently, there is a strong need to design simple methods capable to yield information on the most critical features of an ORR EC for screening purposes. In this regard, cyclic voltammetry with the thin-film rotating ring-disk electrode (CV-TF-RRDE) is a very popular approach. The latter allows for the facile study of the kinetics of an electrochemical process as promoted by an EC and minimizes the influence of complex spurious phenomena (*e.g.*, charge and mass transport). In this contribution a general method is discussed allowing for the correlation of the outcome of conventional electrochemical experiments with the critical features determining the performance of an ORR EC. Such features include prominently: (i) the kinetic activation barrier of the ORR; and (ii) the accessibility of O_2 to the active sites. The proposed method: (i) adopts the CV-TF-RRDE setup; (ii) does not lean on the simplifications associated with the conventional Butler-Volmer kinetic description of electrochemical processes; and (iii) does not make assumptions on the specific features of the EC. As a result, the proposed method allows to compare accurately the kinetic performance of ORR ECs exhibiting a completely different chemistry. Finally, it is shown that the figure of merit considered in this method, $E(j_{Pt}(5\%))$, is much more accurate than other popular figures of merit to gauge the ORR such as the half-wave potential $E_{1/2}$.

Acknowledgements

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P5 • A New Frontier in Membranes for Redox Flow Batteries: The Polyketone-Based Membranes

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Zinc iodide flow batteries (ZIFBs) are amongst the most promising chemistries to substitute the expensive and less energy intensive Vanadium Flow Batteries (VFBs). One of main problems related to this technology is the crossover of water due to the transport of Zn^{2+}. One possible approach is the development of new ion-exchange membranes (IEMs). For practical applications they are required to possess high ionic conductivity, high thermal stability, long lifetime, and electrical insulation. The preparation of polymeric materials with such high-performance properties is still challenging and can lead to high prices, hindering their widespread use in energy conversion technologies. This is even more difficult when considering anion conducting membranes [1-3].

Polyketones (PK) are known to be high performance thermoplastic polymers with applications ranging from fire-retardants film coatings, packaging, and fibers, resulting from their high thermal and chemical stability. They can be obtained in high yields by copolymerization of inexpensive and readily available feedstocks such as ethylene and carbon monoxide. Our group proved that PK with alternating 1,4-dicarbonyl repeating units constitute an ideal starting point to access a wide class of modified polymers by simple Paal-Knorr cyclization, to gain pyrrole-N-bound functional groups stemming from the aliphatic backbone [4-5]. Different ion-conducting membranes have been developed and the effect of reaction conditions on their thermal properties, chemical stability, and their conductivity in a wide range of frequencies have been assessed by broadband electric spectroscopy to shed light on the conduction mechanisms [4, 6]. The more promising material developed has been tested in a single cell redox flow battery obtaining promising results. The proposed conducting polymers combine the thermal stability of the aliphatic PK structure with the chemical flexibility given by the groups derived from functionalized amines branching out, proving to be highly tailorable, with possible applications in current energy conversion technologies.

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P6 • Self-healing biodegradable polymers

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Recently, the interest for biodegradable polymers, employed in packaging, agriculture, medicine and other areas, has raised as a consequence of the need to counter the environmental pollution caused by synthetic plastics. Biodegradability has been included into polymers in everyday use through slight modifications of their structures [1]. In this context, the new biodegradable highly amorphous vinyl-alcohol (HAVOH) polymer based on the modified poly-vinyl-alcohol (PVOH), patented and commercialized with the trade name of G-Polymer (Nippon-Goshei, Japan) is a noteworthy example. This material shows excellent characteristics, such as high-water solubility, good rheology for extrudability (low melting temperature, low melt tension, ease of extrusion, orientation, transparency) and remarkable gas barrier properties [2], which have allowed its wide use [3]. This work proposes the preparation of a self-healing HAVOH-based film obtained by incorporating the Murexide compound which acts as auto-repair agent due to its ability to boost up self-healing mechanisms, based on supramolecular chemistry, inside the polymeric matrix. This biodegradable eco-friendly material is potentially suitable for different industrial applications, such as coating or food and biomedical packaging.

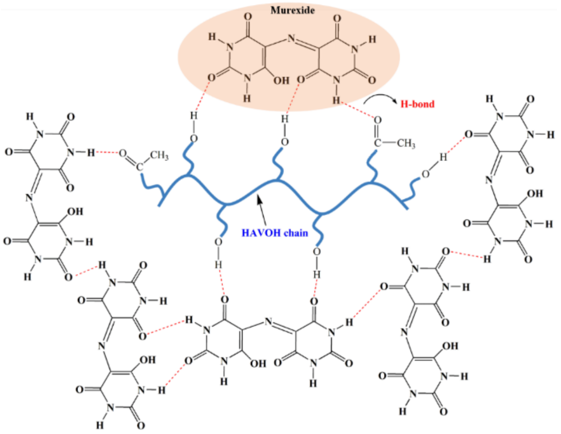

Figure 1. Picture showing the supramoleculat network established inside HAVOH matrix.

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P7 • Molecular Dynamics study of Silica-Ketoprofen hybrid materials synthesized by Sol-Gel: Interaction study for drug delivery

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Controlled drug delivery systems are drawing increasing attention thanks to their possible pharmaceutical and biomedical applications [1]. In this work a theoretical study based on Molecular Mechanic (MM) and Molecular Dynamic (MD) methods is performed to investigate possible surface interactions between the amorphous SiO_2 surface and the ketoprofen molecules (an anti-inflammatory drug), considering the role of drug concentration. The hybrid materials were synthesized by Sol-Gel route [2] and the MM and MD results were compared to those obtained by Fourier-Transform infrared spectroscopy. The results revealed that the loaded drug in these amorphous bioactive material forms hydrogen bonds with the silica surface (see Figure 1). The surface interactions are essential to have a new generation of biomaterials not only important for biocompatibility [3], with specific structural and functional properties, but also able to incorporate anti-inflammatory agents for efficient release into the human body [1].

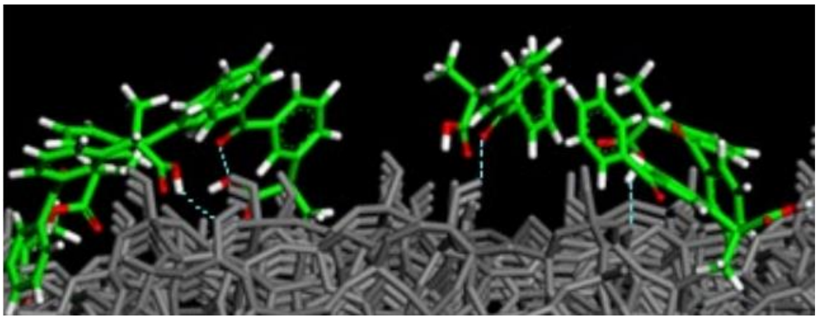

Figure 1. H-bonds between the amorphous silica surface and the Ketoprofen molecules.

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P8 • Natural Methylxanthines: electrochemical oxidation methods and MS techniques as synergic tools to evidence intermediates

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Methylxanthines (MXs) are present in many products as coffee, tea and chocolate, resulting the most widely consumed psychoactive substance in human dietary. Besides the well-known physiological effects, antioxidant properties have been also suggested for MXs. Nowadays, the relevant biological effects and a relatively low toxicity with a potential antioxidant capacity make MXs pharmacological tools with increasing therapeutic potentialities. Few studies on the oxidation of MXs have been reported,[1] so further investigations on its behavior under oxidative condition are still requested.

We will present some results regarding the electrochemical oxidation of natural methylxanthines (MXs) in aprotic medium by cyclic voltammetry (CV) and controlled potential electrolysis (CPE) carried out in UV cell modified for spectroelectrochemistry, to investigate on the radical intermediates involved in the primary oxidative process and their possible fate.[2] Typically, the choice of the aprotic medium comes because it is a good medium to evidence radical intermediates by reducing the effect of fast following chemical reactions occurring in aqueous system.

Aim of the work is to get a new insight into the oxidative mechanism of this natural compounds, and to elucidate the reactivity of caffeine CAF, theobromine (TBr) and theophylline (TPh) in organic solvents as well in aqueous medium, by using HPLC-PDA-ESI-MS/MS analysis to support mechanisms.[3,4] Great regard will be payed to the reactivity of radical species.

Figure 1 Natural Methylxanthines

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P9 • Free *N*-heterocyclic Carbenes from Bronsted Acidic Ionic Liquids: Direct Detection by Electrospray Ionization Mass Spectrometry and Study of their Speciation

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In recent years, task-specific Brønsted acidic ionic liquids (BAILs) have become increasingly popular and widely used in industrial processes since, as non-volatile materials, they are considered less harmful and corrosive than traditional liquid acids.[1] The presence of carboxylic acid groups into the cation scaffold of BAILs represents indeed an important opportunity for the discovery of novel applications and new materials. *In situ* formation of free *N*-heterocyclic carbenes (NHC) from Brønsted acidic ionic liquids will be studied, highlighting the crucial role of the anion basicity in promoting the C2-H proton abstraction from imidazolium cations with a carboxylic side chain. The question of the presence of free NHC in the reaction medium is current and of utmost importance being related to the interest in NHC in synthetic chemistry and catalysis, which remains as high as ever.[2] The acidic carboxylic group inserted on the *N*-side chains of the cation can act as a "charge tag" for the direct detection of NHCs in ILs by mass spectrometry (MS). The coupling of MS techniques with soft ionization methods, such as electrospray ionization (ESI), allows one to intercept elusive intermediates, and gently transfer them from the solution to the gas-phase environment for structural and reactivity investigations.[3] This experimental study can prove the possibility of using BAILs to furnish proper amounts of stable NHCs. The results can pave the way to the use of the novel compounds as MAIAc (see Fig. 1) and other customized BAILs as catalysts in carbene-mediated reactions, avoiding the use of other bases, generally added to the reaction bulk, with high benefits for organic synthesis.

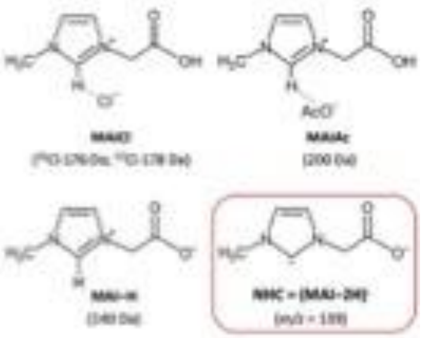

Figure 1. Brønsted acidic ionic liquids studied and their molecular mass (Da). In the inset, the structure of the carbene that can be obtained by C2-H deprotonation and its *m/z* value.

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P10 • Interactions for drug delivery: a Molecular Dynamics study of inclusion complexes between anticancer 5-fluorouracil and β-cyclodextrin

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Cyclodextrins (CDs) are cyclic oligosaccharides known by more than 100 years, recognized as pharmaceutical adjuvants for the past 20 years. Thanks to their capability to form noncovalent water-soluble complexes, they are useful as functional excipients for solubilization, delivery and greater bioavailability of drugs in many different applications. The complexation of 5-fluorouracil (5-FU) with natural or synthetic cyclodextrins permits the solubilization of this poorly soluble anticancer drug. In this theoretical work the complex between β-CD and 5-FU is investigated using Molecular Mechanics (MM) and Molecular Dynamics (MD) simulations in explicit water using a simulation protocol proposed in previous work [1,2]: non-covalent inclusion complexes are easily formed thanks to favorable intermolecular interactions between β-CD and 5-FU. Different drug concentrations were modeled, so that both a 1:1 and a 1:2 β-CD−5-FU stoichiometries could be investigated, giving insight on the geometry and stability of the complexes. The intermolecular interactions in the complex can affect the 5-FU release kinetics, suggesting a two-step mechanism: a fast release for the molecules that interact with the outer β-CD surface, and a slow one for the encapsulated molecules. Molecular dynamics simulations are an interesting tool to study in detail the interactions between hydrophobic drugs and a hydrophilic carrier and also the release mechanism [3].

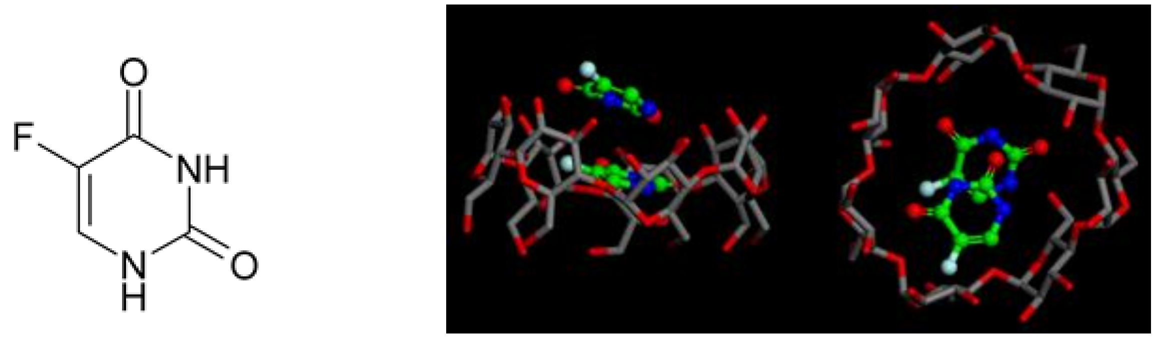

Figure 1. Line drawing of 5-FU (at left) and the stable inclusion complex for β-CD and 5-FU in a 1:2 stoichiometry in explicit water. Water molecules are omitted for clarity.

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P11 • MgAl-CO_3 layered double hydroxide (LDH) nanoscopic crystallites: Physico-chemical and biological characterization

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The aim of this study is to evaluate the physico-chemical and the antibacterial properties of MgAl-CO_3 layered double hydroxide (LDH): this material, synthesized via co-precipitation route (direct method) followed by hydrothermal treatment[1], has nanoscopic crystallites (with a partially disordered or turbostratic structure). The physico-chemical features were investigated by employing X-ray powder diffraction (XRPD), field emission scanning electron microscope (FESEM, Figure 1), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and Fourier transform infrared spectroscopy (FT-IR). The thermal behaviour of the MgAl-CO_3 LDH compound was also studied by thermogravimetry (TG) and differential thermal analysis (DTA), and a kinetic analysis of dehydration and decomposition was also performed. Finally, the antibacterial properties were assessed against Gram-positive and Gram-negative bacterial strains according to the Kirby-Bauer Method.

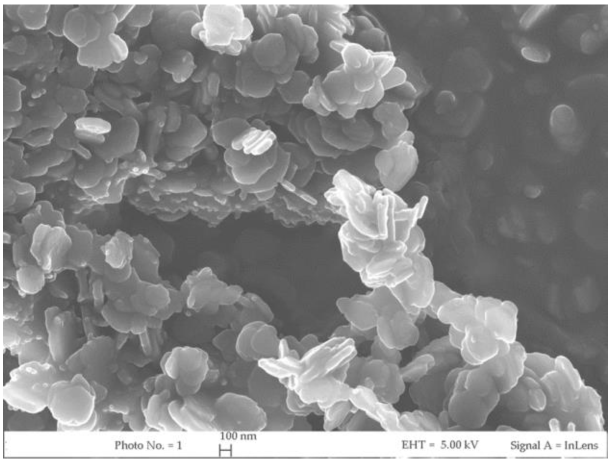

Figure 1. FESEM image of MgAl-CO_3

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P12 • Production of Monolayer and Bilayer Nanofibers via Electrospinning Process

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Electrospinning is one of the processes that allows efficiently producing nanofibers with very small diameters. It shows great potentialities for effective upscaling, especially in the biomedical field, thanks to its operational simplicity [1]. In the current research, electrospun membranes made of Polycaprolactone (PCL) and Gelatin (GN) have been produced and analyzed, according to the procedure reported by Longo et al. [2]. In literature, comparisons between uniaxial electrospinning (blending the two polymers) and coaxial electrospinning (forming bilayer nanofibers) are reported mainly to highlight the differences of surface properties between the systems (e. g. wettability, drug delivery, etc.). [3] In the current research, the differences in mechanical and structural properties depending on the type of process (coaxial or uniaxial electrospinning) are analyzed. In the coaxial configuration, since GN and PCL are spun by two different polymeric solutions, the interaction between the two polymers is less intimate than the one in uniaxial configuration. For this reason, coaxial electrospun membranes show mechanical properties intermediate between GN and PCL alone. Indeed, the strain at break is between 10% and 25% for coaxial systems, whereas is 3% for GN alone and 79% for PCL. In blend electrospun membranes, very different mechanical properties are reported. The strain at break increases from 79% of the PCL alone to 349% for PCL/GN blend, probably because the interaction between GN and PCL affects the crystalline structure of PCL, leading to form smaller crystals. In this way, these materials can be considered for new types of applications in which very high strainability is required. Moreover, it is proved that it is possible to significantly vary the properties of the nanofibrous membrane by choosing adequately the process configuration.

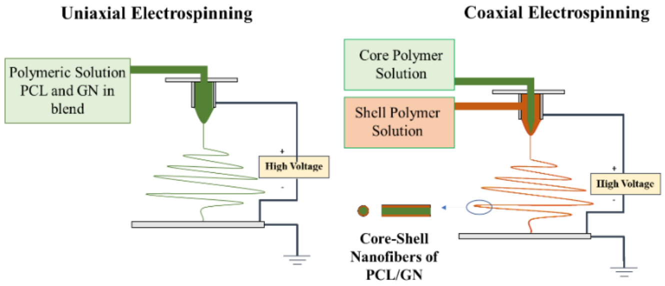

Figure 1. Uniaxial and Coaxial Electrospinning Process

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P13 • Modified POSS nanoparticles for the stabilization of styrene-isoprene-styrene triblock copolymer

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The modification of polyhedral oligomeric silsesquioxane (POSS) nanoparticles by the presence of different substituents in the benzene ring attached to the structure of POSS changes the thermal and radiation stabilities of polymers [1,2], for example styrene-isoprene-styrene triblock copolymer (SIS) used as packaging material. The inspection of differences that exist between the seven hybrids consisting of SIS and modified POSS with benzene rings where CH_3, OCH_3, F and Cl are present [3] indicates the influence of electronic density on the degradation of inorganic filler and, consequently, the unlike protection effect against oxidation. The isothermal chemiluminescence determinations show that the pristine polymer is stabilized by all POSS structures, while the non-isothermal chemiluminescence measurements reveal the differentiated decreasing in the oxidation start temperature after γ-irradiation at 50 kGy. The existence of various substituents in the POSS configurations makes possible the selection of suitable filler for the lowest oxidation rate. The protection efficiency of modified POSS filler is more evident at the temperatures exceeding 150 ˚C, when the electronic effect of substituents becomes evident on the evolution of thermal degradation. If the temperatures characterizing the start of oxidation in SIS/POSS hybrids are unlike for the seven compounds acting as stabilizers in unirradiated samples, the 50 kGy irradiated patterns present about the same temperature for the oxidative degradation illustrating the severe damage of fillers.

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P14 • Metakaolin(MK)-based geopolymers filled with volcanic fly ashes: spectroscopic and thermo-mechanical characterizations

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Metakaolin-based geopolymers, prepared with 20 wt% of volcanic recycled fly ashes derived from Etna's eruptions, are synthesized aiming at reuse the huge quantity of ash erupted by the sicilian volcano in the last two years, which constitutes a disposal problem for the local population (Figure 1).

Figure 1. Three different problems linked with the fly ashes derived from Etna volcano.

The synthesized samples were cured 1 day at 25 or 40°C, and characterized at different ageing time up to 56 days. After their preparation the systems with different percentages in weight of ash were characterized to evaluate its effect on the mechanical and thermal properties of these new geopolymers. Fourier transform infrared spectroscopy (FTIR) has allowed us to verify the bonds formation between the geopolymeric matrix and the ash, whilst scanning electron microscopy (SEM) to speculate about their structures. Dynamic Mechanical Analysis (DMA), Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were performed in order to evaluate the thermo-mechanical performance of this new geopolymer in comparison to its counterpart pure geopolymer.

P15 • Effect of formulation of physico-chemical properties of MK-based geopolymers added with waste corundum powder

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Recycling of corundum abrasive powder in metakaolin-based geopolymer formulations is proposed in this study with the aim to decrease the quantity of waste to be treated or disposed of in landfills allowing to both diminish the ecological damage and reduce the costs of transportation for removal. The addition of waste corundum (RC), as an important source of Al_2O_3, has proved to increase the low ionic conductivity of the leachate solution obtained after immersion in water of samples at 28 days of curing at room temperature. With the same curing conditions, the geopolymerization process has not been disturbed as evidenced by the FT-IR peak shift and XRD patterns. It was recorded a decrease in resistance to compression of the consolidated geopolymers of about 5% with 10wt% addition and of about 77% with the addition of 20wt% of waste corundum. In any case, the waste abrasive powder does not release heavy metals when added to a geopolymeric formulation based on MK, NaOH and Na-silicate, and does not show relevant antibacterial properties, indicating the formation of a stable and safe final product with a ceramic-like appearance.

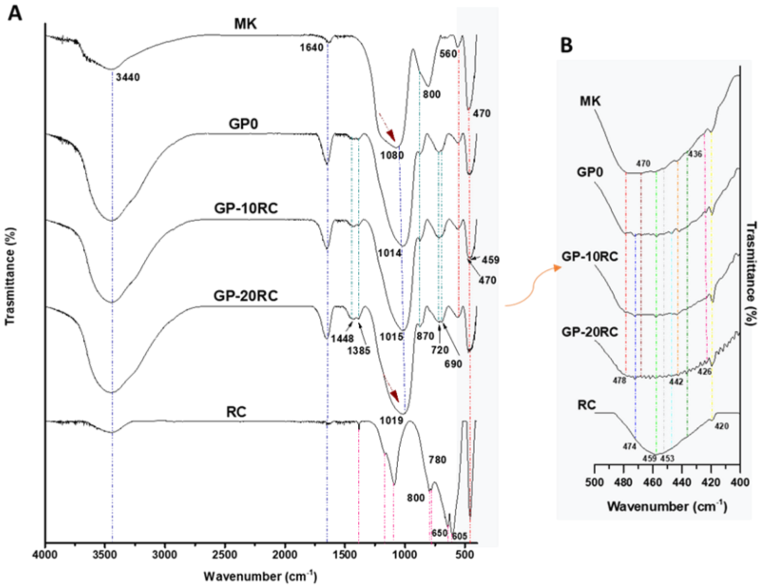

Figure 1. A) FT-IR spectra of MK powder, GP0 (0% RC), GP-10RC (10% RC), GP-20RC (20% RC) and RC powder. B) Focus on 500-400 cm^{-1} IR range.

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P16 • Multivariate statistical analysis applied to UV-Vis/NIR spectra for Determination of Diisocyanate Group Content in Polyurethanes

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Due to the functional group –N=C=O, the diisocyanates are essential reagents for the production of polyurethanes (PUs) in combination with an appropriate polyol. Depending on the nature of the diisocyanate compounds, PUs can possess an aliphatic, cycloaliphatic or aromatic hard segment. The diisocyanate choice for the PU production is very important for the modulation of the physico-chemical and mechanical properties of PUs constituted by methacrylate as an end group (PUA). In Figure 1 the synthetic pathway of the PUA preparation is represented. In the first step the diisocyanate compound is reacted with a polyol (in a suitable molar ratio) to obtain a urethane prepolymer with two terminated –N=C=O groups. In addition, in the second step the as-obtained urethane prepolymer was functionalized with a hydroxy methacrylate derivative.

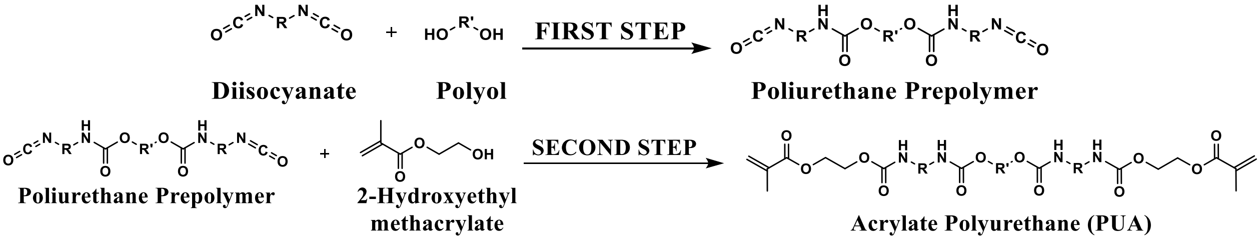

Figure 1. Synthetic pathway of the preparation of PUs with methacrylate as end groups (PUA).

Aliphatic isocyanate such as isophorone diisocyanate (IPDI) and aromatic isocyanate as 2,4-toluene diisocyanate (TDI) were used. The first step reaction has been monitored quantifying the content of the free isocyanates by means of a titration[1] method or IR analysis[1]. The main objective of this study was the application of a fast methodology which comprises the use of UV-Vis/NIR spectroscopy in combination with a multivariate statistical analysis, in order to control the first step of the PU prepolymer preparation. Multivariate statistical analysis was applied to UV-Vis/NIR spectra of reaction medium aliquots recorded in the wavelength range between 400 and 2500 nm. The resulting prediction model permitted the monitoring of the first step of the PU prepolymer preparation. For comparison, a conventional methodology based on IR analysis was performed.

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P17 • Microwave effect on silane functionalized cellulose nanofibrils: a ^{13}C and ^{29}Si solid state NMR investigation

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Plastic pollution is widespread all over the world and is responsible of severe consequences both on the environment and on human health. The necessity to overcome these problems suggested the development of new materials characterized by a lower impact on environment. Among them, nanocellulose is gaining more and more interest[1] 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[2], allowing the tuning of mechanical and physico-chemical properties and providing the possibility to develop new eco-sustainable materials. Cellulose modifications can be attained after heating at moderate temperatures. Microwave is an advantageous tool to obtain a uniform and fast heating with a good control of the process time.[3] In this contribution, cellulose nanofibrils (CNFs) were functionalized with a silane coupling agent, using conventional and microwave heating. Multinuclear NMR spectroscopy was performed for the evaluation of the effects of the microwave heating compared to the conventional one. In particular, crystallinity index and substitution degree of the functionalized CNFs were investigated using ^{1}H-^{13}C CP-MAS (Figure 1). In addition, ^{1}H-^{29}Si CP-MAS was used to evaluate siloxane structure formed on surface of functionalized CNFs.

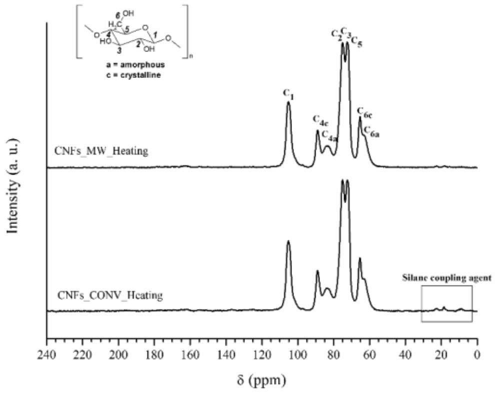

Figure 1. ^{13}C CP-MAS of CNF samples functionalized with silane coupling agent using conventional and microwave heating.

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P18 • Sulfonated Poly(ether ether ketone) membrane optimization for the set-up of an in-house built small-sized Vanadium Redox-Flow Battery

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Vanadium redox flow battery (VRFB) has been considered as one of the most promising large-scale electrical energy storage systems due to a partition between energy and power rating, a fast response, a room working temperature, and an extremely long life.[1] The commercialization of the VRFB is still hindered by the low stability of vanadium precursors which compose the electrolyte and the high costs of some key components such as the membranes.

In this contribution, sulfonated poly(ether ether ketone) (SPEEK) membranes with different sulphonation degrees and filler contents were prepared and tested in a lab-scale VRFB system. An optimized mixed sulphuric/hydrochloric acid was used as electrolyte.[2] Electrochemical impedance spectroscopy (EIS) measurements and consecutive charge-discharge cycles permitted to select the suitable membrane to configure an in-house built small-sized VRFB. The performance of the configured small-sized VRFB was evaluated by means of consecutive charge-discharge cycles carried out at different current densities (Figure 1).

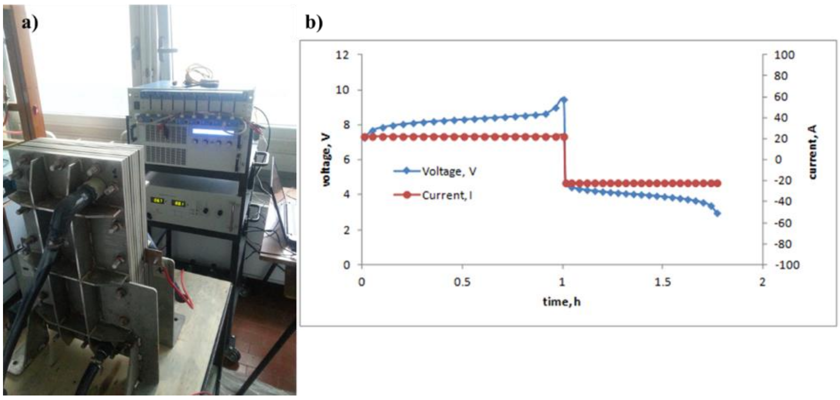

Figure 1. a) In-house built small-sized Vanadium Redox-Flow Battery and b) a charge-discharge cycle profile.

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P19 • The use of PLGA-Encapsulated Epigallocatechin 3-Gallate nanoparticles as a new potential biomedical system: a combined computational experimental approach

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Biodegradable polymers are widely used in the design of biomedical devices and tissue engineering applications because of their biocompatibility, non-toxic, and non-immunogenic nature. Despite the large variety of synthetic biodegradable polymers, poly(lactic-co-glycolic acid) (PLGA) copolymer is the most commonly used one following its first introduction in the second half of the 20th century and subsequent approval by the Food Drug Administration (FDA) [1]. On the other way, Epigallocatechin 3-Gallate (EGCG) is one of the most interesting and prominent polyphenols with high antioxidant and anticancer properties. Despite this, its bioavailability is conditioned by low stability. In this study, we designed and produced PLGA nanoparticles (NPs) able to encapsulate EGCG (figure1), and we explored the interactions between the molecules and the polymer. Four different systems have been produced (with no EGCG, 1.4 mM, 4.3 mM, and 6.6 mM) to identify the role of the EGCG amount on the stability of NPs. Infra-Red (IR) spectroscopy and Molecular Dynamics (MD) simulations showed that EGCG is always encapsulated in PLGA NPs without aggregation, preserving the molecular integrity. These findings encourage the use of these particles to increase the concentration of small molecules and allow them to reach the target site avoiding inflammatory processes.

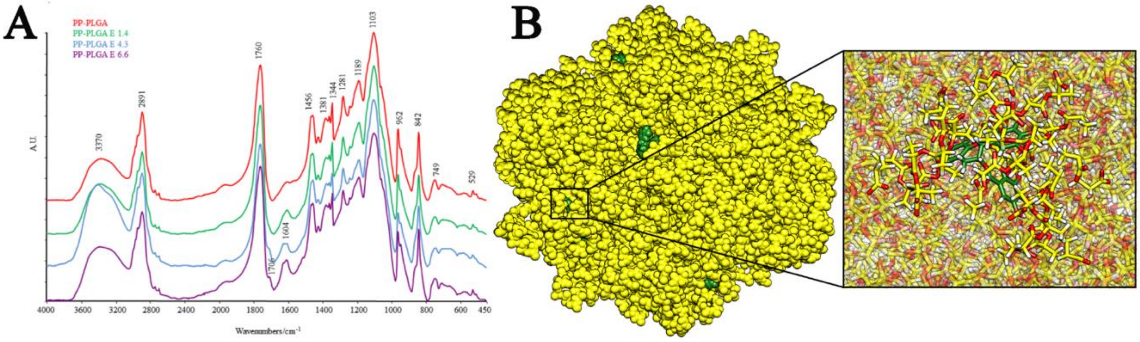

Figure 1. FT-IR spectrum NPs (a) and atomistic model of PLGA (yellow) and EGCG (green) NPs (b)

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P20 • Steel slags-based materials as catalysts for transesterification and reduction reactions

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Waste products 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 can play a significant role in catalysis and their use is of great economic importance and contributes also to the reduction of solid waste.[1] In this work, new catalysts with magnetic properties were synthesized in order to facilitate their recovery and reuse. These catalysts were obtained from the deposition of metal nanoparticles or metal oxides on steel slags as a support. The synthesized catalysts were used in hydrogenation reactions. Thanks to their basic properties, these catalysts were employed in the transesterification reaction for producing biodiesel (Fatty Acid Methyl Esters, FAMEs) starting from Waste Cooking Oil (WCO),[2] replacing the common procedure that involves a homogeneous catalysis in the presence of NaOH (Figure 1). The same catalysts could be used in the subsequent upgrading of the obtained FAMEs by partial hydrogenation with the aim of mainly obtaining C18:1 monounsaturated chains which are a good compromise between the fluidity of the fuel and oxidation stability.[3]

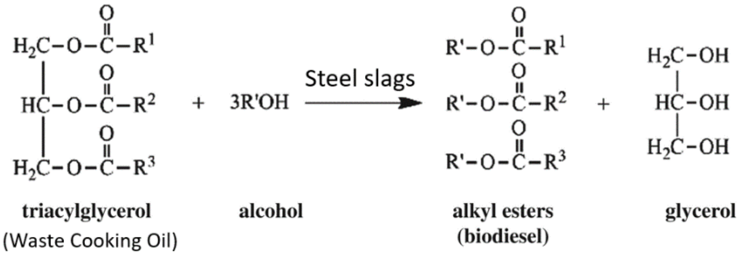

Figure 1. Transesterification reaction with steel slags as catalyst

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P21 • Vapor explosive detection through PbS colloidal quantum dots-based optical sensors

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Colloidal quantum dots (CQD) have attracted lot of interest in the fabrication of optoelectronic devices including light sources, solar cells and photodetectors, due to their strong quantum confinement that provides unique optical properties such as increased absorption and emission as well as size tunability. Thanks to their large effective surface-to-volume ratio and outstanding surface reactivity, combined with tunable surface chemistry and processability, CQD have been recently proposed also for gas sensing applications [1]. Because of their typical low vapor pressure trace detection of explosives is still very challenging. Existing instruments and procedures are bulky, expensive and require trained personnel, therefore, there is a strong demand for portable devices suitable for both security and military applications.

In this work we report on a compact optical sensor for nitroaromatic explosive (NE) detection based on the measurement of the photoluminescence quenching produced by exposing PbS nanoparticles. The sensor consists of a silicon substrate with both surfaces provided with a quantum dot film. The upper suitably functionalized CQD layer acts as photoluminescent probe, pumped by a pulsed blue LED. The change of photoluminescent intensity associated to the interaction between the PbS CQD and the analyte is measured by the Pbs CQD photodetector fabricated on the opposite side. We report on the sensor fabrication and characterization in terms of sensitivity, response time and selectivity, and discuss the proposed sensing mechanism. Due to its sensitivity, simple architecture, and small footprint, we believe the proposed device may have great potential for practical applications as either portable device or element of sensor networks.

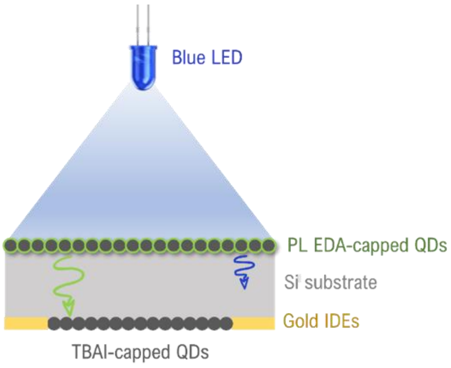

Figure 1. Schematic of the optical arrangement.

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P22 • TACTICITY OF FUNCTIONAL POLYMERS STUDIED BY SOLUTION AND SOLID STATE NMR SPECTROSCOPY

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Functional materials are defined as materials capable of exerting a special function, which can be intrinsically related to the chemical structure or can be triggered when such materials are exposed to external stimuli, such as electrical, magnetic, or optical signals. This type of material is finding vast technological use in many fields. Indeed, in recent years intense research has been directed toward the development of new materials to be used in the collection and storage of energy, in biomedical applications, and technologies for the mitigation of climate change.[1,2]

The chemical-physical characterization of this material is fundamental to predicting its behavior in the presence of external stimuli. In this work, high-resolution Nuclear Magnetic Resonance (NMR) is proposed as a valid tool for analyzing the primary structure of the functional material along with the dynamic phenomena it encounters in solution. A special focus is on the investigation of polymer tacticity, which is a function of its stereochemical placement, determining crucial properties as the degree of crystallinity of a polymer, its melting temperature, rheological properties, or its glass transition temperature.

Here are described the results of a spectroscopic study by MAS-NMR and NMR in solution carried out to establish the dual control of molecular weights and tacticity of the functional synthetic polymers obtained in our labs though radical polymerization processes. Free-radical polymerization is one of the synthetic strategies most used in the chemical production of polymeric material on an industrial and laboratory scale, because it allows to convert a wide variety of vinyl monomers into high molecular weight polymeric materials with reduced purification steps and the possibility of use different types of solvents available on the market.

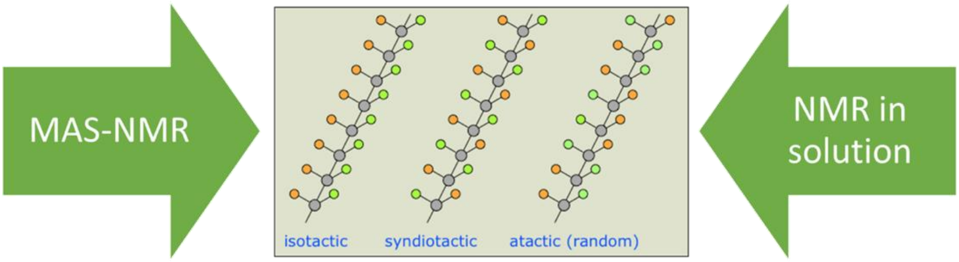

Figure 1

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P23 • Innovative approach for the synthesis of carbon dots by conversion of beer bagasse via Hydrothermal Carbonization Processes

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Biomass is the biodegradable fraction of waste and residues of biological origin from agriculture and related industries, including fishing and aquaculture, as well as the biodegradable fraction of industrial and municipal waste. The conversion of biomass into fuels and chemicals is becoming a very viable alternative to diversify energy sources and reduce global warming. In fact, biomass, in addition to being a renewable source for energy production, generates fewer greenhouse gas emissions than fossil fuels, because the CO_2 released is consumed in the growth process of the biomass itself. Biomass can be converted by thermochemical treatment in which the main biomass conversion product is a carbonaceous material, called char. The char obtained from woody biomass has a high carbon content and interesting characteristics such as the porous structure, the high energy density, the aromatic surface and the presence of functional oxygen groups on the surface, characteristics that allow a wide range of applications as in the remediation of soil[1], wastewater pollution[2], solid fuels[3] and energy[4]. Among the thermochemical methods, hydrothermal carbonization is a simple, scalable and economical synthetic method that allows to produce high quality biocarbon materials based on the conversion of biomass waste under mild conditions (180-300 ° C) and autogenous pressure. In this work, the hydrochar obtained from HTC of beer bagasse was characterized and treated to obtain nanodots of activated carbon. The resulting hydrochar was used to manufacture high-performance electrochemical sensors for monitoring hazardous environmental pollutants, such as heavy metals in water.

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P24 • Attribution of Pollution Source in Apulian Ports by means of Multivariate Statistical Analysis

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In conventional environmental research, the attribution of a pollution source is essentially based on concentration values of specific Persistent Organic Pollutants (POPs), determined by analytical methods and then evaluated by means of standardized univariate statistical tests. This approach is often not exhaustive, more likely due to the unstability of some contaminants, and it is time-consuming, since the description of an area generally involves tens of POPs.

Multivariate statistical techniques could be applied to reduce the dimension of a dataset, thus allowing an easier interpretation of the analytical data [1].

In the present work, concentrations of POPs were measured in marine sediment samples, collected from four apulian ports that showed different levels of anthropogenic activity (negligible, moderate, and strong). Unsupervised and supervised multivariate statistical analyses were performed, in order to point out relationships existing between POPs and to identify patterns of POPs as potential markers of specific pollution sources/paths. Then, a model, aimed to classify the anthropogenic activity acting on the areas under study, was constructed and validated, obtaining a good predictive performance (Figure 1).

Hence, multivariate statistical approaches could provide a useful tool for the routine procedures of environmental monitoring.

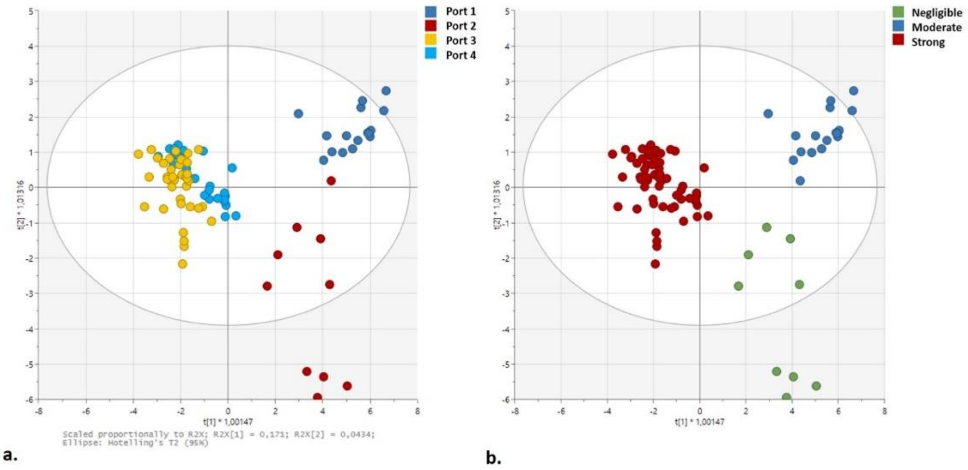

Figure 1. Orthogonal Partial Least Squares Discriminant Analysis (OPLS-DA): t1/t2 score plot displaying the observations coloured according to the ports (a) and to the level of the acting anthropogenic activity (b).

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P25 • TiO_2 nanotube arrays decorated with metallic nanoparticles: a versatile tool for a wide range of applications

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Due to its well-known physico-chemical properties, e.g. photocatalytic activity and biocompatibility, TiO_2 has been widely exploited for a variety of applications, ranging from hydrogen production to self-cleaning devices.[1-2]

Within this context, the use of nanostructured TiO_2 is highly convenient, allowing the coupling of the abovementioned features to the peculiar properties of the material at the nanoscale.[3] In the last decade our group has been involved in the electrochemical synthesis, fundamental studies, and application in the field of energy of TiO_2 nanotube arrays, which are characterized by easily tunable morphological parameters and high internal order.[4-6]

Here we describe a facile route for the decoration of TiO_2 nanotube arrays with Ag and Si nanoparticles and their detaching from the metallic layer on which they are synthesized, giving rise to self-standing membranes. Moreover, we show preliminary results concerning the use of the thus obtained samples respectively as biocompatible, anti-microbial surface and as anodes in lithium-ion batteries.

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P26 • Waste wood biomass valorisation by using Deep Eutectic Solvents (DESs)

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Deep Eutectic Solvents (DESs) are a new class of sustainable solvents, whose unique features conjugate the properties of conventional organic solvents with those of ionic liquids.[1] In recent years, the application of DESs as green solvents in valorization of the lignocellulosic biomass has gained significant attention because they are able to cleavage the covalent bonds between cellulosic and hemicellulosic fragments and lignin, thus overcoming the so-called recalcitrance of wood biomass, and acting as biorefinery. In addition, DESs promote the hydrogen bond disruption between the long cellulose chains, facilitating the mechanical disintegration of the extracted cellulose into more valuable nanosized materials.[2, 3] Herein, we report on the use of DESs for the microwave assisted extraction of cellulose from waste wood flours and the subsequent treatments for obtaining nanocellulose for various purposes.

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P27 • Evaluation of the sustainability for Lithium-Ion batteries recycling technologies

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The need for urgent and more intensive actions against climate change is largely recognized around the world. To mitigate the climate change and create a fossil fuel-free economy, the global community has agreed that GHG emissions must be significantly reduced. In this context, Li-ion batteries (LIBs) represent an effective solution to reduce the GHG emission from one of the major GHG emitters which is the transportation sectors. Furthermore, the supply of the raw metals for batteries could result precarious in order to meet the overly growing demand due to a centralized distribution of minerals in just few countries. Therefore, recycling of spent LIBs can play a significant role to secure the sustainable supply of critical metals (Li, Co, Ni) to new LIBs production and also to reduce landfill waste.

In this study the ESCAPE "Evaluation of Sustainability of material substitution using CArbon footPrint by a simplifiEd approach" approach was used to evaluate the sustainability of 8 Co extraction processes available in literature. This novel method introduced by Bontempi [1] is a sustainability assessment technique applied as a preliminary screening to the Life Cycle Assessment. It allows to establish, through the ESCAPE index, based on the Embodied Energy (EE) and Carbon Footprint (CF), the environmental impact evaluation of wastes if used as substitution of natural resources.

It appears that the recovery processes that involve the use of inorganic acids as leaching agents are generally more sustainable compared to organic acids. However, through the ESCAPE method, it was demonstrated that, by varying the experimental conditions of Co extraction process (S/L ratio, acids concentration, and time of process), it is possible to optimize the sustainability parameters (EE and CF) as long as the Co recovery efficiency does not drop drastically. Finally, the country where it is assumed to carry out the LIBs recovery processes is important. EE and CF parameters depend on the country's energy source. As a result, the most sustainable recovery processes are those developed in countries where energy comes mainly from renewable sources.

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P28 • Non-isothermal kinetic study of pyrolysis of multi-layered plastic food packaging. Effect of zeolite catalyst

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The recycling of multi-layered plastic food packaging (MPFP), which account for 40% of 55 Mt produced plastic in Europe, represents a significant challenge because the available technologies cannot identify and separate the individual layers [1]. Most MPFP contains several types of polymers, making mechanical recycling difficult and ultimately resulting in disposal or incineration. Pyrolysis, as a method of thermochemical recycling, is an alternative technology that can utilize multi-layered plastic food packaging and transform it into valuable goods such as fuels and chemicals. To get a deeper insight towards the understanding of the role of the selected zeolite catalyst in affecting the pyrolysis process of multi-layered plastic food packaging, thermogravimetric (TG) analysis was used to assess their thermal stability and kinetic parameters. The experimental TG conditions were: nitrogen flow at 60 cm^3 min^{-1}, heating rates of 5, 10, 15 and 20 °C min^{-1} in the temperature range from 40 to 600 °C. The raw data collected from TG experiments were processed according to the isoconversional model-free Friedman method [2], along with a statistical approach to conduct a kinetic study of pyrolysis. TG analysis revealed that decomposition occurs in the temperature range 350 − 510 °C, accompanied by a mass loss >90%, thus indicating high volatile matter content, hence potentially interesting for pyrolytic oil production. The results of kinetic analysis confirmed that pyrolysis of multi-layered plastic food packaging is a complex multi-step process consisting of three decomposition stages, characterized by diffusion and Avrami-Erofeev reaction models. The activation energy values determined by Friedman showed a rising trend with the degree of conversion α from 127 kJ mol^{-1} at $\alpha = 0.01$ to 219 kJ mol^{-1} at $\alpha = 0.95$. It is reasonably to make the assumption that the activation energies related to the processes occurring in the presence of the catalyst are lower by 44% and 8% for the first and the second steps, respectively, while they are substantially comparable for the third step. As a consequence, the onset decomposition temperature in the presence of the catalyst is likewise reduced, as determined by TG analysis, resulting in less energy required to heat the pyrolysis reactor.

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P29 • Cobalt(II) complex formation in [C$_4$mim][Tf$_2$N]

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Room temperature ionic liquids (RTILs) have been used as "green" substitutes of organic solvents in a number of applications, due to several advantages over the latter and numerous useful physicochemical properties.[1]
As far as the separation and recycling of "critical" metals is concerned, the use of hydrophobic RTILs as extracting phases in hydrometallurgical processes has been proposed in the last decade.[2]
In particular, the recycling of cobalt assumed growing importance due to the increased demand related to his use in expanding markets, such as Li-ion batteries or electric motors.[3] Therefore the knowledge of speciation and structure of the Co(II) ion in RTILs can provide key information for developing efficient recylcing processes. Among the available RTILs, those based on the N,N'-alkylimidazolium ($C_nC_m im^+$) cation and bis(trifluoromethylsulfonyl)imide (Tf_2N^-) anion (Figure 1) have been extensively studied for metal extractions and electrochemical depositions. However, only few works[4] are focused on the nature of the dissolved metals and their speciation in RTILs. With the aim to fill this gap, in this communication, we report the results on Co(II) complex formation with nitrate and chloride anions in [C$_4$mim][Tf$_2$N] (C$_4$mim = 1-methyl-3 butylimidazolium). The nature of the species formed in [C$_4$mim][Tf$_2$N] is determined experimentally by means of spectrophotometry and calorimetry. Density Functional Theory (DFT) and molecular dynamics (MD) calculations are employed to get information on the structure and solvation of the complexes. Our results show that stable CoX$_j$ (j = 1-4 and 1-3 for Cl^- and NO_3^-, respectively) are formed. In the case of Cl^-, a change of coordination (octahedral → tetrahedral) occurs (Figure 1) in the 1:2 species. MD simulations provided the Co(II) coordination number and information on the arrangement of the $[Tf_2N]^-$ anions in solution. Also, it is observed that the second solvation shell, mostly composed by $[C_4mim]^+$ cations, contracts with the increase of the number of bound ligands (j).

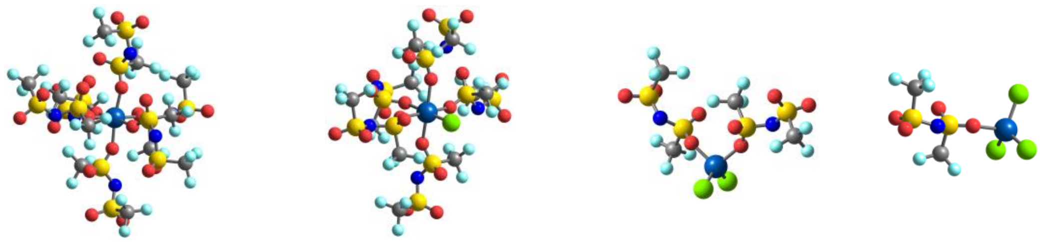

Figure 1. [Co(Tf$_2$N)$_i$Cl$_j$]$^{(2-i-j)}$ complexes.

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P30 • Photothermal responsive core-shell nanosystem based on Cdots functionalized with poly(N-isopropylacrylamide) for light-triggered drug release

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In these last decades, great efforts have been focused on the development of nanostructured materials that hold promise in chemo-photothermal combination therapy, which represents a new frontier for the cancer therapy application.[1] Core-shell nanocomposites are one of the most important achievements in the field of nanotechnology. The combination of multi-responsive shell with luminescent and photothermal carbon-based core has led to promising applications in various fields. In this work, a core-shell nanosystem, composed by carbonized dots (Cdots) core and poly(N-isopropylacrylamide) (PNIPAM) shell, was developed and the photothermal triggered release of doxorubicin was demonstrated. The system was fully characterized by ^{1}H NMR, DLS, Z-potential, AFM, optical absorption and fluorescence measurements. A photothermal conversion efficiency (η) value of about 67.9% was measured. Molecular dynamic (MD) simulations data agreed with experimental results, at 310 K the coil-to-globule transition and a consequent desorption of doxorubicin from the polymer were observed. Both the radius of gyration and the fluctuation of the distance drug-shell pointed that a temperature above the LCST and an acid pH facilitated the polymer transition. Moreover, MD simulations suggested an influence on the LCST exerted by the number of polymer chains anchored to the carbon core.

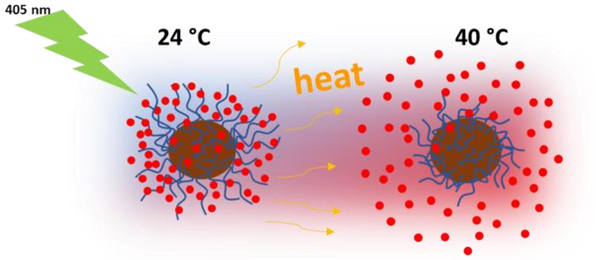

Figure 1. Photothermal-trigegred drug release from CPDs-PNIPAM nanosystem

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P31 • Adsorption of cisplatin by dithiocarbamate-functionalized silica

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Cytostatic drugs (CD), characterized by their environmental persistence have been detected in water bodies at concentrations up to µg/L levels.[1] Several methods for the removal and degradation of CDs, have been developed,[2] but they are relatively expensive and sometimes inefficient for CDs complete removal from the treated water. Among CDs, platinum-based chemotherapy agents are widely used for the treatment of a variety of cancers and demonstrate a high toxicity and low biodegradability. Such compounds, after administration, are excreted into hospital wastewater intact or as toxic metabolites in significant percentage.[1] Effectively, Pt-based drugs have been detected in the mg/L range in hospital effluents and water treatment plants, raising concerns about the long-term exposure of living organisms to low levels of such compounds.

A potentially efficient strategy to treat such low levels of Pt-containing contaminants is to selectively pre-concentrate the sample by adsorption, and then to further treat it e.g., by means of advanced oxidation processes.

In this contribution, the adsorption of cisplatin by dithiocarbamate (DTC) modified silica is evaluated. The choice of this material is based on the high affinity of the thiocarbamate group for Pt^{2+}, which, upon metal binding, causes the destruction of the original toxic compound. Also, the low-cost starting materials for the preparation of the adsorbent phase makes it attractive from an economic point of view.

The functionalization of silica was carried out with a slightly modified literature procedure[3] and characterized by IR, TGA and PZC analysis. Adsorption kinetics and isotherms have been built by analysing the free concentration of Pt by using UV-Vis spectrophotometry. The obtained material showed that equilibrium was reached after about 60 minutes of contact time with the cisplatin-containing solution. The mass/volume ratios between 1 and 10 mg/mL of adsorbent were tested. The adsorbent material retained up to 70% of the platinum present in the experimental conditions adopted.

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P32 • Synthesis and photophysical characterization of Donor-Acceptor molecular architectures with potential Thermally Activated Delayed Fluorescence (TADF) behaviour

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In the research field of organic materials for electroluminescence, conjugated systems exhibiting thermally activated delayed fluorescence (TADF) have received a considerable interest[1] connected to their potential to harvest both singlet and triplet excitons and realize a theoretical Internal Quantum Efficiency of 100%. An accepted synthetic strategy for the obtainment of TADF materials consists in the adoption of a suitable donor-acceptor architecture, enabling the spatial separation of the frontier orbitals (HOMO and LUMO), leading, in turn, to a small difference in energy levels between singlet and triplet states (ΔE_{ST}). To this effect, a large dihedral angle between the donor and accepting units allows sufficient spatial HOMO and LUMO separation to warrant the desired electronic feature. A survey of the available literature indicates that among the typical acceptors, several types of ketones or ketone derivatives are commonly used, while typical electron donor groups involve aromatic heterocycles containing different heteroatoms.[2] In this presentation, we will discuss the synthesis and characterization of three new molecular architectures exhibiting TADF. The structures are reported in Figure 1.

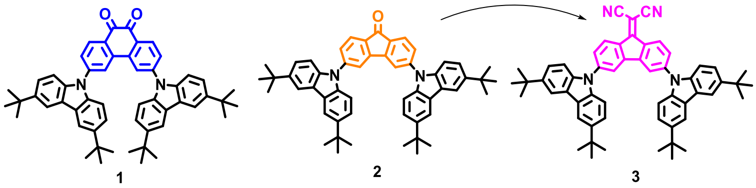

Figure 1. 9,10-phenantrenequinone- and 9-fluorenone-based molecules with potential TADF properties.

The structures **1** and **2** have been synthesized by organometallic coupling between 3,6-dibromofluorenone or 3,6-dibromophenanthrenequinone with two equivalents of the suitable donor, while **3** has been obtained by suitable Functional Group Interconversion starting from **2**. The three structures have been characterized by standard spectroscopic and spectrometric techniques (ESI-MS, FT-IR, NMR, UV-vis, PL) followed by more thorough photophysical investigations, directed to the ascertaining of TADF.

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P33 • Versatile Indanone/Indandione-based Thermally Activated Delayed Fluorescence Organic Materials with Diversified Emissive Behaviors of AIE and RTP

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The design of versatile luminescent materials possessing thermally activated delayed fluorescence (TADF), aggregation-induced emission (AIE), room-temperature phosphorescence (RTP) and high luminescence efficiency is a crucial step in the development of efficient organic electroluminescent devices.[1] In this presentation, we describe the molecular design, synthesis, and characterization of a class of organic emitters adopting different indanone/indandione-based electron-accepting units (A) (Figure 1). By adopting the donor–acceptor (D-A) design, in order to enhance the separation of the HOMO and LUMO, we selected di(tert-butyl)carbazole and di(tert-butyl)phenothiazine as donors. The synthetic strategy culminated with a Pd-catalyzed Buchwald-Hartwig coupling between the electron-accepting (A) and the electron-donating (D) building blocks enabling the C-N bond formation. The optimized synthetic protocol allowed to synthesize two structures, in which the indan-1-one acceptor unit was coupled with 3,6-di(tert-butyl)carbazole donor unit or 3,6-di(tert-butyl)phenothiazine. Furthermore, the influence of the additional ketone functionality on the optical properties of the corresponding molecules was evaluated by introducing indan-1,3-dione as electron accepting unit. The obtained compounds were characterized by investigated thermal, electrochemical and photophysical properties, the latter supported by theoretical analyses. Due to the large dihedral angle between donor and acceptor, the obtained compounds were exhibited TADF and AIE phenomena in peculiar conditions. The pursued results indicate that, through a suitable molecular design strategy, relatively straightforward synthesis allows the obtainment of efficient multifunctional luminescent materials.

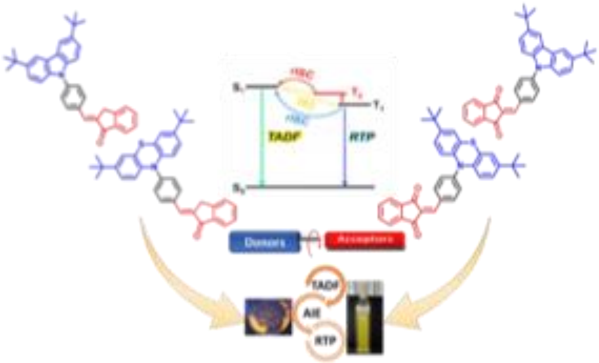

Figure 1. Molecular structures designed as D-A ketone-based emitters.

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P34 • Perspectives and challenges of micro/nanoplastics issues

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There is increasing knowledge on the sources, levels, and environmental fate of microplastics, with models on sampling and analysis, but reliable data is still needed for assessing management options. Indeed, an effective management policy requires a clear scientific vision of the issues arising from micro and nano plastics (M/NPs). However, there are currently different, dissimilar, and non-standardised methods for sampling and analysing M/NPs in environmental and biological matrices making difficult to get to reliable conclusions, despite the large amount of scientific literature available. To understand their impacts on the environment and health, more high-quality results are needed, but to guarantee reliable results, researchers must agree on the analysis and adopt shared protocols.

The VAMAS Technical Working Area (TWA) “Micro and Nano Plastics in the Environment” wants to give to the scientific community an international platform to assess the scientific topics related to the MPs and to support national and international projects in developing reliable protocols. This TWA acts in synergy with the PRIORITY COST European Action, in which more than 250 researchers from 38 Countries are involved to create a transnational team, supporting the sharing of the know-how and the discussion on future challenges due to the environmental plastic litter. The final goal is to allow the decision-makers to be able to protect the resources, such as waters, air, food products, and soils, thus the environment and the humans’ health.

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P35 • Synthethic and formulation studies for the development of new polymeric environmental-friendly materials

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The growing use of information technologies has led to a growing demand for a large number of materials characterized by excellent chemical-physical features, high resistance, and durability over time.

A project is underway in our lab focused on the development of synthetic processes characterized by increased sustainability both for the operators and for the environment. The project aims to develop innovative materials to be included in composite products. Therefore, it is crucial to further extend the research to develop innovative materials, the production of which should be more sustainable for the environment and the operators working close to the production line.

In particular, the research project includes the generation of new functional polymeric materials and the development of their formulations in compliance with the requirements of Health, Safety, and Environment (HSE). New polymers showing special functional features, such as improved mechanical properties, are synthesized and, thus, exploited for the preparation of innovative composite products. Formulation studies are performed on the prepared polymers. During the research activity, a special focus is on the principles of eco-design and green chemistry, looking at the ecological and toxicity profile of the reagents e solvents used. 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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P36 • Synergistic effects of combined UVA light and atmospheric plasma for efficient chemical decontamination and microbial inactivation of packaged fish products

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Fish products require specific attention to avoid possible contamination which can readily occur during different stages of production. In fact, prior to packaging, eliminating pathogenic microorganisms and chemical compounds which can reduce the shelf life or alter the organoleptic properties of the product is often necessary. Among the novel techniques to ensure bacterial inactivation and chemical decontamination of packaged food, "cold plasma" produced under atmospheric conditions has been often proposed as a sustainable method.[1] The use of UVC light (100-280 nm), also known as "cold pasteurization", is also a well-established method to reduce or eliminate pathogens, but it is highly energetic and represents an expensive investment. Irradiation at lower energy (such as UVA, 320-400 nm) would be desirable but generally ineffective (see Figure 1) for the required tasks.[2] We hereby report that simultaneously performing UV-A irradiation and cold plasma discharge results in substantial process intensification, both in terms of microbial inactivation of foodborne pathogens and chemical oxidation of a model organic compound such as methylene blue (see Figure 1). The process do not significantly affects the properties of the fish product and allows to reduce the decontamination costs, thus justifying the application for this aim. A possible mechanism based on the generation of photo-active peroxynitrite species has been proposed to justify the observed synergistic effects.

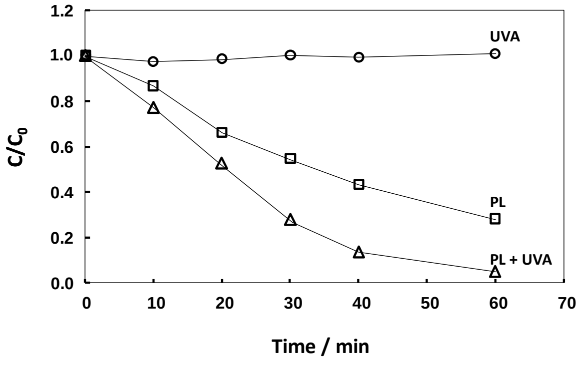

Figure 1. Normalized concentration of methylene blue versus time during a treatment with UVA light (UVA, circles), atmospheric plasma (PL, squares) and combined plasma and UVA light (PL+UVA, triangles).

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P37 • Characterization and treatment of non-recyclable plastics fraction in municipal solid waste streams - RECOVER project.

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Over 360 million tons of plastic are produced annually worldwide, of which up to 40% and 3.5% are consumed by the packaging and agricultural industries, respectively, while just about 30% of waste plastic is recycled, the rest is incinerated, disposed in landfills or released to the environment. and Inefficient collection of recyclable materials, multilayers in plastic items are among the barriers to achieve a higher recycling rate. New recycling routes for non-recyclable mixed plastics are proposed using a combination of insects, microorganisms, earthworms and enzymes to convert plastics into biofertilizers and bio-based materials for food packaging and agricultural applications.

Figure 1. Municipal solid waste selection at Idelux facilities

This study provides a preliminary overview of the main non-recyclable plastics in municipal waste streams, and their characteristics as well as an overview of the logistic chain for their collection and present management was performed. In agriculture plastic waste is mainly constituted by Polyethylene (PE) both linear low density, low density and high density, in food packaging polyethylene is still present together with a large presence of polypropylene, polystyrene (PS) and polyethylene terephthalate (PET). Representative samples of plastics (PE, PET, PS) were selected for analysis of deterioration, after pre-treatments and subsequent biodegradation, by biological treatment using insects. LLDPE is one of the main plastic type in these waste streams mostly coming from food packaging. Exposure of LLDPE to UV treatment for long time produce significant changes in the structure of the polymer that could facilitate further biological treatment. The insect Galleria mellonella was capable to feed on LLDPE.

Acknowledgment: This project has received funding from the Bio Based Industries Joint Undertaking (JU) under grant agreement "GA887648" project RECOVER "Development of innovative biotic symbiosis for plastic biodegradation and synthesis to solve their end-of-life challenges in the agriculture and food industries" The JU receives support from the European Union's Horizon 2020 research and innovation programme and the Bio Based Industries Consortium.

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