



Chimica Verde

Energie Rinnovabili

Salute

Materiali

Modelling

Beni Culturali

CONFERENZA DI DIPARTIMENTO 2018

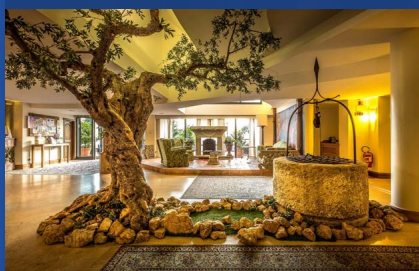
DS@TM

Department of Chemical Sciences and Materials Technology

24-25-26 SETTEMBRE

ASSISI

GRAND HOTEL ASSISI



Consiglio Nazionale delle Ricerche
Dipartimento Scienze Chimiche e Tecnologie dei Materiali

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Piazzale Aldo Moro, 7 - 00185 Roma
www.edizioni.cnr.it - bookshop@cnr.it - 06 49932287

ISBN 978 88 8080 339 3

Atti della Conferenza del Dipartimento Scienze Chimiche e Tecnologie dei Materiali
Assisi 24-25-26 settembre 2018,
a cura di **Doriano Lamba e Francesco Verginelli**

Organizzazione Giornate di Dipartimento 2018 24-25-26 Settembre, Assisi

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PROGRAMMA

24 settembre 2018

13.30 - 14.30

Registrazione

14.30 - 14.40

INTRODUZIONE
Dr. Maurizio Peruzzini

Direttore Dipartimento di Scienze Chimiche e Tecnologie dei Materiali



Chimica Verde

14.40 - 14.45

Chair - Dr. Mauro Marchetti (ICB-CNR) & Dr. Alessandro Mordini (ICCOM-CNR)

14.45 - 15.05

A paper-based algal biosensor for nanoatrazine optical detection

Scognamiglio Viviana - IC

15.05 - 15.25

A coordination-driven triangle as nanoreactor

Rancan Marzio - ICMATE

15.25 - 15.45

β -Cyclodextrin inclusion complexes of natural occurring compounds and their evaluation as insect repellents in a push-pull strategy

Delogu Giovanna - ICB

15.45 - 16.05

Green Analytical Chemistry (GAC) at ICCOM: the role of analytical methodology development

Bramanti Emilia - ICCOM

16.05 - 16.25

Permeation of Light Gases through Zeolite Membranes

Barbieri Giuseppe - ITM

16.25 - 16.45

Micro-engineered capsules: a powerful tool in green chemistry

Costa Anna - ISTECC

16.45 - 17.15

Coffee Break

17.15 - 17.45

Invited Lecture - **Dr. Nicola Armaroli (ISOF-CNR)**
Chemistry and the Great Energy Transition



Chimica per l'Energia Rinnovabile

17.45 - 17.50

Chair - Dr. Alessandra Sanson (ISTEC-CNR) & Dr. Alessandro Mordini (ICCOM-CNR)

17.50 - 18.10

Organic Components of Perovskite Solar Cells

Orlandi Simonetta - ISTM

18.10 - 18.30

Catalysts 2.0: a New Technology at the Forefront of Processes at the Heart of Renewable Energy Technology

Giambastiani Giuliano - ICCOM

DSCTM

18.30 - 18.50 Supported Pd and Pd-Au Membranes for Hydrogen Generation and Purification Iulianelli Adolfo - ITM

18.50 - 19.10 Keynote Lecture - **Dr. Armida Torreggiani** (ISOF-CNR)
There isn't any science without communication: collaborative dialogue between research and school

19.10 - 20.00 Sessione Poster

20.00 Apericena

21.00 Riunione Giunta - Direttori



25 settembre 2018



Materiali Avanzati

08.30 - 08.35	Chair - Dr. Maria Lucia Curri (IPCF-CNR) & Dr. Alessandra Sanson (ISTEC-CNR)	
08.35 - 08.55	New anti-fraud method: the proteomic technique applied to the identification of luxury animal fibers	Tonetti Cinzia - ISMAC
08.55 - 09.15	Thiazole and Pyrazole-based Metal-Organic Frameworks for Gas Storage and Catalysis	Rossin Andrea - ICCOM
09.15 - 09.35	Bio-hybrid Nanostructured Cellulose Membranes as Functional Tools for Bio-separation and Bio-recognition Applications	Militano Francesca - ITM
09.35 - 09.55	From Tailored Molecules to Advanced Nanomaterials and Devices: Surface Protection, Light Absorption and NIR-Emission	Bossi Alberto - ISTM
09.55 - 10.15	Development and Application of an Analytical Method to Determine Polyethylene in Compostable Carrier Bags	Rizzarelli Paola - IPCB
10.15 - 10.35	Microstructure, wettability and surface reactivity of AlSiMg system used in additive manufacturing	Bassani Paola - ICMATE
10.35 - 10.55	Smart amphiphobic surfaces for challenging industrial applications	Blosi Magda - ISTEC
10.55 - 11.35	Coffee break	



Modeling Computazionale

11.35 - 11.40	Chair - Dr. Filippo De Angelis (ISTM-CNR)	
11.40 - 12.00	Advanced Methods and Software for the Characterization Crystalline Materials by Powder Diffraction Data	Corriero Nicola - IC
12.00 - 12.20	Exploiting Quantum Phenomena to Design Electron Transport in Nanojunctions	Trioni Mario I. - ISTM
12.20 - 12.40	Computational Multi-Scale Modeling of Metal Oxide Nano-Particles and Surfaces	Barcaro Giovanni - IPCF
12.40 - 13.10	Invited Lecture - Prof. Luigi Nicolais (Materias S.r.L) <i>The Evolution of University-Industry Relationship</i>	



13.10 - 14.30 Pranzo



Chimica per i Beni Culturali

14.30 - 14.35 **Chair - Dr. Costanza Miliani (ISTM-CNR)**

14.35 - 15.05 **Invited Lecture- Prof. Antonio Sgamellotti (Univ. Perugia)**
Chemistry for Art: a non-invasive in situ approach by MOLAB

15.05 - 15.25 Low cost, disposable and self-sustainable paper-based platforms for SERS analysis applied to the study of natural dyes **Campanella Beatrice - ICCOM**

15.25 - 15.45 Non-invasive investigations on Max Ernst's masterpieces: materials, painting technique and alterations products **Nodari Luca - ICMATE**

15.45 - 16.05 Assessment of weathering steel corrosion inhibition in NaCl solution by the natural extract of *Brassica Campestris* **Casaletto Maria Pia - ISMN**

16.05 - 16.35 **Keynote Lecture Dr. Rinaldo Psaro (ISTM-CNR)**
Materials Science and Art

16.35 - 17.15 Coffee Break



Chimica per la Salute e le Scienze della Vita

17.15 - 17.20 **Chair - Dr. Giuseppe Palmieri (ICB-CNR) & Dr. Dorian Lamba (IC-CNR)**

17.20 - 17.40 Creating neurodegenerative diseased tissue model in a membrane bioreactor **De Bartolo Loredana - ITM**

17.40 - 18.00 Mass spectrometry proteomic platforms: discovering molecular signatures in clinical proteomics studies **Desiderio Claudia - ICRM**

18.00 - 18.20 New Molecules for Drug Discovery by Screening Platform of Marine Natural Products **Nuzzo Genoveffa - ICB**

18.20 - 18.40 Effects of Prion Protein on β -Amyloid Peptides Oligomerization and Toxicity **Pagano Katuscia - ISMAC**

18.40 - 19.00 Toward Personalized Medicine: RGD-Peptide as Scaffold for the Comprehension of Structural Determinants for Integrin Specific Recognition **Saviano Michele - IC**

19.00 - 19.20 Nanophotosensitisers based on cyclodextrin for bio-imaging and PDT **Mazzaglia Antonio - ISMN**

19.20 - 20.00 Sessione Poster

20.30 Cena Sociale



26 settembre 2018

08.45 - 09.00	Premiazioni & Presentazioni YIA 2018
09.00 - 09.30	Chimica Verde: Guerriero Antonella - ICCOM
09.30 - 10.00	Chimica per l'Energia Rinnovabile: Gondolini Angela - ISTECH
10.00 - 10.30	Chimica per la Salute e le Scienze della Vita: Posati Tamara - ISOF
10.30 - 11.00	Coffee Break
11.00 - 11.30	Materiali Avanzati: Silvestroni Laura - ISTECH
11.30 - 12.00	Modeling Computazionale: Mosconi Edoardo - ISTM
12.00 - 12.30	Chimica per i Beni Culturali: Giuliani Chiara - ISMN
12.30 - 12.45	Menzioni d'Onore YIA2018 & Premiazioni Posters Chimica Verde: Balzarelli Fabio - ITM; Chimica per l'Energia Rinnovabile: Bossola Filippo - ISTM; Chimica per la Salute e le Scienze della Vita: Panseri Silvia - ISTECH; Materiali Avanzati: Biffi Carlo Alberto - ICMATE; Modeling Computazionale: Rinaldi Silvia - ICRM; Chimica per i Beni Culturali: Campanella Beatrice - ICCOM
12.45 - 13.00	Contributed Presentation - Dr. Mario Malinconico (IPCB-CNR) <i>2019: 100 years of IUPAC and 150 years of the Periodic Table of Chemical Elements</i>
13.00 - 13.30	DISCUSSIONE PLENARIA & CONCLUSIONI Dr. Maurizio Peruzzini Direttore Dipartimento di Scienze Chimiche e Tecnologie dei Materiali
13.30 - 14.30	Pranzo
15.00 - 17.30	Visita Basilica di Assisi



ABSTRACT

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Chemistry and the Great Energy Transition

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Istituto per la Sintesi Organica e la Fotoreattività - CNR, Bologna, Italy

The investigation of fundamental phenomena in photochemistry and photophysics is a privileged path to explore molecules, supermolecules and materials of wide and sometimes unexpected interest in the area of sustainable chemistry and energy conversion [1-4]. This fundamental research will be framed in the context of the ongoing energy transition from conventional to renewable energy sources [5]. Some key challenges and bottlenecks of this complex process will be discussed, highlighting the leading role that chemistry can play in this context, also in the frame of large interdisciplinary projects [6].

Keywords:

Photochemistry; Photophysics

References:

- [1] M. Mohankumar, M. Holler, E. Meichsner, J.-F. Nierengarten, F. Niess, J.-P. Sauvage, B. Delavaux-Nicot, E. Leoni, F. Monti, J. M. Malicka, M. Cocchi, E. Bandini, N. Armaroli, *J. Am. Chem. Soc.* **2018**, *140*, 2336-2347.
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- [4] T. Miletić, E. Pavoni, V. Trifiletti, A. Rizzo, A. Listorti, S. Colella, N. Armaroli, D. Bonifazi, *ACS Appl. Mater. Inter.* **2016**, *8*, 27966-27973.
- [5] N. Armaroli, V. Balzani, *Chem.-Eur. J.* **2016**, *22*, 32-57.
- [6] www.sunriseflagship.eu



There isn't any Science without Communication: Collaborative Dialogue between Research and School

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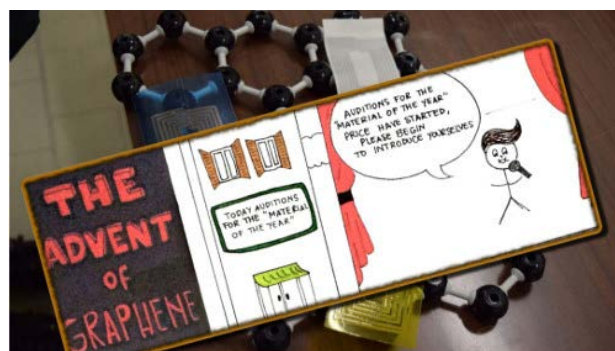
Scientific culture is seen by youth with less and less interest, probably due to the way science is taught in schools, to the difficulties in the understanding of the real impact on the everyday life and finally, to the shortage of attractive career perspectives. Schools often do not focus on technology promotion, awareness and collaboration with industry. As reported by the UNESCO document, the education is the primary agent of transformation towards sustainable development, increasing people's capacities to transform their visions for society into reality. Education not only provides scientific and technical skills, it also provides the motivation, justification, and social support for pursuing and applying them. Thus, it is necessary to individuate a real breakthrough in science dissemination, which can be attractive for the youth.

A **collaborative dialogue between students, teachers, researchers, and industries** is the most effective mean to transfer the scientific progress and to promote the technological advances. In this perspective the proposal "**From Research to School and...back – METHOD, LANGUAGE AND SCIENTIFIC APPROACH FOR HIGH QUALITY SCHOOL**", funded by MIUR in 2017 (ACPR15T4_00327; 01/11/2017-31/10/2019 <http://www.bo.cnr.it/linguaggiodellicerca/>), represents a key action to introduce and promote research in school. In fact, the general scope of the project is to promote and assist a wide dissemination action on current Research topics in Schools thanks to the strategic integration between Schools, CNR, other research organizations and non-profit organizations. It aims to turn on young people's interest in respect of scientific research, methods and results as well as communication of scientific data and information through their involvement in a work of popularization. In fact, **the core process of the project is to make Research meeting the Schools, that in turn, need to meet Society, in a common learning environment.**

The methodological approach can be divided into five steps:

(1) the researchers meet pupils at school: interactive lessons exercises/hands on activities are organised at school on about 30 topics and their connection with societal challenges;

(2) the students are asked to become science communicators themselves and create informative materials focused on the learned contents by using both Italian and English languages (web site, poster, comic strip, power point presentation, video, etc.);



What is it?!
This is a magazine created by class 3A
from Liceo Copernico of Bologna.

History of Graphene
p. 3
Applications p. 6-7
And there is a lot
more!



(3) organization of annual Conferences for the exhibit of the material and the awarding of the most deserving;



(4) possibility for the most motivated students to deep their knowledge of the research world through summer stages in the CNR labs;

(5) possibility for students to collaborate with researchers in supporting public events, i.e. EU Researchers' Night.

The project is coordinated by the Institute for Synthesis Organic and Photoreactivity (ISOF-CNR) and its Consortium is composed by ENEA, Melting Pro. org, and the CNR Institutes of the Research Areas of Bologna and Rome 1 (ISMAR, IMM, ISAC, IBIMET,

ISMN, IGM, ISM, ITD IIA, IC, ITABC, IMC), ITD in Genoa and the CNR Press Office in Rome. In 2018 the project is involving more than 4500 pupils, their teachers and more than 30 researcher scientists.

It is working in order to build a national network that will strength and implement the already collaborative processes activated by CNR and Local Actors (Schools and Companies), as well as European ones (Universities and Research centres, i.e. <https://rmschools.isof.cnr.it/network.html>), and will valorise peculiarities of territorial contexts.

This project can be of help in answering more efficiently to the MIUR requests about the combined study/work experience in youth training (Alternanza Scuola-Lavoro). In fact, it will share in the national network the “good practices” for an active learning, create educational material (hands on toolkits, video-lessons, etc.) and a virtual centre (e-learning platform) to diffuse it, and support each partners in overcoming difficulties.

Keywords: research-school, scientific active learning, creative thinking

References:

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Acknowledgement:

This work was supported by MIUR (ACPR15T4_00327) and by the Raw Matters Ambassadors at Schools European project (RM@Schools- Project N. 17146/2018/EIT/EIT Raw Materials, European Institute of Innovation and Technology, a body of the European Union under Horizon 2020) which are gratefully acknowledged.



The Evolution Of University-Industry Relationship

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President and Ceo of Materias s.r.l.

In order to diffuse in Italy an entrepreneurial culture of research, encourage the dissemination of scientific outcomes and support scientists through the stages of commercialisation of the results of their study, several Universities have established Technology Transfer Offices (TTO).

These offices have been joined by specific tools operating as “intermediary structures” in the field of knowledge, innovation and technology transfer to SME’s. An overview of these tools and their evolution starting from Science and Technology Parks, Competence Centers, Technological District and Pôle de Competitivité is presented.

At European Level the new framework program Horizon Europe with the Open Innovation pillar aims to make Europe a frontrunner in technological transfer and market-creating innovation.

Despite, the level of innovation and competitiveness of Italian research is at the top of world rankings, the industrial impact of Italian scientific research, is not among the best. This handicap derives from low investments in research, the weakness of venture capital system and low tech-transfer ability.

Materias s.r.l. is a new model that is born as a tool to overcome the "valley of death", through the connection of the research world with the world of industrial companies, the development of innovative solutions in the field of advanced materials and the creation of new business science-based.

Keywords: advanced materials, technology transfer



Chemistry for Art: a Non-Invasive *In Situ* Approach by MOLAB

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Chemistry provides powerful tools to solve problems in art-historical studies and may be used to suggest appropriate procedures for conservation and restoration.

A multi-technique approach by MOLAB will be presented for investigations on different typologies of artifacts:

- i) paintings by ancient Masters (*Perugino, Raffaello*) and by modern and contemporary Artists (*Mondrian, Burri*);
- ii) sculptures (*Michelangelo's David, Calamita Cosmica* by *Gino de Dominicis*);
- iii) manuscripts (Mexican pre-Columbian codices);
- iv) ceramics (Renaissance lustres).

Keywords: Investigations, In situ, Non-invasive

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Acknowledgement:

Thanks to the MOLAB team



Materials Science and Art

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Science, Technology and Art has always plotting major horizons and constitute essential fields of research, although sometimes seem mutually incompatible or even turned against each other. The purpose of this seminar, which is deliberately informative, intends to look at the history of art, focusing on the materials used. The seminar starts from the glass passes to gold and titanium finally trying a "common thread" with a scientific approach and artistic.

Vitrum: glass between art and science in the Roman world. Historical sources on the discovery of glass and production techniques in Roman times; examples of artifacts from the time of the eruption of Vesuvius; it was a revolution of architecture and costume?

The gold but what's special about this metal? Properties and use of gold in the ancient world; Etruscan artifacts with advanced technology; colloidal gold used by the Romans from the middle ages to the purple of Cassius in today's examples.



La coppa di Licurgo, applicazione nano tecnologica ante litteram?

Titanium one of the last discovered metals. Properties and use of titanium in particular in architecture: the case of the Guggenheim in Bilbao; from goldsmiths to the invention of the titanocromie of Pedefferri.

From titanocromie to the opal's chromatic properties, what is the explanation from a material science point of view?

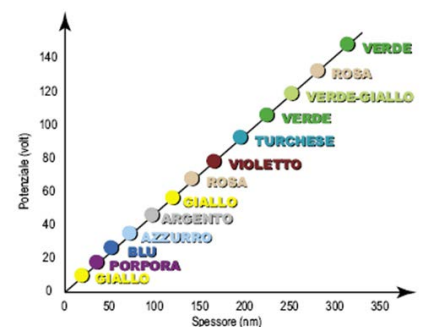
Primo Levi, wrote that if there really exists a "schisi" between Science and Art, it is an "unnatural schisi": because this separation knew neither Dante, nor Galileo, nor even Empedocles, Leonardo, Descartes, Goethe, Einstein, neither the anonymous builders of Gothic cathedrals, nor Michelangelo; neither the good artisans of today know it, nor the physicists hesitating on the edge of the unknowable.

Even today, it is more than ever, faced with the separation between Science and Art, it is useful and necessary to take Primo Levi's approach. If there is a "schisi" between culture and science, this is an "unnatural schisi". Levi's approach to the problem of the separation between the two cultures is really important. Because it tells us that Art and Science are different, but deeply interpenetrated, manifestations of a single culture, human culture. Art and Science intertwine and therefore influence each other: much more than, in the first instance, we are led to believe.

Keywords: scienza dei materiali, arte

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Potenziali, spessori e colori della pellicola di ossido su titanio.



2019: 100 years of IUPAC and 150 years of the Periodic Table of Chemical Elements

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The year 2019 marks the 100th anniversary of IUPAC founded in Paris from representatives of 5 nations, including Italy, and the 150th anniversary of the Periodic Table of Chemical Elements [1-2].

On December 20, 2017, the 72nd session of the United Nations General Assembly (UN) has proclaimed 2019 as the International Year of the Periodic Table of Chemical Elements (IYPT 2019) [3].

The IUPAC Centenary is an opportunity to reflect on the value and work carried out by the IUPAC.

The theme of the anniversary is "A Common Language for the Chemistry".

The anniversary of the Periodic Table of Chemical Elements and its central role in Chemistry is celebrated by IUPAC with a global online competition.

Keywords: IUPAC, United Nations Organization - International Years

References:

[1]<https://iupac.org/iupac-100th-anniversary-celebrated-2019/>

[2]<https://iupac.org/100/>

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GREEN CHEMISTRY



ORAL COMMUNICATION



A Paper-Based Algal Biosensor for Nanoatrazine Optical Detection

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The increasing democratic pressure, climate change, industrial globalization and the intensive use of resources of last decades represent nowadays a few main global challenges, being factors that generate a huge impact on the environment and people's health [1]. Among human practices, agriculture is one of the main cause of environmental pollution since farming activities have been oriented toward the indiscriminate use of resources as land and water, high-tech machinery, and chemicals as pesticides and fertilizers, with the aim of producing ever higher food volumes. For these reasons, consumer demand for more sustainable agricultural practices and waste minimisation has become imperative in modern agrifood sector. In this context, smart agriculture entails the exploitation of different multifarious approaches based on more energy efficient and environmentally friendly cross-cutting technologies, including among others i) the use of nanomaterials to increase the dispersion and wettability of agricultural formulations [2], and ii) advanced diagnostic tools for the analysis of ground/drinking water to assess water matrices pollution level [3].

In this overall scenario, we developed a paper-based algal biosensor for the optical detection of nanoatrazine, a forefront nanoformulated herbicide with a high effective post-emergence herbicidal activity constituted by poly(ϵ -caprolactone) nanocapsules loaded with atrazine. In particular, the effects of both poly(ϵ -caprolactone) nanocapsules alone and loaded with atrazine on the unicellular green photosynthetic algae *Chlamydomonas reinhardtii* was evaluated, to study the response of the microorganism and optimise the analytical conditions of the biosensor. Then, the experimental set up was optimised for nanoatrazine detection, as well as, interference studies, matrix effect and recovery studies, and stability studies. Any variation in the growth, photosynthetic activity in terms of maximum fluorescence yield, and content of photosynthetic pigments was observed in the presence of both poly(ϵ -caprolactone) nanocapsules alone and loaded with atrazine, a part from the variable fluorescence $I-V_f$ which decreased in dependence with the increase of nanoatrazine concentrations. This parameter was thus exploited as algal response towards nanoatrazine in a concentration range between 0.5 and 200 nM indicating a linear relationship in the measured dose-response curves and detection limits of 4.8 pM. Interference studies demonstrated the suitability of the algae to detect nanoatrazine also in drinking water, a defenseless matrix in case of terroristic attack, where copper and arsenic could be present at safety limits. Very slight matrix effect was evidenced, with ratios of 0.86 for calibration curve in tap water samples with respect to standard solutions. A recovery value of $100 \pm 5.7\%$ was achieved for a nanoatrazine concentration of 75 nM in tap water. Once optimised all the experimental conditions, algae were immobilised on a paper substrate soaked with an agar hydrogel to form a sort of tin film for algae absorption. The obtained paper algal biosensor was challenged for nanoatrazine detection demonstrating its suitability for applications in smart agriculture, providing a detection limit of 4.2 pM in both standard solutions and real samples, very slight interference from the presence of copper and arsenic at safety limits, as well as slight matrix effect and a satisfactory recovery value of $96 \pm 4.9\%$ for 75 nM nanoatrazine in tap water. This study open perspective for the use of biosensors for nanoatrazine detection in drinking water in special due the high persistence in the environment and consequently the contamination of soil, water resources, food and humans.

Keywords: Paper-based biosensor, nanoherbicides, photosynthetic algae,

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Acknowledgement:

This work was supported by NanoSWS project EraNetMed - RQ3-2016. The authors express gratitude to the staff of the Institute of Crystallography (National Research Council) in the person of Loredana Caccavale for her precious help in working on laboratory experiments with photosynthetic microalgae.



A Coordination-Driven Triangle as Nanoreactor

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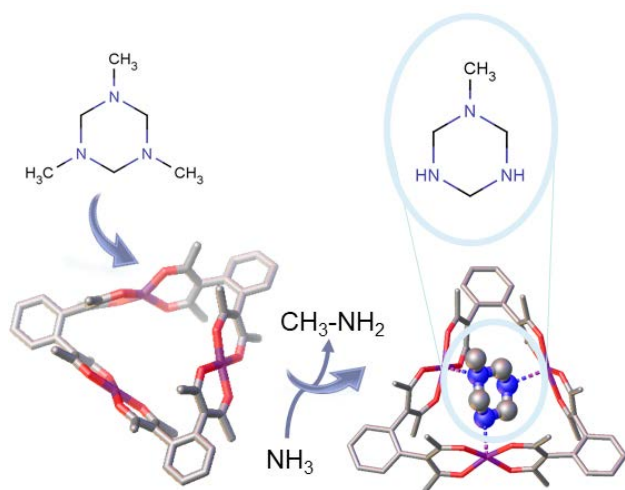
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Metallo-supramolecular architectures generated from metal centres and well designed polytopic ligands are an excellent bench test for supramolecular and self-organization concepts and a wide source of new functional materials. In particular, coordination-driven discrete boxes and capsules have drawn increasing attention due to their hollow superstructure. Such architectures provide space confined cavities for a variety of applications including storing, sensing, and nanoreactors.



In this context, we studied the metallo-supramolecular triangle $[\text{Cu}(\text{o-L})_3]$ generated by self-assembly between Cu(II) ions and a bis-acetylacetonate ligand [1,2]. $[\text{Cu}(\text{o-L})_3]$ is a metallo-macrocyclic with a triangular cavity endowed with host-guest properties. We show that this system can act as nanoreactors for the oxidation of PTA (1,3,5-triaza-7-phosphaadamantane) under soft conditions and for de-alkylation of hydrotriazines. The role of the solvent as oxidation trigger and its influence on the stability of the metallo-supramolecular host is also discussed. These results are supported by a combination of FT-IR analysis, absorption spectroscopy and single crystal structural studies.

Keywords: metallo-supramolecular systems – oxidation – confined space reactivity

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β -Cyclodextrin Inclusion Complexes of Natural Occurring Compounds and Their Evaluation as Insect Repellents in a Push-Pull Strategy

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β -Cyclodextrin (β -CD) is an amphipathic toroid consisting of seven D-(+)-glucopyranose units linked by α -(1-4) bounds with a hydrophobic cavity that is capable of forming inclusion complex with hydrophobic guests of suitable size and shape and an outer hydrophilic surface [1]. β -CD has the ability to form inclusion complexes resulting in significant improvement in water solubility and stability of the guest molecule whose taste and odor are partially masked. β -CD is produced from a renewable natural material (starch) by a sustainable biotechnological process, it is commercially available in large bulk at relatively cheap price, it is nontoxic in consumable concentration and it is biodegradable. Its use in pharmaceutical, textile, food industry and recently in cosmetics and detergents is widely known, however, a few examples are present in agriculture as sustainable matrix to improve agrochemicals effect.

Drosophila suzukii (Matsumura) (Diptera: Drosophilidae), spotted-wing drosophila, has recently become a common and serious pest of temperate fruit crops (small fruits, cherries and kaki) in many countries [2]. Crop damage is caused when adult females, using a serrated ovipositor, lay eggs in ripe and partially ripe fruit before harvest. Developing larvae cause soft and unmarketable fruit, moreover oviposition wounds provide access to pathogens that may enhance fruit deterioration leading to increased risk of secondary rot infections with an economic losses up to 80%. Push-pull strategies (stimulus deterrent diversionary strategies) attempt to reduce crop injury by modifying pest distribution using adversative stimuli to push the pest organism away from the crop while also using attractive stimuli to pull the pest organism out of the crop [3]. A novel and more sustainable method for repelling *D. suzukii* was evaluated by spraying edible repellents (alone and in mixture) on fruit surface during ripening period in combination with conventional natural attractive traps.

The project, started in March 2018, join expertise in organic chemistry, physical chemistry, entomology, insect physiology and crop protection.

Both edible repellents and synergists were selected from commercially available natural occurring compounds and their inclusion complexes with β -cyclodextrin (β CD) were prepared under sustainable conditions. All β -CD complexes were characterized by 1NMR spectroscopy and release time of the guest were calculated in aqueous solution.

Preliminary studies on effectiveness of complexes were carried out with laboratory-reared *D. suzukii* on artificial fruits. Under electrophysiological assay *D. suzukii* appeared to be sensitive to all selected edible repellents. Field experiments have been planned.



Keywords: β -cyclodextrin, natural occurring compounds, repellents

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Acknowledgement:

Regione Autonoma Sardegna, LR 7/2007, project CPR SDULCIS-821008



Green Analytical Chemistry (GAC) at ICCOM: the Role of Analytical Methodology Development

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Green analytical chemistry (GAC) emerged from green chemistry in 2000 after Anastas and Warner formulated the 12 principles of green chemistry [1].

One of the most active areas of Green Chemistry R&D is the development of new methods and techniques that reduce and eliminate the use and generation of hazardous substances [2], as well as the increase of knowledge to avoid threats to human health and the environment.

The analytical chemistry group at ICCOM Pisa has a long-term experience in the development of analytical methodologies for the determination of substances at trace and ultra-trace levels as well as in the chemical characterization of materials with spectroscopic and chromatographic techniques, achieving relevant objectives in this area. The main topics explored are the following:

(i) Development of microwave technology to improve catalytic processes, for the on line green photodecomposition and photodegradation of organic compounds for analytical applications and remediation strategies;

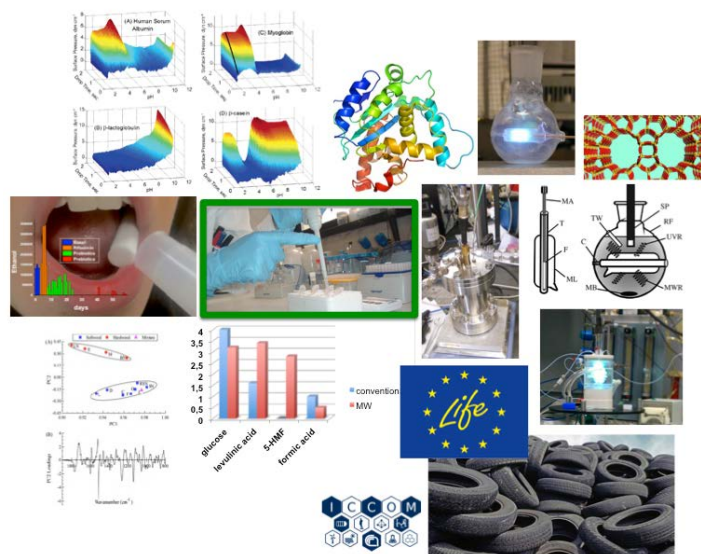
(ii) Development of spectrophotometric chemometric methods to avoid the sample treatment, the use of reagents, long procedures and the production of hazardous wastes;

(iii) Development of a miniaturized Dynamic Surface Tension Detector (DSTD) for the study of the rheological properties of water-soluble polymers, nanoparticles, proteins and complex matrices;

(iv) Non invasive, multi-analyte chromatographic methods coupled to multivariate analysis for the analysis of microbiota;

(v) Development of sustainable processes and novel "green" materials (LIFE+ projects 2012-2017)

Several topics will be discussed in the perspective of valorizing the possible interaction with research groups in other areas (green chemistry, chemistry for life sciences, advanced materials...).



Keywords:

Green Analytical Chemistry; microwave technology; non invasive methods.

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Acknowledgement:

The authors acknowledge Dr Carlo Ferrari and Dr Iginio Longo (INO-CNR) for supporting all the activities related to microwave technologies.



Permeation of Light Gases through Zeolite Membranes

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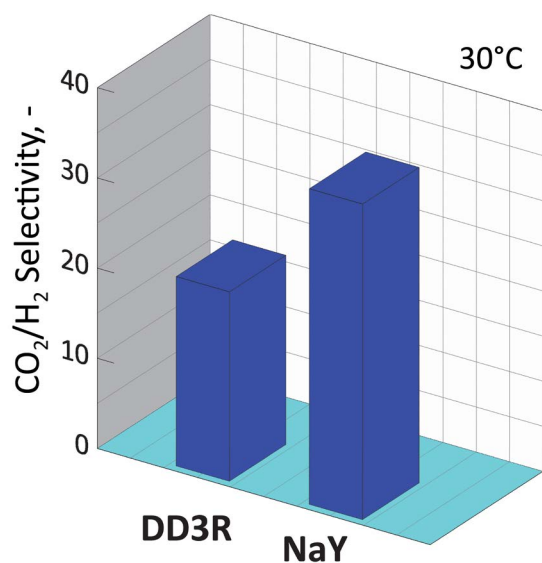
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Membranes are a suitable green alternative to the traditional technologies to separate light gas mixtures, requiring lower energy and operational costs, avoiding the use of solvents, as well as the necessity for extreme operating conditions, thus making the separation more sustainable. In this field, zeolite membranes are quite interesting owing to their high thermal and chemical stability allowing an effective use in a wide range of temperature and pressure. Zeolites are aluminosilicates having crystalline and microporous structure, which can be used for several applications, such as adsorption, catalysis, ion exchange, liquid and gas separation. In the field of gas separation, zeolite membranes show promising performance in terms of high permeance and selectivity.

Different zeolite membranes (NaY, DD3R, Silicalite, Sapo-34) were investigated for light gases separation (H_2 , CO_2 , CH_4 , CO and N_2) [1-3]. A particular attention was paid to the CO_2/H_2 and flue gas (CO_2-N_2) mixtures. In fact, H_2 is well recognized as an alternative energy carrier with zero-emissions, whilst CO_2 is today considered as one of the main greenhouse gases. Therefore, CO_2 separation and capture for an eventual further utilization is, today, one of the most important pillars to support and promote sustainability and to make the chemical industry competitive. Permeation of these gases through zeolite membranes was analyzed considering the presence of surface and Knudsen diffusion. In particular, Knudsen diffusion was affected by surface diffusion, since the presence of an adsorbed phase hinders the free gas permeation inside the channel. This blocking effect was quantified in terms of a change of some zeolite pore parameters, such as the effective porosity, passage diameter and tortuosity [1]. This new model was validated in both single gas and mixture conditions for FAU-NaY [1] and MFI-Silicalite-1 [2] and was used for prediction of several gas mixtures in a wide range of temperature (270-800 K) and feed pressure (100-1000 kPa) [3]. The permeation in DD3R happens only to surface diffusion.

Adsorption of gases in these zeolites was also estimated by a deep analysis of the isotherm available in the literature [4-6] and the Langmuir and Sips model parameters were used as input for evaluating the surface diffusion contribution to permeation.

Among the main results achieved, zeolite membranes was found appropriate for CO_2 separation from other light gases in particular at low temperatures. The NaY membrane showed high CO_2/H_2 and CO_2/N_2 selectivity values (about 35 at 303 K), tending to the Knudsen value at high temperatures. This was attributed to the strong CO_2 adsorption, which hinders the permeation of the weakly adsorbing species (i.e., H_2 and N_2). On the other hand, adsorption tends to disappear with increasing temperature and, thus, selectivity strongly decreases. The DD3R was found also indicated for CO_2/H_2 separation, showing a selectivity of ca. 20 at room temperature. On the other hand, Silicalite-1 showed worst performance, having a CO_2 adsorption similar to DD3R but a bigger pore size. However, an increment of feed pressure positively affects the CO_2/H_2 selectivity.



CO₂/H₂ selectivity in DD3R and NaY for an equimolar mixture at 30°C

The obtained results suggest operating at a low temperature, in order to exploit the competitive adsorption and the consequent blocking effect in increasing the membrane selectivity. The NaY membranes are the best candidates for separation of CO₂/H₂ and flue gas mixtures for environmentally sustainable applications within an appropriate temperature range.

Keywords: Membrane selectivity; gas separation; permeance;

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Acknowledgement:

P.F. Zito gratefully acknowledges the “SIACE” Ph.D. Course held at the University of Calabria, Rende (CS), Italy.

The research project PON 01_02257 “FotoRiduCO2 - Photoconversion of CO2 to methanol fuel”, co-funded by MiUR (Ministry of University and Research of Italy) with Decreto 930/RIC 09-11-2011 in the framework of the PON “Ricerca e competitività 2007-2013”, is gratefully acknowledged.



Micro-Engineered Capsules: a Powerful Tool in Green Chemistry

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To truly take advantage of the benefits offered by advanced materials, engineers need to adopt a “multiscale” approach to materials design (from molecular to nano, meso, micro and macro), considering how different length scales and diverse structures contribute to the bulk properties of their final product. Cutting-edge technologies such as nanotechnology and biomimicry address such challenge, and become successful when the deliver structure (nano-enabled products, powders, scaffolds, coatings preserves the active/functional properties exhibited at molecular or nanoscale. The particle enlargement by agglomeration technique (granulation), that transforms fine powders into free-flowing, dust-free granules easy to encapsulate active phases and to be easily compressed, handled, stored or recovered, is a key step of many multi-length state processes. In order to succeed in passing from a liquid state, in which nanoparticles together with molecular additives are dispersed (colloidal state) to solid micro-granules, the spray methods (spray-drying, spray-freeze-drying) are the best candidates. These techniques allow obtaining spheroidal and homogeneous micrometric powders by nebulization and subsequent elimination of the solvent from the drops of dispersion. We will show three case studies, to empathising the high versatility of such techniques and of the resulting micro-engineered ceramic capsules. Indeed they represent powerful design solutions in very different field of application: photocatalysis [1], luminescent materials [2] and nano-safety [3] (Figure 1).



Micro-engineered capsules used as a) photocatalyst; b) luminescent materials; c) carrier of potentially hazardous nanoparticles.

The possibility to characterise precursor at wet colloidal state and to optimise charges in order to promote an electrostatic attraction between host matrix and embedded active phase, is a fundamental step of these multiscale processes. Before any encapsulation/granulation step we fully characterised colloidal properties of precursor suspension and found the best condition to maximise stability but also interactions between each component. We tested for case study 1) the photocatalytic efficiency in the degradation of synthetic organic pollutants; for case study 2) the luminescent properties and the washing fastness; for case study 3) the stability of encapsulating organic granules and estimated the release of nano-Ag when granules are dispersed in water.

Keywords: engineered microcapsules, photocatalyst, safe by design



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CHEMISTRY AND ENERGY



ORAL COMMUNICATION



Organic Components of Perovskite Solar Cells

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Hybrid organic-inorganic perovskites of various nature are actively investigated as basic components in many optoelectronic devices, because of their peculiar properties including strong light absorption properties, high charge-carrier mobility and small exciton binding energy. In particular, perovskite solar cells (PSCs) have undergone a remarkable and surprising development over a few years, with certified power conversion efficiency values (PCEs) rising rapidly from 3.7% to 22.1%. PSCs have thus the potential to complement silicon-based photovoltaic technologies.

The success of PSCs is strongly related to the development of suitable organic compounds (small molecules and polymers) that proved to be essential in the fabrication of highly efficient devices.

As a part of an ongoing research program aimed at the design and synthesis of organic compounds for PSCs, we developed two broad families of molecular hole transporting materials (HTMs), namely spiro-configured molecules containing dithiophene derivatives, [1] and diarylamino-substituted metallo-phthalocyanines [2]. A systematic investigation of PSCs featuring these HTMs has been performed in collaboration with the team of Prof. M. K. Nazeeruddin (EPFL, Switzerland). PCEs up to 20.2% were obtained in the case of molecules characterized by a mixed fluorene-cyclopentadithiophene core [3].

We have recently turned our attention to the design of solvophobic ammonium salts and their use in perovskite formulations. These organic cations have a deep influence on the phase dimensionality of the inorganic lattice and on the optoelectronic properties of the resulting hybrid perovskite materials, as highlighted by a study undertaken in the frame of the CNR-Short Term Mobility Program 2017 at the EPFL laboratory. Preliminary results obtained for PSCs fabricated with the new materials showed an increase in device stability without detrimental effects on PCEs.

Keywords: Organic synthesis, Hybrid perovskite, Solar cells

References:

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Acknowledgement:

We gratefully acknowledge continuous support by Prof. M. K. Nazerrudin and coworkers at the Group for Molecular Engineering of Functional Materials of the École Polytechnique Fédérale de Lausanne-Valais. SO gratefully thanks CNR-Short Term Mobility Program 2017.



Catalysts 2.0: a New Technology at the Forefront of Processes at the Heart of Renewable Energy Technology

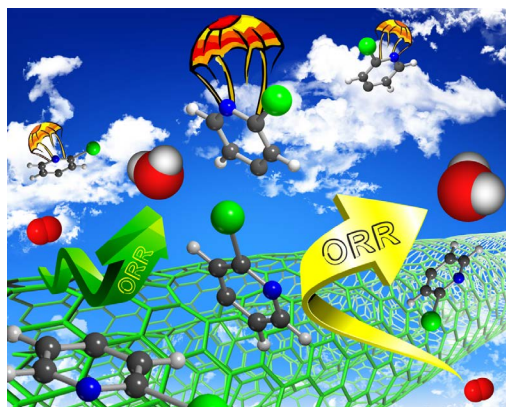
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With their unique physical and chemical properties, carbon nanomaterials (CNMs) represent nowadays one of the most valuable tools in heterogeneous catalysis. Beyond their application as simple supports for metal nanoparticles, CNMs as such or in the form of light-heterodoped systems have shown excellent properties as metal-free heterogeneous catalysts in a series of key transformations. The real nature of the active sites responsible of their ultimate catalytic activity is far from being definitively unveiled, as well as their final mechanism of action. However, it is commonly accepted that surface topological defects and electronic redistributions driven by the presence of functional groups play a crucial role on the (electro) catalytic performance of these materials. For this reason, the last decade has shown a real boost towards the development of carbon nanomaterials, particularly in their doped form with light elements (mainly N, B) as metal-free promoters for a number of key industrial processes. The development of cheap, highly efficient and selective catalytic materials (catalysts 2.0) for the sustainable development of devices and processes at the heart of renewable energy technology passes through the accomplishment of the following points: 1) the tailored bottom-up synthesis of complex nanostructures with at least one dimension at the nanometer scale; 2) the intensive research effort in reducing or replacing critical raw materials (e.g. PGMs) from catalysts; 3) the in-depth comprehension of the underpinning mechanisms which drive and control the activation and (electro) chemical conversion of challenging small molecules for their valorization as renewable energy sources.

Our recent outcomes in the field move from a rational bottom-up design and synthesis of a series of metal-free 1D-3D carbon-based materials decorated ad hoc with chemically tethered surface functionalities and applied as heterogeneous (electro)catalysts to promote a variety of key industrial transformations:



from the challenging activation and electro-reduction of small molecules (i.e. O_2 and CO_2)^[1,2] to the rethinking of the current alkanes dehydrogenation technology^[3], one of the most energy demanding transformation at the core of polymer industry.

The tailored nature and composition of the catalytic materials offer unique clues to debate on the structure/activity relationship of these systems in catalysis.

Keywords: heterogeneous catalysis, materials chemistry, renewable energies

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Acknowledgement:

Thanks are due to the Italian MIUR through the PRIN 2015 Project SMARTNESS (2015K7FZLH) “Solar driven chemistry: new materials for photo- and electro-catalysis” and TRAINER project (Catalysts for Transition to Renewable Energy Future) of the “Make our Planet Great Again” program (Ref. ANR-17-MPGA-0017) for support.



Supported Pd and Pd-Au Membranes for Hydrogen Generation and Purification

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In the last years, hydrogen utilization as energy carrier has involved a high demand on hydrogen permeable membranes as compact devices for its separation and purification [1]. As reported in the specialized literature, composite Pd-based membranes demonstrated to be very effective for the aforementioned purposes [2], particularly if compared to the utilization of unsupported Pd-based membranes, because less expensive and more mechanical resistant [3]. The aim of this work is to propose a short summary about some Pd-based membranes used at ITM-CNR, paying particular attention to the preparation and characterization of composite Pd-alloyed membranes for hydrogen production (from reforming reactions of renewable feedstocks in membrane reactors) and purification (Figure 1).

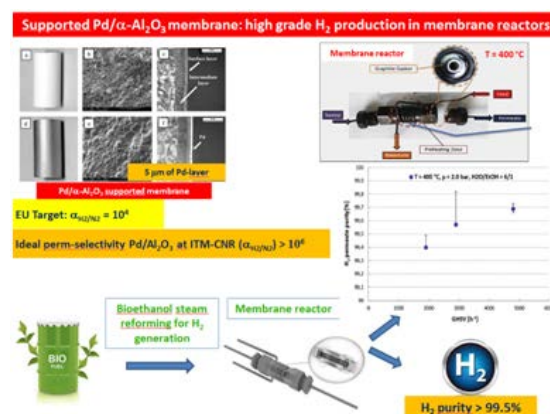


Figure 1. Example of experimental application of a Pd-Al₂O₃ membrane reactor module (bench-scale) for producing high grade H₂ (purity > 99.5%) from steam reforming of a real bio-ethanol mixture.

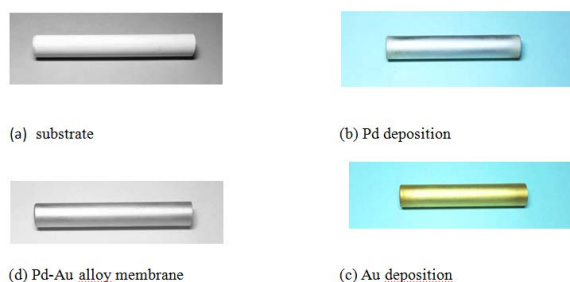


Figure 2. Electrodeposition steps for the Pd-Au/Al₂O₃ membrane preparation (Nanjing Tech University – China): a) ceramic substrate; b) Pd deposition; c) Au deposition; d) Pd-Au/Al₂O₃ membrane.

As a case study, a new generation of Pd-Au membranes supported on a porous substrate (Figure 2) is considered and an experimental characterization in terms of SEM analyses, XRD patterns, hydrogen permeance and pure gas selectivity is given.

Furthermore, the effect of temperature and pressure variation on the hydrogen perm-selectivity characteristics of the membrane is also considered and discussed. Last but not less important, the influence of thermal cycles on the membrane performance is also included.

Keywords: palladium membrane, hydrogen, membrane reactors

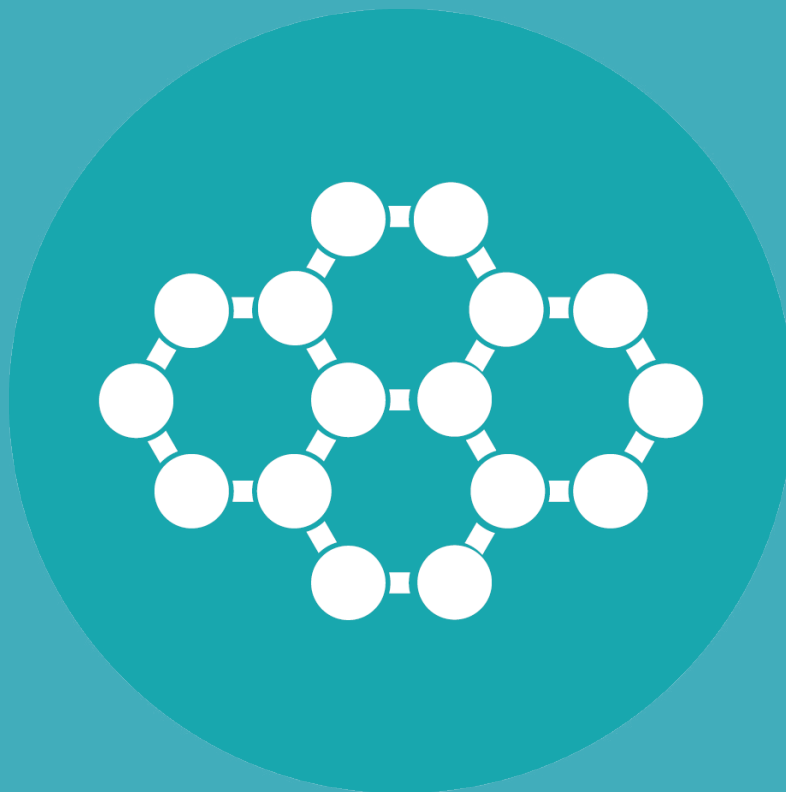
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Acknowledgement:

Stanford University (USA), Worcester Polytechnic Institute (USA) and Nanjing Tech University (China) are kindly acknowledged for their collaboration in the preparation and development of Pd and Pd-Au based membranes of this work.

ADVANCED MATERIALS



ORAL COMMUNICATION



New Anti-Fraud Method: the Proteomic Technique Applied to the Identification of Luxury Animal Fibers

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Leading companies in the textile sector need objective and precise analytical methodologies able to univocally identify and quantify animal hair fibers present in textile articles, to guarantee that no falsification occurs, especially when cheaper fibers, like wool and yak, are blended with expensive fibers, like cashmere.

Traditionally, the methods used for fibers identification are: light microscopy, that gives information on the internal and external structure of the fibers, reveals details of the shape, cuticle morphology, internal pigmentation and medullation; and scanning electron microscopy (SEM) that shows the fine structure of the cuticle cells at high resolution. Anyway, these methodologies are subjective, depending on the expertise of the operator, and often are affected by chemical treatments to which the fibers have been submitted during textile processing. Several methods have been developed in the past to remedy these problems, with poor results.

CNR-ISMAL of Biella in collaboration with the Department of Food and Drug of the University of Parma developed a new method for qualitative and quantitative analysis of animal hair fibers. The method based on electrospray (ESI) mass spectrometry (MS) combined with liquid chromatography (LC) follows a proteomic approach to assess molecular markers for species identification [1-3]. In particular, the method focuses on the identification and quantification of wool, cashmere and yak fibers. Keratin from sheep, cashmere goat and yak are similar but not identical, because in some specific parts there are amino acidic variants resulting in specific peptide-markers which can be used to distinguish each animal fiber. The procedure includes an enzymatic digestion of the keratin after the protein extraction in order to obtain similar but not identical homologous peptides, which can be discriminated by LC/ESI-MS analysis. These markers have been successfully used not only for qualitative analysis of wool, cashmere and yak blends, but also for quantitative ones, with a limit of detection of 3%.

Recently, this proteomic method has become international standard: "ISO 20418-1 Textiles - Qualitative and quantitative proteomic analysis of some animal hair fibres Part 1: Peptide detection using LC-ESI-MS with protein reduction". The standard method will be also adopted by CEN (European Committee for Standardization) and UNI (Ente Nazionale Italiano di Unificazione) soon.

In the meantime, ISMAC Biella is continuing its research to verify the applicability of the proteomic method also to the South American camelids (lama, alpaca, vicuna and guanaco) and camel hairs, so that in the future it will be possible to extend the standard to these fibers as well.

Keywords: animal fibers, LC/ESI-MS, proteomic method.

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Thiazole and Pyrazole-based Metal-Organic Frameworks for Gas Storage and Catalysis

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Metal-Organic Frameworks (MOFs) are coordination networks containing potential voids formed by metal ions or oxo-metallic clusters connected by polytopic ligands, with over 80,000 crystal structures reported so far. The extraordinary versatility in MOFs design (achieved through the tailored combination of linkers and metallic nodes) is the main reason of the applicative success of this class of materials. MOFs have unique advantages including the control of pore shape and dimensionality, tailored chemical environment and large surface area. The presence of heterocycles in the MOF organic linker opens new perspectives for a number of practical applications, like gas storage and catalysis. Among the various options, pyrazoles and thiazoles are intriguing, for different reasons. The former give rise to exceptionally stable (bridging) coordinative bonds with transition metals, imparting high thermal and chemical stability to the final material; the latter are the simplest (N,S) heterocycles conceivable and exhibit fluorescence properties (benzothiazoles are present in luciferines, bioluminescent substances that are produced by fireflies). MOFs featuring pyrazole- and thiazole-based linkers as organic building blocks (Figure 1) have been prepared and fully characterized in the solid state. Their performance as CO₂ storage materials [1] and as heterogeneous catalysts for carbon dioxide conversion into cyclic carbonates under green conditions [2] has been scrutinized. The results will be presented.

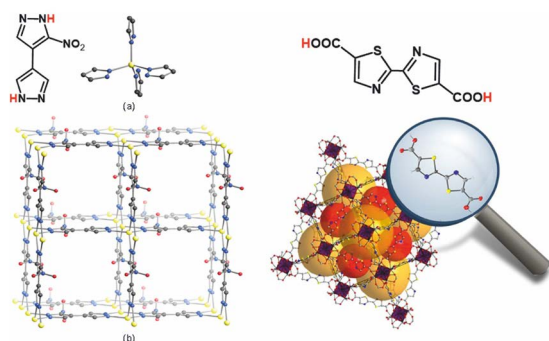


Figure 1. Left: (a) Zinc coordination sphere and (b) portion of the crystal packing viewed along the [001] direction of $[Zn(BPZNO_2)]_\infty$, where $BPZNO_2 = 3\text{-nitro-}4,4'\text{-bipyrazole}$. Right: The “UiO-67 analogue” $[Zr_6(O)_4(OH)_4(L)_6]_\infty$. $L = 2,2'\text{-bis(thiazole)-}5,5'\text{-dicarboxylic acid}$.

Keywords: Metal-Organic Frameworks (MOFs), thiazole, pyrazole

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Acknowledgement:

S.G. acknowledges Norberto Masciocchi (Università dell'Insubria) for fruitful discussions and Università dell'Insubria for partial funding. G.T. and G.G. thank the Italian MIUR through the PRIN 2015 Project SMARTNESS (2015K7FZLH) for financial support. A.R., S.G. and C.P. acknowledge the COST Action CM1302 “European Network on Smart Inorganic Polymers” (SIPs) (<http://www.sips-cost.org/home/index.html>).



Bio-hybrid Nanostructured Cellulose Membranes as Functional Tools for Bio-separation and Bio-recognition Applications

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The conjugation of biomolecules with synthetic materials is an advanced technique to date used in a wide range of biotechnological applications, e.g. diagnostic, separation, bioprocess applications. This 'hybrid' combination of a biological entity and a support material confers advanced 'biological' functionality to the support material and, at the same time, promotes the stabilization and permits the reuse of the costly biological molecule, giving also the possibility to tailor the properties of the solid surface. Today, a great interest is devoted to nanostructured materials as solid supports, among which membranes are increasingly attractive because of their unique properties: they allow to combine separation with molecular recognition in a single operation unit.

The development of a bio-hybrid surface need consideration of different parameters. Indeed, the immobilization of a protein and the related bio-activity and stability are dependent on several factors including the method used for the bio-conjugation, the properties of the surface, the properties of the protein and the immobilization conditions. After the immobilization, biomolecules have to maintain their function, to retain their biological activity, to remain closely bound to the surface. The choice of the appropriate membrane material and immobilization method are of primary importance. Also, a deep knowledge of factors affecting the immobilization process is required in order to tune the degree of bio-functionalization.

In this work, the development of bio-hybrid cellulose membranes for application in bio-recognition and bio-separation processes is presented. In particular, the study on the influence of protein bulk properties on the immobilization process and the development of bio-hybrid membranes able to recognize and capture target molecules of diagnostic interest on the base of immuno-affinity interactions is illustrated.

Cellulose membranes were chemically activated in order to introduce reactive aldehyde groups on its surface for proteins attachment. The immobilization process was studied by using three model proteins having different properties and behavior: BSA, protein G, the enzyme lipase from *C. Rugosa* [1]. The effect of the proteins bulk properties (concentration, size and aggregation phenomena) on the i) kinetics of binding, ii) surface coverage, iii) structural rearrangement and the proteins bio-activity after immobilization were studied. The bio-functionalized membrane with protein G was employed to develop immuno-affinity membranes, with immobilized specific antibody, for the capture and recognition of interleukin 6 (IL-6), a cytokine involved in inflammatory processes. In particular, the ability of protein G to bind antibody with spatial orientation was exploited for the site specific and oriented immobilization of the antibody to IL-6. Two different strategies were used: 1) the immuno-affinity membrane was directly used for the IL-6 capture; 2) the specific antibody was stabilized by chemical cross-linking before IL-6 capture [2]. Several aspects and parameters were studied and optimized: the ability of protein G to bind the antibody; the bio-recognition properties of both immuno-affinity membranes; the stability and selectivity of the antibody and the possibility of reuse; the improvement of the specificity of the system.

The results demonstrated that the aggregation behaviour of a protein has a significant influence on the bio-layer formation on the membrane surface (including surface coverage, protein distribution and rearrangement and protein bio-activity). Thus, a close correlation between the protein properties in solution and during immobilization was found.

The bio-functionalized membrane with protein G was successfully used for the oriented immobilization of the antibody to IL-6 showing a high antibody binding efficiency (88 %). The immuno-affinity membranes, prepared by the two different strategies, efficiently captured the IL-6 antigen with a capture efficiency up to 91 %, also revealing a linear relationship between the amount of the captured IL-6 and the initial IL-6 concentration. Thanks to the cross-linking, the second strategy permitted the antibody stabilization and the regeneration and efficient reuse of the immuno-affinity system with similar performances of the first use.



Keywords: bio-functionalized membranes, proteins immobilization, molecular recognition

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Acknowledgement:

The authors gratefully acknowledge for the financial support to the project Nanomax (N-CHEM): "Nanomax-integrable sensors for pathological biomarkers diagnosis" from Programma Nazionale della Ricerca 2011-2013 (Progetto Bandiera).



From Tailored Molecules to Advanced Nanomaterials and Devices: Surface Protection, Light Absorption and NIR-Emission

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The current development of optoelectronics and nanoscience takes great advantage from the ability of organic, organometallic and hybrid compounds to fulfill specific needs and requirements.

Organic and organometallic molecules can be easily and judiciously engineered to tune the optical absorption and emission features, the electronic energy levels, the sterical hindrances and the solid state aggregation. Once a molecular framework has been identified as the suitable candidate for a given application, different techniques allow for the growth of the material as ultrathin film or in multilayer structures. Physical vapor deposition (PVD) is an extremely versatile technique; it benefits from the precise control on the deposition parameters (temperature, rate, thickness control down to few Angstroms) and contaminant-free environment.

In this contribution, three examples are going to be reported in which the molecular design and synthesis interplay with the film growth and device fabrication (Figure 1); considering our group expertise, two class of molecules will be presented: *iridium complexes*, which represent the emitters of choice in organic light emitting diodes (OLEDs), and *porphyrins*, as chromophores for organic solar cells (OSCs) and as organic two-dimensional layer inhibitors for the protection of graphite electrodes.

1- Commercial OLED displays and light panels are produced by PVD method. Our research in the field of OLED is devoted to the design of new emitting materials, in particular octahedral Ir(III) cyclometalated complexes and use PVD technology for the fabrication of prototype devices. The photophysical and electrochemical properties of these complexes are controlled by the chemical structure of the ligands and their emission can be finely tuned giving different colors, from UV to near-IR. Herein, we report our studies on modulation of color emission of OLED based on iridium emitters and the investigations of the degradation mechanisms acting in a model blue OLED based on the FIrpic complex.

2- Graphite electrodes are traditionally employed in batteries and graphene production but suffer from stability issues due to the severe working conditions. In this context, due to their stability and assembling properties, porphyrins represent a promising and unexplored class of organic molecules suitable as corrosion inhibitors. Our recent works reported the growth by PVD of ultra-thin (0.5 Å) and thin (12 Å) films of porphyrins on highly oriented pyrolytic graphite (HOPG), the latter used as model electrode-surface. The films grow as 2D wetting-layer with the presence of 3D-structure as a function of the thickness. Electrochemical-AFM investigations highlight the protective effect of porphyrin when HOPG undergoes oxidative stress. We move from a simple case study (metal-free tetra-phenyl-porphyrin, H2TPP) and explored the role of different peripheral groups on the porphyrin core. The groups are chosen to tune the electronic properties and the sterical hindrance of the molecules and their orientation on the graphite surface

3- Porphyrins have emerged in the last years as promising active layers for OSC due to their interesting optical and electrochemical properties. Rational design strategies can be adopted to best match their absorption



with the solar spectrum, introducing substituents at *meso*- or β - positions. Here, granted the morphological studies investigated in the graphite protection, we employed the same porphyrins (*i.e.* having different bulkiness and solid state packing) as donor materials in fully evaporated bilayer heterojunction OSCs.

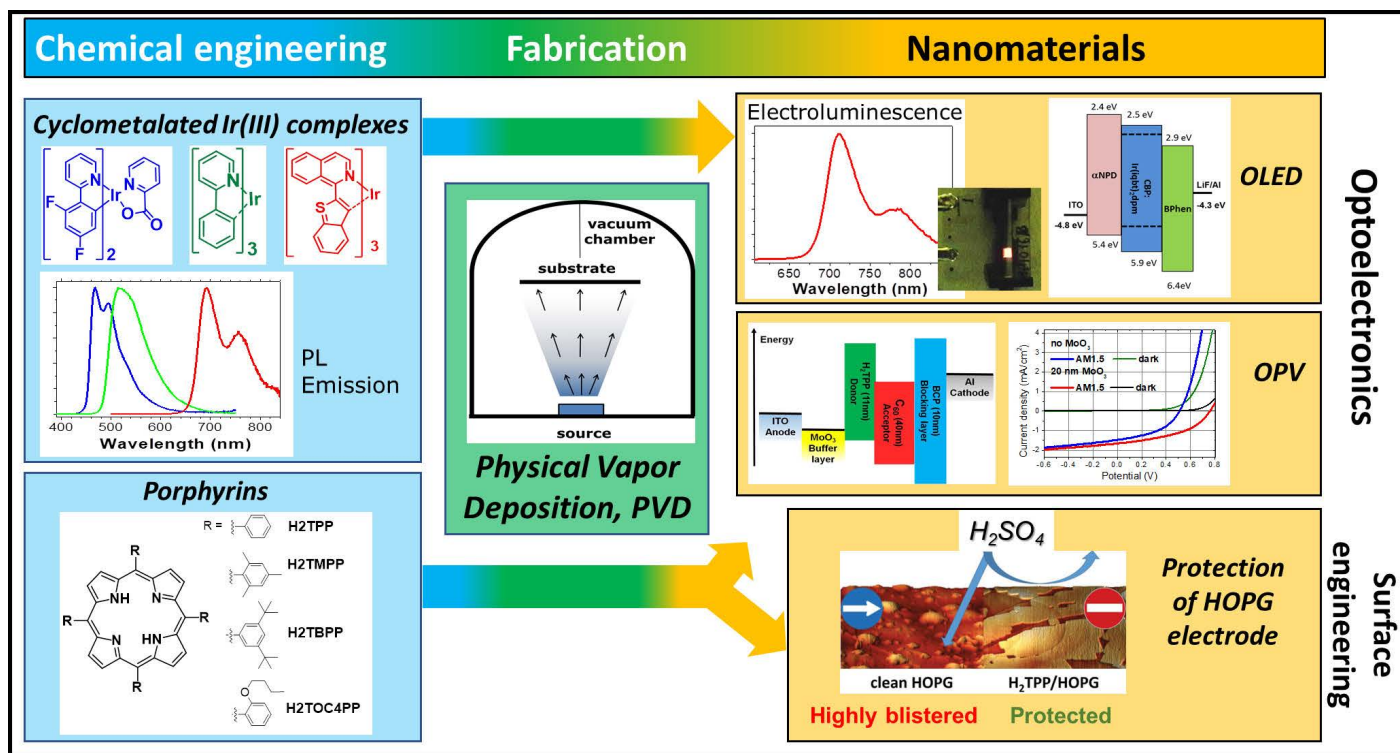


Figure 1. Selected examples of molecularly engineered materials and their applications

Keywords: Porphyrins – NIR-Emission – Graphite protection

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Acknowledgement:

SAMSUNG GRO 2014-2015; Progetto integrato Regione Lombardia – Fondazione Cariplo “SmartMatLab Center”; Accordo Quadro tra Regione Lombardia e Consiglio Nazionale delle Ricerche, progetto “I-ZEB Verso Edifici Intelligenti a Energia Zero per la crescita della città intelligente”



Development and Application of an Analytical Method to Determine Polyethylene in Compostable Carrier Bags

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The simple mixing of polymeric materials in the melt state, with or without chemical reactions taking place, is accomplished to create new materials with the desired combination of properties. Blending can be carried out by using conventional machinery, i.e. no expensive investment is necessary, which is an important feature for industry. In general, the specific motivation for blending is not to change the properties of the components drastically, but cost reduction, improvement of mechanical properties, impact resistance or the decrease of sensitivity to water. Polyolefins are widely used in blends, in particular polyethylene (PE) for its versatility, mechanical properties and low cost. The introduction of a polyolefin component in a biodegradable matrix may have some significant advantages in terms of processability and properties, as well as cost. However, it is well known that PE cannot be considered biodegradable. According to European Standard EN 13432-2000, each significant organic constituent of a compostable packaging material must be biodegradable. "Significant" constituent is any constituent present in a concentration higher than 1% of dry weight of that material. This requirement implies that a concentration of PE of maximum 1% is considered to be as an acceptable contamination of the biodegradable and compostable material, while a concentration higher than 1% would make the material not compliant with EN 13432. The identification and quantification of the PE component in complex polymer blends can be difficult. Traditional techniques, such as FTIR, or wet methods with selected solvents can be useful but time-consuming and not reliable.

In this work, the amount of PE contained in complex biodegradable polymer blends and in carrier bags claimed to be compostable was determined by thermogravimetry analysis (TGA) and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). To validate the method, polymer blends based on polylactide (PLA, Ingeo 4043D, Natureworks), poly(butylene adipate-co-butylene terephthalate) 53/47 (PBAT, Ecoflex 7025 - Basf), native starch (NS, Cargill), and CaCO_3 (Sigma Aldrich), with known amount of PE (Lupolen 3020K, Basell) ranging from 0 to 10%, were prepared by melt mixing. In the first step at 400 °C of Py-GC/MS, pyrolysis products originated from thermal cracking of PLA, NS and PBAT were detected. In the second step carried out at 500 °C, GC triplet peaks characteristic for PE, consisting of α,ω -dienes, α -alkenes and n-alkanes, were revealed together with some signals related to PBAT (Figure 1).

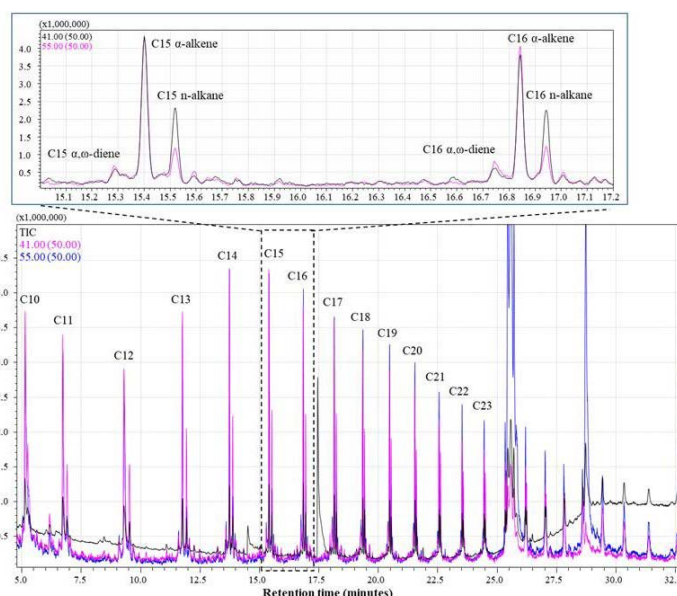


Figure 1. TIC and single ion current (SIC) traces of m/z 41 and 55 of the degradation products at 500°C of the blend with 10% of PE.

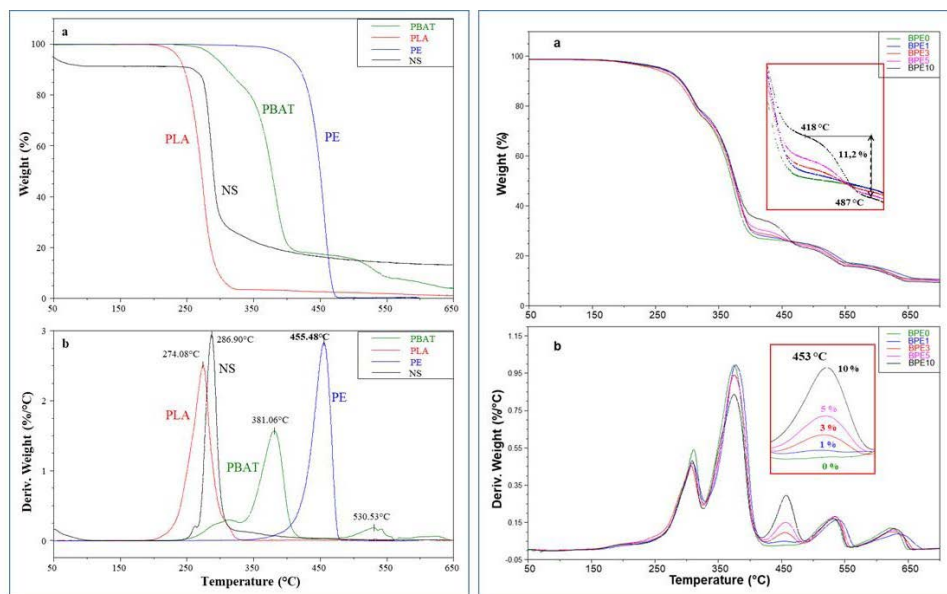


Figure 2. TGA (a) and DTG (b) curves of the single polymeric components and of the blends with different percentage of PE.

TGA under nitrogen atmosphere was used to determine the amount of PE in the blends. Figure 2 shows the TGA e DTG curves of the single polymeric components (PLA, NS, PBAT and PE) and of the blends with different percentage of PE. The thermal degradation curves of PLA and PE samples display a single decomposition process, while that of PBAT shows three steps of degradation. Several steps of degradation due to the various components and a good separation of the degradation step of PE can be observed. At

about 455 °C the degradation step of PE can be clearly distinguished from the others. The percent amount of PE, determined by the weight loss of TGA, show an overestimation of about 1.2%, respect to the nominal value, which is constant in all the polymer blends. The overestimation was attributed to the partial overlapping of one of the steps of degradation of the commercial PBAT and that of PE.

Additionally, the analytical approach was successfully applied in the characterization of carrier bags claimed to be “biodegradable and compostable” according to EN 13432. Since February 2016, the method has been regularly applied and further extended to check the presence of PE in more than 60 carrier bags certified as compostable and has contributed to reveal the incidence of illegal carrier bags on the market. Analyses were commissioned by Legambiente, private companies and laboratories. About the 33 % of the carrier bags analysed had a content of PE higher that the limit (1%) established in the European Standard.

Keywords: Biodegradable polymers, Polyethylene, Compostable carrier bags

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Acknowledgement:

This work was financially supported by the project “SHELF-LIFE—Integrated use of innovative technological approaches to improve the shelf-life and preserve the nutritional properties of food products” carried out by the Cluster Sicily Agrobio and Fishing Industry and funded by the Research Fund PON R&C 2007–2013, DD 713/Ric. (PON02 00451 3361909).



Microstructure, Wettability and Surface reactivity of AlSiMg System Used in Additive Manufacturing

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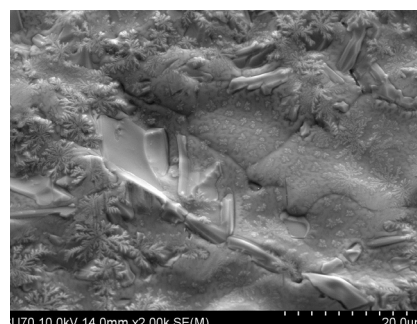
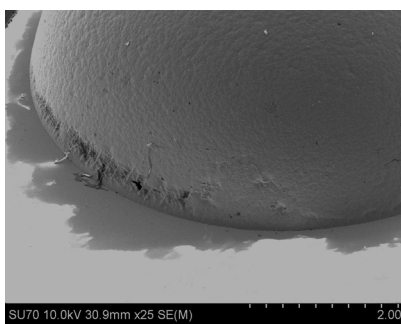
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Additive manufacturing processes, among which Selective Laser Melting (SLM) is one of the more promising, are transforming the traditional approach to metal fabrications, allowing not only to obtain challenging shapes, but also to induce particular microstructures that affect functional or structural properties. Several alloys are proposed for additive manufacturing and those of AlSiMg system are largely applied. AlSiMg system belongs to the wide family of the aluminum-silicon casting alloys, widely used for conventional casting and die-casting technologies. Magnesium addition allows precipitation hardening, obtained through the formation of beta phase (Mg_2Si) nanometric particles during post-cast ageing thermal treatment.

The thermal histories experienced by the material during additive processing, especially SLM, are quite different from those of conventional casting: rapid heating/cooling cycles and re-melting above pre-existing melted pools are typical of these new processes. Consequently, a reasonable concern aroused about suitability of conventional alloys to these processes. It is well known that AM microstructures are finer than conventional ones, but are also characterized by solidification defects such as porosity and, possibly, presence of oxides. The latter strongly affects stability, wettability and reactivity of the alloy at high temperature.

A study of the behavior of Al-Si10-Mg0.4 (wt. %) alloy at high temperature was undertaken in order to evidence differences from eutectic Al-Si12.6 (wt. %) alloy and pure Aluminum: wettability tests on Al_2O_3 were performed considering two different atmospheres (vacuum and Argon). Contact angle from sessile drop tests were compared and surface morphology and microstructures were analyzed by SEM/EDS.

In all cases surface oxidation was observed, even if to different extent and morphology. As expected, silicon was observed both as primary silicon crystal as well as eutectic structure, while magnesium effect need to be deepened.



SE micrographs of Al-Si10-Mg0.4 (wt. %) sample after sessile drop tests: a) side view at low magnification, b) higher magnification surface micrograph: aluminum matrix decorated with lichen-like oxides and smooth silicon crystals are visible.

Keywords: AlMgSi alloys, microstructure, wettability

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Smart Amphiphobic Surfaces for Challenging Industrial Applications

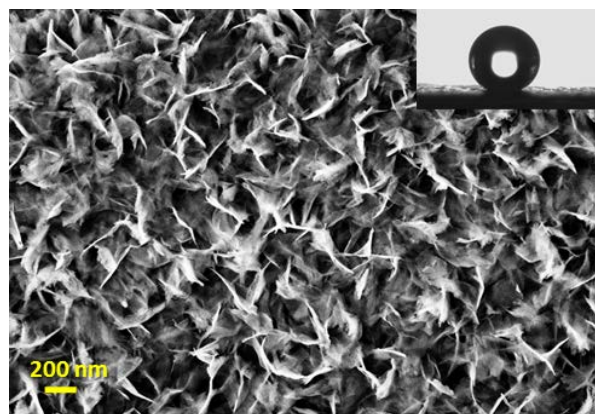
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The control of surface wettability has become an interesting area of investigation owing to its wide range of promising applications in different industrial sectors (maritime, aeronautic, hydraulic, energy, etc.) [1]. Furthermore, non-wettable surfaces have drawn huge interest due to their related self-cleaning, de-icing, anti-fouling, anti-soiling, friction-, drag- or noise-reduction properties. In order to create a surface allowing extreme repellence to water and oils and mimicking some living organisms (e.g. lotus leaf, taro leaf, shark skin etc.), a combination of micro and nano-structures with low surface energy have to be applied [2]. The replica of such natural surfaces allowed us to synthesize coatings able to change the material response to different environments by the control of their wettability.

In this work we produced amphiphobic (super hydrophobic/oleophobic) surfaces by means of a multistep process which acts by following the double approach: nano-structuration and chemical modification. Particularly we present a widespread comparative study among different coatings on aluminum surfaces, obeying the Cassie-Baxter model, which allowed us to identify for each tested coating their strength/weakness points. We have systematically changed several variables, investigating their influence both on anti-wetting performances and on durability. This way we have explored the effects impaired on the surfaces by considering the influence of: roughness of the aluminum substrate, surface nanostructure produced by the nanoparticles, composition of the inorganic layer (Al_2O_3 , TiO_2 , SiO_2), composition of the organic layer and employed solvent.



Typically the samples were dip-coated with different ceramic oxide nanoparticles prepared by sol-gel methods, thermally cured at temperature between 150-400°C and finally treated with a properly selected fluorine-organic compounds to introduce low energy functional groups. Here we focus on aluminum, but the same versatile process can be successfully applied to different substrates: glass, ceramics, metals and paper. A wide-range characterization revealed outstanding properties of the final aluminum surfaces, with features different from each other depending on the selected combination of variables. Basically we evaluated static and dynamic contact angles, microstructure (FESEM-AFM), surface chemistry (XPS), chemical durability and abrasion resistance.

We achieved really promising results, showing contact angles with water ranging from 130 to 178°, CA hysteresis lower than 3°, implying excellent drop mobility and CA with oils up to 150°. The microstructure evidenced homogeneous hierarchical nanostructures, with morphologies dependent on the kind of nanoparticles applied (fig.1), with a nanometric roughness and a final coating thickness of about 200-400 nm.

Results demonstrated that the prepared coatings hold their properties over time, from the mechanical point of view, tape-test and abrasion-test analyses evidenced a good adhesion to the substrate.

Durability tests were performed on coated samples in severe environments (acid, basic, saline solutions, freezing, UV irradiation) to check their physicochemical resistance and to reveal their potential applications. Results from some functional application tests will be presented as well (anti-icing and drag reduction).



Keywords: amphiphobic surfaces, nanostructured coating, sol-gel, anti-icing surfaces, drug reduction

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Acknowledgement:

This research received support from the U.S. Office of Naval Research Global (ONR Global)

COMPUTATIONAL MODELING



ORAL COMMUNICATION



Advanced Methods and Software for the Characterization Crystalline Materials by Powder Diffraction Data

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Innovative crystallographic methodologies and advanced computational tools are developed. They are also implemented in computer programs of great utility in every scientific and technological field where the characterization of a polycrystalline material is fundamental for the comprehension of the problem under study.

EXPO¹ is a software devoted to reveal the atomic crystal structure of compounds available in the form of microcrystalline powder. It requires only the chemical formula and the experimental diffraction profile. It is able to investigate small molecules (up to 100 non-H atoms in the asymmetric unit), inorganic as well as organic and metalorganic. It can execute the following steps: 1) identifying the crystal cell parameters; 2) determining the space group; 3) solving the structure by locating the atom positions; 4) refining the crystal model.

QUALX² is a software for identifying the crystal phase(s) present in a powder sample. It automatically locates peaks in the experimental diffraction profile, subtracts the background noise, makes a search in crystal phase databanks and brings out the chemical phase(s) which best match the peaks in the experimental pattern. It is widely used in chemistry, pharmaceuticals, mineralogy, forensic science, cultural heritage. An online version of QUALX2.0 is in progress.

OChemDb³ (Open Chemistry Database) is a new free web portal which has been developed for assisting in the crystal structure determination process by surveying on bond distances, bond angles, torsion angles, atom types and space groups. It uses a suitably designed database of solved crystal structures. The use of OChemDb requires only a web browser and an internet connection. Every device (mobile or desktop) and every operating system is able to use OChemDb by accessing to its web page.

The software we develop, free for academic and non-profit research institutions, is based on sound theoretical principles and the most recent and advanced programming languages. It is supported by a high level of automatism and graphic interface, which makes its use simple also to non-expert in crystallographic knowledge and worldwide used. Moreover, it is continuously improved in terms of computational and graphic performances and tested on a large powder diffraction data bank. Examples of application will be presented.

Keywords: crystal structure solution, qualitative analysis, crystal chemical database

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Exploiting Quantum Phenomena to Design Electron Transport in Nanojunctions

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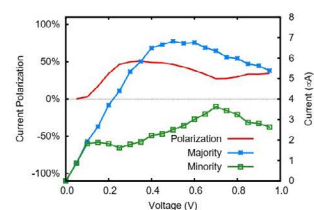
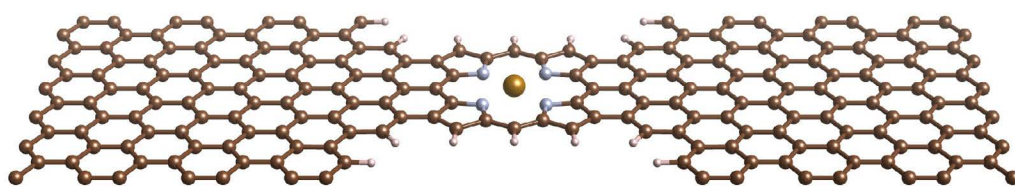
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The miniaturization of electronic devices requires a novel approach in the design of such apparatuses. Indeed, as their size scales down towards the atomistic level, their electronic transport properties cannot be rationalized by classic physics, and the use of quantum mechanics becomes mandatory. In this talk I will show that the choice of a quantistic approach paves the way towards the conception of a new class of nanojunctions in the emerging field of nano-electronics and spintronics.¹

The following test cases will be shortly illustrated:

- 1) A two-dimensional device made of a single graphene sheet. The regular adsorption of transition metal atoms allows for the filtering of electrons of one spin component only.
- 2) A one-dimensional porphyrine junction between two semi-infinite graphene sheets. Since electrons are forced to run through the molecule, the spin-dependent flow of the current is strongly influenced by the structure and the chemical properties of the molecular junction.
- 3) A prototypical Ag/MgO/Ag nanojunction. Though classically no current flow is allowed in this system, electrons do flow from one electrode to the other by the tunnel effect. Engineering the presence of defects in the oxide layer allows to tune the response of the system to an external voltage, obtaining devices suitable for selected applications.
- 4) A junction built with the following sequence of materials: Pt/Cr/MgO/Pt, thus containing both an insulating layer (MgO) and an antiferromagnetic one (chromium). The presence of alternate magnetic moments, combined with the oxide layer at just one side of the junction, makes this system a valuable spin filter based on the tunnel effect.



Keywords: Electron transport, spintronics, molecular junctions, electronic devices

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Computational Multi-Scale Modeling of Metal Oxide Nano-Particles and Surfaces

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The widespread growth of nanomaterials in many technological sectors has led to planned industrial investments for improving both nanomaterial properties and large-scale production strategies. In this context, appropriate computational protocols at the atomic and mesoscale levels have the potential to reveal valuable information for interpreting the experimental data and for predicting and driving the production procedures. As a matter of fact, numerical simulations can in fact identify important effects regarding the growth mechanism of any given material and disclose the physical chemical properties at the nanoscale [1-3].

In this presentation, we will describe a multi-scale computational approach developed in our group able to provide peculiar structural information and shed light on structure/property relationships at the nanoscale, with particular attention to disclose chemical and physical processes taking place at the interphase between two different materials. Our protocol relies on the use of accurate first-principles (mainly DFT) models to derive a structural and energetical database to train and/or validate both Unreactive (Classical) or Reactive Force Field (ReaxFF) describing the different part of the systems. Both Classical and Reactive Molecular Dynamics (MD/RMD) simulations, based on the use of Force Fields trained for specific purposes, are then carried out in order to get access to static and dynamical structural information on length and time scales unreachable at the first-principles level. In general MD/RMD simulations are used for two purposes: (i) explore the Potential Energy Surface (PES) to single out low-lying energy structures (in conjunction with the use of a Global Optimization Monte Carlo statistical algorithm) and (ii) to investigate the time evolution of a given system. Our final goal is to derive physico-chemical descriptors which can feed meso/macro scale (coarse-grained) models aiming at going beyond atomistic resolution and extending time and length scales.

This research has been applied to metal-oxide-based materials with a great interest in both basic research and technological applications, in particular in the development of new catalyst systems. Three examples will be briefly discussed: (i) early growth stages of zinc oxide Nano Particles (NP) in plasma conditions focusing on the structural and stoichiometric features characterizing the growing particles; (ii) static, dynamical and catalytic properties of small platinum NP adsorbed on amorphous alumina; (iii) adsorption mode of fluorinated alkane chains on low-index crystalline ceria surfaces.

Keywords: Multi-Scale Modelling, Nano-Particles, Surfaces

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Acknowledgement:

This work is part of the European project NanoDome that has received funding from the European Union's Horizon 2020 Research and Innovation Programme, under Grant Agreement number 646121.

CHEMISTRY FOR CULTURAL HERITAGE



ORAL COMMUNICATION



Low Cost, Disposable and Self-Sustainable Paper-Based Platforms for SERS Analysis Applied to the Study of Natural Dyes

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Anthraquinoid dyes, aromatic compounds derived from anthraquinone, have been the most applied red organic colorants in the history of art. Their identification and characterization in artworks, such as textiles, can provide important information for dating, authentication, and conservation treatment of these objects. Generally, reversed-phase liquid chromatography is the method of choice for the analysis of dyes after a wet sample treatment, since most of their chromophores are polar and water-soluble compounds. Optical spectroscopic techniques cannot be compared with liquid chromatography, in that they do not separate the various components of a dyestuff, nevertheless their ability to rapidly analyze much smaller samples is remarkable in a museum context.

In this study, the surface enhanced Raman scattering (SERS) performances of paper-based substrates were investigated for application to the analysis natural organic dyes used in antiquity, especially in textile dyeing. For this purpose, SERS-active silver nanoparticles were produced by Pulsed Laser Ablation in Liquid (PLAL). PLAL presents some advantages when compared to conventional chemical preparation methods, namely the absence of reagents in the suspension and a higher control over the nanoparticles morphology that can be obtained by changing the ablation conditions. After characterized, PLAL nanoparticles were used to prepare disposable paper SERS substrates *via* drop-casting.

For the application to dyes analysis, two strategies were investigated. In the first, laboratory-dyed vegetable and animal textiles were micro-extracted with a mild aqueous treatment, and the liquid fraction deposited and pre-concentrated on the functionalized substrates. In the second method, Japanese rice paper functionalized with silver nanoparticles was tested for the direct analysis of solid samples to avoid any chemical treatment (“dry-state” SERS).

Keywords: SERS, paper-based sensing, natural dyes

Acknowledgement:

This work has been supported by Regione Toscana (Progetto INDACO – POR FSE 2014-2020). We would like to acknowledge prof.ssa Ilaria Degano (Università di Pisa, Dipartimento di Chimica e Chimica Industriale) for providing the samples.



Non-Invasive Investigations on Max Ernst's Masterpieces: Materials, Painting Technique and Alterations Products

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The present study, in the frame of a collaboration project with the Peggy Guggenheim Foundation in Venice, deals with non-invasive *in situ* investigations on three Max Ernst's masterpieces: Antipope, Zoomorphic Couple and Attirement of the bride. These investigations were focused on the understanding of the Ernst's painting techniques, in order to highlight the used materials and the possible presence of alteration products. The project is based on a multi-disciplinary approach which involves *in situ*, contactless spectroscopic techniques: Vis-NIR multispectral imaging, X-Ray Fluorescence spectrometry (XRF), External Reflection Fourier Transform Infrared Spectroscopy (ER-FTIR) and Raman spectroscopy. The multi spectral acquisition of the painted surfaces allows the detection of a variety of information about the used pigments and the presence of chromatic alterations related to the aging of varnishes, etc. Furthermore, the images acquired in individual spectral bands can be analysed statistically for revealing hidden features not directly visible in the single images as tighter and thicker brushwork in applying the paint. Concerning the used pigments, analyses has shown a complex palette, in which modern pigments coexist with the traditional ones. For instance red areas are mainly composed by azo pigments and ferric oxides. Moreover different pigments are mixed to produce particular hues and shadows. For instance, blue areas are mainly composed by phtalocyanine and/or prussian blue, mixed with TiO₂, depending on the desired lightness. The combination of XRF, ER-FTIR and Raman results has also allowed the discrimination between pigments and additives. Lithopone (BaSO₄ and ZnS) and bassanite (CaSO₄•H₂O) were identified in all the *oeuvres*, independently from the analyzed spots. The presence of these compounds can be associated to paint tubes additives rather than their use in a preparatory layer. This hypothesis is supported by considering the hefty pictorial layer and the detection of barium sulphate and bassanite overtones by ER-FTIR, which investigates tens of micron in depth. Vice versa the ubiquity of Pb, detected by XRF, a more penetrating techniques, could be associated to the use of a lead carbonate in the canvas preparation. Neither ER-FTIR or Raman, have shown ubiquitous signals attributable to lead carbonate. The nature of the paint binders and the related alteration compounds were thoroughly investigated by ER-FTIR. All the artworks show a broad C=O stretching absorptions, at $\approx 1740\text{ cm}^{-1}$, typical for a lipid based binder. The broadening towards low wavenumbers could be ascribed both to the presence of photo-oxidative products and to other C=O bearing materials, as bee-wax or synthetic varnishes. In general, alteration products, in the form of carboxylate and oxalate, were detected in all the paints. The presence of Zn carboxylate was especially identified in white/whitish areas, while oxalate are more evident in colored areas. The on-going project highlights that an integrated approach based on non-destructive techniques can successful provide useful information for the study of modern and contemporary oil paintings, by overcoming the intrinsic limitation of each single method.

Keywords: in situ analyses, paintings, Vis-NIR multispectral imaging, XRF, ER-FTIR, Raman

Acknowledgement:

Bando Torno Subito 2017, by Regione Lazio Fondo Sociale Europeo Programmazione 2014 – 2020 – Asse III Istruzione e Formazione is kindly acknowledged for the project grant of Martina Zuena



Assessment of weathering steel corrosion inhibition in NaCl solution by the natural extract of *Brassica Campestris*

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Weathering steels (known by the trademark COR-TEN) are widely used in industrial engineering for structural purposes (bridges, roads, high voltage towers, soundproof and sound adsorbing screens), in architectural cladding and urban finishing (buildings, façades and roofs), due to their good mechanical properties, good atmospheric corrosion resistance and a pleasant aesthetical appearance. Originally designed for industrial purposes, weathering steels have been also used in modern and contemporary art since the beginning of the 1960s, due to the bright colors of the protective and uniform layer (iron oxides/oxyhydroxides) which turn from yellowish to purplish, as well as reddish and brownish.

The remarkable performance of COR-TEN steel needs some crucial pre-requisites to occur: regular variation of wet/dry cycles; low concentration of chlorides ions; low concentration of atmospheric pollutants; surface orientation and construction details (1). Dry or wet climates or areas that remain permanently damp are not suitable for the formation of the adherent and protective layer. Coastal areas and harsh-weather environments represent two adverse conditions for the use of unpainted COR-TEN steel. In the presence of NaCl (marine context) or acidic rain water (polluted urban environment), it suffers high corrosion rates and the protective patina degenerates into severe corrosion products.

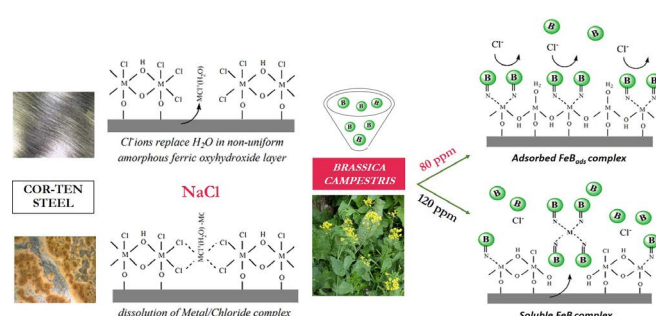
In this work the corrosion of COR-TEN steel by NaCl and by acidic solutions was investigated in order to simulate the conditions of a marine environment and a polluted urban atmosphere (2), respectively. The natural extract of *Brassica Campestris* was tested as potential corrosion inhibitor as a function of the concentration at room temperature. *Brassica campestris* is a widespread plant in Southern Europe, easily available and commonly cultivated. Powerful spectroscopic techniques, such as Electrochemical Impedance Spectroscopy (EIS) and X-ray Photoemission Spectroscopy (XPS) were used for the assessment of the inhibition efficiency and the electrochemical modelling of the processes.

The best inhibition efficiency (80-84%) was found for the addition of 80 ppm of *Brassica campestris* to NaCl solution, because of the formation of insoluble complexes resulting from the combination of the metal cations and the organic molecules adsorbed on COR-TEN surface.

The addition of higher concentration (120 ppm) of *Brassica campestris* resulted detrimental, since a decrease in the charge transfer resistance was observed. This effect can be explained by the formation of highly soluble organometallic complexes that induce the dissolution of the metal, similarly to the action of pure chlorides ions.

In Figure 1 the dissolution mechanisms of COR-TEN steel in NaCl solution and the effect of the addition of different concentrations of *Brassica Campestris* extract are shown.

Fig. 1. COR-TEN corrosion/inhibition mechanisms in NaCl solution.





A very weak inhibiting effect of *Brassica campestris* on COR-TEN corrosion was detected in acidic solutions, where the highest inhibition efficiency (~ 31%) was obtained for 120 ppm Brax.

The synergetic use of these surface and electrochemical techniques proved to be a powerful tool for understanding the mechanism of COR-TEN corrosion/inhibition in NaCl in the absence and in the presence of different concentration of natural extract of *Brassica campestris* [3].

Keywords: Weathering steel - Marine corrosion - ‘Green’ corrosion inhibitors

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Acknowledgement:

Financial support by the PON03PE_00214_1 TECLA Project: “Nanotecnologie e nanomateriali per i Beni Culturali”, Distretto di Alta Tecnologia per l’Innovazione nel settore dei Beni Culturali della Regione Sicilia, is gratefully acknowledged.

CHEMISTRY FOR LIFE SCIENCES



ORAL COMMUNICATION



Creating Neurodegenerative Diseased Tissue Model in a Membrane Bioreactor

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One of the most common goals in neuronal tissue engineering is to provide systems and devices that can reproduce tissue-like microenvironments *in vitro* promoting and guiding neuronal regeneration. The challenge is to create 3D neuronal models for neurorepair and/or for the study of neurobiological events, pharmacological screening, and as investigational platform for neurodegenerative disease [1-2]. Notably, polymeric membranes can promote the formation of membrane–neuron hybrid systems that, thanks to their selective structural, physico-chemical, mechanical and transport properties, are able to drive neurite outgrowth and branching, network connectivity, and synaptic plasticity leading to the successful *in vitro* reconstruction of neuronal tissue. Within this scenario, our strategy was to develop high performing neuronal membrane bioreactors as a platform for the *in vitro* reconstruction of neuronal networks with defined functional, geometric, and neuroanatomical features [3]. Our approach was to combine membrane characteristics such as geometry and configuration, as well as the intrinsic structural features of the poly-L-lactic acid highly aligned microtube array (PLLA-MTA) membranes, with the uniform fluid dynamic conditions within the bioreactor, in order to develop a well-controlled microenvironment able to trigger neuronal differentiation.

We tested the ability of the membrane bioreactor to provide a well-controlled microenvironment with suitable conditions for promoting neuronal regeneration *in vitro*. The neural membrane bioreactor was used as *in vitro* model of Amyloid beta (A β)-induced toxicity associated to Alzheimer's disease to test the neuroprotective effect of a phytoestrogen, Glycitein.

The bioreactor configuration provided a wide surface area for cell adhesion in a small volume, and offered a peculiar arrangement that directed neuronal orientation. The combination of an appropriate membrane porosity, pore interconnectivity and very thin walls ensured optimal indirect perfusion to cell compartment, and enhanced the mass transfer of metabolites and catabolites protecting neurons from shear stress. The PLLA-MTA membrane bioreactor promoted the growth and differentiation of neuronal cells toward a neuronal phenotype, and guided neurite alignment giving rise to a 3D neuronal tissue-like construct. In particular, neurites linearly extended along the membranes and the elongation of neuronal processes followed the orientation and the alignment of the membranes (Figure 1).

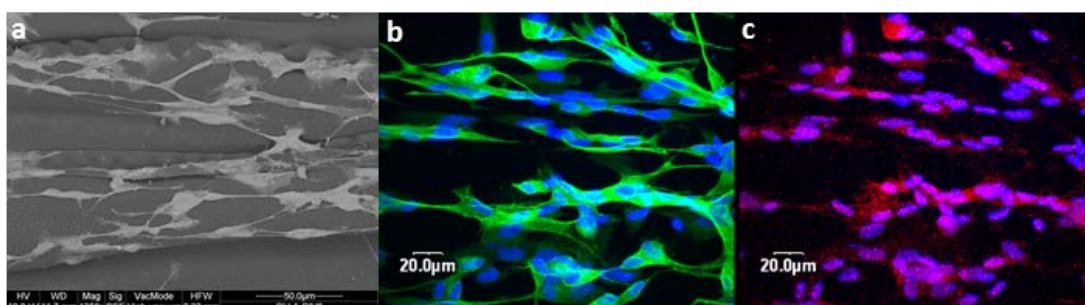


Figure 1. SEM micrographs of neuronal cells adhered on PLLA-MTA membrane surface (a), (b) Confocal Laser micrographs of neuronal cells in PLLA-MTA membrane bioreactor after 13 days of culture. Cells were stained for neuronal markers β III-tubulin (green), synaptophysin (red), and nuclei marker (DAPI, blue).



Cells in the bioreactor were treated with a mixture of Amyloid beta and glycitein at different concentrations to test the effect of glycitein against Abeta-induced cytotoxicity. Glycitein protected neurons against Abeta-induced apoptosis and abrogated Abeta-induced cytotoxic events (ROS). This bioactive neuronal membrane bioreactor represents a valuable tool to test the neuroprotective effect of phytoestrogen, Glycitein. Our findings emphasized that Glycitein can inhibit Abeta aggregation and the subsequent Abeta-induced neurotoxicity. PLLA-MTA membrane bioreactor is an innovative investigational platform that could be used to study neurodegenerative disorders as well as neurobiological phenomena in order to gain new insights on neurological functions and protection.

Keywords: membrane bioreactor, neuronal cells, neuronal differentiation, neurite orientation

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Acknowledgement:

The authors acknowledge the Italian Ministry of University and Research for granting the project Nanomax-integrable sensors for pathological biomarkers diagnosis (N-CHEM).



Mass Spectrometry Proteomic Platforms: Discovering Molecular Signatures in Clinical Proteomics Studies

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Proteomic analysis represents a useful tool for studying diseases at molecular level contributing to elucidate the mechanisms involved in their onset and progression and to discover potential biomarkers as well as possible therapeutic targets. Proteomic analysis can follow a targeted or an expression approach. Expression proteomics, evaluating the qualitative and quantitative differences in protein expression profile under healthy and disease conditions is currently the most widely approach used, especially in the biomedical applications of proteomics.

Among the analytical techniques and the methodologies used in proteomics, mass spectrometry (MS) interfaced with pre-separation tools such as liquid chromatography (HPLC) or capillary electrophoresis (HPCE) or bi-dimensional electrophoresis (2DE) emerged as tool of excellence for protein characterization providing information on both protein mass and molecular structure.

MS based proteomic analysis can follow diverse strategies: the bottom-up and the top-down approach. In the bottom-up, largely applied, protein mixtures or protein fractions are analysed in mass spectrometry after chemical or enzymatic digestion. Proteins are therefore characterized by the identification of their unique tryptic peptides by tandem MS experiments. This strategy can be applied to purified or pre-separated proteins, i.e. after mono- or bi-dimensional electrophoretic separation, or, directly to protein mixtures (shot-gun proteomics) that are separated after digestion by liquid chromatography prior to MS detection. Differently, in top-down approach, proteins are analysed in their entire, undigested, or native form and directly fragmented in mass spectrometry by tandem MS² or Msⁿ analyses. Together with their pros and cons, the two approaches are complementary each other, allowing a wide and precise characterization of the proteome under investigation. Particularly, while the bottom-up strategy provides a large dynamic range of protein identification, including high molecular weight proteins, the top-down approach, although applicable to proteins with a relatively low molecular weight, is challenging for the identification of post-translational modifications (PTMs), isoforms and characterization of biologically active peptides or peptides fragments from major proteins. Protein fractionation is often required together with careful removal of most abundant proteins and lipid components to remove interferences and allowing the characterization of the intact proteome.

Proteomic analysis involves different steps including protein extraction, separation, identification and characterization, software and bioinformatics data analysis and elaboration. The sample pretreatment step is critical and has to be carefully optimized to purify the sample and to access to the identification of low molecular weight and low abundant proteins and peptides present in the biological matrix under investigation. Clinical proteomics represents the biomedical application of proteomics and includes proteomics, epidemiology, clinical chemistry and medical disciplines. A clinical proteomic approach is based on the determination of the total protein pattern expressed by the genome of a specific cell, tissue, or body fluid at a given time, evaluating the qualitative and quantitative differences under health and disease conditions. By characterizing the protein content and the alterations produced by genetic or epigenetic variations on the proteome, the molecular mechanisms involved in the disease and/or diagnostic/prognostic biomarkers can be disclosed for potential clinical applications.

The top-down and bottom-up strategies have been both applied to protein profiling of biological fluids and tissues in clinical proteomics studies particularly in relation to brain tumours [1-3] and neurodegenerative diseases. The results obtained with the diverse approaches will be illustrated and discussed. The top-down



strategy was particularly challenging in studying the naturally occurring protein fragmentome and the protein/peptide PTMs relevantly modulated in diseases. The analysis of the intact proteome allowed to identify bioactive peptides, belonging to alpha- and beta-thymosin families, and bioactive haemoglobin protein fragments naturally occurring in the samples together with proteoforms, especially C-terminal truncated forms, and isoforms, interestingly modulated in diseases.

Keywords: Mass spectrometry, proteomics, biological samples

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Acknowledgement:

Acknowledgements are due to the Institute of Biochemistry and Clinical Biochemistry of the Catholic University and to the Pediatric Neurosurgery Unit-Fondazione Policlinico Gemelli-Catholic University in Rome and to the Department of Surgery "P.Valdoni" of University La Sapienza in Rome for the valuable scientific cooperation in clinical and neuroproteomics studies.



New Molecules for Drug Discovery by Screening Platform of Marine Natural Products

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It is known that Marine Natural Products (MNPs) represent an area of interest in many fields of biomedical science, especially in the discovery of compounds with pharmaceutical interest. The number of molecules for drug development from this source has been steadily increasing. The development of a screening platform represent an useful tool to improve the hits in drug discovery field and at the same times to reduce laboratory times and work. With this aim, we have developed and validated an SPE-based method to fractionate marine natural extracts in order to obtain few enriched fractions of the main major chemical classes, to build a "library of MNP" available for drug discovery.¹ Biological analysis of library samples (which includes raw extracts and SPE-fractions) reveal that at least 50% of the activity was detectable only after extract fractionation demonstrating that the method ensures the recovery of minor components, whose activity may be masked in the raw extract. At the moment, we have applied our library for the screening of antitumor and immunomodulatory compounds and both screening allowed us to reach interesting molecules, both from a chemical and biological point of view. As an example, during the screening for anticancer molecules, the extract of the Atlantic soft coral *Stragulum bicolor* was selected for its cytotoxic activity. Further fractionation of the active extract led us to isolate, together with known compounds, new members of amphidinolide family,² an active polyketide class of compounds, including more than 40 macrolides, with extremely high cytotoxicity against several carcinoma cell lines.³ Due to their diverse functionality, stereochemical complexity and promising bioactivity, amphidinolides have attracted great interest in the research field of drug lead. Our chemical study of *S. bicolor* permitted the identification of minor compounds with unprecedented carbon skeleton, which assessment of the cytotoxicity on different tumor cell lines has revealed a powerful and selective activity at nanomolar level on melanoma A2058 cells. Resistance to apoptosis is a hallmark of malignant melanoma and A2058 cells show a set of dysregulated survival-apoptosis genes that govern survival of the melanoma cells. Thus, the effect this new compound on A2058 cells suggest a specific mechanism that is able to overcome the bypass of the apoptotic machinery that is responsible for the poor outcome of the current therapy of malignant melanoma.

Particular attention in our studies was done to the complete structure elucidation of these molecules, which required the application of multiple methodologies. First of all, an intense study of spectroscopic data to assign the relative stereochemistry and methods of chemical derivatization to define the absolute stereochemistry of some stereocenters. To complete the assignment of the configuration of all chiral carbons, a computational method was also applied to the study of these molecules.

Keywords: Marine Natural Products – Drug discovery

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Acknowledgement:

Part of the work has been carried out in the frame of Italy-Brazil bilateral project (Grant # 490247/2011-3) founded by CNR and CNPq. The authors are grateful to both institutions.



Effects of Prion Protein on β -Amyloid Peptides Oligomerization and Toxicity

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Soluble A β peptide oligomers are widely recognised as the toxic forms responsible for triggering Alzheimer disease (AD). A β receptors are hypothesized to represent the first step in a neuronal cascade leading to dementia [1] and cellular prion protein (PrP) has been reported as a high-affinity binder of A β oligomers [2]. Structural chemical biology approaches, based on NMR, ThT fluorescence and TEM, are employed to depict, at a molecular level, the interactions between PrP with A β 42 and the highly toxic N-truncated pyroglutamylated species (A β pE3-42).

We demonstrate that soluble PrP binds both A β 42 and A β pE3-42, preferentially interacting with oligomeric species and delaying fibril formation. Residue level analysis of A β 42 oligomerization process reveals, for the first time, that PrP is able to differently interact with the forming oligomers, depending on the aggregation state of the starting A β 42 sample. A distinct behaviour is observed for A β 42 1-30 region and C-terminal residues, suggesting that PrP protects A β 42 N-tail from entangling on the mature NMR invisible fibril, consistent with the hypothesis that A β 42 N-tail is the locus of interaction with PrP.

Interaction data are validated and complemented by cellular tests performed on Wt and PrP-silenced neuronal cell lines, clearly showing the role of PrP in A β oligomer cell internalization and toxicity [3](Figure 1)

Further project development, in progress in the lab, is related to unravel the role of small molecules and bare gold nanoparticles in influencing self-aggregation processes in pathological and functional amyloids, such as silk fibroin.

Keywords: Alzheimer Disease; Amyloids; Nuclear Magnetic Resonance.

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Acknowledgement:

This work was supported by the Alzheimer Association (NIRG-14-321500 Grant) and CARIPLO Foundation (2015-0503). KP, ST, HM, and LR acknowledge Fondazione Antonio De Marco for financial support.

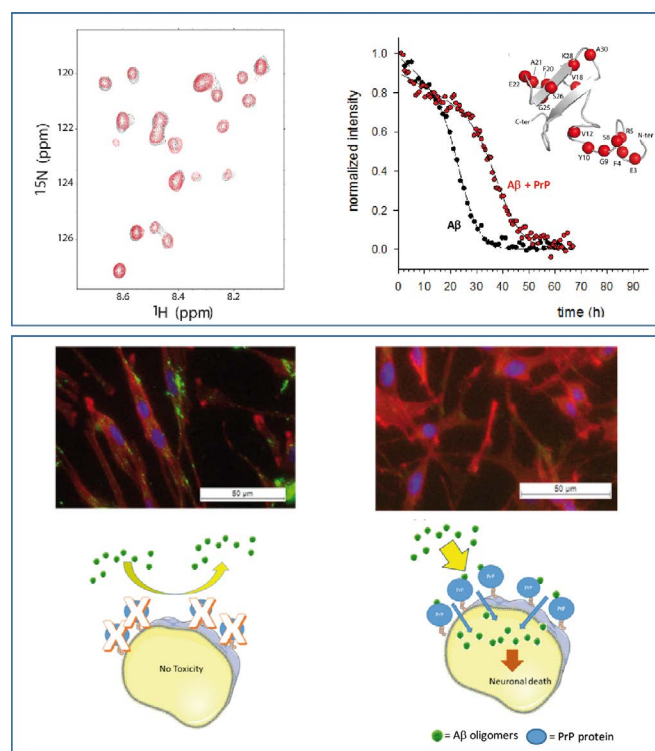


Figure 1. Residue-level NMR based analysis of A β 42 oligomerisation kinetics (upper panel). A β 42 cell internalization into WT or PrP-KO neuronal cells (lower panel)



Toward Personalized Medicine: RGD-Peptide as Scaffold for the Comprehension of Structural Determinants for Integrin Specific Recognition

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In the past decades, the scientific community has focused the attention mainly on $\alpha_v\beta_3$, $\alpha_v\beta_5$, and $\alpha_5\beta_1$ integrins due to their relevance in tumor vascularization and metastasis, in wound healing acceleration, drug resistance and tumor recurrence in different types of solid cancers, as well as in hematological malignancies. Unfortunately, the precise roles in pathological angiogenesis and in tumor progression of these proteins, alone or combined with other integrins, are not yet fully understood and thus the availability of integrin sub-type-exclusive antagonists is highly desirable. The majority of the ligands described so far as selective agents have residual, yet significant, affinity for the other integrins, thus stimulating extensive research to develop novel integrin specific molecules.

Over the last decade we developed the selective peptide RGD_{dechi}, a chimeric molecule encompassing a cyclic portion containing the RGD triade for integrin binding and a linear sequence for the β_3 subunit specificity [1]. We demonstrated anti-adhesive and pro-apoptotic effects on tumor cells and antiangiogenic activity in vivo [1]. SPECT, PET and optical imaging studies in xenograft models confirmed the ability of RGD_{dechi} peptide to selectively visualize this integrin [2]. NMR and computational analyses on cell membranes allowed us to understand the $\alpha_v\beta_3$ /RGD_{dechi} recognition mechanism [3], and consequently prompted us to use RGD_{dechi} for its bifunctional nature as scaffold to elucidate the molecular determinants to drive the selectivity toward $\alpha_v\beta_5$ or $\alpha_5\beta_1$ integrins.

Keywords: Drug design, integrin, peptidomimetics

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Nanophotosensitisers based on cyclodextrin for bio-imaging and PDT

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Cyclodextrins (CDs), either as molecule or in self-assembled form, can complex PS guests by non-covalent interactions. In the recent past, we reported different supramolecular assemblies based on amphiphilic CDs (aCD) with high efficacy for application in Photodynamic Therapy (PDT), antimicrobial Photodynamic Therapy (aPDT) and bio-imaging [1]. Actually, the design of novel nanophototherapeutics for PDT generally complies with efficient uptake of PS within tissues, cell membranes and/or intracellular components with production and diffusion of singlet oxygen in the neighboring areas to the sites of action. Here we report a brief overview on the most recent outcomes on aCD nanoassemblies entrapping different PSs with high photodynamic activity or bio-imaging properties such as Zn(II)-phthalocyanine, Pheophorbide A and Bodipy (see Figure 1) [2-3]. The choice of CD carrier and its modification with receptor targeting group can modulate the amount of entrapped PS within of nanoassemblies, its aggregation state and hence the in vitro activity, thus allowing spatial-temporal control of PS release in targeted cells.

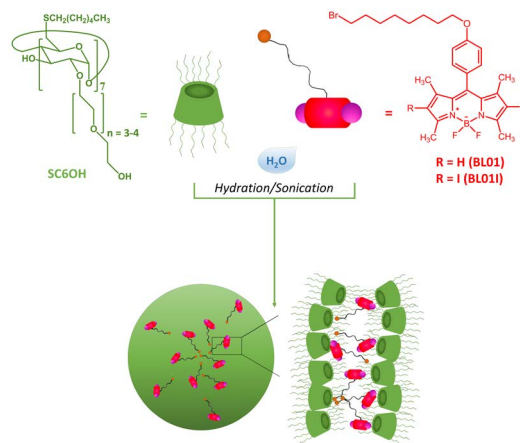


Figure 1: Sketched view (from Ref 3) of Bodipy/aCD nanoassemblies for PDT and bio-imaging purpose (aCD is SC6OH and Bodipy are BL01 and BL011, respectively).

Keywords: cyclodextrin, nanophototherapeutics, PDT

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Acknowledgement:

H2020 MADIA Project ID: 732678



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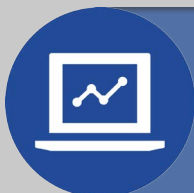
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Water Purification with Active Cotton Membrane: Photo- and Photoelectrochemical Treatments in Semi-Pilot Plant

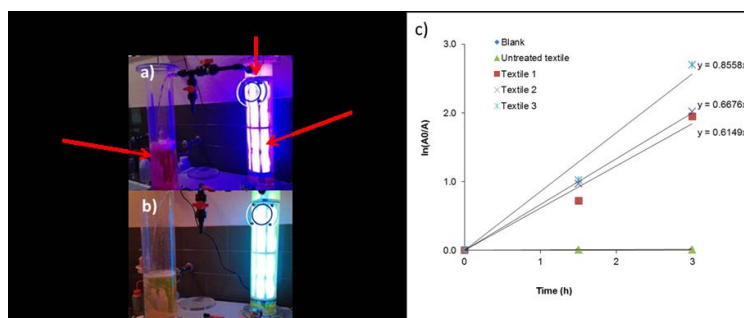
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Semiconductor photocatalytic technology using either UV or solar light has recently come into prominence owing to its mineralization aspects and its advantages as compared to other oxidative processes that require the use of potentially dangerous chemicals or disinfectants. The ProBioType II project, funded by the Italian national program Fabbrica del Futuro, investigated the development and up-scaling of photocatalytic reactors, designed to be downstream modules of chemical plants or more traditional purification systems. This activity meets the need of ISTEC-CNR to transfer to large scale plants the long experience gained in photocatalytic technologies and in the development on nano-TiO₂ based photocatalytic materials¹⁻⁴. The project allowed the up-scaling of a lab-scale pilot plant (1L) to semi-pilot plants with different geometries (6L and 10L), up to a pilot-scale plant (100L). Using UV or visible LEDs irradiation, the degradation of Rhodamine B was used as a

probe reaction. In particular, this study is focused on the developments of 10L capacity semi-pilot plant. Several kinds of photocatalytic membranes based on commercial cotton fabric coated with nano-TiO₂ were used within semi-pilot photoreactor and compared. The preliminary test in semi-pilot plant by the standard photocatalytic approach showed very promising results, with photocatalytic efficiencies around 90% within four hours of UV irradiation (Figure 1), and



performance conservation even after five complete recycling tests. An implementation of the photocatalytic approach was also pursued in which an additional electrochemical functionality was added to the system employing palladium-doped TiO₂/Ti anodes obtained by thermal oxidation of ASTM Grade 1 titanium mesh (Figure 2). Results show that an increase of the rate of degradation of Rhodamine B can be obtained as compared to that measured with photocatalytic membranes only. The dependence of the RhB degradation reaction rate and degradation kinetics on the type of salts added as support electrolyte was investigated. The electrochemical performance of TiO₂(Pd)/Ti anodes was found to be constant over many four-hour cycles. The proof of concept achieved at the pilot scale level, will allow a sound evaluation of environmental impact as well as of other technical feasibilities and costs, pushing the proposed technology towards its commercialization.

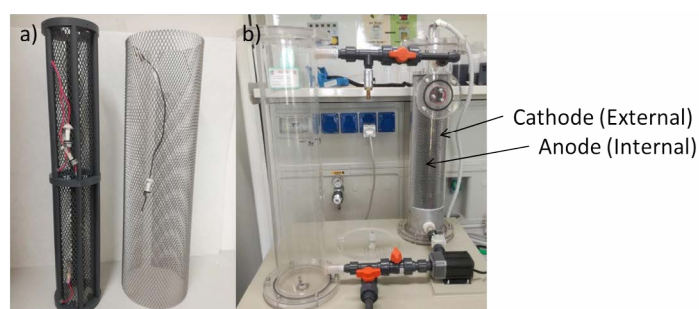
Keywords: Photoelectrochemical process, nano-TiO₂ coated textile, semi-pilot plant

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Acknowledgement:

This work has been funded by the Project Probiopol (Flagship Project “La Fabbrica del Futuro,” call FdF-SP2-T4.1), coordinated by the National Research Council of Italy (CNR) and funded by the Italian Ministry of Education, University and Research (MIUR).





Direct Air Capture (DAC) Of CO₂ Accomplished By Different Alkanolamines

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The chemical capture of carbon dioxide from ambient air (Direct Air Capture - DAC) represents one of the negative emission technologies (NETs) with the potential of reduce the global atmospheric CO₂ concentration. Moreover, the capture of CO₂ from air is suitable to supply pure CO₂ wherever it is needed. Because of the very low concentrations (about 400 ppm), to date the most widespread technologies for CO₂ removal from the air are based on alkaline aqueous solutions, but the process is high energy demanding and prohibitively expensive.

In recent papers, we have reported some experimental studies on the CO₂ capture from gas mixture by different amine-based sorbents. [1-3] Herein, we have investigated the possibility of transferring our previous studies to DAC technology, with the goal of formulating absorbents capable to efficiently react with aerial CO₂ featuring lower energy demand for thermal regeneration. To this purpose, we have selected 2-aminoethanol (monoethanolamine, MEA), the benchmark in CCS technologies, 2-(2-aminoethoxy)ethanol (diethylene glycol amine, DGA), 2-amino-2-methyl-1-propanol (AMP) and 2-(butylamino)ethanol (BUMEA), and we have investigated their performances for low-concentrated CO₂ capture either in aqueous and non-aqueous solutions. The 2-(2-methoxyethoxy)ethanol (diethylene glycol monomethyl ether, DEGMME) was used as non-aqueous solvent because of the solubility of most of the carbonated compounds in this solvent, the high boiling temperature and low viscosity of the solutions. We have carried out batch experiments to evaluate the CO₂ loading capacity, the CO₂ absorption profile as a function of time and the CO₂ absorption efficiency from air for 24 h. The ¹³C NMR spectroscopy has been used to identify and quantify the carbonated species in the solution equilibria originated by CO₂ absorption, to better understand the absorption mechanisms. The heat of CO₂ absorption (ΔH_{abs}), which is a significant parameter to evaluate the overall energy demand for the regeneration of the different amine solutions, has been calculated by the Gibbs-Helmholtz equation. Considering both the absorption and the desorption features of the different solutions, aqueous DGA is the most attractive option and should be a promising absorbent for DAC applications.

Keywords: Negative Emission, Direct Air Capture, alkanolamine solutions

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Acknowledgement:

Authors acknowledge ICCOM - CNR, POR-FSE 2014-2020 Regione Toscana and STM Technologies SRL for funding this research activity. Thanks are expressed to the Department of Chemistry, University of Florence, for the facilities.



Environmentally Friendly Treatment of Olive Mill Wastewaters and their Valorization by using Membrane Technology

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Nowadays, it is well recognized that advanced clean technologies, able to work in mild conditions and with low energy input are necessary to face challenges in environment protection, rational use of water, production of naturally derived stable bioactive compounds. Membrane technologies fulfill these requirements. The treatment of olive mill wastewaters (OMWWs) coming from olive oil production is among the critical issues in agro-food industry. These wastewaters represent a severe environmental problem due to their high organic load and phytotoxic and antibacterial phenolic compounds, which resist to biological degradation. On the other hand, OMWWs represent a significant source of biophenols for health benefits, which can be revalorized and used for medical or agro-alimentary purposes. The development of new strategies for the disposal of these by-products appears to be extremely useful from an environmental and economic point of view. In this context, integrated membrane systems can permit the selective recovery of bioactive compounds, such as biophenols as well as water recovering and purification. The system proposed based on a pre-treatment unit and a combination of different membrane operations including microfiltration (MF), nanofiltration (NF), osmotic distillation (OD) on lab scale prototype; membrane emulsification (ME) was studied for the encapsulation of concentrated fractions of biophenols. The influence of materials, configurations, molecular weight cut-off (MWCO) or pore size of membranes on permeate flux, total organic carbon (TOC) removal, biophenols rejection and fouling index were investigated. The overall integrated membrane system produced an enriched fraction of biophenols, as well as a water stream that can be reused for irrigation or membrane cleaning. Relatively high fluxes, with respect to literature data, were obtained in both MF and NF steps (60 and 7 L/m²h, respectively). In addition, high biophenols rejections (98%) were measured for the NF operation using a polymeric membrane with MWCO of 200 Da [1]. The NF retentate was further concentrated with a factor of 7 by OD at low operating temperature, producing an enriched fraction of biophenols. This concentrated has been used as functional ingredients for the production of bioactive formulation by water-in-oil (W/O) emulsions. The pulsed back-and-forward ME has been selected as low shear encapsulation method because it is particularly attractive for the production of highly concentrated emulsions without causing coalescence phenomena [2]. In addition, a novel procedure for encapsulation of amphiphilic biophenols into solid lipid particles (SLPs) by using traditional method and membrane emulsification was studied [3]. The best operating conditions in ME process to control particles size and size distribution for W/O emulsions and SLPs were studied. Moreover, the comparison of two emulsification methods (pulsed back-and-forward ME and rotor-stator homogenizer) regarding particles size, size distribution and EE are presented. The results showed that the membrane emulsification process was more efficient than the homogenizer in producing monodisperse particles with improved encapsulation efficiency and low energy consumption. This work promoted advances in the development of novel membrane systems for olive mill wastewaters valorization through the enhancing of water recycling, biophenols recovery and formulation of emulsions loaded with biophenols.

Keywords: Olive mill wastewaters, membrane operations, biophenols

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Acknowledgement:

The authors acknowledge for the financial support the project PON01_01545, Olio più, within the framework PON Ricerca e Competitività 2007–2013.



BiO⁺-Based Nanocomposite for Environmental Remediation: Modulation of the Functional Properties by Composition Tailoring

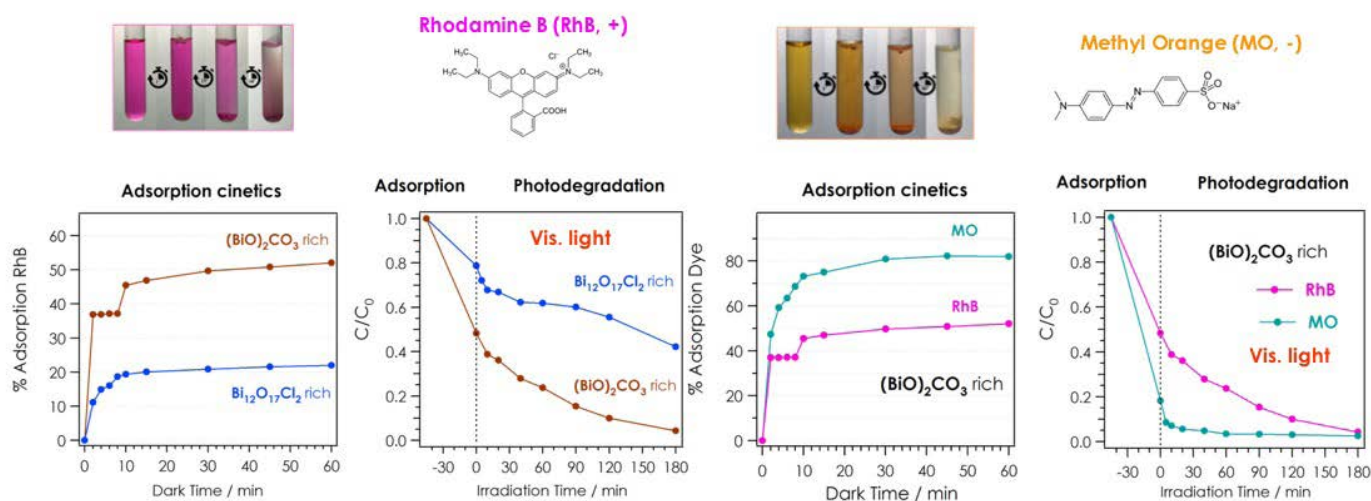
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In the field of environmental remediation strategies, multifunctional materials able to act for pollutants adsorption and degradation at the same time are highly desirable. In this framework, post-synthesis treatments represent a powerful tool for the modulation of the chemico-physical and functional properties of nanocomposite materials. In this study, Bi₁₂O₁₇Cl₂/(BiO)₂CO₃ nanocomposite materials were studied as bifunctional systems for depuration of wastewater and synthesized at room temperature and ambient pressure by means of controlled hydrolysis of BiCl₃, in presence of a surfactant (Brij 76). Cold treatments with UV-light or thermal annealing at different temperatures (370 – 500 °C) and atmospheres (air, Ar/30 % O₂) of the pristine samples were adopted in order to modulate the Bi₁₂O₁₇Cl₂/(BiO)₂CO₃ relative amounts and hence morphology, surface areas, ζ-potential, optical absorption in the visible range and the adsorption/degradation of Rhodamine B (RhB) and Methyl Orange (MO), used as model pollutants.

Dye adsorption and photodegradation



The best performance was achieved by (BiO)₂CO₃-rich samples which adsorbed 80 % of MO and decomposed the remaining 20 % by visible light photocatalysis. Irrespective of the dye, all the samples were able to almost complete the adsorption step within 10 minutes contact time. Bi₁₂O₁₇Cl₂-rich composite materials displayed a lower adsorption ability, but thanks to the stronger absorption in the visible they behaved as more effective photocatalysts. The obtained results evidenced the ability of the employed strategy to modulate sample properties in a wide range thus pointing out the effectiveness of this approach for the synthesis of multifunctional inorganic materials for environmental remediation.

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1D-Zigzag Lanthanides Coordination Chains endowed with temperature dependent luminescence

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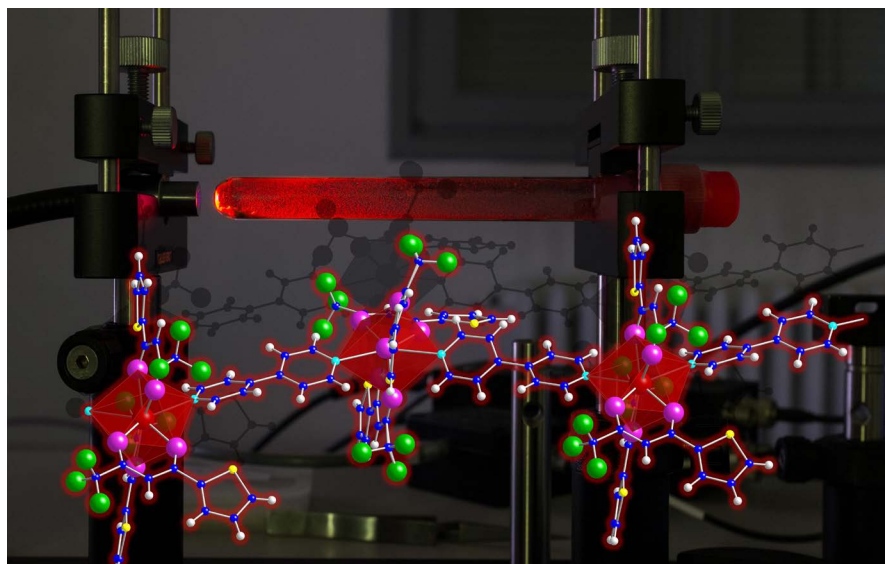
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In last few years Lanthanide-based Coordination Polymers (LCPs) of various dimensionality have been increasingly employed as self-calibrated luminescent molecular thermometers due to lanthanides unique luminescent properties [1]. However, the rational design of LCPs is an intriguing challenge still far from be rationalized and hampered by the high coordination number of these ions and their lability.



Recently, we developed a convenient and high-yield synthesis of mono-dimensional CPs based on lanthanide β -diketonate complexes as nodes and 4,4'-bipyridine (bipy) as unique connector with molecular formula $[\text{Ln}(\text{dike})_3(\text{bipy})] \cdot \text{C}_7\text{H}_8$ were $\text{Ln}=\text{Eu}^{3+}$ or Tb^{3+} , dike= dibenzoylmethide (DBM), 2-thenoyltrifluoroacetate (TTA) or hexafluoroacetylacetonate (HFA) and C_7H_8 = toluene [2]. All three $[\text{Eu}(\text{dike})_3(\text{bipy})] \cdot \text{C}_7\text{H}_8$ complexes have a bright red emission whereas only $[\text{Tb}(\text{HFA})_3(\text{bipy})] \cdot \text{C}_7\text{H}_8$ displayed an intense green luminescence. We studied the

temperature effect on the photoluminescence properties of $[\text{Eu}(\text{HFA})_3(\text{bipy})] \cdot \text{C}_7\text{H}_8$, $[\text{Tb}(\text{HFA})_3(\text{bipy})] \cdot \text{C}_7\text{H}_8$ and their mixtures having different Eu/Tb molar ratios. These experiments showed composition dependent thermometric properties which are influenced by Tb^{3+} -to- Eu^{3+} energy transfer processes.

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Acknowledgement:

The authors thank Ministero Istruzione Università e Ricerca MIUR PRIN 2015 20154X9ATP Progetti di Ricerca di Interesse Nazionale for financial support.



Advanced Membrane Operations in CO₂ Separation

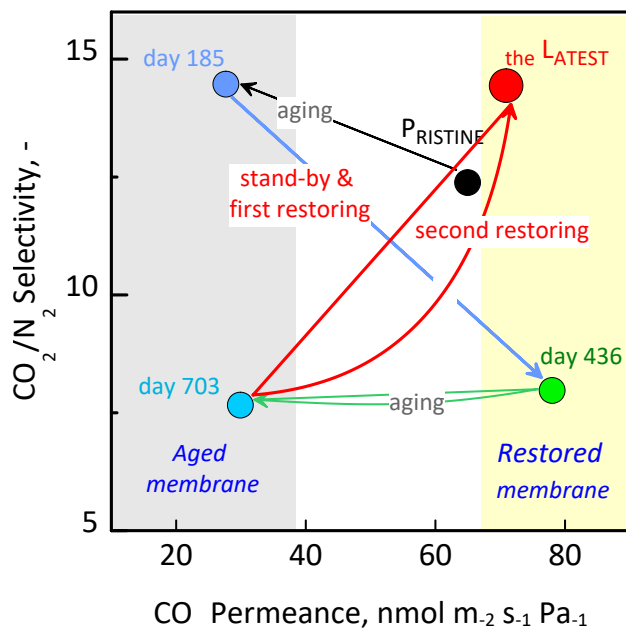
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Membrane-based gas separation systems are today widely accepted and, in many cases, used as a unit operation for generation, separation and purification of gases in gas, chemical, petroleum and allied industries. There are several applications of membrane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

CO₂ separation from flue gas coming out from a power plant or a cement industry, as well as CO₂ from biogas and natural gas is one of these fields. Polymeric membranes, thermally rearranged polymer membranes, mixed matrix membranes, zeolite membranes, etc. are some examples of membranes investigated c/o the ITM-CNR for separating gases, such as, CO₂, CH₄, etc. of interest for many industrial cycles. The mass transport properties of these membranes are analyzed feeding gas streams, with different content of water vapor and other aggressive components; these being one of the crucial assets for moving towards to real applications [1,2]. Other aspects, such as aging, clustering due to water vapor, physical compaction, thermal



Evolution of permeance and selectivity, covering all major steps during the entire course of the experiments

cycles and contaminants were and are currently under investigation, also with long term characterizations [3]. To this purpose, together with material science, membrane engineering covers a fundamental role in the development of this technology and its scale-up. Modelling assists experimental analysis for a unified approach in advanced membrane unit operations. In this logic, a tool was developed in terms of performance maps suitable for analyzing also membrane-integrated systems identifying proper operating conditions and proposing possible process schemes for achieving the desired targets for the various streams of interest [4,5].

Among the main results achieved, most recently, thermally rearranged polymer membranes showed interesting properties for their use in CO₂ separation. The presence of micropores, appropriately tuned cavities size and distribution in their polymer matrix makesb them highly permeable and, selective, in the meantime.

At ITM-CNR we carried out a deep analysis of their performance, passing from the understanding of permeation behavior in dependence of the various gases fed to restoring of permeation properties after aging. For instance, long term measurements carried out for ca. two years on a membrane module with thermally rearranged membranes under a saturated flue gas stream, showed, in fact, a certain drop in permances that can be attributed to aging effects and to clustering of water. We demonstrated that this clustering is reversible: by feeding dry gases into the membrane module, the mass transport properties was fully recovered and reached performance levels similar to those prior to wetting. More importantly, we developed an in-situ procedure to restore initial separation properties, an option particularly attractive from an applicative point of view.



Keywords: Membrane Engineering; CO₂ separation; Aging;

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The “Ministero per l’Istruzione, l’Università e la Ricerca” of Italy, Ricerca e competitività 2007-2013, is gratefully acknowledged for the financial support of the project PON01_02257 “FotoRiduCO₂ - Photoconversion of CO₂ to methanol fuel”, (“Studio e sperimentazione di sistemi di foto conversione con luce solare di CO₂ in metanolo, da utilizzare come combustibile”).



Axe7A: A Novel CE7 Acetylxylan Esterase for Biomass Degradation

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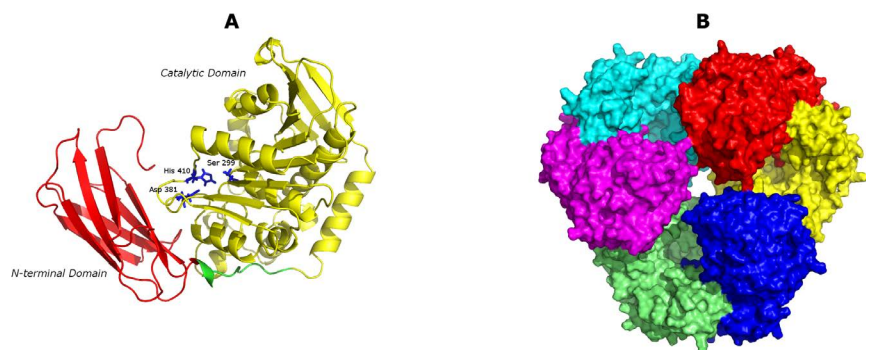
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As a clean and readily available agricultural residue, corn bran may have the potential of becoming a source for new C5 biofuel products or for the manufacture of food ingredients. These novel uses require partial or complete degradation of the biomass to its constituent monomers. Corn bran originates from a graminaceous plant having a primary cell wall, a complex macromolecular composite whose degradation by microorganisms requires a large and diverse panel of hydrolytic enzymes. Moreover, the degradation and fermentation of complex polysaccharides by microbiota is essential for many ecosystem-processes including nutrient cycling and herbivores nutrition. Among the different structural polysaccharides composing the plant cell walls, xylan is the second most abundant one and its degradation involves the removal of O-acetyl esters decorating the O-2 and O-3 positions of the D-xylanopyranosyl moiety.

A transcriptomic analysis of a gene cluster, present in the ruminal anaerobe *Prevotella ruminicola* 23, revealed a repertoire of xylanolytic enzymes with different functions and cellular localization [1]. Among them Axe7A, an acetylxylan esterase belonging to the CAZy CE7 carbohydrate esterase family, has been established [2]. Interestingly Axe7A amino acid sequence includes, besides the characteristic catalytic domain, an additional 100 residues long N-terminal domain not previously found in the CE7 family members, showing low similarity (around 10% identity) with any other structurally characterized protein annotated in the PDB.

In order to gain insights into the functional role of its N-terminal domain, the crystal structure of Axe7A has been determined at 2.6 Å resolution (A). Axe7A shares the 32 hexameric doughnut-shape (B) commonly found in CE7 deacetylases [3], while the unique protomer architecture has been disclosed in the CE7 family, for the first time. The N-terminal domain, characterized by a β -sandwich fold, is actively engaged in the oligomer formation. We are further investigating, by SAXS, the behaviour of Axe7A in solution aiming at validate the crystallographic oligomeric assembly in nearly-physiological conditions.



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Membrane-assisted Crystallization of Monoclonal Antibodies by Novel Customized Membranes: the AMECRYS – Project

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This work describes a sustainable way to produce customized PVDF membranes in which DMSO is employed as non-hazardous solvent in place of substances of very high concern (SVHC), by a combination of vapor-induced and liquid-induced phase separation (VIPS and LIPS) stages, and without using any chemical additive as pore forming. Namely, combining VIPS and LIPS techniques in a controlled way, allowed to produce symmetric porous membranes with customized rough surface topography and hydrophobicity, according to a biomimetic behaviour as that of lotus leaves surfaces, through an environmental friendly fabrication process. The resulting membranes are characterized by a high porosity with well-interconnected pores, despite no pore-former additives were included in the dope solution, making them ideal candidates for application in membrane contactors.

Customized membranes have been used for the first time in membrane-assisted crystallization of an antitumor monoclonal antibody (mAb), aiming to develop an innovative downstream purification processing (DSP) in mAbs manufacture. In fact, in the biopharmaceutical industry, separation and purification of therapeutics are primarily based on labour-intensive and expansive chromatographic methods, which cause a bottleneck in the production and impact goods and facility costs. Therefore, alternative procedures to replace chromatographic operations are currently subject to extensive research.

Crystallization has been recognized as a method for purification or formulation. Nevertheless, the use of this technique is far to be a routinely procedure for the purification of protein therapeutics, since competitive phenomena or contaminants hamper crystal formation. To address these issues, we envisaged an innovative Continuous Template-Assisted Membrane Crystallization process for the purification of therapeutic monoclonal antibodies. Major challenges include the establishment of a robust membrane crystallization process, able to maintain suitable performances in a certain range of working conditions. Furthermore, process design comprise the availability of customized membranes, compatible with the processed solutions, and the setting of appropriate working parameters.

This work is performed in the frame of AMECRYS, a project funded by the European Commission's Horizon 2020 Programme in the framework of Future and Emerging Technologies actions (FET-OPEN), which supports the early-stages of the science and technology research and innovation around new ideas toward radically new future technologies. The AMECRYS network involves two public research organizations, four academic institutions, and three industrial/SME from four European Countries (Italy, England, Belgium, and France). CNR is involved in the project with three research institutes, two of which belonging to DSCTM of CNR: the Institute on Membrane Technology (CNR-ITM) Rende (CS), coordinating the entire project, and the Institute of Crystallography (CNR-IC), Bari (CNR-IAC, Bari, is also involved).

Keywords: Bioseparations, Membrane preparation, Monoclonal Antibodies purification

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Acknowledgement:

The authors would like to thank the European Union's Horizon 2020, Future and Emerging Technologies (FET-OPEN) programme, for funding this work within the AMECRYS project (<http://www.amecrys-project.eu/>) under grant agreement no. 712965.



A Sustainable Bioprocess Based on the Marine Microorganism *Thermotoga Neapolitana* for the Production of Energy and Functional Products: Perspectives and Potential Industrial Applications

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Thermotoga neapolitana is a marine anaerobic bacterium with an optimal growth temperature of 80°C, suitable for conversion of sugars into hydrogen with yields close to theoretical values¹. The fermentation process has shown general robustness, reproducibility and consistency and a low risk of contamination because of the hyperthermophilic conditions. We have recently reported in *T. neapolitana* an unprecedented pathway involved in the recycling of carbon dioxide through the coupling of acetate and carbon dioxide with the concomitant production of lactic acid, without affecting hydrogen production^{2,3}. This metabolic mechanism, called Caphnophilic (CO₂-requiring) Lactic Fermentation (CLF), may become the cornerstone for economically attractive biotechnological applications. In fact, the patented process offers the potential advantage of combining carbon capture, energy production from renewable source and synthesis of highly added value products such as lactic acid, using CO₂ and carbohydrate-rich feedstocks such as agroindustrial wastes.

Complete and deep understanding of mutual cross-talk of the biochemical pathways related to hydrogen and lactic acid production is crucial to further improve rate and yield of the process for guaranteeing its sustainability. However, this needs optimization of upstream and downstream processes including improvement of final product titer, definition of operational parameters, reactor design and the separation of the fermentation products. Another aspect concerns the development of metabolic engineering tools and strategies for *T. neapolitana* to improve the non-competitive production of H₂ and lactic acid.

These tasks are objectives of an H2020 Project (European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement No. 760431). The high-level goal of BioRECO2VER project is to demonstrate the technical feasibility of more energy efficient and sustainable anaerobic biotechnological processes for the capture and conversion of CO₂ from industrial point sources into 2 valuable platform chemicals, The project, started on January 2018, will be executed by a well-balanced and experienced group of 2 Research and Technology Organizations, 2 universities, 4 SMEs and 4 large industries.

Keywords: energy, metabolism, added value products

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This work is based upon research supported by: PON01_02740 project "Sfruttamento Integrato di Biomasse Algali in Filiera Energetica di Qualità" (SIBAFEQ), Programma Operativo Nazionale—Ricerca e Competitività 2007–2013, in collaboration with FERRERO SPA; European Horizon-2020 project "Biological routes for CO₂ conversion into chemical building blocks BioRECO2VER)" (Project ID: 760431).



Safe-by-Design Approach for Winning the Nanorisk Challenge

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The unique properties of nanomaterials (NMs) arise from their nanoscale. Unfortunately, such peculiarity is also the main source of their potential toxicity when they come in contact with biological systems. Safe-by-Design (SbyD) strategies are very promising solutions for the preventive risk management of nanoparticles and nano-related products [1]. They aim to design NMs with the desired functional properties, but with reduced (or no) toxicity and/or potential exposure. In order to reach such an ambitious goal a lot of aspects have to be taken into account and multidisciplinary efforts have to be put in place. We made the first steps in this direction in the frame of two European collaborative research projects addressed to mitigate the risk from NMs for the human health in workplaces (SANOWORK) and to make the production of NMs sustainable (SUN). Nevertheless a right compromise between the potential reduction of risk and preservation of expected functional properties should be achieved. At this aim, in this work, we suggest a step-wise approach as supporting tool for the individuation and selection of a SbyD strategy in relation with the physicochemical properties of NMs, their evolution in testing media, and their biological reactivity, as well as their technological functionality. Moreover, we will present some results taken by case studies developed in the EU projects abovementioned where we modified commercial NMs with inorganic or organic coatings to control their biological reactivity or tried to limit exposure by purifying nanosols from the excess of toxic ions or controlling powder dustiness by granulating pristine nanopowders. In particular, we coated titanium dioxide (TiO₂) with silica (SiO₂) and copper oxide (CuO) with several organic capping agents (sodium citrate, sodium ascorbate, PVP, PEI) and ultrafiltered silver (Ag) nanosol to remove silver ions in excess. We measured and compared the physicochemical properties of pristine and modified samples and their evolution in testing media (water, biological and environmental fluids) in terms of size, zeta potential, and risk-relevant physicochemical properties, such as ion distribution and reactive oxygen species (ROS) production, in order to evaluate the effects of the treatments applied.

Keywords: Safe-by-Design, Nanomaterials, Nanorisk.

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Acknowledgement:

This work was supported by EU FP7 SANOWORK (Grant no. 280716) and EU FP7 SUN (Grant no. 604305).



New Ru-arene Complexes of the Water-soluble Ligand CAP: Synthesis, Characterization and Applications in Catalysis and Medicinal Chemistry

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After many years dedicated to investigate the coordination chemistry of the neutral water-soluble aminophosphine PTA (1,3,5-triaza-7-phosphadamantane, Figure 1a) and its derivatives to obtain PTA-based transition metal complexes,^[1] the interest of our research group switched to the higher homologue CAP, namely 1,4,7-triaza-9-phosphatricyclo[5.3.2.1]tridecane (Figure 1b). Although CAP has similar properties in terms of solubility and stability, it demonstrated a different behaviour compared to PTA, for example towards hydrogenation and alkylation reactions.^[2]

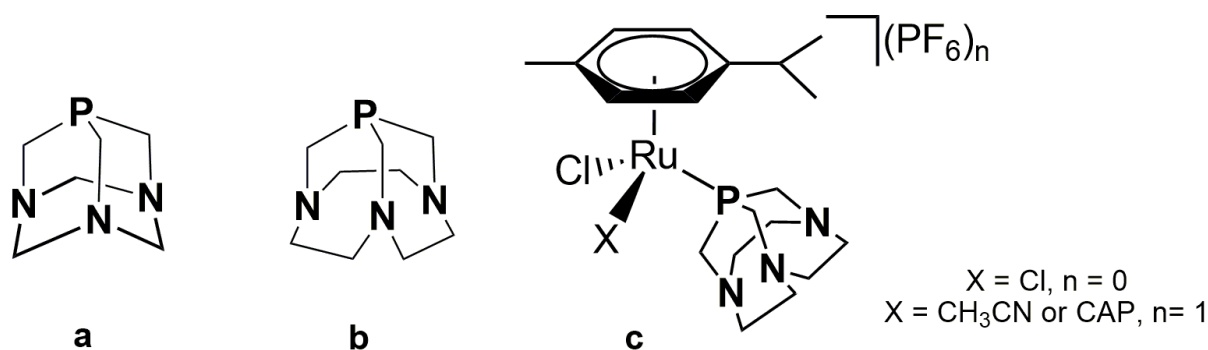


Figure 1. Phosphine ligands PTA (a), CAP (b) and general formula of new Ru(II)-CAP compounds (c).

Taking into account our expertise on PTA chemistry, we started to explore the reactivity and coordination ability of CAP, obtaining three novel ruthenium(II)-arene half-sandwich complexes bearing CAP as monodentate ligand (Figure 1c).^[3] These new Ru(II)-CAP complexes have been tested as catalyst precursors in homogeneous catalytic hydrogenations of some selected unsaturated substrates under very mild transfer hydrogenation conditions, using exclusively sodium formate in water phase as reductant. Furthermore, these complexes have been tested in vitro as cytotoxic compounds against selected cancer cell lines, revealing higher activity than the corresponding PTA analogues and a reasonable degree of cancer cell selectivity when used on noncancerous cells.

Keywords: ruthenium-phosphine complexes; catalysis; anticancer agents.

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Acknowledgements:

The Italian Ministry for Education and Research (MIUR) is kindly acknowledged for financial support through Project PRIN 2015 (grant number 20154X9ATP).



Pd@Sulfonated Monoliths Catalysts: Synthesis, Characterization and Application to Selective Hydrogenation Reactions under Continuous Flow

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Continuous flow fine chemical synthesis by supported heterogeneous catalysts is receiving increasing interest in large scale applications, due to the considerable safety, environmental and economic benefits compared to conventional batch operations. However, the need to overcome the common drawbacks associated with the mesoporous catalysts usually employed to this purpose requires a constant effort to develop innovative materials with improved properties. Monoliths featuring an isotropic, hierarchically porous structure of interconnected flow-through macropores and diffusive mesopores have shown a unique hydrodynamic behavior in the liquid-phase. Indeed, few inorganic monoliths with grafted functionalities have been described. A facile synthesis of functionalized, dual porosity silica monoliths will be described in these presentation as reported in the last our work.¹ Hierarchical macro- / mesoporous silica monoliths were first synthesized using the combination of sol-gel process and spinodal decomposition accordingly to our previous paper.² The resulting monoliths (MonoSil) were then sulfonated by grafting of 2-(4-phenylsulfonic)ethyl silane (MonoSil-ArSO₃) with a one-pot, batch treatment of monolith, hence Pd nanoparticles were grown *in-situ* onto MonoSil-ArSO₃ by a simple two-steps, one-pot flow procedure. (Figure 1) The procedure afforded PdNP of small size evenly distributed within the monolith and resulting in a 4.6% wt bulk metal loading. Compared to previous synthetic methods,³ the actual strategy provides significant advantages in terms of higher metal content and smoother, environmentally friendlier, procedure. The catalytic performance of Pd@MonoSil-ArSO₃ were investigated in the selective hydrogenation of 3-chloro-nitrobenzene and 3-hexyn-1-ol under continuous flow conditions, as test reactions showing remarkable versatility and very good activity and chemo/stereoselectivity. 3-chloro-nitrobenzene and 3-hexyn-1-ol were hydrogenated in > 75.5% and > 90% selectivity at nearly complete conversion, respectively, under very mild conditions.

The catalyst showed pretty nice constant efficiency over prolonged time on stream, with no regeneration treatments required. Compared to the known catalysts for the flow processes, the reported catalysts provide a good compromise solution between product purity and productivity, with no need of additives to achieve satisfactory selectivity.





Keywords: monoliths, selective hydrogenation, continuous flow reactor

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Acknowledgement:

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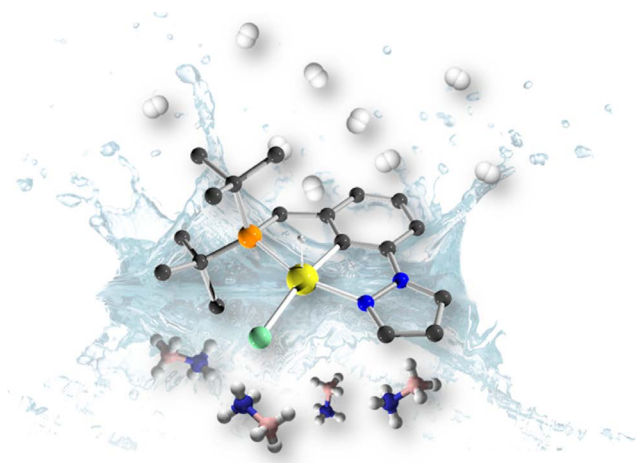
Amine Boranes Dehydrogenation Mediated by a Pyrazole-Based Unsymmetrical PCN Pincer Iridium(III) Hydride

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Lightweight inorganic hydrides are at the forefront of contemporary chemical hydrogen storage research due to their easy handling, thermal stability and relatively high hydrogen content.¹ Following our interest in developing new and efficient homogeneous catalysts for the dehydrogenation of amine-boranes mediated by transition metal hydride complexes,² a new Ir(III) hydride species stabilized by a tridentate monoanionic unsymmetrical *pincer* ligand [$(^{tBu}PCN)]^3$ has been prepared and fully characterized.



$(^{tBu}PCN)IrHCl$ has shown an improved catalytic performance with respect to its symmetrical analogue $(^{tBu}PCP)IrHCl^{2b}$ at ambient temperature. The reaction of [$(^{tBu}PCN)IrHCl$] with amine boranes in catalytic regimes have been studied through multinuclear (VT)-NMR and (VT)-IR spectroscopies, kinetic rate measurements and kinetic isotope effect (KIE) analysis. The results will be presented and discussed in details.

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Acknowledgement:

Italian MIUR (PRIN 2015 Project SMARTNESS (2015K7FZLH)) is acknowledged for financial support to this research activity.



Unconventional Hierarchically Porous Niobium-Titanium Oxide Monoliths for the Catalytic Dehydration of Xylose to Furfural under Continuous Flow

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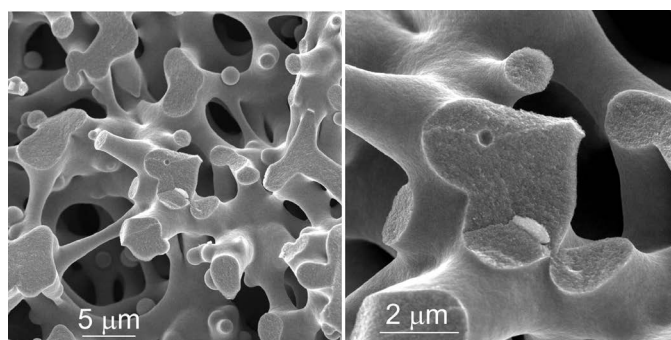
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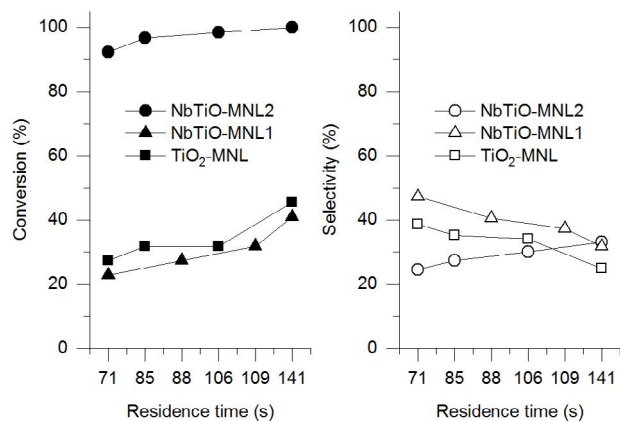
The environmental situation in the last period and the future expiration of fossil resources has driven the research community to invest efforts in searching an alternative to a fossil-based lifestyle. Biomass may represent a suitable option to decrease the current fossil dependence, mainly composed by C, H, and O, it can be found as a nearly infinite reservoir for the production of fuels and chemicals, without compromising human needs since only ca. 3% of the total is dedicated to food consume. However, the transition from fossil to biomass technologies implies many difficulties that must be overcome. The sustainable conversion of vegetable biomass-derived feeds to useful chemicals requires innovative routes matching environmental and economical criteria. One solution may be the development of heterogeneous acid catalysts featuring high efficiency, stability and tolerance to water, combined with catalysis under continuous flow operations.

The approach herein pursued is the synthesis of unconventional solid acid monolithic catalysts based on a mixed niobia-titania skeleton building up a hierarchical open-cell network of mesopores (2 nm < x < 50 nm), what allows efficient processing, and macropores (x > 50 nm) with benefits in terms of reduced pore clogging, better active sites accessibility and improved mass transfer.



Typical SEM images of NbTiO-MNL2 (secondary electrons, 5 keV, high vacuum). Left: 11000 magnifications. Right: 29000 magnifications

The materials were characterized by spectroscopic, microscopy and diffraction techniques showing a reproducible, isotropic structure and an increasing Lewis / Brønsted acid sites ratio with increasing Nb content. Application of the synthesized monoliths in the development of sustainable methods for biomass valorisation was tested through a reaction of great relevance; the acid-catalyzed dehydration of xylose to furfural.



Selected data for the continuous flow dehydration reaction of xylose over monolithic catalysts at different residence times (130 °C, xylose 0.02 M in H₂O : GVL = 1:9 v/v) Left: conversion. Right: selectivity to furfural

The efficiency of the catalyst showed to be dramatically affected by the niobia content in the titania lattice. The presence of as low as 2% wt niobium resulted in a furfural yield of 39% at 140 °C reaction temperature and 224 s residence time under continuous flow conditions, using H₂O / γ -valerolactone as safe monophasic solvent system. The interception of a transient 2,5-anhydroxylose species suggested the dehydration process to occur via a cyclic intermediates mechanism. The catalytic activity and the formation of the anhydro intermediate were related to the LAS/BAS ratio and indicated a significant contribution of xylose-xylulose isomerization. No significant catalyst deactivation was observed over 4 days usage.



Keywords: monoliths, flow, biomass

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Acknowledgement:

European Community's Seventh Framework Program through the Marie Curie Initial Training Network NA-NO-HOST, (Grant Agreement no. 215193)



Lactic Acid from Glycerol by Pt and Ir Nanoparticles

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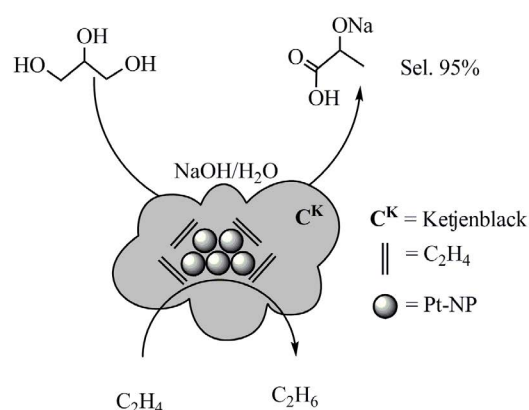
Lactic acid (LA) is an important platform molecule which can be converted into acrylic acid, 2,3-pentandione, 1,2- and 1,3-propanediol.[1] Its polymerization gives the biodegradable poly(lactic acid), which finds many applications. The conversion of glycerol (GLY) to LA is an appealing process, due to the availability of GLY from biodiesel production. Most of the heterogeneous synthetic approaches, used for the latter process, employ supported metal nanoparticles (NPs) as catalyst in combination with air or oxygen as hydrogen acceptor, leading very often to undesired side products which stem from the oxidation of glyceraldehyde (*i.e.* key intermediate in LA synthesis from GLY).[2] We present two recyclable metal-NP-based catalytic processes for the selective conversion of GLY to LA (Scheme 1):

A) Pt-NPs supported onto a high surface-area carbon (*i.e.* Ketjenblack) were used to catalyze the selective conversion of GLY to LA, using ethylene as NPs' stabilizer during catalysis and hydrogen scavenger.[3]

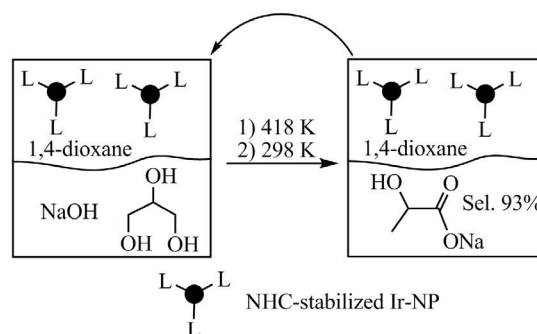
B) N-heterocyclic carbene (NHC)-stabilized Ir-NPs were employed to catalyze very efficiently (TOF of 10^4 h^{-1}) the selective GLY to LA conversion (93%) in 1,4-dioxane.

Both catalytic systems were recyclable for at least three times, without alteration of the catalytic performances.

A) Ethylene-stabilized Ir-NPs for GLY to LA conversion



B) NHC-stabilized Ir-NPs for GLY to LA conversion



Keywords: metal nanoparticles, glycerol, lactic acid

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Acknowledgement:

C. Evangelisti thanks MIUR-Italy (FIRB 2010; contract RBFR10BF5 V) for financial support.



Sustainable Production of PLGA-Peg Microparticles by Membrane Emulsification/ Solvent Diffusion-Evaporation Method

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Degradable microparticles have broad utility as vehicles for drug delivery and form the basis of several therapies approved by the US Food and Drug Administration [1]. As the field of drug delivery is expanding into consumer products, it is essential to advance in the development of efficient synthesis technologies while preserving the quality of the resulting microparticles. Conventional emulsion-based methods of manufacturing produce particles with a wide range of diameters in each batch. This outcome has a negative effect on the kinetics of drug release and subsequently in the final application. In addition, the production of particles with high yield, minimizing solvent and energy consumption and with a reduced waste production is a significant challenge for the particle-engineering technologies. There is a plethora of particle- production methods, where the main target is achieving high quality products. However, they generally do not fulfil some key requirements for the commercialization of a medical product: energy consumption, scalability, pharmacopeia fulfillment and environmental impact.

Herein we report the production of PLGA-PEG (one of the most common polymers used in drug delivery applications) microparticles by membrane emulsification [2] and solvent diffusion-evaporation methods. Considering that membranes are a new “green process engineering” alternative to some traditional procedures, for the first time the sustainability assessment of this fabrication technique has been evaluated [3]. To determine the green impactful of the particles production method proposed, the metric based on the Green Aspiration Level™ (GAL) was used. The “greenness” of membrane emulsification was measured and compared with some data reported in the recent literature to convince demonstrate that membrane emulsification is an environmentally improved method for the production of drug delivery systems.

Particles with sufficiently narrow distribution in the droplet size and mean diameter tending to the membrane pore diameter were produced by increasing the dispersed phase flux to 12.84 L h⁻¹m⁻², minimizing the shear stress to 1.12 Pa and the energy consumption to 3.9 10⁵ Jm⁻³. The impact of solvent used on size distribution, particles morphology and green performance scores was also studied. Solvents used during polymer particle synthesis are often volatile organic compounds and their use is associated to some concerns about their potential environmental impact (some of them are able to form low-level ozone and smog through free radical air oxidation processes), their adverse health effects (ranging from carcinogenic properties to headaches and allergic skin reaction, eye irritations) and their hazardous properties (they are often highly flammable). Dichloromethane (DMC) is one of the most used solvents for the production of polymeric particles via emulsification and subsequent solvent-evaporation due to its high volatility, low boiling point and high



immiscibility with water. Ethyl acetate (EA) has been proven to be a potential substitute of DCM with less toxicity. It has been classified as “recommended” considering the safety, health and environmental scores while DCM is considered “problematic” or “hazardous”. More uniform particles, with dense and slightly rough surface, high encapsulation efficiency and drug loading were obtained by replacing DCM with EA.

Results demonstrated that membrane emulsification is an environmentally improved method for the production of drug delivery systems with enormous impact in terms of formulation quality, energy consumption reduction and waste minimization. The simplicity and versatility of the method combined with the use of green solvents hold much promise for the development of a sustainable chemical manufacturing industry. Considering that a broad spectrum of micro-nanostructured materials with predictable and controllable sizes, different chemical compositions, morphologies, and functionalities can be produced by using the proposed method, membrane-based technologies result a best green process choice.

Keywords: drug-loaded particles, membranes, green solvents

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Acknowledgement:

Program Erasmus Mundus Doctorate in Membrane Engineering-EUDIME (2011–0014) is grate fully acknowledged. The authors acknowledge for the financial support the project PON01_01545, Olio più, within the framework PON Ricerca e Competitività 2007-2013.



Novel and “Safe” Inorganic Antibacterial Coatings for Cotton Fabrics

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Ag and TiO₂ nanoparticles (NPs) are known for their antimicrobial effect and their use in commercial products is increasing, thus raising the attention of European nano-safety research. A good antimicrobial candidate needs to be “intentionally toxic” (towards bacterial colonization) but “non-toxic” (not-harmful against other organisms). In fact, dealing with antimicrobials always implies a basic cost-benefit evaluation of the material balancing between toxicity and antibacterial efficiency. Ag and TiO₂ NPs are found as antiseptic additives in several every-day products, an interesting application is their use for producing auto-sanitizing textiles for healthcare, studied within the H2020 collaborative project PROTECT. In this work we present the design of safe alternatives modifying Ag and TiO₂ NPs with different coatings (Ag-HEC and TiO₂-SiO₂) in order to mitigate their toxicity but preserving their antibacterial function, following the “safe-by-design” principles.

Ag-HEC is an innovative antibacterial hydrogel achieved by means of a green synthesis performed at room temperature and based on spherical Ag NPs (15-20 nm) capped with hydroxyethylcellulose (HEC) [1]. The outstanding potentialities of this process stem from its low environmental impact combined with the absence of any kind of heating treatment. An excellent and prolonged antimicrobial activity jointly with a reduced cytotoxicity (tested on skin cell models) found in Ag-HEC sample validate its use as safe and active antimicrobial product.

TiO₂-SiO₂ core-shell nanoparticles (NPs) is the other promising material here presented as safe alternative and studied for producing antibacterial textiles, as well as photocatalytic ceramic tiles [2]. TiO₂-SiO₂ NPs have been prepared by means of a colloidal versatile heterocoagulation process [3], practical and easy transferable on large scale production which allows the surface covering of the active TiO₂ with the inert SiO₂ inorganic phase. The SiO₂ modified TiO₂ NPs showed a decreased production of reactive oxygen species (ROS), representing a positive response as reduction of potential hazard, jointly with an improvement of the photocatalytic activity assessed in terms of deNO_x performance, in addition the antibacterial activity was preserved on TiO₂-SiO₂ coated fabrics. The outstanding result is that it is possible to dilute the amount of TiO₂ with silica, decreasing the production of ROS, but improving the functional performances of pristine sample.

Keywords: Safe-by-design; Nanoparticles, Antibacterial fabric.

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Acknowledgement:

This research received support from the H2020 EU PROTECT (Pre-commercial lines for production of surface nanostructured antimicrobial and anti-biofilm textiles, medical devices and water treatment membranes) Collaborative Project (H2020-NMBP-PILOTS-2016-720851).



Effect of Ionic Liquids on the Activity and Conformation of Formate Dehydrogenase from *Pseudomonas Sp. 101* in the Presence of Lyoprotectants

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Ionic Liquids (ILs), thanks to their tailor-made chemical, physical and biological special properties, are emerging as new solvents for applications in electrochemistry, biocatalysis and drug formulation.

The possibility to use enzymes in neat non-conventional media (i.e., ILs, organic solvents) is usually exploited for synthetic applications because of several advantages, such as the possibility to avoid side reactions due to water, to increase the solubility of hydrophobic substrates or to modulate some properties as regio- and enantioselectivity of the biocatalyst. In this perspective the use of ILs as media for synthetic purposes seems to be very promising because of the large number of available ILs.

Contrarily to biocatalysis carried out in organic solvents, where enzymes are usually suspended in the reaction system, with an appropriate ILs it is possible to use them in soluble form, which can be a situation helpful to reduce diffusional limitations and to improve enzyme performances.

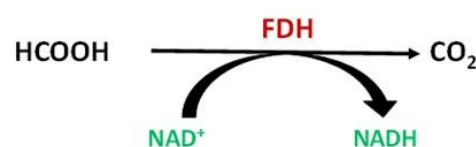
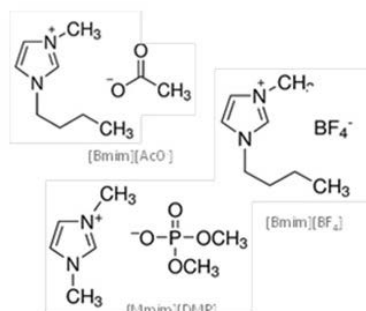
Besides biocatalysis, ILs might be exploited as solvent and/or co-solvents in other protein-based biotechnological applications. ILs can favor the solubilization of protein based polymers from biomasses (e.g., fibroin, keratins) [1] or the refolding of proteins of intracellular inclusion bodies [2]. However, media that do interact with proteins making them soluble (e.g. some ILs or DMSO or DMF) usually also interfere with intramolecular bonds, causing unfolding and deactivation [3].

In order to shed light on the use of neat ILs for enzyme dissolution, we studied the solubility of formate dehydrogenase from bacterium *Pseudomonas sp. 101* (FDH) in different ILs and their effects on the enzyme stability. The aqueous solution of the enzyme was lyophilized and the dry product re-dissolved with ILs. However, since freeze-drying can cause different type of stresses including low temperatures, ice crystal formation and pH shift that can lead to denaturation or inactivation, we co-lyophilized FDH with different lyoprotectants (saccharose, trehalose, mannitol and PEG4000).

The lyophilized FDH with and without lyoprotectants was dissolved in neat imidazole-based ILs ([Mmim][Me₂PO₄], [Bmim][BF₄] and [Bmim][OAc]) and the residual activity measured in water.

The data obtained showed that the lyoprotectants allow a recovery of catalytic activity up to 40 % of the initial activity (before lyophilization). On the contrary, when the enzyme was lyophilized in the absence of lyoprotectants, the activity recovery was not higher than 10% of the initial activity. However, lyoprotectants shows only in the case of trehalose a modest stabilizing effect (preservation of activity as a function of time) of the enzyme in [Bmim][BF₄].

Figure. Structures of the studied ILs: 1-Butyl-3-methylimidazolium acetate - [Bmim][OAc]; 1-Butyl-3-methylimidazolium tetrafluoroborate - [Bmim][BF₄]; 1,3-Dimethylimidazolium dimethyl phosphate - [Mmim][DMP] (left) and reaction catalyzed by formate dehydrogenases (right).





Keywords: ionic liquids, enzyme formulation, protein stability

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Acknowledgement:

This work was supported by joint grant between Italian National Research Council (Prot. n. 421- 09-03-2015) and Russian Foundation for Basic Research 15-54-78035



Project 65: Strengthening Chemical and Biological Waste Management in Central Asia Countries for Improved Security and Safety Risk Mitigation

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European Union (EU) CBRN Risk Mitigation Centres of Excellence (CBRN CoE) project 65 is an EU funded project which aims to address the issue of chemical and biological waste management in the Central Asia (CA) region. The aims and objectives of the project were agreed with the National Focal Points of the CA partner countries and were outlined in the Project Terms of Reference upon which the current project plan is based. The aim of the project is the need to strengthen existing chemical and biological waste management capabilities.

In order to achieve all the points attended for Project 65, the latter has been structured around the delivery of nine work packages (WPs). The Institute of Molecular Science and Technology (CNR-ISTM) is the leading organization of WP4, whose main purpose is to raise or enhance the awareness of the main actors across the beneficiary Countries on the correct management of chemical and biological wastes and to design, plan and organise training sessions on safety & security aspects related to the generation, handling, transportation, containment and disposal of C and B waste materials at different level, i.e. from laboratory scale, to minor and major production sites. These activities will aim at building or strengthening a local capability to foresee, prevent, minimize and/or mitigate chemical or biological incidents and emergency situations involving hazardous chemicals at both national and regional level among beneficiary Countries.

In detail, the activities within WP4 are grouped in two main tasks:

- Task 1 – Awareness raising on chemical and biological waste management
- Task 2 – Implementation of a sustainable training system for lifelong learning.



Keywords: chemical waste management, chemical risk, recycling and regeneration



Carbon Nanomaterials as Efficient Catalysts for Organic Reactions

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Carbon based materials such as carbon black (CB), carbon nanotubes (CNTs) and graphene or chemically modified graphenes (CMGs), have been used for various applications in energy storage, electronic, optics, biomedical engineering, medical devices, sensors, etc.¹ Some of these nanomaterials have also been applied in catalysis² above all as supports for catalytically active transition metals, thanks to their unique properties such as high surface area, stability and high conductivity.

The replacement of environmentally hazardous Brønsted and Lewis acid catalysts with environmentally benign heterogeneous catalysts is currently an intriguing research area and, in this context, the application of nanostructured carbon materials as metal free catalysts for facilitating synthetic organic reactions is a new emerging area with great potential.

As part of our research program in developing innovative synthetic methodologies, herein³ we report the highly efficient activity of some of these nanomaterials as catalysts for condensation reactions with particular attention to the experimental conditions (low impact solvents and very small amounts of catalyst), according to the growing demand for highly sustainable chemical procedures. Interesting aspects such as the recycling and reusability performance of the nanocatalysts were also investigated. Finally, the elaborated methodologies were conveniently exploited for the synthesis of the 1,5-benzodiazepine nucleus, that is a very interesting heterocyclic scaffold with a wide range of application in the pharmaceutical industry.

Keywords: Carbocatalysis – Solvent-free – Benzodiazepine

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Acknowledgement:

Financial support of “Ministero dell’Istruzione, dell’Università e della Ricerca” is gratefully acknowledged.



Hydrogen and Acrylate Generation by Electrochemical Reforming of Bioalcohols

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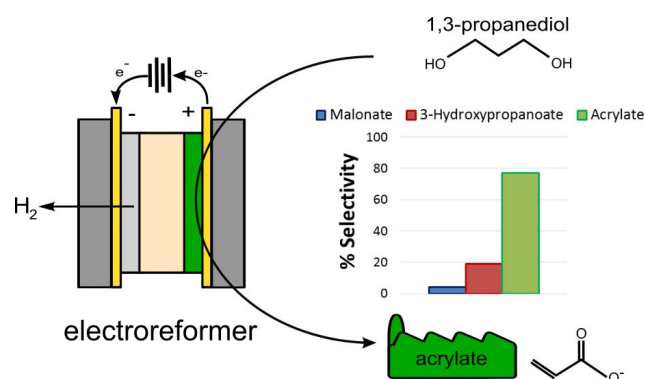
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The production of hydrogen by the electrolysis of water is a well-established technology. However, it does not have a significant commercial impact due to its high-energy cost. A traditional Proton Exchange Membrane (PEM) electrolyzer needs more than 45 kWh kgH₂⁻¹ to achieve a significant rate of hydrogen production.^[1] This is the main reason why water electrolysis accounts for only a small proportion of the world's hydrogen production (circa 4%). Since the thermodynamic barrier of water electrolysis consumes 68% of the whole energy input of the device, our strategy for reducing the energy cost is the replacement of the unfavorable anodic oxygen evolution reaction with a more suitable reaction: the partial oxidation of an alcohol to a carboxylate. This process needs only 20 kWh for the evolution of one kilogram of hydrogen at the same working conditions of traditional PEM electrolyzers, with a net energy saving of about 44%. Such electrolytic processes that lead to the concomitant generation of hydrogen and industrially relevant chemicals, like acetate and lactate, are often indicated as “electrochemical reforming”, or “electroreforming”.^[2] In order to obtain selective oxidation of alcohols to carboxylic compounds of interest to the fine chemical industry, several anodic catalysts have been investigated, ranging from nanostructured palladium catalysts to rhodium organometallic compounds.^[2,3] Here we present an anode based on palladium nanoparticles deposited onto a carbon-ceria support Pd(10%)/C:CeO₂ (50%/50%) which is able to selectively oxidize the 1,3-propanediol biomass derived alcohol to potassium acrylate, a very important raw chemical. The production of acrylate is coupled with the generation of pure hydrogen (99.99%). We had and in depth study of the operative conditions of the electroreformer to optimize the selectivity of the alcohol oxidation reaction to potassium acrylate: at 400 mV and 80°C in a “single pass mode”, the selectivity is of the 80% for acrylate.^[3]



Keywords: Hydrogen production, renewable alcohols, electrocatalysis

References:

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First-Principles High-Throughput-Screening Catalyst Design for Ammonia Synthesis

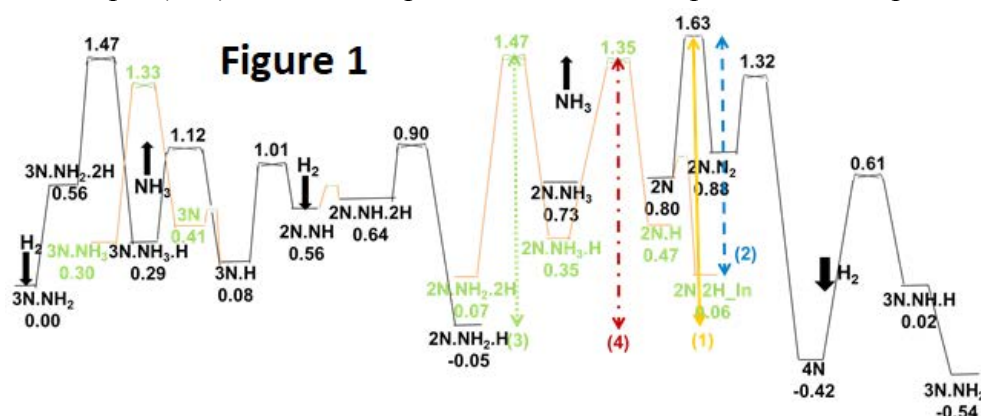
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The Haber-Bosch industrial process for synthesis of ammonia (NH₃) from hydrogen and nitrogen produces the millions of tons of ammonia gas annually needed to produce nitrates for fertilizers required to feed the earth's growing populations. This process has been optimized extensively, but it still uses enormous amounts of energy (2% of the world's supply), making it essential to dramatically improve its efficiency. To provide guidelines to accelerate this improvement, we used Quantum Mechanics (QM) to predict reaction mechanisms and kinetics for NH₃ synthesis on Fe(111) - the best Fe single crystal surface for NH₃ synthesis. We predicted the free energies of all reaction barriers for all steps in the mechanism (see Fig. 1) and built these results into a kinetic Monte Carlo model for predicting steady state catalytic rates to compare with single-crystal experiments at 673 K and 20 atm. We find excellent agreement with a predicted turnover frequency (TOF) of 17.7 s⁻¹ per (2×2) unit cell compared to TOF = 10 s⁻¹ per site from experiment [1].

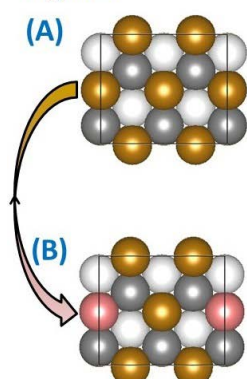


Next, we developed a hierarchical high-throughput screening (HHTS) approach to catalyst design based on the thus-derived detailed reaction mechanism and we applied it to the Haber-Bosch ammonia-synthesis process as a prototype test case [2]. We started from the QM-based free-energy diagram for HB over Fe(111), we selected the

key reaction steps that might become rate-determining, which we arranged hierarchically by decreasing free-energy barriers, we defined a reduced set of reaction energies to quickly predict the effect of catalyst changes on each barrier, we defined a catalyst change strategy as single-element substitutional top-layer doping, and screened sequentially 34 candidate dopants to single out the subset satisfying all criteria, including stability (see Fig. 2).

Among the 4 dopants (Rh, Pt, Pd, Cu) expected to accelerate NH₃ production, we tested the best candidate (Rh) by a complete free-energy and kinetic analysis, finding an acceleration by ≈4 times in the rate of NH₃ synthesis compared to Fe(111), in excellent agreement with predictions from HHTS, validating our approach.

Figure 2



(C) ■ N₂ads-dis-I ■ N₂ads-dis-II ■ hydrogenation

■ NH₃desorption ■ stability

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
21	22	23	24	25	26	27	28	29	30
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
39	40	41	42	43	44	45	46	47	48
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
57	72	73	74	75	76	77	78	79	80
Ce			Eu			Er	Tm		Lu
58			63			68	69		71



Keywords: heterogeneous catalysis- rational design - density-functional theory

References:

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Acknowledgement:

A.F. gratefully acknowledges financial support from a Short-Term Mission (STM) funded by Italian Consiglio Nazionale delle Ricerche (CNR). This work was supported by the U.S. Department of Energy (USDOE), Office of Energy Efficiency and Renewable Energy (EERE), Advanced Manufacturing Office Next Generation R&D Projects under contract no. DE-AC07-05ID14517.



Synthesis of Ceramic Powders for Energy Applications

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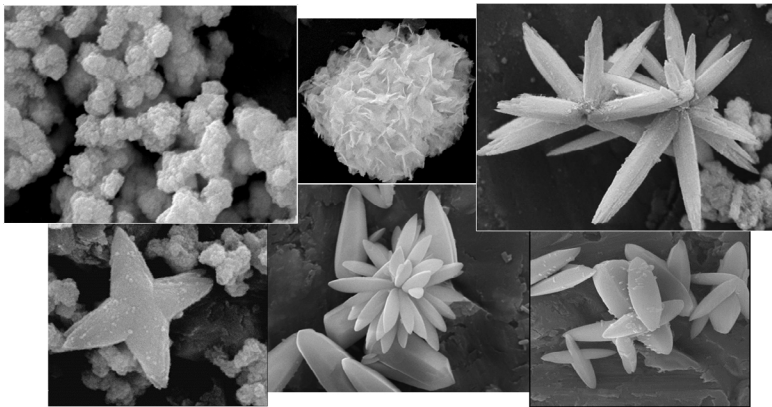
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Ceramic powders (ceria-based, titania-based, silica-based, etc.) have been extensively studied and used in a wide range of energetic and catalytic applications. Several synthesis methods were proposed to obtain these type of powders, however an accurate study of the most appropriate method and of the parameters involved is necessary to obtain morphology, size, composition and properties suitable for each application.

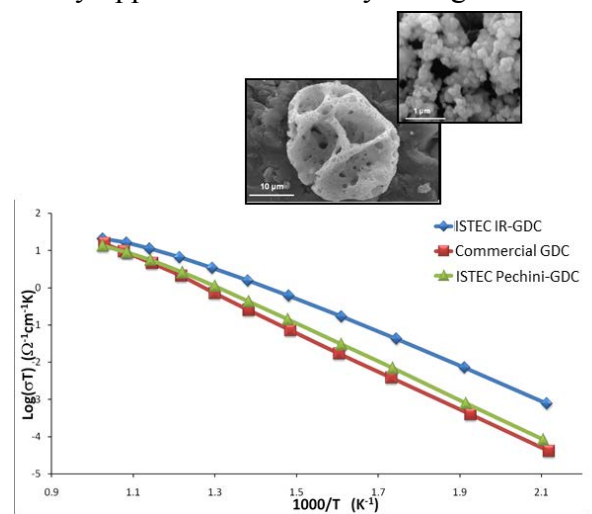
In this work, the effect of different synthesis methods and parameters were accurately studied in order to control the properties of the powders. The synthesis of CeO_2 , Gd-doped CeO_2 and $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ were investigated as case study.

Ultrafine CeO_2 and Gd-doped CeO_2 (GDC) powders were obtained using standard chemical routes coupled with non-conventional heating processes (IR and Microwave) [1-3]. Ceria were found to be active in the catalytic oxidation of toluene whereas GDC obtained through the optimization of the synthesis parameters exhibited high values of ionic conductivity suitable for Intermediate Temperature Solid Oxide Fuel Cells applications.

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ were produced using the conventional solid state reaction and sol-gel route. The effect of cations doping and additional milling procedure were considered to increase the performance and the specific surface area of the synthesized powders. These materials were successfully applied for the catalytic degradation of pollutants.



Powder morphologies obtained with non-conventional heating processes



Conductivity of the synthesized GDC powder (ISTEC) compared to the commercial one

Keywords: Ceramic nano-powder, Synthesis Method, Synthesis Parameters

References:

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Acknowledgement:

The authors would be very grateful to Prof. S. Albonetti for the toluene oxidation measurements and to S. Boldrini and L. Doubova for the conductivity measurements of GDC powders.



Synthesis of Nanoparticle Oxides via Flame Spray Pyrolysis

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In the last years, flame spray pyrolysis (FSP) process has been proven to be an efficient method for synthesis of single- and multi-component nanoparticles oxides with tailored characteristics. Properties such as crystallite size, crystalline phase, degree of aggregation and agglomeration, surface area and porosity can be very challenging in different applications including catalysis, gas sensors as well as energy storage.

In our laboratory in Milano, nanoparticles oxides are produced with a flame spray pyrolysis using an oxygen-assisted spray apparatus in order to inject the precursor coaxially with the pilot flame. The liquid precursor is normally feed through the spray nozzle by using a syringe pump. The apparatus has been designed and developed in order to produce nanoparticles in powder as well as in film. In fact, in the case of catalytic application, e.g. air and water treatment or industrial chemical transformations, the availability of supported photocatalyst can be very useful to overcome several problems of process design and implementation.

To obtain the film, the nanoparticle oxides are deposited by orthogonal impingement on a cooled substrate (alumina or stainless steel) holder placed at 30 cm height above the burner. Cooling temperature was kept at about 100 °C to avoid water condensation on the holder. A pneumatically operated mechanical shutter placed above the target substrate allows the control of the exposure time of the aerosol-generated powder deposition. Temperature field along the synthesis process and nanoparticles collection is properly changed and monitored in order to obtain nanoparticles of particular chemical and physical characteristics. After synthesis, nanoparticles films are annealed in order to improve film-substrate adhesion.

Synthesis of TiO₂ and SnO₂ are performed with this method and then characterised by means of XRD, STEM and FT-IR analysis.

The results prove the potentials of the method as a scalable technology for synthesis of advance materials in powder as well as powder supported deposit.

Keywords: nanoparticles, oxides, flame spray pyrolysis

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Acknowledgement:

The authors would like to acknowledge the financial support from the CNR- Regione Lombardia Agreement in the framework of the project: I-ZEB (Towards Intelligent Zero Energy Buildings for smart city growth)



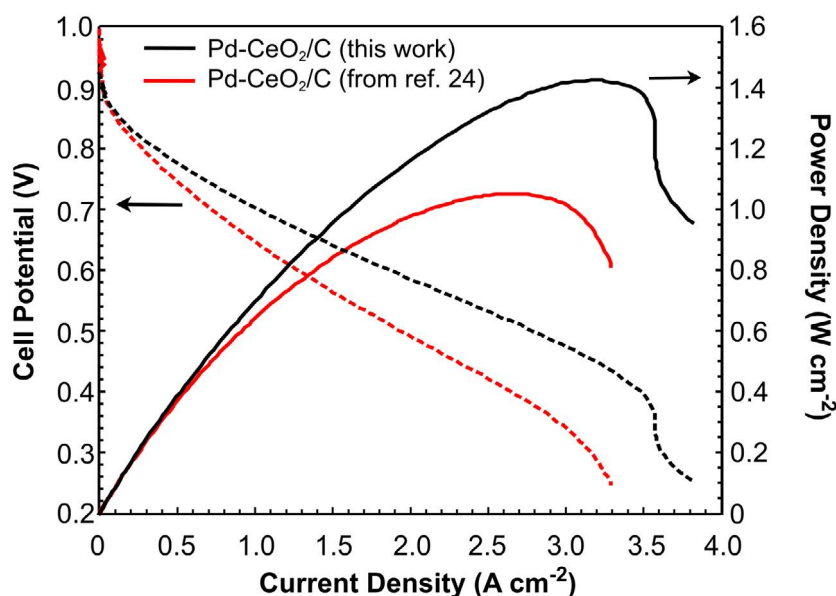
Anion Exchange Membrane Fuel Cells: Enhanced Alkaline Hydrogen Oxidation Activity for Ceria-Palladium Nanoparticle Catalysts

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Anion exchange membrane fuel cells (AEMFCs) offer several important advantages with respect to proton exchange membrane fuel cells (PEMFCs), which can contribute to overcoming the high cost of fuel cell systems that has largely slowed large-scale implementation. The poor kinetics of the hydrogen oxidation reaction (HOR) and other limitations in performance such as the instability of membranes have stalled AEMFC development. Replacing Pt at the anode with a cheaper catalyst that has also enhanced activity for the HOR is a key objective for those working in the field of AMFCs. We recently reported a new class of HOR catalyst based on Pd nanoparticles supported on carbon and CeO₂ that allowed us to achieve 0.5 W cm⁻² peak power density in a Pt-free AEMFC.¹ In this presentation, we report further enhanced HOR kinetics due to a maximized Pd-CeO₂ contact between these two phases on the nanoscale. To date, this is the only alternative non Pt HOR catalyst yet reported that matches state of the art fuel cell performances (> 1 W cm⁻²). We present here a reproducible synthesis (on the gram scale) that consists of the addition of CeO₂ to carbon using an organometallic precursor followed by Pd deposition. With this catalyst more than 1.4 W cm⁻² peak power density in fuel cell testing is achieved (Figure 1).



Keywords: Fuel cells, Platinum free, Anion exchange membrane

References:

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3D Engineered Photoanodes for Dye-Sensitized Solar Cells

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The extensive use and growing dependence on electrical and electronic equipment increased the energy/power requirements on a global scale. With dwindling fossil-fuel reserves, there is an urgent need to find alternative energy resources to meet the growing demand; they must be efficient, cost-effective and ecologically friendly. In this context, the harnessing of solar energy and its conversion into electricity made by photovoltaic devices, becomes very attractive. Among all the different technological options, in the recent past lot of scientific community efforts have been focused on a rapidly evolving technology, the Dye-sensitized Solar Cells (DSCs)[1]. Their key features are high versatility, low cost and the use of environmental-friendly materials. A fundamental DSCs component is the photoanode (typically composed of a mesoporous TiO₂ screen-printed film), which represents the device nucleus. The afore-mentioned random porous TiO₂ structure is perfectible in order to overcome some undesired characteristics like low conductivity and limited access, for dye and electrolyte, to the entire film surface. Consequently techniques for fabricating photoanodes, with improved both conductivity and accessibility to the semiconductor, are of great interest. In this work, 3D engineered photoanodes (Figure 1), composed by micro-pillars supported onto a mesoporous layer, were produced using a combination of wet-powder spraying (WPS) and the additive manufacturing technique called micro-extrusion (or robocasting)[2].

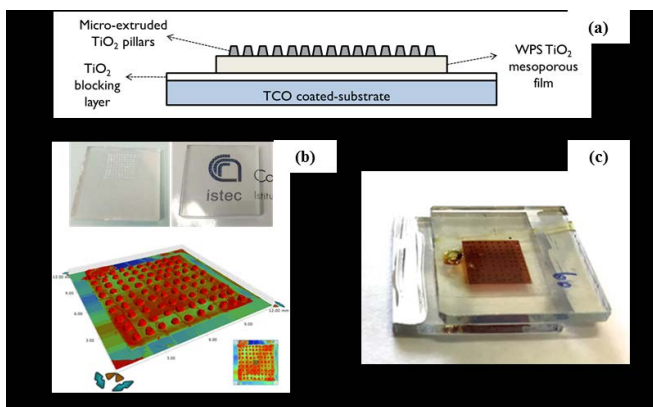


Figure 1 – (a) Schematic representation of the 3D engineered photoanode (b) Photoanode topography and (c) DSC prototype

These processes were performed using a fully-automated multi-head machine highlighting their easier scalability. High-transparent mesoporous TiO₂ films were obtained through WPS technique. The target was properly pursued optimizing, (in terms of stability and substrate/suspension interactions), a modified commercial aqueous-based colloidal TiO₂ suspension and evaluating the impact of the main process parameters (fluid flow, the number of consecutive depositions, etc.) on the film quality. The most performing TiO₂ mesoporous sprayed layer (thickness about 3 μm) showed definite improving in the substrate coverage and a very smooth surface, confirmed by the optical and SEM images. A

highly mesoporous microstructure was observed and its great transparency confirmed by a T% of about 95%. The sprayed TiO₂ film showed an improved dye adsorption capability and higher photovoltaic performance than a common screen-printed film having same area and thickness. 3D coarse micro-pillars were deposited on the optimized WPS film using the micro-extrusion technique. Following a colloidal-based formulation approach, the initial TiO₂ content was set at 5 vol.% and two different amounts (4.70 and 5.60 wt.%) of cellulosic blend were investigated. Micro-pillars with a highly porous microstructure and a mean aspect ratio (AR) of about 0.060 were obtained with the most concentrated paste and carefully optimizing the different process parameters (nozzle diameter, deposition time, etc.). Consequently DSC prototypes, constituted by 3D engineered photoanodes were built and characterized.



The mean DSCs efficiency value with sprayed films was around 2.4% while it exceeded 3.0 % for the ones with 3D structures. The augmented performances were due to a progressive increase in both the current density (Jsc) and open circuit voltage (Voc). Regarding the IPCE measurements of the prototype with the engineered photoanode, the maximum conversion efficiency was about 30%. This improvement was mainly ascribed to the perfected properties of the electrode containing the micro-pillars and, secondly, to its higher dye loading capability. Electrochemical Impedance Spectroscopy (EIS) showed a reduced charge transfer resistance (Rct), therefore an improvement of the charge transport and of the generated photocurrent.

Keywords: Dye-sensitized Solar Cells, Wet-powder spraying, Additive Manufacturing.

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Platinum-free Dye-Sensitized Solar Cells

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Dye-Sensitized Solar Cells (DSSCs) represent one of the most interesting solar technology for low powered application (portable electronics, internet of things) and for Building-Integrated Photovoltaic (BIPV). Most of these applications require transparent device and the absence of liquid parts. In particular, for portable electronics no-liquid parts should be present on the other hand highly transparent device are required as well as for BIPV application where the light can reach the solar cell from both sides (bifacial solar cells). Moreover, increasing the device stability, reducing the production costs and increase the overall sustainability are fundamental challenges that need to overcome in the next future for complete DSSCs commercialization. In order to achieve these goals, Platinum as counter-electrode must be replaced with other catalytic materials such as conducting polymers (CPs), carbon based materials or metal alloys ^[1].

In this work, some of keys aspects related to the influence of the properties of polymer counter-electrode on the efficiency of bifacial and gel-state DSSCs will be presented. Suitable and low cost conducting polymer such as polypyrrole (PPy) are considered as counter-electrode. PPy films were prepared by electrochemical method and doped with different anions in order to assess the properties that affect the efficiency of a bifacial solar cell. The study revealed the importance of the optical properties of the electrolyte/counter-electrode interface on the overall efficiency of a transparent device. On the other hand the application of Molecular Imprinting Polymers (MIPs) as counter-electrode in DSSCs was introduced for the first time to enhance the selectivity towards triiodide molecule contained in the electrolyte and the final efficiency of the solar cells. The DSSC electrolyte is commonly a complex matrix containing other than the triiodide (the target molecule) also other compounds used as additives and stabilizers that can interfere with the triiodide reduction lowering the cell efficiency. Molecular Imprinting Technology (MIT) is traditionally applied into a wide range of application areas where high selectivity versus a target molecules is required (like high performance sensors)^[2]. The application of MIPs counter-electrode allowed a definite increase in the photovoltaic efficiency of the device as a consequence of the lowering of charge transfer resistance at the counter-electrode side. These results open the possibility to apply MIP materials into energy systems based on photo-electrochemical cell improving their properties.

Keywords: DSSCs counter-electrode; Molecular Imprinting Technology; Polipyrrole.

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RM@Schools 3.0: A Wider Society Learning Project

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Raw Matters Ambassadors at Schools 3.0 (RM@Schools) is an innovative program to make science education and careers in raw materials (RM) attractive for youngsters, involving RM experts and teachers (RM Ambassadors). It proposes to schools an active learning by involving students in experiments with RM-related hands-on educational kits and in communication activities. Indeed, as pointed out also by the known phrase of Confucius “If I hear I forget, if I see I remember, if I do I understand”, the use of an active learning by the experimental approach, i.e. set-up of laboratories where students can meet science by experiments, is an improvement of science teaching.

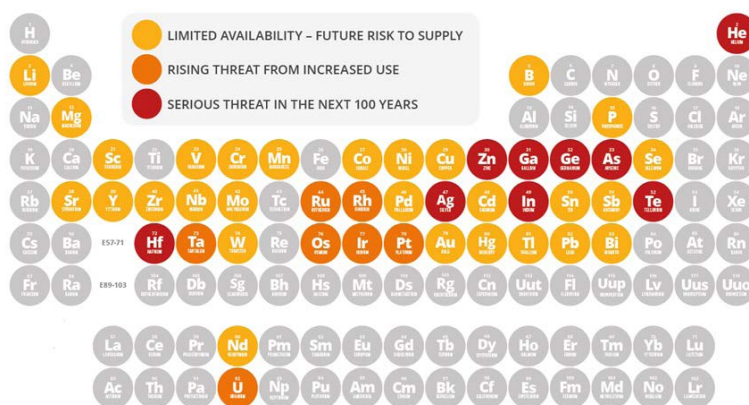
The project is carried on by a consortium which comprises 21 partners from 13 EU countries with complementary expertises in the field of RM and education: (1) CNR (project coordinator) –Italy, (2) Stichting Wetsus - The Netherlands, (3) University of Liege – Belgium, (4) Technische Universität Clausthal – Germany, (5) Universidad Politecnica de Madrid – Spain, (6) Bay Zoltán Nonprofit Ltd. – Hungary, (7) Fraunhofer Institute - Germany, (8) Montan-Universitaet Leoben – Austria, (9) KTH - Royal Institute of Technology –, (10) Fundação para a Ciência e a Tecnologia-, (11) Politecnico di Milano –Italy, (12) RWTH Aachen University – Germany, (13) Tallinn University of Technology- Veiko Karu, (14) University of Milano- Bicocca – Italy, (15) University of Bologna – Italy, (16) Geological Survey of Slovenia – Slovenia, (17) Geological Survey of Sweden – Sweden, (18) ECODOM – Italy, (19) Commissariat à l'énergie atomique et aux énergies alternatives – France (19) ASTER- taly; (21) Aalto University – Finland. The consortium is coordinated by ISOF-CNR, but also other CNR institutes are strongly involved in the project, such as ISTM in Milan, IMM and ISTM in Bologna, and ISM in Rome.

RM@Schools 3.0 aims to **promote and assist a wide dissemination action on RM-related themes in Schools and Society** through a wider collaborative dialogue and networking between European and Local Actors, and strategic partnership between Research, School, and Industry. The specific objective RM@Schools 3.0 is to set-up and diffuse a common and replicable dissemination approach within the Raw Material Academy dedicated to young students (10-19 years old), starting from Research versus Schools and, in turn, reaching Society, in terms of not only families but the general public.

RM@Schools 3.0 originates from Raw Matters Ambassador at Schools (**RM@Schools 1.0 and 2.0** - <http://rmschools.isof.cnr.it/>), born in 2016 by a Consortium constituted by 6 EU partners, and has elaborated a **strategic planning of dissemination capacity and methodology** to improve the image of science & technology in schools (student age: 10-19 yrs), with a specific focus on raw materials themes and to promote new professional careers in this sector. This year it has become the Flagship Program in the segment of Wider Society Learning of EIT Raw Materials, by involving about 1300 students in all Europe and promoting many open-access Events.

Keywords: critical raw materials, education, 3R

THE PERIODIC TABLE'S ENDANGERED ELEMENTS



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Semax, a Copper Chelator that Influences the Cu(II) Induced Aggregation, Ros Production and Cytotoxicity of A β by Metal Ion Stripping and Redox Silencing

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Alzheimer's disease (AD) is the most common neurodegenerative disorder associated with cognitive decline and loss of memory, a degeneration of cognitive skills and a loss of neurons that occurs in the cerebral cortex and hippocampus of the brain. There is a general consensus that copper ion participate in two processes related to AD pathology: i) the aggregation of A β peptides to form senile plaques and neurofibrillary tangles, and/or ii) the augmentation of metal ion mediated oxidative stress. It is postulated that aggregation of A β in the presence of redox-active metal ion like copper is responsible for the additional trait of cellular toxicity by the generation of reactive oxygen species (ROS) in Fenton-like reaction connected with Cu(II)/Cu(I) redox cycling of the Cu(II)-A β complex. Moreover A β -metal ion complexation influences the aggregation pathway of A β and is shown to stabilize the toxic oligomeric state in vitro. The multifaceted toxicity induced by A β oligomers and aggregates with metal inclusion leads to cell death. Interestingly, recent evidence showed that Cu(II) enhances the effect of A β on microglial activation and neurotoxicity involving mitochondrial ROS production and potentiates the spatial memory deficit induced by A β in the hippocampus of rats. In this context molecule that inhibit the formation of more toxic A β -metal aggregates, disrupt the A β -metal ion complex by metal stripping and prevent ROS generation and membrane disruption is a promising therapeutic strategy for preventing the progression of AD. The peptide Semax (Met-Glu-His-Phe-Pro-Gly-Pro) is a synthetic peptide consisting of the ACTH(4–7) fragment and the C-terminal tripeptide Pro-Gly-Pro (PGP) which exhibits neuroprotective, neurotrophic and nootropic properties, stimulates learning and memory formation in rodents and humans and is the basis for a number of drugs that are used in the clinical practice for the treatment of CNS diseases. Recently, we demonstrated that Semax possesses a high affinity for Cu(II) ions (ATCUN binding site) and a protective ability against metal-induced cell toxicity. The ability of the peptide Semax to influence the Cu(II) induced A β aggregation, to inhibit the copper catalyzed oxidation of A β and silence the Cu(II)-A β complex were studied in vitro and in-cell and discussed. The results indicate that Semax is able to modulate A β aggregation in presence of Cu(II), to extract Cu(II) from Cu(II)-A β species as well as to influence the redox cycling of the Cu(II)-A β complex and decrease the level of associated reactive oxygen species (ROS) production. Finally we find that these properties of Semax confer cytoprotection to SH-SY 5Y cells against oxidative stress induced by copper catalyzed oxidation of A β peptide. This study provides further insights in the potential role of Semax in neurodegenerative disorders and into the design of new compounds with therapeutic potential for Alzheimer's disease.

Keywords: Beta Amyloid, Semax, copper

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Data-Matrix Technology for Multiparameter Monitoring of Cell Cultures

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Cells can be used as efficient sensors exploiting their change upon external/internal stimuli morphology, shape, immunofluorescence and so on. Moreover, cell cultures are one of the most powerful activity for the initial stage of a variety of application in life science, ranging from the mono-cellular level study to complex multicellular tissue and regenerative medicine. The number of cells adhered on a substrate, their morphology, spatial distribution and the capacity to migrate are widely used information to establish cell wellness and as a first order characterization the differentiation stage. In N-CHEM project we developed a new method, in which we addressed the problem of multiparameter monitoring of cell cultures by introducing the data-matrix technology in cell biology as an efficient method for facile, real time, multi-parameter monitoring of cell cultures. The method exploits the know-how developed for error handling in digital information technology developed for satellite communications and used for data-matrix technology. The method is based on the measure of reading errors induced by intervening cells upon checking a fluorescent data-matrix code placed behind them. By reading fluorescence images via a modified data-matrix reader of a smartphone, the method delivers number of fluorescent cells, coverage and time evolution. The process has been demonstrated with several immunostained model cell cultures as well as by monitoring the evolution in time of green fluorescent protein in a fibroblast culture and for cell sorting.

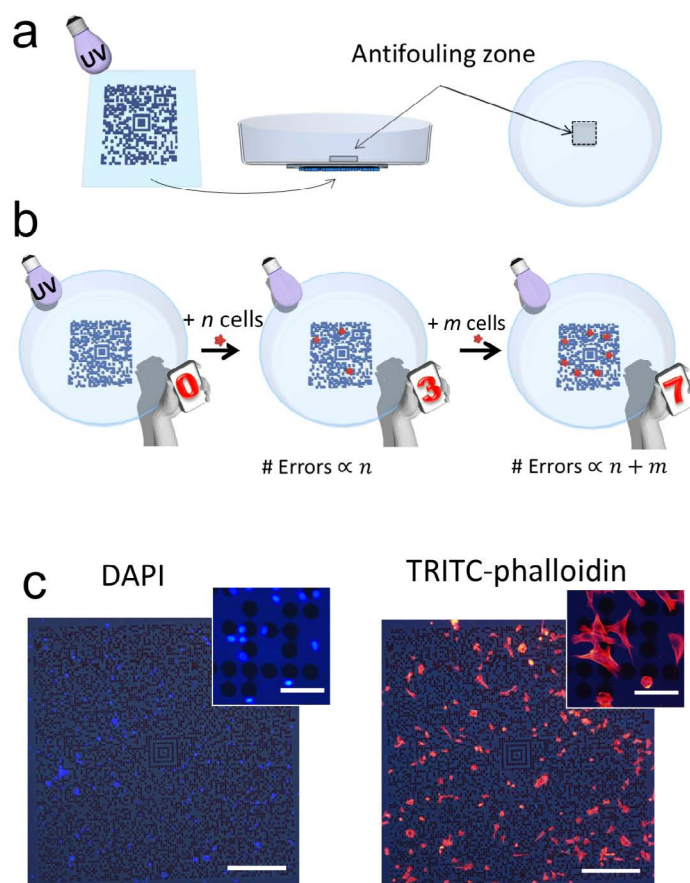


Figure 1. Concept of data-matrix cell monitoring device and method. a) Structure of the device. The data matrix, which becomes visible in fluorescence mode, is placed under the substrate. An antifouling zone is printed on the substrate in contact with a Petri-dish in correspondence of the reference markers of the data matrix. b) Concept of the method. Cells proliferation generates a number of errors proportional to the number of cells. c) Real cell culture observed through a fluorescent data-matrix code placed on the background. DAPI immunofluorescence image of NIH-3T3 cell culture showing the nuclei of the cell. The contrast is artificially enhanced to better visualize the nuclei and corresponding immunofluorescence image expressed by TRITC-phalloidin. The insets show a zoom. Bars are 200 μm ; insets 20 μm .



Keywords: ell culture devices, data matrices, soft lithography

References:

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Acknowledgement:

This work was supported by Italian flagship NANOMAX, N-CHEM. The project Air Force AFOSR-ASTRO-MAT-(FA9550-16-1-0502) and AFOSR ASTRONIR, FA9550-17-1-0052) are acknowledged.



Glial Interface: Engineering Tools for Brain Study and Health by Using Materials, Device and Approaches Targeting Astrocytes Physiology and Biophysics

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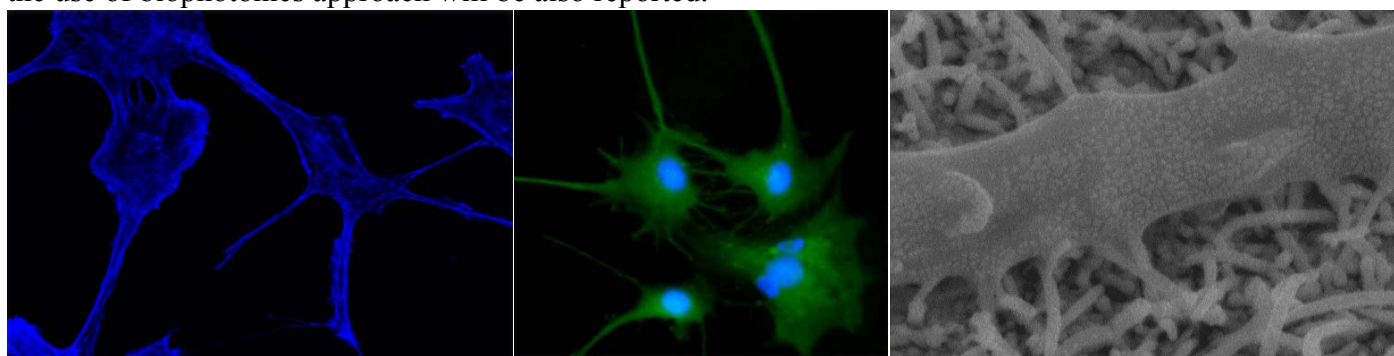
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Exploiting the potential of nanostructured material to interface and modulate molecular and functional properties of brain cells in the central nervous system, will be critical to increase our understanding of nervous system function and dysfunction. Results produced over the past 30 years have moved the neurocentric vision of brain science towards the study of the role of non-excitabile glial cells, called astrocytes. Astrocytes are the most numerous type of cells in the central nervous system (CNS). Their ion channels and aquaporins play crucial roles in the maintenance of cerebral homeostasis as well as in the modulation of synaptic activity. Consolidated evidence demonstrates the causal role of astrocytes in acute neurophathologies and chronic disease. Nonetheless, the study of astrocytes/material interaction is essential for engineering biosensor and bioelectronic device targeting the brain, as astroglial reactivity is a major cause of failure of implant performance over long term.

In this view, our studies are devoted to the design, engineering, implementation and validation of glial interface i.e. to take advantage of bioelectronic and biophotonic materials, devices and approaches to study, understand and manipulate astrocytes physiological and pathological processes.

Here results obtained with organic bioelectronic device as well as with hybrid and polymeric materials will be reported. We will show the ability of glial interfaces to control and to manipulate acutely and chronically the molecular and biophysical properties of protein channel in astrocytes *in vitro* such as calcium signaling, ionic conductance and water permeability. Insight on astrocyte biosensing and transduction capability, provided by the use of biophotonics approach will be also reported.



Keywords: glial chemistry, neuroregenerative medicine, glial interface

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Acknowledgement:

This work is supported by AFOSR research grant Astromat and Astronir



Combined HS-SPME-GC-MS and HPLC Analysis of Saliva Metabolites after the Assumption of Rifaximin, Prebiotics and Probiotics as an Indirect Assessment of Gut Microbiota

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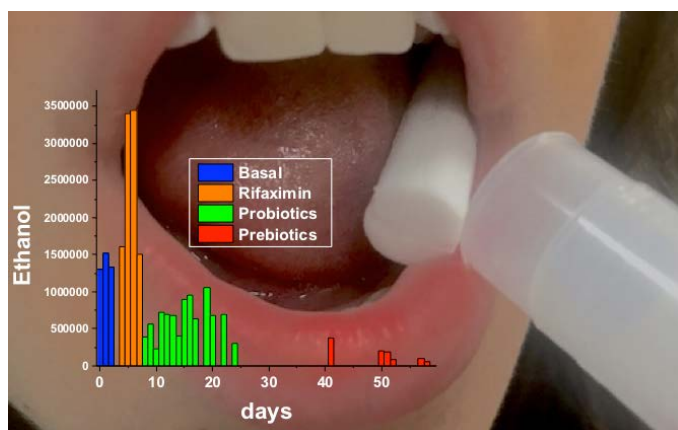
We investigated by headspace-solid phase microextraction-gas chromatography-mass spectrometry (HS-SPME-GCMS) and liquid chromatography (HPLC) the dynamics of volatile and non-volatile metabolites in saliva of a single subject undergoing treatment with antibiotic followed by probiotics and prebiotics. Multivariate analysis (Principal Component Analysis, Linear discriminant analysis and Hierarchical Cluster Analysis) was applied for the analysis of data.

Non-stimulated saliva samples were collected for 31 days from a nominally healthy volunteer during the antibiotic treatment with rifaximin, followed by probiotics (*Saccharomyces boulardii*) and prebiotics (*Aloe vera*). Salivary volatile organic compounds (VOCs) were detected by HS-SPME-GCMS and non-volatile metabolites by HPLC with UV-visible detection.

Saliva is a very feasible biological specimen as it can be easily collected and comprises metabolites absorbed in all gastrointestinal (GI) mucosae. Metabolites flow in the blood stream and are partitioned from blood through salivary glands in saliva, thus reflecting globally the GI microbiota. This would represent an advantage with respect to the faecal analysis, considering that the composition of microbiota is different in the various parts of gut and that faeces composition reflects only the last part of gut. Furthermore, the results obtained from culture-based methods are not always in agreement with those obtained from culture-independent techniques [1]. Moreover, the processing of faecal samples requires optimised and standardised protocols for their collection, homogenisation, microbial disruption and nucleic acid extraction [2].

Although the vast majority of studies on VOC biomarkers have been conducted using exhaled breath samples, thanks to the non-invasiveness and safety of the sampling process, VOCs analysis in exhaled breath is still challenging due to the low concentrations of the VOCs, the difficulty in breath storage and to the absence of standard sampling and analysis protocols [3].

Several metabolites were found to be significantly associated with the administration of rifaximin (1-butanol, 2-butanol, 2-butanone, 2-pentanone, ethyl acetate, methyl acetate, ethanol, isopropanol, decanol, 1-ethanol, dimethylsulfide) and *Aloe vera* (oxalate, acetic acid, 2,3-butanedione, acetone, 3-hydroxy-2-butanone, uric acid). Different kinetics of metabolites produced by the gastrointestinal tract microbiota suggest that their changing pattern in saliva reflects the state of gut microbiota. Thus, although derived by a single case, this approach can be considered novel from an analytical standpoint and it encourages further studies combining saliva metabolite profiles and gut microbiota dynamics.





Keywords: Volatile Organic Compounds; Cromatographic analysis; Saliva.

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Protective Effects of Punicalagin Against UVA-induced Damage in Retinal Pigment Epithelial

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Oxidative injury and functional impairment of retinal pigment epithelial (RPE) cells plays an important role in the pathogenesis of a lot number of degenerative ocular pathologies including cataract, glaucoma, diabetic retinopathy and age macular degeneration (AMD). During ocular injuries in fact there is an overproduction of reactive oxygen species (ROS) and free radicals with a switch in pathological conditions. Exposure to ultraviolet (UVA) may induce the production of reactive oxygen species (ROS) resulting in oxidative damage to retinal pigment epithelium (RPE) cells and in a consequent dysfunction of neural retina and photoreceptors. In this framework, one of the plausible ways to prevent or slow down cellular disorders induced by oxidative stress is to augment or potentiate the cellular defence capacity through an adequate intake of antioxidants particularly of natural origin which constitute today a new wave of therapies to defend against free radicals. Studies have shown that Punicalagin, a major polyphenol abundant in pomegranate fruit, husk and juice, can protect several cell types from oxidative stress. It may be useful in the prevention of early AMD. To determine whether Punicalagin protects RPE from UVA-induced damage, we used ARPE19 cells, an human cellular line of retinal pigment epithelium, treated with UVA. Cellular viability and intracellular ROS levels were measured, moreover mRNA expression of principle genes involved in cellular protection by oxidative stress (Nrf2, OH-1 and NQ01) were measured. The results obtained evidence which pretreatment with Punicalagin enhances cells survival after UVA exposure. Moreover Punicalagin reduces cellular oxidative stress in particular both increasing the mRNA nuclear factor erythroid 2-related factor 2 (Nrf2) and its translocation at the nuclear level. The results indicated that Punicalagin has an important effect in preventing UVA-induced damage in RPE cells and may be suitable for further developments as a chemoprotective factor for the primary prevention of early AMD.

Keywords: Age macular degeneration (AMD), Punicalagin, Oxidative stress

References:

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Drug Discovery Research Using Virtual Screening with Homology Models

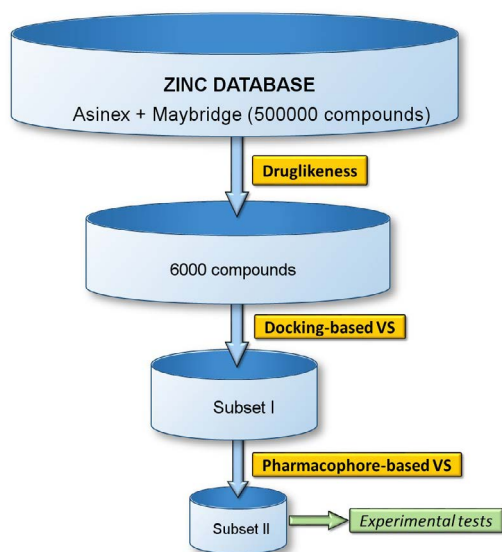
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Homology modeling is a reliable method to predict the three-dimensional structures of proteins when NMR or X-ray crystallographic data are not available. It bases on experimentally determined structures of the target's homologues, under the assumption that similar protein sequences imply similar three-dimensional structures. Although docking using comparative models is more challenging, several comparative protein models have been successfully employed to aid inhibitor discovery [1]. The development of computational strategies for identifying new and potent small molecules able to interfere with life processes, having thus therapeutic potential, is a major research activity at ICRM-Rome.



Here, we describe the applications of virtual screening methods in the discovery of inhibitors of protein-protein interactions and protein targets whose three-dimensional coordinates were generated adopting various molecular modeling approaches including homology modeling, fold recognition, protein-protein docking and molecular dynamics simulations. Selected successful case studies will be discussed which led to the identification and patenting of families of pharmacologically active molecules with putative therapeutic role [2,3]. Overall our findings demonstrate that structure-based virtual screening represents a viable approach to the development of new drug candidates, despite the fact that no experimental structures are available for targets.

Keywords: inhibitors, molecular docking, molecular dynamics simulations

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Acknowledgement:

Fondazione Policlinico Universitario Agostino Gemelli IRCCS



3D Eumelanin Electrospun MicroFibers as Tool to Guide Dopaminergic System Regeneration

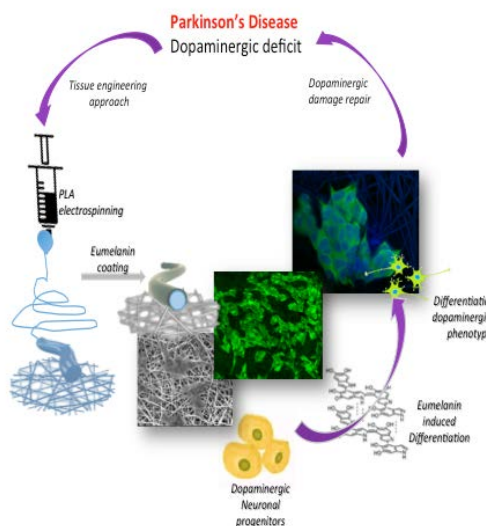
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Parkinson's disease (PD) is characterized by an altered integrity of the presynaptic striatal dopaminergic system consisting of a low dopamine storage capacity and a decreasing of functional dopamine reuptake sites. These pathological conditions reflect a loss of nigro-striatal nerve terminals, which determine cognitive and loco motor disfunctions in PD's patients. Nowadays an effective treatment of PD is limited by the development of tolerance to pharmacological therapy over time. The fabrication of eumelanin-coated microfibrillar structures represents a novel strategy to realize tissue-engineering scaffolds able to guide dopaminergic cell phenotype development by providing biological signals to direct the axonal growth cone to the distal stump.



To fabricate the scaffolds based on random eumelanin microfibers, an appropriate protocol combining electrospinning, spin coating and solid-state polymerization process was established [1]. For biological investigations, a human derived cell line from neuroblastoma was used. Cell growth and differentiation on random eumelanin microfibers were evaluated through Class-III β tubulin and GAP-43 expression, marker of dopaminergic differentiating neurons, by using confocal analysis. Furthermore, cell morphology by using SEM analysis and β III tubulin expression was tested.

3D matrices as electrospun fibers, spheroid-based systems or porous materials are useful *in vitro* to reproduce more realistically 3D *in vivo* neuronal microenvironments thus promoting cell-cell interaction and cell response in terms of viability, growth and differentiation [2-3]. Biological results demonstrated that random

eumelanin microfibers support biological response in terms of cell survival and adhesion. Morphological studies (SEM and confocal microscopy) showed that eumelanin microfibers were able to induce a good cellular spreading.

Furthermore, eumelanin random microfibers induced the formation of network of neuritic processes and promoted GAP-43 expression over cell culture time thus suggesting dopaminergic differentiation processes.

Keywords: eumelanin, tissue engineered scaffold, neurodegenerative applications

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Acknowledgement:

The study was supported by PNR Aging program 2012-2018 from the Ministero dell'Università e della Ricerca. The authors also thank Mrs. Cristina Del Barone of LAMEST laboratory for SEM investigations and Mrs Stefania Zeppetelli for supporting biological investigations.



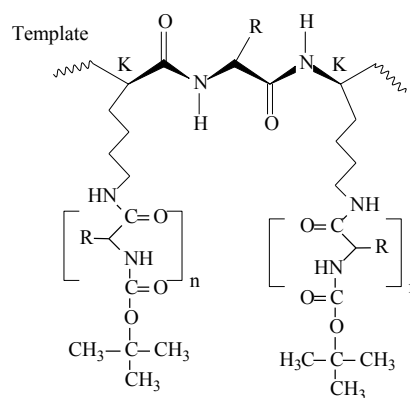
Synthetic Model of Nanostructured, Functionalized Peptide Matrix

Emma Fenude

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The concept of intramolecular catalysis, in which a reaction is accelerated by the participation of a neighbouring group in a reactant, is well established in organic chemistry. We look to intramolecular catalysis in enzymes by substrate participation. The catalytic efficacy of enzymes stems, in part, from their well-defined folded structure. Within the active site, catalytic residues are precisely oriented in space to accommodate well orchestrated, and often highly stabilized, transition states. Our approach involves the synthesis of minimal peptides containing the key features of enzymatic active sites and the insertion of this sequence in a peptidic matrix in order to obtain a substantially simplified chiral environment. In general, the design of peptide-based catalysts have largely focused on sequences that are predisposed to specific secondary structures. The β -turn motif has proved particularly fruitful in this regard. Based on our studies of synthetic homologues of protein-derived exorphins [1], we sought to take advantage of predictable β -turn geometry in our catalyst design. In many cases, the tendency of certain β -turn-containing peptides to adopt double stranded structures provides further conformational support through additional interstrand hydrogen bonds. This approach allows for the possibility of positioning catalytically active amino acid side chains in close proximity to the substrate as well as to other functional groups that further stabilize the catalytic complex. Several factors are for key importance in design of a peptidic matrix that contains the catalyst and serves as template for the growing polypeptide chain, including (i) conformational and dynamical properties of template, (ii) the nature and role of β -turn, (iii) nature of the stabilising weak interactions. Here we report about synthesis and conformational characteristics of model systems containing two bioactive sequences covalently bonded to side chains functional groups of the template peptide.

Image1 Schematic representation of peptidic system presented, n=4,6



Keywords: peptide matrix; peptide catalyst;

References:

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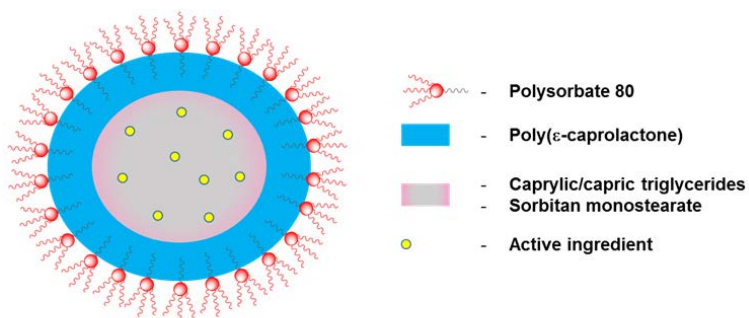
Nanoencapsulation of Biologically Active Compounds in a Biocompatible Polymer for Potential Food Applications

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The production of healthier and more functional food, and safe food storage systems is in constant interest. [1]

Nanoencapsulation of functional molecules is an efficacy strategy to increase their solubility, bioavailability and activity, to protect them from degradation and to mask eventual unpleasant taste. [2] The interfacial deposition of the preformed polymer represents a useful encapsulation method as it furnishes polymeric lipid-core nanocapsules (LNCs), which are efficient systems easy to prepare and cheap. These LNCs are formed by the diffusion of the organic solvent into the aqueous phase followed by the solvent evaporation. They have a polymeric wall coated by a surfactant, and a lipid inner core, where bioactive compound is allocated.



Schematic representation of a PCL-nanocapsule

In this context we prepared lipid-core nanocapsules based on biodegradable and biocompatible poly(ϵ -caprolactone) (PCL) with potential applications in the nutraceutical field following two approaches:

1) *Nanoencapsulation of active ingredients for potential functional food applications.* The approach involves the encapsulation of active ingredients (hydroxycinnamic acids [3] or vitamin E or ascorbyl palmitate) in lipid-core nanocapsules (NCs) based on PCL polymer, coated by a surfactant (polysorbate 80), and an inner core formed by a dispersion of triglycerides/sorbitan monostearate, where bioactive compound is dispersed. The nanoparticles loaded with active ingredients (AI-NCs) showed monomodal distribution with nanometric diameter size, very low polydispersity index (PDI), good or excellent encapsulation efficiency, and stability over time. In vitro tests of simulated gastro/intestinal digestion were performed to obtain useful information regarding the stability of AI-NCs in the different biological compartments.

2) *Nanoencapsulation of natural essential oil as potential food preservatives against food-borne bacteria.* The approach involves the encapsulation of essential oils (EOs) from *Thymus capitatus* and *Origanum vulgare* in PCL-nanocapsules. Differently to the previous approach, the triglycerides in the inner core are substituted by the same essential oil. The EO-NCs showed monomodal distribution with nanometric diameter size, very low PDI, high efficiency of encapsulation, stability and high retention of EOs during prolonged time storage. The antibacterial and bactericidal activity of EO-NCs against food-borne pathogens in comparison with the corresponding pure essential oils were also assayed.



Keywords: polycaprolactone nanocapsules, active ingredients, essential oils

References:

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Acknowledgement:

Part of this work was carried out with the support of Italian MISE, project POR “Imprese e competitività” 2014-2020 FESR for technological development in food science, leader company Dolfin S.p.A. (Italy, Catania)



Donepezil-like Compounds as Acetylcholinesterase and β -Secretase-1 Inhibitors

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Alzheimer's disease (AD) is a multi-factorial progressive neurodegenerative disorder, clinically characterized by age-related loss of memory and cognitive impairment.

Cholinergic enzyme deficiency, increased accumulation of β amyloid ($A\beta$) in the senile plaque neurites, the formation of neurofibrillary tangles composed of a highly phosphorylated form of the microtubule-associated protein tau, oxidative stress, dyshomeostasis of biometals, mitochondrial abnormalities, and neuroinflammatory processes are among the major factors implicated in the multi-faceted pathogenesis of AD.

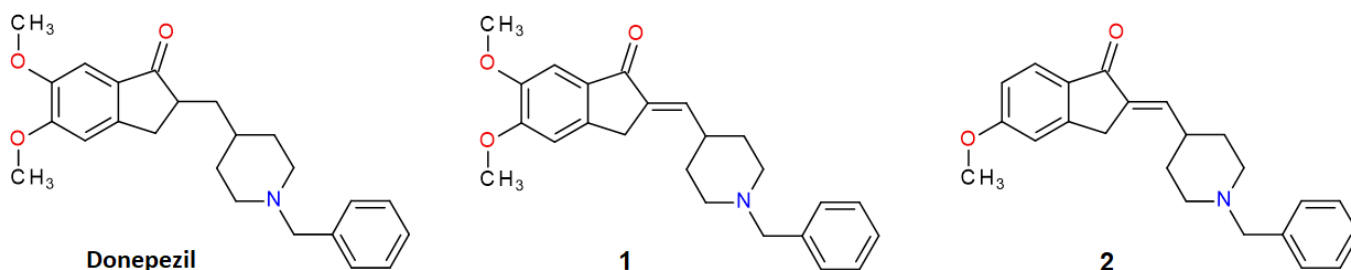
Despite the extensive research in the field, AD pathogenesis is still at some extent obscure.

The most significant of these are: (i) the *cholinergic hypothesis* which postulates that the cognitive decline can be linked to a decrease in the amount of the neurotransmitter acetylcholine and (ii) the *amyloid hypothesis* which instead ascribes AD symptoms to the Amyloid Precursor Protein (APP) that undergoes a sequential post-translational proteolysis/processing by β -secretase 1 (BACE-1) and γ -secretase leading to the formation of hydrophobic $A\beta$ peptide fibrils that readily accumulate and deposit on neuritic plaques in the gray matter of the brain.

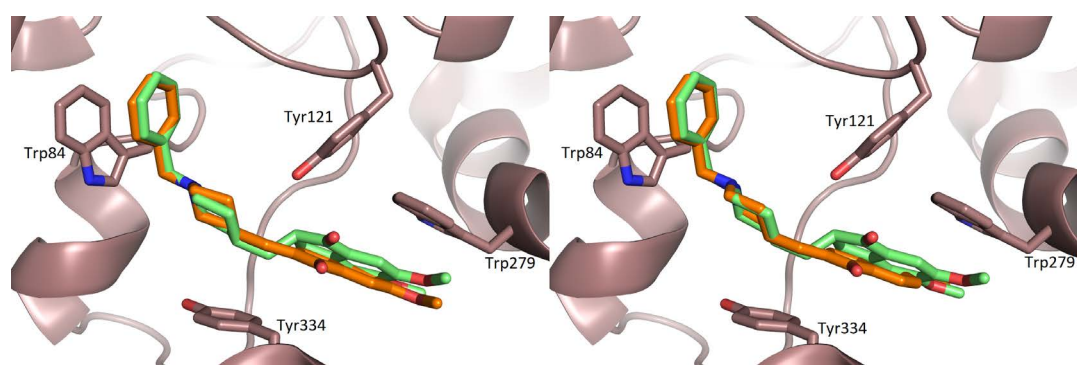
Acetylcholinesterase inhibitors were introduced for the symptomatic treatment of AD. Among the currently approved inhibitors, Donepezil is one of the most preferred choices in AD therapy.

The X-ray crystal structures of *Torpedo californica* AChE in complex with two novel rigid Donepezil-like analogues [1], compounds **1** and **2**, have been determined. Kinetic studies indicated that **1** and **2** show a mixed-type inhibition against *TcAChE*, with K_i values of 11.12 ± 2.88 nM and 29.86 ± 1.12 nM, respectively [2]. The Donepezil rigidification results in a likely entropy-enthalpy compensation with solvation effects contributing primarily to AChE binding affinity.

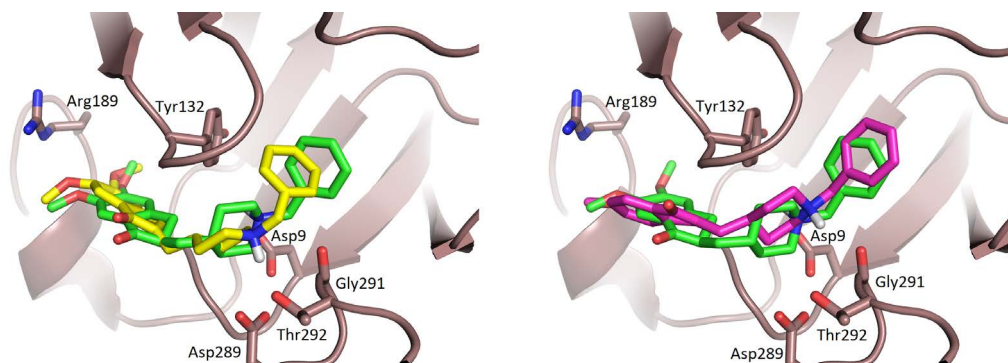
Molecular docking highlighted the molecular determinants for the binding of compounds **1** and **2** to the active site of β -secretase-1



Overall, these simplified Donepezil derivatives may represent new structural templates for the design of lead compounds for a more effective therapeutic strategy against AD by foreseeing a dual AChE and BACE-1 inhibitory activity.



Superimposition of the crystal structure of the *TcAChE*-Nonepezil complex [3] (carbon atoms colored in green) with the *TcAChE*-1 (Left) and *TcAChE*-2 (Right) complexes (carbon atoms colored in orange).



Superimposition of the top ranked docking poses of hBACE-1 in complex with Donepezil and **1** (Right), and **2** (Left), respectively. Donepezil, **1** and **2** are shown as stick models with carbon atoms colored green (Donepezil), yellow (**1**) and magenta (**2**).

Keywords: Donepezil analogues; Acetylcholinesterase inhibition kinetics; X-ray Crystallography

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Multiple Target Detection of Circulating MiRNA in Celiac Disease

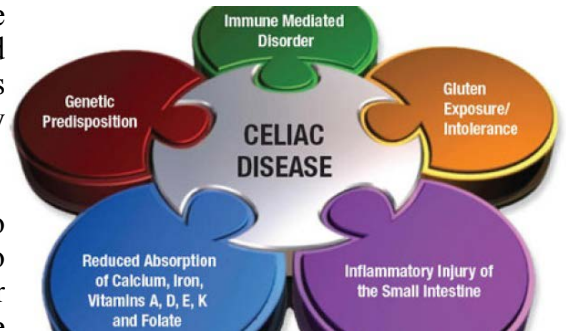
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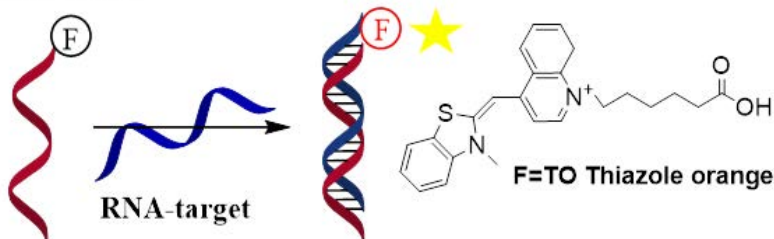
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Celiac disease (CD) is an immune related disease triggered by the interaction of environmental and genetic factors.¹ It is diagnosed on the basis of symptoms, the detection of CD specific antibodies and intestinal mucosal biopsy. To date, a screening test that totally avoids an invasive approach is still unknown.

The only available treatment for CD is a lifelong adherence to a gluten-free diet (GFD). Numerous researchers have tried to unravel the mechanism of CD and to discover new molecular biomarkers to employ for the diagnosis, or to find alternative methods to avoid biopsies. Recently miRNA, a class of small non coding RNAs have emerged not only as a new group of cellular regulators, but also as significant biomarkers being deregulated in several diseases including the celiac one.² MiRNAs are optimal biomarkers owing to high stability under storage and handling conditions and their presence in blood, urine and other body fluids. In particular, detection of levels of miRNAs in blood, plasma and serum has the potential for an earlier disease diagnosis and to predict prognosis and response to therapy. Based on that, a group of miRNAs deregulated in celiac disease have been identified in literature such as: miRNA-449a, miRNA-492, miRNA-21, miR-486. Thus, we have designed and synthesized peptide nucleic acid (PNA) based anti-miRNA probe for their early detection in CD.



PNA-Probe



Peptide nucleic acids (PNAs)³ are DNA synthetic mimics in which the deoxyribose phosphate backbone is replaced by a pseudo-peptide polymer to which the nucleobases are linked. The high affinity and excellent specificity towards nucleic acids immediately suggest their use as diagnostic tool. In addition, a broad range of salt tolerance and stability to enzymatic

degradation are added benefits of PNA probe.³ The detection of miRNA is obtained through a light up probe, using a thiazole orange (TO) dye as a fluorescent tag. PNA based probes were prepared by solid phase peptide (SPPS) using commercially available Fmoc/Bhoc monomers; exploiting a synthetic protocol developed in our laboratory. Structural characterization and hybridization properties of the PNA probes, with the target miRNAs, was provided by UV, CD and fluorescence spectroscopy.

The use of PNA as a diagnostic probe in a smart kit for miRNA detection is an emerging technology; and represent a great promise for rapid and convenient recognition of specific RNA sequences.

Keywords: Celiac Disease, miRNA, PNA.

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Acknowledgement:

Horizon 2020-PON 2014/2020-MISE: Progetto n. F/050013/03/X32



Detection of Germline Mutations in Sardinian Patients with Breast and Ovarian Carcinoma using Next-generation sequencing (NGS)

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Tumor suppressor genes BRCA1 and BRCA2 are the two main breast and ovarian carcinoma (BOC) susceptibility genes, and their genetic testing is necessary to evaluate the risk of the hereditary tumor.

Additionally, genetic testing for BOC cases has been introduced into the clinical practice as predictive of therapeutic response. Patients with advanced BOC carrying *BRCA1/2* mutations are highly sensitive to PARP inhibitors and platinum-based chemotherapies.

Overall, Sardinian BOC patients (n=137) unselected for family history of breast or ovarian cancer were consecutively collected, from January 2017 to May 2018.

We have analyzed for *BRCA1/2* mutations 106 patients with breast cancer and 31 with ovarian cancer.

Next-generation sequencing (NGS) strategies were applied on the genomic DNA samples isolated from peripheral blood, for the detection of small insertion/deletion frameshift, nonsynonymous, truncating and splice-site alterations and large genomic rearrangements in BRCA1 and BRCA2 genes.

NGS analysis was performed using the ION Oncomine BRCA assay panel based on proven Ion Ampliseq Technology (ThermoFisher scientific). All exons are covered 100%, with an average of 64 bases of flanking sequence into the introns upstream and downstream of each exon, allowing for over 99% confidence of detecting 5% somatic variants across both genes.

The sequence data were processed using standard Ion Torrent Suite Software running on the Torrent Server (ThermoFisher scientific) version 5.4.

We identified a total of 11 missense variants (8%, 11/137) of uncertain significance (VUS), including a single, specific BRCA1 variant detected in 3 breast cancer patients and 5 BRCA2 variants carried in 8 different patients, 3 of which occurring exclusively in breast cancer patients.

The observed BRCA1 and BRCA2 VUS are rare variants according to 1000 Genome Project data, with a value of population minor allele frequency less than 1% (MAF < 1%).

Eight BRCA1 and nine BRCA2 variants (17/137; 12.5%) were present at high frequencies in analyzed patients and in $\geq 1\%$ of the general population according to GMAF (Global Minor Allele Frequency), indicating as common polymorphisms.

Four (4/137; 2.9%) pathogenic BRCA1 variants were detected: all frameshift mutations were interpreted as



deleterious in according to genetic testing guidelines.

We classified three truncation variants including, respectively, one frameshift mutation and two nonsense variants in BRCA2 gene. Furthermore, a founder mutation - 8765_8766delAG/p.Glu2846fs - [1] in BRCA2 gene, previously described by our group in Sardinian breast cancer population was detect in 5 BOC cases, 4 of whom with breast carcinoma and one with ovarian cancer (8/137; 5.8%).

Another important finding was that a vast majority of BOC patients did not show any pathogenic or uncertain variant (113/137; 82.5%).

High prevalence of deleterious mutations in BRCA2 as compared to those in BRCA1 confirms a large heterogeneity of pathogenic mutations and an inverse involvement of the two genes in our population in comparison to the general one. The use of expanded panels may increase the number of clinically relevant results, aimed at identifying a greater number of genes associated with hereditary predispositions in breast and ovarian cancers.

Keywords: BRCA1, BRCA2 ,NGS

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Eucaryotic-like Ser/Thr kinase from *S. Pneumoniae*: *in Silico* Structural Characterization of a New Target for Alternative Antipneumonal Drugs

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In silico molecular modelling techniques, in the last two decades, are increasingly employed in many fields of chemistry, biochemistry and related fields due to the synergistic evolution of the machines' technology and of the models describing a chemical/biochemical system. A huge number of examples of the application of classical molecular mechanics to the structural characterization of the proteins, nucleic acids and their interaction with other macro- or small molecules, are present to date in literature, confirming the molecular modelling as a useful guideline for the "wet" work and as well as a tool for shed light on unclear data from the experiments. Here is presented a recently published study showing the contribution of the molecular modelling and molecular dynamics simulations to the solution of a life science problem represented by the characterization of the structure of a novel macromolecular drug-target and the mechanisms at the basis of its activation [1].

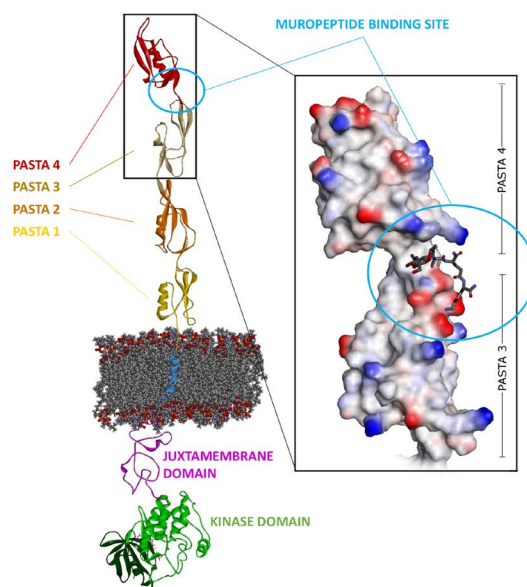
The human pathogen *Streptococcus pneumoniae* is a gram-positive bacterium which is a frequent causative agent of the hospital-acquired pneumonia but also responsible for other infections, such as sepsis, endocarditis and peritonitis, in particular in immunocompromised individuals. *S. pneumoniae* possesses a unique eSTK (eukaryotic-like Serine/Threonine protein Kinases) termed StkP, that plays an important role in many aspects of the bacterial cell-cycle, and that has become an attractive target for the design of new antibacterial drugs with an alternative mode of action by which it could be possible to overcome the multidrug resistance phenomenon.

The StkP is a 651 residues-long transmembrane protein, composed of an intracellular catalytic kinase domain connected to a transmembrane helix by a juxtamembrane domain, and an ectodomain divided into four extracellular PASTA subdomains. The four-PASTA extracellular domain was shown to modulate the cell-wall synthesis by acting as sensor of the uncross-linked peptidoglycan fragments [2]. Here we report the full-length structural model of StkP, generated by the combination of the data from small-angle X-ray scattering experiments and *in silico* molecular modelling techniques. The generated three-dimensional model of the StkP was used as a target for molecular docking calculations aimed to reveal the binding orientation of a peptidoglycan molecular fragment (muropeptide) on the surface of the StkP extracellular domain. A comparative molecular dynamics simulations study of the StkP model, bound to the muropeptide and in its unliganded form, in the presence of the explicit lipidic membrane bilayer, confirmed the orientation of the ligand on the hinge between the two c-terminal PASTA domains and the relative orientation of the PASTA domains.

Keywords: Eucariotic-like Ser/Thr Kinase, *Streptococcus pneumoniae*, Molecular Modelling

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The Life of Extremophiles from Polar Regions to Volcanic and Hypersaline Area: Surviving in Hostile Habitats by Exopolysaccharide Production

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Extremophiles have developed various adaptations, enabling them to compensate for the deleterious effects of extreme conditions as high temperatures, salt presence, low pH values, or high radiation levels. Among the adaptive strategies, exopolysaccharide (EPS) biosynthesis is one of the most common protective mechanisms. Although the EPS production is a process that requires a significant carbon investment for microorganisms, the benefits are significantly higher than costs considering the cell survival in their presence^[1]. These biopolymers have emerged as new polymeric materials with novel and unique physical characteristics that have found extensive applications in food, pharmaceutical, and other industrial fields^[2]. The increasing demand of natural polymers for industrial applications has led to a vibrant interest in the EPS production by microorganisms^[3]. There has been a substantial attractiveness in the isolation and identification of new microbial polysaccharides that might have innovative uses as emulsifiers, stabilizers, and gelling or texture-enhancing agents. Recent research on polysaccharide produced by extremophiles, isolated from Arctic and Antarctic regions, hypersaline environments, deep-sea hydrothermal vents, and volcanic areas, will be reported including chemical structures, fermentation technology, biotechnological and biomedical applications^[3].

Keywords: extremophiles, exopolysaccharides, biotechnological application

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Acknowledgement:

This work was partially supported by PNRA16_00020.



Do Size, Coating, and Composition of Magnetic Nanoparticles Really Affect Interaction with Living Systems? A Tightly Controlled Systematic Approach

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How the properties of nanoparticles (NPs) affect their interaction with living systems (from single cells to whole organisms) is still a largely open question. A major difficulty is that the comparison of literature data is hampered by differences in both the biological system (different animals, cell lines, assays, experimental conditions, etc.) and the nanosystem (composition, size, shape, surface chemistry, aggregation state, etc.). In order to shed some light on this very complex issue, we investigated the interaction of NPs with cells (immunogenicity, internalization,) and organisms (distribution after IV) by systematically varying a *single* morphological or chemical parameter of the NPs in order to shed some light on the effect of the *varied* parameter. Of course, we had to choose which NPs investigate, which NP parameters vary, and which biological endpoints measure. Such decisions were based on the current state of the art in nanomedicine.

We focused on magnetic NPs since they are widely employed in nanomedical research and are deemed to be promising supports for theranostic nanosystems since the magnetic inorganic core provides diagnostic (MRI), targeting (magnetic localization) and therapeutic (hyperthermia) functionality. In particular, NPs made of iron oxide, a low toxicity material, have a relatively well-known chemistry that allowed us to accept the challenge of synthesizing NPs which differ by just one morphological/chemical feature while keeping all other ones fixed. We chose to vary three basic NP parameters, *i. e.*, size, core composition, and surface charge distribution *one at a time*, while keeping other parameters (such as shape) fixed. The measured endpoints are immunogenicity, phagocytic internalization, and *in vivo* distribution. They are critical endpoints since successful NPs in medicine do not elicit inflammation, are captured to the least extent, and have favorable biodistribution. It is unlikely that NPs not satisfying these requisites may be used even as a support for theranostic nanosystems.

We managed to synthesize magnetic NPs which differed from the reference NPs (11 nm, Fe₃O₄ core, ZDS coating) [1] for size (3, 17, 22 nm), or core composition (MnFe₂O₄, CoFe₂O₄), or ionic coating (dopamine sulfonate, lithium caffeate, coryneine iodide). In total, we prepared 9 different NP types. All NPs were fully characterized as to morphology, structure, and colloidal behavior in biological media) before using them in biological assays.

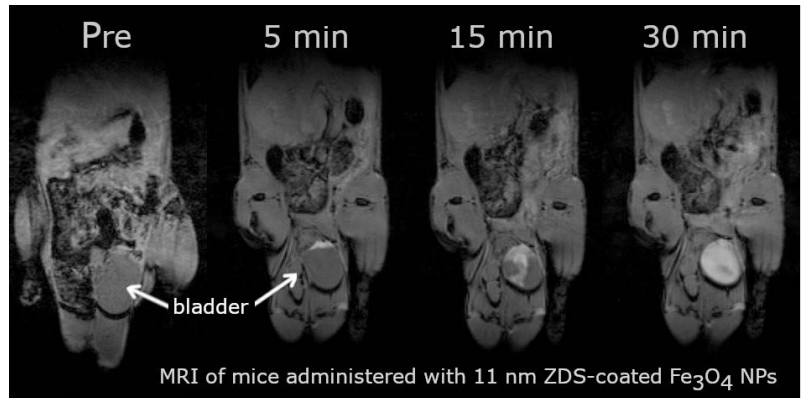
Incubating whole human blood with LPS-free NPs for 24 h and the measuring cytokine production and genic expression we were able to show that none of the NP types elicits immunological response or interferes with the inflammation process. This is a critical *sine qua non* condition for any foreseeable application in medicine.

The internalization of NPs by phagocytic cells is at the center of the current debate in nanomedicine since NP sequestration is the major hurdle to the real application of NPs in medicine. [2] We compared the *in vitro* internalization of NPs by BV-2 cells, which are a good model for primary microglia. The dose-dependent NP uptake was found to be insensitive to the core composition and, rather unexpectedly, to the largely different coatings. Size has a strong impact on NP uptake: aggregated NPs are internalized more than tenfold with



respect to colloidal NPs and mass uptake of the latter is inversely proportional to the NP curvature radius.

Finally, the biodistribution of 3 and 11 nm ZDS-coated Fe_3O_4 was compared after IV injection in healthy mice. NPs are quickly captured by the liver and disappear after 14 days; no NP was detected in kidneys, heart, dorsal muscle. Unexpectedly, not only 3 nm but also 11 nm NPs are rapidly excreted through the kidneys to a significant amount, in contrast to previous results [3] limiting at 6 nm the size of renally clearable NPs.



Keywords: magnetic nanoparticle, immunogenicity, internalization

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Acknowledgement:

This work has been financially supported by Fondazione CARIPO (Grant No. 2011-2114) and Regione Lombardia (RSPPTech Project).



Hyaluronic Acid-Based Nanocomposite Hydrogels Obtained by Sol-Gel Method for Tissue Engineering Applications

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INTRODUCTION

Over the past years, natural hydrogels have been widely employed in regenerative medicine, as they can promote efficient biomolecular interactions with cells, also through the regulation of their basic functions, guiding the spatially and temporally complex multi-cellular processes of tissue growth [1]. Hyaluronic acid (HA) is widely used for numerous medical applications, such as viscosupplementation, eye surgery and drug delivery [2]. Hyaluronic acid sodium salt (HAs) was chemically modified in order to obtain a photocrosslinkable hydrogel with tailored mechanical properties. Moreover, to improve both mechanical and biological properties, a composite hydrogel was developed based on chemical modified HA and *in situ* synthesized hydroxyapatite (HAp) by sol-gel approach [3]. It has been assumed that the reduced enzymatic degradation and improved mechanical properties of the nanocomposite HAs can lead to a valuable biomaterial for tissue engineering purpose.

MATERIALS AND METHODS

Hyaluronic acid sodium salt (HAs, $M_w \sim 340$ kDa, BloomageFreda Biopharm Co. Ltd., Shandong, China) was methacrylated (MeHA) and maleated (MaHA) using different degrees of substitution (DS) in order to have a photocrosslinkable hydrogel with tunable properties. Composite hydrogels have been synthesized by sol-gel method varying the amount of HAp from 25 to 50wt%. Composite disc shaped samples were photocrosslinked by UV radiation as showed in Figure 1.



Figure 1: Photocrosslinking of nanocomposite MeHA/MaHA + CaP

Nuclear Magnetic Resonance (NMR), Fourier transform infrared spectroscopy (FTIR) were performed in order to identify the functional groups on MeHA and MaHA. Dynamic mechanical analysis (DMA) was carried to study mechanical properties of neat and composite hydrogels. Morphology and distribution of CaP were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Finally, to assess if the chemical composition of the biomaterials could lead to cytotoxicity, compromising the cellular viability, the CCK-8 quantitative cell viability assay was performed.

RESULTS AND DISCUSSIONS

¹H NMR characteristic peak at 5.6 and 6.0ppm for MeHA and at 6.1 and 6.7ppm for . Results from DMA analysis performed on MeHA and MaHA showed that mechanical properties of MeHA are strongly influenced by the DS. In particular, all the MeHA based composites showed values of the elastic modulus generally higher than MeHA neat hydrogel based ones. MaHA hydrogels followed the same trend found for MeHA. Furthermore, no significant statistical differences in terms of mechanical properties were observed between the two different DS. SEM analysis showed a good distribution of HAp particles into the hydrogel. Furthermore, the cytotoxicity demonstrated that after 3 days of culture neat hydrogels and composite with 25wt% of HAp showed the best biological behaviour.



CONCLUSION

Hydrogels are versatile and appealing biomaterials for tissue engineering application due to their unique combination of physico-chemical features similar to natural ECM. Nanocomposite hydrogels based on chemically modified HAs and *in situ* synthesized HAp were developed and characterized by their morphological, mechanical and biological properties. Results showed that the mechanical properties of the modified HAs can be controlled by adjusting the chemical reaction and through the sol-gel method it is possible to realize a finely dispersed HAp particle into the hydrogels. Finally, both neat and composite hydrogels showed no cytotoxic effect when seeded with fibroblast cell.

Keywords: Tissue Engineering, Hydrogel, Sol-gel synthesis

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Acknowledgement:

The authors would like to thank the *H2020-MSCA-RISE-2016*, SECOND.R.I., Grant Agreement No 734391 for financial support.



Gas Permeable Membrane Bioreactor for Engineering a Liver Construct by using Human Skin Derived Mesenchymal Stem Cells with Hepatocytes and Endothelial Cells

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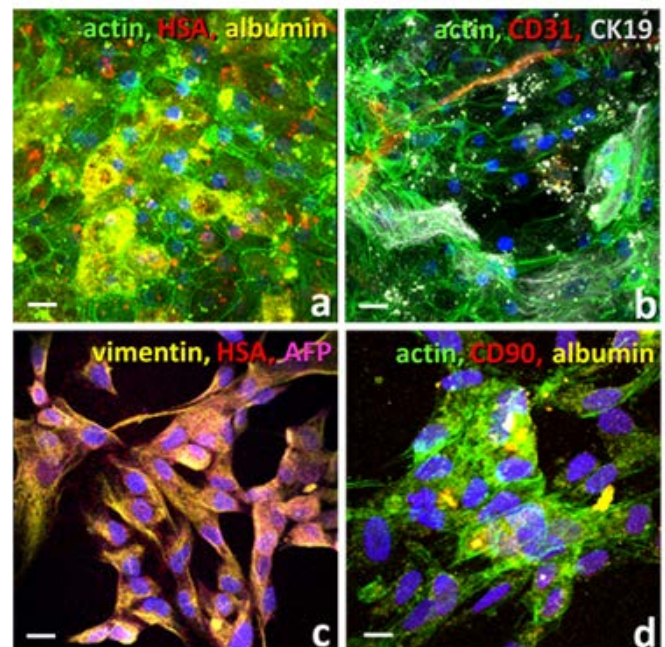
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In this study a human liver tissue construct was created by using human skin derived mesenchymal stem cells (hSSCs), primary human hepatocytes (hHeps) and human endothelial cells (hECs) co-cultured in a gas permeable membrane bioreactor developed in two different configurations in order to create direct and interconnected co-cultures. A single chamber configuration consisting of two flat-sheet gas permeable fluorinated ethylene propylene (FEP) membranes was used for the direct co-culture of cells in contact each other and with membrane. To establish interconnected co-culture a compartmentalized bioreactor was developed, in which hHeps and hECs adhered to FEP membrane were separated from hSSCs through a microporous polycarbonate (PC) membrane that allows the communication between cells by means of their secreted paracrine factors. FEP membranes ensured the mass transfer exchange of O₂ and CO₂ and aqueous vapour between cells and external environment, PC membrane the selective mass transport of molecules secreted by cells, avoiding the direct contact between hSSCs and the other cells. Direct and interconnected co-culture conditions were compared in order to elucidate the influence of the hSSCs interactions on the liver specific functions and morpho-functional characteristics of the liver construct. The designed bioreactor offered to cells a highly perfused and homogeneous microenvironment allowing an adequate O₂/CO₂ mass transfer exchange that is crucial for the maintenance of liver functions. A computational model was implemented to investigate the concentration profiles of the main metabolites (i.e. urea and albumin) produced into the bioreactor and to compare them in direct and interconnected co-culture conditions. In both gas permeable membrane bioreactors, biliary ducts and vascular capillaries were tightly distributed, mimicking the natural hepatic lobules. Cells displayed relevant albumin and urea synthesis as well as drug metabolism in both direct and interconnected cultures. In the compartmentalized bioreactor, the liver specific functions were prominent thanks to the biochemical communications between the different compartments as confirmed by the experimental and computational analysis. The investigation on the expression of specific mesenchymal, hepatic and endothelial markers suggested the ability of hSSCs to start the differentiation in hepatocyte phenotype expressing specific hepatocyte markers (e.g., albumin, α fetoprotein AFP, hepatocyte specific antigen HSA and hepatic biliary duct marker



Confocal laser scanning microscope micrographs of cells in the gas permeable membrane bioreactor after 19 days of interconnected co-culture: hHeps and hECs on FEP membrane stained for actin (green), HSA (red) and albumin (yellow) (a), and for actin (green), CD31 (red) and CK19 (grey) (b); hSSCs on PC membrane stained for vimentin (yellow), hepatocyte specific antigen HSA (red) and α -fetoprotein AFP (magenta) (c), and for actin (green), mesenchymal surface antigens CD90 (red) and albumin (yellow) (d). Cells were counterstained for nuclei (blue). Scale bar 20 μ m.



CK19). A dual purpose accomplished the bioreactor: the creation of a vascularized liver microtissue displaying specific phenotypical characteristics and functional performance thanks to the positive influence of biochemical signaling and stimuli from hSSCs; the production of partially differentiated hSSCs-derived cells that could be harvested as a cell source for liver tissue engineering.

Notably, the gas permeable membrane bioreactor provided a 3D culture environment suitable for the creation of a liver construct with the presence of vascular structures that was functionally active for an extended period of time. These characteristics address the applicability of the device in toxicity and drug testing studies and in the biofabrication of hepatic tissue analogues.

Keywords: Gas permeable membrane bioreactor, bioartificial liver, mesenchymal stem cells

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Zeolites as Chameleon Biomaterials: Assessment of the Zeolite Scaffold Physical-Chemical Characteristics on Interactions with Human Cells

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The ability of cells to recognize and interact with the substrate is the first essential step, without which processes such as adhesion, proliferation, migration, cell differentiation and carrying, which presuppose continuous exchanges of ions and molecules among cell and support, would not be possible. Therefore, the possibility of modifying and controlling surface properties at the micro/nano level constitutes one of the major breakthroughs [1-3]. In order to prepare a new generation of biomaterials with enhanced properties, novel pure and hybrid zeolite membranes were synthesized with appropriate different physicochemical characteristics such as frameworks, hydrophilicity, crystal size, chemical composition, acid-base properties and surface morphology and used in inorganic cell/scaffold constructs. The XRD analysis of self-supported membranes reveals patterns corresponding to MOR, FAU, BEA, MEL and MFI type structures demonstrating that all samples prepared are pure highly crystalline membranes. The morphologic analyses both zeolite crystals of membranes and grown cells on the inorganic support were investigated by scanning electron microscopy and they reveal that fibroblasts adhered strongly to some zeolite scaffolds, whereas poorly to others. The viability of the cells grown on the membranes was significantly higher with respect to fibroblast controls for all samples, as assessed by acridine orange test. The analysis of density for unit surface of adhered cells to membranes versus the culture time revealed that zeolite membranes favoured the cell growth for all zeolite structures examined. The ability of these zeolite membranes to support cell adhesion was examined in the absence of serum proteins, to complement the analysis conducted in the presence of serum. As expected, significantly fewer cells adhered to the surfaces in the absence of serum relative to the serum-containing conditions.

In conclusions, this study evidences that synthetic self-supported zeolite membranes provide ideal, economic, reusable, pH and bacterial resistant, undegradable supports for cell adhesion, because many of their physical-chemical characteristics like the PZC can be modulate by chemical manipulations in order to obtain, in this way, the best performance of fibroblast adhesion, good-spreading and growth. On the basis of these results, we propose that zeolite membranes could be used for extensive massive future application to all type of cell cultures.

Keywords: Zeolites; Hydrothermal synthesis; human cell cultures.

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Acknowledgement:

The authors are grateful for financial support to PON R&C (Programma Operativo Nazionale Ricerca e Competitività 2007-564 2013) project PON_01 00293 «SPREAD BIO-OIL».



Synthesis of Hydantoin-based Universal Peptidomimetics as potential Inhibitors of Protein-Protein Interactions

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The protein-protein interactions are involved in most biological processes even in the onset and development of diseases. In modern medicinal chemistry, the design of small molecules acting as protein-protein interaction inhibitors (PPI) became increasingly important even if challenging, due to the large and shallow surface area of contact involved in those interactions. However, it's known that the PPI free Gibbs energy binding (more than 90%) depends mainly on the interaction of certain protein side chains present in secondary structural elements known as "hot spot". A "hot spot" is defined as a residue which substitution by an alanine leads to a significant decrease in the free energy of binding. Actually, the "hot spot" are molecular portions showing interactions between hydrophobic residues of the two proteins belonging to secondary structures of the proteins themselves (α -helix and β -turn). They are excellent targets for the demolition of the global interaction between the two proteins and this is the reason why the entire strategy focuses on the synthesis of small organic molecules - with favourable enthalpic and entropic profiles - mimicking the protein secondary structures.

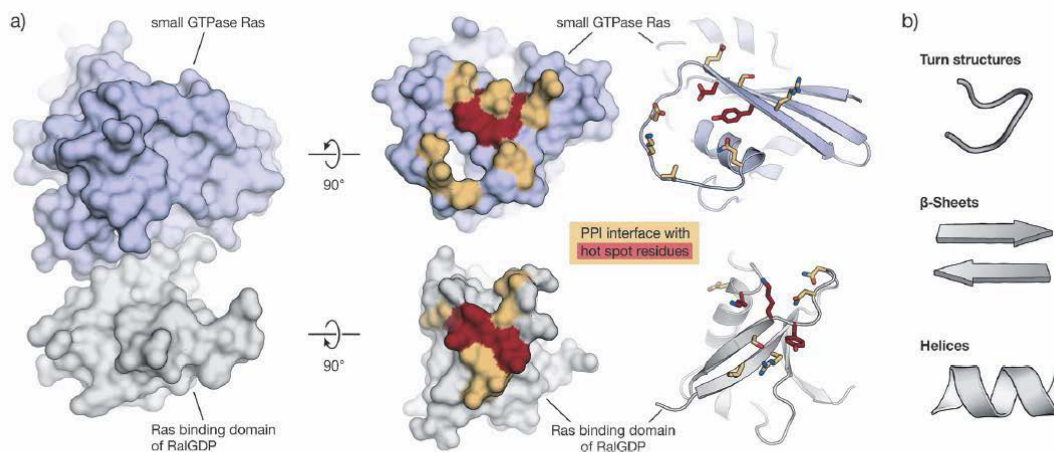
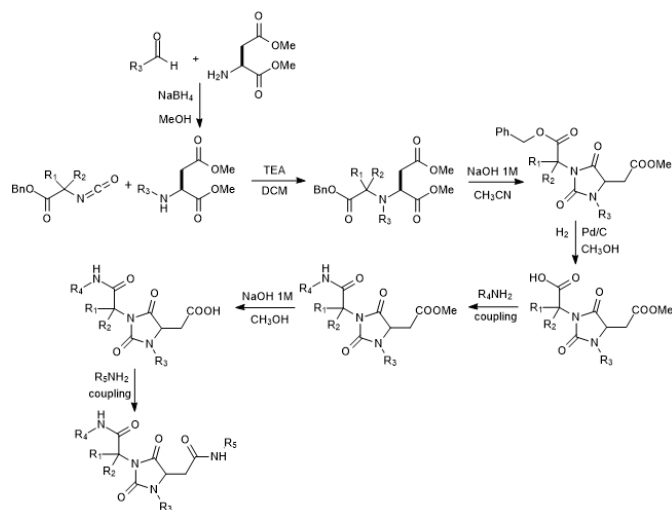


Figure 1. Example of a PPI with its interaction area and hot spots: a) Left: Crystal structure in surface representation of the complex between Ras (light blue) and the Ras binding domain of RalGDP (gray, PDB: 1LFD).^[5] Right: The same proteins with their PPI interface (orange/red). Hot-spot residues are highlighted in red. Proteins are shown in surface and schematic representation (interacting residues are shown as sticks).^[6] b) Peptide secondary structures in schematic representation.

Recently, 3-cyclo-butylcarbonyl hydantoin scaffold was designed [1] having the following properties: (a) side chain mimicking secondary protein structures, (b) flexibility for adapting to a broad range of kinetically and thermodynamically accessible conformations, (c) limited degrees of freedom leading to a favorable entropic profile, (d) easy and versatile synthesis with incorporation of a wide range of amino acid side chain suitable for a combinatorial approach. Computer molecular modelling, conformational analysis (NMR) and X-ray studies of those molecules showed them to be secondary structure mimetics, very promising as PPI inhibitors.



Through a modular synthetic pathways and a large variety of natural and unnatural amino acid side chains that can be placed in key positions, similar mimetics having other carbocycles or acyclic residues in position 3 are reported.



Scheme. Synthetic way to hydantoin-based universal peptidomimetics.

The synthetic way to the preparation of the hydantoin-based universal peptidomimetics involves the formation of the hydantoin scaffold through the condensation of an L-aspartic acid diester and an isocyanate derived from an orthogonal protected amino acid followed by a base induced ring closure. The R^3 , R^4 , and R^5 substituents are important for the PPI inhibition while R^1 and R^2 can be hydrogen, alkyl or cycloalkyl substituents.

Keywords: Peptidomimetics, PPI inhibitors, Hydantoin

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Acknowledgement:

Mr Walter Panzeri is gratefully acknowledged for analytical (Mass and NMR spectroscopies) support.



Tuning Polymorphism in 2,3-Thienoimide Capped Oligothiophene Based Field-Effect Transistors by Implementing Vacuum and Solution Deposition

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We investigated the impact of the molecular packing and film morphology on the field-effect charge mobility in 2,3-thienoimide-based oligothiophenes semiconductors (C_n-NT4N) [1]. Organic field-effect transistors were realized by implementing both vacuum and solution methods in order to control the solid-state phase of the active layer. Indeed, controlling the polymorphism of the active layer is an effective strategy for tuning the electrical properties in organic devices [2]. Thermal sublimation in high vacuum chamber and Supersonic Molecular Beam Deposition were used as vacuum-based fabrication approaches while Lithographically Controlled Wetting was used as a solution-deposition technique. Thermal sublimation led to thin-films with a phase packing showing ambipolar behaviour. By tuning the deposition rate, Supersonic Molecular Beam Deposition enabled the formation of two crystal phases showing different electrical behaviour. On the other hand, Lithographically Controlled Wetting allowed the formation of C_n-NT4N microstructured active layers and their implementation in field-effect transistors.

Keywords: Polymorphism, Oligothiophene, Organic Field-Effect Transistor

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Acknowledgement:

This work received funding from the European Union’s Horizon 2020 research and innovation program under grant agreement N. 644742 (LEO Project), national project “Premiale” EOS funded by Italian Ministero dell’Istruzione dell’Università e della Ricerca (MIUR) and the Italian flagship NANOMAX, N-CHEM.



Ecosustainable MgO-based Cements: Unravelling the Role of Phosphate Additives by Means of Solid State NMR Spectroscopy

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MgO-based cements are receiving great attention both because their production could in principle involve negligible or “negative” CO₂ emissions and especially because they are particularly promising for the containment of radioactive waste. The important binder phase in cements obtained from hydration of MgO and silica is the completely amorphous magnesium silicate hydrate (M-S-H), the structure of which has been recently deeply investigated and characterized [1]. In order to pave the way to extensive and optimized applications of these promising cements, many aspects, both fundamental and practical, need to be investigated and understood. So far Solid State NMR (SSNMR) and Relaxometry techniques have given a crucial contribution to the comprehension of these materials at the molecular and nanometric scale, providing a detailed picture of the structure of the silicate binder phase, of the dynamic properties of water included in the pores and on the pore features, also clarifying their time evolution [2,3]. In the practice of cement preparation, additives are always necessary to achieve different goals, such as: accelerate or retard setting or hardening, decrease the amount of water necessary to obtain a given degree of workability, improve the mechanical performances, entrain air, etc. In the case of MgO/silica cements, sodium hexametaphosphate (HMP) nowadays is the only additive used as plasticizer and its mechanism of action is still not understood. In this work we have carried out a wide-ranging investigation on the effects of three different phosphate salts (HMP, sodium trimetaphosphate, TMP, and sodium orthophosphate, OP) on MgO/silica cements by combining fluidity tests, calorimetric measurements, XRD and SSNMR experiments. In particular, ²⁹Si and ³¹P SSNMR experiments clarified in detail and quantitatively the effects of the different additives on the formation kinetics and structure of M-S-H, highlighting at the same time the chemical modifications underwent by the additives and the interactions with the silicate phase. Combining these results with those of the other techniques it has been possible to propose a rationale behind the macroscopic effects observed for the different additives.

Keywords: Solid State NMR, cements, silicates.

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Acknowledgement:

This work was performed with the financial support of Ministero dell’Istruzione, Università e Ricerca scientifica MIUR (FIR2013 Project RBF132WSM).



Photoluminescence and evolution of polar order in $\text{Eu}:\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ ceramics

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BaTiO_3 -based ferroelectric ceramics show interesting properties such as high dielectric constant, low losses, high hydrostatic piezoelectric coefficient and PTCR effect. For these reasons, barium titanate is widely used in the electronic industry for manufacturing miniaturized multilayer ceramic capacitors, underwater transducers and self-regulating thermistors [1]. $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ (BZT) solid solution has the perovskite structure and shows a series of phase transitions and a progressive evolution of ferroelectric order, from long-range order typical of classic ferroelectrics ($x = 0-0.15$), via a diffuse transition behaviour ($x = 0.15-0.25$), to short-range order typical of relaxors ($x \geq 0.25$) and finally paraelectric non polar state for neat BaZrO_3 .

The trivalent europium ion (Eu^{3+}) is well known for its strong luminescence in the red spectral region. Even very small variations in the coordination sphere of europium ions induce major changes in the emission spectrum. Thanks to these features, Eu^{3+} is a unique and powerful local structural probe [2].

In this framework, we have investigated the photoluminescence (PL) emission of dense BZT ceramics doped with Eu^{3+} at the Ba site with composition $\text{Eu}_y\text{Ba}_{1-y}\text{Zr}_x\text{Ti}_{1-x-y/4}\text{O}_3$ ($y = 0.01$; $x = 0, 0.05, 0.15, 0.30, 0.50, 0.70, 1$) in the temperature range -100 to 140°C . The ceramics were prepared by the classical solid-state route and sintered at $1450-1550^\circ\text{C}$. The dielectric permittivity of the samples was measured from -150 to 150°C at 10^2-10^6 Hz to determine reference values of the phase transition temperatures and the type of polar order. The PL spectra underwent significant shape and intensity variations as a function of both composition and temperature, which can be correlated with the nature (long-range or short-range) of polar order.

The observed behavior can be rationalized considering the off-center displacement of Eu^{3+} ions with respect to the lattice position occupied by barium. The strong variation of the PL spectra induced by temperature change can be exploited to develop ratiometric self-calibrating luminescence thermometers [3] working from room temperature down to liquid nitrogen.

Keywords: Perovskites, Ferroelectrics, Luminescence

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Engineered Ferroelectric PVDF Composites Containing BaTiO₃-based Core-shell Inclusions: Dielectric Properties and 3D FEM Modelling of Field Distribution

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The demand for high dielectric constant materials and high energy density capacitors has rapidly increased in recent years due to the continuous and rapid development of the electronic industry and the need to store electrostatic energy more efficiently. The high breakdown field typical of polymers can be preserved while increasing the effective permittivity, if ferroelectric inclusions are embedded in the polymer matrix by forming a composite, thus improving the stored energy density. The dielectric properties of the composite can be tailored by varying size, shape and volume fraction of the inclusions as well as the dielectric constant of the polymeric matrix, thus altering the electric field distribution inside the material. Moreover, the distribution of the electric field can be modified by coating the particles used as inclusions with an oxide layer with a different dielectric constant.

In this work we have fabricated polyvinylidene fluoride (PVDF) composites containing 30 vol.% BaTiO₃@AO₂ (A = Si, Ti) particles and measured their dielectric properties. Barium titanate particles with a diameter of ~100 nm were synthesized using a hydrothermal-like method and coated with a thin shell (~10 nm) of SiO₂ or TiO₂ by means of colloidal chemistry methods. The composites were prepared by solution casting followed by compression moulding.

The dielectric properties of the composites (permittivity and loss tangent) were measured at different frequencies and several temperatures. The coating results in a significant modification on the effective permittivity, which is mainly determined by the value of its dielectric constant. To gain insight into the role of the coating layer, the electric field distribution and the effective dielectric constant were calculated for the different composites using a 3D finite element modelling and compared to experimental results.

Keywords: Dielectrics, composites, dielectric constant

Acknowledgement:

Work carried out in the framework of project Polycom funded by Fondazione Bancaria Compagnia di San Paolo.



Environmental Applications of Electrospun Keratin Nanofibers

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Electrospun nanofibers have gained increasing interest for solving critical environmental issues such as air pollution and water contamination. Electrospinning is based on the application of a high voltage to the viscous polymer solution in order to generate an electrified jet stream from an electrically charged liquid drop that solidifies into nanofibers by solvent evaporation. Electrospinning process parameters lead the production of nanostructured layers with different characteristics (e.g. fiber size, morphology, layer density and thickness).

Highly porous and flexible web can act as a membrane separating two distinct phases through processes such as adsorption, distillation, and extraction. High porosity, interconnected open pore structure, high permeability and high surface area per unit volume are very attractive properties in separation technology. One of the advantages of nanofiber membranes is that they can offer, at the same time, filtration and adsorption. Moreover, electrospinning process is scalable; to increase both productivity and covering area, large-scale nanofiber production by multi-jet electrospinning systems can be designed [1].

Many natural materials such as agricultural wastes or industrial by-products have been proposed as low cost adsorbents available in large quantities for heavy metals. Among them, keratin proteins are characterized by a great number of functional groups able to bind cationic species. Keratin is the most abundant non-food protein in nature is available as waste (more than $5 \cdot 10^6$ t/y) from textile and breeding industry. Considering its applications, it is worth to note that is biocompatible and biodegradable and can be electrospun pure or in blend with other polymers, such as polyamides. Among the natural electrospinnable polymers, keratin is able to remove toxic substances such as formaldehyde, metal ions and dyes efficiently [2]. Moreover, keratin nanofibers integration with nanoparticles as TiO_2 and Ag colloidal properly dispersed in the electrospinning solutions improves membrane functionalities such as biocidal action and photocatalytic properties [3].

Keywords: electrospinning, keratin, filtration

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ANFISOL - amphiphobic coatings with self-cleaning properties for photovoltaic panels

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The solar modules are subject to various factors that reduce their performance. In addition to the endogenous phenomena of the module, (i.e. reduction of cell efficiency, oxidation of the electrical contacts, increase of the reflectance of the receiving surfaces) there are other phenomena that affect the glass front layer: a) progressive dirtying of glass by deposition of fine particles, b) deposition of liquid or solid organic components c) dew formation.

Highly hydro and oleophobic (amphiphobic) coatings can be used as an effective solution to reduce the negative effect due to surface alteration due to the "self-cleaning" effect which allows to prevent the entry into the surface cavities of powders, particulate, organic residues as well as the formation of dew.

In this work a superhydrophobic/ amphiphobic coating has been prepared, characterized and tested for its employ on solar panels. The produced coating is easily applicable and have high transmittance.

Preliminary tests for wearing, thermal stress and durability have been also performed in order to study amphiphobic systems for solar panel application.

Keywords: amphiphobic, superhydrophobic coatings, fotovoltaic

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Acknowledgement:

Compagnia San Paolo



Self-cleaning Photocatalytic Paints: Efficiency Under Indoor Lighting Systems

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The awareness of a healthy living environment is increasing in recent years and it concerns either outdoor or indoor spaces. Recently, buildings and indoor living spaces have often been objects of dedicated studies aiming to optimise the energy demand in relation to heating and ventilating systems, as well as Indoor Air Quality (IAQ) management [1].

Designers and architects tend to limit the air mass exchanges with outdoor environment in order to minimise the energy demand for air conditioning, thus preferring the recycling of indoor air. This involves the gradual increase in indoor pollutants and the decay in IAQ. The pollutants content in indoor spaces often reaches a concentration higher than outdoor, thus requiring the introduction of adequate control and remediation systems in order to maintain a suitable air quality.

Several remediation systems are available and indoor pollutant removal takes currently advantage of various technologies. Air filtration through filtering and/or adsorbing cartridges is often used, but they involve continuous maintenance operations (i.e. increased costs). An alternative and low-cost VOCs remediation system is based on the Advanced Oxidation Processes (AOPs). Thanks to the employment of suitable photocatalytic self-cleaning wall paints, VOC can be removed from air while organic dirty stains are removed from the surface. Both pollutant typology are completely mineralised towards carbon dioxide and water.

Dedicated scientific papers have always taken into account the performance of the photocatalysts themselves, but rarely the photocatalytic paint formulations have been characterised nor their performances accurately assessed in real or simulated indoor conditions [2, 3]. The paint components, indeed, can significantly affect and modify the performance of the active photocatalytic compounds.

The self-cleaning photocatalytic paints can be designed for specific applications such as outdoor or indoor environments. In the latter case, the paint formulation should consider different light sources with respect to the outdoor one (i.e. the sun), with very different energy content for the activation of the photocatalytic compounds. Nevertheless, the technical sheets of the paints often reported that they are “active under artificial lights” and “effective without UV light”, while the specific lighting requirements for their activation are not reported.

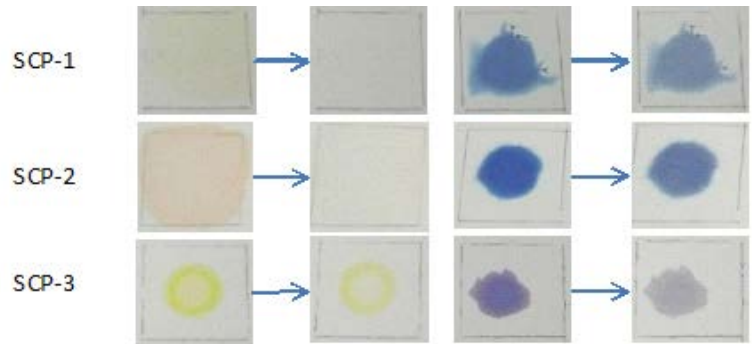
The aim of the present contribution is to assess the performances in different conditions of three commercial indoor self-cleaning photocatalytic paints with respect to their photocatalytic performances in different conditions.

The selected paints have been fully characterised and their photocatalytic performances have been



investigated toward NO_x (i.e. for the indoor air quality improvement) and methylene blue removal (i.e. for self-cleaning action), according to ISO standards 22197-1 and 10678 respectively. Ad-hoc experiments were furthermore designed for testing their action in bleaching methyl red and methylene blue stains under different light sources: UVC, Xenon, fluorescent and LED lamps.

The paint producers usually refer to ISO standards for the certification of the photocatalytic properties and these protocols are generally planned under UVA light. This light source, however, is not used in the ordinary indoor conditions. Therefore, the paints were tested under prevalent indoor lights (fluorescent and LED lamps) in order to provide a valuable comparison with respect to more energetic sources.



Keywords: Photocatalysis, Indoor paints, Visible light.

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Acknowledgement:

This work was partially funded by the European Union's Seventh Programme for research, technological development and demonstration under grant agreement No 609180, Ecoshopping. Energy efficient & Cost competitive retrofitting solutions for shopping buildings. The authors acknowledge Dr. L. Nodari and Dr. A. Gambirasi for the FT-IR analyses and their helpful discussions.



Reactivity of Silane Compounds with few-layer Black Phosphorus

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2D materials have attracted the interest of researchers around the world due to their outstanding properties and potential applications in many fields such as optoelectronics and sensing. Among those 2D materials, phosphorene, which consists on a single layer derivative, atomically thin nanosheet of bulk orthorhombic black phosphorus, seems to be one of the most promising. Yet, the instability of this material in air and its tendency to degrade very quickly via reaction with low concentrations of oxygen and water is a major drawback that impedes its direct application.¹ Therefore, for the last couple of years, most research efforts have been devoted to the chemical functionalization of this fascinating nanomaterial in order to improve its stability.

On the other hand, SiO₂ coating is a common process that has been previously used in many nanomaterials, such as carbon nanotubes.² This kind of coating is not covalently bond to the nanomaterials, therefore, it does not alter its electronic structure significantly. It can, however, passivate the nanomaterials, improving their resistance to degradation, thus making them more stable in air.

In this work, we have studied the reactivity of few-layers black phosphorus with various silane compounds such as, TEOS, APTES, PDMS, etc. Characterization of the reaction products (IR, Raman, TEM, etc.) shows the layers of BP are containing silicon compounds and the stability of these flakes over time is improved. In particular, the Raman spectrum provides a significant shift in the wavenumber of A²g mode while the A¹g mode remains practically unchanged in comparison to pristine BP, which can be interpreted as an indication for the occurrence of a strong interaction or a covalent bond with the phosphorus atoms of BP.

Keywords: black phosphorus, silicon, coating, stability

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Thanks are expressed to the European Research Council (ERC) for funding the project PHOSFUN “Phosphorene functionalization: a new platform for advanced multifunctional materials” (Grant Agreement No. 670173) through an ERC Advanced Grant to M. P.



Interfacial Properties of Binary Dispersions of Titania and Silica Nanoparticles and Applications to Foams and Solid Foams

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Partially hydrophobic nanoparticles in a dispersion are energetically favoured to segregate irreversibly at the liquid interface, forming compact layers which influences the mechanical properties and in particular the stability of the interface. Based on these concepts, these NPs have been proposed as efficient foam and emulsion stabilisers, in alternative to common emulsifiers or foaming agents and conveniently utilised in the development of capsules, porous materials and solid foams [3]. While several physical methods have been proposed to control the philic nature of NPs, a particularly simple approach consists in adsorbing surfactants at the NP surface, which can be straightforwardly done by adding proper amounts of surfactants to the dispersion [1, 2].

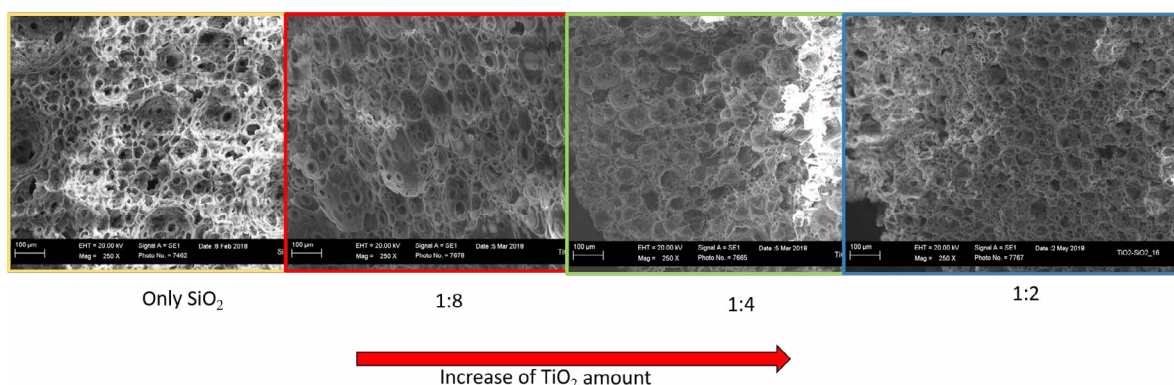
Recently we have investigated the possibility to apply such approach to binary nanoparticle systems, namely composed by titanium dioxide (TiO_2) and colloidal silica particle (SiO_2). Both particles are highly hydrophilic under standard conditions, due to the presence of a large negative surface charge. The adsorption of a cationic surfactant, such as CTAB, can be therefore suitably utilised to impart controlled degrees of hydrophobicity to these NPs, promoting their segregation at the dispersion interface.

The studies evidence that important synergetic effects exist in these binary systems, in relation to the ability to modify the mechanical properties of the interface. As a result, foams produced by the corresponding dispersions, shows outstanding features, remaining stable for times of the order of several days under room conditions.

In addition, specific routes in the formulation of these binary dispersions have been shown as effective to control selectively the segregation of the different species of NPs at the liquid-air interface.

In order to exploit these remarkable properties, we have developed solid foams starting from these binary dispersions, based on a protocol already utilised to obtain solid foams from particle-stabilised aqueous foams. The preliminary results show the possibility to conjugate the specific features of the single particles in porous materials with tailored functional and structural characteristics.

$\text{TiO}_2/\text{SiO}_2$ foam





Keywords: porous materials; nanoparticles, foams

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Acknowledgement:

This work is supported by the ESA MAP projects “Soft Matter Dynamics” and “Particle Stabilized Emulsions -PASTA”, and the by the related Italian Space Agency contract (ASI n. 2013-028-R.O.).



Synthesis of Sulfur-Rich Polymers: Copolymerization of Cyclohexene Sulfide and Carbon Disulfide Using Chromium Complexes

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The copolymerization of cyclohexene sulfide (CHS) and carbon disulphide (CS₂) to afford poly(cyclohexene) tritriocarbonates catalysed by a chromium complex with salen-type ligand **1** (R,R)-N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-diaminobenzene has been studied in the presence of [PPN]N₃ (bis(triphenylphosphine)iminium azide) as cocatalyst at different temperatures and comonomer loading (Figure 1).

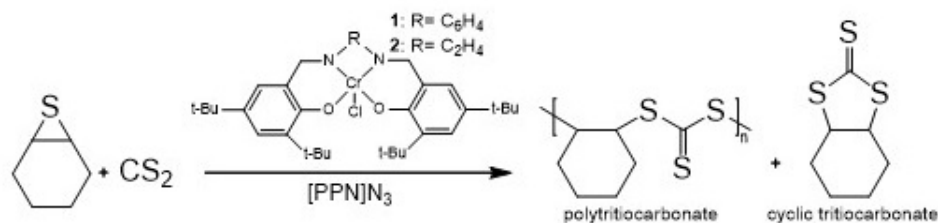


Figure 1. Copolymerization of cyclohexene sulphide (CHS) and CS₂.

A kinetic study was carried out in order to identify the optimal conversion and selectivity. The reaction proceeds with higher selectivity values at 25 °C, with 2:1 CS₂ to CHS loading ratio and the polytritriocarbonate copolymer is the dominant product. Moreover, the ¹H and ¹³C NMR spectra shown only 3% of signals related to the thioether moiety. Therefore, it can be assumed that the samples are mainly alternating copolymers.

The polytritriocarbonate copolymer synthesized with salen-type ligand **1** shows higher molecular weight than copolymers from literature prepared with chromium complex with salen-type ligand **2** (N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-ethylenediamino) where the copolymerization yields only 15 % of copolymer with a molecular weight (Mw) of about 5000 g/mol.¹

The thermal behaviour of the copolymers was studied by TGA and DSC. The sulphur-rich polythiocarbonates decompose with a midpoint temperature of about 250 °C. A crystallization temperature, not observed in polycarbonates, is detected at 113 °C and additionally the sulphur-rich samples exhibit a melting temperature around 147°C.

Keywords:

Cyclohexene sulfide, carbon disulphide, polytritriocarbonates

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Investigation of the Modulation of the Non-Covalent Interaction Between 2D Bp and Fluorescent Pyrene Derivatives Endowed with Different Functional Substituents

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Owing to its semiconductor nature, phosphorene (bidimensional black phosphorus, 2D BP) is one of the most studied 2D material of the last years. Surface functionalization is a key factor in the development of this 2D semiconductor as an effective material platform to be implemented in real-setting applications. Indeed, several chemical strategies can be adopted in this framework in order to modulate phosphorene band gap [1], to realize active hybrid heterostructure [2] and to protect 2D BP from oxidation [3].

Herein, we perform a throughout photo- and chemical-physical study in order to get insights on the nature of the chemical interactions between 2D BP with organic luminescent conjugated compounds bearing different functionalities. Together with their unsubstituted counterpart, we selected two pyrene derivatives with boron-functionalities such as the pyren boronic acid (PBA) and the pyren boronic ether (PBE), which have been dispersed in 2D BP exfoliated suspension. Specifically, the presence of the boron-functionalities is correlated to the widely-recognized chemical affinity between phosphorus atom (P) with boron atom (B). Moreover, the presence of hydroxyl and ether terminal groups in the compounds allows to evaluate the role of oxygen in two different chemical and hindrance environments in establishing weak interactions (such as H-bonds and Van der Waals forces) with 2D BP.

As a first output, ^{31}P deuterated magic-angle spinning NMR spectrum (DE-MAS) performed for the first time in a suspension highlighted a non-covalent nature of the interaction between 2D BP and PBA.

Then, DFT calculations were performed in order to discriminate the effectiveness of the different functionalities in mastering the interactions between the 2D BP and the organic conjugated moieties. Indeed, the stabilization energy between phosphorene and PBA is expected to be higher than that of the phosphorene/PBE system. Moreover, the stabilization energy increases when BP is oxidized.

As a final experimental validation, time-resolved lifetime fluorescence spectroscopy revealed that PBA and PBE are energetically stabilized with respect to unsubstituted pyrene given they present almost 5-time-higher emission decay time constants.

Collectively, all these results showed up that (i) the multi-technique and inter-disciplinary experimental approach here presented is suitable assessing the intimate nature of the interaction between 2D BP and active molecules and (ii) the energy-stabilized semiconductor hetero-system comprised by 2D BP and suitably-functionalized pyrene moiety is prone to be use as active layer optoelectronic devices.

Keywords: phosphorene, pyrene, functionalization

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Acknowledgement:

The authors thank the ERC under the Horizon 2020 research and innovation program (Grant Agreement No. 670173) for funding the project PHOSFUN “Phosphorene functionalization: a new platform for advanced multifunctional materials” through an ERC Advanced Grant to MP (PI).



Interfacial Phenomena in Ni Alloys-Oxides systems of Interest for Investment Casting of Superalloys

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The project “Innovative Surfaces for Superalloys Casting Processes” (INSURFCAST) has the objective of designing appropriate ceramic surfaces and procedures which would enable the use of innovative superalloys for the production of complex-shaped blades by precision investment casting.

In any casting process, a liquid alloy is poured into a refractory container, typically a ceramic, that must be inert to avoid surface and bulk defects in the final product.

Issues related to high-temperature metal-ceramic interactions arise dramatically when dealing with innovative superalloys: these high-performance Ni- or Co-based alloys have very high melting temperatures (up to 1500°C) and contain highly reactive elements (e.g. Al, Ti, Hf, Y) that, even when present at very low concentration, form, in contact with the ceramic mould, non-metallic inclusions as internal and surface casting defects. In addition, well-defined microstructures and precise external surfaces are requested to the final products.

Therefore, acquiring knowledge on interfacial phenomena may assist the choice of the right alloy-refractory combination in relation to the processing parameters as surface finishing, temperature, heating-cooling rates, atmosphere conditions, etc.

In this poster, results aimed at elucidating these issues are presented. In order to deepen the knowledge about the role of active elements in the interfacial behaviour of superalloys, the wetting of “simple” binary and ternary Ni alloys containing small amounts of other elements (e.g. Cr, Hf) in contact with oxides chosen among those used in contact with superalloys (e.g. Al₂O₃, mullite) was studied. The results are discussed in terms of chemical interactions, and as a function of the alloys composition. Moreover, thermodynamic data (phase diagrams, energy quantities) are also presented in order to interpret and predict phenomena occurring during industrial high-temperature liquid-assisted processes.

Keywords: superalloys, investment casting, metal-ceramic interfaces

Acknowledgement:

This work is part of the Project INSURFCAST (Innovative Surfaces for Superalloys Casting Processes) financed within the ERA-LEARN 2020 support action funded by EU-H2020, M-ERA.NET Joint Call 2016.



Recent Progresses in Catalyzed Butadiene and Isoprene Polymerization

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The first generation of catalysts for the polymerization of butadiene and isoprene was obtained by a combination of transition metal compounds (*e.g.*, chlorides, alcoholates, carboxylates) with aluminum-alkyls [1]. These systems permitted to prepare all the stereoisomers of polybutadiene, but their activity was rather low, and the selectivity too was not very high, since the stereoregular polymer often represented only a small fraction of the crude polymer.

With the advent of MAO as alkylating agent, in the 1980s, new catalytic systems were introduced, in some cases much more active and stereospecific than those based on common aluminum-alkyls. Metallocene catalysts could also be used for the polymerization of 1,3-dienes, allowing to obtain novel polymers from substituted butadienes which were not possible to prepare with the conventional Ziegler-Natta catalysts. The results obtained, however, were particularly interesting from the scientific point of view – useful for a better comprehension of the diene polymerization mechanism – but did not lead to any real improvement with regard to the catalysts used for the polymerization of butadiene and isoprene, the only monomers of industrial interest. Starting from the 2000s, a new generation of catalysts, based on well defined complexes of transition metals and lanthanides with various ligands containing donor atoms such as P and/or N and/or O (*e.g.*, phosphines, imines, imino-pyridines, keto-imines), has been introduced [2,3]. These novel catalysts permitted better control of the polymerization regio- and stereo-selectivity, of the molecular weight and molecular weight distribution of the resulting polymers. It was possible to prepare polybutadienes and polyisoprenes with a higher *cis* content, 99.9% and $\geq 99\%$ respectively, with catalysts based on lanthanide (Nd, Pr, La) complexes with bis-imino, bis-iminopyridine, keto-imino and keto-imino-pyridine ligands, upon activation with various types of aluminum-alkyls (*i.e.*, $\text{Al}(\text{Bu})_2\text{H}$, MAO, TIBAO). This result is extremely important from the industrial point of view since even a slight increase in the polymer *cis* content may lead to a great improvement in the elastic properties of the polymers. A high *cis*-1,4 polybutadiene ($\geq 85\%$) was also prepared with catalysts based on various types of titanium and vanadium complexes (*e.g.*, phosphine, keto-imines, bis-imines, pyridine-imines complexes) with MAO; in particular the obtaining of a *cis* polymer from vanadium was quite unexpected since vanadium catalysts are mainly known in the field of stereospecific diene polymerization for their ability to give highly *trans*-1,4 polymers, and are by far the most important systems for preparing *trans*-1,4 polybutadiene. With these novel catalytic systems it was possible to obtain new, highly stereoregular polymeric structures that were not possible to prepare before. This is the case with syndiotactic and isotactic 3,4 polyisoprene obtained by iron and lanthanide catalysts, respectively, and *cis*-1,4-*alt*-3,4 polyisoprene obtained by cobalt catalysts. The catalytic systems based on well-defined cobalt complexes were however, without a doubt, those giving, up to now, the most interesting results. New catalytic systems have been developed by combination of MAO with phosphine- CoCl_2 complexes. The peculiarity of such novel complexes lies in their ability *i)* to allow the



formation of poly(butadiene)s with controlled microstructure (*cis*-1,4 or 1,2) by simply varying the type of ligand coordinated to the Co atom and *ii*) to give living polymerizations. Taking advantage of these features, we were able to prepare new butadiene di-block stereoregular polybutadienes (BDSPs), in which the two blocks, linked through a single junction point, have different characteristics (amorphous *cis*-1,4 and crystalline syndiotactic 1,2); these novel polymers will allow to prepare compounds for applications in several fields such as tires, soles and technical articles, with improved properties compared to those nowadays available.

Based on what reported above, it is clearly evident that investigations into the synthesis of novel transition metal and lanthanide complexes, with particular regard to their environmental sustainability, and their use as catalyst components for the polymerization of 1,3-dienes, seem to pave the way for future studies. Preparation of homo- and multi-block copolymers exploiting the "living" character of these catalytic systems, and the possibility of controlling and/or modifying the catalytic regio- and stereoselectivity during polymerization, through an appropriate choice of type of ligand, type of aluminum-alkyl and Al/Mt ratio, nature of the monomer, will represent another way to go in the future.

Keywords: catalysts; polymerization; polybutadiene.

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The P-Sc Structure in Phosphorus: Bringing Order to the High Pressure Phases of Group 15 Elements

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In the recent years, the renaissance of black Phosphorus (bP) has been strictly related to the increasing interest for Phosphorene, a newly-synthesized and promising 2D corrugated monoatomic layer of P. In fact, bP is made by the periodic stacking of Phosphorene [1] and has a layered orthorhombic A17 structure, stable at room conditions. The A17 phase transforms into a layered rhombohedral A7 structure above ~5 GPa, and the A7 phase is reported to further convert into a non-layered, simple cubic structure at ~11 GPa. The sequence of the high pressure (HP) structures of P at room temperature presents two striking anomalies if compared to the other group 15 elements with higher Z. First, the A17 structure is an isolated exception along the group; second, whereas the HP limit for the A7 structure decreases in group 15 with increasing Z, according to current literature its pressure value in P (11 GPa) is located below that of As (25 GPa). A recent experiment [2], in good agreement with theoretical predictions, has revealed a two-step mechanism for the A7 to sc transition and the existence of a previously unreported, intermediate pseudo simple-cubic (p-sc) structure from 10.5 up to at least 30 GPa. The presence of this p-sc phase significantly raised the HP limit for the layered structures of P and provided new experimental evidences to account for the long debated anomalous pressure behaviour of the superconducting critical temperature (T_c) of P in the 10-30 GPa range. In this study, synchrotron X-ray diffraction (ID27, ESRF) during room temperature compression of bP up to 30 GPa in Diamond Anvil Cell (DAC) was performed in the presence of He, H₂, N₂ and Daphne Oil 7474. The data demonstrated that the p-sc structure is an intrinsic feature of P that does not depend from the pressure transmitting media. Furthermore, the EOS's of A17, A7 and p-sc phases were derived and the A7 to p-sc transition was demonstrated to follow a first order mechanism. Highlighting the structural relations between A7 and p-sc, we were finally able to solve the apparent contradictions emerging from previous literature data, bringing order to the sequence of HP A7 layered structures in group 15 elements [3].

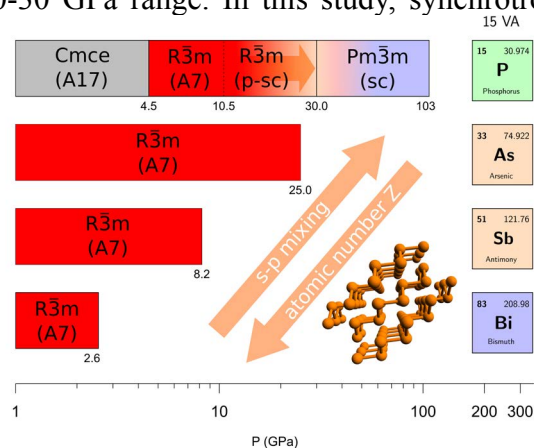
Keywords: x-ray diffraction, phase transitions, black phosphorus

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Acknowledgement:

Thanks are expressed to EC through the European Research Council (ERC) for funding the project PHOSFUN "Phosphorene functionalization: a new platform for advanced multifunctional materials" (Grant Agreement No. 670173) through an ERC Advanced Grant.





Hi-Tech Ceramics and Composites for Severe Environments

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This lecture traces the main research activity concerning Hi-Tech Ceramics and Composites for severe environments. Harshness characterizes extreme working conditions where thermo-chemical, thermo-physical and thermo-mechanical attacks may concurrently take place. New composite concept designs make feasible the overcoming of the ceramic's brittleness merging damage tolerance and capacity of withstanding ultra-high temperature regimes in chemically aggressive environments. Added-value materials with self-repairing capability are under development.

The R&D activities span from the fundamental understanding of the process-microstructure-property correlations, to the materials functionalization through suitable procedures up to the realization of technological demonstrators to be validated in relevant environment.

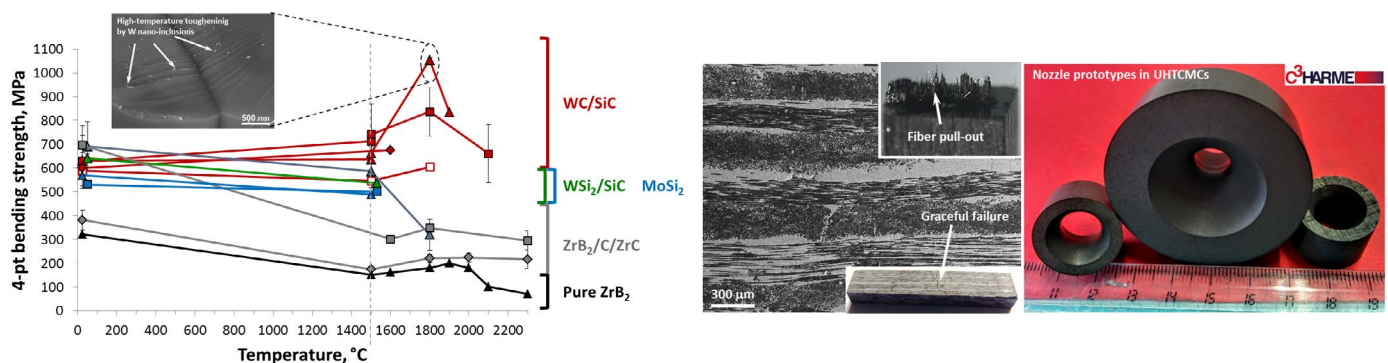
The materials investigated include damage tolerant ultra-high temperature ceramic matrix composites (UHTCMCs), extremely strong ceramics, super hard and light carbides for structural applications in various harsh environments.

The talk shows the last results on a variety of advanced ceramic materials.

First, ultra-high temperature ceramics are considered. This class of composites includes borides and carbides of the 4th to 6th group which possess melting point above 3000°C and a combination of thermo-mechanical properties that make them adequate for application in highly corrosive and ablative hot environments, like component of space vehicles and parts of rocket nozzles. Their major drawbacks include a difficult densification, sensitivity to oxidation, high brittleness and low thermal shock resistance.

Here we show that upon suitable incorporation of sintering agents, different types of fibers or suitable powder processing we can manipulate the microstructure to obtain desired properties and stem the above mentioned limits. For example, we obtained ceramics possessing strengths exceeding 1 GPa at 1800°C, when normally their strength at these temperature are around 200 MPa, composites with fracture toughness above 14 MPa·√m, with a tremendous improvement compared to conventional bulk UHTCs (typically 3.5 MPa·√m), and near Zero-ablative oxidation-resistant UHTC, being thus suitable for reentry and propulsion applications

In addition, we also show recent progresses on super light and hard materials intended for wearable ballistic protections.





Keywords: ultra-high temperature ceramic composites, extreme environments, damage tolerance.

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Acknowledgement:

Part of the research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2011-2014) under grant agreement LIGHT-TPS No. 607182 and from the European Union's Horizon 2020 "Research and innovation programme" under grant agreement No. 685594 (C3HARME).



Lightweight Composites with Hollow Glass Microspheres for Rotational Molding Technology

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The present work is aimed at obtaining lightweight materials suitable for the manufacturing of plastic products by rotational molding. Rotational molding or rotomolding (RM) is a low-shear technology used to produce one-piece hollow items for various applications, like liquid storage tanks, containers, toys, indoor and outdoor furniture [1]. About 85% of RM worldwide production is based on different grades of polyethylene (PE) resin. Hollow glass microspheres (HGMs) are mainly used as an inert, low density filler in polymeric matrices. In particular, HGMs made of chemically stable soda-lime-borosilicate glass with high crush-strength allow to attain, also in high-shear processing conditions, lightweight composites with a reduced resin content [2].

In this work, we reinforced medium density polyethylene (MDPE) and poly(ϵ -caprolactone) (PCL) with HGMs to study innovative composites. In the first case, materials were prepared with MDPE, which is traditionally used in RM manufacturing. HGMs were used as such or surface modified by treatment with dodecyl(triethoxy)silane (DDTES), a commercial coupling agent bearing an alkyl chain, in order to enhance compatibility between the inorganic particles and the polyolefin matrix. The effectiveness of the silanization process was established using FTIR spectroscopy and TGA. A polyethylene grafted with maleic anhydride (PE-g-MA) was also tested as coupling agent to enhance material properties. MDPE composites at various HGMs content were prepared by melt blending at 200°C, 10 min, and 60 rpm in a Brabender internal batch mixer. In the second case, composites were prepared with PCL, an aliphatic polyester fully biodegradable and biocompatible. Although PCL has a good flexibility, characterized by high fracture strain, it shows low thermal resistance and heat deflection temperature due to its low melting point (~60°C). Moreover, the Young modulus of PCL is very low, typically 200-400 MPa. These drawbacks have limited its commercial application to some extent. The HGMs were used as such or surface modified by treatment with (3-aminopropyl)triethoxysilane (APTES) [3] in order to enhance the compatibility between the inorganic particles and the PCL matrix. PCL-based composites at different compositions were analogously prepared using the Brabender mixer in the following conditions: 100°C, 10 min and 60 rpm, under nitrogen atmosphere. The composites either based on MDPE or PCL were characterized in terms of morphological, rheological and mechanical properties. On the basis of scanning electron microscopy (SEM) inspections, a good filler dispersion in the composites was found as a result of HGM-surface modifications. The addition of HGM particles has relevant implications on the rheological and mechanical properties enhancing the stiffness of the composites. In particular, the MDPE-based composite reinforced with 20 wt% of silanized HGM exhibits an increase of Young modulus up to 90% compared to neat MDPE accompanied by a reduction of density of about 10%. The PCL-based composite reinforced with 20 wt% of silanized HGM exhibits better mechanical properties (Young modulus enhancement of 120%, tensile strength enhancement 20%) and a lightening of about 12% compared to the neat polymer matrix. Moreover, several rotomolded parts in composites based on MDPE and PCL were prepared successfully through uni-axial benchtop rotomachine showing their potential use in RM technology. As an example, in Fig. 1 PCL-based parts at increasing percentage (0, 5, 10 wt% from left to right) of HGMs prepared with the uni-axial benchtop rotomachine are shown.



Fig. 1



Fig. 2

A few formulations based on MDPE were then selected and used to successfully produce some prototypes in the actual industrial environment, that is under bi-axial rotation in the experimental conditions normally used for polyethylene. In Fig. 2 MDPE-based prototypes prepared by RM are shown. With respect to the neat MDPE (Fig. 2, left), the presence of 10 wt% HGMs (Fig. 2, right) confers to the composite item a good aesthetical quality, characterized by a uniform translucent finishing put in evidence by interior lighting.

Keywords: Polymer-based composites; Lightweight materials; Rotomolding

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Acknowledgement:

The authors would like to acknowledge the financial support of Regione Lombardia through the Research Project "Arred'Arte - Multipli plastici per l'arredamento di design artistico" (ID 187022).



Aziridine Functionalized Carbon Nanotubes as Highly Efficient Electrocatalysts for the Selective CO₂ Reduction to CO

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The constant increase of CO₂ levels in the atmosphere as a result of anthropic activities is directly linked to climate changes and global warming issues. Multiple approaches need to be implemented to curb with these phenomena, including carbon sequestration, electrification of the transportation sector and switching from fossil fuels to renewable energy. One of the most promising methods to mitigate CO₂ impact while providing a means of mass energy storage, is the electrochemical reduction of CO₂ (CO₂RR) into chemicals and fuels of added value.^[1] However, electrocatalysts for CO₂ conversion into products such as CO, formic acid, methanol, and small hydrocarbons, still suffer of moderate productivity and/or poor selectivity. To date, Ag and Au-based electrocatalysts exhibit the best performance for the conversion of CO₂ to CO, but they irremediably suffer of poor sustainability. On this ground, metal-free systems have recently emerged as highly attractive candidates to replace metal-based systems in the process. To date, relatively few examples of metal-free catalysts for CO₂RR exist, most of them raising from the class of light-heterodoped carbon nanomaterials (CNMs). In particular, a series of N-doped systems have been investigated but the nature of active sites responsible for CO₂RR remains highly controversial.^[2]

Recent findings from some of us have demonstrated how a fine tuning of the surface properties of CNMs can be conveniently achieved by chemical functionalization of their outer surface with tailored N-containing heterocycles.^[3] The chemical approach allows a precise control of N-dopants in terms of N-configuration and electronic charge distribution, offering a unique tool for the comprehension of the role of specific N-functionalities in the activation of small molecules. In this contribution we report the chemical decoration of MWCNTs with NH-aziridine functionalities (MW@N^{Az}) and their application as highly efficient and selective metal-free electrocatalysts for CO₂ reduction into CO. With a Faradaic efficiency (FE) close to 90% at -1.2V (vs. Ag/AgCl/KCl_{sat}) and productivity as high as 48 NLCOh⁻¹gN⁻¹, MW@N^{Az} ranks among the metal-free systems with the highest performance reported so far providing, at the same time, a privileged view-point on the structure-reactivity relationship of light-heterodoped CNMs and a powerful tool to the unambiguous comprehension of the underlying CO₂RR mechanism.

Keywords: inserire massimo 3 keywords - Times New Roman 12

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Acknowledgement:

Authors thank the Italian MIUR (PRIN 2015, Project SMARTNESS 2015K7FZLH) for financial support.



Polypyrrole Nanoparticles Synthesis and Deposition by “Throwing Stones” for Antibacterial Textiles

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Antibiotic resistance is one of the most critical health issues to human health in the world. The emergence has stimulated intensive research in many fields, including the development of antibacterial fabrics and novel broad-range biocides for textiles.

Polypyrrole (PPy) is a conjugated polymer that showed excellent antibacterial properties on textiles [1]. Bioactivity of PPy is likely due to the presence of positive charges along the backbone chain able to open the membrane cell of bacteria [2]. PPy has been easily synthesized and deposited on fabrics by chemical oxidative polymerization from solutions of the monomer. However, at industrial level, the separation between polymer synthesis and fabric coating would lead to benefits in terms of productivity, evenness, cost, wastewater and chemicals usage.

In this work, chemical synthesis of PPy was carried out in presence of poly(styrene sulphate) (PSS) in order to produce stable water dispersions of PPy nanoparticles. Viscosimetric analysis displayed a significant interaction between PPy and PSS with the presence of PSS solution between the PPy nanoparticles. However, this feature seems to be positive for the high shear rates locally generated during the ultrasonic coating process.

PPy nanoparticles were deposited on polyester fabrics by an ultrasound-assisted deposition process. In this case, the ultrasound “throwing stones” technique produces microjets that push the nanoparticles in water towards the fibres surface enhancing particle collision, penetration and deposition.

Since PPy is black, a colorimetric analysis was used to quantify the amount of PPy deposited on fabrics. Moreover, scanning electron microscopy, infrared spectroscopy and thermogravimetric analysis were used to assess the PPy content. Antibacterial tests were carried out according to ISO 20743 against *Staphylococcus aureus* and *Escherichia coli*. The fabrics with the higher amount of PPy (4 g/m²) showed excellent antibacterial properties against both bacteria. In particular, a bacterial reduction of 99.99999% (Log 7.00) was found against *S. aureus* and 99.999996% (Log 7.35) against *E. coli*.

Keywords: antibacterial fabrics, conjugated polymers, ultrasound.

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Acknowledgement:

This work is funded by the EU Horizon 2020 research and innovation programme under Grant Agreement No. 720851, project PROTECT. Authors greatly acknowledge Ilana Perelshtein and Aharon Gedanken (Bar-Ilan University, Israel) for ultrasound depositions and antibacterial tests.



Thermo-Mechanical Characterization of NiMnGa Melt Spun Ribbons

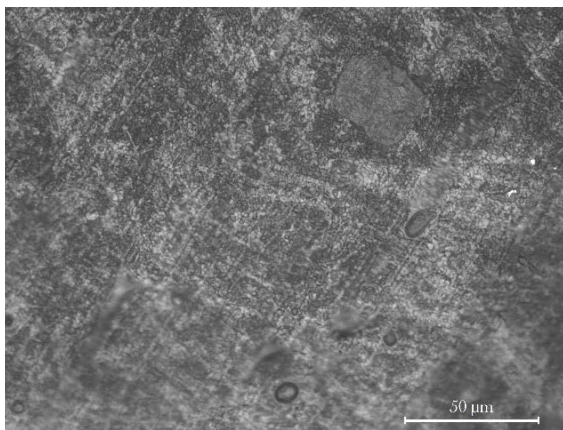
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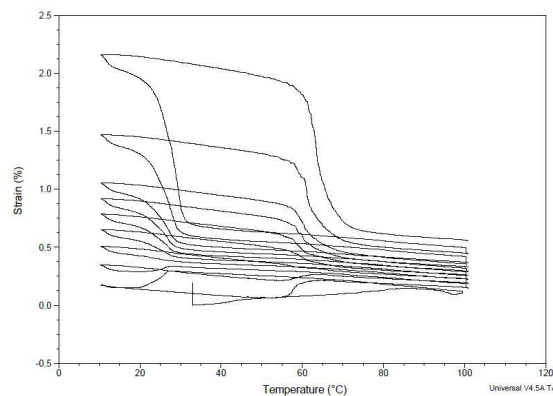
The NiMnGa alloy is the principal and the most investigated system in Ferromagnetic Shape Memory Alloy field (FeSMA). The best performances as giant magneto-strictive material were obtained with single crystal sample (12% in strain), but as lot of attempt was performed to obtain new system NiMnGa-based and new products to reach good results in many functional properties like magneto-caloric effect, magneto-resistive effect, magnetic shape memory induced transition and elasto-caloric properties. Moreover many investigation were aimed to overcome the principal technological problem of these alloys: the high brittleness.

Therefore the melt spinning procedure is a good way to obtain ribbons for the development of active element in actuator devices.



Microstructure of NiMnGa melt spun ribbons

In our study we show the study of calorimetric and mechanical, dynamic-mechanical and functional properties of two series of NiMnGa ribbons.



Measure of strain recovery vs T under load

The modulation of microstructure by thermal treatment and its influence on mechanical properties was investigated.

Keywords: FeSMA, NiMnGa, Melt spun ribbons

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Acknowledgement:

Authors are grateful to Marco Pini and Giordano Carcano of CNR-ICMATE (Lecco Unit) for technical assistance.



Solid-Gas Biocatalysis Using PVDF Enzyme-Loaded Membrane

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Enzymes have been generally employed in aqueous solution, organic solvent systems, two phase water/organic mixtures or microemulsions either for homogeneous or heterogeneous catalysis. Anyway, biocatalysis can also be applied to vapour phase systems, in which substrates and products are in gaseous phase and enzymes are in solid phase. Solid-gas biocatalysis is a special type of reaction system that exploits the ability of some enzymes, being in the solid state, to catalyze reactions of substrates in the gas phase. This approach has been proposed with the aim to develop new technologies for applications in production, waste treatment, biosensing and so on [1]. Solid-gas biocatalysis with respect to traditional solid-liquid biocatalysis has many advantages such as an higher thermostability of the dehydrated enzyme, absence of leakage, reduction of microbial contamination, improvements in mass transfer and product recovery. Several enzymes, such as lipases, esterases, cutinases, alcohol oxidases, alcohol dehydrogenases, that traditionally converts substrates in aqueous solutions has been tested in solid-gas systems showing significant activity [2]. Optimal supports for solid-gas biocatalysis are porous membrane materials, which allow to obtaining high flow rate and low pressure drop. The objective of this work was to develop a biocatalytic membrane reactor for hydrolysis of substrates in gaseous streams. As model reaction has been selected the hydrolysis of ethyl acetate (eq. 1) since it is relatively less toxic compared to other solvents.



Lipase from candida rugosa (LCR) immobilized onto functionalized polyvinylidene fluoride (PVDF) membrane was used as model enzyme. The functionalization strategy consisted in grafting reactive amino groups on the hydrophobic PVDF [3]. The PVDF hydrophobicity is a valuable property because their interaction with water remains very low even at high water activities. In order to investigate the best immobilization strategy LCR was immobilized either by ionic adsorption or by covalent bond (in this case using glutaraldehyde as crosslinker). In the developed biocatalytic membrane reactor, process parameters such as reaction temperature, flow rates of water and ethyl acetate were investigated. In addition, under the optimized condition the amount of LCR immobilized on the membrane was varied between 13 and 72 $\mu\text{g cm}^{-2}$. The ethyl acetate hydrolysis, which end up in ethanol and acetic acid production, was monitored following the ethanol production by gas chromatography analysis. Interestingly, the dehydrated-immobilized lipase showed higher thermostability and productivity when compared with the free-hydrated one at certain operating temperature. In particular, in experiments carried out at temperature of 50°C only the dehydrated LCR showed biocatalytic activity. In the biocatalytic membrane reactor, the best performance in terms of ethanol production were obtained at 40°C feeding 0.4 mL h⁻¹ of water and 1.3 mL h⁻¹ of ethyl acetate, for a membrane loaded with 72 $\mu\text{g cm}^{-2}$ of LCR attached by ionic adsorption. Under these conditions about 5 $\mu\text{mol h}^{-1} \text{mg}_{\text{LCR}}^{-1}$ of ethanol (one of the two reaction products) during 12 h of reaction were produced. A first comparison with the literature data shows that the gas phase reaction in our biocatalytic membrane system has an enzyme activity about 50% higher. This strategy, in which the enzyme immobilized on membrane has been used to catalyze a reaction in gaseous phase, can be also promising for other enzymes and substrates of interest (e.g. phosphotriesterase).



Keywords: biocatalytic membrane, solid-gas biocatalysis, lipase

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Acknowledgement:

The authors gratefully acknowledge for the financial support by ProjectPON01_01585 “Innovative products for monitoring and detoxification/decontamination of nerve agents and explosives in the environment and/or for handling of emergency” (BIODEFENSOR) within the framework PON Ricerca e Competitività 2007–2013.



Ab Initio Study of the Insulating Power of Defective Magnesium Oxide Ultrathin Films in Ag/MgO/Ag Tunnel Junctions

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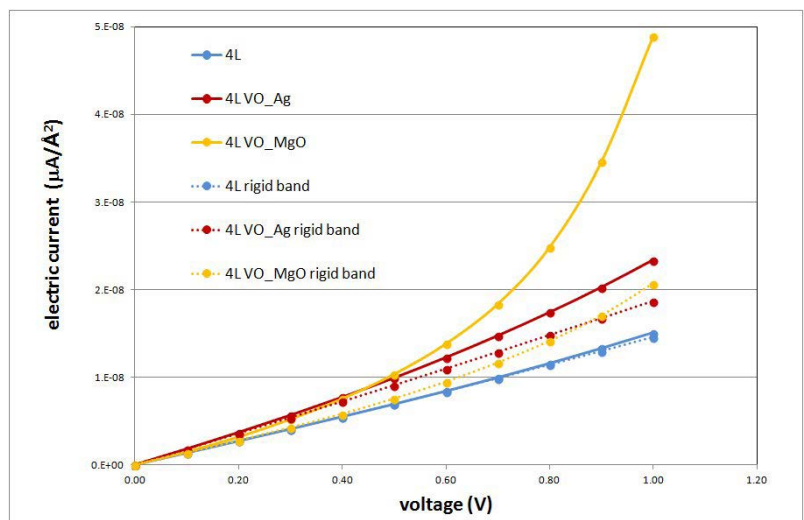
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MgO based tunnel junctions received great attention since the theoretical prediction of a 100% magnetoresistance in Fe/MgO/Fe,^{1,2} a result partially confirmed experimentally³ that paves the way towards the engineering of miniaturized spintronic devices. Despite a large amount of literature available on this subject, a comprehensive study on the insulating power of MgO ultrathin films inserted between two conducting leads is still missing, especially concerning the presence of defects in the insulating barrier.

In this study we present a systematic ab initio study of the electronic and transport properties of defective Ag/MgO/Ag tunnel junction. We performed Density Functional Theory computations using the SIESTA code, modeling nanodevices with 2 to 5 MgO layers inserted between the Ag leads, considering in each case the presence of oxygen vacancies, either at the Ag/MgO interface and in the inner oxide layers. To explore the effects of the non equilibrium electronic properties in the presence of finite voltages, we took advantage of the TransSIESTA code, which combines the non-equilibrium Green's function (NEGF) formalism with DFT, and worked out the Transmission Function and the electronic current with the TBTrans tool.

The main results of our investigation, shown in the figure for the case of 4 MgO layers, can be summarized as follows: (a) in the non defective system the current increases linearly with voltage; (b) when oxygen vacancies are inserted at the MgO/Ag interface with 3% concentration (4L VO_Ag), the current still increases linearly but is about 50% larger with respect to the non defective case; (c) when oxygen vacancies are inserted in the middle MgO layer, far from the interface, the current increase exponentially with voltage in the bias range considered, an unexpected and intriguing result; (d) to determine the electric current in a "rigid band" approximation (dashed curves), a widely used approach to save computational time skipping self-consistency of the Ag/MgO/Ag open system at finite voltages, proves inadequate in the system under investigation.



Keywords: tunnel junctions, defective metal-oxides interfaces, electronic transport

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An Accurate High-Throughput Framework for Materials Discovery

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In the last few years, the field of materials modeling has witnessed a important *paradigm shift*, from single technically-involved calculations on a handful of materials, to *high-throughput* high-volume, automatic exploration, of entire classes of materials, without constraints on chemical composition, structure and variations.

The requirement of a high-throughput framework is: speed, robustness, reproducibility of results (i.e. data-base-storage), consistency of results (independence from human choice of input parameters), accessibility and accuracy. Several groups and large-collaborations are already active in this field (AFLOW, AiiDA, NOMAD, Materials Genome just to name a few). Each existing framework created with a different goal in mind, such as to compute properties of existing materials vs discovering new materials, to automate a calculation framework vs analyzing band structures in search of topological signatures.

However, all the greatest powers of high-throughput calculations are lessened if the underlying calculations are not accurate. Presently, Density Functional Theory (DFT), the computational workhorse of choice in materials science, still suffers from many drawbacks: (1) even a 1% error in the DFT-predicted lattice spacing can lead to the large under-estimation and suppression of soft phonon modes; (2) the typical ~50% underestimation of the band gap, strongly affects optical and transport properties; (3) the lack of strong electronic correlations prevents the exploration of a huge class of materials: Mott insulators and superconductors.

Therefore, in this talk, I will illustrate our strategic plans to overcome all aforementioned limitations. To obtain accurate results, we propose the recently developed ACBN0 functional [1,2], which has been shown to yield structural parameters, band gaps and phonon dispersions in strikingly good agreement with experiments. The ACBN0 calculated band structures are in very good agreement with expensive many-body (GW) calculations, and the equilibrium volume of weakly-correlated perovskites is well reproduced. We highlight that the computational cost of ACBN0 is comparable to that of conventional DFT (whereas hybrid functionals are 10× to 30× more expensive, and high-throughput GW calculations on more than 50/100 atoms basically impossible). Furthermore, to address strongly correlated materials (Mott insulators, superconductors), we propose the Slave-Boson Gutzwiller method, which in the current implementation, has the same computational cost of plain DFT calculations.

The ACBN0 functional is implemented in our open-source AFLOW π [3] (www.aflowlib.org/src/aflowpi) high-throughput framework (written entirely in Python), which runs on Quantum-Espresso (QE). The advantages of AFLOW π over other frameworks are the simple installation (there is no need to run a daemon on every machine), the small size of the code-base (yet it's extremely powerful), the possibility to create custom workflows and the large number of physical observables (optical, magneto-transport, topological, thermal-transport), that can be calculated out of the box.

The construction of a high-throughput database of accurate, strongly-correlated calculations is the essential pillar to build upon Machine Learning models, for accelerated materials discovery. But this will be the topic of future DSCTM meetings.

Keywords: DFT, strongly-correlated, high-throughput

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Correlation between Creep and Relaxation Behaviour in a Cr Martensitic Steel

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There is a growing number of papers in literature concerning the possibility, for high temperature component design purpose, to generate creep rate data using stress relaxation tests and viceversa. According to these papers, relatively short stress relaxation tests could allow to estimate the creep strain rates spanning in several decades. Similarly, quite simple and inexpensive creep tests could predict stress relaxation performances. In order to check if stress relaxation tests can be a quick experimental way to obtain long term creep data, the primary creep and stress relaxation behaviour of a martensitic steel, has been investigated at 350°C with tests lasting up to 15.000h. Different kind of stress relaxation tests have been performed, in particular:

- multiple stress relaxation tests where the specimen, after some stress relaxation, is reloaded at the initial load and stress relaxed again,
- stress relaxation tests performed on specimens crept up to the steady state.

The experimental results show that anelastic-reversible-kinematic hardening processes control the initial stages of creep and relaxation, while creep-irreversible-isotropic hardening mechanisms control the creep and relaxation behaviour at longer times.

The results indicate that the experimental curves obtained in multiple stress relaxation tests can give important information on the steady state creep behaviour of the alloy.

Finally, the experimental results have been modelled using coupled differential equations of the Kachanov form, that are consistent with physical deformation mechanisms of the studied alloy.

The parameters of the proposed constitutive equation are functions of microscopic parameters like the density of mobile dislocations and their curvature between pinning points, but they are also related to easily measurable characteristics of the experimental creep curves, so that they can be determined using macroscopic creep data only.

The use of differential formalism of the equations allows to describe the creep behaviour also at variable stress and temperature, and to cope also with more complicated load/temperature histories as, for example, variable loading creep, constant strain rate and stress relaxation tests without appealing to arbitrary strain or time hardening rules.

In order to further validate the proposed equations, creep tests with one step change of load and/or temperature have been performed.

The proposed differential equations have been successful both in interpolating the constant load/temperature tests and in predicting the stress relaxation behaviour and the effect of step changes in load on the creep behaviour of the alloy.

Keywords: Stress relaxation, Constitutive Equation, Creep



Pushing the Limits of Solving Crystal Structures by Powder Diffraction Data

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In the last decades, structure solution from powder diffraction data has become more and more popular although it is usually hindered by problems. Indeed, the greatest limitations are related with 1) the diffraction peak overlap that prevents from reliably extracting of the experimental information from the diffraction profile, 2) the estimate of the background and 3) the preferred orientation(s) of microcrystallites. For all of these reasons, structure solution from powder diffraction data is not trivial. EXPO [1] is a computing program able to perform structure solution by powder data in a) reciprocal space (by Direct Methods) that needs only chemical formula and experimental profile, as well as in b) direct space that needs also the knowledge of the molecular geometry. The solution processes by reciprocal and direct spaces have different performances, limits and advantages. The choice of the kind of solution process mainly depends on the level of complexity of the compound under study in terms of number of non-H atoms in the asymmetric unit and/or number of variable degrees of freedom which describe the molecular structure. Our research activity regards the development of advanced methods of structure solution (both in reciprocal [2] and direct [3] space) with the aim of pushing more and more the limits of solving powder structures. The methods are implemented in EXPO which is characterized by efficient computational and graphical performances and easy use. An advanced parallel version of part of EXPO has been very recently developed for tackling the solution of complex structures in reasonable time. EXPO is one of the software most widely used by the international scientific community for the structure determination of materials of interest in several scientific and technological fields (Chemistry, Physics, Material Science, Life Science, Earth Science, Pharmaceuticals,..). We are now at the point, unimaginable some years ago, that EXPO can solve in standard way structures with about 30 non-H atoms in the asymmetric unit in the case of reciprocal space and 20 varied degrees of freedom (DoFs) in the case of direct space. Solution of structures with more than 100 non-H atoms in the asymmetric unit and 40 DoFs can be now approachable. Examples of increasing complexity will be presented.

Keywords: structure solution; powder diffraction; crystallography.

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Dft Calculations and Raman Spectroscopy of as(III) Complexation with Thiol Ligands

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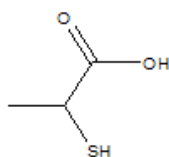
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The interest in the chemistry of arsenic complexes has increased in recent years. This metal is a natural pollutant, present in trace in the environment and living organisms [1]. About 60% of arsenic is released by volcanic activity and largely derives from anthropogenic sources. It is well known, indeed, that arsenic compounds have several applications in many industrial fields, such as pesticides and herbicides in agriculture, as chemioterapeutic agent in medicine and as constituent of numerous consumer goods. For these reasons, humans are usually exposed in food, water, air and soil. Accordingly, the extensive arsenic contamination is considered one of the most important toxicological problem.

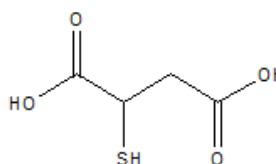
The significance of the metal pollution, as well as its mobility and bioavailability, depends on arsenic speciation, which represents the distribution of the different chemical species in a given system. The predominant species in aqueous solutions are the inorganic As(III) and As(V) ones, derivatives of the arsenous and arsenic acids, respectively. It was found, already in the past, that arsenite(III) compounds are more poisonous than arsenate(V) ones and even more dangerous of its organic species. This toxicity is mainly due to its high affinity for the sulfhydryl groups present in active biomolecules, such as enzymes and proteins [2]. Nevertheless, few data on the As(III) interaction with thiols are reported in the literature.

In the light of these considerations, an investigation on the As³⁺ complexation with S-donor ligand in aqueous solution was performed, in particular with thiolactic (TLA) and thiomalic acids (TMA).

This study is based on a speciation analysis on As³⁺-TLA and As³⁺-TMA systems and a Raman spectroscopic investigation combined with density functional calculations (DFT). Up to now, detailed Raman investigations of thiolactic and thiomalic ligands are missing in the literature.



2-mercaptopropanoic acid or
thiolactic acid (TLA)



2-mercaptosuccinic acid or thiomalic
acid (TMA)

The Raman spectroscopy results combined with DFT calculations shed light on the arsenic chelation mechanisms with these S-donor ligands.

Keywords: Arsenic, Raman spectroscopy, DFT calculations.

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Exploring the Boundary of 3D Perovskites Domain: The Case of $\text{FAPb}_{1-x}\text{Sn}_x\text{Br}_3$ Perovskites

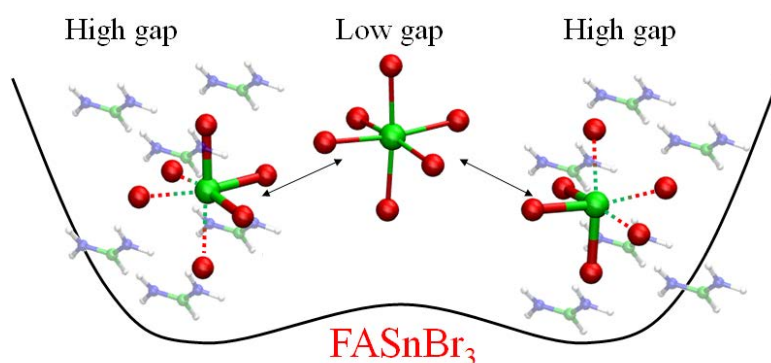
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Metal-halide perovskites are promising photovoltaic materials for the next generation of solar cells. Perovskites based on the formamidinium (FA) A-site cation show interesting properties compared to the parent MAPbI_3 compound, including a generally smaller band-gap due to a cation-induced pseudo-cubic crystal structure. The larger molecular size of FA compared to MA leads, however, to a structural instability in FAPbI_3 , related to a non-perovskite phase, placing FA at the border of tolerance factor for lead-iodide 3D perovskites. Based on the huge interest in mixed Sn/Pb perovskites for tandem devices, here we investigate $\text{FAPb}_{1-x}\text{Sn}_x\text{Br}_3$ perovskites in a full compositional range ($0 \leq x \leq 1$). We find a non-monotonic band-gap evolution with increasing the Sn content, which, through first-principles computational analyses, we relate to an increasingly structurally distorted structure that dynamically averages to an overall cubic structure, as determined by XRD. The large FA cation size induces an instantaneous distorted structure in FASnBr_3 , made by partly decoupled SnBr_3 units, which leads to the observed band-gap opening. As such, FASnBr_3 likely represents the border of the 3D perovskite domain. Intermediate $\text{FAPb}_{(1-x)}\text{Sn}_x\text{Br}_3$ compositions maintain a band-gap of ~ 1.8 eV up to an Sn content of ca. 85%, making them interesting candidates for applications in tandem devices.



Keywords:

Perovskite Solar Cell, DFT Calculation, Sn-based Perovskites

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Acknowledgement:

The authors gratefully acknowledge the project PERSEO- “PERrovskite-based Solar cells: towards high Efficiency and lOng-term stability” (Bando PRIN 2015-Italian Ministry of University and Scientific Research (MIUR) Decreto Direttoriale 4 novembre 2015 n. 2488, Project Number 20155LECAJ) for funding.



Charge Traps in Lead-halide Perovskites: a Computational Study

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Lead halide perovskites are promising materials for new generation photovoltaics, exceeding 22% of efficiency in solar cells devices.[1] The presence of native defects, however, can strongly affect their efficiency due to charge trapping processes which can limit the lifetime of the photogenerated charge carriers. In this work a state of the art Density Functional Theory (DFT) study of native defects in the MAPbI₃ perovskite is presented, aimed to unveil the nature of deep charge traps in this material and the associated defects chemistry.

The defects formation energies (DFEs) of native defects in different conditions of growth of the perovskite is discussed, based on hybrid functional DFT and including spin-orbit corrections. The trapping activity of the most stable defects is investigated through the analysis of the associated thermodynamic ionization levels diagrams.

Our analysis shows that charge trapping processes in MAPbI₃ are intrinsically dominated by iodine chemistry, with a coexistence of long-lived and short-lived recombination centers, which have different impacts on the photoluminescence properties.

[2] Furthermore, the mechanisms of charge traps passivation induced by external agents, such as oxygen, and isovalent halide doping is discussed, providing a microscopic interpretation of the beneficial effects of these agents on the PL properties of the perovskite reported by experiments.[3]

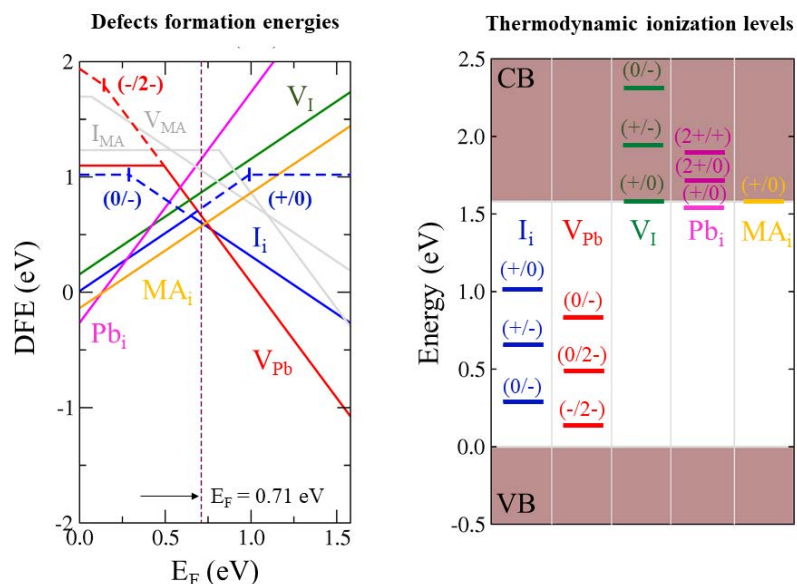
Keywords: perovskites, defects, DFT

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Acknowledgement:

I would like to acknowledge funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 763977 of the PerTPV project.





Conformational Dynamics of Non Visual Arrestin Subtypes

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Proteins in the Arrestin (Arr) family are downstream effectors propagating signaling starting at ligand bound G-protein coupled receptors (GPCRs). Together with G proteins and GRKs, arrestins orchestrate an interplay underlying the functional selectivity of the receptors.

Arrestins exhibit a well-conserved structural fold that nevertheless allows for significant differences in their selectivity for different GPCRs and their phosphorylation states. To reveal the mechanism of activation that prepares arrestin for selective interaction with GPCRs, and to understand the basis for these differences, we used unbiased Molecular Dynamics (MD) simulations to compare the structural and dynamic properties of several arrestin subtypes. Previous findings have highlighted a significant dynamic modulation of Arr3, which in ~400ns MD simulations explores active like structures, characterized by a relative active-like orientation of N terminal and C terminal domains, in contrast to the more rigid visual Arr1. The higher intrinsic flexibility was hypothesized as inducing a higher propensity to activation and higher promiscuity of Arr3. Here, the conformational dynamics of Arr3 is compared to the other non-visual subtype Arr2 by means of multiple microsecond time scale MD simulations in the absence and in the presence of a bound activating phosphopeptide. Monitoring several activation-related measures such as N-C domain rotation, exposure of the C tail and of the surface loops involved the GPCR complex reveals remarkable differences in the conformational dynamics of the subtypes, which might be related to function and confirm smFRET based observations.

Keywords: Molecular Dynamics, arrestin, GPCRs



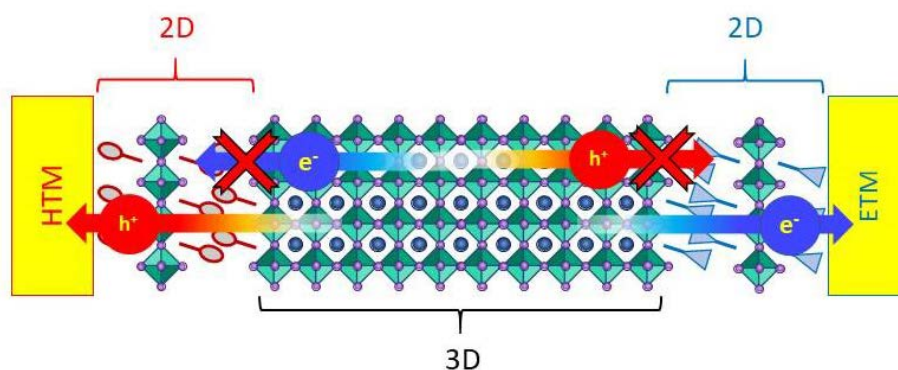
First Principles Modeling of Mixed 2D/3D Organohalide Perovskites

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Harvesting solar energy through photovoltaic devices is the most accredited answer to the requirements for sustainable and environmentally compatible energy of the future. Within this field, organohalide perovskites (ABX_3) have revolutionised the scenario of emerging photovoltaic (PV) technologies, with recently lead-based materials delivering certified $> 22\%$ efficiency in solid-state solar cells. The great potential of this class of materials is mainly due to the unique set of optoelectronic properties [1], combined with the promise of low cost techniques for their production and the solid-state character of the corresponding devices. The prototype $CH_3NH_3PbI_3$ perovskite ($CH_3NH_3^+$ =methylammonium=MA) and the mixed halide $MAPb(I_{1-x}Br_x)_3$ and $MAPb(I_{1-x}Cl_x)_3$ analogues have dominated the field. Along with the low embodied energy and cost of materials and solution processed fabrication techniques, further optimization of perovskites composition and optoelectronic quality may represent a giant leap towards the rapid uptake of PV technology. While 3D perovskites are the materials currently leading the field for photovoltaics, 2D hybrid organic/inorganic layered materials have a much broader versatility in accommodating a vast variety of organic molecules and are providing a long-term devices stability. In particular, we obtained a one-year stable perovskite device by engineering an ultra-stable 2D/3D perovskite junction with a PCE of 14.6% in standard mesoporous solar cells [2]. Hybrid organic-inorganic multidimensional perovskites, also known as Ruddlesden-Popper perovskites, are composed of 3D domains separated by large organic cations. The mixing of the two mainly studied types of perovskites supposes the combination of the good properties from each one. Due to the 3D domains, Ruddlesden-Popper perovskites can absorb radiation in a wide range of the electromagnetic spectrum. Moreover, the environmental stability issue characteristic of 3D perovskites is solved thanks to the good stability provided by the 2D domains, in which the larger amount of organic phase acts as barrier against water and moisture penetration [2]. The main problem of this material arises from its photoexcitation and the consequent generation of the electron-hole pairs. Holes and electrons keep confined in the inorganic layers due to the electric isolation of the organic cations in 2D domains, i.e.: while their diffusion along the 3D domains is excellent, it is quite poor across the 2D ones. In order to find a solution, we will explore the possibility of improving the conductivity of charge carriers across 2D domains by the insertion of specifically designed conducting organic cations. The chemical structure of these cations should be suitable for the purpose, for instance by embedding aromatic rings or conjugated multiple bonds and allowing the selective transport of a single carrier type. The desired cation properties will be finely computed in order to realize a Ruddlesden-Popper perovskite with high and selective vertical conduction, see Fig. 1.





Keywords: Perovskite, DFT, photovoltaics

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Acknowledgement:

We acknowledge funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 604032 of the MESO project.



Vibrationally Excited Hydrogen Molecules Formation on a Cesium Surface

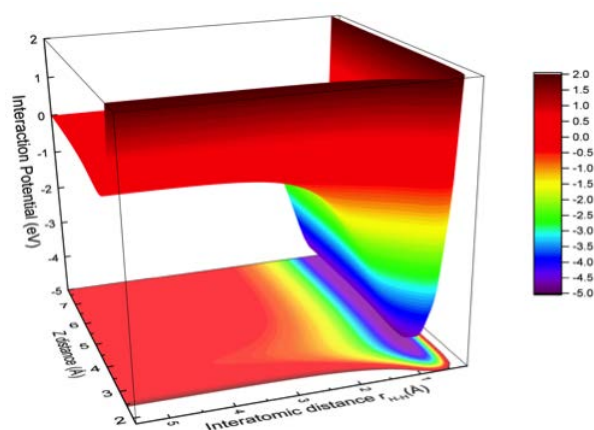
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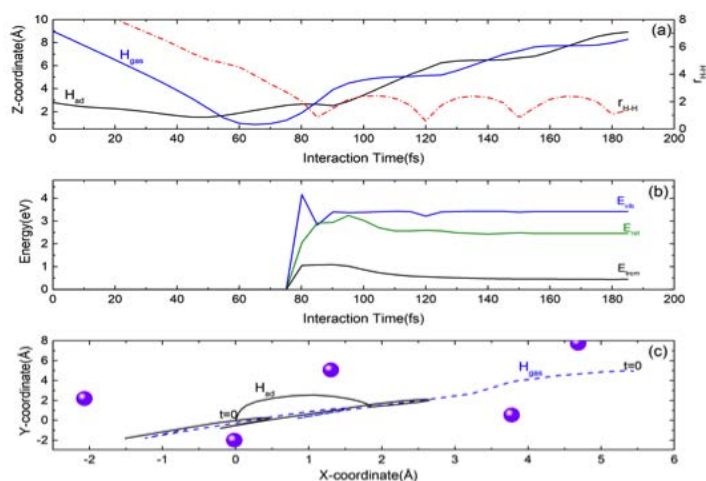
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Hydrogen atoms recombination *via* the Eley-Rideal mechanism on a cesiated surface was studied using a semiclassical collisional model [1]. The Potential Energy Surface governing the reaction was evaluated by *ab initio* calculations in the framework of Density Functional Theory.

The recent results obtained for H interaction potential with the same surface model were used together the first principle results obtained for H₂ interaction potential with Cs and Mo surface atoms. Molecular Dynamics calculations have been performed for two different typical adsorption sites identified on the surface. The probabilities for recombination reaction and for the complete set of elementary surface processes arising from different reactions were evaluated. It appears that the recombination occurs only for one adsorption site on the surface and with low probability, while for the other site H atoms are mainly scattered from the surface with a partial negative charge [2].



The vibrational distributions of formed H₂ molecules exhibit a non-Boltzmann behaviour and are peaked on medium-high lying vibrational levels. The considered surface appears promising for negative ion sources [2,3], contributing to the formation of ions by means of both usually considered mechanisms, surface production and volume production *via* dissociative attachment. The global and state-to-state recombination coefficients were also calculated to be used in kinetic modelling of negative ion sources.



Keywords: Negative Ions production, surface processes, semiclassical dynamics

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Acknowledgement:

CINECA for computational facilities in the framework of ISCRAs calls under the project IsC42_HyonMoCs.



Theoretical Investigations on the Solution Chemistry of Organohalide Perovskite Precursors

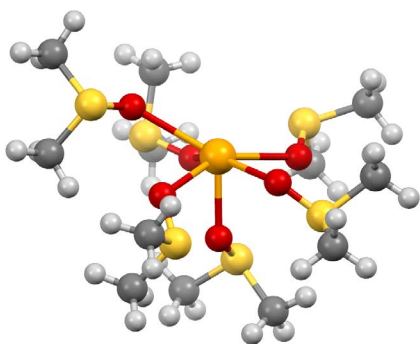
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Among the methods of synthesis of the perovskite materials for photovoltaic applications, the solution approach has attracted many interests thanks to the possibility of production of high quality materials at a low cost. Nevertheless, the paths that link the solution-based precursors to the solid-state perovskite are not yet completely understood and so investigations on the solution chemistry of organo-halide perovskites is necessary to understand which species and equilibria are more likely to dominate during the synthesis of perovskites. Here we are going to clarify the nature of these species and the involved solution equilibria by combining experimental analysis and theoretical methods.

In agreement with previous experimental work, [1] we found that the use of solvents with different coordinative power regulates the type of species that we can find in solution. As an example, in a strong coordinative DMSO solution of PbI_2 we cannot easily find species with high coordination of I⁻, such as $[\text{PbI}_3]^-$ and $[\text{PbI}_4]^{2-}$. The average coordination number of the complexes is expected to be found between 5 and 6. In Figure 1 we report the optimized structure of $\text{Pb}^{2+}(\text{DMSO})_6$ in its hemi-directed configuration, that is the main species that is found in a DMSO solution of $\text{Pb}(\text{NO}_3)_2$. [2]



Considering an experimental strategy similar to that employed by Stamplecoskie *et al.* [3] and thanks to our theoretical results, we also predicted the equilibrium constants that dominate some of the most important reactions involved in the synthesis of perovskites.

Keywords: perovskite – coordination chemistry – solution synthesis

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Acknowledgement:

ESPReso project— H2020-LCE-2016-2017 No. 764047

European Union's Horizon 2020 research and innovation programme for grant agreement No. 763977 of the PerTPV project.



A Theoretical and Experimental Investigation of the Mechanism Underlying Response Enhancement of CNT-Si Based Devices upon NO_2 Exposure

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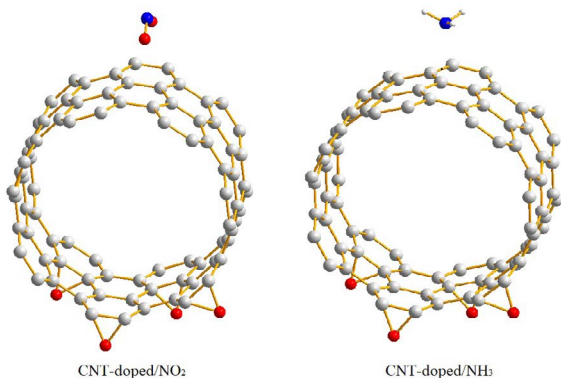
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Hybrid heterojunctions between carbon nanotubes (CNT) and Si wafers have demonstrated the possibility to achieve low-cost, high efficiency devices for photovoltaic (PV) applications. The hybrid CNT-Si architectures can be ranked among the most promising systems for the next generation PV with power conversion efficiency (PCE) up to 17%. Recent investigations on hybrid CNT-Si junctions have shown that the performances of CNT-Si photovoltaic (PV) cells can be strongly affected by the exposure to selected molecules, with the aim to: (i) produce a chemical etching of the device interface, (ii) steer the formation of a SiO_x buffer layer, (iii) dope the CNT layer.^{1,2} In particular, a large sensitivity of cell performances on both NO_2 and NH_3 exposure is observed, where NH_3 resulted to be detrimental to cell efficiency, while NO_2 improves the PV cell performances (up to 300%).

Through a combined experimental and theoretical investigation, we have tried to understand the mechanisms underlying this kind of response. A systematic ab initio study of the electronic properties of CNT-doped/ NO_2 and CNT-doped/ NH_3 junctions has been performed through Density Functional calculations. We have considered a (7,7) single-walled CNT while varying the density of adsorbed molecules, in order to characterize the most important factors that influence the PV parameters, namely the CNT-doping, the change of the CNT work function (WF) and the occurrence of trap states at the interface that reduce the carrier recombination.



In particular here we show that the measured changes in the open circuit voltage (V_{oc}) are perfectly reproduced by the changes in the work function at the estimated working concentration.

Keywords: heterojunctions, power conversion efficiency, carbon nanotubes

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Temperature Behaviour of PEG Treated Historic Wood by FTIR and Raman Investigations

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The aim of this contribution is to report Fourier Transform InfraRed spectroscopy and Raman scattering findings collected on wood fines extracted from a 800' dated wooden crucifix. More specifically, different Polyethylene Glycol (PEG) aqueous solutions were investigated by FTIR and Raman; then the wood fines, after having been treated by immerging them into the PEG aqueous solutions, were studied by IR and Raman spectroscopies through a thermic cycle in the 25 ÷ 350 °C temperature range. From the present study it emerges that, in the PEG200/PEG600 comparison, the lighter polymer shows a higher effectiveness in terms of thermal restraint.

Keywords: Wood conservation, Infrared and Raman spectroscopy, polymeric aqueous solutions



Analysis of Trehalose Treated Wood Fines by Portable Raman and Infrared Spectrometers

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InfraRed and Raman spectroscopies represent non-invasive and non-destructive tools for cultural heritage diagnostics. A great advantage is obtained nowadays thanks to new generation of portable spectrometers (Bruker ALPHA-IR and Bruker BRAVO-RAMAN) which allow to collect spectra in a straightforward way. In the present paper, the results of a FTIR and Raman analysis, performed as a function of temperature on wood fines, extracted from a 800' dated wooden painting frame, under a trehalose treatment are reported. In particular, at first, the wood fines were investigated, as a function of temperature during a thermal cycle; then wood finds treated with trehalose-water mixtures were investigated in order to perform a comparison of the two samples temperature spectral features under the same thermal cycle. It clearly emerges that trehalose provides the investigated wood fines a higher thermal restraint.

Keywords: trehalose, preservation, cultural heritage



The “Scream” by Edvard Munch: An Exemplary Case Study of Synergism Between Chemistry and Conservation

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In this contribution the outcomes of a wide research project on the “Scream” painting by Edvard Munch, made in collaboration with the Munch Museum (MUM) of Oslo, are presented and discussed with the final goal of showing how a synergic interplay between chemistry and conservation science offers an invaluable approach for knowledge, valorisation and fruition of our cultural heritage when based on high level competences, advance technologies and interdisciplinary collaboration. Edvard Munch (1863–1944) is considered one of the fathers of the Modernism and his most famous painting the “Scream” is the iconic representation of the universal anxiety of modern man in early ‘900. In his artistic experimentation E. Munch used a wide variety of materials and techniques leading to a huge production of paintings, drawings and graphic works. The same “Scream” motif has been represented in many different versions, including two paintings on cardboard (one at the Munch Museum and the other at the National Museum of Art in Oslo), pastel/crayon drawings, lithographs and ink sketches. The diverse use of techniques, working processes and treatments of the pictorial surface experimented by E. Munch and the availability of new materials from industrial revolution during his life make it very difficult to outline the artist’s creative process but, most important, to front the challenging conservative issues posed by his art. As matter of fact a large number of paintings authored by Munch suffers from a range of problems related to the artist’s choice of materials and techniques as well as to past restorations or unsuitable storage. In this scenario, the MUM is developing a large core project aimed at providing a new scientific knowledge of the museum painting collection, giving specific attention to the “Scream” motif, with the support of a robust interdisciplinary collaboration among scientists, conservators, restorer and art-historians [1]. In 2017 a wide MOLAB diagnostic campaign through the transnational access granted by the Eu IPERION-CH project was carried out on six versions of the “Scream” motif held at the MUM, with particular focus on the one painted in 1910 (date still debated) which is, probably, the universally most known. The study was aimed at providing a thorough examination of the painting materials and supports and of their present condition by a total non invasive diagnostic approach. Advanced analytical imaging techniques, such as scanning XRF and hyperspectral VIS-NIR imaging, along with other complementary non-invasive spectroscopic tools available in the MOLAB platform (UV-Vis-NIR reflectance and fluorescence spectroscopy, reflection FTIR and Raman spectroscopy) allowed the identification and mapping of organic and inorganic painting components (pigments, binders, additives and industrial production residuals) as well as of their possible degradation products (as for example oxalates). Results demonstrated how Munch was open to the introduction of new synthetic pigments such as ZnO, cadmium sulphides (CdS, in the hexagonal and cubic forms) or lead chromates (possibly as $\text{PbCr}_{1-x}\text{S}_x\text{O}_4$) applied in the “Scream (1910)” as dense oil paint brushstrokes or pastel drawings on the bare cardboard support; more traditional materials such as vermilion (HgS) or red lead (Pb_3O_4) were also found. Overlaid pure paints as well as pre-mixed pigments were localised on the painting surface as a result of different creative processes. Signs of materials migration, probably due inappropriate storage, were observed possibly following the theft of the painting in 2004 or the habit of the same Munch of leaving his paintings in outdoor environment. The detailed identification and localization of the Zn-, Cd- and Cr- based pigments is crucial for conservation purposes in consideration of the proven sensitivity of these materials to decay



processes. As a matter of fact, previous extensive scientific investigations carried out by the researchers of the ISTM and SMAArt on these classes of pigments both on original artist's materials, such as J. Pollock or V. van Gogh, and on dedicated laboratory model paints (see for example [2,3] and references therein) evidenced their remarkable reactivity as a consequence of the type of the industrial formulation they were produced with, the environmental conditions and the interactions with the binder.

Overall, the outcomes of the MOLAB access provided a new body of scientific knowledge of the Munch's paintings in comparison with previous studies ([1] and literature therein) which will help in furthering the understanding of the Munch's artistic technique, but most important will provide new hints for addressing targeted preventive conservation strategies of these masterpieces.

Keywords: Munch's painting materials, non invasive diagnostics, preventive conservation

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Acknowledgement:

The authors acknowledge the transnational MOLAB access offered by the IPERION-CH project (Integrated Platform for the European Research Infrastructure ON Cultural Heritage - H2020-INFRAIA-2014-2015, GA n. 654028), funded by the European Commission.



Corrosion of archaeological bronzes and modern steel artworks: Surface and Electrochemical Investigations

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Metals degradation is a crucial issue that involves industry, buildings, infrastructures and ancient and modern artworks. Metallic materials are naturally involved in corrosion processes, especially when they are in contact with humidity of air (oxygen and water) and aggressive agents, such as acidic and chlorides environments. Metals from Cultural Heritage could be subjected to corrosion due to archaeological post-burial phenomenon or to outdoor exposure. In addition, the uncontrolled conditions of the microclimate in museum storage and exhibition halls could threaten the suitable conservation of the artworks.

The surface analysis of a metallic artifact, both before and after an anticorrosive treatment, and the knowledge of the electrochemical processes taking place at the interface between the metal matrix and the aqueous environment are essential for the evaluation of the conservation conditions and for the validation of novel anticorrosion coatings and corrosion inhibitors.

X-Ray Photoemission Spectroscopy (XPS) is a very surface-sensitive analytical technique, commonly used in the field of materials science at the nanoscale level. Historically applied to the field of industrial research, it is also successfully used in the investigation of Cultural Heritage, both for diagnostics and for conservation purposes.

The nature and the state of conservation of artifacts can be defined by surface analysis, evidencing the presence of patinas, corrosion products, coatings and protective layers from previous restoration treatments. Due to the ability of understanding the chemical processes taking place at the metal surface in many aggressive environments, XPS contributes to the choice of adequate restoration and conservation protocols and to validate new restoration products, such as anticorrosion coatings or corrosion inhibitors.

Electrochemical Impedance Spectroscopy (EIS) and dynamic polarization are effectively used for obtaining electrical and kinetic parameters (corrosion current, potential and rate, charge transfer resistance etc.), related to the corrosion phenomena. In such a way, the corrosion inhibition efficiency of novel compounds and the validation of novel treatments of the metallic surfaces can be successfully determined.

In this work, some case studies about the synergetic application of these techniques to the conservation of copper-based and iron-based alloys in the field of Cultural Heritage are reported. In particular, the focus is on the evaluation of the conservation state and the identification of degradation phenomena of archaeological bronzes [1] and on the formation of different corrosion products on the surface of modern iron-based artworks. These investigations are essential for the formulation and the assessment of eco-compatible corrosion inhibitors for a sustainable conservation of ancient bronze and modern steel artworks [1, 2].

Keywords: Archaeological Bronzes, Modern Steel artworks; X-Ray Photoemission Spectroscopy, Electrochemical Impedance Spectroscopy.

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Acknowledgement:

Financial support by the PON03PE_00214_1 Project: "Nanotecnologie e nanomateriali per i Beni Culturali", TECLA, Distretto di Alta Tecnologia per l'Innovazione nel settore dei Beni Culturali della Regione Sicilia, is gratefully acknowledged.



Innovative and Sustainable Approaches to Inhibit Corrosion Processes in Cultural Heritage Artefacts and Monuments

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The degradation processes that typically occur in unique and valuable artefacts and monuments can irreversibly compromise their conservation status and modify their appearance due to the formation of alteration products and reactive compounds. The preservation of cultural heritage still represents a critical issue and the development of high-performance materials that satisfy the demanding requirements related to environmental sustainability and cost-effectiveness is a serious challenge for the scientific community. Specifically, in the field of art conservation, the research of effective and non-toxic corrosion protective treatments has recently registered a significant increase, due to new strict health and safety regulations.

Many approaches have been developed for the protection and conservation of metal artefacts, mainly based on passive coatings with barrier properties for external aggressive species and usually toxic corrosion inhibitors that chemically stabilize the metal surface hindering the interaction with degrading agents. A particular attention has been paid to the occurrence of degradation processes in copper-based works of art, with special emphasis for chloride-induced processes. There are still many concerns related to the conservation of metal artefacts since the most effective protective materials are commonly based on the use of toxic corrosion inhibitors and large amounts of harmful organic solvents for their application and removal. Therefore, innovative approaches to fulfil the protective, aesthetic and safety requirements are demanding.

In this context, within the EU H2020 Nanorestart project “NANOmaterials for the REStoration of works of ART”, we have focused our attention on the development of smart nanostructured coatings able to provide an “active” protection of modern metal works of art and easy to be applied and removed by using not toxic water-based solvents. To achieve a long-lasting and safe protection, we have developed innovative coatings based on environmentally friendly polymers from renewable sources, such as chitosan, and with stimuli responsive nano-containers for a tailored release of the corrosion inhibitors that have been first validated at laboratory scale on model substrates [1-3]. Thanks to their superior protective and aesthetic properties, and high safety with respect to commercial benchmarks, the developed materials have been applied on real works of art in collaboration with Peggy Guggenheim conservators and will be used also for other case studies.



Based on these successful results, a similar approach based on the use of smart nanocarriers will be applied to the conservation of concrete monuments within the EU H2020 InnoVaConcrete project “Innovative materials and techniques for the conservation of 20th century concrete-based cultural heritage”. Corrosion inhibitors, properly selected to protect the steel bars, will be confined into the nanocarriers and released under stimuli related to the corrosion processes in the reinforced concrete, such as an increased concentration of chloride ions and a pH decrease. The nanocarriers will also contribute to the sequestration of aggressive species by acting as “nanotraps” and



hindering their diffusion toward the steel bars. To achieve a long-lasting protective efficacy, the nanocarriers that act as a inhibitor reservoir will be incorporated into appropriate consolidants thus producing innovative multifunctional protective systems that will be applied on the concrete surface for an integral protection by combining the action of the different components.

After validation at laboratory scale, the products developed within the project will be applied and validated in situ on the XX century concrete monuments identified as representative case studies that will be fully characterized to get information about the compositional-structural features and their state of conservation. Among the case studies in Italy, War Memorials will be considered for their social values, as symbol of collective identity of European citizens, and relevant monuments in Rome as the Flaminio Stadium by Pier Luigi Nervi will be also investigated.

Keywords: Smart Materials; Corrosion Inhibition; Sustainable Conservation.

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Acknowledgement:

The work has been carried out within the NANORESTART project funded by the European Union's Horizon 2020 Research and innovation programme under the grant agreement No 646063 and within the InnovaConcrete project funded by the European Union's Horizon 2020 Research and innovation programme under the grant agreement No 760858



SERS Substrates for Pigments Detection in Works of Art: a Combined DFT and Experimental Study

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Characterization of organic pigments used in works of art is essential in order to identify both geographic area of provenience and manufacturing historic period. Some pigments can be indeed connected to a determinate historic time or to a specific artist; To this particular purpose Raman spectroscopy is a valid approach for its non-destructive nature. However conventional Raman of organic substances is heavily affected by the intense fluorescence which makes the identification of the molecule difficult or more often unreliable. Surface-enhanced Raman scattering (SERS) spectroscopy allows for overcoming the drawback associated with fluorescence representing a valid alternative in the identification of organic dyes. [1]

In this work we present SERS substrates, made by a thin layer of silver and gold nanoparticles deposited on sandpaper sheets by means of the pulsed laser ablation technique (PLA). [2] SERS substrates are designed and realized specifically to detect pigments in work of art. [3] The so obtained substrates can be gently swabbed, for example, on a painted surface or on small decorated fragments in order to collect small quantities of the superficial layer. Then Raman spectra are acquired -on the substrate surfaces avoiding in such a way direct laser exposition of the work of art. The substrates were tested on laboratory prepared layers of some dyes (methylene blue, rodamine-6G and indigo dyes). Moreover, DFT (density functional theory) calculations were carried out in combination with SERS experiment to understand the nature of interactions between pigment and nanoparticles for indigo and methylene blue. In particular we modeled the Ag-dye and Au-dye structures in various configurations to evaluate their energetic stability together with their Raman and SERS theoretical spectra, to be compared with the outcomes of the experimental results.

Keywords: SERS; DFT-calculations; organic pigments

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X-Ray Analysis *in situ*: The Importance of Adaptive Instrumentation

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In the field of the material analysis of cultural heritage artefacts is necessary the use of non-invasive and non-destructive methods such as those based on X-Rays (es. X Rays Fluorescence and Radiography). Moreover, due to the fact of immobility artworks from the places where they are exhibited or conserved, therefore is essential the use of portable instrumentation in order to perform analysis *in situ*.

Artworks can have different sizes, from some centimeters to several meters, and can be placed on the ground, on a pedestal or suspended several meters above the ground, this is why it is necessary the use of portable instrumentation easily adaptive to the case in question.

At ICLA (Institute of Crystallography Archaeometric Laboratory) X-Rays instrumentation, is adapting and modifying in order to obtain the best solution to the case in question. Through this approach, we were able to study several artworks: from architectural elements (rosette of the cupola of SS. Luca and Martina church in Rome), to modern canvases (by Capogrossi, Guttuso), from Latin bronze artifacts (in Archaeological Museum of Ager Faliscus - Sangallo Fortress Civita Castellana, Vt) to soil blocks from Crustumerium (east of Rome). Moreover, we perform analysis for forensic investigations, for example required by *Comando Carabinieri Tutela patrimonio Culturale* (CC TPC) and by court experts.



Moreover, from 2014 until now, during the annual excavations in the archaeological area of Roman Crustumerium and with the cooperation of *Soprintendenza Speciale Archeologia, Belle Arti e Paesaggio di Roma* we have been successfully able to set up an X-Rays laboratory in the farm building State property to support the restorer's work.

Keywords: X-Ray, analysis in situ

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Acknowledgement:

The authors are grateful to:

- *Soprintendenza Speciale Archeologia, Belle Arti e Paesaggio di Roma*
- *Galleria Nazionale di Arte Moderna*
- *Università degli Studi di Urbino*
- *Università La Sapienza di Roma*
- *Comando Carabinieri Tutela patrimonio Culturale*
- *Università degli Studi di Napoli L'Orientale*

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