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PROGRAMMA SCIENTIFICO workshop AICIng 2022

Giovedì 16 giugno – Aula Mario Giordano

8:30-9:00	**Registrazione**
9:00-9:20	**Saluti di benvenuto**: - Magnifico Rettore - Presidente AICIng
Sessione 1: ***Prof. Piero Mastrorilli (Politecnico di Bari)***	
9:20-9:35	**O1-Elena Cazzaniga (Politecnico di Torino):** Determination of lipid content in hazelnuts using NIR spectroscopy.
9:35-9:50	**O2-Nico Zamperlin (Università di Trento):** Barium Titanate functionalization with Organosilanes: enhancing particle-matrix compatibility in nanocomposites.
9:50-10:05	**O3-Martina Lippi (Politecnico di Milano):** Nanocellulose-based aerogel as urea-controlled release systems.
10:05-10:20	**O4-Massimo Zambito Marsala (Politecnico di Milano):** Bionanocomposites based on a covalent network of chitosan and edge functionalized graphene layers.
10:20-10:35	**O5-Roberto Martini (Università di Roma Tor Vergata):** Solvent-induced Aggregation of Prolinated Porphyrin Derivatives: Comparison between Solution Behavior and Solid-State Morphology
10:35-10:50	**O6-Mattia Sozzi (Politecnico di Torino):** 1H NMR Spectroscopy as a tool for monitoring and optimizing lentil flour extraction and enzymatic hydrolyzation processes.
10:50-11:20	*Coffee Break*
Sessione 2: ***Prof. Salvatore Failla (Università di Catania)***	
11:20-11:35	**O7-Giulia Calabrese (Università di Messina):** Perovskite oxides for hydrogen storage.
11:35-11:50	**O8-Martina Bortolami (Università di Roma La Sapienza):** Anodic generation of BF_3 from imidazolium ionic liquids: a safe and effective alternative to commercial etherate form.
11:50-12:05	**O9-Ivan Pietro Oliveri (Università di Catania):** Tunable transmetalation properties of a new Lewis acidic Zn(II) Schiff-base complex
12:05-12:20	**O10-Manfredi Caruso (Politecnico di Milano):** One (benzene) ring to rule them all: overcoming solubility and reactivity issues of N-hydroxyphthalimide in the oxidation of hydrocarbons.

12:20-12:35	**O11-Fatima Margani (Politecnico di Milano):** A green approach to the edge functionalization of graphene layers with a bio-based 2-pyrone.
12:35-12:50	**O12-Claudio Gioia (Università di Bologna):** Synergic cooperation for the synthesis and advanced modelling/characterization of novel functional bio-polymeric architectures.
12:50-13:05	**O13-Cristina Minnelli (Università Politecnica delle Marche**): Layered double hydroxide as versatile and sustainable platform for biomedical applications.
13:05-14:30	*Pranzo*
Sessione 3: ***Prof.ssa Michelina Catauro (Università degli Studi della Campania*)**	
14:30-14:45	**O14-Viviana Bressi (Università degli Studi di Messina):** Rilevamento elettroanalitico di ioni metallici pesanti in acqua di mare mediante sensori TPYP-SPEEK/SPCE.
14:45-15:00	**O15-Fabrizio Caroleo (Università di Roma Tor Vergata**): Colour Catcher® : low-cost colorimetric sensor and laundry. Kill two birds with one stone.
15:00-15:15	**O16-Simona Crispi (Università degli Studi di Messina):** Gas sensing modulation of CNTs and m-TiO_2 nanomaterials by atomic layer deposition (ALD).
15:15-15:30	**O17-Alberto Taffelli (Università di Trento):** Large area photodetectors based on sol-gel-derived MoS_2 films.
15:30-15:45	**O18-Francesco Moriggi (Politecnico di Milano):** Chemical functionalization of graphene surface as filler for rubber compounds: modeling of supramolecular interactions.
15:45-16:15	*Coffee Break*
Sessione 4: ***Prof. Roberto Paolesse (Università di Roma Tor Vergata)***	
16:15-17:00	**Conferenza Plenaria-Prof. Luca Prodi (Università di Bologna):** Luminescence-based systems for analytes of biomedical and environmental interest.
17:00-17:15	**O19-Daniele Veclani (Università di Udine):** Thermodynamic of Adsorption of Diclofenac on graphene by molecular dynamics simulations.
17:15-17:30	**O20-Elaheh Mohebbi (Università Politecnica delle Marche**): $VO_2(B)$ Nanostructures as Promising Cathode Materials for rechargeable Li-ion Battery.
17:30-17:45	**Dott.ssa Maria Grazia Garavaglia (Perkin Elmer)**
17:45-19:00	**Sessione Poster**
20:30	**Cena Sociale -** ***Bar Caffè Giuliani - Corso Giuseppe Garibaldi, 3***

Venerdì 17 giugno (Sessione Parallela A) - Aula Mario Giordano

Sessione 4A: *Prof.ssa Isabella Chiarotto (Università di Roma La Sapienza)*	
8:30-8:45	**O21-Simone Naddeo (Politecnico di Milano):** Two steps one pot process for the conversion of dimethylfuran to pyrrole compounds with almost null E factor.
8:45-9.00	**O22-Anna Paola Panunzi (Università di Roma Tor Vergata):** Enhancing electrocatalytic activity of $La_{0.6}Sr_{0.4}FeO_3$ by Pt-doping for IT-SOFC cathodic applications.
9:00-9:15	**O23-Beatrice Ricciardi (Università di Roma Tor Vergata):** 3D Spherical Fe-N-C Oxygen Reduction Electrocatalysts for Energy Conversion.
9:15-9:30	**O24-Francesco Lanero (Università di Padova):** Functionalized co-polypyrrole-polyketone anion exchange membrane.
9:30-9:45	**O25-Emanuele Previti (Università di Messina):** New Calcium Lactate-SPEEK composite Coatings for Thermal Energy Storage Applications.
9:45-10:00	**O26-Gloria Nicastro (Politecnico di Milano):** Co-Polymeric Nanosponges from Cellulose Biomass as Heterogeneous Catalysts for Organic Reactions.
10:00-10:15	**O27-Laura Riva (Politecnico di Milano):** Cellulose Nanofibers as Additives for Sustainable Buildings: LCA and Analysis on Raw Earths.
10:15-10:30	**O28-Rida Jbr (Università Politecnica delle Marche):** Chemical separation: a step towards a full recycling and recovery of Cotton and PET fibers from blended textile.
10:30-11:00	*Coffee Break*
Sessione 5A: *Prof.ssa Giuseppina Raffaini (Politecnico di Milano)*	
11:00-11:15	**O29-Giovanni Dal Poggetto (Università di Modena e Reggio Emilia):** Effect of acid attack on geopolymers based on recycled corundum.
11:15-11:30	**O30-Edoardo Bondi (Università di Bologna):** Comparison between films and scaffolds of cyclohexane-based random copolyesters for vascular repair.
11:30-11:45	**O31-Edoardo Testa (Politecnico di Milano):** Innovative bioplastics from polypeptides of Hermetia illucens.
11:45-12:00	**O32-Elena Battaglini (Università di Bologna):** Sealing properties of fully bio-based poly(butylene 2,5-furanoate).

Venerdì 17 giugno (Sessione Parallela B) - Aula A 7/8

Sessione 4B: *Prof.ssa Simona Sabbatini (Università Politecnica delle Marche)*	
8:30-8:45	**O33-Enrico Bianchi (Università di Bologna):** Isomerism, glycol chain length and copolymerization as tools to achieve outstanding furan-based sustainable food packaging

8:45-9.00	**O34-Nicola Cavallini (Politecnico di Torino):** Chemometric differentiation of sole and plaice fish fillets using three near-infrared instruments.
9:00-9:15	**O35-Arianna Rossetti (Politecnico di Milano):** TEMPO-oxidized cellulose nanofibers/polyvalent cations hydrogels: A multifaceted view of network nteractions and inner structure.
9:15-9:30	**O36-Laura Fazi (Università di Roma Tor Vergata):** Towards an understanding of the connection between micro e macro behaviour of CNT/polymer composites: a 3D Raman imaging approach.
9:30-9:45	**O37-Serena De Santis (Università di Roma tre):** FTIR spectral fingerprints in Colorectal Cancer derived Tissues and Cancer Associated Fibroblasts.
9:45-10:00	**O38-Enrico Lemma (Università Campus Bio-medico Roma):** Selective positioning of different cell types on 3D scaffolds via DNA hybridization.
10:00-10:15	**O39-Emanuela Muscolino (Università degli studi di Palermo):** Recombinant mussel protein Pvfp5b enhances cell adhesion of poly(vinyl alcohol)/k-carrageenan hydrogel scaffolds.
10:15-10:30	**O40-Fabiana Pandolfi (Università di Roma La Sapienza):** New deferiprone derivatives as antibiofilm and antimicrobial agents: design, synthesis and biological evaluation.
10:30-11:00	*Coffee Break*
Sessione 5B: *Prof.ssa Paola Astolfi (Università Politecnica delle Marche)*	
11:00-11:15	**O41-Marco Parlapiano (Università Politecnica delle Marche):** Molecularly Imprinted Polymers for the CECs selective removal as tertiary treatment in Municipal Wastewater Treatment Plant.
11:15-11:30	**O42-Alessia Foglia (Università Politecnica delle Marche):** Assessment of alternative value chains for Polyhydroxyalkanoate recovery from municipal wastewater treatment plant.
11:30-11:45	**O43-Aurelio Bifulco (Università di Napoli):** PVP-based composites containing sol-gel nanosized SiO_2 and hybrid TiO_2 microparticles for water purification.
11:45-12:00	**O44-Grazia Maria Cappucci (Università di Modena e Reggio Emilia):** Assessment of impacts caused by local scale emissions introduced in USEtox model.

SESSIONE CONGIUNTA - Aula Mario Giordano

12:05-12:30	**Premiazioni e chiusura lavori**

Conferenza Plenaria

Luminescence-based systems for analytes of biomedical and environmental interest

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The research of our group has recently focussed on the development of photoactive nanostructures for nanomedicine. In this context, light can be a powerful tool to obtain (i) bright contrast agents for *in vivo* imaging, (ii) efficient probes for real time and real space measurements of analytes of biological interest, (iii) promising agents for therapy, and (iv) high analytical performances in *in vitro* diagnostics. In particular for this last application, the many ways in which the excited state can be generated lead to different techniques, such as photo-, chemi-, electrochemi- and thermo-luminescence, offering, together with high sensitivity, high versality to address the different analytical needs. One of the most urgent one, as the last pandemics has clearly showed, is the design of accurate, fast, cheap, and portable platform to detect infectious agents. Thanks to the experience acquired so far [1], we present here a sensitive methodology based on electrochemiluminescence to detect the genome of the virus of the hepatitis B, with analytical performances comparable or even better respect to PCR ones [2]. To note, this approach can be extended to other infectious pathogens, including bacteria and parasites.

Furthermore, our know-how on the design of systems for nanomedicine [3] led us to design a derivatized hyaluronic acid that, thanks to a proper design, can allow the detection of micro- and nano-plastics [4], whose presence in waters is creating a problem of great relevance worldwide, but that is still unsolved from an analytical point of view.

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Contributi Orali

Determination of lipid content in hazelnuts using NIR spectroscopy

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Hazelnuts (*Corylus avellana* L.) are one of the most largely farmed and exported dry fruits all over the world (Oliveira, et al., 2008), produced in tons per year (FAOSTAT). Their popularity is linked to their high nutritional and nutraceutical properties: among other types of nuts, hazelnuts are particularly rich in lipids (Köksal, Artik, Şimşek, & Güneş, 2006). The present work is focused on investigating if near infrared (NIR) spectroscopy is suitable to obtain information concerning the lipids and polyphenols contents of 57 samples of hazelnuts, mainly differing by country of origin (Italy, South America, Turkey, Georgia and Azerbaijan), using both an expensive benchtop spectrometer and a cheap portable instrument. To this aim, two near-infrared (NIR) instruments were used: a benchtop FT-NIR spectrometer (Multi Purpose Analyser–MPA, by Bruker) equipped with an integrating sphere device, and the hand-held, battery powered SCiO Pocket molecular sensor (by Consumer Physics).

Multivariate data analysis was exploited to inspect the NIR collected spectra. Firstly, a Principal Component Analysis (PCA) model was built to explore the information contained in the samples. Then, a Partial Least Square (PLS) regression model was developed to predict the lipids and polyphenols contents. The best results were obtained both for PCA and regression models when using the MPA instrument. The PLS-regression results regarding the lipids content showed much better performances than the polyphenols. The robustness of the model was tested through cross-validation and the regression parameters were $R^2 = 0.939$ and RMSE = 0.440 in calibration and RMSEP = 0.419 in prediction for the lipids, while the same parameters for the polyphenols were much lower. The SCiO portable instrument showed similar but slightly worse results concerning the lipid content in samples. The PLS-regression parameters were $R^2 = 0.811$ and RMSE = 0.787 in calibration and RMSEP = 1.097 in prediction, suggesting the reliability also of the model obtained through this portable instrument.

References:

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Oliveira, I., Sousa, A., Sa Morais, J., Ferreira, I. C., Bento, A., Estevinho, L., & Pereira, J. A. (2008). Chemical composition, and antioxidant and microbial activities of three hazelnut (*Corylus avellana* L.) cultivars. *Food and Chemical Toxicology*, 1801-1807.

Barium Titanate functionalization with Organosilanes: enhancing particle-matrix compatibility in nanocomposites

Nico Zamperlin[1], Andrea Bottacini[1], Emanuela Callone[1], Alessandro Pegoretti[1], Marco Fontana[2], Sandra Dirè[1]

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The interest around polymer-based nanocomposites for electronic applications (sensing, wearable, energy harvesting) has continuously grown during the last decade [1]. These composites must combine flexibility and softness given by the polymeric matrix with dielectric and piezoelectric performance conferred by ceramic nanofillers. Titanates are largely employed for these application, in particular barium titanate (BT) that enables good performance avoiding the use of lead-based ceramics. The main issue of polymer-ceramic nanocomposites consists in the poor matrix-filler compatibility [2] that is responsible for non-homogeneous filler dispersion and, consequently, for poor and inhomogeneous dielectric and piezoelectric response. To solve this problem, the surface of ceramic nanoparticles (NPs) can be modified with several functionalizing agents to enhance their dispersion and chemical compatibility with the polymeric matrix. In this work we successfully grafted different organosilanes on the surface of both commercial and sol-gel synthesized [3] BT NPs. A fundamental requirement is a proper BT surface activation due to its poor pristine reactivity. The hydroxylation treatment with H_2O_2 (30% vol) aimed to create -OH active sites for reaction with organosilanes was optimized with commercial BT NPs. Oxidized commercial NPs have been functionalized with 3-glycidyloxypropyltrimethoxysilane (GPTMS) and the yield of the functionalization was evaluated by solid state Nuclear Magnetic Resonance (NMR), and thermogravimetric analysis (TGA). Once the optimal reaction parameters were identified, sol-gel synthesized particles were functionalized with three different Organosilanes: GPTMS, 2-[(acetoxy(polyethyleneoxy)propyl]triethoxysilane (APEOTES) and triethoxysilyl-propoxy(polyethyleneoxy)dodecanoate (TESPEOD). The presence of surface grafted organosilanes was proven thanks to Fourier transform infrared spectroscopy (FTIR) and NMR also evaluating the grafting density (molecules per nm^2). Finally, particles were embedded in two different polymeric matrices, namely epoxy resin and polydimethylsiloxane, and the effect of the functionalization on the particles' dispersion and alignment was studied by scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDXS).

References

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Nanocellulose-based aerogel as urea controlled release systems

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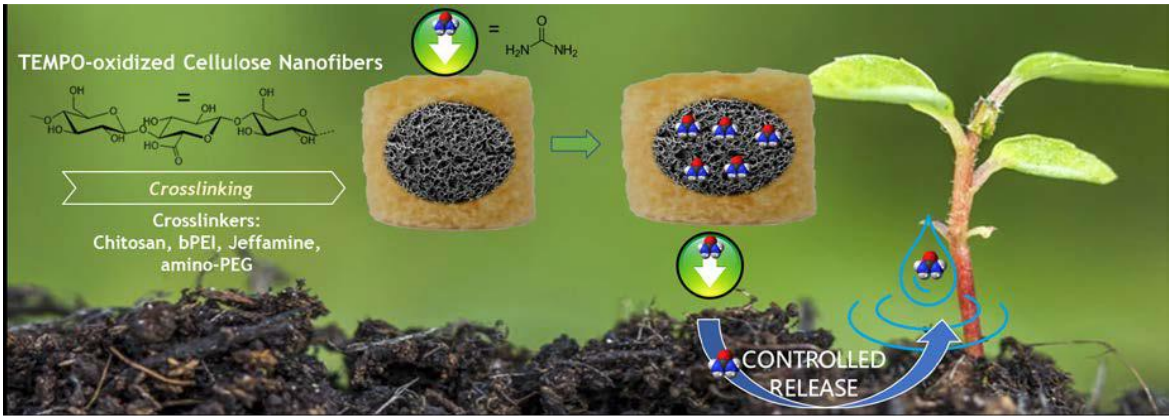

Nowadays agriculture industry needs to face all the compliance due to the global climate change and the increasing urbanization [1]. While nitrogen-rich fertilizers can help to improve the crop and plants growth [2], their intensive use has consistently contributed to the emission of nitrous oxide (N_2O) in the atmosphere, a potent greenhouse gas that is one of the main responsible of global warming. To overcome this issue, the design of highly efficient fertilizers (Enhanced Efficiency Fertilizers, EEF) is mandatory [3]. Herein we report the development of hybrid versions of urea-based fertilizers for a controlled release of nitrogen in the soil, with the aim of reducing nutrient loss as well as the dangerous emissions into the atmosphere. Aerogels build upon the crosslinking between TEMPO-oxidized cellulose nanofibers (TOCNFs) and polyamines [4] were studied for controlled release of urea in water. During the processing of the materials, three operational parameters were varied in order to modulate the morphology of the final systems and to investigate how it could influence the urea release: i) the degree of cellulose oxidation, ii) the freezing temperature of the intermediate hydrogel, and iii) the type of crosslinker used (linear and branched polyamines). Two different approaches for urea loading were proposed and urea release was monitored by UV-Vis Spectroscopy, by means of a specific commercial kit. Results showed different behavior depending on materials' composition, especially in relation to the different crosslinker used.

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

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Graphene has outstanding thermal, mechanical and electronic properties. Bionanocomposites are an emerging class of materials, designed with the aim of achieving advanced structural and functional properties by using biobased polymers. As biopolymer, a great interest is for chitosan (CS), poly (*N*-acetyl-D-glucosamine), a copolymer of linked 2-acetamido-2-deoxy-D-glucopyranose and 2-amino-2-deoxy-D-glucopyranose. Graphene and graphene related materials are increasingly used for the preparation of bionanocomposites.

In this study, a high surface area graphite was edge functionalized with hydroxyl groups (G-OH) through the reaction with KOH. G-CHO, with 4.5 mmol/g of functional group, was prepared from G-OH by means of the Reimer-Tieman reaction. [1]

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

References

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Solvent-induced Aggregation of Prolinated Porphyrin Derivatives: Comparison between Solution Behavior and Solid-State Morphology

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Porphyrin derivatives covalently linked to L- or D-proline enantiomers organize in solution in chiral suprastructures thanks to the amplification of chiral information stored in the single proline residue [1]. Such systems could be used as active materials in sensors to detect chiral pollutants produced, among all, by pharmaceutical and agri-food industries [2]. Recently, aggregation studies carried out on the derivatives, both as free-base and Zn complex (**Figure 1A, M = H_2, Zn**), in EtOH/H_2O 25:75 (v:v) showed the formation of chiral assemblies, where the the metal inserted had a crucial role both on the aggregation mechanism and on the resulting chiroptical features [1].

In this work we extended these studies on the two enantiomers of Co(II) porphyrin complex, namely (L) and (D)CoP (**Figure 1A, M = Co**), with the aim of evaluating the effect of this metal on the aggregation process. The supramolecular organization is triggered by the addition of an appropriate amount of water - in which the porphyrins are poorly soluble – to EtOH solution (**Figure 1B**)), until a concentration of around 5 μM is reached. The kinetics of the process is followed by UV-Vis and Circular Dichroism (CD) spectroscopy. **Figure 1C** reports the CD spectra at equilibrium of the three (L)-prolinated derivatives-based aggregates. In particular, the Co porphyrin gives assemblies with a remarkably different spectral pattern in comparison to the others, with an intense band at wavelengths below 400 nm that reveals a distinctive aggregative behavior. Studies on the size and morphology of the aggregates were conducted by means of Dynamic Light Scattering (DLS) and Atomic Force Microscopy (AFM) measurements.

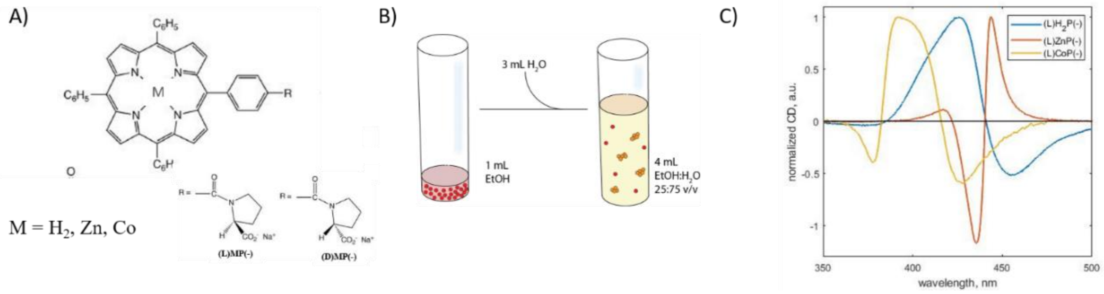

Figure 1: (**A**) structures of porphyrin derivatives (L)/(D)MP(-). (**B**) Aggregation process driven by hydrophobic effect. (**C**) CD patterns of the different aggregates from (L)MP(-).

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^{1}H NMR Spectroscopy as a tool for monitoring and optimizing lentil flour extraction and enzymatic hydrolyzation processes

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In past years, the interest towards bioeconomy concepts has been considerably growing. In particular, the development of sustainable and renewable bio-based technologies for food production is becoming increasingly important. One of the most interesting applications of bioeconomy in the "food" area is the use of enzymes for the transformation of food materials [1], to improve food safety and optimize the overall food treatment process.

In this perspective, the present study is focused on the optimization of the parameters used for lentil flour treatments. Lentil flour, which is known as a "functional food" in the field of food supplements, was treated under different experimental conditions. First, an extraction process with $Ca(OH)_2$ at a controlled pH value of 8 and a fixed 60 °C temperature was performed. Half of the flour was treated with a stirring rate of 60 RPM, while the other half was treated with a stirring rate of 120 RPM. At the beginning of this process, a 0.2 % quantity of protease enzyme for hydrolysis was added to 20 samples (10 treated at 60 RPM and 10 treated at 120 RPM). To get an overall view of the process, the sampling procedure was performed at different time points, with 10 points for the hydrolysed samples and 6 points for the non-hydrolysed samples, leading to a total amount of 32 liquid samples to be analysed. All samples were analysed with a Jeol ECZR NMR spectrometer operating at 600 MHz with 128 scans, 32k points and a relaxation delay of 3 s. In addition, a solvent suppression procedure ("watergate") was applied to suppress the water signal.

Multivariate exploratory analysis tools such as Principal Component Analysis (PCA) was used on the NMR spectra to explore similarities and differences among the samples. As expected, hydrolysed samples acquired after 15 minutes of treatment can be easily distinguished from non-hydrolysed samples. Curiously, hydrolysed samples at zero time and after 1 minute of treatment, despite the presence of the enzyme, are similar to the non-hydrolysed samples. Moreover, by exploring the domain of hydrolysed samples after 15 minutes of treatment, an interesting time-trend response was found. Finally, a classification analysis performed with PLS-DA (Partial Least Squares – Discriminant Analysis) allowed obtaining a classification model able to distinguish hydrolysed samples from non-hydrolysed samples with very high sensitivity, specificity and precision for both classes, and a very low error rate.

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Perovskite oxides for hydrogen storage

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Nowadays the human society relies essentially on fossil fuels for energy production but these are not inexhaustible sources and they are not sustainable due to emissions of greenhouse gases. So a cleaner and more sustainable energy source is being actively pursued, especially for the transport sector which currently accounts for almost 60% of world energy consumption. Hydrogen is a promising candidate due to its high energy density (120 MJ/kg = 33.33 kWh) and also because its only reaction products are H_2O and warm air. Given the extremely low density of this gas (0.089 kg/m^3), solid-state storage system is the most viable solution.1 For this purpose metal hydrides are the most exploited materials because they have high hydrogen storage densities (6.5 H atoms/cm^3 for MgH_2) at moderate temperatures and pressures and this gives these systems an advantage in terms of safety over other accumulation methods in the liquid and gaseous state. However, these materials are characterized by slow kinetics and are unable to release hydrogen at low temperatures, as the applications require.[2] So we are investigating perovskite oxides as an alternative for H_2 storage because they are thermally stable and 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. In particular, we are evaluating $ABO_{3\pm\delta}$ type perovskite oxides with a non-stoichiometric content of oxygen to investigate whether the presence of oxygen vacations can promote the amount of hydrogen absorbed. Specifically, among the materials we are studying $CaMnO_3$, according to our analyses, is able to absorb and release an amount of H_2 equal to 2.76 kg/m^3 at 308.15 K and under a gas pressure of 40 bar. In order to determine the theoretical maximum hydrogen amount that can be stored in the structure of this material structural evaluations were applied. In particular, due to orthorhombic structure of $CaMnO_3$ and considering the presence of octahedral voids (whose dimension is 2.82 $Å^3$), we evaluated the fitting of both molecular hydrogen and hydride ion. So, approximating the species to a sphere, we can observe that hydrogen as H^-, with a ionic radius of 1.34 Å cannot fit into the material structure considered, while molecular hydrogen, with a radius of 0.74 Å, can theoretically fit into an octahedral void. Further analysis are ongoing to evaluate in which form hydrogen is absorbed by these materials and to consider the presence of structural defects in order to understand the mechanism by which hydrogen is stored and improve the storage efficiency consequently.

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Anodic generation of BF_3 from imidazolium ionic liquids: a safe and effective alternative to commercial etherate form

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Boron trifluoride is a toxic and highly reactive gas, and to make it easier to handle and apply in acid catalyzed reactions its current commercial form is a liquid complex with an organic ether. Nevertheless, BF_3-etherate still retains some critical issues both in handling and storing, due to its toxicity, corrosive properties, flammability and high sensitivity to moisture [1]. In the light of Green Chemistry principles, the identification of an alternative and less dangerous source of BF_3 could be of great importance. With this aim, based on literature data reporting the generation of BF_3 from tetrafluoroborate anion by electrochemical oxidation of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (BMIm-BF_4) [2], we carried out some classical acid catalyzed reactions in anodically oxidized BMIm-BF_4. Compared to the use of BF_3-etherate, analogous or improved results were obtained for the investigated reactions. The noteworthy advantages of the developed method are: the *in situ* generation of the BF_3, without the necessity of storing; the possibility to generate the amount of required catalyst using the electron as redox reagent; the reduced sensitivity to moisture; the possibility of ionic liquid recycling for subsequent reactions [3]. Subsequently, we used different tetrafluoroborate-based ionic liquids for BF_3 electrogeneration and we studied the effect of the electrochemical configuration (*i.e.*, divided or undivided cells) on BF_3 reactivity, taking as model reaction the styrene oxide isomerization. The different experimental conditions led selectively to the formation of phenylacetaldehyde or of 2-benzyl-4-phenyl-1,3-dioxolane. Moreover, computational analysis strongly suggested a higher stability for BF_3/BMIm-BF_4 system compared to $BF_3 \cdot Et_2O$, and confirmed the formation of N-heterocyclic carbene-BF_3 adduct when carrying out the electrolysis in an undivided cell [4]. All together, these results allow the definition of the BF_3 electrogenerated in tetrafluoroborate-based ionic liquids as an efficient and less harmful alternative to BF_3-etherate for organic syntheses.

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Tunable transmetalation properties of a new Lewis acidic Zn(II) Schiff-base complex

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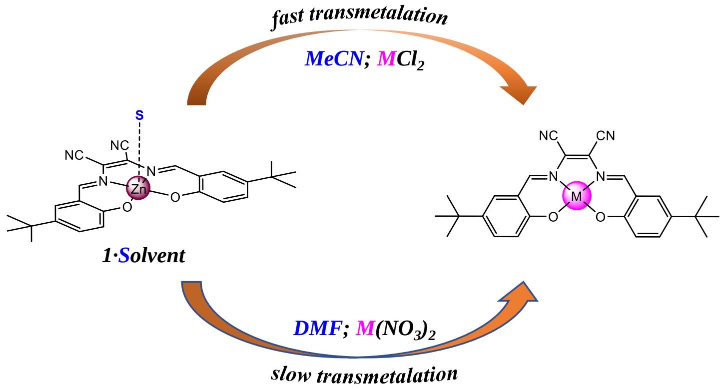
Zn(II) Schiff-base complexes are Lewis acidic species which form aggregates in absence of Lewis bases and monomeric adducts in presence of Lewis bases. The switching from the aggregate to the adduct involves dramatic variations of optical spectroscopic properties, both in solution and in solid state.[1-2] The stability of monomeric adducts influences dramatically the properties of these complexes. Transmetalation, or metal exchange, represents a powerful tool in the synthesis of multimetallic and supramolecular structures, and allows to modulate the catalytic and sensing properties of inorganic systems.[3] Nevertheless, in the literature only few studies are reported on the transmetalation properties of Zn(II) Schiff-base complexes.[4-6]

Here, we present the first systematic transmetalation study of a new Lewis acidic Zn(II) Schiff-base complex, **1**, in relation to the stability of the starting monomeric adducts.



The lower stability of adduct **1**·MeCN allows transmetalation with Cu^{2+}(fast), Co^{2+} and Ni^{2+}(slow) using nitrate/perchlorate salts and a fast transmetalation with divalent ions of the first transition series (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}) using chloride metal salts. On the other hand, in DMF the transmetalation of **1** is slower than in MeCN, according to the greater stability of **1**·DMF adducts. Thus, transmetalation properties of these Zn(II) Schiff-base complexes can be tuned in relation to the Lewis basicity of the coordinating solvent[7] and the nature of the counteranion of metal salts.

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One (benzene) ring to rule them all: overcoming solubility and reactivity issues of N-hydroxyphthalimide in the oxidation of hydrocarbons

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The liquid-phase aerobic autoxidation of hydrocarbons is a key tool for the industrial production of bulk chemicals.[1] The implementation of these transformations is under continuous investigation for both economical and ecological reasons. In this context, N-hydroxyphthalimide (NHPI) has emerged as a valuable organocatalyst able to improve a wide range of oxidation reactions by efficiently mediating hydrogen atom transfer (HAT) processes.[2] The typical substrate scope of this catalyst is represented by alkylaromatic compounds. However, given the poor solubility of NHPI in these apolar media, toxic polar co-solvents (*e.g.* acetonitrile, benzonitrile, acetic acid) are often required to ensure homogeneous conditions.[3] To overcome this problem, the synthesis of NHPI derivatives bearing lipophilic chains has emerged as a promising strategy [4,5]. Nonetheless, a key structural feature improving the solubility of these compounds has not been found yet.

Along this line, in the present work, we synthesized a small library of lipophilic NHPI derivatives bearing different functional groups to investigate their influence on the solubility of these catalysts.

Unexpected preliminary results revealed the importance of introducing a benzene ring in the structure of these compounds to significantly improve their solubility in both aromatic and aliphatic hydrocarbons.

Starting from these findings, we designed the lipophilic version of an NHPI analog known as N-hydroxynaphthalenimide (NHNI), having a potentially wider substrate scope and improved solubility in alkylaromatic compounds.

The ultimate goal of this work is to provide further useful information allowing for the final launch of this class of catalysts in scaled oxidation processes.

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A green approach to the edge functionalization of graphene layers with a bio-based 2-pyrone

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Increasing awareness and concerns about climate change have spotlighted the need for a sustainable development. Green chemistry, defined as “the design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances” [1], pursues the aim to transform hydrolyzed biomass, mainly composed by carbohydrates, into suitable building blocks.

In this context, 2-*pyrones* build up a class of C-6 unsaturated lactone from lignocellulosic feedstock and intriguing building blocks for the preparation of key intermediates in synthetic organic, medicinal and polymeric chemistry [2].

In this work, a green and efficient pathway for the preparation of a 2-pyrone starting from mucic acid [3] is presented. Furthermore, a 2-pyrone derivative, ethyl 3-hydroxy-2-oxo-2*H*-pyran-6-carboxylate (Pyr-COOEt, Fig.1) was used for selectively decorating the edge of a nano-sized graphite with high surface area (HSAG), without altering the graphitic bulk structure. [4]

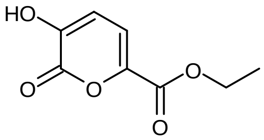

Figure 1. Chemical structure of ethyl 3-hydroxy-2-oxo-2*H*-pyran-6-carboxylate (Pyr-COOEt)

The preparation of adducts between HSAG and Pyr-COOEt was performed through a sustainable method [4,5], with the help of either thermal or mechanical energy, reaching high functionalization yield (up to 90%). Few layers of graphene were easily obtained by means of a mild sonication of a water dispersion of the HSAG/Pyr-COOEt adducts.

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Synergic cooperation for the synthesis and advanced modelling/characterization of novel functional bio-polymeric architectures

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The recent advent of green chemistry and the development of social awareness concerning the current environmental issues are promoting an unprecedented effort to achieve new safe and sustainable materials, particularly shifting from petrol-based feedstocks in favor of sustainable alternatives. Fortunately, nature can provide a variety of compounds that can be exploited in material science. Indeed, the unique structures of natural phenols, such as vanillic or ferulic acid, lipids such as ricinoleic acid as well as bio-itaconic acid, can be successfully subjected to chemical modification and polymerization thus obtaining new families of polymeric architectures presenting additional desirable properties (antioxidant and/or antimicrobial effect). Framed in this scenario, we report examples of novel lines of research specifically designed to valorize the unique chemical structures of natural compounds by creating novel macromolecular architectures. Such structures are then subjected to EPR and IR analysis to assess and correlate antioxidant activity and chemical structure while modeling investigates the unusual behavior of selected architectures in a simulated biological environment drawing a correlation between chemical structure and antimicrobial properties.

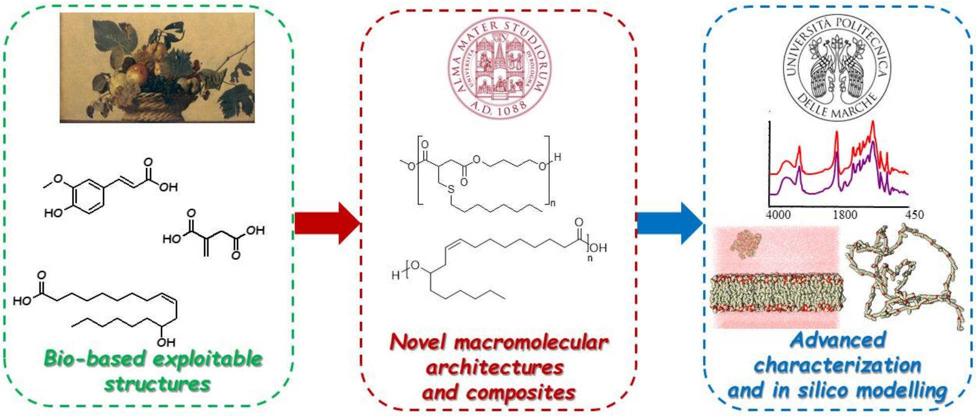

Figure 1. Strategy for the development of novel biobased functional materials: synergic efforts between synthesis and advanced modelling/characterization

Layered double hydroxide as versatile and sustainable platform for biomedical applications

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Layered double hydroxides (LDHs), are multifunctional powder materials with a brucite-like structure characterized by anion exchangeability, high chemical-physical stability, and a low-cost preparation method that allows to fabricate of environmentally friendly and biocompatible materials [1]. LDH consists of hydroxide layers where some of the divalent cations have been replaced by trivalent ions giving a material with a general composition formula of $(M_{1-x}^{2+}\ M_x^{3+}(OH)_2)^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are a divalent and trivalent metal cation, and $A^{n-}\cdot mH_2O$ is the interlamellar anion in the hydrated state (Figure 1A). The resulting positively charged sheets could be used for different applications including solar energy conversion, catalyst, and biomedical fields. In this context, we successfully intercalated in BSA-coated LDH resveratrol molecule, a stilbenoid polyphenol with interesting antitumor activity (Figure 1B). The physico-chemical characteristics of the resulting nanocomplexes were studied by X-ray powder diffraction and transmission electron microscopy. Molecular dynamics simulation shed light on the intermolecular interactions involved in complex stabilization. The nanohybrids showed slow-release properties and an anticancer activity higher concerning bare RES [2]. The same approach was used to encapsulate biological extracts from *Humulus lupulus* in alginate-coated LDH for potential antireflux applications by exploiting the intrinsic feature of LDH and alginate as antiacid and raft-forming agents, respectively. Overall, the results showed that the nanocomposites are suitable for biomedical applications.

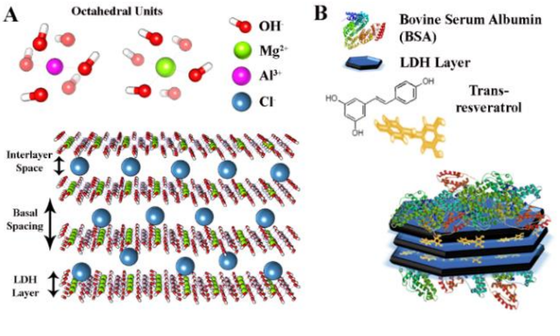

Figure 1. (A) In silico model of layered double hydroxides (LDH) and (B) representation of BSA-coated LDH.

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RILEVAMENTO ELETTROANALITICO DI IONI METALLICI PESANTI IN ACQUA DI MARE MEDIANTE SENSORI TPyP-SPEEK/SPCE

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I metalli pesanti possono diventare particolarmente dannosi per la salute dell'uomo che può entrarne a contatto per via indiretta, per esempio tramite le acque inquinate [1]. Appare quindi fondamentale il monitoraggio costante e altamente sensibile delle concentrazioni, anche minime, di metalli pesanti che si possono accumulano nell'ambiente. In questa sede presenteremo i risultati preliminari di uno studio finalizzato allo sviluppo di sensori SPCE modificati per aumentare la selettività ai metalli pesanti. Tali sensori sono stati modificati depositando sull'elettrodo di lavoro una membrana solfonata di polieter-eter-chetone (sPEEK), precedentemente solubilizzata in DMAc (1% in peso). La membrana è stata quindi modificata incorporando una fenil porfirina meso-sostituita (TPyP) e modulando la sua percentuale nei canali di conduzione protonica della membrana fino al 12,8% in peso. I sensori sviluppati sono stati caratterizzati e studiati dal punto di vista elettrochimico per la loro capacità di rilevare i metalli pesanti nell'acqua di mare. La tecnica della voltammetria di stripping anodico (SWASV) è stata impiegata per valutare l'attività elettrocatalitica dei sensori bare SPCE e dei sensori modificati TPyP-sPEEK/SPCE nella rilevazione simultanea di Pb2+, Cd2+ e Hg2+. Le misure sono state condotte direttamente in acqua di mare, immergendo l'elettrodo SPCE modificato e aggiungendo i singoli cationi metallici con concentrazione crescente a partire da 1μM. È stato notato l'effetto di amplificazione sulla corrente di picco anodica dovuto alla presenza della porfirina nella membrana sPEEK, che può essere facilmente spiegato dall'effetto complessante del gruppo porfirinico con gli ioni metallici in soluzione. Ulteriori studi saranno finalizzati all'ottimizzazione delle condizioni operative per migliorare le caratteristiche di sensibilità, selettività e stabilità del sensore, necessario per la determinazione di basse concentrazioni di metalli pesanti in acqua di mare, acque reflue e acqua potabile.

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Colour Catcher®: low-cost colorimetric sensor and laundry. Kill two birds with one stone.

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The detection of mercury ions in drinkable water is a challenging task, because should be detected in very low concentrations [1]. While analytical laboratory instruments can allow reaching the required sensitivity, the need for continuous monitoring of water samples by chemical sensors is more difficult. In this work is reported the development of a low-cost colorimetric sensor, based on the color variation of a free base porphyrin upon interaction with Hg(II) ions [2]. The solid support is made by Colour Catcher® strip embedded by the tetra (4-carboxyphenyl)porphyrin, *TCPPH₂*; the anionic character of the porphyrin allows a uniform deposition onto the positively charged solid support. An optical platform, composed of low-cost electronic devices, such as LED and webcam, has been developed to digitalize the images of the strip color changes upon the flux of water solution containing Hg(II) ions. Homemade software was exploited to analyze the color changes, allowing reaching a LOD three times below the Hg(II) legal limit stabilized by WHO. The device also showed good selectivity towards other potential interferent metal ions, demonstrating the potentialities in the real field.

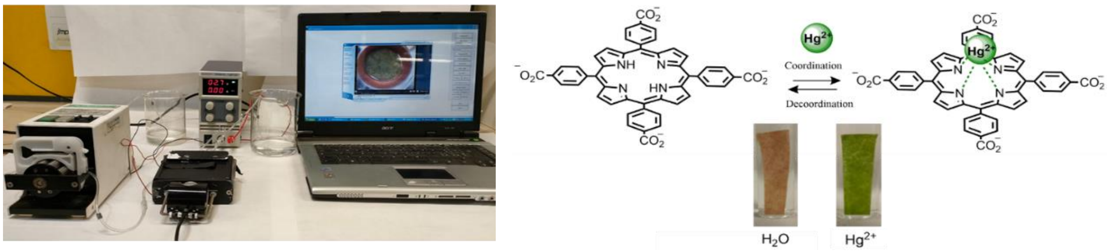

Figure 1 On the left, the optical setup (webcam, LED, homemade holder, PC, bench power supply, peristaltic pump). On the right, the reversible coordination of mercury ion in the central core of $TCPPH_2$. Is reported, the colorimetric variation of CC@TCPPH2 caused by the mercury coordination, from dark pink (non-coordinated

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Gas sensing modulation of CNTs and m-TiO$_2$ nanomaterials by atomic layer deposition (ALD)

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Nanoscale materials are referred as nanomaterials. They show large surface areas, quantum effects, unique electrical and thermal conductivity, excellent mechanical properties, and antimicrobial activity. These characteristics allow them to be used in many applications such as in paints, cosmetics, storage devices, electronics, and sensors. Further, the huge development of these nanomaterials is linked to the possibility to modulate their morphology and dimensions, following top-down and bottom-up approaches [1].

In particular, the modulation of their electrical properties has allowed to adopt them as sensitive materials for the development of high performance conductometric gas sensors. In this work we demonstrated the gas sensing modulation of some widely used nanomaterials such as Carbon Nanotubes (CNTs) and mesoporous Titania (m-TiO$_2$), through the coating of a thin layer of suitable semiconductors by the Atomic Layer Deposition (ALD) technique [2].

In the specific, the gas sensing properties of CNTs were modified through the deposition of tungsten sulfide (WS$_2$) layers. We found that the layered WS$_2$-CNTs sensors exhibit higher nitrogen dioxide (NO$_2$) sensitivity compared to naked CNTs one. Furthermore, the sensitivity to the same gas varies in according to the thickness of WS$_2$ coating on the CNTs surface.

The same phenomenon was found with M-TiO$_2$. In this case, the mesoporous m-TiO$_2$ sensors showed good sensitivity towards many gases such as ammonia (NH$_3$), hydrogen (H$_2$) and ethanol (C$_2$H$_5$OH), resulting then not selective. On the other hand, coating nickel oxide (NiO) layers on this oxide, we make the sensor more sensitive and selective to hydrogen.

The results presented showed as the modification of the external surface of the base nanomaterial, allowed to develop sensors with tailored and improved sensing performances.

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Large area photodetectors based on sol-gel-derived MoS_2 films

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Two-dimensional molybdenum disulfide (2D-MoS_2) has been extensively studied in the last decade, due to its great optoelectronic properties allowing production of devices for several applications, ranging from optoelectronics, environmental monitoring, gas sensing, and energy harvesting.

Major limitations in the common MoS_2 production methods regard the scalability of the process and the possibility to produce large area films. Moreover, production methods often require high annealing temperatures and introduction of hydrogen and sulfur in the process, making fabrication environmentally impactful.

In this work large area MoS_2 films were produced by the sol-gel process, adapting a synthesis protocol previously reported in literature [1], which leads to crystalline MoS_2 by thermal annealing in Argon atmosphere at temperatures below 600°C without additional hydrogenation or sulfurization processes. Large area and uniform MoS_2 thin films were achieved on different substrates, demonstrating the versatility of the fabrication route, and were exploited to fabricate a first example of MoS_2-based photodetector produced via sol-gel process. The fabricated photodetector displays a responsivity of few mA/W in the NUV-VIS-NIR spectrum, widening the spectral response of previously reported MoS_2 based photodetectors [2]. At present, the response time of the detector limits device applications to low frequency operations, and work is in progress to improve its performance.

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Chemical functionalization of graphene surface as filler for rubber compounds: modeling of supramolecular interactions

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Over the last few years, the surface modification of fillers for high-level technological applications such as polymer composites for tyre industry, conductive inks and coatings has seen a considerable increase in interest since it can increase mechanical, electrical, and thermal properties of the final material. Nano-sized carbon allotropes such as graphene and carbon nanotubes are a suitable class of compounds for these purposes: high thermal and electrical conductivity along with considerable mechanical reinforcement are the main improvements that these fillers bring to the composite and their elevated surface area allows to reduce the filler volume ratio compared to more common alternatives. An efficient and reliable method to modify the surface of these nano-fillers is the so-called pyrrole methodology, [1] a mild procedure that involves bio-sourced reagents to introduce functional groups on the graphitic planes and that has been recently employed in the fabrication of elastomeric composites with improved mechanical properties [2]. In order to understand the mechanism beneath the interaction between the pyrrole and the substrate and thus the behavior of the functionalized filler, a more in-depth analysis is requested. A theoretical work based on molecular dynamics simulations and a DFT study were performed in order to investigate the interaction energy, the geometry of interaction and the mobility of N-substituted pyrrole molecules adsorbed on the graphene planes. This theoretical study at atomistic level can help design a new class of high-performance fillers by better understanding the interaction mechanism [3] given the important role of supramolecular interactions.

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Thermodynamic of Adsorption of Diclofenac on graphene by molecular dynamics simulations

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Over the last two decades, pharmaceutical and personal care products (PPCPs) are being detected in surface waters at appreciable levels [1]. This finding raised a great concern, as the long-term the exposure to low levels of these persistent compounds (or their metabolites) has a potential negative impact in on living organisms [2]. Since the quality of drinking water is directly connected with human welfare and sustainable development, efficient water treatment (WT) processes are needed. The fact that current WT technologies are unable to completely remove PPCPs [1] stimulated a strong effort in the research of more efficient and cost-effective approaches. Adsorption of PPCPs by regenerable, high-surface/high-affinity materials could be an answer to this problem [3]. Carbon-based materials, in principle, have all these required features for removing from wastewater organic PPCP at low concentrations [4].

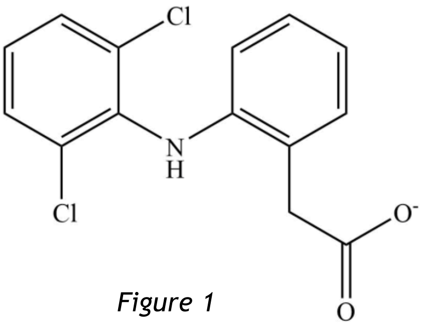

Figure 1

In this contribution, the interaction of graphene materials with non-steroidal anti-inflammatory Diclofenac (DCF, Figure1), commonly detected at relatively high concentrations (up to ppm range) [5], is studied by means of molecular dynamics (MD) simulations and the results compared with available thermodynamic data [6]. Different graphene models were employed: *i)* graphene (pG), *ii)* graphene oxide (GO), *iii)* hydroxyl-graphene (GOH) and iv) epoxy graphene (GCOC). Free energy calculations, based on umbrella sampling technique, allowed to determine the ΔG of adsorption which results negative and close to the values obtained from experimental data.

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VO_2(B) Nanostructures as Promising Cathode Materials for rechargeable Li-ion Battery

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With the development of energy storage technology, lithiumion batteries (LIBs) have been widely applied in smart phones, laptops, and electric vehicles because of their high energy density, high capacity, and good electrochemical performance. A thin layer of vanadium dioxide type B (VO_2(B))(Figure 1) is found to be effective to promote electrochemical performance of the cathode material in LIBs, mainly because of its prominent advantages of large specific capacity, remarkable rate capability and capable cycling stability. Using the fundamental principles of green chemistry, sustainable design process of high-performance VO_2(B) cathode materials without introducing extraction chemicals and with much lower environmental impacts seems to be a great idea, as compared to traditional metallurgical technologies.To this end, here we reported a systematic investigation of the efficacy of advanced theoretical methods for computing chemical and physical properties of VO_2(B) before to starting the experimental process for the synthesize. Our present work is focused on the complete theoretical description of the morphology, stability, electronic, magnetic, and optical properties of VO_2(B) polymorph. The insight provided by theoretical framework in our study will be useful to address future practical applications from nanoscale smart materials and promote their sustainable utility.

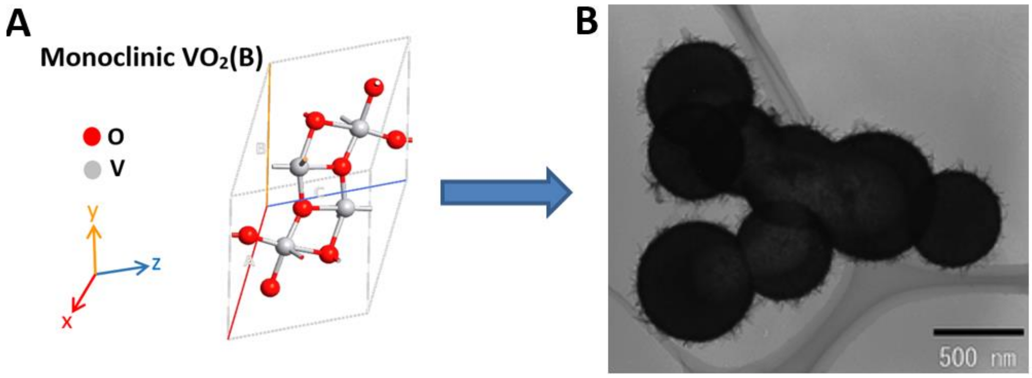

Figure 1. Schematic representations of (A) 3D frameworks of VO_2(B) unit cell, and (B) synthesized VO_2(B) spheres as a cathode material for a lithium-ion battery [1].

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Two steps one pot process for the conversion of dimethylfuran to pyrrole compounds with almost null E factor

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The replacement of the oil-based chemicals with those derived from biomasses is one of the most exciting challenges of the last decades. For example, 1,4-dicarbonyl compounds have a great importance in chemical synthesis, thanks to their high chemoselectivity and there is an increasing interest for preparing them from biomasses. In particular, 2,5-hexanedione could be synthesized starting from lignocellulosic sources, through the acid-ring opening reaction of 2,5-dimethylfuran as the bio-based feedstock.[1] The reaction of 2,5-hexanedione and a generic primary amine leads to pyrrole compounds. Many examples have been reported by some of the authors.[2]

In this work a sustainable process for the preparation of pyrrole compounds starting from a bio-based reagent has been developed. The selected starting material was 2,5-dimethyl furan.

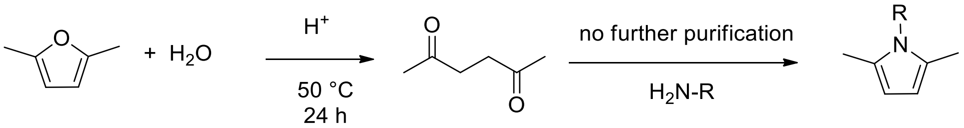

Figure 1: Process for the synthesis of pyrrole compounds starting from DMF

In this work, the ring opening reaction of 2,5-dimethylfuran was optimized by tuning parameters such as the amount of water, type and amount of acid, time and temperature. 2,5-hexanedione was obtained with a high yield (95%) without the need of purification. Then, different primary amines, in particular biosourced, have been used to prepare a variety of pyrrole compounds, with high yield (at least 90%) and with high carbon efficiency, without producing waste. The pyrrole compounds have then been used for the functionalization of a nanosized graphite, promoting the exfoliation to few layers graphene.

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Enhancing electrocatalytic activity of $La_{0.6}Sr_{0.4}FeO_3$ by Pt-doping for IT-SOFC cathodic applications

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One of the main issues in the development of efficient and cost-effective Solid Oxide Fuel Cells (SOFCs) is the choice of electrode materials [1]. Among all, the ABO_3 perovskite oxides appear to satisfy all the requirements for the fabrication of the SOFCs electrodes in the intermediate temperature operation range (500-750°C), such as structural stability, electrical conductivity, and electrocatalytic activity [1]. The employment of lanthanum strontium ferrites for SOFC, especially for cathodic applications, has been widely reported. Moreover, the cathodic characteristics of these materials, such as mixed ionic and electronic conductivity (MIEC) and Oxygen Reduction Reaction (ORR) activity, can be easily improved by B-site doping with different atoms [2]. Among all LSF-based perovskites, $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ (LSFCo) shows the best ORR performance [3]. However, the economic and ethical problems related to the extraction of cobalt, make the study of other performing materials extremely important. For this purpose, noble metals B-site doping has been found to enhance the ORR catalytic activity of LSF at intermediate temperatures, making it a cobalt-free compound suitable for cathodic applications [4][5][6]. Here, a Pt-doped LSF perovskite as innovative IT-SOFC cathode is presented. The introduction of a small amount of platinum (from 0.5 to 5 mol%) in the LSF structure has proven to have a great impact on the LSF performance, keeping the cost compatible with the widely used LSFCo. The catalysts, synthesized by Solution Combustion Synthesis (SCS), were characterized by XRD, showing a single-phase structure and a shift of the peaks towards lower angles as compared to the undoped LSF, due to the complete inclusion of large Pt ions within the perovskite lattice. The effect of Pt introduction in the structure was also studied by TGA and XPS measurements, highlighting an increase of oxygen vacancies in the LSF structure upon Pt-doping. The electrical conductivity was tested by the 4-point probes method, and Electrochemical Impedance Spectroscopy (EIS) was used to investigate the ORR performance in oxidizing conditions. A deeper study of the ORR mechanism by the Distribution of Relaxation Times (DRT) analysis highlights a relevant improvement of the charge transfer process with low Pt doping, approaching the LSFCo performance in the IT range. Consequently, the choice of low platinum doping seems to be an efficient, cost-effective, and “green” alternative for the fabrication of a performing cathode for IT-SOFC. Preliminary fuel cell tests on LSFPt/LSGM/LSFPt symmetrical cell show promising results in terms of power output and polarization resistance at 650°C.

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3D Spherical Fe-N-C Oxygen Reduction Electrocatalysts for Energy Conversion

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The potentialities of porous organic polymers (POPs) have been investigated to obtain Pt-free catalysts for oxygen reduction reaction (ORR) for energy conversion applications. Currently, Pt-based catalysts are still the state-of-the-art ORR catalysts, but the shortage of platinum supplies, high cost, and low durability limit the commercial applications of Pt-based fuel cells.[1] In this context, phenol (P) and melamine (M) have been used as substrates for the preparation of POP precursors. Pluronic F 127, a soft template, was introduced to increase the surface area and wettability. The obtained materials were impregnated with different amounts of Fe followed by pyrolysis treatments. Combining electrochemical and spectroscopical techniques (i.e., Cyclic Voltammetry, Linear Sweep Voltammetry with rotating disk electrode, X-Ray Photoelectron and Raman Spectroscopy) allowed elucidating the effect of Fe content on materials structure, surface chemistry, and electrocatalytic activity towards ORR.[2] The obtained results demonstrated the potential applicability of POP-based electrodes in alkaline fuel cells.

Acknowledgments

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Functionalized co-polypyrrole-polyketone anion exchange membrane

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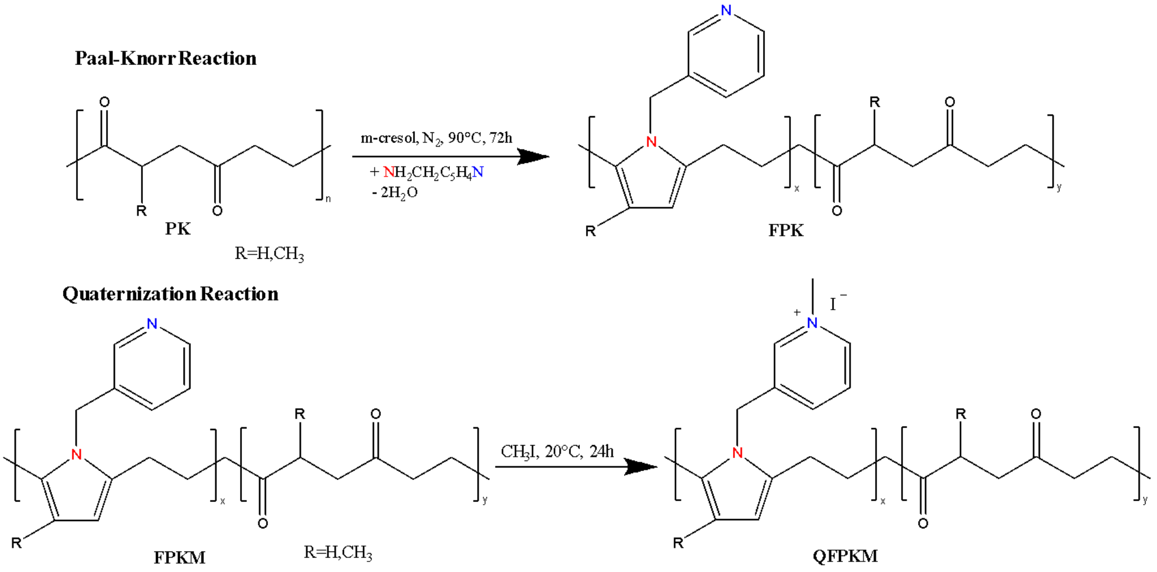
We prepared new anion exchange membranes (AEMs) based on a polypyrrole-polyketone backbone, for electrochemical application [1], starting from a terpolymer polyketone (from ethylene, propylene, and carbon monoxide) with great mechanical and chemical resistance. Polyketones shows γ-diketonic repeating units that allow the grafting of different side chains and functionalities through Paal-Knorr cyclization reaction with a primary amine [2].

In this work, 3-(Aminomethyl)pyridine was used to obtain functionalized polypyrrole-polyketone copolymers, with a functionalization degree tuned by changing the amount of amine and/or the reaction conditions like temperature and time. The obtained polymers were casted to obtain the final membranes which were suspended in iodomethane for quaternization.

The prepared membranes were characterized to investigate the structure, the functionalization degree, and their thermal and ion conductivity properties to evaluate the possible application in electrochemical devices.



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New Calcium Lactate-SPEEK composite Coatings for Thermal Energy Storage Applications

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The aim of Thermal Energy Storage (TES) applications consists in recovering waste heat, from buildings or industrial sector, and to use it for later usage technologies. In this regard, thermochemical materials exploit a reversible chemical reaction to store (and subsequently release) energy, generally, during a dehydration (hydration) process. Inorganic hydrated salts were extensively studied for this purpose, because of their high energy storage density. Nevertheless, these materials often undergo the phenomenon of deliquescence, which causes some operational issues during the hydration/dehydration process.1 To overcome this drawback, we propose here an organic hydrated salt derived from lactic acid: Calcium Lactate Pentahydrate (CLP). This salt does not incur deliquescence notwithstanding under high relative humidity (100%). What is more, CLP is suitable for working under typical operating conditions of low-temperature heat storage systems (dehydration temperature 80°C and hydration temperature between 20-65°C) and presents a dehydration heat of 1021 kJ/kg. The interest towards CLP is also justified by the fact it is a low cost, non-toxic, non-corrosive and non-explosive reactant; which promote this salt as a promising material for TES.

A new Calcium Lactate-SPEEK (sulfonate polyether ether ketone) composite coating was realized to enhance the diffusion of vapour during the hydration process and, at the same time, to increase the heat transfer efficiency with the heat exchanger. The sulfonation reaction of PEEK polymer allows to obtain a microstructurally porous binder with high water vapour permeability.2 The SPEEK is preventively dissolved in DMF and then mixed with salt. The amount of CLP added is proportional to polymer content (i.e. 50-50 in %wt., 60-40 in %wt., 70-30 in %wt., 80-20 in %wt., respectively). The coating deposition of resulting solutions was performed, using drop test technique, on aluminium strips. The hydration tests have shown that SPEEK is flexible enough to resist the process of volume shrinkage/expansion of the salt caused by the cyclic dehydration/hydration reactions. On the other hand, the performed mechanical test (scratch test, pull off test and impact test) demonstrate a good resistence of investigated coatings, especially the ones with a major content of binder. In conclusion, the selection of this organic salt paves a new way towards the choice of a new class of thermochemical materials promoting, meanwhile, coating technology as a new area of investigation.

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Co-Polymeric Nanosponges from Cellulose Biomass as Heterogeneous Catalysts for Organic Reactions

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Heterogeneous catalysts prepared from biopolymers and biomass waste sources are attracting increasing interest [1,2]. The reasons can be related to the possibility of combining the virtuous approach of circular economy with the consolidated advantages of heterogeneous catalysis, specifically the recycling of the system and the possibility to drive selectivity towards desired products.

Recently our group reported a highly porous cellulose-based nanosponge (CNS) used as heterogeneous and recoverable catalyst for organic reactions. The material is obtained by a thermal cross-linking between TEMPO-oxidized cellulose nanofibers (TOCNF) and branched polyethyleneimine 25 kDa (bPEI) in the presence of citric acid [3].

This material resulted efficient in promoting both Henry and Knoevenagel reactions [4]. Moreover, by considering also the high sorption capacity of CNS towards a wide range of transition metal ions, previously exploited in the field of water remediation [5,6], it was possible to extend the scope of CNS by preparing new classes of catalysts, loaded with different metals [7].

Herein we present a new Pd(II)-loaded CNS as sustainable heterogeneous catalyst for promoting cross-coupling Suzuki reactions [8].

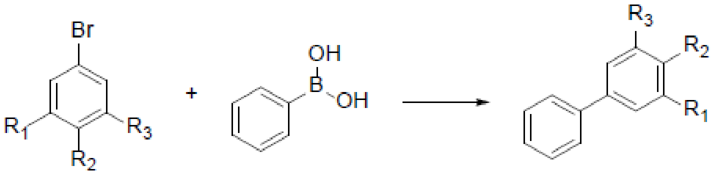

Figure 1: Suzuki reaction

With this catalyst, high yields of reaction were reached. Recycling and re-use efficiency of the catalyst were also investigated, showing promising results [4,7,8].

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Cellulose Nanofibers as Additives for Sustainable Buildings: LCA and Analysis on Raw Earths

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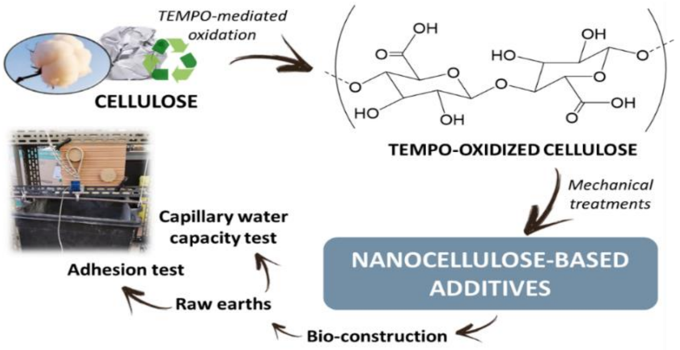

Interest towards biopolymers, and in particular cellulose nanofibers (CNF), has seen a significant growth, mainly thanks to the increasing sensitivity towards the concept of circular economy. CNF can be easily obtained through different approaches, acting on the hierarchical structure of cellulose. TEMPO-mediated oxidation pre-treatment [1], combined with mechanical methods allow to obtain cellulose nanofibers by reducing the energy demand of the production process. The proposed study includes the use of CNF, obtained from both virgin and waste sources, as additives for sustainable bio-building [2]. The role of CNF was verified by performing adhesion test, conducted to determine the maximum vertical load sustained, and capillary water absorption test [3]. This latter provides an important parameter, as water ingression is a major issue in earth-based structures. CNF were able to modify the behavior of earth blends depending on i) cellulose original source, ii) process used to obtain CNF, and iii) oxidation degree of the fibers. Promising results were obtained also with CNF derived from waste sources, opening new opportunities for the re-use of discharged materials. The use of these sustainable additives in raw earths was also supported by a Life Cycle Assessment study conducted on the production process of CNF, bringing out interesting considerations on the choice of the original sources from which they can be produced [4].

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Chemical separation: a step towards a full recycling and recovery of Cotton and PET fibers from blended textile

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The increasing global demand on goods from textile industry, and the large production volume from fast-fashion companies is already a serious environmental issue. If prevention of waste generation (and thus production) and reuse of clothes are not feasible options, recycling of textile fibers can represent a sustainable effort to the matter.

Cotton and Polyester, i.e., poly (ethylene terephthalate) (PET), represent the most common textile materials in the fiber market [1] and within textile blends. This is mainly because blending fibers made from those two materials will impart the textiles with property profiles suitable for most apparel applications, ranging from high quality and durability to relative cheapness when a high PET content is used. Advancing findings from literature [2], chemical separation of these two types of fibers has been studied in this research to optimize reaction conditions (i.e., finding best parameter settings for type of reagent, concentration, time, temperature) to completely solvate, in a first step, 100% pure Cotton and 100 % pure PET fibers. This was carried out using sulfuric acid (H_2SO_4) and sodium Hydroxide (NaOH*)* solutions to hydrolyze Cotton fibers and PET fibers respectively, without the need to using a catalyst. In a second step, the optimal conditions, obtained from removing the pure fibers, were applied on blended textiles that consisted of those two fiber types, to hydrolyze one fraction of them and obtaining the other fraction in its fiber form.

Promising results were obtained at laboratory scale and at pre-pilot scale (25 liters), where a 95%±5 removal efficiency was achieved to hydrolyze Cotton fibers from the blends using a solution of 50% by mass fraction of H_2SO_4 in water at 60 C° after 120 minutes and using a magnetic stirring table. Vice versa, PET fiber hydrolysis from blends using a solution of 15% by mass fraction of NaOH in water at 90 C° after 120 minutes and using a magnetic stirring table.

Future steps will be followed to decide, from a life cycle point of view, which is the best method to be adopted to separate Cotton and PET fibers from blends. For instance, an additional method – yet generally more time-consuming – is using enzymatic hydrolysis to remove Cotton fibers. Moreover, an important step would be to recover the fraction present within the solution after the treatment of the blends, as high recovery rates are also in the focus of legislature, which has just recently been highlighted again by the EU [3].

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Effect of acid attack on geopolymers based on recycled corundum

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The term "geopolymer" is used to indicate synthetic solids obtained by mixing powders of aluminosilicate with alkaline solutions, and is synonymous with alkali-activated materials. A number of different formulations have been optimized so far, most of them based on industrial wastes. Geopolymer synthesis consists on the reaction of a powdered precursor, with high content in amorphous aluminosilicate (high SiO_2 to Al_2O_3 ratio), with a strong alkaline activator solution. One potential use of these materials is as a Portland cement replacement, within the area of green buildings, with associated CO_2 emissions avoided and the requirement to be a good acid resistant binder because Portland cement concretes are susceptible to acid attack. The higher durability of alkali-activated material (AAM) with respect to ordinary Portland cement (OPC) is attributed to low Ca content of the first, as reported by T. Bakharev [1] which attributed AAM performance to its low Ca content (≈ 40% CaO) compared to OPC (≈ 65% CaO). Based on studies [2-4] that have already investigated the use of acids on geopolymers, in this paper we focused on the effect of sulfuric, nitric and hydrochloric acids on geopolymers based on recycled waste corundum at different granulometry.

The study continues with the examination of the corrosion process focusing on the chemical composition and microstructural changes of geopolymer sample before and after the acid attack. The tests carried out were the weight loss, mechanical properties degradation as well as microstructural modifications detected by MAS-NMR, x-ray diffraction, and FT-IR.

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Comparison between films and scaffolds of cyclohexane-based random copolyesters for vascular repair

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In the European Union (EU) cardiovascular diseases (CVDs) have caused 1.68 million deaths in 2018 (37.1% of all deaths) and were the leading cause of death; the second cause, malignant neoplasms, is at the 25.8% of all deaths [1]. The current treatment of CVDs includes surgery and implant of autologous grafts, although donor site is not always available. The use of synthetic grafts could be a good choice, but when small diameters are involved ($d < 6$ mm) failure often occurs [2]. In this context, the creation of artificial vascular grafts by electrospinning represents a valid alternative [3]. This technique permits the fabrication of fibrous scaffold which have physical properties close to those of extracellular matrix (ECM) [4]. Poly(butylene trans-1,4-cyclohexanedicarboxylate) (PBCE) is an aliphatic polyester with good thermal properties but, due to its high crystallinity and rigid chain, its application in vascular tissue engineering is limited. For this reason, copolymerisation with Pripol 1009, a commercial diacid containing PE-like segments, might be a good solution. Four copolymers, named $P(BCE_xBPripol_y)$, were synthetized with different molar ratio between monomers. After the synthesis, the so-obtained polymers were first purified, then the chemical composition and structure were confirmed by ^{1}H-NMR. After that, PBCE and the four copolymers were compression molded in films and electrospun in scaffolds. Both films and scaffold were subjected to thermal analysis (TGA and DSC) and tensile tests. All the materials showed a calorimetric behaviour typical of semicrystalline materials, similar in films and scaffolds. As to mechanical properties, elastic modulus and elongation at break are smaller in scaffolds than in films, but anyway copolymerisation has permitted to reach, in some cases, the elastomeric behaviour required for vascular applications. Scaffolds were also analysed through SEM to check the morphology of the fibres. Preliminary *in vitro* cytotoxic assay was carried out on films, showing promising results, making these materials potential candidates for the treatment of CVDs.

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Innovative bioplastics from polypeptides of Hermetia illucens

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The environmentally sustainable waste management, together with waste valorization, is one of the actual challenges pursued by the European Commission. UE policies are thus contributing in the frameworks of circular economy by promoting the extraction of high quality materials from wastes [1]. At the European level, the generation of municipal solid waste (MSW) is estimated to be 500 kg per capita, of which 70% (discarded food, yard trimmings, paper and wood) is represented by the so-called organic fraction of municipal solid waste (OFMSW) [2]. In this scenario, organic waste valorization is gaining major relevance within circular economy models, with bioconversion mediated from insects being one possible and effective answer to the problem. The project RICH (Turning Rubbish Into biobased materials: a sustainable CHain for the full valorization of organic waste) aims to develop an innovative and integrated circular economy chain, which, starting from the biotransformation of the organic fraction of municipal solid waste (OFMSW), allows the targeted production of biobased materials with high technological value, such as bioplastics and other advanced protein-based materials. In the present study, proteins and polypeptides were extracted from larvae and pupae of *Hermetia illucens*, also known as Black Soldier Fly. The extraction efficiency from both stages was assessed. Crude extracts were characterized by means of proteomics techniques such as BCA, SDS-PAGE, and LC-MS analyses. State of art [3] materials were prepared, investigating the correlation with the molecular structure through physical techniques (FTIR, Contact Angle, TGA). Results clearly points out a correlation between film-forming ability and the chosen larval stage, with extracts from Larvae at the 6th instar leading to the best results. A correlation with polypeptide chain length is proposed.

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Sealing properties of fully bio-based poly(butylene 2,5-furanoate)

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Fossil fuel-based plastics have been largely used to produce goods on industrial scale for the past 150 years. The only solutions for the disposal of plastic waste have been incineration and landfill so far. However, this linear economic model can no longer be sustainable in the future because of the increase of global population, and the corresponding increase of plastic waste.[1] Therefore, the European Parliament adopted several political measures contributing to the development of a circular economic model, which reduces the plastics waste production. Nowadays, about 30% of plastic packaging ends up in landfills, or is disposed via incineration for energy recovery. Bioplastics represent a valid solution, since we can also produce them from agro-food wastes.[2] One of the most relevant bio-based building blocks is 2,5-furandicarboxilic acid (2,5-FDCA), considered the *alter-ego* of fossil-based terephthalic acid.[3] From it, several furan-based polyesters, characterized by aliphatic diols with different lengths, have been prepared and deeply investigated for their potential use in food packaging.[4,5]

In the present work, the welding properties of poly(butylene 2,5-furanoate) (PBF) – based compression molded films have been investigated. Different welding techniques have been considered, i.e. ultrasonic, thermal and Thulium laser. In all cases, from the results obtained, PBF films showed to be characterized by outstanding welding properties.

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Isomerism, glycol chain length and copolymerization as tools to achieve outstanding furan-based sustainable food packaging

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2,5-furandicarboxylic acid (2,5-FDCA) is an extremely appealing biobased chemical building block because of its potential to replace the petrochemical and industrially widespread terephthalic acid [1]. A family of high molecular weight polyesters was synthesized using one of its structural isomers, 2,4-furandicarboxylic acid (2,4-FDCA), and biobased, linear glycols of various length (Figure 1). Within this family of polyesters, poly(trimethylene 2,4-furanoate) (2,4-PTF), was improved by reactive blending with biobased poly(trimethylene succinate) (PTS). These copolymers were compression moulded into films and subjected to NMR, GPC, WAXS, DSC, TGA and PLOM analyses. Their functional properties for food packaging applications were evaluated with linear and cyclical tensile tests and gas permeability tests. Among the best results, it was possible to achieve gas barrier properties comparable to poly(ethylene vinyl alcohol), and elongation at break up to 2400%, with shape recovery (Figure 1). From the characterization, new insights on the partially-ordered phase of these systems allowed the establishment of interesting structure-property relationships. Overall, these results highlight the great potential of 2,4-FDCA-based homopolymers and copolymers as promising candidates for the production of biobased, flexible, monolayer, easily recyclable and sustainable food packaging.

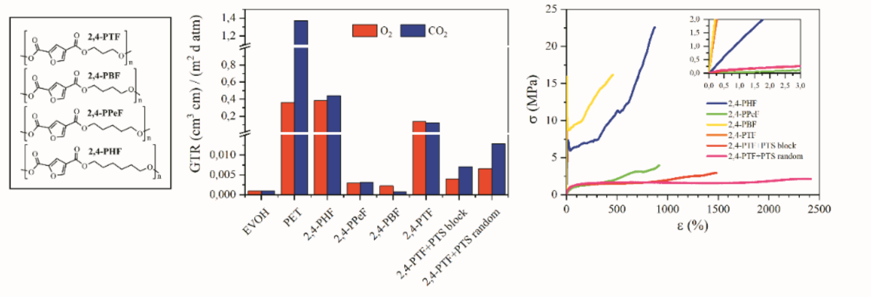

Figure 1. From left to right: chemical structure, gas transmission rates and mechanical properties.

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Chemometric differentiation of sole and plaice fish fillets using three near-infrared instruments

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Fish species substitution is one of the most common frauds all over the world, as fish identification can be very challenging for both consumers and experienced inspectors in the cases of fish sold as fillets. Along the fishery production chain, one of the most vulnerable food chains [1], species replacement can often occur [2–4]: indeed, the difficulties in distinguishing among different species may generate a "grey area" in which mislabelling can occur. Thus, the development of fast and reliable tools able to detect such frauds in field is of crucial importance.
In this study we focused on the distinction between two flatfish species largely available on the market, namely the Guinean sole (*Synaptura cadenati*) and European plaice (*Pleuronectes platessa*), which are very similar looking. Fifty fillets of each species were analysed using three near-infrared (NIR) instruments: the handheld SCiO (Consumer Physics), the portable MicroNIR (VIAVI), and the benchtop MPA (Bruker). Exploratory principal component analysis (PCA, [5]) models and classification partial least squares–discriminant analysis (PLS-DA, [6]) models were built using the spectral datasets, and all three instruments provided very good results, showing high accuracy in classification: 94.1 % for the SCiO and MicroNIR portable instruments, 90.1 % for the MPA benchtop spectrometer.

The good classification results of the approach combining NIR spectroscopy, and simple chemometric classification methods suggest great applicability directly in the context of real-world marketplaces, as well as in official control plans.

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TEMPO-oxidized cellulose nanofibers/polyvalent cations hydrogels: A multifaceted view of network interactions and inner structure

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In the last years, hydrogels have stood up as important materials for different biomedical applications [1,2]. The ones from renewable biopolymers and low-cost row materials, including cellulose-based ones, are particularly appealing for the increasing importance of circular economy and the request of a sustainable chemistry [1,3]. In this context, cellulose nanofibers are considered suitable building blocks for the synthesis of many biocompatible products, with a variety of chemical-physical properties which drive their applications [4]. The aim of the present study is to analyse, with a multi-technique and multi-scale investigation, the sol-gel transition in aqueous medium of a biocompatible formulation composed of TEMPO-oxidized cellulose nanofibers (TOCNFs) and different polyvalent cations. In particular, Small Angle Neutron Scattering analysis, UV Resonant Raman spectroscopy and Transmission Electron Microscopy provided information on the inner structure of the nanofibers in the system, and their intra- and inter-molecular interactions, both in the gel and in the liquid state, as a function of the concentration of both TOCNFs and cations, the ions species, and the pH of the system [5]. The merging of the different techniques allowed us to elucidate the structural organization and the chemical-physical properties of the material, that is helpful for a fine tuning of the macroscopic properties in biomedical applications (*e.g.* injectable formulations).

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Towards an understanding of the connection between micro e macro behaviour of CNT/polymer composites: a 3D Raman imaging approach

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The increasing interest in stretchable conductive composite materials for wide-ranging application has sparked a growing demand for studies of scalable and widely applicable fabrication techniques and geometries[1].
In this context, Single Wall Carbon Nanotubes (SWCNTs) deposited and self-grafted on polymer films offer appealing characteristics: conductivity, stretchability, strength, thinness, combined with an easy and low cost manufacture[2] [3]. Since each application requires specific polymers, targeted studies to understand the interface between CNT and the polymer film are required. In particular, the stability and durability of CNT grafting into the surface of polymer film is paramount.
In this work, such analysis is performed by Raman micro-spectroscopy and 3D mapping. This technique offers the possibility to understand microscopic characteristics of the composite (from which the macroscopic behaviour follows) at the interface between CNT bundles and the polymeric material. We analyse different composites made of SWCNT dispersions combined with a selection of five polymer films, with the purpose of understanding the spatial distribution and penetration of the CNT bundles into the polymer films and of correlating these penetration profiles with the macroscopic properties of the resulting composite.

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FTIR spectral fingerprints in Colorectal Cancer derived Tissues and Cancer Associated Fibroblasts

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Cancer is a major cause of death worldwide. Patients are frequently diagnosed at a stage that is not responsive to current treatments, and this is one major cause for the poor survival rates too often observed. A more comprehensive multiOMICs approach may ultimately contribute to a reliable early diagnosis and a deeper understanding of cancer progression. In this context, Fourier Transform infrared (FTIR) spectroscopic imaging, whit its ability to recognize and spatially locate macromolecules within single cells and tissues, has emerged as an independent modality for disease characterization and diagnosis enabling significant advances in the field of clinical evaluation. Infrared parameters related to cellular biosynthetic activity may in fact be valuable prognostic indicators obtainable with good sensitivity in a time window compatible with driving therapeutic decisions.

Here we report on the micro-FTIR investigation of colorectal carcinoma (CRC) tumor stroma. Applying multivariate analysis, it was possible to identify collagen as the major responsible for spectral variation between normal and tumor tissues. Collagen fibers remodeling is reasonably one of the most significant events in tumor progression and we demonstrated that following just four of its IR signals out of the many composing a complex system such as human tissue, is sufficient for highly accurate diagnosis at a stage at which morphological changes are still not detectable. We further investigated stromal microenvironment main cellular component, Cancer Associated Fibroblasts (CAFs), as they actively drive tumorigenesis and cancer progression by establishing cell-cell interactions with tumor cells or through secretion of several growth factors and extracellular matrix (ECM) proteins. We believe that interference-free spectra of patient derived CAFs will allow for precise biochemical composition tracing and reliable biomarker identification to be used in direct tissue analysis for diagnostic purposes.

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Selective positioning of different cell types on 3D scaffolds via DNA hybridization

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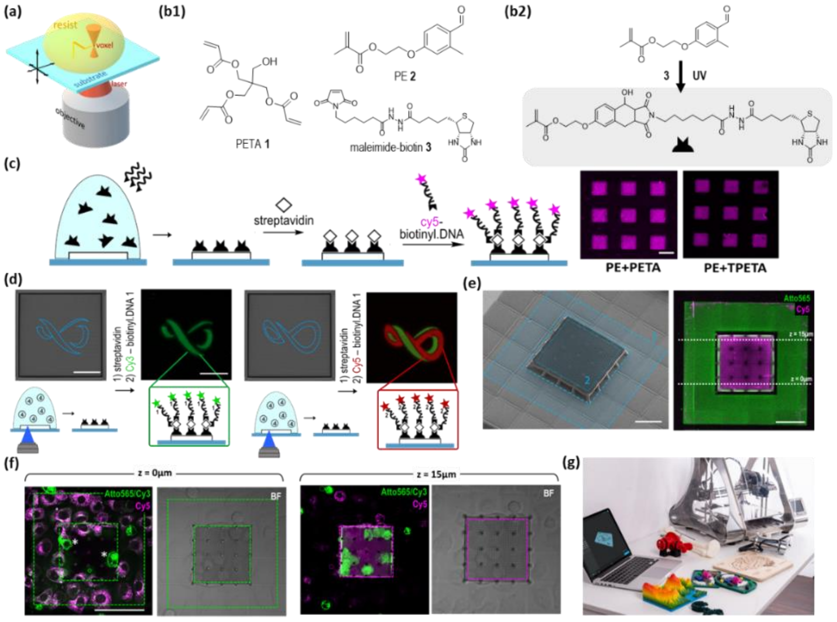
In the last decade, a great effort has been devoted to the establishment of in vitro platforms mimicking the complexity of cellular and tissue microenvironment. Two-photon lithography (2PL, fig. 1a) has given a major contribution to the field, and several scaffolds for studying cell biology made via 2PL have been reported [1]. A further improvement is represented by techniques for the precise positioning of distinct cell types in a 3D microenvironment. Current techniques, e.g., antigen-antibody interaction, pose severe limitations for selective single-cell-type tagging as they lack of specificity. Here, we report the decoration of 2PL-obtained 3D microscaffolds with single-strand DNA (ssDNA) exploiting light-induced click chemistry. An acrylate-based 2PL resin was formulated, including an UV-reactive molecule (i.e., photo-enol, PE, fig.1b1) for further surface decoration with biomolecules. According to the literature, the aldehyde group of the photo-enol enolizes upon UV irradiation and subsequently reacts with a carbon double bond (e.g. of a maleimide molecule) via a Diels-Alder [4+2] cycloaddition click reaction (fig.1b2) [3]. Therefore, a solution of biotinylated maleimide in DMF was placed on the 2D and 3D microstructures and exposed to a focused 405 nm laser, resulting in the covalent binding of the maleimide to the PE; streptavidin was then incubated, followed by an incubation step with a fluorescently-labelled biotinylated oligonucleotide (fig.1c). The degree of functionalization could be controlled by tuning the laser intensity and exposure time. The procedure was repeated sequentially on the for two different oligonucleotides both on 2D (fig.1d) and on 3D structures (fig.1e). To test the selective binding affinity of cells to ssDNA, two different cell lines (i.e., NIH3T3 and U2OS) were decorated with cholesterol-TEG complementary strands and incubated for 30 min on functionalized 3D scaffolds. As expected, cells hybridize more effectively on complementary oligonucleotides than on surfaces with non-complementary ssDNA (fig.1f). Current studies focus on scaling up the methodology to the meso- and macroscale and on widening the palette of acrylate-based photoresists, thus enabling the fabrication of 3D scaffolds using consumer-grade stereolithographic 3D printers (fig.1g).



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Recombinant mussel protein Pvfp5β enhances cell adhesion of poly(vinyl alcohol)/k-carrageenan hydrogel scaffolds

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Polymeric hydrogels are increasingly being considered as a scaffold for tissue engineering because they show similarity to the extracellular matrix (ECM) of many tissues. To control various cellular processes, hydrogels are often functionalized or loaded with various bioactive molecules such as: specific ligands for adhesion receptors, growth factors, hormones, enzymes, and other natural or synthetic regulators of cellular behavior [1]. Cell adhesion is essential for cell communication and regulation of the cell cycle and is therefore of vital importance in tissue engineering. Biomimetic approaches have been investigated to facilitate cell-scaffold adhesion interactions. In particular, the recombinant mussel Perna viridis foot protein 5β (Pvfp5β) was developed. Mussel adhesion is made possible by the secretion of a waterproof protein-based adhesive composed of a mixture of proteins called mussel adhesive protein (MAP) or mussel foot protein (mfps). This allows it to be fixed to almost any type of surface when wet [2].

In this work, a two-step physical gelling process is used to create hydrogel scaffolds with a 50 wt% mixture of k-carrageenan (kC) and polyvinyl alcohol (PVA), which are coated with Pvfp5β. The mechanical and morphological properties of hydrogels were investigated both after conditioning in a typical cell culture medium and after coating with Pvfp5β. The protein was strongly adsorbed on the surface of the hydrogel and, as shown by confocal analysis, was able to interact primarily with the kC component of the scaffold and penetrate into it to some depth. NIH-3T3 mouse embryonic fibroblasts were seeded in hydrogel and cultured for up to 2 weeks. The role of Pvfp5β in promoting cell adhesion, diffusion and colonization of scaffolds was verified.

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New deferiprone derivatives as antibiofilm and antimicrobial agents: design, synthesis and biological evaluation

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The role of iron in microbes growth and virulence is widely investigated by the scientific community. In this work we present a series of new deferiprone (3-hydroxy-1,2-dimethyl-4(1*H*)-pyridinone, DFP) derivatives, designed with the aim to interfere with microorganisms metabolism by chelating metal ions (iron and copper). DFP moiety was connected in N1 position with various aryl, alkyl groups of different sizes and polarity, in order to increase its lipophilia, and with some non-steroidal anti-inflammatory drugs. The chelating capability of synthesized DFP derivatives was evaluated by chelation studies on Fe^{3+} and Cu^{2+} using UV-visible spectrophotometric methods. All synthesized molecules were tested against *Candida albicans* planktonic cells and biofilm [1], *Salmonella typhimurium* and *Pseudomonas aeruginosa* [2]; some of them showed interesting activities. The results suggest that the antimicrobial activity of DFP can be largely modified through the introduction of limited chemical modifications in its structure, and is related to the interference with iron absorption/activities. In particular, this work allowed identifying a hit compound with broad spectrum of action, demonstrating also low toxicity on *Galleria mellonella* larvae.

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Molecularly Imprinted Polymers for the CECs selective removal as tertiary treatment in Municipal Wastewater Treatment Plant

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Abstract: Agriculture is the largest consumer of water for the Food and Agriculture Organization (FAO) of the United Nations (UN), with an annual water withdrawal from natural water bodies estimated to be around 3000 km3 in all the world [1]. Moreover, the sustainable agriculture production is facing challenges due to global climate change issues that cause intense and frequent droughts and floods and make inevitable the search for non-conventional water sources. In the frame of the circular water economy, the re-use of wastewater coming from treatment plants is a commonly applied practice in several European countries [2]. However, conventional water treatment processes cannot efficiently remove micropollutants (I.e., Contaminants of Emerging Concerns - CECs) that include among other pharmaceuticals and personal care products. In this context, non-conventional adsorption technology based on molecularly imprinted polymers (MIPs) may represent a useful tool to remove selectively one or more target molecules from the treated wastewater [3]. Within the PRIMA-funded Fit4Reuse project, an adsorption fixed-bed column filled with specifically synthetized novel Molecularly Imprinted Polymers (MIPs) was designed and realized as an innovative tertiary treatment to reduce diclofenac (DCF) concentration from the final effluent to be reused for agriculture application. MIPs were synthetized, and characterized by Braunauer-Emmet-Teller analysis, FTIR, and SEM spectroscopy. DCF adsorption behavior was evaluated at laboratory scale in batch and flow continuous tests through an UV-Vis spectrophotometer reading absorbance values at 276nm wavelength. Then, a MIPs column was inserted in the pilot treatments train located in the wastewater treatment plant (WWTP) of Falconara Marittima, which is composed by five operation units: optional dynamic rotating belt filter (RBF), up-flow anaerobic sludge blanket reactor (UASB), anaerobic membrane bioreactor (AnMBR, ultrafiltration membrane working in the submerged-side stream configuration), optional UV disinfection and Molecular Imprinted Polymers (MIPs) column. Pilot tests were conducted to confirm the MIPs adsorption properties on a real wastewater matrix with a spiked concentration of DCF of 0.5 μg/L. Finally, data were analyzed by isotherms and column adsorption models to evaluate the adsorption performance of MIPs during the conducted experimental tests (Figure 1).

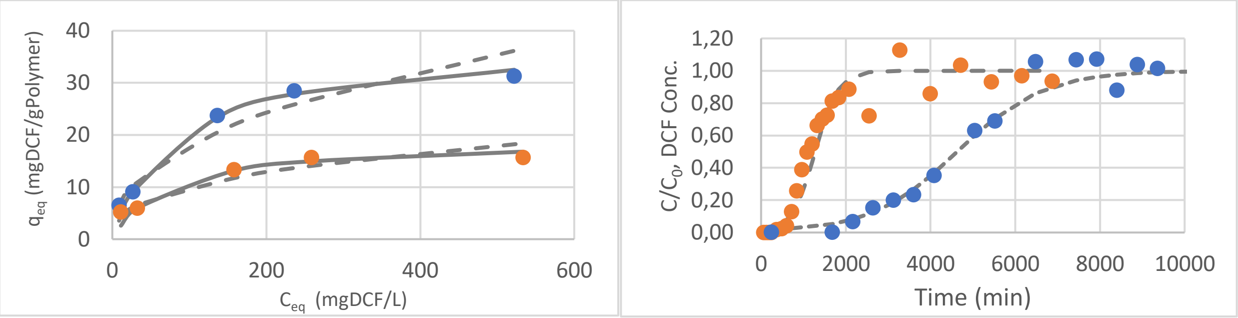

Figure 2. (LEFT) Batch adsorption results of MIPs (blue) and NIPs (red) with isotherm models (grey lines), and (RIGHT) fixed bed column pilot scale results at 33% (red) and 100% (blue) of MIPs with Thomas Model curves (dotted lines)

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Assessment of alternative value chains for Polyhydroxyalkanoate recovery from municipal wastewater treatment plant

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Nowadays, plastic pollution is one of the most severe problems that our society has to deal with. Moreover, recent trends show that plastic consumption is expected to double in the next 20 years. To partially fulfil the transition from fossil plastic production to recycled content in commercial products, bio-based degradable plastics like polyhydroxyalkanoates (PHAs) are becoming an interesting solution over the last years. PHAs are a class of biodegradable polyesters produced as intracellular storage material by a large number of microbial species under nutrient-stress conditions and can have elastomeric/thermoplastic properties, according to their co-monomer composition. In this context novel and alternative value chains for PHA-enriched sludge (PHAES) produced in wastewater treatment plants (WWTPs) has to be considered. Within H2020 SMART-Plant project [1] PHAs were produced in a pilot plant installed in Carbonera WWTP (Northern Italy), with a treatment capacity of 40,000 Population Equivalent. Briefly, the PHAs were produced at pilot scale through an integrated process aiming the integration of via-nitrite nitrogen removal from anaerobic reject water and the selection of PHA-storing mixed microbial cultures (MMC) by means of (aerobic) feast and (anoxic) famine regime [2]. The PHA production capacity of the pilot plant was up to 1.2 kg PHA per day. After the accumulation stage, the PHA enriched sludge (PHAES) with 35-40% of PHA content was dewatered and evaluated for two different recovery pathways: 1) it can be used directly as raw material to produce biocomposites or 2) it can be extracted in order to increase the purity of the PHAs level higher than 90% and sold in the market as bioplastic precursor.

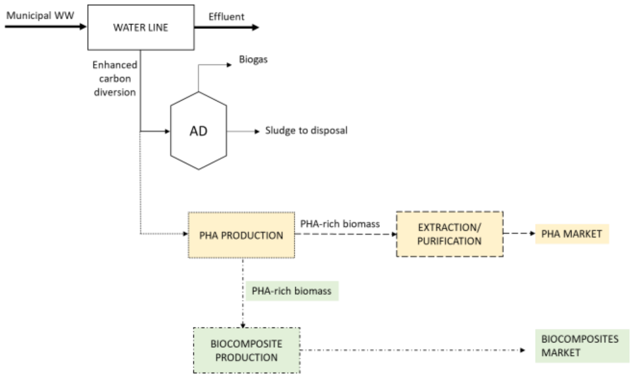

Figure 3 PHA recovery routes in WWTPs

In the first case, the production of biocomposites was formulated by using different contents of PHA enriched sludge, polyethylene, PHA and Wood flour. In the second case, intracellular PHA-rich biomass needs to be extracted and purified using physico-chemical methods. Several methods exist for extraction of PHA from the PHA-rich biomass produced. They are categorized mainly in physical separation processes, cell lysis-based processes and solvent-based processes. An economic assessment of different PHA recovery routes was carried out in this study to evaluate different value chains and payback periods, in order to screen potential and effective value chains driving the conversion of WWTPs into Water Resource Recovery Facilities (WRRFs). Different WWTP sizes (from 50 kPE to 3000 kPE) were considered to evaluate the economic assessment. The market price of extracted PHA was considered in the range from 2 to 5 €/kgPHA, which was the main parameter besides the sludge disposal cost to drive the economic feasibility of the process. As result, the implementation of PHA recovery process in WWTPs is economically feasible for plant size bigger than 300 kPE.

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PVP-BASED COMPOSITES CONTAINING SOL-GEL NANOSIZED SiO_2 AND HYBRID TiO_2 MICROPARTICLES FOR WATER PURIFICATION

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Non-woven composite fiber mats are used in several applications including catalysis, filtration, etc [1]. The electrospinning process is a sustainable approach, because benign solvents and biocompatible polymers can be exploited. Poly(vinylpyrrolidone) (PVP) has been extensively studied, as its pyrroles can interact with several organic and inorganic compounds, leading to membranes with tailored interface. The Sol-Gel methodology can be coupled with electrospinning to prepare organic-inorganic composite with novel properties, working with controlled stoichiometry and mild process conditions. It is possible to obtain hybrid TiO_2-acetylacetonate (TiO_2acac, hybrid titania) amorphous xerogels with intrinsic oxidative ability, which are able to degrade different aqueous organic pollutants without need for light irradiation [2]. Besides, the incorporation of silica nanoparticles (SiO_2NP) into thermally treated electrospun PVP fibers results in the manufacturing of sustainable water- and self-extinguishing ternary composite mats (TCMs) [3]. Herein, SiO_2NP and TiO_2acac microparticles (~90 μm) were synthetized via Sol-Gel to be used in the fabrication of electrospun TCMs based on PVP. The spinning solution was prepared with different amount of TiO_2acac to study the effect of hybrid titania on the electrospinning performance. The chemical composition of TCMs and the incorporation of the fillers into the nanofiber matrix was confirmed through spectroscopic (FTIR, EPR) and microscopy (SEM, TEM) analysis. The Zeta potential and EPR measurements were exploited to assess the surface charge value and the presence of superoxide radicals on the TCMs, respectively. TiO_2acac microparticles generated stable superoxide radicals on the TCMs, which oxidatively degraded methylene blue in absence of light, with an initial rate ~70 % higher with respect to a binary composite mat containing only SiO_2NP. These results highlight the possible application of PVP/SiO_2NP/TiO_2acac mats as functional membranes in water purification process [4].

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Assessment of impacts caused by local scale emissions introduced in USEtox model

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Nowadays the global scale effects of climate change are the most feared environmental problem, but if attention is shifted to local-scale effects, chemicals (and plastics) pollution is of greatest concern to people. The local dimension of damage on human and ecosystem health is not fully considered in the calculation models, or often limited air compartment on the urban scale, for Life Cycle Assessment (LCA) [1,2] analyses.

The aim of this study was to develop an assessment model for public administrations interested in damage on human health and ecosystem caused by local emissions that occur near settlements. This was achieved by introducing a local scale into USEtox 2.12 [3], the UNEP/SETAC scientific consensus model for characterizing human and ecotoxicological impacts of chemical emissions in life cycle impact assessment.

The local scale, i.e. a small scale box with an extension of 1 x 1 km^2 nested in a continental box and including the point of ground-level emissions in air, water natural soil and agricultural soil compartments and an exposed population of 4166 people, was modelled on the simplifying assumption of well-mixed boxes.

The results are analyzed at two levels, by assessing the magnitude of the local and continental impacts in the modified USEtox model (called "USEtox local") and then by comparing the total impact score generated by the "USEtox local" model with the impact score of the USEtox model, assuming the whole amount of chemical is emitted at the continental scale.

For both analyses, considering a unit emission of benzene, chosen as reference chemical to explore the behaviour of the newly introduced scale, preliminary results show that the local scale results to be relevant in terms of damage, particularly for human health and for water and soils emissions, due to the high concentration to which the local population and the ecosystem are exposed to. A limited increase occurs for air compartment compared to the other local compartments, due to the relevance of advective process.

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Contributi Poster

New bio-based copolymers of poly(butylene trans-1,4-cyclohexane dicarboxylate) for sustainable food packaging: effect of camphor on functional properties

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The global pollution problems related to accumulation of plastics wastes in the environment is one of the most important challenges in view of a sustainable society. The highest percentage of these wastes come from packaging sector, especially from food one [1], which involves large amount of single-use plastic. The development of new materials from renewable sources with properties as close as possible to those of fossil-based PP, PE and PET currently widely employed in food packaging applications, is an important goal to achieve. In this work, we propose new 100% bio-based cycloaliphatic copolymers of trans-1,4-cyclohexanedicarboxylic acid, containing different amounts of camphoric acid [2,3]. The copolymers, obtained by optimized solvent-free 2-step polycondensation, were processed into compression moulded films, and characterized by molecular (1H-NMR, GPC), thermal (DSC and TGA), structural (WAXS) and mechanical (via tensile tests) point of view. Gas barrier performances against O_2 and CO_2 were also investigated. The properties were discussed as a function of the different amount of camphor in the copolymers. The obtained results evidence copolymerization is an efficient strategy to improve the unsatisfactory properties of a polymer for a given application without affecting the already good ones. Indeed, the goal of reducing the excessive stiffness of PBCE film keeping the good gas barrier properties, chemical and thermal stability was fully achieved.

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Induced electrochemical mineral deposition on mild steel in seawater by cathodic polarization

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A sustainable decommissioning option for oil and gas offshore platforms close to the end of their productive phase can be achieved by low voltage Induced Electrochemical Mineral Deposition (IEMD). The technology is based on the cathodic protection of steel by impressed currents in neutral chloride environments, resulting in the increase of the pH of the protected surfaces and thus inducing the precipitation of minerals, such as aragonite and brucite. The deposited mineral on the substrate is suitable for the colonization of marine organisms, hence can support the local biodiversity [1].

In this work, the IEMD has been performed on mild steel working electrodes in a laboratory-scale electrochemical cell filled with natural seawater, to investigate the electrochemical and morphological properties of calcium carbonate deposit by means of Electrochemical Impedance Spectroscopy and Optical Microscopy.

The results suggest that the mineral coating of aragonite on mild steel can provide good protection against corrosion in seawater, thus this technology could be promising for decommissioning the offshore platforms by increasing their average lifetime.

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Inclusion complexes between anticancer 5-fluorouracil and β-cyclodextrin for drug delivery: a Molecular Dynamics study

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Cyclodextrins (CDs) are macrocyclic polysaccharides that form interesting carriers for drug delivery since they can solubilize hydrophobic drugs in water, thus enhancing their bioavailability. Thus, complexation of 5-fluorouracil (5-FU) with natural or synthetic cyclodextrins permits the solubilization of this poorly soluble anticancer drug. The complex between β-CD and 5-FU is theoretically investigated here through 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].

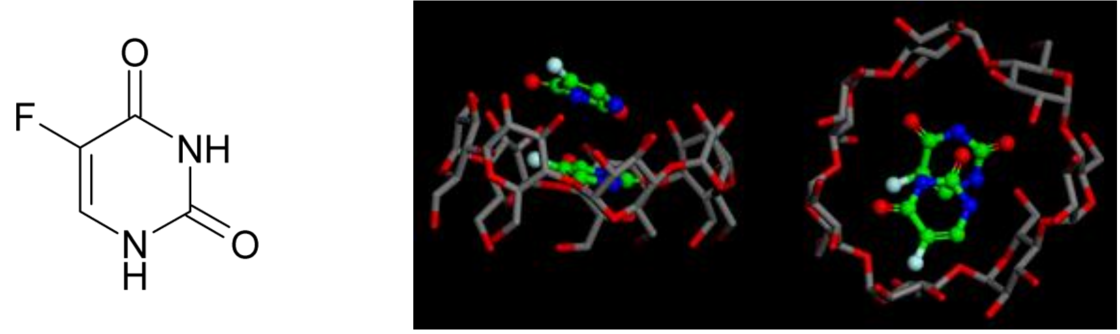

Figure 1. Line drawing of 5-FU (at left) and the stable inclusion complex for β-CD and 5-FU in a 1:2 stoichiometry in explicit water. Water molecules are omitted for clarity.

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Differentiation of fresh and thawed cephalopods using NIR spectroscopy and chemometrics

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One of the most occurring frauds in fish products concerns the declaration of freshness, which can be faked in the case of frozen and thawed products, leading to potentially negative impacts on the consumers' safety and health [1]. In this frame, the development of simple, affordable, and reliable methods able to quickly detect such kind of frauds is of considerable importance for both suppliers and consumers.

In this study, the differences between fresh and thawed cephalopods were investigated using Near infrared (NIR) spectroscopy [2] and a chemometric modelling approach. Fifty fresh specimens of both cuttlefish (*Sepia officinalis*) and musky octopus (*Eledone spp.*) were analysed at refrigerated temperature (~5°C). Then, the samples were frozen at -20°C for 48 hours, and finally thawed and re-analysed. Spectral data were acquired on each sample with three NIR instruments: the handheld SCiO (Consumer Physics) and MicroNIR (VIAVI), and the benchtop MPA (Bruker).

Principal component analysis (PCA, [3]) exploratory models and partial least squares-discriminant analysis (PLS-DA, [4]) classification models were developed using the acquired spectra, and all the three instruments provided a very good discrimination between fresh and thawed samples, with classification accuracy from 82.3% to 94.1% for cuttlefish, and from 91.2% to 97.1% for musky octopus. Moreover, the best classification results were obtained using portable instruments.

To date, there are no reference methods able to provide similar performances, suggesting the practicability of NIR spectroscopy for future screening and confirmatory analyses directly in situ, to the benefit of both producers and official authorities.

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Green sol-gel route to phosphorus-based acid catalytic materials

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Solid acid catalysts characterized by water tolerance and tuneable acidity play a central role in the renewable industrial chemistry based on biomass conversion. Phosphorus-containing oxides with moderate protonic acidity can be supplemented with transition metals, such as niobium, achieving a distribution of Brønsted and Lewis acid sites and improved stability to hydrolysis [1,2]. We investigated Nb-P-Si mixed oxides synthesized by sol-gel technique, which showed remarkable catalytic performances in biomass valorization reactions: hydrolysis of inulin, dehydration of fructose to 5-hydroxymethylfurfural and esterification of fatty acids [1].

Recently we have developed a new sol-gel route for the synthesis of these ternary oxides, inspired by the principles of green chemistry and sustainable production. This one-pot procedure occurs in water at room temperature, with safe, available and inexpensive precursors (i.e. phosphoric acid and ammonium niobium oxalate), and does not require any catalyst, additive or organic solvent [2]. The annealed gels containing 2.5 mol% P_2O_5 and 2.5 – 5.0 mol% Nb_2O_5 have a highly cross-linked amorphous porous structure, with Nb-O-P bonds stably anchoring phosphorus to the silicate matrix, as endorsed by solid state NMR spectroscopy [2]. Their surface characterization revealed medium-strong Brønsted and Lewis acidity and temperature-programmed catalytic tests evidenced an interesting activity in the gas-phase conversion of ethanol to ethylene, with unusually low yield of diethylether, a common by-product [3].

Next developments include the modulation of acidic and catalytic properties by the introduction of different transition metals in the mixed oxides system.

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Devices for the capture of rare cells from biological samples for diagnostic purposes

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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].

This research aims at making 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 in order 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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Chemistry and Sustainability@Tor Vergata: Materials for Energy and Environment

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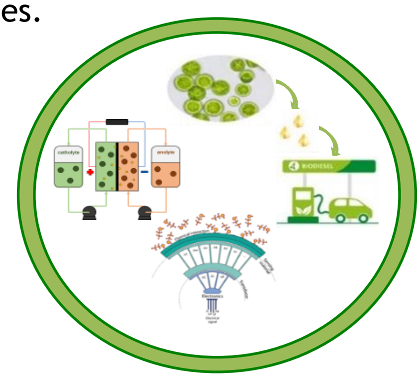
The term sustainability deals with policies and strategies able to agree with the current economic, social, and environmental needs of society with the welfare of future generations. Chemistry works to find sustainable solutions for various ambitious challenges, such as guaranteeing access to inexpensive and sustainable energies for everyone and reducing the impacts of anthropic activities for environmental preservation. At Tor Vergata we are working on the following three research fields to meet such goals:

Materials for Energy Conversion and Storage: nanostructured organic, inorganic, and hybrid materials for energy applications are prepared and characterized. Catalysts, polymer electrolytes, and ceramic oxides for high and low-temperature fuel cells, redox flow batteries, and bioelectrochemical systems are obtained by tailoring the interplay of morphology, microstructure, and surface chemistry on electrochemical properties.

Biomass for Energy and Fuels: microalgae are an ideal third-generation biofuel feedstock because of their rapid growth rate, CO_2 fixation ability, and high production capacity of lipids. Microalgal biomass is studied and selected to obtain high lipids production with a good percentage of unsaturated fatty acid extracted.

Chemical Sensors for Environmental Monitoring: sensitive materials based on porphyrinoids combined with inorganic nanostructures are finely prepared. The developed chemical sensors used as single devices or in array configuration are exploited for the analysis of complex gaseous and liquid matrices for purposes of environmental monitoring, industrial processes control, foodstuffs quality assessment, and clinical analyses practices.



(S) o (R): questo è il problema

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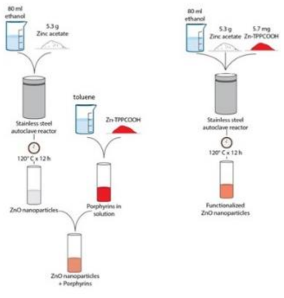
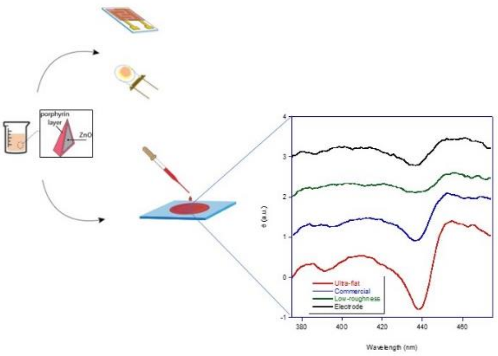
Le porfirine sono tra i più versatili composti di partenza per la costruzione di aggregati supramolecolari chirali. Il problema principale nell’utilizzo di questi composti come materiali sensibili per realizzare sensori enantioselettivi consiste nel trasferimento delle proprietà chirali della singola molecola al film a stato solido. Un possibile approccio consiste nell’utilizzo di materiali ibridi basati su ossidi metallici (ZnO) funzionalizzati con porfirine chirali [1]. In questo contributo si riportano i risultati relativi alla realizzazione di film basati su analoghi sistemi ibridi, ottenuti variando il metallo coordinato al macrociclo e le condizioni di preparazione (post-funzionalizzazione o co-crescita). Le misure al dicroismo circolare hanno mostrato che il materiale inorganico permette di ottenere film chirali su differenti substrati in modo riproducibile, anche con tecniche semplici come il drop casting. I materiali più promettenti sono stati selezionati per realizzare due piattaforme multisensoriali basate su trasduttori gravimetrici e conduttometrici. Nel primo caso, l’analisi delle componenti principali ha evidenziato la capacità del sistema di separare sia diversi composti achirali sia di distinguere tra i due enantiomeri del metil lattato. Nel secondo caso è stata verificata la possibilità di realizzare sensori conduttometrici chirali, in cui sia la conducibilità che le proprietà di sensing sono fotoattivate da irraggiamento con luce visibile.





Riferimenti

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Nanotubi di titanato con Au in superficie per la foto-ossidazione selettiva di alcoli ad aldeidi

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La fotocatalisi è stata ampiamente utilizzata per processi di disinquinamento; tuttavia, ha un ruolo come alternativa verde ai processi di sintesi catalitica industriale. La reazione di ossidazione selettiva di alcoli alle corrispondenti aldeidi ha una notevole importanza da un punto di vista industriale. Considerando la luce solare come fonte di energia verde e sostenibile, l'uso di fotocatalizzatori attivi sotto luce solare può rappresentare un'alternativa ai tradizionali processi catalitici. A questo proposito, sono state studiate nanoparticelle metalliche per le loro proprietà uniche associate al foto-assorbimento nella regione della luce visibile per il cosiddetto "effetto plasmonico". Nanoparticelle di Au supportate su TiO_2 o CeO_2 sono state utilizzate come fotocatalizzatore sotto irradiazione di luce visibile (assorbono a ca. 550 nm) [1].

In questo lavoro è stato preparato un set di nanotubi di titanato (TiNT) puri o caricati con Au (1 o 3% in peso) [2]. Questi solidi sono stati utilizzati come fotocatalizzatori per l'ossidazione selettiva di tre alcoli aromatici e un alcol furanico alle corrispondenti aldeidi. Le reazioni sono state condotte in sospensione acquosa e condizioni ambientali sotto irraggiamento UV, visibile o con luce solare naturale. Tutti i materiali risultati attivi sotto radiazione UV, Vis o solare per l'ossidazione parziale fotocatalitica dei quattro alcoli. Il tipo e la posizione dei sostituenti nell'alcol aromatico influenza sia la conversione che la selettività all'aldeide. La presenza di Au ha migliorato la selettività della reazione verso l'aldeide particolarmente sotto irraggiamento visibile e solare. In generale, l'utilizzo della luce visibile e solare ha dato luogo a conversioni inferiori ma maggiori selettività ad aldeidi.

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Transition metal nanoparticles on pyrrole-decorated sp^2 carbon allotropes for selective hydrogen isotopic exchange

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Compared to homogeneous catalysts, heterogeneous systems possess more attractiveness in the chemical industry because of the easier separation from the reaction products, lower amount of wastes, larger recyclability and lower toxicity and corrosiveness. Preparation of supported metal nanoparticles often requires energy demanding techniques such as laser ablation, electrochemical reduction, and high temperature heat treatments. In this work we present a facile and sustainable method to functionalize multi-walled carbon nanotubes (MWCNTs) and exploit the novel surface reactivity to deposit Ruthenium nanoparticles. Serinol pyrrole (SP) was synthesized and, through a Domino reaction, grafted on carbon nanotubes' surface.[1-3] Mild reducing conditions were employed to decorate CNT-SP with Ruthenium nanoparticles. The latter adduct was characterized by means of X-ray diffraction and transmission electron microscopy. Ru/CNT-SP was then tested in the selective deuteration of quinoline. High selectivity and conversion, determined through H-NMR, were achieved compared to commercial Ru/C catalysts. The results obtained in this work led to the filing of two patent applications.[4,5]

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Insights into the photocatalytic behaviour of doped $LaFeO_3$ oxides for oxytetracycline degradation

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Lanthanum ferrite ($LaFeO_3$, LF) is a perovskite-type photocatalyst, which has been proposed as visible-light and UV photocatalyst for aqueous reactions [1-3]. As many ABO_3 perovskite-type oxides, LF shows a high recombination rate of photogenerated electron-hole (e^--h+) pairs [4]. Several strategies are developed to reduce the unfavourable electron-hole recombination process. In this work, doped LF nanopowders are evaluated in the photocatalytic degradation of Oxytetracycline (OTC). Pd 3%, Pd 5%, Cu 10%, Mg 5% - Mg 10% - Mg 20%, Ga 10%, Y 10% and Y 20% doped LF are studied and the influence of the doping metal and the specific surface areas (SSA) on the photocatalytic degradation efficiency of OTC is assessed. The lowest degradation values occurred with Ga 10%. The most extensive photodegradation of 78% is noticed with Cu 10%. A good result is also obtained with 10%Mg-doped photocatalyst. The results of the performed characterizations suggest that the SSA of the catalysts is the parameter that has the greatest influence on degradation kinetic, except for the sample with 10% Cu.

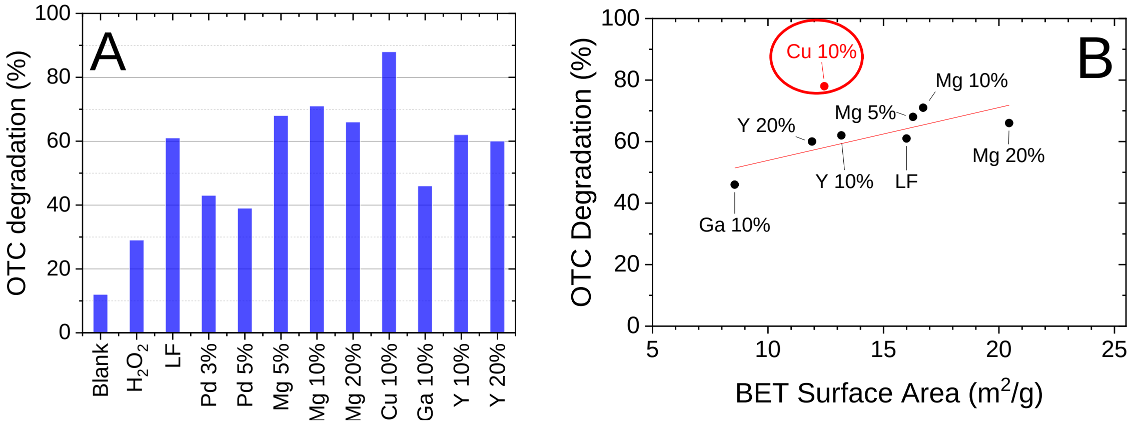

Figure 1: (A) OTC Degradation vs catalyst. (B) OTC Degradation vs BET Surface Area.

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Chiral N-methyl corroles : a re-discovery

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Environmental pollution by chiral agents is progressively becoming a serious problem for both health and the environment. The development of methods and sensors capable of detecting these substances in the best possible way is therefore of vital importance.
An idea that came to Professor Roberto Paolesse's research group was to use corroles, porphyrinoid molecules with excellent properties and used for sensing, having chirality induced by the methylation of one of the nitrogens of the ring core. The induced chirality of these substrates would allow the modulation of the sensing properties and the directing of the chiral selectivity towards the pollutant.
These compounds were first synthesized in 1965 by Johnson and Kay [1], and a small number of studies have been published since then, possibly due to low yields and the difficulty of separating isomers [2].
An effective synthetic strategy was therefore developed, thanks to which it was possible to obtain to a large extent two N-methylated isomers of 5,10,15-tri-p-tolylcorrole (TTC), to the detriment of a minimum amount of di-methylated compound, the main reaction by-product.
At this point, numerous alkylation tests were carried out with chains with variable carbon numbers and complexation reactions with different metals, obtaining interesting results with Palladium and Cobalt. Being able to obtain different derivatives would also allow application in the photophysical field and asymmetric catalysis.
Last but not the least, the synthesis of a new type of corrole-corrole dimer bonded through the nitrogen atoms of the core was carried out using the same synthetic strategy of the N-methylates, using five and ten-membered alkyl chains as a bridge.

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Functionalized carbon black for elastomer composites with low hysteresis

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The prime application of elastomeric composites is tire compounds. The tuning of dynamic rigidity and hysteresis is key to achieve the desired tire performances. Car tires require hysteresis to be high at low temperatures, to promote wet traction, and low at medium-high temperatures, for low energy dissipations. To achieve these properties amorphous precipitated silica is commonly selected as reinforcing filler due to its nano dimensions and the possibility of establishing chemical bonds with the elastomers' chains. Carbon black (CB), another common filler for tire compounds, does not have functional groups able to promote chemical bonds with the rubber matrix yet it would be highly desirable. A CB with a cradle to gate LCA comparable if not even better than silica's LCA could be used in replacement of silica in tire compounds.

In this work, a pyrrole compound (PyC) containing a thiol group was used to functionalize CB by the so-called "pyrrole methodology" [1-3]. The thiol group was expected to react with the sulphur-based crosslinking system, thus forming chemical bonds with the rubber chains [4]. The synthesis of the PyC and the functionalization reaction were characterized by high atom efficiency. A poly(styrene-co-butadiene) copolymer from anionic solution polymerization was used as the main rubber for the compound preparation. The crosslinked composite material filled with functionalized CB revealed substantial improvements with respect to the composite with pristine CB, in particular: high rigidity and low hysteresis at high temperature. These findings seem to confirm the formation of the expected rubber-filler chemical bond and are even comparable to those of silica- based rubber composites. The results here reported pave the way to CB-based rubber composites with a low environmental impact.

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Interactions for drug delivery: a molecular dynamics study of Ketoprofen on amorphous SiO_2 hybrid materials synthesized by Sol-Gel

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Biomaterial-based drug delivery systems for a controlled drug release are drawing increasing attention thanks to their possible pharmaceutical and biomedical applications. It is important to control the local administration of drugs, especially when the drug exhibits problems diffusing across biological barriers [1]. Molecular Mechanics (MM) and Molecular Dynamics (MD) simulations at atomistic level are performed in order to investigate surface interactions [2] between the amorphous SiO_2 surface and the (*R*,*S*) ketoprofen molecules, an anti-inflammatory drug, both at smaller and at higher concentration [3]. The simulation results are compared with the experimental data obtained using Fourier-Transform Infrared Spectroscopy (FT-IR) at two percentages of the ketoprofen drug entrapped in a silica matrix obtained via the Sol–Gel methods. The loaded drug forms hydrogen bonds with the silica surface, as found in this theoretical study (see Figure 1). MM and MD simulations at the interface provide insights about this new generation of biomaterials able to incorporate anti-inflammatory agents for release *in situ* after implantation [3].

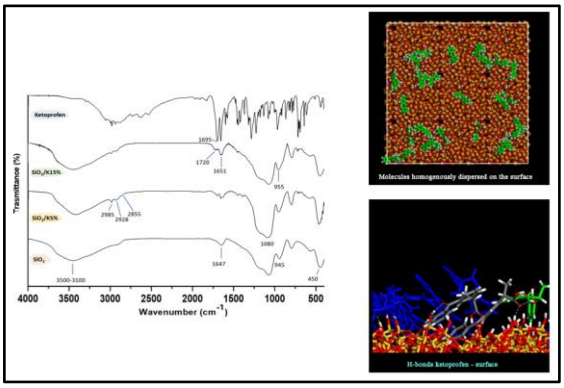

Figure 1. At left, the FT–IR spectra of Ketoprofen, SiO_2/Ketoprofen (5 and 15 wt%) hybrid materials and pure SiO_2. At right, the theoretical results.

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Upgrading grape pomace containing ethanol into hexanoic acid: a Life Cycle Assessment study.

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Grape pomace is an agricultural-industrial by-product generated during the wine production process. Several products can be recovered from this waste of the wine industry, including ethanol, tartaric acid and the anthocyanins. One of the most recent ways regarding the valorization of this product was developed by some of the present authors[1]. It is based on the conversion of the ethanol residues in red grape pomace, remainings after the wine production process, into hexanoic acid. This new process could be a more environmentally sustainable alternative to the more traditional method for recovering ethanol from grape pomace, i.e distillation. This work aims to carry out a Life Cycle Assessment (LCA) study, in order to reliably quantify the environmental impacts associated to the whole life cycle of the innovative valorization procedure based on the use red grape pomace, arising from the winemaking process of red wine. In the modellization of the process on the SimaPro calculation tool[2], two different red grape pomaces have been selected. In this way it will be also possible to notice any different impacts that can be obtained by using red grape pomaces obtained with slightly different processes (one of the two grape pomaces is indeed obtained through an organic an biological winemaking process).

In parallel to this, a modelling of the conventionally performed valorization strategy, i.e. the distillation process, for the recovery of the residual ethanol in red grape pomace, was carried out.

For both processes the environmental assessment was carried out at a laboratory scale, so the future idea is to scale up both of the two processes at an industrial level to see how the results could change.

The present work therefore has the objective of comparing the results obtained by the two processes, in order to determine whether the new and more recent valorization of red grape pomace proposed by some of the authors[1] con be effectively considered less environmentally impactful with respect to distillation.

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Environmental Impact Assessment of 2D Materials synthesis by LCA methodology: the case of Ti_3C_2MXene

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The interest of scientists in 2D transition metal carbides has rapidly increased, due to their unique physical properties, that make them useful in a wide range of applications such as energy storage, optoelectronic, biomedical, communications, and environmental [1].

Most common synthetic routes of 2D MXene materials employ the selective etching of metal layers from the MAX phases (Ti3AlC2), using aqueous solutions of hydrofluoric acid of different concentrations [2]. In order to overcome the hazard associated with the handling of hydrofluoric acid, there are currently several developments such as: the use of a lower concentrations of the hydrofluoric acid solutions or the generation of hydrofluoric acid in situ [3].

In the current work, the Life Cycle Assessment (LCA) methodology was applied to quantify the environmental impact of most synthetic strategies of 2D Ti_3C_2 material. LCA is a holistic approach that quantifies the environmental and human health impacts associated with the inflows from nature and outflows to nature, related to the human activities involved in the whole life cycle of a product or process [4].

In this study, LCA method was applied for the well-known synthesis of Ti_3C_2 MXene, as well as for the newly proposed methods, to accurately and objectively quantify and compare their environmental burdens. These calculations allow a significant progress towards the greenness and sustainability of the preparation of transition metal carbides.

Further work requires the LCA calculations for the preparation of different transition metal carbides, as well as its application to the synthesis of other 2D materials.

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