Chimica Verde | Energie Rinnovabili | Salute | Materiali | Modelling | Beni Culturali

CONFERENZA DI DIPARTIMENTO 2019

DSCTM
Department of Chemical Sciences and Materials Technology

28-29-30 OTTOBRE
BRESSANONE
HOTEL GRÜNER BAUM

Consiglio Nazionale delle Ricerche
Dipartimento Scienze Chimiche e Tecnologie dei Materiali

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Bressanone 28-29-30 ottobre 2019,
a cura di Doriano Lamba e Francesco Verginelli

Organizzazione Giornate di Dipartimento 2019
28-29-30 Ottobre, Bressanone

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PROGRAMMA

28 ottobre 2019

14.00 - 16.00	Registrazione
16.00 - 16.10	INTRODUZIONE **Dott. Maurizio Peruzzini** Direttore Dipartimento di Scienze Chimiche e Tecnologie dei Materiali

Chimica Verde

16.15 - 16.20	**Chair - Dott. Mauro Marchetti** (ICB-CNR) **& Dott. Alessandro Mordini** (ICCOM-CNR)	
16.20 - 16.35	Bio-based production of energy and CO_2 valorization	d'Ippolito Giuliana - ICB
16.35 - 16.50	The role of the constrained amorphous interphase on physical and mechanical properties of bio-based polymeric materials	Righetti Maria Cristina - IPCF
16.50 - 17.05	ZrO_2-based catalysts: a versatile tool for the production of oxygenated biofuels from alcohols and furans	Scotti Nicola - ISTM-SCITEC
17.05 - 17.35	Coffee Break	
17.40 - 18.10	**Chair - Dott.ssa Alessandra Sanson** (ISTEC-CNR) Keynote Lecture - **Dott. Massimo Mazzer - (DIITET-CNR)** *Fotovoltaico: come Ricerca e Innovazione possono contribuire agli obiettivi del piano Nazionale Energia e Clima e del SET-plan Europeo*	

Chimica per l'Energia Rinnovabile

18.10 - 18.15	**Chair - Dott.ssa Alessandra Sanson** (ISTEC-CNR) **& Dott. Alessandro Mordini** (ICCOM-CNR)	
18.15- 18.30	Chemical Looping Combustion With Oxygen Uncoupling (CLOU) Using Novel Geopolymer Oxygen Carriers For Fluidized Bed	Natali Murri Annalisa - ISTEC
18.30 - 18.45	Benzo-bisthiazole and quinoxaline derivatives as fluorophores in LSC photovoltaic devices	Calamante Massimo - ICCOM
18.45 - 19.00	Design of Ni/La_2O_3 catalysts for dry reforming of methane: Influence of synthesis conditions on the structural properties and catalytic performances	Liotta Leonarda - ISMN

DSCTM

19.00 - 20.00	**Sessione Poster I** (Modeling Computazionale; Chimica per i Beni Culturali; Materiali Avanzati)
20.15	Cena
21.30 - 22.00	**Chair - Dott. Maurizio Peruzzini** (DSCTM-CNR) Post-Dinner Speech - **Dott. Chryssostomos Chatgilialoglu** (ISOF-CNR) *Free Radical Chemistry From Science To Market Innovation: A Success Case*

29 ottobre 2019

08.45 - 09.15 **Chair - Prof.ssa Lidia Armelao** (ICMATE-CNR & Università di Padova)
Keynote Lecture - **Prof.ssa Milena Salvo** (Dipartimento Scienza Applicata e Tecnologia - Politecnico di Torino)
Advanced Glasses, Composites and Ceramics for High Growth Industries

Materiali Avanzati

09.15 - 09.20 **Chair - Prof.ssa Maria Lucia Curri** (IPCF-CNR & Università di Bari) **& Dott.ssa Alessandra Sanson** (ISTEC-CNR)

09.20 - 09.35	Graphene oxide enhanced membranes for tap water purification	Bianchi Antonio - ISOF
09.35 - 09.50	Improvement Of Dental Implants Properties By Surface Dual-Step Functionalisation	Galenda Alessandro - ICMATE
09.50 - 10.05	Luminescent Organometallic Complexes: Multiple Perspectives in Technological Applications	Bossi Alberto - ISTM-SCITEC
10.05 - 10.20	Non Covalent Porphyrin Architectures from Structure to Applications	Castriciano Mariangela - ISMN
10.20 - 10.35	Recent developments in the preparation and characterization of advanced polymeric membranes for gas and vapour separation	Jansen Johannes Carolus - ITM
10.35 - 10.50	Spectroscopic signature of quantum dot dimers at subnanometric interparticle distance	Striccoli Marinella - IPCF

10.50 - 11.20 Coffee break

Modeling Computazionale

11.20 - 11.25 **Chair - Dott. Doriano Lamba** (IC-CNR)

11.25 - 11.40	Innovative Methodologies and challenging applications of Software for the Characterization of Polycrystalline Compounds	Rizzi Rosanna - IC
11.40 - 11.55	Computational tools to investigate structure and chemical ordering in metal / metal-oxide Nano Particles	Barcaro Giovanni - IPCF

12.15 - 13.45 Pranzo

14.00 - 14.30 **Chair - Dott. Mauro Marchetti** (ICB-CNR)
Keynote Lecture - **Dott. Vittorio Maglia** (Federchimica)
Chimica: Scienza e Industria per un Futuro più Sostenibile

Chimica per i Beni Culturali

14.35 - 14.40	**Chair - Dott.ssa Alessandra Sanson** (ISTEC-CNR)	
14.40 - 14.55	Unveiling the composition of iconic objects of the Italian design through MOLAB access to non invasive & portable spectroscopies	Rosi Francesca - ISTM-SCITEC
14.55 - 15.10	Active Multifunctional Materials to Inhibit Degradation Processes: from Remedial to Preventive Conservation	Di Carlo Gabriella - ISMN

15.15 - 15.45 Coffee Break

15.45 - 16.15 **Chair - Dott. Doriano Lamba** (IC-CNR)
Keynote Lecture - **Prof. Enrico Domenici** (COSBI & Università di Trento)
Omic approaches in Drug Discovery: from Big Data to Novel Targets

Chimica per la Salute e le Scienze della Vita

16.20 - 16.25	**Dott. Doriano Lamba** (IC-CNR)	
16.25 - 16.40	Molecular and structural basis of dystroglycanopathies	Cassetta Alberto - IC
16.40 - 16.55	Discovery of a selective NEK6 kinase inhibitor: toward precision medicine against solid tumours	De Rosa M.Cristina - ICRM-SCITEC
16.55 - 17.10	Cyclodextrin Nanomagnetes Decorated with Peptides: from Aβ-Amyloid Detection to Theranostic	Mazzaglia Antonino - ISMN
17.10 - 17.25	Selective Response of Healthy and Cancer Osteoblast Cells to 2D Black Phosphorus	Raucci Maria Grazia - IPCB
17.25 - 17.40	Synchrotron Radiation Circular Dichroism (SRCD) UV photostability assay: a useful tool to study protein oxidative stress damage	Ruzza Paolo - ICB
17.40 - 17.55	Ti and Fe doped hydroxyapatite: novel biomimetic hybrid UV-filter for sunscreen formulation	Sandri Monica - ISTEC

18.00 - 18.20 **Chair - Dott. Maurizio Peruzzini** (DSCTM-CNR)
Contributed Talk - **Dott. Michele Guerrini** (DSCTM-CNR)
From Horizon 2020 to Horizon Europe – Next steps towards the new framework programme for Research and Innovation 2021-2027

18.30 - 19.30	**Sessione Poster II** (Chimica Verde; Chimica per l'Energia Rinnovabile; Chimica per la Salute e le Scienze della Vita)
20.00	Cena Sociale

30 ottobre 2019

08.45 - 09.00	**Chair - Dott. Maurizio Peruzzini (DSCTM-CNR) & Dott. Doriano Lamba (IC-CNR)** Premiazioni & Presentazioni YIA 2019	
09.00 - 09.15	Premio YIA2019 - Chimica Verde	Esposito Elisa - ITM
09.15 - 09.30	Premio YIA2019 - Chimica per l'Energia Rinnovabile	Dessì Alessio - ICCOM
09.30 - 09.45	Premio YIA2019 - Chimica per la Salute e le Scienze della Vita	Gallo Carmela - ICB
09.45 - 10.00	Premio YIA2019 - Materiali Avanzati	Castaldo Rachele - IPCB
10.00 - 10.15	Premio YIA2019 - Modeling Computazionale	Ambrosio Francesco - ISTM-SCITEC
10.15 - 10.30	Premio YIA2019 - Chimica per i Beni Culturali	Monico Letizia - ISTM-SCITEC
10.30 - 10.45	**Chair - Dott. Maurizio Peruzzini (DSCTM-CNR) & Dott. Doriano Lamba (IC-CNR)** Menzioni d'Onore YIA2019 & Premiazioni Posters	
	Menzione d'Onore YIA2019 - Chimica Verde	Ortelli Simona - ISTEC
	Menzione d'Onore YIA2019 - Chimica per l'Energia Rinnovabile	Pagliaro Maria Vincenza - ICCOM
	Menzione d'Onore YIA2019 - Chimica per la Salute e le Scienze della Vita	Zagami Roberto - ISMN
	Menzione d'Onore YIA2019 - Materiali Avanzati	Hostaša Jan - ISTEC
	Menzione d'Onore YIA2019 - Materiali Avanzati	Fuoco Alessio - ITM
	Menzione d'Onore YIA2019 - Modeling Computazionale	Meggiolaro Daniele - ISTM-SCITEC
10.45 - 11.15	Coffee Break	
11.15 - 12.15	**Chair - Dott. Maurizio Peruzzini** (DSCTM-CNR) Round Table Discussion - **Dott.ssa Cristina Battaglia** (UVR-CNR); **Dr. Liborio Capozzo** (ISTEC-CNR); **Dr. Antonio Cusmà** (DSCTM-CNR) *Il Trasferimento Tecnologico e la Valorizzazione dei Risultati della Ricerca al CNR*	
12.15 - 12.45	**Discussione Plenaria & Conclusioni - Dott. Maurizio Peruzzini** Direttore Dipartimento di Scienze Chimiche e Tecnologie dei Materiali	
13.00 - 14.30	Pranzo & Partenza	

ABSTRACT

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CHEMISTRY AND ENERGY

ADVANCED MATERIALS

COMPUTATIONAL MODELING

CHEMISTRY FOR CULTURAL HERITAGE

CHEMISTRY FOR LIFE SCIENCES

POSTER COMUNICATION

GREEN CHEMISTRY

CHEMISTRY AND ENERGY

CHEMISTRY FOR LIFE SCIENCES

ADVANCED MATERIALS

COMPUTATIONAL MODELING

CHEMISTRY FOR CULTURAL HERITAGE

KEYNOTE LECTURE

ORAL COMMUNICATION

Fotovoltaico: Come Ricerca E Innovazione Possono Contribuire Agli Obiettivi Del Piano Naz. Energia E Clima E Del Set-Plan Europeo

Massimo Mazzer
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Referente Nazionale Set Plan per il Fotovoltaico, CNR-DIITET

Nell'ambito della sfida globale posta dai cambiamenti climatici al futuro del genere umano su questo pianeta, il tema dell'energia è uno dei più importanti ed urgenti da affrontare visto l'impatto che gli attuali sistemi di generazione, distribuzione e uso di energia, basati ancora prevalentemente sui combustibili fossili, hanno sulle emissioni di gas serra.

I notevoli avanzamenti tecnologici ottenuti nell'ambito delle energie rinnovabili e del risparmio energetico, grazie agli investimenti in ricerca e innovazione soprattutto nel corso degli ultimi 10 anni, hanno di fatto azzerato, e in alcuni casi già invertito, il gap fra il costo delle nuove soluzioni tecnologiche a basso impatto ambientale e le tecnologie convenzionali basate sull'uso intensivo di combustibili fossili. E' il caso, ad esempio, di Eolico e Fotovoltaico che, secondo le più recenti stime di autorevoli analisti, sono già le fonti di energia elettrica meno costose in gran parte del mondo al netto di qualsiasi incentivo economico ai produttori e/o ai consumatori di energia.

Grazie a questi risultati il mercato delle energie rinnovabili si espande esponenzialmente e si stima, ad esempio, che la capacità totale di impianti fotovoltaici installati globalmente raggiunga 1 TW di potenza di picco entro il 2022, sufficiente a generare circa il 5% dell'energia elettrica consumata in tutto il mondo. Se combinate con le previsioni di sviluppo dell'accumulo elettrico e della mobilità elettrica, questi dati indicano come la transizione verso un sistema energetico compatibile con gli attuali obiettivi di contenimento del riscaldamento globale, sia non solo possibile ma anche realizzabile su una scala di tempi ben più ambiziosa di quella attuale.

In Italia il Piano Nazionale Energia e Clima, ancora in fase di discussione e criticato da più parti per la scarsa ambizione degli obiettivi, prevede tuttavia una crescita di quasi il 300% della capacità di generazione di energia elettrica da fotovoltaico portandola dagli attuali 25 TWh/anno circa, a 75TWh/anno entro il 2030. Il rapido sviluppo di strumenti di mercato come i "Power Purchase Agreements" (PPA) anche in Italia, combinato con il trend di riduzione del Levelised Cost of Energy (LCOE) da fotovoltaico sono importanti driver per il raggiungimento di questo obiettivo ma, quella economica non è l'unica barriera all'adozione delle nuove tecnologie energetiche come il fotovoltaico.

Oggi l'obiettivo di ricerca e innovazione nel settore dell'energia non è più dimostrare che esiste un'alternativa sostenibile, dal punto di vista economico, ai combustibili fossili ma sviluppare soluzioni che permettano di accelerare la transizione energetica agendo sulle barriere di altra natura a partire da quelle tecnologiche. Nel caso del fotovoltaico vi sono soprattutto l'inadeguatezza della rete elettrica nazionale a gestire la generazione diffusa da fonti rinnovabili e la scarsità di soluzioni e prodotti innovativi per un approccio integrato all'autosufficienza energetica degli edifici non solo di nuova costruzione.

Il sistema della ricerca pubblica possiede il know-how e l'indipendenza
di azione necessarie per affrontare queste problematiche e per sviluppare, insieme alle imprese, prodotti processi e soluzioni innovative da portare rapidamente sul mercato. Per fare questo è in atto un'azione coordinata a livello nazionale e internazionale che sta mettendo a sistema il meglio delle competenze all'interno di un programma ambizioso basato sullo stesso spirito che ha caratterizzato il programma spaziale delle grandi superpotenze degli anni '60 che ha portato i primi esseri umani a sbarcare sulla Luna in meno di un decennio.

Lo Strategic Energy Technology Plan (SET Plan) dell'Unione Europea, a partire dal 2017 è diventato il quadro di riferimento strategico dei programmi nazionali di Ricerca e Innovazione nel settore dell'Energia all'interno del quale i Paesi Membri dell'Unione hanno condiviso obiettivi e roadmap in 14 aree strategiche fra cui il Fotovoltaico. A questo quadro strategico si è affiancato "Mission Innovation", un piano straordinario di investimento pubblico per accelerare l'innovazione nel settore delle "energie pulite". I Paesi che hanno aderito, tra cui l'Italia, si sono impegnati a raddoppiare in cinque anni i fondi pubblici destinati a questo obiettivo.

SET Plan e Mission Innovation vengono oggi considerate due aspetti complementari di un unico piano attuativo, coordinato congiuntamente dai Ministeri della Ricerca (MIUR) e dello Sviluppo Economico (MISE). In Italia, è parte integrante di questo piano anche un'altra iniziativa strategica di rilevanza nazionale. Al fine di massimizzare l'impatto delle iniziative progettuali e di raggiungere la necessaria massa critica per affrontare con efficacia le sfide dettate dall'urgenza ambientale e climatica è stata promossa la costituzione di una rete nazionale per la ricerca e l'Innovazione in ciascuna delle aree strategiche del SET Plan. Della rete fanno parte enti di ricerca, università e stakeholders industriali che condividono gli obiettivi del SET Plan e intendono coordinare i propri sforzi per raggiungerli nello spirito delle future "Mission" strategiche di Horizon Europe.

Acknowledgement:
Desidero ringraziare sia i membri del comitato promotore della Rete Nazionale di R&I del Settore Fotovoltaico, Fabrizio Bizzarri (Enel Green Power), David Moser (EURAC Research), Simona Binetti (UniMIB), Franco Roca (ENEA), Aldo di Carlo (CHOSE), Claudia Barolo (UniTO), che i colleghi del CNR Alessandra Sanson (DSCTM) e Salvatore Lombardo (DSFTM)

KEYNOTE LECTURE

Free Radical Chemistry From Science To Market Innovation: A Success Case

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ISOF - CNR

The research activity of our group concerns free radical chemistry, embracing the structure-reactivity relationship of free radicals and their various applications in synthetic methodologies, material science, and life sciences. The wide competence on free radical chemistry has been achieved and developed with an interdisciplinary approach for almost four decades, starting from the fundamental knowledge of organic and physical chemistry, skilfully applied to the fields of synthetic, bioorganic and biological chemistry, and more recently come to envision the new interdisciplinary sector of biomimetic chemistry of radical stress and related biomarkers.

The early work and the discovery of (Me3Si)3SiH as radical-based reducing agent

The studies in physical organic chemistry were predominant in the first ten years of the group activity. Knowledge of kinetic methodologies and time-resolved spectroscopies constituted a solid background for the expansion of our activity, focusing in particular on the structural properties and reactivity of sulfur- and silicon-centered radicals. (Me3Si)3SiH was disclosed as a very convenient and non-toxic radical-based reducing agent and awarded with the Fluka prize “Reagent of the Year 1990”. More than a thousand publications in chemical research deal with the use of this reagent from groups all over the world, well known as a very versatile compound for carrying out several types of radical reactions.

Biomimetic radical chemistry and applications

We contributed to the development of free radicals for bio-technological applications, evaluating biomolecules such as DNA, proteins and lipids, having specific supramolecular structures and radical reactivity in aqueous systems. We opened the field of biomimetic radical chemistry, leading also two COST Actions and European research on this subject. Our discoveries in this sector attracted worldwide attention on two main topics: (i) the endogenous formation of trans-geometrical lipids and of the n-10 fatty acids in human body, developing the fatty acid-based membrane lipidomic analysis, (ii) the 5‘,8-cyclopurine formation and associated mechanisms as tandem lesion with specific biological significance for human diseases and aging. Our biomimetic studies and analytical protocols with complete characterization of reaction or transformation products brought us up to clinical research.

The birth of a spin-off company and the promotion to the market

Research on lipidomics led to the setting up of an innovative analytical platform to examine erythrocyte membrane lipidome, which is nowadays also implemented with an original designed high-throughput robotics for the isolation and analysis of mature red blood cell membranes. The company Lipinutragen srl was approved as a spin-off initiative of the CNR to bring our science to the market, and is now a successful example of research that is translated into innovative products for molecular medicine, health care and prevention.

References:

1) Chatgilialoglu, C. *Organosilanes in Radical Chemistry*; Wiley: Chichester (UK), **2004.**
2) Chatgilialoglu, C.; Studer, A., Eds. *Encyclopedia of Radicals in Chemistry, Biology and Materials* (4 volumes); Wiley, Chichester (UK), **2012.**
3) Ferreri, C.; Chatgilialoglu, C. *Membrane Lipidomics for Personalized Health;* Wiley: Chichester (UK), **2015.**

KEYNOTE LECTURE

Advanced Glasses, Composites And Ceramics For High Growth Industries

Milena Salvo

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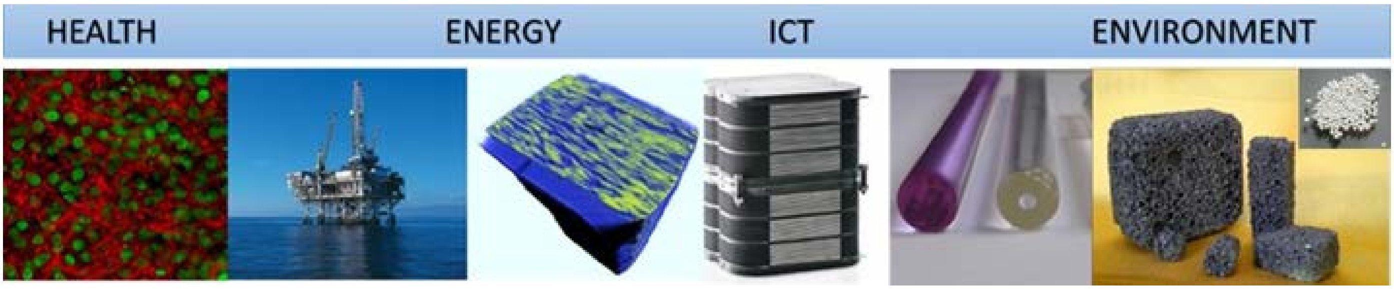

The “Advanced glasses, Composites And Ceramics for High growth industries” (CoACH) project is a European Training Network co-funded by the European Commission through the Marie Sklodowska-Curie action of Horizon 2020. CoACH involved multiple actors in the innovation ecosystem for advanced materials; five universities and ten enterprises in seven different European countries. A total of 15 early stage researchers worked in close relationship with industrial and business partners, developing new antibacterial materials, innovative materials for energy production and harvesting, sensors for harsh environments and building materials from industrial wastes. The CoACH research outcomes are poised to be commercially exploited in industrial applications and commercial products. The individual research projects of the 15 researchers concerned:

- novel, antibacterial and nanostructured coatings for medical devices and implants for dental, orthopaedic and tissue engineering applications. They can help to reduce bacterial infections and cut the use of antibiotics by patients
- innovative glass fibre sensors that can monitor the degradation of polymer composites in harsh environments
- innovative thermoelectric materials using non-toxic elements and new manufacturing techniques for more efficient thermoelectric devices
- new glass-ceramic and ceramic materials that are able to increase the reliability of solid oxide electrolysis cells
- materials for eco-sustainable buildings produced from industrial waste

Chimica: Scienza E Industria Per Un Futuro Più Sostenibile

Vittorio Maglia

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Federchimica

La caratteristica della chimica di avere una scienza e un’industria con lo stesso nome dà un posizionamento forte sia nello scenario di globalizzazione sia in quello di sostenibilità.

Ciò potrà essere rafforzato da parte delle imprese da una più forte consapevolezza di dover sviluppare da un lato maggior ricerca strutturata e dall’altro di dover operare sulla frontiera tecnologica e su aree scientifiche non sempre proprie dell’impresa.

Ciò significa l’apertura di una necessaria e rafforzata collaborazione tra ricerca pubblica e privata, nella consapevolezza di un maggior impegno nella ricerca da parte delle imprese ma anche della realtà di queste che spesso non hanno esperienza di interazione con il CNR.

Il CNR è per l’industria chimica l’interfaccia ideale per rafforzare l’impegno nella ricerca.
Insieme si dovrà anche operare nei confronti delle Istituzioni perché ci sia una corretta comprensione del ruolo fondamentale della chimica non solo come settore ma come infrastruttura tecnologica al servizio dei settori a valle.

Questa realtà riguarda in particolare la green chemistry da considerare non solo come chimica da biomassa ma come chimica sostenibile.

Omic Approaches In Drug Discovery: From Big Data To Novel Targets

Enrico Domenici

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Fondazione The Microsoft Research-University of Trento Centre for Computational and Systems Biology (COSBI), Rovereto (TN)

Drug discovery and development is associated with a high rate of failures, especially when dealing with molecular targets lacking a robust association to the disease of interest and in the absence of biomarkers that can help to identify the right patient population. That notwithstanding, in recent years a number of genomic targets have been translated from basic research discoveries into clinical practice, showing the potential of genetic information in supporting the development of innovative medicines. The advent of large-scale genomic technologies is creating the premises nowadays for a revolution in drug discovery. Scientists are joining their efforts into large consortia aimed at deciphering the genetic basis of complex diseases, thus increasing our understanding of their molecular underpinnings and setting the basis for the identification of innovative targets. In psychiatry, the advent of big data might revamp drug development, which has been stalled for many years, and, in perspective, help in the identification of biomarkers enabling for tailored medicines.

In the present talk, I will showcase several of examples in support of the ability of genome-wide association studies to point to putative targets and describe how the availability of large-scale functional genomic data can guide to the selection of the most appropriate drug discovery strategy. Moreover, I will show how the integration of omic data and clinical data can guide to the identification of patient subgroups, paving the way for precision medicine approaches. Finally, I will illustrate how multiple layers of omic information can be integrated to develop a knowledge-based network to search for novel indications for known targets, leading to novel drug repositioning approaches.

CONTRIBUTED TALK

ORAL COMMUNICATION

From Horizon 2020 To Horizon Europe – Next Steps Towards The New Framework Programme For Research And Innovation 2021-2027

Michele Guerrini

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Department of Chemical Science and Materials Technologies
National Research Council of Italy – Brussels Liaison Office

On 7 June 2018 the European Commission presented the proposal for Horizon Europe, the next Framework Program for research and innovation 2021-2027, successor to Horizon 2020. In this year the proposal was negotiated by the co-legislators (Council and European Parliament), at the end of a tight legislative negotiation, the EU institutions - Parliament and Council, in agreement with the Commission - reached and approved a provisional agreement, defining a "consolidated" legislative text of the next framework program (April 2019) . The "roadmap" of the new program is tight and it is therefore essential to have a clear picture of the new program, to be able to anticipate what will happen in the coming months in order to intercept in time what we are interested in and be competitive.

The topics discussed are:

- General architecture of the program - the new pillars of Horizon Europe.
- Strategic planning - the process that, starting from the "consolidated" legislative text, will lead to the definition of the EU's strategic plan and research and innovation priorities for the years 2021 to 2024, preparing the contents of work programs and calls for funding for the first four years of the next program.
- Missions - The contributions and recommendations to identify specific R&I missions in the strategic plan will come from the 5 Mission Boards: one for each possible "mission area" identified in the legislative text.
- Partnerships - The review of the partnerships proposed by the European Commission. At the beginning of May the EC presented the package of 44 partnerships foreseen for Horizon Europe, articulated in the three different types: institutionalized partnerships; co-programmed partnerships; co-financed partnerships

The issues addressed will decipher the mechanisms that govern the processes of co-decision in the definition of the funding programs. Understanding the moment of transition we are going through, between a programming cycle and another, will give the possibility to take the necessary actions that help the scientific network to be more competitive on the European scene.

ROUND TABLE DISCUSSION

ORAL COMMUNICATION

Il Trasferimento Tecnologico E La Valorizzazione Dei Risultati Della Ricerca Al CNR

Cristina Battaglia, Antonio Cusma, Liborio Capozzo

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UVR, DSCTM, ISTEC

Con oltre undici mila fra dipendenti e collaboratori, il 60% dei quali a vario titolo coinvolto in attività di ricerca e di formazione alla ricerca, Il Consiglio Nazionale delle Ricerche (CNR) è il maggiore Ente pubblico di ricerca italiano ed ha il ruolo istituzionale di svolgere, promuovere e valorizzare ricerche nei principali settori della conoscenza, di trasferirne e di applicarne i risultati per lo sviluppo scientifico, culturale, tecnologico, economico e sociale del Paese e di fornire supporto tecnico-scientifico al governo e alle amministrazioni pubbliche.

Sulla base dei principi statutari e di una forte esperienza in ambito nazionale e internazionale, il CNR promuove l’avanzamento delle conoscenze, anche attraverso la valorizzazione del patrimonio dei trovati, delle infrastrutture e delle competenze presenti presso la propria rete scientifica e il trasferimento sul mercato dei risultati della ricerca, promuovendo e conducendo un dialogo, continuo e strutturato, con tutti i settori strategici – pubblici e privati – per lo sviluppo e l’innovazione. Il trasferimento tecnologico – processo complesso, articolato su tematiche, expertise e competenze apparentemente molto diverse, che vanno dalla conoscenza tecnologica alla giurisprudenza, alla negoziazione, al profitto, all’innovazione – assume dunque un ruolo istituzionale molto forte, come seconda Missione di Ente, accanto alla primaria Ricerca.

Negli ultimi anni il CNR ha voluto dare coerenza e visione a percorsi di trasferimento tecnologico, ponendo la valorizzazione al centro, e non semplicemente al termine, dei processi di produzione scientifica. Obiettivo che si è cercato di raggiungere armonizzando compiti e funzioni legati alle attività di trasferimento tecnologico e associando agli stessi azioni di promozione, tutela e valorizzazione dei risultati della ricerca, coordinandone strategia e vision.

Nella tavola rotonda verranno brevemente introdotte le attività del CNR in materia, le recenti modifiche, o proposte di modifica, ai regolamenti Spinoff e Brevetti dell’Ente e la future azioni previste a sostegno del trasferimento tecnologico e della valorizzazione dei risultati della Ricerca.

GREEN CHEMISTRY

ORAL COMMUNICATION

Bio-Based Production Of Energy And CO_2 Valorization

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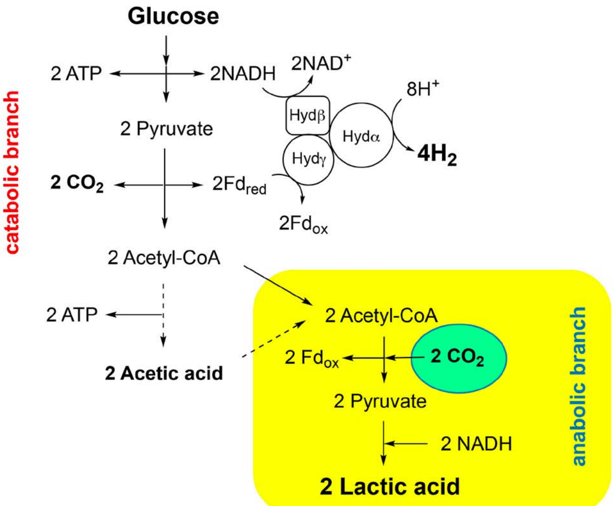
Bio-based processes can make the economy more sustainable and lower its dependence on fossil fuels, converting low cost renewable feedstocks and CO_2 into valuable bio-products with the help of microorganisms in bioreactors. *Thermotoga neapolitana* is a marine anaerobic bacterium with an optimal growth temperature of 80°C, suitable for conversion of sugars into hydrogen with yields close to theoretical values[1]. 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 unprecendented pathway involved in the recycling of CO_2 through the coupling of acetate and carbon dioxide and the concomitant production of lactic acid (95% e.e), without affecting hydrogen production[2]. This patented process, called Caphnophilic (CO_2-requiring) Lactic Fermentation (CLF) (Figure 1), may become the cornerstone for economically attractive biotechnological applications based on CO_2 valorization.

In this contribution, we present activities and latest results related to the biochemical cross-talking and metabolic engineering of the pathways related to hydrogen and lactic acid production[3], as well as 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. These are crucial aspects to further improve rate and yield of the process for guaranteeing its sustainability.

These activities were developed within the frame of the European Project BioRECO2VER (Horizon 2020, Research and Innovation Programme under Grant Agreement, No. 760431). BioRECO2VER Project started in Januray 2018 and include 2 Research and Technology Organizations, 2 Universities, 4 SMEs and 4 large industries. The high-level goal of the project is to demonstrate the technical feasibility of more energy efficient and sustainable anaerobic biotechnological processes for the capture and conversion of CO_2 from industrial point sources into 2 valuable platform chemicals.



Caphnophilic (CO2-requiring) Lactic Fermentation (CLF) operated by Thermotoga neapolitana for production of hydrogen and L-lactic acid.

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The Role Of The Constrained Amorphous Interphase On Physical And Mechanical Properties Of Bio-Based Polymeric Materials

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The micro- and nanophase structure of semi-crystalline polymers is determined by competition between crystallization and vitrification, which leads to the development of different amorphous regions, which, due to different distance from the crystalline domains, can exhibit different molecular dynamics. A detailed description of the micro- and nanophase structure of semi-crystalline polymers is decisive for a full understanding of the physical properties of these materials. It has been recently proved that many macroscopic properties of semi-crystalline polymers, as for example mechanical and barrier properties, are defined not only by the degree of crystallinity, but also by the percentage of constrained amorphous nanophase present at the amorphous/crystal interface. The quantification of this nanophase is therefore a crucial step in the characterization of a polymeric material, since different processing conditions affect in different ways the evolution of the crystalline and amorphous fractions.

The subject of the presentation will be the evolution, during solidification, of the constrained amorphous interphase in some bio-based polymers, as poly(L-lactic acid) (PLLA), poly(3-hydroxybutyrate) (PHB), and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), which, owing to their biodegradability, can be utilized for a variety of applications.

The contribution of the constrained amorphous nanophase to physical ageing of PLLA, as well as to the mechanical properties of PHB and PHBV will be presented and discussed. In particular, a quantitative estimation of the elastic modulus of the constrained amorphous nanophase in some PHBV copolymers will be described. The calculated elastic modulus turns out to be in agreement with theoretical expectations.

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ZrO_2-Based Catalysts: A Versatile Tool For The Production Of Oxygenated Biofuels From Alcohols And Furans

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In the search for sustainable and renewable alternatives to traditional fossil fuels, oxygenated compounds derived from non-food sources, i.e. lignocellulosic biomass, are very promising candidates. Bioalcohols are among the main output of biorefineries through fermentative processes, with a continuously increasing production. They can be directly used as fuels (e.g. ethanol) in traditional engines or in fuel cells, or further transformed. Alcohols are not the only oxygenated compounds to have been investigated as a replacement of fossil fuels: among the alternatives we find esters (e.g. butyl levulinate) and ethers (e.g. derived from furanics). Compared to alcohols, esters and ethers possess a lower polarity, thus leading to reduced corrosion phenomena, and enhanced physical properties depending on the substituent[1]. The development of green production routes is on the basis of the sustainable employment of these compounds.
In this view we focused our research on the study of efficient catalytic strategies for the synthesis of symmetric esters (from bioalchols) and furanic ethers (from furfural and HMF). The design of the catalyst has revealed the high performances of different zirconium-based materials in complex, multistep reactions.
The first example is the dehydrogenative coupling reaction, a high atom economy process, that allows to produce symmetric esters directly combining two molecules of alcohol, with the release of H_2 as the only "by-product". Using a CuO/ZrO_2 catalyst we were able to produce ethyl acetate and butyl butyrate in high yield, 87% and 98% respectively, in solvent- and additive-free, gram-scale conditions and batch reactor. The characterization of the catalyst put in light the cooperative role of Cu and Zr phases and their high interdispersion, as the reason for the high activity[2]. The catalytic process was also optimized in a continuous flow reactor for the preparation of a butanol/butyl butyrate mixture that was studied as 30% gasoline blend in a real engine and proved to be a valid and sustainable choice for fuel replacement.
The second example involves the synthesis of ethers of furfural and dithers of HMF combining catalytic transfer hydrogenation (CTH) and etherification reactions in a one-pot process[3], using 2-butanol (solvent, H-donor and ether moiety precursor), under mild conditions (120 °C, autogenic pressure). Different ZrO_2-SiO_2 catalysts with an increasing SiO_2 content (0, 3, 10, 30 wt%) were compared: the introduction of silica has a significant impact on the selectivity of the resulting material. Thus, pure ZrO_2 catalyzes only the CTH, selectively leading to the alcoholic products, while on ZrSi30 the –OH groups of the substrates undergo to a further etherification, with the exclusive ethers formation. Therefore furfuryl ether and HMF diether, that are promising biofuels for diesel blend, are here produced in 95% and 96% yield respectively, conversely to the limited amount usually obtained with other systems.

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CHEMISTRY AND ENERGY

ORAL COMMUNICATION

Chemical Looping Combustion With Oxygen Uncoupling (CLOU) Using Novel Geopolymer Oxygen Carriers For Fluidized Bed

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One of the best alternatives to reduce the economic cost of CO_2 capture is represented by the chemical looping Combustion, a process which enables the inherent separation of carbon dioxide simply by water condensation, as the stream exiting the fuel reactor is only composed of CO_2 and H_2O. In Chemical Looping Combustion, with or without oxygen uncoupling (CLC and CLOU, respectively), the fuel is oxidized by a metal oxide, called the oxygen carrier (OC), avoiding a direct contact between the fuel and air. In CLOU processes, the metal oxides reduce by spontaneously releasing O_2, which is directly used in the combustion of fuel, allowing also for the use of solid fuels. Both these technologies are generally carried out using two reactors: an air reactor, where the metal of the OC is oxidized by ambient air, and a fuel reactor where it reduces and the combustion of fuels occurs [1]. In both cases, the selection of suitable OCs is a key factor for the development of such technologies. Indeed, the limited stability at high temperatures and under continuous cycling conditions of most of the current OCs might represent a serious limitation, as well as the heavy environmental and economic impact of their production technologies [2].

In this work, synthetic OCs based on geopolymer composites for CLOU processes have been proposed as alternative to traditional ones, exploiting geopolymers' excellent thermal and mechanical stability, together with their easy, sustainable and low cost production process [3]. Suitable oxides, such as Cu and Mn oxides, also in combination with each other, have been used as the active phase and embedded within a geopolymer matrix. The performances of the produced OCS have been evaluated in terms of red-ox activity, oxygen transport and oxygen uncoupling ability. Laboratory experiments were carried out in a thermo-balance at 700 °C and 900°C, in order to measure the weight change of the sample in alternating inert and oxidizing atmospheres, then in a lab-scale reactor, under more representative conditions. Attrition tests were also carried out to evaluate the abrasion resistance of the materials and their suitability for the use in fluidized bed conditions.

The conducted tests pointed out the good performance of the CuO-based OCs in terms of oxygen carrying capacity, exhibiting a better behavior compared to carriers based on mixed Cu-Mn oxides. However, both systems were able to release oxygen in inert atmosphere, demonstrating potentialities for CLOU applications, and were found to be stable to high temperatures and to repeated cycling, since no relevant modifications to their macro- and micro-structure have been detected.

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Benzo-Bisthiazole And Quinoxaline Derivatives As Fluorophores In LSC Photovoltaic Devices

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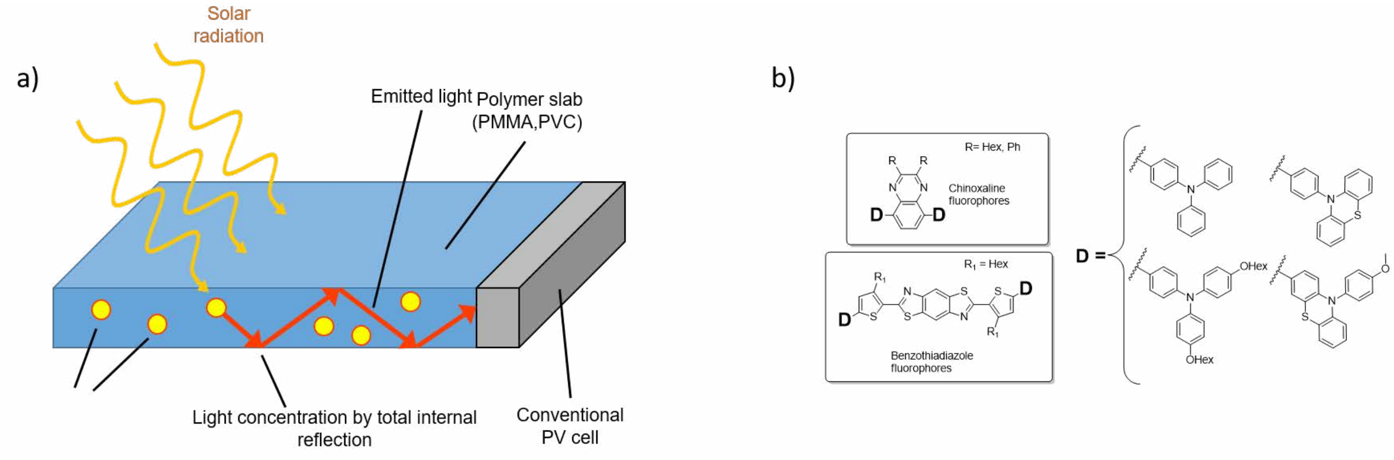
Luminescent solar concentrators (LSCs) is a photovoltaic technology that has shown considerable interest in recent years. The main advantages are the simplicity of preparation of the device, low costs for its preparation, transparency and the possibility of obtaining coloured devices. These features could allow integration into buildings[1] (BIPV-Building Integrated PhotoVoltaic). The heart of the LSC is the fluorophore, that is the compound that absorbs the solar radiation and re-emits it at a longer wavelength. To date, a variety of luminophores have been developed to fabricate LSCs. In this communication we present a series of fluorophores that have been studied with the aim of having high fluorescence quantum yields (important factor for obtaining high optical efficiencies) and high stock shift, (factor that allows to build devices of higher area, minimizing the loss of energy caused by self-absorption).



a) Typical LSC configuration; b) Structure of the studied fluorophores.

The symmetrical organic compounds prepared by us have D-A-D (Donor-Acceptor-Donor) structure, that is composed of a central acceptor system (in our case benzothiadiazole[2] or quinoxaline systems) and of arylamines moieties as lateral donor groups. The various compounds prepared show good quantum yields and excellent stock shifts. LSC devices built with our fluorophores allowed to obtain greater optical efficiencies than the reference dye (Lumogen RED-BASF). Furthermore, through computational analysis and spectroscopic measurements on excited systems, we tried to find a correlation between molecular structure and quantum yield and stoke shift. The aim is to be able to predict such properties in the future, based only on the structure of the molecules.

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Design Of Ni/La_2O_3 Catalysts For Dry Reforming Of Methane: Influence Of Synthesis Conditions On The Structural Properties And Catalytic Performances

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Dry reforming of methane (DRM) is highly endothermic ($\Delta H^{\circ}_{25^{\circ}C}$ = +247 kJ/mol) and normally requires temperatures above 700°C to attain good conversion levels. Nickel is the most frequently reported metal in DRM because of its good catalytic activity and its cost-effectiveness as compared with Rh, Ru, Pt, and Pd-based catalysts. However, the main drawback of Ni based catalysts is represented by the production of significant amount of carbon and by the sintering at the high temperatures of the reaction. Carbon deposits are formed when the rate of methane dissociation is faster than the oxidation of carbon by the surface oxygen species arising from CO_2 dissociation [1]. Currently many studies have demonstrated that metal oxides such as CeO_2, MgO, ZrO_2 have positive effects on catalytic activity, stability and carbon suppression of nickel catalysts for DRM [2,3].

In the present work the physical chemical properties, the related catalytic activity and the long-run stability of Ni-La_2O_3 catalysts have been evaluated in DRM reaction. The aim was to investigate the effect of ammonia addition during the synthesis of La_2O_3 oxide carried out by sol-gel method in presence of citric acid. Ni(10%wt) was deposited by wetness impregnation over two La_2O_3 oxides prepared with and without adding NH_3 solution during the synthesis, the corresponding catalysts were labelled as *Ni-La CA* and *Ni-La CA-*NH_3, respectively. The so far prepared catalysts were characterized by BET, XRD and TPR techniques. The XRD patterns of the supports calcined at 800 °C showed that ammonia addition favors the formation of La_2O_3 phase with respect to $La(OH)_3$. La_2O_3 was the only lanthanum phase detected in the XRD pattern of *Ni-La CA-*NH_3, after calcination at 600 °C and reduction treatment at 700 °C, moreover, weak features attributed to dispersed metallic Ni particles were found. While in the case of *Ni-La CA*, both phases, La_2O_3 and $La(OH)_3$ were present along with well visible peaks of metallic Ni suggesting the presence of big clusters. DRM gradient catalytic test performed between 400°C to 800°C revealed higher catalytic activity of *Ni-La CA*, nevertheless long run test showed a better stability of *Ni-La CA-*NH_3 catalyst. The spent catalysts were characterized by XRD, TGA, Raman and TEM analyses. In both samples $La_2O_2CO_3$ phase was formed together with C graphite peak of higher intensity in the case of *Ni-La CA* in agreement with greater weight loss revealed by TGA and stronger deactivation during long run with respect to *Ni-La CA-*NH_3. The effect of the nature of the catalyst on the amount of carbon coke formed during DRM was also confirmed by Raman and TEM results.

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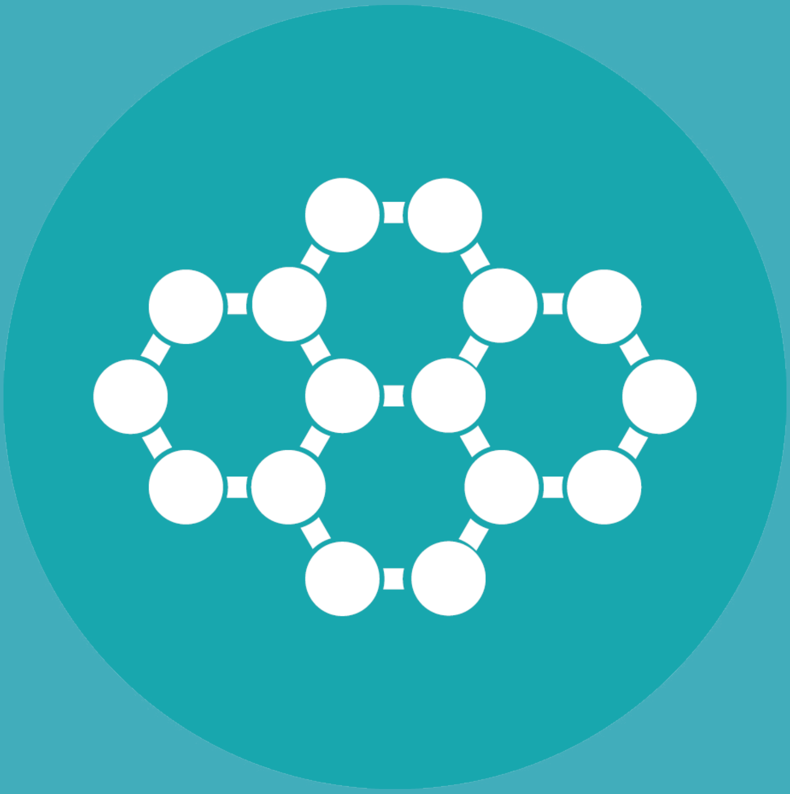
ADVANCED MATERIALS



ORAL COMMUNICATION

ORAL COMMUNICATION

Graphene Oxide Enhanced Membranes For Tap Water Purification

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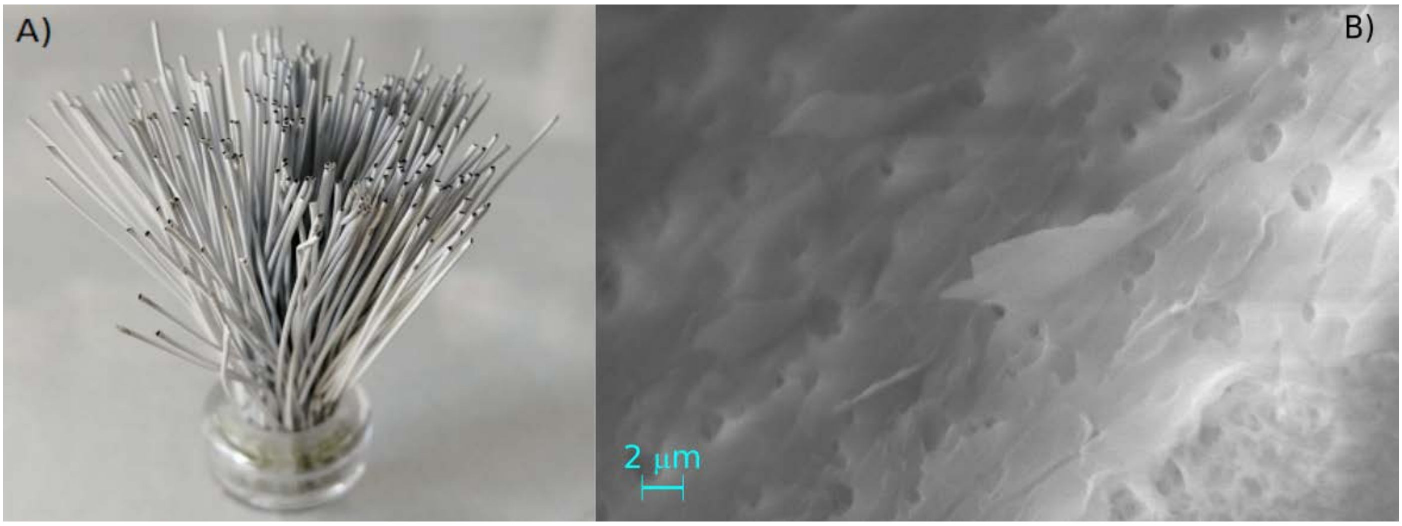
Much of our tap water comes from rivers, streams, lakes and groundwater. These fundamental water resources are increasingly contaminated by discharges of chemicals from industries and urban areas, most of them not fully removed by standard water treatment. Traces of prescription medications, antimicrobial chemicals, pesticides and cosmetics, with suspicious or even proved toxic effects have been found in several EU water bodies. This serious issue calls for the development of new efficient, low cost and sustainable purification technologies. In the last years, due to their outstanding adsorption properties, high processability and versatile chemical modification options, graphene-based materials have emerged as the most promising nanomaterials for advanced water treatment technologies.

Here, we report on polyethersulfone(PES)-graphene oxide (GO) composite membranes obtained by sequential microfiltration of a GO solution and thermal fixation of GO and their use in filters for the removal of three representative contaminants from tap water[1]. Stable fixation of GO on commercial hollow fiber membranes (Versatile PES®, Medica) is achieved by microwave activation or conventional heating under mild conditions.[2,3]. It is demonstrated that GO enhances the removal of polar contaminants, i.e. ofloxacin (antibiotic), with respect to PES-only fibers. As a matter of a fact, a positive correlation has been found on the amount of GO fixed on PES hollow fibers and the system removal efficacy. Working mechanism, regeneration and GO release issues are discussed.

A) PES-GO hollow fibers, B) PES-GO external surface SEM image



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Acknowledgement:

Foundings from Graphene Flagship CORE-2

Improvement Of Dental Implants Properties By Surface Dual-Step Functionalisation

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The dental implant related technologies are under constant implementation for improving the device performance. About 70-80% of dental implants are made of metallic biomaterials and commercial pure titanium (cp-Ti) is widely used for dental applications thanks to the optimum combination of strength-to-weight ratio, corrosion resistance and biocompatibility [1]. Nevertheless, the reduced titanium bioactivity suggests the device surface functionalisation to enhance, accelerate and direct the bone growth. In this way, several methods have been proposed but only a restricted number of them have been actually scaled-up to industrial level [1]. The deposition of calcium phosphate ceramics layers (CPCs) on the implant surface is a typical modification methodology [2]. The CPC presence permits a faster bone-to-implant integration with a strong and stable bond. On the other hand, the CPC layer usually suffers of poor adhesion on Titanium substrates. Moreover, CPCs are reabsorbed by dissolution in body fluids and osteoclasts action. The biological removal of the CPCs layer, obviously, involves the loosening of the implant stability and can lead to its failure. Literature suggests that CPCs adhesion can be improved by the insertion of a dense and compact ceramic inter-layer [3], but the CPCs biological reabsorption phenomena cannot be avoided.

The developed research deals with an original synergic deposition route for the functionalisation of titanium dental implants by a multi-step process. The final composite device is designed with a bioactive, dense, compact and crystalline TiO_2 inter-layer, obtained by Metal Organic Chemical Vapour Deposition (MOCVD) and an homogeneously spread discontinuous calcium phosphate ceramic top-layer, with particular chemical composition, crystallinity and morphology, obtained by means of spray pyrolysis. In detail, the CPC deposition step leads to the presence of hydroxyapatite (HA) islands on the TiO_2 compact layer.

The unique architecture of the device is planned for improving different characteristics that, joined together, define the overall implant performance. In detail, the TiO_2 layer is conceived to act as a protective and functional coating. Indeed, it reduces the titanium ions release into body fluids, improves the tribo-corrosion, mechanical and wettability properties. The HA spots on the surface, on the other hand, are imagined for the improvement of the early stage of the osseointegration process.

Beside the above mentioned properties, the planned architecture takes its advantage in the bioactive synergic role of both TiO_2 and HA. The novelty, indeed, lies in their simultaneous exposure to the body fluids and then their contribution to the healing process: a bioactive, biocompatible and not resorbable TiO_2 inter-layer is available for the long-term integration, whereas a more bioactive and resorbable HA top-layer permits the short-term anchoring. In the here proposed composite device, new bone simultaneously starts to anchor on HA (quickly) and on TiO_2 (slowly) and when the HA is completely reabsorbed the implant is still steadily bound.

During all the experiments, in order to provide a deeper investigation on the role of the coatings, three kinds of titanium substrates commonly used in dental implant applications and with different surficial morphology (i.e. titanium machined, sandblasted, and sandblasted/acid etched, all of commercial grade IV) were considered and compared.

Coated surfaces exhibit better electrochemical performances in artificial saliva, and reduced ions release in lactic acid. The mechanical properties at nano-scale level of the composite materials were improved with the functionalization. The coatings make the composite hydrophilic or even super hydrophilic. Acellular in-vitro bioactivity of all species was tested studying the ability of the materials to form a bone-like apatite layer on the surface after immersion in Dulbecco Phosphate Buffer Saline solution.

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Luminescent Organometallic Complexes: Multiple Perspectives In Technological Applications

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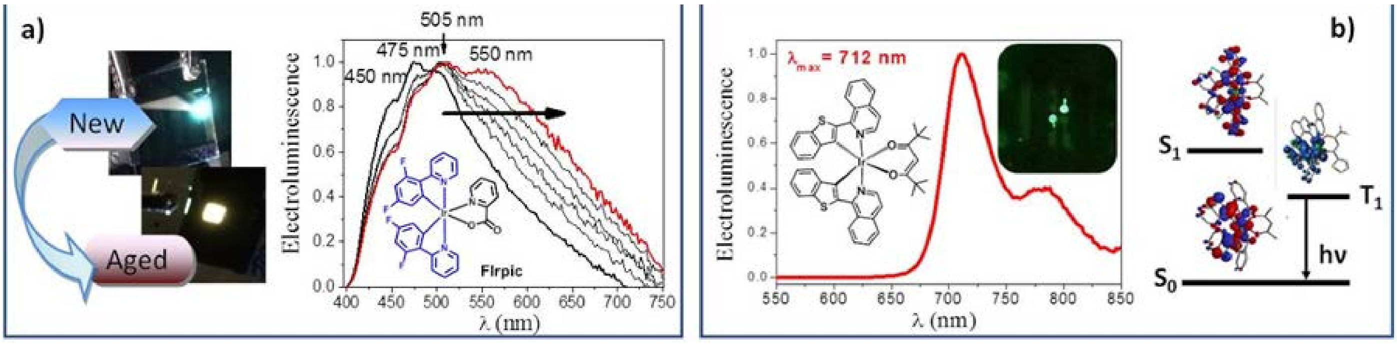
The current developments of optoelectronics and bionanoscience take great advantage from the ability of organic, organometallic and hybrid compounds to fulfill specific needs and requirements. Phosphorescent transition-metal complexes, in particular octahedral Ir(III) ones, have been the target of intense researches given their excellent photophysical properties such as high luminescence quantum efficiency and short radiative lifetime; in addition they can be easily engineered in order to judiciously tune the optical absorption and emission color, the electronic energy levels, the sterical hindrances and the solid state packing. Ir complexes quickly became the emitters of choice in organic light emitting diodes (OLEDs) which is the reference technology employed in energy-saving flat panel displays and a promising alternative to develop solid-state lighting. Although this technology has already been introduced in the market, two big challenges still remain and are going to be the topics of this contribution: i) the instability and degradation of blue-emissive organic materials and ii) the lack of efficient emitters to extend the OLED *applications* into the nearIR region (λNIR > 700 nm) for automotive, surveillance and phototherapy.

1- The study of the degradation pathway leading to OLED failure is essential to meet the device lifetime and efficiency requirements.[2] Our approach combines chemical, photophysical and thermal studies of the molecular emitters; fabrication of multilayered engineered devices and chemical analysis of degradation fragments at the interface; thorough theoretical investigation of exciton induced molecular instabilities. We were able to define the boundary conditions for the suppression of degradation in a model blue OLED based on the archetypal FIrpic complex (Fig. 1a).[1]

2- In the NIR field, we undertook a rational structure-property engineering of Ir(III) emitters with *iso*quinoline-benzothiophene ligand (Fig. 1b) and identified Ir(iqbt)$_2$dpm as the leading system with high NIR quantum efficiency of 16% and short radiative lifetime. Phosphorescent OLEDs were fabricated by solution processes and vacuum thermal evaporation showing state-of-the-art efficiencies exceeding 3% (Fig. 1b).[2]

Finally, in the last part of the talk is going to be outlined a novel development of the research where Ir(III) system are selected as bright emitters with variable visible emission color for electrochemiluminescence applications inside a PRIN 2017 project.[3]

(a) Aging on ***blue****-OLED: color and spectral alteration, FIrpic structures. (b) NIR emissive Ir(III) complex and its OLED application under IR camera.*



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Non Covalent Porphyrin Architectures From Structure To Applications

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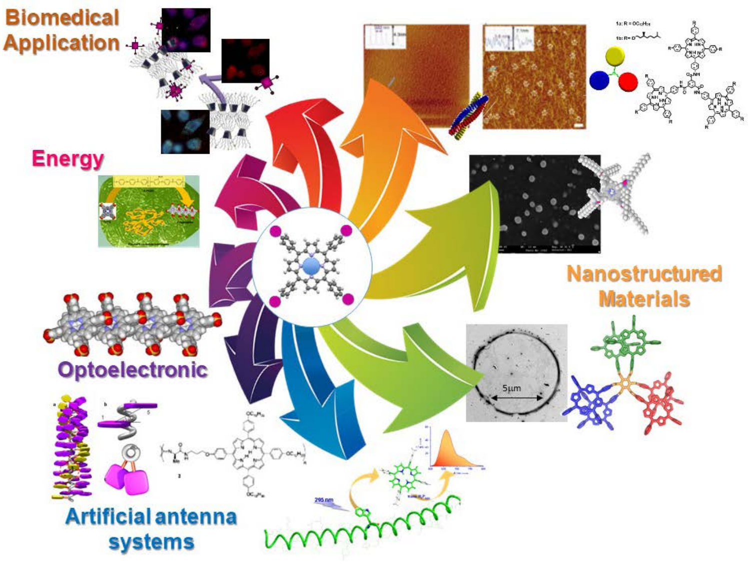
The remarkable recent progress in nanotechnology is mainly due to the ability to synthesize, investigate, and exploit materials with structural modulation on the nanometer scale. Porphyrins are well suited building blocks since they i) are relatively easy to synthesize; ii) show interesting and peculiar photophysical properties that can be tuned through careful choice of peripheral substituents and inserted metal ions and iii) are able to self-assemble spontaneously into dimers or higher aggregates through non-covalent interactions. Porphyrin structure features can be controlled in order to introduce and tune, in the self-assembled material, functional properties for a wide range of application spanning from catalysis, to sensors, optoelectronics or drug delivery. In particular, water soluble porphyrins are very interesting since, taking advantage of the self-correcting nature of the supramolecular interactions, defect-free structures can be achieved whose shape, size and photophysical properties are highly sensitive to external stimuli. In this framework, the water soluble tetrakis(4-sulfonatophenyl) porphyrin ($TPPS_4$) provides an iconic example of such behavior, since its diacid form, in particular experimental conditions, is able to self-arrange in well defined J-aggregates supramolecular structures. In the last decades, our investigations have been manly focused on $TPPS_4$ self-aggregation phenomena, supramolecular organization on biological matrices and in confined environments. The data reported on this system have allowed to gain important information in the field of supramolecular architectures, highlighting the importance of the role of experimental parameters such as concentration and/or mixing order of the reagents. Here we report a detailed kinetic investigations to demonstrate the fundamental role of the various factors in controlling the assemblies sizing and the expression and transmission of chirality at nano and mesoscopic scale.[1] Furthermore, we report on aggregation templated by inorganic nanoparticles to realize hybrids nanocomposite materials[2] and an interesting example of new composite membranes, successfully tested as proton exchange material in fuel cells (PEMFC) technology.[3]



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Recent Developments In The Preparation And Characterization Of Advanced Polymeric Membranes For Gas And Vapour Separation

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The growing threat of global warming and climate change necessitates a strong increment in the use of renewable energy and a strong reduction of greenhouse gas emissions. In this light, membrane processes are increasingly used in important emerging fields such as biogas upgrading, and they form one of the most promising approaches to achieve energy-efficient CO_2 capture. The development of new polymers with higher gas permeability and selectivity would further enhance the efficiency of other membrane gas separations of current industrial interest, including hydrogen recovery during ammonia production (H_2 from N_2), oxygen or nitrogen enrichment of air (O_2 from N_2) and natural gas sweetening (predominantly CO_2 from CH_4).
Increasingly, polymer membranes are also being considered as a practical alternative to solvent absorption for large-scale capture of CO_2 from power plant flue gas (predominantly CO_2 from N_2). For gas separations on such a massive scale, membranes with very high permeance *(i.e.* flux) are desirable to minimise energy costs for gas compression and to reduce the active surface area of the membrane, thereby optimising the overall size and manufacture cost of the membrane system. In this work we will show a number of the most recent developments in the preparation and characterization of high-performance gas separation membranes based on polymers of intrinsic microporosity (PIMs), and in advanced methods for the analysis of their performance. PIMs are characterized by a rigid and contorted polymer backbone, which prevents them from packing space efficiently, resulting in a low packing density and a high fractional free volume. In this work, we will discuss the development of polymers with increasing rigidity in the backbone [1] and with contorted structures or 2 dimensional chain structures that generate a particularly high fractional free volume, and thus a high gas permeability. Usually, the high permeability is associated with a low gas selectivity, or *vice versa*, and this trade-off behavior leads to an imaginary upper bound in membrane performance. Recently, in collaboration with researchers from the University of Edinburgh, we have investigated materials with greatly enhanced performance that break this upper bound [2]. For the complete understanding of the performance of such new materials, it is necessary to study the permeation of gas mixtures. In this light, we will show the results of a newly developed permeation setup with mass-spectrometric analysis of the gas composition, which yields not only the permeability, but also the unique diffusion coefficients of the individual mixture components in the membrane [3]. It will be furthermore shown how the gas transport correlates with the polymer's mechanical properties via the analysis of the Young's modulus, using an innovative method based on AFM force spectroscopy measurements.

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Spectroscopic Signature Of Quantum Dot Dimers At Subnanometric Interparticle Distance

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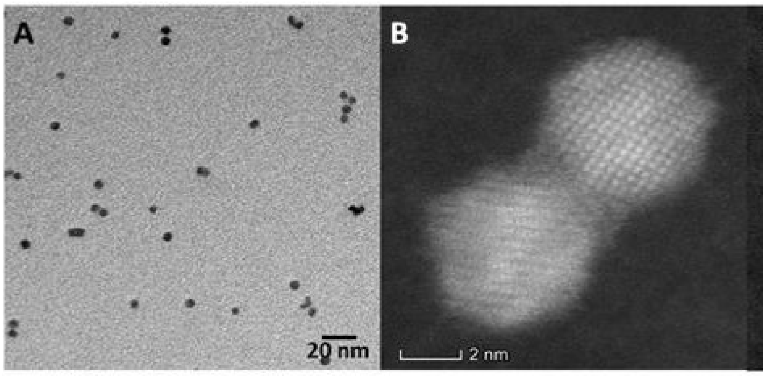
A growing interest has recently been devoted to the synthesis and organization of nanostructured materials. In nanoscopic regime, the electronic properties can be tuned by varying the physical size of the crystal, leading to new phenomena, as size-dependent optical transitions in semiconductor quantum dots (QDs), interesting for device applications. QDs synthesized by solution chemistry approach represent potential building blocks for inexpensive manufacturing of low cost and large area devices. Currently, intensive research has focused on the fabrication of QDs based organized meso-structures in solid state, which have shown new properties due to the collective interactions of nanoparticles [1]. While several studies described the coupling effects in QD disordered solid film [2], only few studies in literature concern the challenging fabrication and characterization of molecular assemblies composed of a low and controlled number of QDs interacting in solution. The investigation in solution of the properties of such QD based molecules can allow a better understanding of the mechanisms underlying the coupling of QDs, avoiding collective phenomena due to a large number of aggregated QDs in close proximity with each other. Here, dimers of CdSe QDs of the same size (homodimers) or of two different sizes (heterodimers) have been fabricated by using alkyl dithiols as bifunctional linkers, bridging the two nanoparticles. The assembled systems have been investigated by morphological (high resolution TEM) and spectroscopic (UV-Vis absorbance, stationary and time resolved photoluminescence spectroscopy) characterization techniques. The diverse alkyl chain lengths of selected dithiols allow to control and modulate the interparticle distance in the nanometric and subnanometric range.

The comprehensive spectroscopic investigation of the dimers shows inter-QD coupling phenomena ranging from energy transfer to tunneling of charge, depending from the interparticle distance. In addition, the QD size affects the exciton dissociation at subnanometric distance. The obtained results demonstrate as the control of the QD geometric parameters (size and distance) in dimers can strongly influence the transfer rate and the coupling efficiency among the nano-objects and, then, their electronic properties, with possible relapse in photonic or optoelectronic application. The preparative approach can be easily extended to colloidal nanocrystals of different size and composition, giving rise to a plethora of original and unexpected phenomena.



TEM (A) and HAADF STEM micrographs (B) of CdSe QDs dimers, linked with propanedithiol

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COMPUTATIONAL MODELING

ORAL COMMUNICATION

Innovative Methodologies And Challenging Applications Of Software For The Characterization Of Polycrystalline Compounds

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New and innovative crystallographic methodologies, associated with advanced computational tools, are developed at the Institute of Crystallography (IC-CNR) of Bari and implemented in computer programs. They are of great utility in several scientific and technological fields where the characterization of a polycrystalline material is necessary to understanding the problem under study.

The developed software are:
EXPO[1]: a computing program devoted to structure solution of materials available in the form of microcrystalline powder, by using X-ray diffraction data. The chemical formula and the experimental diffraction profile are the only information necessary to run it. EXPO is able to investigate small molecules (up to 100 non-H atoms in the asymmetric unit), inorganic, organic and metal-organic. It can execute, in a complete automatic way, all the steps characterizing the structure solution process and consisting of: 1) identification of crystal cell parameters; 2) determination of space group; 3) solution of crystal structure by locating the correct atom positions; 4) refinement of the final crystal model.

QUALX[2]: a software for identifying the crystal phase(s) present in a powder sample. It automatically performs: 1) the location of peaks in the experimental diffraction profile, 2) the subtraction of the background noise, 3) the search in crystal phase databanks. At the end of the process, QUALX brings out the chemical phase(s) which best match the peaks in the experimental pattern. In addition, it can query two databases: one commercial (PDF-2) and one free (POW_COD). QUALX is widely used in chemistry, pharmaceutics, mineralogy, forensic science, cultural heritage. An online version of QUALX is also available.

OChemDb[3](Open Chemistry Database): a new free web portal which has been developed for assisting in the crystal structure determination process by searching and analyzing crystal chemical information of organic and inorganic compounds. It provides statistics on desired distances, bond angles, torsion angles and space groups. OChemDb 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 developed is based on new theoretical algorithms and on the most recent and advanced programming languages. Free for academic and non-profit research institutions, it is supported by a high level of automatism and a graphic interface rich in tools, which makes its use simple also to non-expert in crystallographic knowledge. Moreover, it is continuously improved in terms of computational and graphic performances and tested on a large powder diffraction data bank.
For each software, examples of challenging applications by users around the world covering a wide range of scientific interests will be presented.

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Computational Tools To Investigate Structure And Chemical Ordering In Metal / Metal-Oxide Nano Particles

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Nowadays Nano Particles (NPs) play a fundamental role in both fundamental and applied research, due to peculiar effects related to nano confinement. Due to their reduced dimensions, precise atomistic information on NPs are difficult to achieve at the experimental level and, in this perspective, computational tools based on molecular modeling can provide important information on several aspects such as: nucleation and growth mechanisms, stoichiometry, structural arrangements driven by kinetic/thermodynamic factors, chemical ordering. The precise control of all these features in the synthetic preparation of NPs are of crucial importance, due to the close relations between them and the responsive properties of these systems when subjected to an external perturbation.

In this presentation an overview of the latest computational algorithms, employing both un-reactive and reactive (ReaxFF) force-fields, developed in our group will be presented, aiming at the investigation of: a) the growth modes of metal-oxide NPs of 1st row transition metals [1-2]; b) the chemical-ordering patterns which can be found in alloyed (transition-metal) NPs (nano-alloys) [3]. More specifically, regarding point a), it will be shown how the computational procedure has to be specifically tailored when simulating two completely different reactive environments: the growth of zinc oxide NPs in a high-T gas-phase plasma reactor [1] or the formation of iron oxide NPs in a solution environment from the decomposition of organo-metallic precursors in low-T conditions [2].

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CHEMISTRY FOR CULTURAL HERITAGE

ORAL COMMUNICATION

Unveiling The Composition Of Iconic Objects Of The Italian Design Through MOLAB Access To Non Invasive & Portable Spectroscopies

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The Italian Triennial Design Museum, inaugurated in 2007, is the first Italian design museum. It houses a wide collection of iconic objects (furniture, accessories and electronics) dating from 1927 to the present day and representing the history of Italian design. Aimed at safeguarding and preserving the numerous items made using different types of plastics, the museum recently started a research project to unveil the composition of some of the plastic objects with unknown or uncertain composition. Due to the impossibility of moving the objects and even more to take (micro)-samples the use of non invasive and portable analytical methods was mandatory. Driven by these needs, the museum asked for the access to the mobile laboratory MOLAB of the E-RHIS infrastructure (www.e-rihs.it).

Among the available portable non-invasive analytical techniques of MOLAB, vibrational spectroscopy FT-IR in reflection mode exploring the 4000-400 cm^{-1} range already demonstrated to be a valid tool for determining the class of polymers [1-2]. In the present paper new results from the use of non invasive FT-IR reflection spectroscopy extended to the wider infrared range 10000-400 cm^{-1} (including a portion of the near IR) are presented. Spectral interpretation was performed by comparison with the spectra recorded from the reference ResinKit TM collection both in transmission and reflection modes. No spectral correction (namely Kramers Kronig) was applied to the reflection spectra of the polymer references and museum objects since the co-presence of both surface and the volume reflections [3]. The combined exploration of mid and near FT-IR integrated spectral ranges allowed identifying the nature of the polymer- including variations within the same class of materials - and unveiling mismatching with respect to the compositions reported in the catalogues. The analytical approach also proved to be a valuable tool for highlighting signs of (photo)degradation of acrylonitrile-butadiene-styrene (ABS)-based polymers in non invasive way. X-ray fluorescence (XRF) spectrometry completed the characterization of inorganic fillers, as well as the inorganic pigments for colored objects.

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The authors wish to acknowledge MIUR for e the access to MOLAB at the Italian node of E-RIHS. IPERIONCH (Integrated Platform for the European Research Infrastructure ON Cultural Heritage), funded by the European Commission (H2020-INFRAIA-2014-2015, GA n. 654028) is also acknowledged. The author thanks Prof. E. Richardson, Head of the Material Studies Laboratory at UCL, London UK, for providing the ResinKit reference samples

Active Multifunctional Materials To Inhibit Degradation Processes: From Remedial To Preventive Conservation

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The reliable and long-lasting conservation of cultural heritage is still a critical issue and new sustainable solutions are necessary to preserve them for future generations. Both archeological and modern artworks are typically affected by complex degradation phenomena that can compromise their chemical-physical stability. Among these phenomena, corrosion processes are receiving great attention since they can induce irreversible damages in valuable metal objects, including for example bronze and silver artefacts. Moreover, it is important to highlight that corrosion is also one of the main degradation causes in concrete monuments since can induce serious and visible damages, such as cracking and spalling of concrete cover.

Nowadays, the identification of new conservation strategies, more reliable and effective than state-of-art solutions, is still necessary in order to avoid the loss of unique and valuable cultural heritage based on metals, including metal objects and concrete monuments. In order to face these issues, our research efforts have been addressed to the development of active protective materials with multifunctional properties that can provide long-lasting protection, environmental sustainability and cost-effectiveness by preserving the aesthetic features of artworks [1-3]. In the case of metal works of art, active protective coatings were successfully developed by using stimuli responsive nanocarriers able to release protective molecules only under stimuli related to corrosion processes. The nanocarriers were embedded into a green polymer matrix and can take advantages from the use of multilayered systems.

Based on these findings, stimuli responsive materials were proposed and optimized for the conservation of concrete monuments within the EU InnovaConcrete project. The first step was a proper selection of corrosion inhibitors to protect the steel reinforcements and then the inhibitors were confined into nanocarriers able to release them under stimuli related to degradation processes occurring in reinforced concrete. To achieve a long-term protection, the nanocarriers acting as inhibitor reservoir are incorporated into consolidants thus producing innovative multifunctional systems. After laboratory validation, the optimized products will be applied on European XX century concrete monuments identified as representative case studies. The case studies in Italy include: i) War Memorials selected for their social values, as symbol of collective identity of European citizens, and ii) Flaminio Stadium as relevant monument designed by Pier Luigi Nervi.

These approaches based on nanostructured materials opens the way to novel scenarios for the preventive conservation of cultural heritage. Specifically, the ability of smart materials to selectively interact with degrading species, dangerous for the artworks, can be used to create a stable microenvironment for stored and displayed artefacts. This issue is addressed within the EU APACHE project aimed at the development of active/intelligent packaging materials and display cases.

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CHEMISTRY FOR LIFE SCIENCES

ORAL COMMUNICATION

Molecular And Structural Basis Of Dystroglycanopathies

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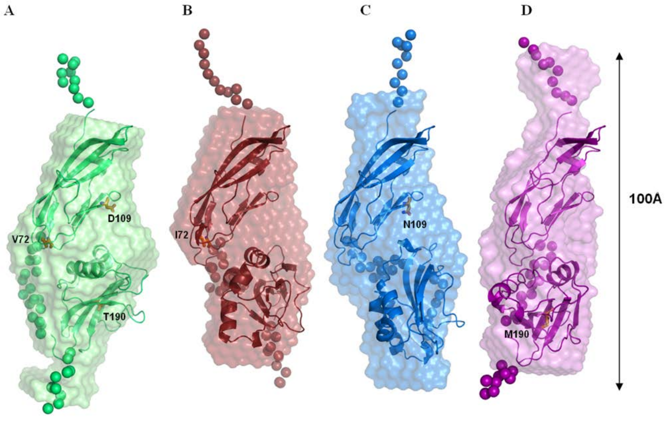
Dystroglycanopathies are neuromuscular disorders associated with abnormal neuronal migration and muscular dystrophy. Clinical manifestations are extremely variable, and include a wide spectrum of phenotypic severity. Dystroglycanopathies are mainly due to abnormal glycosylation of dystroglycan (DG) which is a cell-surface glycoprotein that links the cytoskeleton with the extracellular matrix acting as a receptor for extracellular matrix proteins containing laminin-G domains. Dystroglycan is composed of two subunits: the extracellular highly glycosylated α-DG and the transmembrane β-DG. A multistep glycosylation process is necessary to decorate the α-DG subunit with complex glycans that are crucial for its interaction with the extracellular matrix proteins, such as laminins. Most of the dystroglycanopathies are due to an impaired functional state of the enzymes involved in α-DG maturation. Nevertheless, a set of missense mutations has been recently identified on the N-terminal region of α-DG (a.a. 50-313 in mouse) that determine the hypoglycosylation of the DG complex, due to the impairment of a key step in α-DG glycosylation operated by the bifunctional glycosyltransferase LARGE1. Moreover, a point mutation (C667F) affecting β-DG has been described to lead to a severe pathological state that is not a congenital disorder of glycosylation.

With the aim of elucidating the molecular and structural implications of the pathological mutations leading to dystroglycanopathies, we have undertaken a multi-technique study, including synchrotron radiation approaches to gain insight on the molecular structure of biological macromolecules in both crystals and solution. Indeed we determined the high resolution molecular structures of α-DG point pathological mutants by X-ray crystallography. Moreover, Small Angle X-ray Scattering (SAXS) has been employed as a complementary approach to get low resolution information on the conformations and the structural organizations of α and β DG mutants at near-physiological conditions. The results of the synchrotron radiation -based experiments, combined with biochemical, cellular and microscopic data, allowed us to shed light on the molecular and structural basis of dystroglycanopathies.



Comparison of the structural models of the WT (A) and the three pathological mutants of α-DG-Nt: V72I (B), D109N (C), T190M (D)

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Discovery Of A Selective NEK6 Kinase Inhibitor: Toward Precision Medicine Against Solid Tumours

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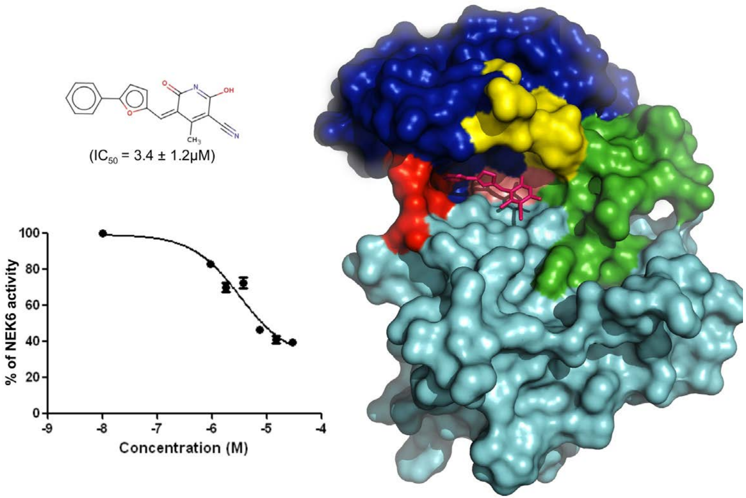
Several therapeutic strategies have been proposed for targeting the cell cycle in cancer. However, these drugs have lacked the therapeutic index which is necessary to obtain a robust response against cancer cells with little or no cytotoxic effect on normal cells. Thus, the next generation of anti-mitotic drugs will need to target cell-cycle features characteristic of tumor cells such as defective checkpoints in mitosis which are deregulated in cancer cells and whose regulators represent potential targets for the design of cancer selective therapies. Among these emerging targets NIMA-related kinases, or NEKs, have been demonstrated to have important roles in cell cycle control. In particular NEK6 was shown to be involved in cell cycle progression and contribute to the establishment of the microtubule based mitotic spindle thus emerging as a promising target for personalized therapies in oncology [1]. The selective inhibitors of NEK6 may therefore become important compounds for identifying novel therapeutic agents. To date none of the natural and synthetic molecules with inhibitor activity on NEKs, reported in the literature, has entered clinical trials for the treatment of cancer. In an effort to identify novel and more efficient NEK6 inhibitors we performed a computer-aided drug design (CADD) study on a model structure of NEK6 generated by molecular modelling, adopting both structure- and ligand-based techniques. *In silico* and experimental screening lead to the identification of a number of hit compounds and, among these, (5Z)-2-hydroxy-4-methyl-6-oxo-5-[(5-phenylfuran-2-yl)methylidene]-5,6-dihydropyridine-3-carbonitrile), which demonstrated to selectively inhibit NEK6, with respect to the homologous NEK7, at micromolar order of magnitude [2,3]. Notably, this compound shows antiproliferative activity against a panel of human cancer cell lines, and displays a synergistic effect with cisplatin and paclitaxel in a BRCA2 mutated ovarian cancer cell line, thus supporting a possible use for personalized therapy.



The identified inhibitor of NEK6 activity. The orientation of the compound within the NEK6 ATP binding pocket, in solid surface representation, is also shown.

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Cyclodextrin Nanomagnetes Decorated With Peptides: From Aβ-Amyloid Detection To Theranostic

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Magnetic nanoparticles (MNPs) are widely utilized in magnetic-field-assisted bio-separation, bio- interaction, imaging and drug delivery, due to their large surface area and easy manipulation by an external magnetic force. MNPs, stabilized with different capping agents and incorporating drugs, were designed as nanotheranostic. In this context, cyclodextrin-based MNPs offer a multipurpose chance in detection, therapy and imaging, since cyclodextrins (CDs) can strongly entrap in its cavity hydrophobic guests to optimize molecular recognition of biomarkers or for sustained therapeutic action in the site where they are directed with the help of the magnetic field and / or serving as contrast agents in magnetic resonance imaging (MRI) . Amphiphilic cyclodextrin (aCD) are efficaciously engaged to entrap and control deliver of drugs and diagnostic probes [1]. Here we propose MNP covered with aCD nanomagnets (aCD is heptakis (2-oligo(ethyleneoxide)-6-hexadecylthio-)-β-CD (SC16OH)) (MNP@SC16OH) and tailored with Adamantanil-(PEG)4-KLVFF (Ada-Pep) for recognition and detection of Amyloid-β(1-42) protein (Aβ(1-42)). MNP@SC16OH/Ada-Pep were prepared by hydration of an organic film of Ada-Pep with a dispersion of pre-made-up MNP@SC16OH. Hence, modified MNPs were isolated by magnetic-filed separation, centrifugation and fully characterized [2]. Furthermore, we investigated the ability of system to fish out Aβ(1-42) from samples prepared in aqueous solutions and analysed by MALDI-TOF MS. Our results indicate that in our experimental conditions the nanomagnets can perform an unbiased Aβ(1-42)-targeted fishing. Moreover the effect of nanomagnetes in delivery of anticancer drugs as sorafenib in hepatocellular carcinoma (HCC) cells as well as in *in vitro* enhancement of MRI relaxivity was investigated [3]. Altogether, results indicate the potential utilize of these nanomagnets based on cyclodextrins as therapeutic and imaging agents.

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Selective Response Of Healthy And Cancer Osteoblast Cells To 2D Black Phosphorus

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Introduction:
Currently, osteosarcoma is the most common bone cancer which mainly affects young people. Surgical resection of tumor followed by chemotherapy for micro-metastasis inhibition constitutes the current standard procedure. However, chemotherapy treatment uses pharmacological agents with the effect of blocking cell proliferation, without any distinction between healthy and cancer cells. In recent years, several studies have focused the attention on the use of Photodynamic Therapy (PDT) as minimally invasive therapeutic procedure that can apply a selective cytotoxic activity toward cancer cells [1]. In this context, we propose the use of 2D substrate based on few-layer black phosphorous (2D bP) as an alternative tool for osteosarcoma treatment and report how 2D bP can inhibit cancer cell proliferation and in the same time to stimulate newly forming bone tissue generation after osteosarcoma resection [2] without photothermal treatment. In our study, we have developed an in vitro model to evaluate the efficacy of 2D bP material with and w/o near-infrared light irradiation treatment on healthy (HOb, hMSC) and cancer (Saos-2) cells and we also propose an *in vitro* co-culture model (SAOS-2 and HOb cell lines) to study the effect of 2D bP on inflammatory response related to cancer.

Experimental methods: The biological studies were performed to investigate the effect of 2D bP on cell proliferation and osteogenic differentiation of human healthy (hMSC and HOb) and cancer cells (SAOS-2) with and without near-infrared irradiation treatment (NIR). The cell morphology was evaluated by SEM, confocal microscopy and hematoxylin-eosin staining. The biocompatibility and osteogenic differentiation were checked in vitro by Alamar blue assay and ALP activity, respectively. Furthermore, the reactive oxygen species (ROS) production was evaluated with and w/o NIR treatment by in vitro model inflammation. The effect of 2D bP on inflammatory response through pro and anti-inflammatory cytokine investigations on co-culture model consisting of SAOS-2 and HOb, was also investigated.

Results and discussions: Our investigations suggested that NIR had no effect on HOb proliferation because 2D bP without NIR stimulation promoted the HOb viability with the best expression of early marker of osteogenic differentiation at day14, thus inducing higher proliferation values than control. Conversely, 2D bP with and without NIR, induced a significant reduction in SAOS-2 proliferation and inhibition of ALP activity. Furthermore, 2D bP is able to increase anti-inflammatory cytokines generation on co-culture model and to inhibit pro-inflammatory mediator synthesis thus suggesting the opportunity to prevent cancer-related inflammation. This study demonstrated that 2D bP enhances the growth and osteogenic differentiation of human healthy cells (HOb and hMSC) and inhibits the proliferation of osteosarcoma cells (SAOS-2) without NIR treatment. The inhibition of cell proliferation (SAOS-2) of 2D bP reveals its anti-inflammatory activity on an in vitro co-culture model of cancer-related inflammation.

Conclusions: The role of exfoliated black phosphorous (2D bP) as a substrate for an experimental *in vitro* model of osteosarcoma (SAOS-2) was investigated. Its effect was also analyzed on healthy bone derived cell line (HOb) in order to test its potential toxicity on tumor-surrounded tissue. The beneficial effects of 2D bP, from one side the enhancement of HOb growth and the osteogenic differentiation, in the other side the inhibition of SAOS-2 proliferation by blocking inflammatory processes without any photothermal treatment, prompt the application of 2D bP as a highly promising candidate for bone biomedical applications.

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Synchrotron Radiation Circular Dichroism (SRCD) UV Photostability Assay: A Useful Tool To Study Protein Oxidative Stress Damage

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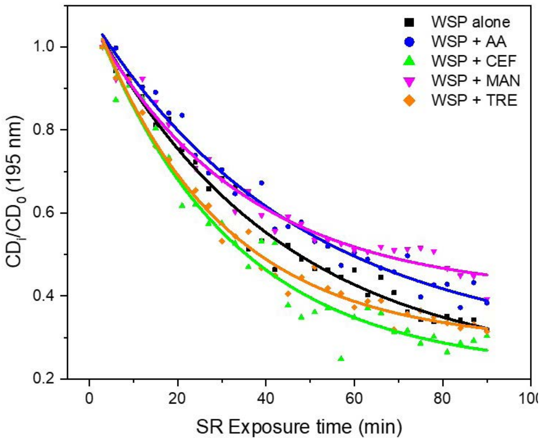
Circular dichroism (CD) spectroscopy is a valuable biophysical tool for studying biomolecules structures. A major practical limitation of CD spectroscopy is represented by the low intensity of light source in benchtop instruments. The use of synchrotron radiation as light source has improved the measurements, expanded the types of samples that could be examined and consented to extend the range of analysis in the vacuum-UV region, leading new applications in structural and functional genomics [1]. The high beamline brilliance and photon flux of the third generation Diamond Light Source synchrotron allowed developing at the B23 beamline a novel method to evaluate protein stability, based on the acquisition of a greater number of repeated scans in the far-UV region [2, 3]. This would cause damage to the protein during the time of data acquisition with a loss of the secondary structure. The rate of protein denaturation is greatly influenced by the presence of ligands enabling the assessment of the potential binding property of small molecules to proteins or peptide. Recently, we demonstrated that the mechanism of structure denaturation of proteins induced by VUV and far-UV irradiation were not originated by local heating of water molecules bound to the proteins but mediated by the formation of reactive free radicals (FR) and reactive oxygen species (ROS). UV photostability assay has been successfully used to assess and characterize the photostability of protein formulations, also mimicking oxidative stress damage, and ligand binding interactions, in particular for ligand molecules devoid of significant UV absorption.

Oxidative stress is involved in the pathogenesis of many ageing diseases, photo-oxidation, and photosensitizers may be activated by UV irradiation and are affected by the photo-stability of proteins. The understanding of the mechanisms that govern the protein photo-stability is essential for its control enabling enhancement or reduction.

Here we will discuss the photostability of eye lens water-soluble proteins, named crystallins, involved in the onset of cataract, and the protective effect of antiamyloidogenic (ceftriaxone, mannitol and trehalose) or radical scavenger (ascorbic acid) molecules, as well as the influence of the medium in the ROS production.



Plot of the SRCD intensity change at 195 nm for WS lens proteins alone or in presence of small molecules: ceftriaxone (CEF), mannitol (MAN), trehalose (TRE) or ascorbic acid (AA).

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Ti And Fe Doped Hydroxyapatite: Novel Biomimetic Hybrid UV-Filter For Sunscreen Formulation

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The use of sunscreens as protective barriers against skin damage and cancer, by absorbing harmful UVA and UVB rays, is becoming an increasingly important issue; such products are usually containing titanium dioxide (TiO2) or zinc oxide (ZnO) as physical filter [1]. TiO_2 is able to reflect, scatter and absorb UV radiation, thus preventing sunlight-related skin disorders such as sunburn and skin photodamage. However, TiO_2 is well known to generate reactive oxygen species (ROS) under photoexcitation, it has to be chemically modified when used in sunscreens [2]. Calcium phosphates (CaPs), especially hydroxyapatite (HA) have been deeply investigated for several applications in biomedical field and nanomedicine due to their high biomimicry and biocompatibility. An interesting feature of biomimetic HA is to incorporate some foreign ions in its lattice, in fact, in the past years we developed a number of protocols for the incorporation of different kind of ions (e.g. Mg, Sr, CO_3, and Fe) and the achievement of multifunctional products for regenerative- and nano- medicine [3]. Regarding sunscreens, unmodified HA, however, does not absorb in the UV range, so it is necessary to modify its structure to obtain a UV-absorbing material. Doping with appropriate elements may provide final compound with promising UV protection. In this study two different hybrid materials were successfully developed exploiting the biomineralization process; one is composed of alginate and Ti-doped HA (alg-TiHA) and the other is composed of alginate and Ti and Fe-doped HA (alg-FeTiHA). During the mineralization process the mineral phase is nucleated on alginate molecules blocking the particles' due to growth and allowing the formation of nanocrystals merged in the polymer matrix suitable to be dispersed in sunscreen cream without damaging skin for the penetration of nanoparticles. Deep investigations were performed to evaluate the particles' morphology (ESEM), chemical properties (XRD, FTIR, TGA) and interaction with UV-VIS radiations (adsorption spectra and photodegradation potential). Results demonstrate that the sample with alg-TiHA revealed a high reflectance in the UVA and UVB range, however, the sample with alg-FeTiHA showed a good absorption only in UVB. Although the worst properties of alg-FeTiHA in terms of reflectance index, its combination with alg-TiHA is important because the presence of Fe ions provide for a brown color range avoiding the whitening effect typical of highly protective sunscreen. Furthermore, both samples do not show photocatalytic effect thus avoiding the formation of radicals and/or reactive species under irradiation and highlighting their potentiality for innovation in sunscreens. In conclusion, we developed hybrid materials capable to protect by UVA and UVB ray, avoiding the whitening effect and the photocatalytic effect which can damage the tissues provoking skin disease.

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GREEN CHEMISTRY

POSTER COMMUNICATION

Influence Of Cocatalysts And Polymerization Conditions On Properties Of Polyesters From ROCOP Of Epoxides And Cyclic Anhydride

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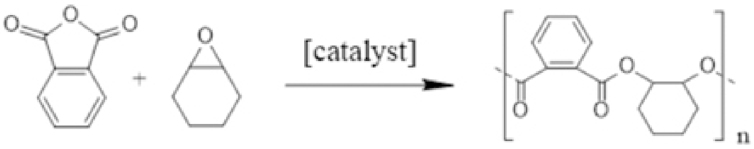
Aliphatic polyesters (PEs) are an appealing class of polymers used in a range of applications such as biomedical devices and bulk packaging owing to their excellent properties and general biocompatibility [1]. Alternating ring-opening copolymerization (ROCOP) of epoxides and cyclic anhydrides (Figure 1) is becoming an attractive method for the synthesis of PEs. However, one of the major challenges faced with ROCOP is that the PEs synthesized via this technique are typically of low number average molecular weight (Mn) that leads poor mechanical and thermal properties and thus limits their applications [2]. In recent years, numerous organometallic catalysts have been developed for the epoxide/anhydride copolymerization, many of which showed markedly higher activity with the addition of a nucleophilic co-catalyst [3].



Ring Opening Copolymerization (ROCOP)

The influence of co-catalysts and polymerization conditions to obtain alternating polyesters with Mn > 10000 g/mol and Tg > 80 °C by ROCOP polymerization with commercial catalysts have been investigated. Cyclohexene oxide (CHO) and Phthalic anhydride (PA) have been reacted in the presence of salen – type complexes of three different metals Cr (1), Al (2), and Mn (3) in combination with DMAP, PPNCl and $PPNN_3$ as cocatalysts.

The polyesters were characterized by size exclusion chromatography (SEC), differential scanning calorimetry (DSC) and nuclear magnetic resonance (NMR). This research work offers access to PEs with good thermal and molecular weight properties suitable for practical applications. Moreover, the percentage of biodegradation of selected polyesters have been determined according to ISO 14851.

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Quaternary Phosphonium Halides As Cocatalysts For Cyclohexene Oxide/CO_2 Copolymerization

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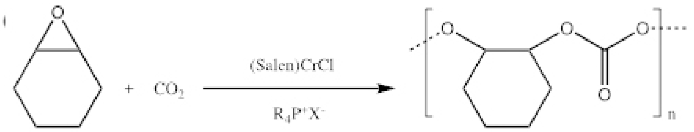
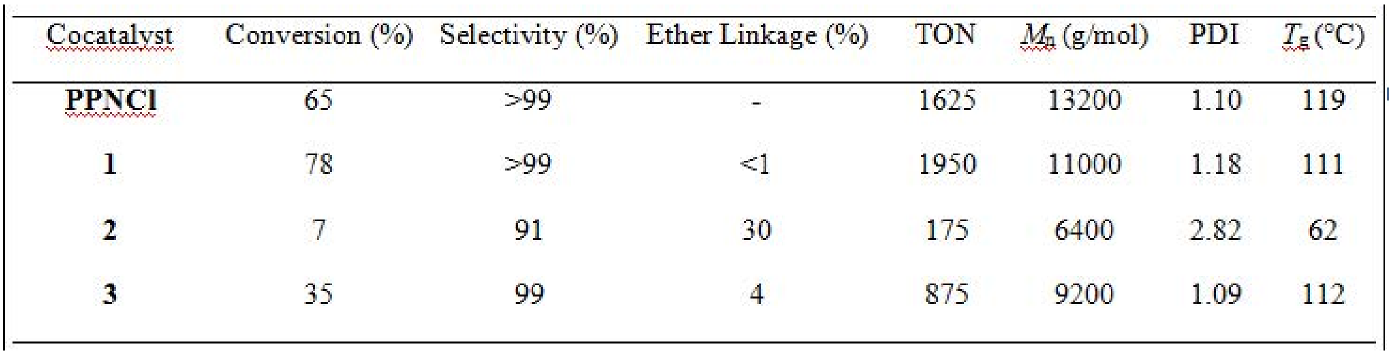
The quaternary organic phosphonium salts 1, 2 and 3 have been tested in conjunction with a chromium Salen complex in the alternating copolymerization of CO_2 and cyclohexene oxide, CHO (Figure 1). Of these, triphenyl(4-pyridinylmethyl)phosphonium chloride hydrochloride 1 can compete with the more traditional PPNCl cocatalyst. Highly efficient formation, in terms of TON and selectivity over cyclic carbonate, of atactic polycarbonates characterized by narrow distribution and molecular weights comparable to those obtained with the reference salts was achieved (Table 1).



Coupling of cyclohexene oxide with CO_2 mediated by SalenCrCl and cocatalysts 1, 2, and 3

Table 1. Coupling of cyclohexene oxide with CO_2 mediated by SalenCrCl and cocatalysts 1, 2, and 3.



Cocatalyst	Conversion (%)	Selectivity (%)	Ether Linkage (%)	TON	M_n (g/mol)	PDI	T_g (°C)
PPNCl	65	>99	-	1625	13200	1.10	119
1	78	>99	<1	1950	11000	1.18	111
2	7	91	30	175	6400	2.82	62
3	35	99	4	875	9200	1.09	112

Remarkably, the use of FTIR/ATR spectroscopy on the *pretreated* catalytic system can reliably predict the success of the copolymerization before the actual introduction of the epoxide monomer.

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Bio-Polyol Grafted On Nanocrystalline Cellulose As Reactive Filler In Polyurethanes Foams

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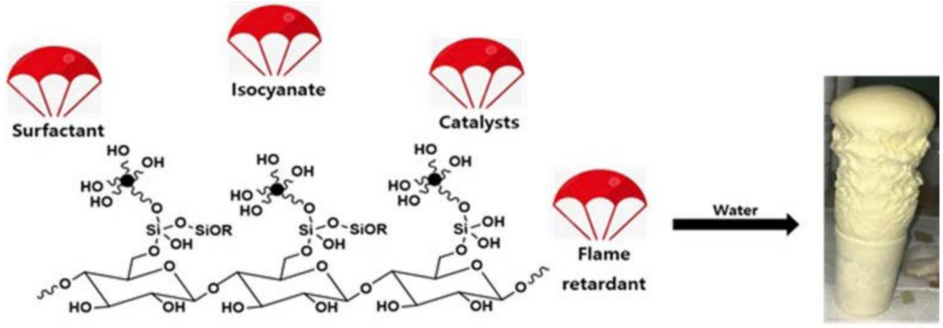
Over the last several years many publications have focused on sustainable monomers to synthesize polymeric materials such as bio-based polyurethane foams (PUs). PUs is a class of materials with a lot of industrial applications (from insulation panels, structural reinforcement, sandwich construction to medical application)1 and are generally composed by polyol, isocyanate and several additives. PUs mechanical and functional properties are determined by the typology of polyols and isocyanate precursors, the distribution of the soft and hard segments from which PUs are composed and by the morphological structure in terms of open or closed cells. To avoid the problem of the big amount of chemicals produced from petroleum source, such as polyols and isocyanate utilized in the PUs formulation (the goal to produce sustainable PUs where both precursors are obtained from renewable resources is still a challenge), nanoparticles made from green and renewable materials are added replacing partially the polyol. Furthermore, by modifying the surface of nanoparticle with isocyanate functional group also the amount of isocyanate can be reduced. An example of suitable nanoparticles that could be used is nanocrystalline cellulose (CNC). The combination of cellulose properties, such as low cost, chemical modification capacity, high Young's modulus, biodegradability, and abundance in nature, with features of the nanosized materials such as very large specific surface area, high aspect ratio, light weight, and outstanding reinforcing potential2 justifies the big interest of scientists towards this issue. On the other hand, the cellulose hydrophilicity leads a bad dispersion in non polar matrices, the consequential nanocrystal aggregation decreases thermo-physical and mechanical properties of the nanocomposite3.

Herein, we propose the use of modified CNC (m-CNC) as reactive filler in polyurethane foams (PUs, fig. 1). To overcome the cellulose hydrophilicity, the CNC has been modified by linking covalently the bio-polyols on the m-CNC surface. In our strategy the silylation reaction in water to modify the surface of CNC followed by bio-polyol grafting was used. The CNC-grafted-polyols has been tested in the preparation of different composite PUs.



PUF synthesis using CNC-grafted-polyol.

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Biocompatibility Or Compostability: Which is the Real Meaning? Some Experiences Of Scientific Divulgation

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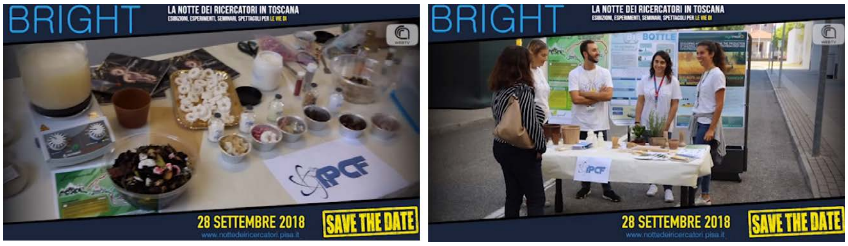
The question of waste management and disposal over the years has taken on an ever greater dimension at national and international level. In addition to the need to promote an economy that can minimize waste production by encouraging reduction and re-use, it is still important to support research into the development of "green" materials which therefore has a zero environmental impact both in terms of production that end of life, for example by promoting the recycling of plastic materials through an adequate recovery of the same and enhancing the waste materials. No less important are the information and training initiatives aimed at changing the still life: education for sustainable development today becomes a strategic objective for the present and for the future of the human species.

Therefore, the activities of information that researchers operating in the synthesis and/or modification of polymeric materials can do to make the consumers aware about the characteristics of the products and how they can be disposed at their end-of-life become important. With the entry into force of the Italian Legislative Decree in August 2017 which introduced the use of ultra-light biodegradable and compostable shoppers but also with the realization of environmental protection campaigns aimed at reducing the use of plastic from fossil fuels, a generalized disinformation emerge on the definitions of biodegradability and compostability.

In particular, the research activities carried out at the Institute for Chemical-Physical Processes and the skills acquired during the development of FP7 Leguval and BBI Agrimax projects on the valorization of waste coming from agriculture or from the canning industry for the realization of new materials with low environmental impact have found a strong response in the public opinion. With the entry into force of the Italian Legislative Decree in August 2017 which introduced the use of ultra-light biodegradable and compostable shoppers and environmental protection campaigns aimed at reducing the use of plastic from fossil fuels, a generalized disinformation emerged on the definitions of biodegradability and compostability.

The result was a training activity through participation in public events, the request of schools to visit the facilities of the Institute where these activities are used.

Furthermore, since last year, these activities are also organized within an environmental awareness program (Win on Waste-WOW) during the Researchers' Night in which the IPCF operates in collaboration with technicians and technicians of other CNR institutes of Pisa (besides IPCF, ICCOM, IBF, IFC, IGG, IIT, IRET, ISTI) and one from La Spezia (ISMAR).



Some pictures of the training activities during Bright 2018 given by the IPCF's researcher

References:

http://www.cnrweb.tv/bright-2018-la-notte-dei-ricercatori-al-cnr-di-pisa/

Acknowledgement:

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Textile Industry And Sustainability: New Challenges From Unexploited Natural Fibers

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Environmental awareness has prompted many industries, particularly in developed countries, to consider more sustainable ways of operating. Now, industries increasingly are looking directly at natural materials in a more positive and proactive manner: they are considered not only as technically valid components, but also as elements that can contribute to the premium pricing of final products because of their superior environmental attributes and their compatibility with socially responsible production and disposal requisites [1].

The textile industry, more specially, has a high environmental impact and is responsible for a significant amount of waste. Today, it creates more plastic waste than Germany's urban waste and consumes more oil than the whole of France. This can be attributed to the massive production and consumption of synthetic fibres. The industrial revolution, the invention of synthetic fibres and ultimately fast-fashion trends have amplified the impact of the textile industry that has even expanded to include industrial applications as airplanes, cars, machinery and construction goods.

Nowadays, there is an emerging demand for sustainable textiles, which a number of key industries are well placed to develop and promote to consumers. For thousands of years the textile industry has developed around traditional natural fibres: cotton, wool, silk, and flax. The new challenge for research is to find the ideal natural fiber unexploited—organically cultivated with zero or minimal artificial assistance, ethically manufactured, sustainable, processed without chemical aid, with reusable by-products, and completely biodegradable. So, many new plant fibers, such as hemp, pineapple leaf fiber, banana fiber, bamboo fiber, kapok fiber, apocynum, mulberry bast fiber and so on, have been evaluated in recent years. Among the conventional and unconventional fibers many of them are still in the research level. The commercialization of the product or development of fibers in the industrial aspect or in the bulk quantity is not achieved due to the technical problems or to inadequate supply of raw material [2]. Especially in the unconventional fibers, the availability of the raw material is in abundance, whilst the utilization in the manufacturing sector is very meager. Hence, the opportunities in this unconventional fiber research opens a new era. At the same time, unlike the synthetic or artificial materials the impact of those products on the environment and ecosystem is considerably less. The research is focused on reducing the carbon footprint of the individual manufacturing process of the material, from plant cultivation to fabric manufacture rather than the cost reduction by using artificial materials and process.

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Sustainable Synthesis And Characterization Of Honokiol, Magnolol Derivatives And Their Anti-Fungal Effect On *Fusarium* Isolates Of Clinical Relevance

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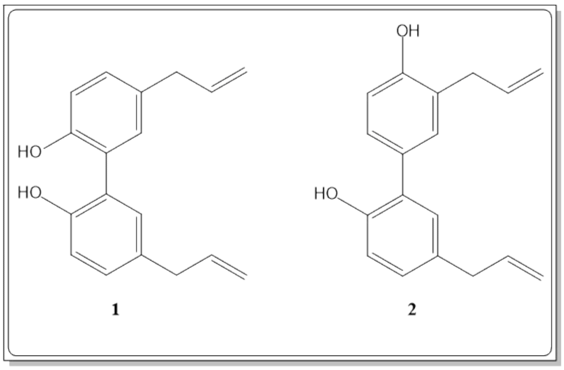
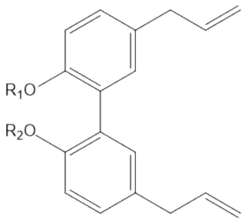
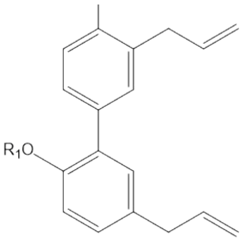
Fusarium spp. are common human pathogenic fungi implicated in invasive mycoses and infections. In humans, *Fusarium* spp., particularly F. *verticillioides*, F. *solani* and F. *oxysporum*, are frequently reported as the cause of several dermatological affections such as onychomycoses and paronychia, but they may also induce keratitis episodes, mainly as a consequence of contaminated lens solutions.

In our previous studies, devoted to the search of effective sustainable fungicides in agriculture, we have observed antifungal activity of magnolol **1** and honokiol **2** against F. *graminearum* and F. *culmorum in vitro* [1] and *in silico* [2]. Magnolol **1** and honokiol **2** are two hydroxylated biphenyls representing the main components of the bark of *Magnolia officinalis*. These compounds have long been important substances in traditional chinese and Ayurvedic medicine due to their wide biological activities. Magnolol **1** manifested the highest anti-fungal activity among a wide range of natural occurring phenols and it is generally recognized as harmless for humans and animal as well as its isomer honokiol **2**. Unfortunately, the poor aqueous solubility of these two hydroxylated biphenyls has hampered their broad clinical application.





3 $R_1 = H$, $R_2 = COCH_3$, magnolol monoacetate
4 $R_1 = R_2 = COCH_3$, magnolol diacetate
5 $R_1 = H$, $R_2 =$ glucosyl, magnolol mono glucopyranoside



6 $R_1 = COCH_3$, $R_2 = H$, honokiol 2-monoacetate
7 $R_1 = H$, $R_2 = COCH_3$, honokiol 4'-monoacetate
8 $R_1 = R_2 = COCH_3$, honokiol diacetate

This study shows a synthetic strategy to improve the bioactivity of magnolol **1** and honokiol **2** by transformation of their hydroxyl groups in an ester group or in an acetal group with a glucosyl unit. The synthetic methodology presented followed diverse sustainable and practical approaches, including the use of green reaction media and alternative technologies such as microwave.

Magnolol **1**, honokiol **2** and their derivatives **3-8** were tested for their anti-fungal activity and specificity towards human and nosocomial isolates and their activity was compared with that of terbinafine and fluconazole, two conventional fungicides [3].

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Acknowledgement:

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SIPCAM ITALIA S.p.A. for **PhD** Research *Fellowship* (SO).

Valorization Of Agro-Food Products And By-Products By Membrane-Based Processes: A Sustainable Approach

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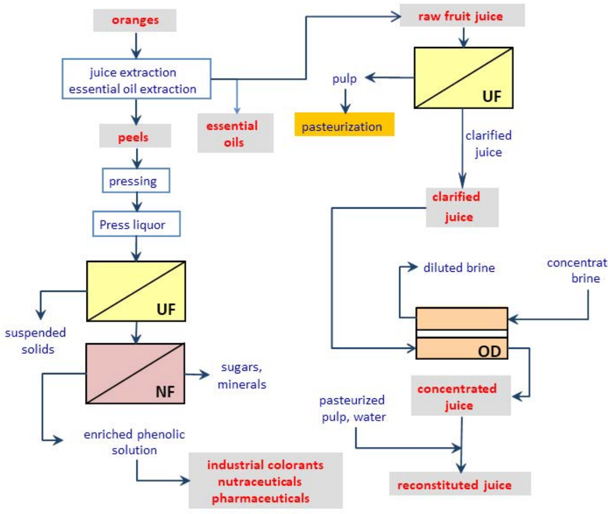
With a market volume of 800-850 million of Euro/year, the food industry represents the second biggest worldwide industrial market for membranes after water and wastewater treatment with a growth of around 7.5% per year [1]. Pressure-driven membrane operations such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are key technologies in the food industry. The basic properties of these processes make them ideal for the treatment of both food products and by-products; high selectivity, minimization of thermal damage, low energy consumption, modularity and easy scale-up, no phase change and use of chemical additives are typical advantages over conventional separation technologies. Other membrane processes, such as membrane bioreactors (MBRs) and membrane contactors (MCs), have been also investigated in recent years for selected applications in the food industry.

The selection of membrane materials and the optimization of operating conditions are key factors in order to improve the efficiency of these processes in terms of productivity and selectivity through the control of concentration polarization and membrane fouling phenomena. Several processes have been investigated at ITM-CNR in the last years in order to improve the quality of food products (i.e. clarification and concentration of fruit juices, wine and must, etc.), as well as to valorise typical wastes of the agro-food production through the recovery of nutri-functional compounds, to be used as supplements or additives in food. Selected applications in different areas of the agro-food processing industry, including olive mill, artichoke, liquorice and citrus wastewaters, are analysed and discussed in relation to separation processes, molecule properties, membrane characteristics and key factors affecting the membrane performance in terms of productivity and selectivity towards target compounds [2,3]. Flow-sheets of integrated membrane processes have been proposed on the basis of experimental results according to a market-competitive and environmentally sustainable way. A conceptual process design in orange juice production is depicted in Figure 1.



Integrated membrane operations in orange juice production (UF, ultrafiltration; NF, nanofiltration; OD, osmotic distillation)

The implementation of hybrid membrane-based processes in these areas permits to rationalize both direct and indirect energy consumption, with improved product quality, process capacity and selectivity, decreased equipment-size/production-capacity ratio and waste production so resulting in cheaper and sustainable technical solutions.

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Toward A Green Integrated Approach For The Extraction And Separation Of Biophenols From Red Wine Lees

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In the last years, industrial ecology concepts like cradle-to-cradle and circular economy are considered as principles for eco-innovation, aiming at zero waste society and economy where wastes are used as raw material for new products and applications. The winemaking process generates a significant amount of wastes such as grape stalks, grape marc, and wine lees characterized by high contents of biodegradable compounds and suspended solids [1]. Conventional treatments of winery wastes are increasingly expensive, requiring significant amounts of effort, resources, and energy for safe discharge into the environment. On the other hand, wine lees contain high concentration of biophenols well recognized for their potential beneficial effects on human health due to their antioxidant, antimicrobial, antiviral and anti-inflammatory activity. The growing interest in the biological activity of biophenols has intensified research efforts to develop novel and sustainable procedures for their extraction, separation, and purification in an efficient and environmentally friendly manner without affecting their stability. In this contest, membrane processes represent a very powerful alternative to conventional methodologies due to their low operating and maintenance costs, mild operating conditions of temperature and pressure, no use of chemical additives, easy control and scale-up, and high selective separations, ensuring high quality of the produced extracts. Their intrinsic properties well fit the requirements of *green* and *intensified processes*. In agreement with a *biorefinery* approach applied to winemaking, sustainable extractive technologies followed by membrane separation methods have been investigated for the recovery and purification of biophenols from red wine lees before using biomass for energy purposes. Specifically, hydro-alcoholic and aqueous extracts were firstly clarified by using commercial and home-made microfiltration (MF) membranes, in order to reduce their turbidity and to recover phenolic compounds in the permeate stream. Then, the clarified extracts were fractionated with different commercial ultrafiltration (UF) and nanofiltration (NF) membranes in flat-sheet configuration having molecular weight cut-off (MWCO) in the range 150-1000 Da. The performance of selected membranes was evaluated in terms of productivity, fouling index and selectivity towards sugars and bioactive compounds. The obtained results showed that the innovative integrated processes allowed to obtain individual fractions enriched in bioactive compounds of interest for specific applications in pharmaceutical, cosmetic, food, and functional food industries. Overall, they turn up as clean and low-cost methods to valorize red wine lees through the recovery of natural ingredients within the logic of both *process intensification* and zero discharge strategies [2, 3].

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Circular Economy Declined For The Ceramic Tile Industry

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The circular economy is a trending concept, currently promoted by several governments. It is viewed as a concrete way to implement the much-discussed notion of sustainable development through the 4R framework (reduce, reuse, recycle, recover). The most influential background conceit wants the future business modelled around a cradle-to-cradle circle run through industrial symbiosis. In this reference frame, ceramic tile manufacturing is often seen as an example of linear economy, where many Rs are difficult to be carried into effect and all the efforts reside on recycling processing wastes in cannibalistic loops. However, this perception is distorted because novel technologies and ongoing innovation are changing the way ceramic tiles are designed and produced. This contribution reviews the current situation in the ceramic industry, assessing the extent by which the circular economy principles are implemented into the tile-making value chain. Attention is paid to Rs (reducing the resource consumption, reusing materials and recovering energy) with special care on challenges of waste recycling (in-house residues, end-of-life products, secondary raw materials from other sectors). This analysis was carried out in the MATER_SoS project ("Sustainable materials for refurbishment and construction of new buildings" funded by Emilia Romagna region (Italy) with European funds (POR-FESR) and shows the hindrances to fit a rigid circular model to a complex value chain and products with a long lifetime that are sold worldwide. About a dozen of residues have been selected, recycled from Emilia-Romagna region, Italy, and suitable as ceramic raw materials (mostly glasses, ashes and sludges). the wastes are introduced as fluxes, to replace feldspathic raw materials in a standard porcelain stoneware batch, contents up to 60% were reached. Bodies underwent a laboratory simulation of the industrial process, stressing on technological obstacles to a large-scale utilization and fully evaluating their behavior. Thus, a waste classification was allowed, and obtained technological profiles summarize preliminary treatments needed, compositional features and the effects on technological behavior of the porcelains stoneware tiles.

POR FESR EMILIA-ROMAGNA 2014/2020

RegioneEmilia-Romagna

Progetto cofinanziato dal Fondo Europeo di Sviluppo Regionale

MATER SOS

MATERiali SOStenibili

per il ripristino e la realizzazione di nuovi edifici

Coordinamento: CENTRO CERAMICO Partner Progetto: Consiglio Nazionale delle Ricerche Certimac Ri.Cos

Aziende: MARAZZI (Settore ceramico) - CONCAVE (Settore aggregati e calcestruzzi) - FILI&FORME (Settore: Estrusione di monofili sintetici)

DURATA DEL PROGETTO 24 MESI (Inizio 1 aprile 2016)

OR0 - Coordinamento e gestione del progetto

OR1 - Mappatura e selezione dei rifiuti in ambito regionale e loro caratterizzazione

OR2 - Materiali con funzione strutturale a diversa matrice sostenibile

OR3 - Materiali per intonaco, massetti e adesivi a diversa matrice sostenibile

OR4 - Piastrelle ceramiche funzionali a diversa destinazione d'uso

OR5 - Attività di diffusione e disseminazione dei risultati

MATER_SOS project: "Sustainable materials for the recovery and realization of new buildings", funded by Emilia Romagna region (Italy) with European funds (POR-FESR)

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Simultaneous Production Of Renewable Energy And CO$_2$ Re-Use: A Close-Loop Of Biorefinery

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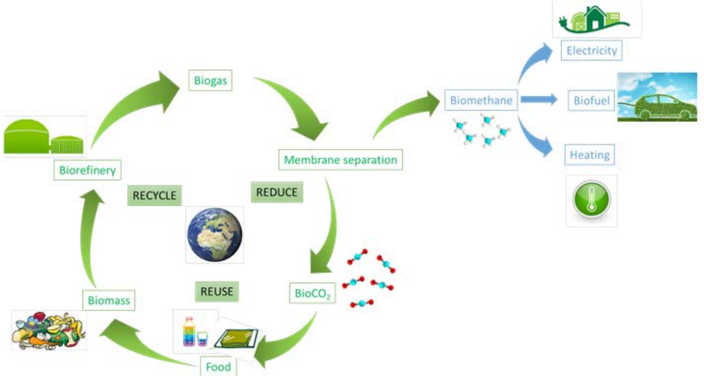
The interest for renewable resources and eco-sustainable processes that allow production of renewable energy with low environmental impact is currently one of the driving forces in the field of green chemistry. Emission of CO$_2$, related to the use of fossil fuels, is considered one of the main causes of global warming and climate change. The reduction of CO$_2$ emission into the atmosphere as a result of human activity is one of the most important environmental challenges to face in the next decennia. A possible solution is the increased use of renewable sources of energy, with the promotion of plans for CO$_2$ capture and reutilization (CCU). In this scenario, the production of biomethane from organic waste, is one of the most promising strategies to reduce fossil fuel consumption and greenhouse gas emission. Unfortunately, traditional biogas upgrading still produces CO$_2$ as a waste product. This work presents a study on an advanced biogas upgrading process, aimed at the simultaneous purification of methane and CO$_2$ via different steps, including CO$_2$/CH$_4$ separation by polymeric membranes. The innovative aspect is the further purification of CO$_2$, from a useless by-product to a food-grade quality gas for commercial application in the food industry. The final result is a biorefinery, that produces bioenergy from biomass and closes the CO$_2$ loop in biogas production, completely eliminating its release into the atmosphere.



Schematic representation of the sustainable cycle of anaerobic digestion with simultaneous production of renewable energy and food grade BioCO$_2$

The study was performed on a pilot plant constructed by Tecno Project Industriale Srl, Italy. The anaerobic digestion plant (Montello Spa), has a digestive capacity of 400.000 ton of biomass/year and can treat over 6.250 m^3/hour of biogas from FORSU. The chemical purity of the gas streams was analysed and compared with the guidelines of the European Industrial Gases Association and the International Society of Beverage Technologists (EIGA /ISBT) for CO$_2$ used in the food industry. The microbiological purity was compared with the limit values defined in the European Collaborative Action. With a purity of 96.3 vol%, the produced methane respects the purity requirement for the household network. With a purity of 98.1% before, and 99.9% after the final distillation process, CO$_2$, proves to be chemically and microbiologically suitable for food-grade applications. The process produces renewable energy and it is environmentally impact-free CO$_2$, respecting the principles of green chemistry and of the circular economy.

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Insights Into The Substrate Promiscuity Of Hydroxysteroid Dehydrogenases

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Bacterial hydroxysteroid dehydrogenases (HSDHs) are NAD(P)H-dependent enzymes belonging to the superfamily of short-chain dehydrogenases/reductases (SDRs) [1]. These enzymes are attractive for industrial applications as they catalyze the reversible oxidoreduction of the hydroxyl/keto groups of neutral steroids, bile acids and other steroid derivatives with exquisite selectivity. Specifically, HSDHs have been shown to display very high regioselectivity for the hydroxyl groups at different positions, e.g., at C-3, C-7, and C-12 of bile acids. Moreover, for each one of these positions, HSDHs usually show high stereoselectivity for either the hydroxyl group above (β configuration) or below (α configuration) the plane of the steroid molecule [2].

Although largely investigated during the last years, there is still only a little knowledge regarding their possible uses on substrates not showing the core structure of steroid molecules. For instance, some years ago a study reported the stereoselective reductions of α-ketoesters catalyzed by HSDHs [3].

Therefore, the presented work aimed at filling this gap by investigating the substrate promiscuity of this highly selective class of enzymes. To this goal, a library of microbial HSDHs, showing either 7α, 7β, or 12α activity, and originated by already reported sources, as well as from newly identified (meta)genomic sequences, was prepared by recombinant expression in *E. coli.*

These enzymes were then tested as biocatalysts for the stereoselective reduction of a panel of substrates including two α-ketoesters of pharmaceutical interest and selected ketones that partially resemble the structural features of steroids. All the reactions were optimized and coupled with a suitable cofactor regeneration system. Regarding the α-ketoesters, nearly all of the tested HSDHs showed a good activity toward the selected substrates, yielding the reduced α-hydroxyester with high conversion and high enantiomeric excess. On the other hand, only few among these HSDHs showed appreciable activity toward more complex ketones, but with interesting selectivity.

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Green Solvents In Membrane Preparation For A More Sustainable Future

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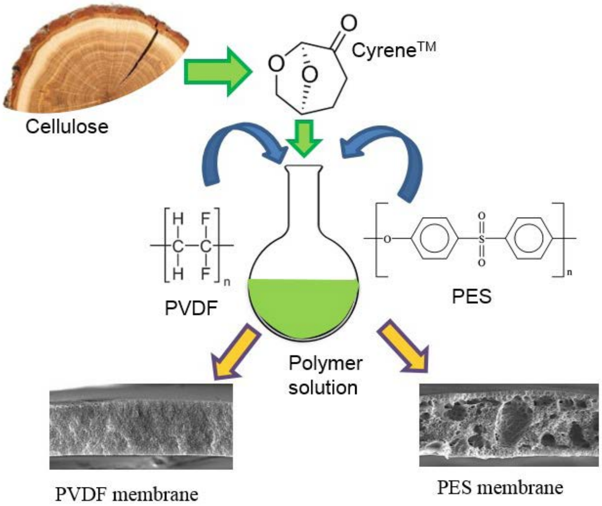
Membrane processes have emerged during the last decades as a valid and efficient technology for the abatement of many environmental problems. High efficiency, low energy requirement and environmental sustainability are among the major benefits displayed by membranes. However, in the logic of a complete sustainability, polymeric membranes should not require the use of toxic and harmful solvents, such as NMP, DMF and DMAc, normally employed during their preparation [1]. Replacing a traditional solvent with a green alternative is not an easy task since the solvent play a crucial role in membrane formation influencing its morphology and properties. In this work, two case studies are reported where two green solvents (Cyrene™ and ethyl lactate) were used for the preparation of polymeric membranes by phase inversion technique.

Cyrene™, a new green solvent derived from cellulose, was used, for the first time, for the preparation of polyethersulfone (PES) and poly(vinylidenefluoride) (PVDF) membranes [2]. Without the use of any additive, but just acting on the exposure time of the nascent membrane to a relative humid environment, it was possible to tune the pore size of prepared membranes in the range of micro and ultrafiltration. Membranes with different morphology (sponge and finger-like), pore size (from 0.01 to 0.13 µm for PES and from 0.05 to 0.55 µm for PVDF) and properties could be prepared with comparable results respect to the membranes prepared with conventional toxic solvents.

In the second case study, the green solvent ethyl lactate, derived from processing corn, was used as alternative to chloroform for the preparation of polylactic acid (PLA) membranes [3]. In this case, the combination of a green solvent with a biopolymer allowed to prepare totally green membranes. By varying the evaporation time of the cast film, it was possible to change membrane morphology from finger-like to spongy-like structure and finally to a dense one. The dense membranes were, then, tested in the pervaporation process for the selective separation of a methanol (MeOH)/methyl tert-butyl ether (MTBE) azeotropic mixture. The membranes resulted selective for the alcohol with a selectivity (α ≈ 75) comparable to the one reported in literature for analogous membranes produced with more hazardous and traditional solvents.



Cyrene™ as a green solvent for the preparation of porous PVDF and PES membranes

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Synthesis And Characterization Of Bio-based Polyols From Epoxidized Soybean Oil And Their Use For The Synthesis Of Polyurethanes

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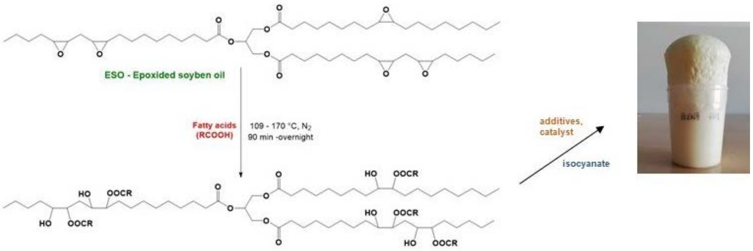
Nowadays, the polyurethane (PU) industry is looking for renewable raw materials to replace two major feedstocks, polyols and isocyanates, which derive from petroleum sources, because of the uncertainty about the cost of petroleum in the future and the need to move toward more environmentally friendly feedstocks. PUs industry is making research efforts for replacing oil-based polyols with polyols from renewable resources, such as bio-polyols from vegetable oils.
Until now, different synthetic strategies have been developed to obtain polyols, including the modification of epoxidized triglycerides by fatty acids. Herein, an epoxidized soybean oil (ESO) with a percentage of epoxy groups equal to 4.8% and 21% oleic, 60% linoleic and 7% linolenic chains was used. A wide screening was performed to identify the best fatty acids to obtain low molecular weight polyols with narrow polydispersity using solvent- and catalyst-free reactions (Step 1). Then a selected bio-based polyol has been tested in the preparation of different composite PUs and their properties have been evaluated as well (Step 2).



Reaction between ESO and various fatty acids and preparation of polyurethanes

Step 1-Synthesis of bio-based polyols: Glutaric acid ($C_5H_8O_4$), caprilic acid ($C_8H_{16}O_2$), thioglycolic acid ($C_2H_4O_2S$), 3-phenylbutyric acid ($C_{10}H_{12}O_2$), stearic acid ($C_{18}H_{36}O_2$) and oleic acid ($C_{18}H_{34}O_2$) were used. Different substituents (such as carboxy, aryl groups and heteroatoms), variable chain length and several unsaturation grades have been evaluated to estimate how the chemical nature of the acidic reagent affects the functionalization degree, OH and pH value. Reactions were carried out at temperatures higher than melting point of each acid, while the ratio carboxyl group to epoxide group was varied to obtain the maximum degree of functionalization.
Step 2-Synthesis of bio-based flexible polyurethane foams (PUs): to synthesize PUs, the oleic bio-based polyol (code MB174), produced by step 1, was blended with polyol mustard oil-based (at 18.5 wt%), MDI was used as isocyanate source, water as blowing agent and catalysts and silicone surfactant to control the polymerization and blowing reactions. The chemico-physical and mechanical properties were evaluated and compared to those of a conventional flexible polyurethane foam produced by using commercial-synthetic polyol. Preliminary results showed that the addition of MB174 positively affects the mechanical properties of the produced foam.

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Acknowledgement:

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Phase Change Materials Integrated Into Glass Scraps-Based Tiles For Ventilated Façades Application: A Laboratory Scale-Up Case Study

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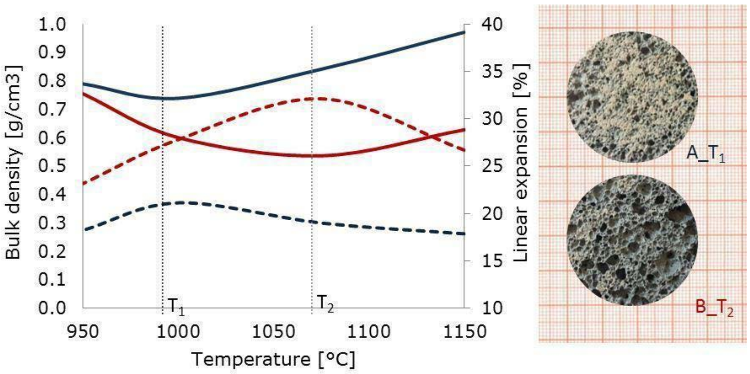
Ceramic foams represent an interesting class of materials for insulation applications, thanks to their low flammability, which makes them a safer alternative to polymeric insulation products. Ceramic foams are characterized by peculiar microstructures with a porous texture, which formation can be induced by the introduction of an expanding agent. Its activation within the ceramic batch is achieved during the firing process. The integration of Phase Change Materials (PCMs) into the pores of the ceramic matrix represents a challenging goal to importantly improve the thermal insulating performances and comfort of buildings. The possibility to embody PCM into porous fired tiles is strictly related to the size and number of pores formed during the process. For this purpose, the capability to control and predict the bloating phenomena as a function of the tiles size is a key point to define the thermal performances of the final device. Starting from a typical porcelain stoneware tile formulation, silicon carbide (SiC) powder was added as expanding agent. Furthermore, the bulk composition was optimized by addition of glass scraps. The presence of glass reduces the carbide stability leading to observe bloating phenomena in a temperature range typical of the industrial ceramic tiles production. To evaluate how the tile size can influence the microstructures, in terms of pores amount, shape and size, a laboratory scale up process was carried out. It was done passing from 30 mm of diameter specimen to a 150x150 mm demonstrator device. The samples were characterized by bulk density, linear expansion, water absorption and pores distribution. The effects of the firing process parameters on the specimens' physical properties were studied. The increase of temperature led to an initial decrease of the bulk density, given by gas formation due to SiC oxidation, followed by a progressive densification regardless the increased expansion potential. The pores amount size and shape showed to be dependent on both the efficiency of SiC decomposition and glass viscosity. The changes in terms of density are matched to the number of pores, affecting the potential amount of PCM that could be incorporated. Linear bloating and pores size showed an evident relationship to the specimens size, emphasized by the reduction of the heating rate.

Effect of composition and firing temperature on 3 cm specimens properties (Full lines: bulk density - Dotted lines: linear expansion – Blu lines: A formulation - Red lines: B formulation).



Acknowledgement:
Authors thank the Emilia-Romagna Region for financial support through the project INVOLUCRO "Sistemi innovativi, adattativi e sostenibili per l'involucro edilizio ad alte prestazioni energetiche ed acustiche" (CUP J42F17000130009), POR FESR 2014-2020 (Axis 1, Action 1.2.2).

Nitrogen-Doped Carbon Quantum Dots: An Electrochemical Insight

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Carbon quantum dots (CQDs) are considered to be a next-generation green multifunctional nanomaterial because of their advantages in terms of high chemical stability, broad excitation, low toxicity, flexible surficial functionalization, and good solubility. In comparison to fluorescent semiconductor quantum dots (QDs), which are usually composed of heavy metals as the essential elements to achieve high performance fluorescence, CQDs are advantageous both in their green synthesis and good biocompatibility for biomedical applications. So far, various methods have been explored to prepare the CQDs, which may be mainly grouped into two classifications: top-down synthetic route, such as laser ablation, electrochemical exfoliation, and arc discharge, and bottom-up synthetic method, just like ultrasonic-assisted route, microwave pyrolysis, and hydrothermal means1.

Doping with heteroatoms (e.g., oxygen, nitrogen, or sulfur) is one way of tuning the electronic and optical properties in CQDs. In particular, nitrogen doping is considered to be the most effective strategy at present because the small atomic size and rich valence electrons of nitrogen atom can bond with the carbon atoms. Moreover, nitrogen-doped CQDs can effectively adjust their electronic characteristics, surface and local chemical reactivity[2a]. In nitrogen-doped CQDs (N-CQDs), some of the carbon atoms at the core/edges of the CQDs honeycomb matrix are replaced by nitrogen, or N-containing groups reside at edges. The most common types of nitrogen atoms found in N-CQDs are graphitic, pyridinic, pyrrolic, and amino centers. In recently reported N-doped CQDs, pyridinic, pyrrolic, and amino N atoms were mainly located at edge sites, with pyridinic and pyrrolic N centers being more abundant[2b].

Recent studies have shown that N-CQDs display reversibly switchable “on-off” fluorescence via redox reactions3a and photoluminescence spectro-electrochemistry determinations provided direct in-situ evidence of the dependence of the N-CQDs luminescence and their redox state[3b]. By contrast, the electrochemical behavior of N-CQDs is considered quite complex and a detailed interpretation of their oxidation/reduction processes is less investigated[3b].

Herein, citric acid (CA) and urea were used as the precursors to synthetize luminescent nitrogen-doped CQDs by facile hydrothermal method, in which urea acted both as base and N-doping source. The resulted materials were characterized by UV-vis and FT-IR spectroscopies, X-Ray Diffraction (XRD) and X-Ray Photoelectron Spectroscopy (XPS). Cyclic Voltammetry (CV) combined with UV-vis and XPS spectroctospies has been employed to give an interpretation of N-CQDs oxidation/reduction processes.

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CHEMISTRY AND ENERGY

POSTER COMMUNICATION

Effect Of The Ancillary Ligand On The Luminescence Of Eu^{3+} Diketonate Complexes

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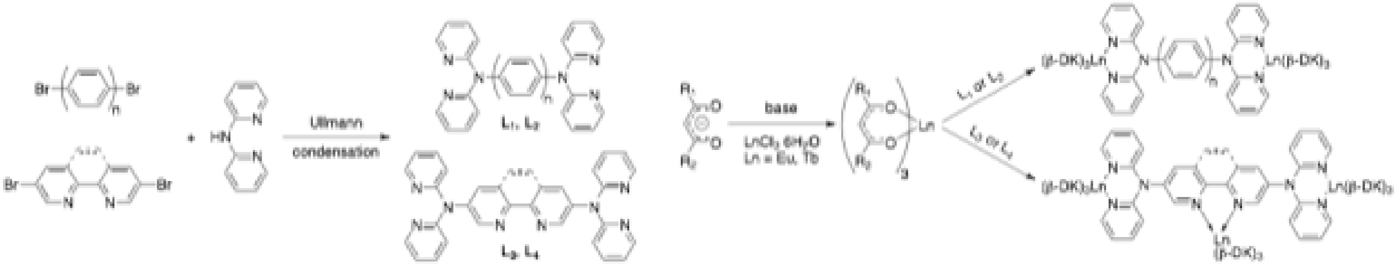
The need to reduce energy consumption has prompted a considerable research effort for developing new energy-efficient lighting systems. Devices based on white emitting OLEDs (WOLEDs) are good candidates to replace conventional light sources (*i.e.*, incandescent and fluorescent lamps) [1]. White light production requires the generation and the intensity control of the three fundamental (red, green and blue) or two complementary (blue and yellow) colors in order to cover the whole visible range from 400 to 700 nm [2].
The target materials of this study are supramolecular multichromophoric arrays containing Eu^{3+} (red emitter) and Tb^{3+} (green emitter) lanthanide ions, whose emission is sensitized by bis(2-pyridyl)amine (2PA) based ligands (blue emitter), prepared according to the scheme below.
Here, we present the results of the preparation and photophysical investigation (absorption, emission, quantum yield, excited state lifetime, energy transfer processes) in solution and in polymer matrices.



Schematic representation of the syntheses of the bridging ligands L_n (left), the lanthanide complexes and arrays (right); R_1 and R_2 are phenyl, thiophenyl, furanyl, or pyridyl derivatives.

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Phase Change Materials Nano-Emulsions For Thermal Energy Transfer And Storage

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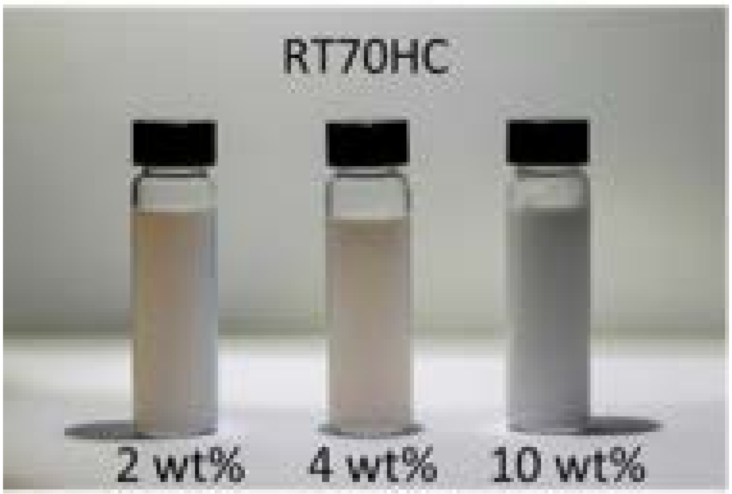
Phase change material emulsions (PCMEs) or phase change slurries have risen interest in scientific community in the last years as potential heat transfer and heat storage fluids [1]. These systems consist on a base fluid, which is a suitable heat transfer fluid, and an emulsified phase change material (PCM). The idea is to exploit the latent heat of melting and crystallization of PCM to increase the thermal energy storage capacity of the base fluid and, at once, confer higher thermal conductivity and lower viscosity by the fluid with respect to PCM. Moreover, the large interface between base fluid and PCM favors the heat transfer between the two phases. Main barriers to their application are the difficulty in maintaining emulsion stability and the sub-cooling effect (i.e. the cooling of the paraffin drops below their melting point before recrystallization).[2]

Water– and (ethylene glycol+water)–based emulsions with fine droplets of various paraffins were produced by a solvent–assisted emulsification method. Concentrations from 2 to 10 wt% were obtained with paraffins with various melting temperatures between 20 and 70°C. The droplet dimensions were verified and resulted below 100 nm for lower concentrations and slightly higher for 10 wt%.[3] No phase separation or significant growth in PCM drops was observed for the prepared emulsions through storage, after freeze–thaw cycles and under mechanical shear. A sub-cooling effect was verified and reduced by testing some nucleating agents. The heat of melting was lower than expected, probably due to PCM molecules on the surface of the nanoparticles anchored to the surfactant. Although the emulsions exhibited diminutions in thermal conductivity with respect to the carrier fluids, enhancements in energy storage capacity with respect to base fluid reached up to 40%. In addition, the thermal reliability of the nanoemulsions was corroborated analyzing the changes in latent heat after several thermal cycles.



Examples of nanoemulsion in water of commercial Rubitherm paraffin melting at 70°C.

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Platinum Free Catalyst For Anion Exchange Membrane Fuel Cells

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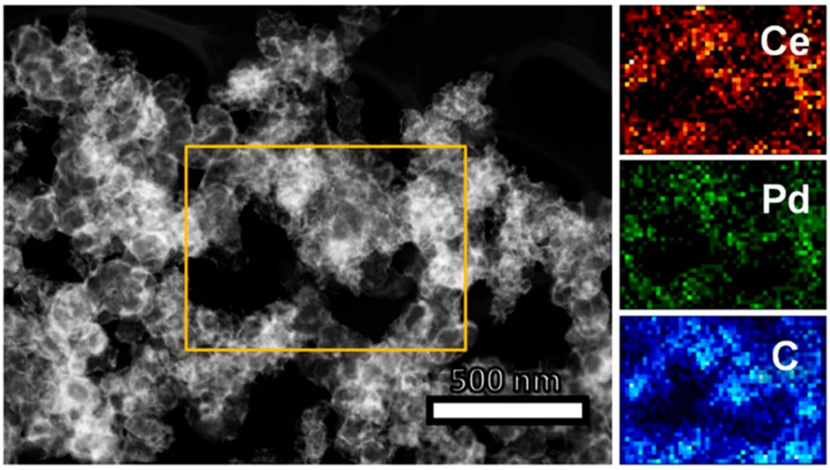
Anion exchange membrane fuel cells (AEMFCs) offer several important advantages with respect to proton exchange membrane fuel cells, including the possibility of avoiding the use of platinum catalysts to help overcome the high cost of fuel cell systems. Despite such potential benefits, the slow kinetics of the hydrogen oxidation reaction (HOR) in alkaline media and limitations in performance stability (because of the degradation of the anion conducting polymer electrolyte components) have generally impeded AEMFC development. Replacing Pt with an active but more sustainable HOR catalyst is a key objective. Herein, we report the synthesis of a Pd–CeO_2/C catalyst with engineered Pd-to-CeO_2 interfacial contact. The optimized Pd–CeO_2 interfacial contact affords an increased HOR activity leading to >1.4 W cm–2 peak power densities in AEMFC tests. This is the only Pt-free HOR catalyst yet reported that matches state-of-the-art AEMFC power performances (>1 W cm–2). Density functional theory calculations suggest that the exceptional HOR activity is attributable to a weakening of the hydrogen binding energy through the interaction of Pd atoms with the oxygen atoms of CeO_2. This interaction is facilitated by a structure that consists of oxidized Pd atoms coordinated by four CeO_2 oxygen atoms, confirmed by X-ray absorption spectroscopy.



STEM images of Pd−CeO2/C: HAADF image and STEM-EDS mapping of the selected area showing the CeO2 (red), Pd (green), and carbon (blue) elemental maps.

References:

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$CsPbBr_3$ Nanocomposite For Photocatalytic Application

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Nowadays, the requests of high-performance technologies for energy and environment are increasing and the development of new kind of materials is crucial for this purpose. Nano-hybrid structured materials condense the features of starting components to reach a composite with improved characteristics. For this reason, in recent years, they are becoming more and more attractive. In this work new nano-hybrid materials, composed by 2D sheets of graphene oxide (GO) or black phosphorus (bP), and nanocrystals (NCs) of all inorganic halide perovskite with formula $CsPbBr_3$, were developed and studied. Nanocrystals were synthesized[1] mixing cesium and lead precursors and subsequently adding bromide precursor to the Cs-Pb compound. The different nano-hybrids were easily achieved by adding the bP or GO sheets in the reaction environment before the additions of bromide precursor. To confirm the success of the reaction, XRD analysis was conducted on the products. Furthermore, SEM and TEM were used to check the morphology of the powders, while absorption spectroscopy was used to determine the right NCs absorption wavelength in the UV-Vis region. The photocatalytic activity of nano-composites was studied carrying out degradation tests of rhodamine B, which is considered as a water pollutant, and using bare $CsPbBr_3$ NCs as a reference. The behavior in terms of degradation activity of hybrids compared to the NCs showed better results thanks to the improved photo-catalytic properties of $CsPbBr_3$ due to the synergic effect between perovskite and bP or GO. To the author knowledge, this is the first work that reports the use and comparison of the $CsPbBr_3$-bP and $CsPbBr_3$-GO composite for photocatalytic applications.

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Thermoelectric Properties Of Zn_4Sb_3 Obtained By Cold Sintering Process

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Zn_4Sb_3 is a p-type thermoelectric material with one of the highest thermoelectric figure of merit in the intermediate temperature range [1]. It received considerable attention in the last two decades especially because of its low thermal conductivity, about 0.9 W/mK at room temperature. Nanostructuring this material is considered a strategic route to reduce its thermal conductivity and improve thermoelectric performance limiting the bipolar effect by selectively scatter minority carriers.

Cold sintering process was recently introduced [2] and demonstrated effective to obtain good levels of densification for various ceramic materials at temperatures below 200°C. It normally uses water and temperature to drive a dissolution-precipitation process that significantly reduces the sintering temperature. Cold sintering process was tested on several compounds, on ceramic-polymer composites, and it was considered for bonding applications.

We investigated the cold sintering process to obtain dense Zn_4Sb_3 at temperatures well below 200 °C, reported as the minimum temperature for Zn loss under dynamic vacuum. We also present and discuss thermoelectric properties of the obtained material, together with mechanical and morphological properties, and we compare results with other low temperature sintering techniques [3].

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A Double-Step Compression Molding To Improve The Dielectric Properties Of PVDF And PVDF-Based Composites

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The demand for lighter and smaller devices with higher energy storage capability has created a strong motivation for research and development in the field of dielectric capacitors. Polymer-ceramic composites provide an ideal solution to combine the good dielectric properties of ceramic fillers with the resistance to high electric fields, low-temperature processability and suitable mechanical properties of polymers [1]. Poly(vinylidene fluoride) (PVDF), due to its dielectric, piezoelectric and ferroelectric properties and its interesting characteristics, such as good mechanical properties and chemical inertness has been increasingly used in this field. It is known that the electroactive properties of PVDF are strictly connected to its polymorphism. In fact, as a consequence of different processing conditions, this polymer can be obtained in up to five distinct crystalline phases: α, β, γ, δ and ε. Among them, β ,γ and δ are characterized by a neat moment dipole and show useful electroactive properties [2]. In this framework, the study of processing methods able to promote the crystallization of the electroactive phases, in particular of the β form, is one of the most important topics in PVDF research [3].

In the present work, an alternative method to induce the formation of PVDF β phase was proposed, exploiting a well-known technique widely used for the polymer processing: the compression molding. In particular, it was used a double step process (P2), which consists in preparing a plate of material (*i.e.* neat PVDF or composite) and then repressing it at high pressure and at a temperature lower than the PVDF melting temperature. As concerns the neat PVDF, the molding conditions were modified to investigate their influence on the final amount of electroactive phase(s) obtained. The impact of processing on dielectric and dynamic-mechanical properties of the PVDF films was also studied on a selected series of samples.

PVDF-based composites containing different amount of ceramic particles (such as BaTiO3 and PZT), widely used in the field of energy harvesting, were then prepared by solvent casting or melt blending. Besides a single-step (P1) molding carried out on samples with completely molten PVDF, also the P2 process was applied to the composites in order to investigate its effect on their final properties. The ensuing samples were characterized from morphological, spectroscopic, dynamic-mechanical and dielectric point of views.

Gathered results suggested that, with respect to the P1 molding, the P2 process increases the PVDF β-phase amount, modifies the molecular motions and improves the dielectric properties. In particular, the samples obtained from the two-step method are characterized by higher dielectric permittivity and lower dielectric losses than those measured for the corresponding samples prepared by the single-step molding.

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Depletion Of Minerals Resources

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The science of materials had an extraordinary development in the last few decades. New materials were invented and entered the market with a huge variety of applications. In spite of this undeniable success, alarms were raised recently concerning the sustainability of this dynamics in the long run, due to the progressive depletion of mineral resources and, in particular, o metals.[1], [2] Economics of resources is still dominated by the paradigm of free-market automatism, according to which due to the price signal and to human ingenuity, resources becoming scarce are substituted by more abundant resources that can make the same function. A new paradigm is growing rooted in the biophysical approach to resource consumption and depletion. This new approach was first developed to describe the depletion of fossil fuels and, in particular of oil. The calculation of the Energy Return on (Energy) Investment (EROI) is a valuable tool to estimate the convenience of the different energy sources. As far as petroleum (oil & gas) is concerned we developed a model that recently showed a steep decline of the global average quality of the oil sources exploited by petroleum companies [3] and the possible multi decades variation of EROI. Our analysis concerns the EROI values of the major oil companies worldwide in 2015, determined using the CO_2 as a proxy to calculate how much energy can be delivered to the society.

The biophysical approach to the study of energy resource depletion can, and should, be applied to the study of the depletion dynamics of metals and of other resources strategic to industrialized societies.

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Production Of Syngas By Electrochemical CO_2 Reduction In Water At Carbon Cloth Electrodes Functionalized With A Fac-Mn(apbpy)$(CO)_3$Br Complex

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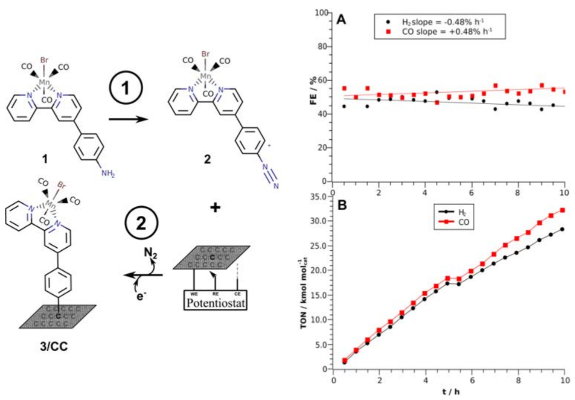
The electroreduction reaction of carbon dioxide represents one of the most challenging strategies for excess renewable energy storage into carbon-neutral high-energy-density forms such as CO, CH4 and liquid fuels (ethanol, methanol, formic acid). Particular interest is aroused by the production of carbon monoxide, as it is a fundamental building block for many industrial processes including Fisher-Thropsch and hydroformilation of olefines. An innovative approach is to use organometallic complexes as electrocatalyst allows, in principle, a higher metal utilization efficiency (i.e. lower metal loading needed), compared to metal-nanoparticle-based electrocatalyst. In addition this strategy opens the the possibility to fine tune the selectivity by varying the electronic properties and the coordination geometry of the complex. In addition, anchoring the complex on electro-conductive supports helps to overcome the mass transport limitations of the electroactive species from the bulk to the electrode surface and allows a much higher electrocatalyst stability. Among many types of electro-conductive supports, carbon cloth (selected as support for this study) represent an excellent material for the fabrication of electrodes, both as gas diffusion layers and in immersion in the electrolyte, with high structural strength and high conductivity. Herein we describe the use of a manganese-tricarbonil-bipyridin Lehn-analogue complex (fac-Mn(apbpy)$(CO)_3$Br) grafted on carbon cloth support by diazonium salt reduction, used as electrocatalyst in aqueous media for the reduction of CO_2 to CO. The electrocatalyst, supported in carbon cloth (0.45µgMn cm^{-2}) in aqueous media was able to convert CO_2 into syngas ($CO+H_2$) as the only product with a CO-faradaic efficiency higher than 50% at -1.3V vs Ag|AgCl|KCl_{sat} at a productivity rate higher than 870Nl h^{-1} gMn^{-1}, attaining turnover numbers up to 33000 in 10h of operation with negligible electrocatalyst degradation.



(left) fac-Mn(apbpy)(CO)3Br grafting process on carbon cloth; right) CO-faradaic efficiency and electrocatalyst turnover number (TON) time profiles

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Freeze-Casting Process For The Production Of Catalytic Monolith

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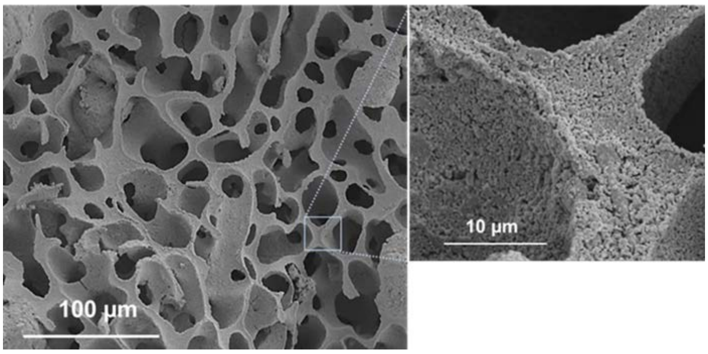
The shaping of engineered porous structures has recently received a lot of attention for the fabrication of ceramic support for energy applications and chemical processes. Among the different shaping techniques, freeze casting is a cost-effective and simple method to allows the fabrication of highly porous substrates (>50vol%) with organized and aligned porosity with good mechanical stability. The interconnected porosity of samples obtained by this technique shows improved gas access and transport, that is known to be the limiting factor for the industrial operation at high flow streams [1].

In this work porous substrates have been produced by camphene-based freeze-casting of ceria-based powders to be applied as support for steam reforming and catalytic partial oxidation reaction. Process parameters (temperatures and freezing conditions) and slurry composition (e.g. dispersant) have been investigated and optimized to obtain engineered porosity with microstructure suitable for the application. One of the main issue linked to the production of freeze cast supports is the obtaining of non-homogeneous microstructure at the samples edges (e.g. dense layer) due to the solvent evaporation and high freezing rate during solidification [2]. Thus, a polishing post-treatment necessary to obtain substrates with homogeneous properties is typically applied as common step of the whole process. On the contrary, in this work thanks to parameters optimization, porous supports “ready-to-use” with more than 70vol.% of porosity, good permeability and homogeneous microstructure were produced. Catalytic tests of the infiltrated samples were performed in real reaction conditions confirming better methane conversion in respect to the starting powder for, particularly, steam reforming reaction.

Microstructure of the final freeze cast sample



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A Phosphate Stabilized PdCo@Ni$_{foam}$ Electrocatalyst For Self-Pressurized H$_2$ Production From The Electrochemical Reforming Of Ethanol At 150 °C

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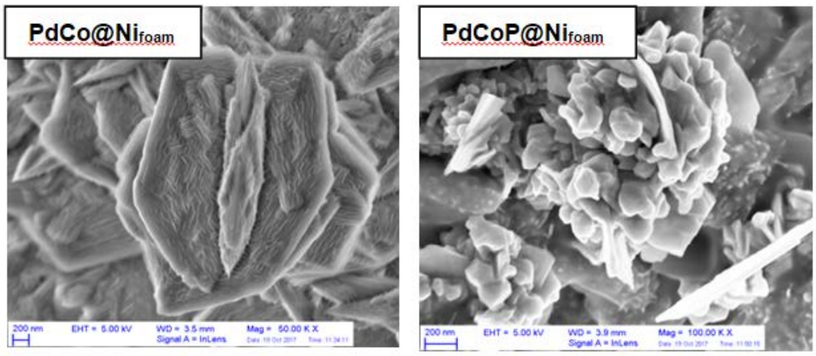
The electro-oxidation of short chain aliphatic alcohols at intermediate temperatures (100-250°C) in devices like Direct Alcohol Fuel Cells (DAFCs) and Alcohol Electro-Reformers is an essentially unexplored field. At temperatures above 150°C in acidic conditions, the kinetics of ethanol oxidation on Pt catalysts are fast and proceed through the C-C bond breaking pathway, thus improving the efficiency of the electro-oxidative process due to the total conversion to CO_2 [1]. Electro-Reformers and DAFCs are more efficient devices using strong alkaline environments (pH ~ 14) due to faster alcohol oxidation kinetics and lower corrosion of the cell components. However, the partial oxidation of alcohols to carboxylates at high pH limits their energy efficiency [2]. In order to achieve total conversion of alcohols to CO_2, we have set up an electrochemical autoclave to study, for the first time, the electrooxidation of alcohols in 2m aqueous KOH at temperatures up to 180°C. Palladium is the most suitable catalytic material for the electro-oxidation of alcohols in alkaline environment [2]. We have synthesized nanostructured palladium-based catalysts supported on nickel foam with a "nanoflower" morphology. The three-dimensional structure of these catalysts guarantees fast mass transport of the alcohol fuel in the liquid phase. In addition, the 3D open structure exhibits enhanced gas permeability, avoiding the formation of bubbles on the electrode. These catalysts are electrochemically characterized both in half-cells and in a complete *Intermediate Temperature Electro Reformers*. The Pd catalysts are used as anodes and are coupled with a nanostructured NiCoP@Ni$_{foam}$ cathode for the hydrogen evolution reaction [3]. Alcohol electroreforming at temperatures over 100°C in a pressurized vessel, couples the advantages of increased catalyst's activity and selectivity with the production of pure and safe pressurized hydrogen (up to 30 bar).

SEM image of PdCo@Ni$_{foam}$ and PdCoP@Ni$_{foam}$



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Thin-Film Fiber-Shaped Dye-Sensitizer Solar Cells Based On Organic Dyes

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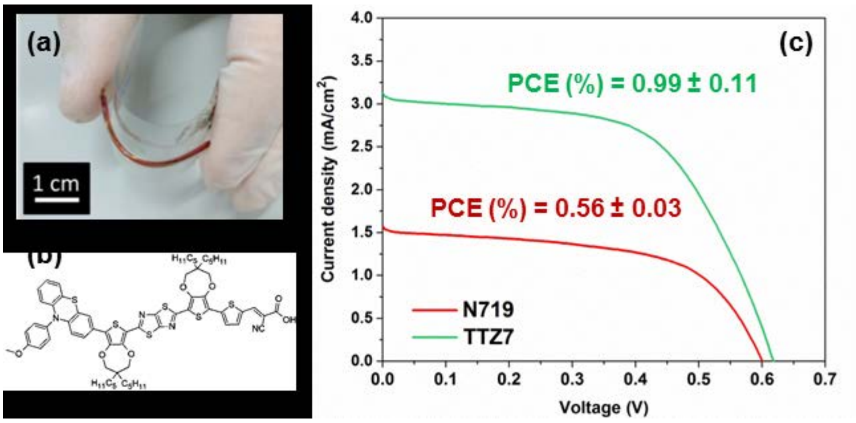
Fiber-shaped Dye-Sensitized Solar Cells (DSSFs) represent the most suitable technology for the development of the next-generation of smart products, namely "electronic textiles" or "e-textiles" able to satisfy the increasing demand of modern electronics for small, portable and wearable integrated optoelectronic devices. Although DSSFs are lightweight, colored and easy to produce, they still suffer for poor mechanical properties (linked to the thickness of the TiO_2 photoanode, around 10 µm) and the presence of metallic dyes (the most efficient based on ruthenium). In this work these issues are faced producing a thinner TiO_2 photoanode and replacing the traditional N719 Ru-based dye with a more efficient organic one. Three different thiazolo [5,4-*d*] thiazole-based organic dyes called TTZ3, TTZ5 and TTZ7, capable of strongly absorb visible light were tested for the first time for this purpose. A thin TiO_2 film (5 µm) was prepared as photoanode active layer by dip-coating and the DSSF structure was completed using a platinum wire as counter-electrode and $I3^-/3I^-$ redox couple as liquid electrolyte. The mechanical properties of the thin film based photoanode were determined as well as the amount of N719 and of the organic dyes adsorbed on the TiO_2 surface. The photovoltaic and electrochemical characterizations performed in different illumination conditions show better performance for all the devices based on organic sensitizers compared with the metallic one. TTZ7-based DSSFs reach the PCE of 0.99±0.11%, JSC of 2.9±0.4 mA/cm^2, VOC 621±18 mV and FF of 55±7% while the N719-based ones produce PCE of 0.56±0.03 %, JSC of 1.6±0.1 mA/cm2, VOC 590±10 mV and FF of 58±1%. The best properties of the TTZ sensitizers were ascribed to their higher light harvesting capability that enhances the current density of the related devices. These results show for the first time the superior efficiency of organic sensitizers instead of the metallic ones for DSSFs application opening the possibility to develop efficient thin-film devices reducing the production costs.



DSSF prepared (a), chemical structure of TTZ7 sensitizer (b) and J-V curves under illumination of DSSFs based on TTZ7 and N719 (c).

CHEMISTRY FOR LIFE SCIENCES

POSTER COMMUNICATION

Action Mechanism Study Of The Nootropic Peptide Semax For The Development Of New Therapeutic Solutions

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Natural regulatory peptides are biologically active compounds that are produced by various cells and provide a link among the main regulatory systems of the body. The field of research into the biological activity of endogenous regulatory peptides is extremely vast. These peptides alter energy metabolism, affect the regulation the cardiovascular, immune, reproductive, endocrine, digestive systems and especially influence the central nervous system. Semax (Met-Glu-His-Phe-Pro-Gly-Pro) is a synthetic regulatorypeptideconsisting of the adrenocorticotropic hormone (ACTH 4–7) fragment and the C-terminal tripeptide Pro-Gly-Pro (PGP) [1]. Semax exhibits neuroprotective, neurotrophic and nootropric properties stimulates learning and memory formation in rodents and humans, and it has been effectively employed in cerebral stroke therapy. The action mechanism of regulatory peptides lie in the ability to affect target cells by modulating the release of other regulatory peptides or proteins [2]. Regardless of the large body of experimental evidence testifying the activity of Semax, it remains unclear to date which is the action mechanism. Therefore, the therapeutic potential of Semax is far from being exhausted and new indications for its application could be discovered by an in-depth study of its biological activity and mechanism of action. The aim of this work was to investigate the mechanism by which Semax acts and describes the effects induced at the cellular level on the RA-differentiated SHSY5SY neuroblastoma cell line. The results indicate that Semax is able to modulate the BDNF expression inducing the phosphorilation of the transcription factor CREB by activation of the AKT and ERK pathways. Moreover, cells differentiated in the presence of Semax are more resistant to different stresses having a higher membrane potential and an increased mitochondrial mass compared to cells differentiated in retinoic acid only. By increasing mitochondrial metabolism Semax provides neurons with the ability to better exploit fuels either under basal and stressful conditions. These results in the improvement of neurons viability as demonstrate by the means of several experimental approaches.

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Structural Basis For Inhibition Of Copper Trafficking By Platinum Anticancer Drugs

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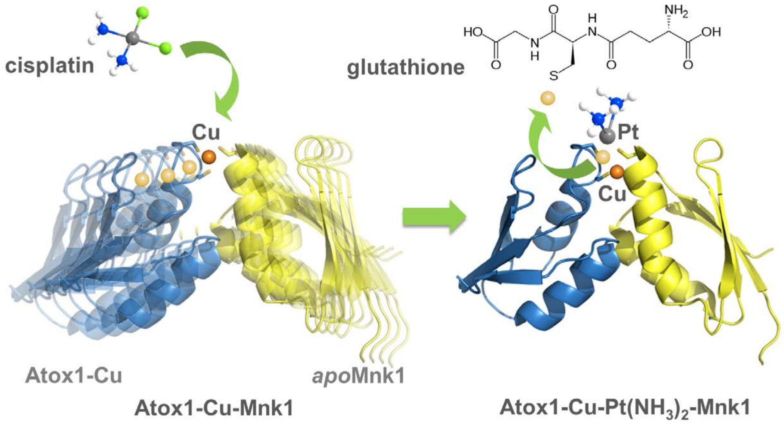
Among anticancer therapeutics, platinum-based drugs have a prominent role. They carry out their antitumor activity by forming stable adducts with DNA, thus interfering with replication and transcription processes. Only a few percent of the platinum (Pt)-based anticancer drugs reaches the nucleus and binds to DNA, whilst the remaining part can interfere with proteins, comprising those involved in copper (Cu) homeostasis and mediate cytotoxicity or resistance to chemotherapy. In particular, proteins involved in copper transport and regulation such as the human Antioxidant 1 copper chaperone (Atox1), are able to mediate the cellular uptake, sequestration, and efflux from cell of platinum-based drugs, affecting their anticancer activity [1]. X-ray crystallographic investigations have disclosed the Pt binding sites of Atox1, and shown that the metal binding site of the Atox1 dimer is partially occupied by a Pt^{2+} ion, with Cu^{+} ions completing the site occupancy [2]. Thus, the platinum ion is able to replace partially the copper ion, leading to a disruption of the delicate process that regulates copper level in the cell. A further recently published study has revealed the structural mechanisms underlying the interaction between Pt-based drugs and two proteins involved in Cu trafficking (Atox1 and the first domain of Menkes ATPase, Mnk1) [3]. Using X-ray diffraction, it was possible to determine the atomic structure of the heterodimer made by the two proteins in the act of interacting simultaneously with a Cu ion and the Pt drug. Overall, crystallographic and nuclear magnetic resonance investigations demonstrated that the kinetic inertness of the Pt(II) derivative imparts a bullet time effect to the fast process of copper exchange between Atox1 and Mnk1, by freezing the Cu(I) ion or hijacking it to glutathione, a physiological antioxidant in the biological matrix. Thus, the anticancer drugs cisplatin and oxaliplatin can interfere with the rapid exchange of Cu between Atox1 and Mnk1, with possible consequences on cancer cell viability and migration.



Cisplatin breaks the equilibrium of Cu exchange between Atox1 and Mnk1

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Acknowledgement:

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Following In Vivo Bone Regeneration Through A Magnetic Biomimetic Scaffold

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A hybrid biomaterial suitable for bone regeneration and composed of collagen and hydroxyapatite (Coll/MgHA) was developed by exploiting a biomimetic process, which wants to examine nature's models, systems and processes to take inspiration from to solve human problems. Especially, the emulation of biomineralization process is useful to reproduce the natural hard tissues such as bone, teeth, and shell. To mimic this process, the mineral phase, MgHA was nucleated on the organic phase (Coll) exploiting the interaction between those phases and a strict stereo-chemical control performed the polymeric template [1]. Magnetic nanoparticles (MNPs) are used as contrast agent capable to be seen through existing non-invasive magnetic resonance imaging techniques (MRI), iron oxide nanoparticle (MNPs) were coated with 3-(triethoxysilyl) propylsuccinic anhydride (TEPSA) to obtain a thin polysiloxane shell presenting carboxylic acid functions (TEPSA-MNPs) in order to avoid owing aggregation [2].

The aim of this work is to develop hybrid materials functionalized with MNPs with or without TEPSA shell to follow, for the first time, the integration and cell differentiation activity in vivo, using an existing non-invasive MRI techniques. Different labelling protocols (simultaneously and post-synthesis) were evaluated to achieve a homogeneous functionalization with TEPSA-MNPs and MNPs without losing the properties of the hybrid material. TEPSA-MNPs were activated with 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and sulfo-N-Hydroxysuccinimide (sulfo-NHS) (ActMNPs) to promote the bound between collagen and MNPs. Physic-chemical characterizations were carried out to investigate the features of functionalized materials in term of morphology, crystallinity and stability followed by MRI analyses and preliminary in vitro tests.

Results demonstrated that in both protocols the labelling of hybrid scaffold had succeeded using ActMNPs. However, the labelling after mineralization of MNPs through a soaking method revealed as during drying overnight they started to precipitate taking to a heterogeneous labelling. Furthermore, evaluating the amount of iron inside the scaffold was clear that labelling through a soaking method leads to heterogeneous material. Regarding biological characterization, in vitro tests were carried out to confirm that no cytotoxicity effect was due to the presence of MNPs or ActMNPs. MTT highlighted a no cytotoxicity effect of all materials and a better proliferation labelling simultaneously with ActMNPs.

In conclusion, the better protocol found in this research is when a simultaneously introduction was carried out and both nanoparticles (ActMNPs and MNPs) were given a good signal, but ActMNPs result better for cell proliferation. This research has successfully developed a biomaterial allowing at the same time to promote bone regeneration and to follow the regeneration through MRI, providing an accurate tool for bone healing monitoring.

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Acknowledgement:

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Antibacterial Polyurethane-Based Composites: Structure, Properties And Behaviours

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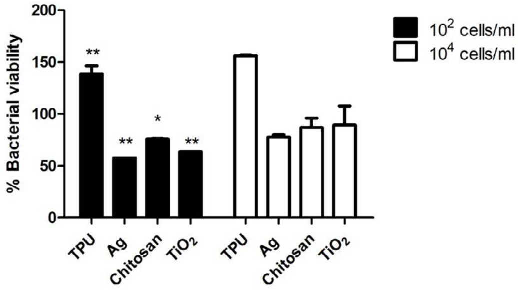
Medical devices used for medical practice are inserted into the human body for short periods of time or to remain in place permanently. Once inserted, they could stimulate the development of an ideal environment for pathogenic bacteria and give rise to resilient infections. The object of this research was the study and the development of innovative materials for the realization of biomedical devices with antibacterial functions. In this work, polyurethane-based composites, containing different antibacterial functions introduced by processing techniques (melt compounding) or post-processing (coatings) were prepared and characterized. TGA, FTIR, SEC, UV, AFM, Contact Angle, Mechanical Tests, Rheology have been performed to investigate the prepared composites. Microstructural characterization of TPU-based starting material was investigated by 1H and 13C NMR spectroscopy highlighting the chemical composition of the monomers and the comonomer sequences. Molecular investigations of finished materials indicates a decrease in the polymer molecular weights after the compounding. For samples loaded with chitosan and silver a slight reduction was registered, whereas the presence of TiO_2 determined a marked reduction of the molecular weights. TiO_2, in the form of anatase, exhibits a catalytic photo activity, which enhances sterilization capabilities beside the generation of hydroxyl radicals capable of degrading the polymer matrix, as evidenced in TGA experiments. Mechanical properties of composites materials, measured by carrying out tensile tests, showed slight differences in Young modulus, tensile strength and elongation at break when compared to the homopolymer, with the exception of TiO_2-based composite which resulted more brittle. Similar rheological behaviors were observed for composites and the homopolymer, performing frequency sweep experiments.



1 Bacterial viability of S. aureus for two bacterial densities measured for the different composites.

The antibacterial activities of the composite materials were evaluated by comparing the behavior of composite surfaces exposed to two different types of bacterial strains. The results show a variable activity depending on the bacterial strains used. The most promising results concern the activity towards S. aureus for which, a reduction of 50% bacterial proliferation was observed in only 24 hours. Summarizing, the whole data confirm a possible inexpensive introduction of the investigated fillers at industrial scale, especially considering the promising antibacterial activities observed for such composites.

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A Microfluidic Module For Extracellular Vesicle Separation Coupled To Microarray Based Phenotyping

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Standard approaches to characterize EVs are usually either low-throughput, laborious or based on sophisticated equipment not applicable to clinical routines. An integrated microfluidic platform that isolates and characterizes EVs available in bodily fluids by combining capture, release and phenotyping of bio-nanoparticles would significantly accelerate the transition of EV-based research to real clinical utility. The realization of such a system is the goal of INDEX a project recently funded in the frame of Horizon 2020 FET-OPEN programs.
The patform consists of two modules one for the extraction of EVs in complex samples and one for the interferometric label-free identification and visualization in a disposable cartridge. In order to integrate the two modules, a new approach for the reversible capture of EVs from serum was developed and demonstrated using the so called magnetic fluidized bed technology recently developed by Pereiro et al (Lab Chip, 2017,17, 1603-1615). This technology is based on the use of functionalized magnetic particles to perform a solid phase extraction step. We report on the progress of the optimization of the technology itself and how it can be used to recover intact EVs.
In the optimization of the magnetic fluidized bed system as tool for the isolation and pre-concentration of EVs in plasma/serum patient samples several steps/issues have been evaluated including: the immobilization chemistry of antibodies on the surface of magnetic particles for increased EV recovery, the dimensions of the chip, the flow rate and sample volume. Capture and release efficiency were evaluated by direct on-chip monitoring of the fluorescence when working with fluorescent samples or by ELISA test . Capturing and release steps were also monitored on anti-tetraspanins antibody microarrays by fluorescence and interferometric detection.
In summary, we have demonstrated that intact EVs can be released from the first module of the sensing platform and transferred to the second module devoted to nanoparticle sizing and phenotyping.

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Liquid Biopsy And Tumors: A New Microarray Method For Genotyping Of Minority Allelic Variants Applied To Colorectal Cancer

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It has now been established that in biological fluids such as blood, it is possible to detect cancer causing genomic alterations by analysing circulating tumour DNA (ctDNA). Information derived from ctDNA offers a unique opportunity to enrich our understanding of cancer biology, tumour evolution and therapeutic efficacy and resistance. Colorectal cancer (CRC) is the second most commonly diagnosed cancer in Europe and a leading cause of death both in Europe and worldwide. In recent years there has been an increase in the diagnosis of CRC and a contextual decrease in mortality, due to screening programs, early diagnosis and improved therapies, which are increasingly targeted and personalized. For the use of molecular target therapies, it is mandatory that patients are selected based on the molecular profile of the tumour and in particular on the presence of mutations that indicate the possible response to treatment (predictive factor). RAS point mutations are found in about 20–25% of solid tumours but in the setting of CRC this percentage rises to 40%. In addition, it is essential to evaluate the *BRAF* mutational status: *BRAF* mutations are found in 8–12% of patients with mCRC and this test has prognostic value because the *BRAF* mutation is a strong and widely accepted indicator of a poor prognosis.

In this context, microarray technology fails in detecting point mutations present in a small fraction of cells from heterogeneous tissue samples or in plasma in a background of wild-type cell-free circulating tumor DNA (ctDNA). The aim of this study is to overcome the lack of sensitivity and specificity of current microarray approaches introducing a rapid and sensitive microarray-based assay for the multiplex detection of minority mutations of oncogenes (KRAS, NRAS and *BRAF*) with relevant diagnostics implications in tissue biopsies and plasma samples in metastatic colorectal cancer patients. In our approach, either wild-type or mutated PCR fragments are hybridized in solution, in a temperature gradient, with a set of reporters with a 5' domain, complementary to the target sequences and a 3' domain complementary to a surface immobilized probe. Upon specific hybridization in solution, which occurs specifically thanks to the temperature gradients, wild-type and mutated samples are captured at specific location on the surface by hybridization of the 3' reporter domain with its complementary immobilized probe sequence. The most common mutations in *KRAS, NRAS* and *BRAF* genes were detected in less than 90 minutes in tissue biopsies and plasma samples of metastatic colorectal cancer patients. Moreover, the method was able to reveal mutant alleles representing less than 0,3% of total DNA.

We demonstrated detection limits superior to those provided by many current technologies in the detection of RAS and *BRAF* gene superfamily mutations, a level of sensitivity compatible with the analysis of cell free circulating tumor DNA in liquid biopsy.

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Acknowledgement:

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A Multifactorial Investigation On The Design Of Injectable Calcium Phosphate Pastes With Enhanced Biological Performance

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Bone cements have been extensively studied in the last century as potential biomaterials to sustain or even regenerate complex-shape bone defects, both for dental and orthopedic applications.

Osteoporosis is a metabolic bone disease that results in bone fragility and increased susceptibility to fracture. One of the most frequent osteoporotic fractures regards the vertebral bodies bone thinning. Vertebroplasty procedures have been established in spinal surgery, involving the injection of acrylic bone cement into damaged vertebrae. Acrylic cements exhibit no bioactivity and their use is accompanied by several drawbacks, such as the strong exothermic effect developed during polymerization and excessive stiffness of the set cement, that can easily induce fractures in adjacent vertebrae.

In order to overcome such limitations, calcium phosphate bone cements (CPCs) have been developed in the 1960s and studied. However, the precise control of their handling properties (setting time, viscosity and injectability) still represents a remarkable challenge because of the inescapable adjustment of multiple correlated processing parameters, especially powder particle size, chemical composition of solid and liquid components or additives.

Similar CPCs can be also used for additive manufacturing technology. In this extrusion-based 3D printing technique, the printed filaments are the elemental building blocks and their accurate and controlled deposition requires careful tuning of the material rheology, to combine a decreasing viscosity during extrusion, with the ability to maintain shape fidelity over time.

The 3D printing of bioceramics generally require high-temperature consolidation steps to improve the mechanical stability of the scaffold. In this case, the major disadvantage is the limited bioactivity of the final scaffold, possibly due to the excessive crystal growth and thermal destabilization of eventually ion-doped ceramic phases [1]. In this respect, the precise control of the material rheology according to 3D printing requirements may represent a useful approach to obtain mechanically competent, self-hardening bioceramic scaffolds for bone tissue engineering.

This work aims to provide for the first time a multifactorial quantitative investigation, based on a Design of Experiment approach, about the role of multiple powder and liquid compositions, as well as milling and mixing parameters on the final performance of Sr-doped apatitic CPCs.

Sr-substituted αTCP powders with different strontium content (i.e. 0-5 mol%) were prepared and mixed with aqueous solutions containing Na_2HPO_4 (i.e. 0-5wt%) and sodium alginate (i.e. 0-5wt%).

In vitro results suggested that the release of Sr^{2+} ions can promote an inductive effect on MSCs and OBs proliferation and osteogenic related genes, as well as an inhibitory effect on OCLs activity [2]. In vivo results showed enhanced bone penetration at 4 weeks after implantation, if compared with a commercial cement as control [3].

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Acknowledgement:

The work has received funding from the national CNR Interest Project "Ageing", PNR-CNR 2012-2014.

Magnetic Particles Sensing: A Novel Dynamic Concept

The MADIA consortium

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Nowadays there is a growing interest in Lab-On-Chip for biomedical applications as fast, compact and cheap platforms for detection of analytes dispersed in a fluid. Among the various transduction approaches, the combination of magnetic nanoparticles (MNPs) and magnetic sensors presents many advantages such as high sensitivity and compactness. An innovative sensing method, based on the different diffusivity MNPs have whether they aggregate or not with targeted bio-analytes, is under development under the Horizon 2020 project MADIA (MAgnetic DIagnostic Assay for neurodegenerative diseases). The primary aim is to develop a Lab-On-Chip platform able to precisely detect amyloids β 1-42 (Aβ1-42) in the concentration range (500 – 1000 ng/ml) critical for Alzheimer's disease early diagnosis. Yet, the same concept can be used for a number of different sensors ranging from ultra-precise sensor for few-molecule detection to rugged field-deployable biosensors. Here we show, along the underlining differential-diffusion-based mechanism, two examples of the above mentioned sensor classes: Planar Hall Effect (PHE) sensors for few-molecule detection and inductive coil magnetometers as robust and (in principle) wearable sensors to detect chemicals and biomarkers in the range of μg/ml and above.

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Michael Acceptor Bearing A Hydroxylated Biphenyl Structure As Molecular Core For New Compounds Against Malignant Melanoma Cells

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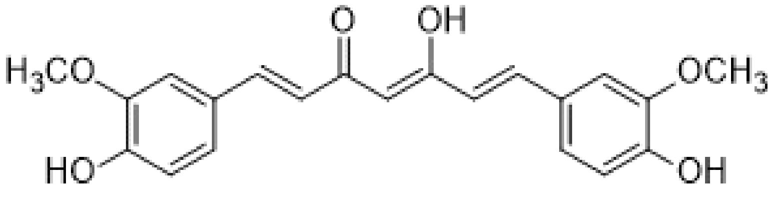
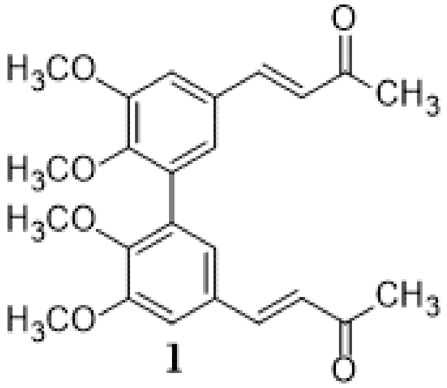
Cutaneous malignant melanoma is the most lethal form of skin cancer that arises from uncontrolled proliferation of melanocytes that are cells producing pigments. Curcumin, the main component of *Curcuma longa*, contains an α,β-unsaturated Michael acceptor pharmacophore that is well recognised in the design of new antimelanoma drugs in virtue of the emerging role of this moiety in interacting with nucleophiles present in the cancer cells[1]. Curcumin exhibits also remarkable anti-oxidant, anti-inflammatory and neuroprotective activities.

Recently, our group has prepared an analogue of curcumin, compound **1**, that showed antiproliferative and proapoptotic activities against malignant melanoma and neuroblastoma ten times stronger than those of curcumin[2].



curcumin



1

The interesting result achieved with compound 1, encouraged us to pursue further structural tuning in order to discover more efficient drug candidates. Hydroxylated biphenyl unit is embedded in many structures of bioactive natural products and provides an ideal molecular framework for structural modifications in the development of drug candidates.

A small collection of C_2-symmetry hydroxylated biphenyls featured with a α,β-unsaturated ketone (Michael acceptor) as lead structure was prepared and the capability to act against different human malignant melanoma cell lines was assayed. The antiproliferative capacity of each compound was calculated as 50% inhibition concentration (IC_{50}) that improved down to 1.2 µM after 72 h of treatment.

The prodrug approach was applied in the synthesis of the compounds in order to improve delivery of compounds into the cell by modulation of Ph-OH protective group. Different functional groups that influenced the physicochemical properties of the molecule were introduced, mainly its lipophilicity and the capacity of hydrolysis into the cell. The effective role of the hydroxylated biphenyl structure in inhibiting growth of malignant melanoma cells was clearly evidenced.

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Functionalization Of Hydroxylated Phenols And Biphenols Bearing An α,β-Unsaturated Ketone As Lead Structure

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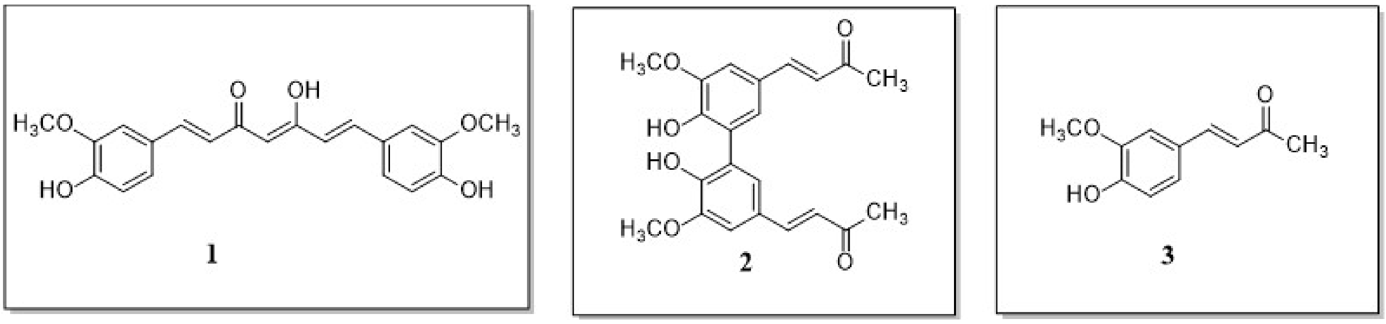
The unique pharmacophore structure of hydroxylated biphenyls has a crucial role in the biological activity of many natural occurring compounds [1]. This structural feature allows the activation of a large and selective number of interactions with the surface of several proteins.

Recently, our group has prepared an analogue of curcumin **1** (biphenol **2**) (Figure 1). We found that compound **2** was an effective breaking-chain activator in bulk lipid autoxidation [2a, showing strong cytotoxicity against rat pheochromocytoma (PC12) cells, a slow-growing neuroendocrine tumoral cells. Compound **2** also interacts with high affinity with alpha-synuclein [2b]. When Ph-OH groups are *O*Me protected, antiproliferative and proapoptotic activities against malignant melanoma and neuroblastoma cell lines were found [3a-c]. Biphenol **2** and its monomer **3** share many pharmacological features with curcumin **1** and, conversely to **1**, compounds **2** and **3** are stable in organic and aqueous solutions.

Chemical structures of compounds 1-3



With the aim of searching for new compounds with enhanced biological activities, in the present study, we prepared a collection of derivatives of compound **2** and of monomeric equivalent **3**. All new prepared compounds possess a common α,β-unsaturated ketone moiety bearing a hydroxylated biphenyl or phenyl structure with Ph-OH group substituted with functionalities with different features (i.e. groups able to increase or decrease lipophilicity of the molecule)

The new compounds were prepared through straightforward synthetic procedures. Different functional groups were introduced giving ether, ester, carbonate, sugar and acetal derivatives that influenced the physico-chemical properties of the molecule. The antiproliferative capacity of all the prepared compounds was preliminarly calculated.

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Solid Lipid Nanoparticles Encapsulating Near Infrared Absorbing Cu2-xS Nanocrystals: A Nanoformulation For Tumor Imaging And Therapy

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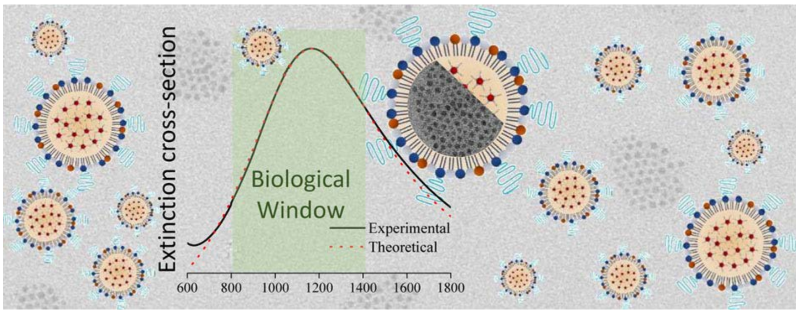
In the last few years, new drug delivery systems have been devolped to improve the efficiency of nanoformulation in the diagnosis and therapies of tumors. Here, a new nanoformulation based on low-density lipoprotein (LDL)-mimetic solid lipid nanoparticles (SLNs) loaded with $Cu_{2-x}S$ nanocrystals (NCs) has been devolped for biomedical application.



Near-Infrared absorbing solid lipid nanoparticles encapsulating plasmonic copper sulfide nanocrystals

$Cu_{2-x}S$ NCs, synthesized by hot injection method, carefully tuning reaction conditions in order to achieve NCs with a narrow size distribution and an intense LSPR in the second biological window, are ideal candidates as photothermal or imaging agents for in vivo cancer treatment, thanks to their plasmonic properties, low toxicity, biodegradability, and low cost. **Among the different nanocarriers**, SLN, mainly formed by crystalline and physiological fatty acids, prepared by a hot homogenization technique using a mixture of cholesterol and triglycerides and phospholipids, are generally recognized as safe and are characterized by high storage stability against degradation, aggregation, and coalescence. Incorporation of $Cu_{2-x}S$ NCs in the LDL-mimetic nanocarriers enhances the nanoformulation potential in biomedical applications, resulting in nanosystems able to provide the concomitant delivery of anticancer molecules and cancer diagnosis and/or therapy by means of optically induced heating and controlled drug release. Besides the optimization of the encapsulation procedures and the comprehensive characterization of the prepared nanostructures, the paper also aims to tackle the challenge accurate determination of the nanoparticles concentration in the final nanoformulation (in terms of $Cu_{2-x}S$ NCs and SLN). Both photothermal therapy and imaging efficiency strongly depend on the concentration of the nanoagents and the concentration of the nanovector is also mandatory for the thorough characterization of the product required for any regulatory approval. However, accurate determination of the concentration is not a trivial issue and currently there is a lack of experimental method recognized as general and reliable. Here a real-time and nondestructive approach for the determination of **NC concentration in the SLNs by means of** Mie theory and Drude model based fitting procedure of the experimental results from the morphological and spectroscopic characterization is proposed for the explanation of the plasmonic properties of the nanoformulation and for the determination of the concentration in terms of $Cu_{2-x}S$ NCs and SLNs.

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Acknowledgement:

The work was partially supported by the Italian National PON TARANTO Project (ARS01_00637) and FONTANAPULIA “Fotocatalizzatori Nanostrutturati e Radiazioni UV per un’ Acqua più Pulita ” (Cod WO BV6K5 -CUPB37H170049000007, 2018-2019).

Experimental/Structural Study Of Conformational Changes In Metabolically Stable Sequences

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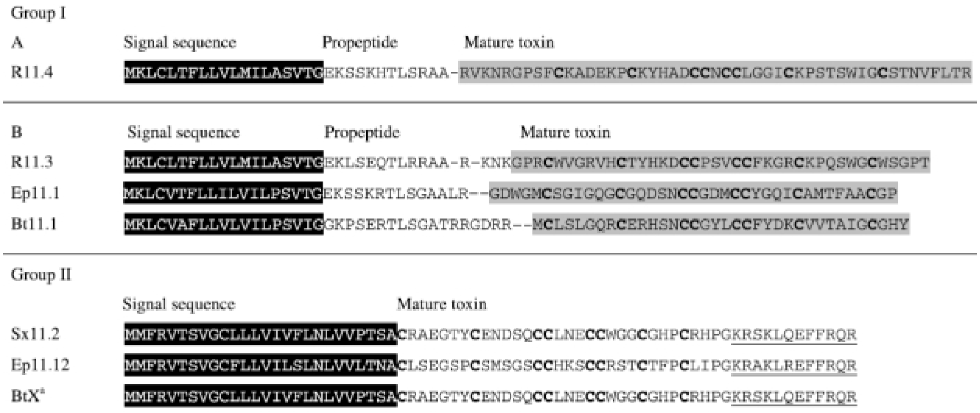
The cone snails (genus Conus) are venomous marine molluscs that use small, structured peptide toxins (conotoxins) for prey capture, defense and competitor deterrence. Most biologically active components of these venoms are small peptides, generally 7-35 amino acids in length. *Conus* peptides generated from genus *Conus* are organized into families and superfamilies with shared sequence elements. The *Conus* peptide precursor has a typical signal sequence (the 'pre-region') and a variable spacer (the 'pro-region). Particularly noteworthy is the extreme conservation of signal sequence within all members of a *Conus* peptide superfamily. The diversity of peptides in different *Conus* species is apparently generated by hypermutation of the C-terminal mature peptide region. Post-translational modification of *Conus* peptides requires both specialized enzyme machinery as well as some recognition signal sequence (with a characteristic structural features) in the peptide precursor to instruct the enzymatic machinery as to which amino acid modify. (Image 01)

We have observed a D-amino-acid-containing excitatory conotoxin belonging to the I-superfamily that have a D-Leu in the third amino acid from the C-terminus. Post-translational isomerization of L-amino acids to D-amino acids is a subtle modification, not detectable by standard techniques such as Edman sequencing or MS. Accurate predictions require more sequences of modified polypeptides. A noteworthy feature of the I2 superfamily is that it lacks a pro-peptide region between signal sequence and mature toxin, differing from all other conotoxin superfamilies in this respect. The great diversity of I-conopeptide sequences provides a rare opportunity for defining parameters that may be important for this most stealthy of all post-translational modifications. Previous work on post-translational epimerization has indicated that there may be a signal sequence that serves as an anchor site for the modification enzyme. In order to verify if the steric effect of signal sequence serves also to create a hydrophobic reaction environment we have studied the conformational changes of the signal sequence identified for conomarphin with synthetic analogues. Here we report about synthesis and conformational analysis of Boc-VIVFL-OMe and Boc-LLLVIVFL-OMe. Furthermore, a comparison was made between structural properties of Boc-LLLVIVFL-OMe and a D,L-alternating octapeptide containing leucine and valine.



Group I

A	Signal sequence	Propeptide	Mature toxin
R11.4	MKLCLTFLLVLMILASVTG	EKSSKHTLSRAA-	RVKNRGPSFCKADEKPCKYHADCCNCCLGGICKPSTSWIGCSTNVFLTR

B	Signal sequence	Propeptide	Mature toxin
R11.3	MKLCLTFLLVLMILASVTG	EKLSEQTLRRAA-R-KNK	GPRCWVGRVHCTYHKDCCPSVCCFKGRCKPQSWGCWSGPT
Ep11.1	MKLCVTFLLILVILPSVTG	EKSSKRTLSGAALR--	GDWGMCSGIGQGCGQDSNCCGDMCCYGQICAMTFAACGP
Bt11.1	MKLCVAFLLVLVILPSVIG	GKPSERTLSGATRRGDRR--	MCLSLGQRCERHSNCCGYLCCFYDKCVVTAIGCGHY

Group II

	Signal sequence	Mature toxin
Sx11.2	MMFRVTSVGCLLLVIVFLNLVVPTSA	CRAEGTYCENDSQCCLNECCWGGCGHPCRHPGKRSKLQEFFRQR
Ep11.12	MMFRVTSVGCFLLVILSLNLVVLTNA	CLSEGSPCSMSGSCCHKSCCRSTCTFPCLIPGKRAKLREFFRQR
BtX[a]	MMFRVTSVGCLLLVIVFLNLVVPTSA	CRAEGTYCENDSQCCLNECCWGGCGHPCRHPGKRSKLQEFFRQR

Complete precursor sequences of I-superfamily peptides

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Bacterial Exopolysaccharides From The Polar Regions: An Environmental-Friendly Microbial Strategy For Bioremediation And Cryopreservation Uses

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The great metabolic and physiological capabilities of extremophilic microorganisms adapted to the cold are widely recognized and supported by numerous studies (Finore et al., 2019). Survival strategies in such harsh environments include the biosynthesis of extracellular polymeric substances (EPSs), adopted by a number of psychrophilic bacteria to cope with extremely low temperatures by protecting microbial cells from the direct contact with the surrounding cold environment (Poli et al. 2017). The ecological roles played by bacterial EPSs in natural environments could find applications in diverse biotechnological fields. EPS production falls within the scope of bioprospecting, where the investigation of new or scarcely explored biological matrices - which could be cold-adapted bacteria is of fundamental importance. This is particularly true given the current extremely urgent need to find new and safety compounds with biotechnological relevance. EPS production by psychrophilic microorganisms has been investigated during recent years, due to the wide versatility, the considerable application possibilities in a wide number of industrial fields, and the ecological and protective roles that such molecules play in microorganisms (Finore et al., 2014). Nevertheless, cold-adapted marine bacteria from several Arctic and Antarctic matrices (e.g. sediment, sea-ice and sponges, lakes) have seldom been explored as a source of EPSs. Ongoing research focusing on polysaccharides produced by extremophiles, isolated from Arctic and Antarctic regions, will be reported including chemical structures, fermentation technology and biotechnological application.

In particular, the description of psychrophilic bacteria from permafrost thaw ponds (thermokarst lakes) in the Sasapimakwananisikw River valley near Kuujjuarapik-Whapmagoostui, in subarctic Québec (Canada), will be described with special attention to *Pseudomonas extremaustralis* strain 2ASCA, producing a levan polysaccharide with cryoprotective capability. Moreover, extracellular polymeric substances produced from sponge-associated Antarctic bacteria (belonging to *Winogradskyella, Colwellia* and *Shewanella* genera) and a *Pseudoalteromonas* sp. MER144, isolated from Antarctic seawater in Terra Nova Bay, will be described for chemical composition and heavy metal adsorption proprierties.

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Acknowledgement:

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N-Glycosylation Analysis As Diagnostic Tool In Neurological Diseases: From Congenital Glycosylation Defects To Alzheimer Disease

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Glycosylation has been shown to be involved in the vast majority of cellular interactions and complex networks. Glycosylation is at the basis of most biological events, including protein structural stability, recognition, immunological responses, cancer metastasis and interaction of pathogens to host cells as first step of infection processes. Furthermore, the importance of glycosylation is highlighted by the extreme consequences of genetic defects concerning the glycosylation machinery. Congenital Disorders of Glycosylation (CDG) are the result of the loss of function of different enzymes involved in N-linked and O-linked oligosaccharide biosynthesis, often resulting in significant neurological impairment, organ failure and premature death. The importance of protein glycosylation requires accurate technologies for structural investigation on the glycan molecular component.

Our research group is part of a European network engaged in the diagnosis and treatment of CDG. In this context, among a number of diagnoses greater than one hundred, we identified by tailored mass spectrometry-based strategies, the distinctive biochemical hallmarks of three new CDG types: DPM2-CDG, MAN1B1-CDG and SLC35A3-CDG (1-2).

We developed over the years, a multiplexed approach for the N-glycome analysis on patient biological fluids such as serum, plasma and cerebrospinal fluid (CSF) and on cell extract and tissues. This methodology was moreover implemented by glycosylation analysis on specific serum-extracted glycoproteins (immunoglobulins, transferrin, and others), giving a significant contribution both to disease diagnosis and to the comprehension of the specific pathological mechanisms.

Our experience gained on glycosylation analysis on CDGs, enabled us to uncover the fundamental role of N-glycosylation in neurological diseases. Evidence of this are our studies on the differential glycomic analysis of CSF in patients with Alzheimer's disease (AD) and mild cognitive impairment (MCI). In particular, we identified a group of AD and MCI subjects (about 45% of the studied sample) showing significant alteration of CSF N-glycome profile, consisting of a decrease in the overall sialylation degree and an increase in species bearing bisecting GlcNAc. Noteworthy, all the MCI patients that converted to AD within the clinical follow-up, had an abnormal CSF glycosylation profile (3). Based on the studied cohort, CSF glycosylation changes may occur before an AD clinical onset. Previous studies specifically focused on the key role of glycosyltransferase GnT-III on AD-pathogenesis, addressing the patho-mechanism to specific sugar modification of BACE-1 glycoprotein with bisecting GlcNAc. Our patients manifested protein N-glycosylation changes at an early phase of the whole biomolecular misregulation on AD, pointing to CSF N-glycome analyses as promising tool to enhance early detection of AD and also suggesting alternative therapeutics target molecules, such as specific glyco-enzymes.

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Acknowledgement:

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Self-Assembling Peptide Hydrogels For Ultrafast Microarray Bioassays

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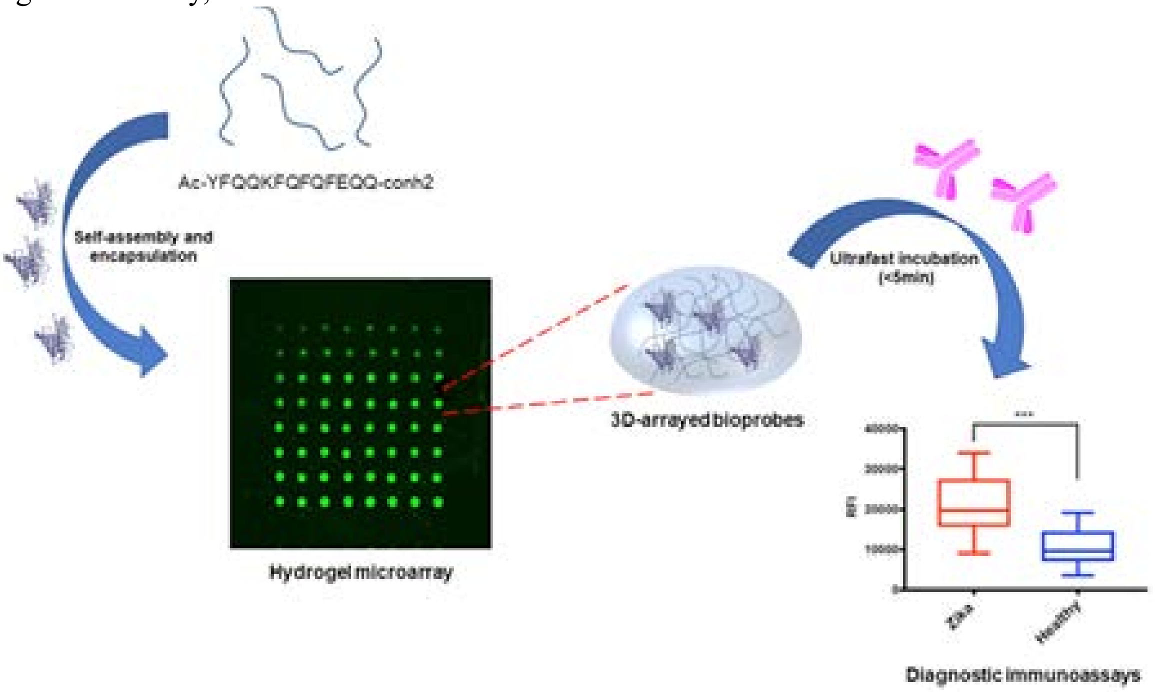
Hydrogels represent ideal environments to locally confine biomolecular probes onto analytical surfaces under solution mimetic conditions. Yet, severe limitations still exist in matching unimpaired analytes diffusion with stable probe entrapment. Here, a peptide hydrogel was used as a highly versatile matrix for the design of 3D microarray immunoassays.1 The hydrogel microstructural and functional properties are easily tunable, resulting in a unique combination of favorable features which include: 1) spontaneous and rapid formation; 2) tunable bio-probes diffusion properties based on gel-forming peptide concentration; 3) direct use in microarrays fabrication due to favorable viscoelastic properties; 4) self-adhesiveness on hydrophobic surfaces. Most importantly, biomolecules diffusion through the gel matrix occurs with ultrarapid kinetics, enabling us to run complete immunoassays in solution-mimetic conditions and unprecedented time frames (<10min). Overall, the developed material overcomes many of the limitations that currently plague hydrogel for immunoassays limiting their widespread applications (limited mass transport, complex fabrication, poor versatility of use), while being user-friendly, robust and cost-effective.



A self-assembled peptide hydrogel is used to fabricate 3D-microarrays for diagnostic immunoassays

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Acknowledgement:

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New Application Of A Versatile Drug Nanocarrier Based On A Choline-Calix[4]Arene Derivative: Supramolecular Nanohydrogel Formation In The Presence Of Curcumin

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The development of nano-structured systems able to deliver drugs to the biological targets are of great interest in biomedical field. In this context, we designed a supramolecular nanoaggregate of a polycationic choline-calix[4]arene derivative (**1**) to deliver drugs towards protected biological compartments (eye and brain) exposing choline-transporters. We demonstrated the potential of the micellar nanoconstruct as nanocarrier for natural and synthetic drugs, [1,2] and as nanoreactor for photoactivatable drugs. [3] The micellar nanoaggregates formed by simple dissolution in PBS medium, significantly increased water-solubility and stability of curcumin. [1,2] Interestedly, at higher concentrations the calix[4]arene **1** and curcumin formed a clear reddish hydrogel (Figure 1), rather than a colloidal solution.

Herein, we report about the preparation, physico-chemical characterization and sustained drug release property of the supramolecular micellar nanohydrogel. Rheological properties, morphology, simulation modelling, protection of curcumin from photodegradation, and low rate of curcumin release upon to dissolution of the hydrogel in drug loaded micellar nanoaggregates, will be discussed. The visco-elastic and injectable supramolecolar nanohydrogel formed by simply addition of a natural drug like curcumin to a self-assembling calix[4]arene derivative, without using other additives and organic solvents, combines the properties of micellar systems and a hydrogel in drug delivery and appears a promising new tool for applications in nanomedicine.

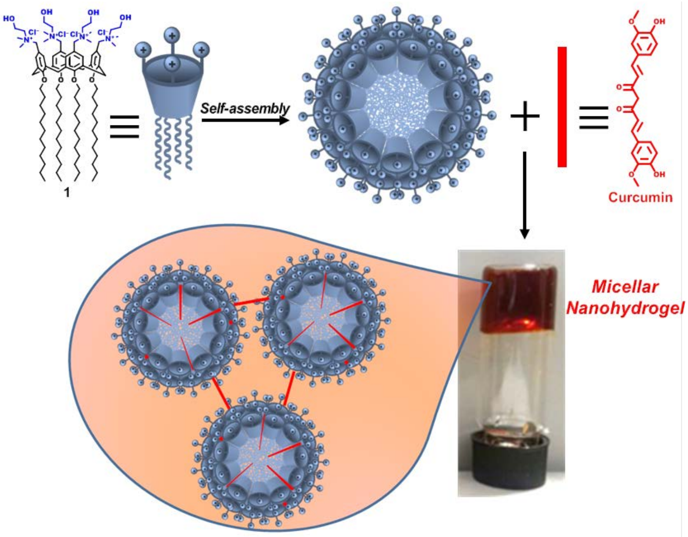

Photo and schematic representation of the calixarene 1–curcumin supramolecular nanohydrogel.

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The Structure Of The Pro-Domain Of Mouse Prongf In Contact With The NGF Domain

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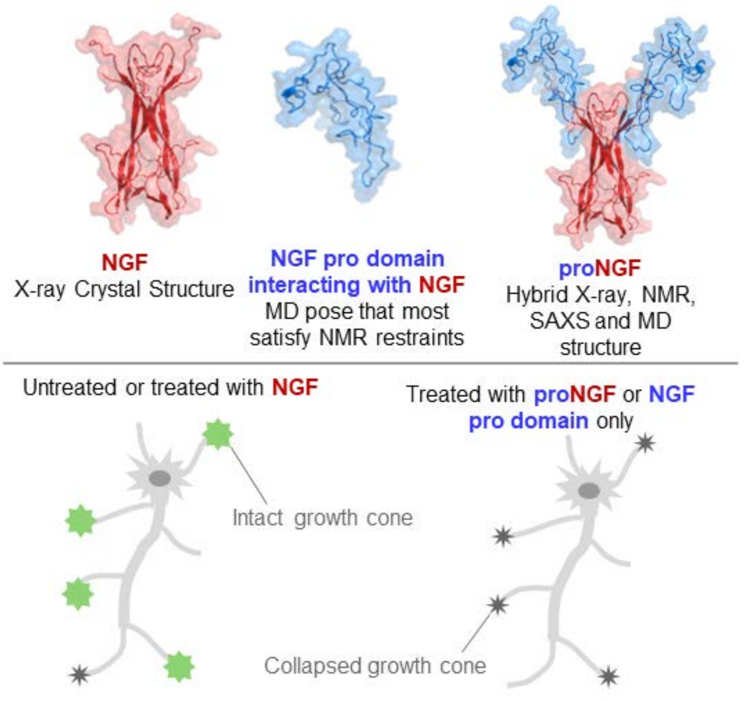
Nerve growth factor (NGF) is an important neurotrophic factor involved in the regulation of cell differentiation and survival of target neurons. Expressed as a proNGF precursor, NGF is matured by furin-mediated protease cleavage.

Increasing evidence suggests that NGF and proNGF have distinct functional roles. While the structure of mature NGF is available, little is known about that of the pro-domain because of its dynamical structural features.

We exploited an ad hoc hybrid strategy based on nuclear magnetic resonance and modeling validated by small-angle X-ray scattering to gain novel insights on the pro-domain, both in isolation and in the context of proNGF [1].

We show that the isolated pro-domain is intrinsically unstructured but forms transient intramolecular contacts with mature NGF and has per se the ability to induce growth cone collapse, indicating functional independence.

Our data represent an important step toward the structural and functional characterization of the properties of proNGF.



Structure and Function of proNGF, NGF pro domain and mature NGF

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Cyclodextrin Polymers As Versatile Platform For The Delivery Of Antibiotics And Antitumorals

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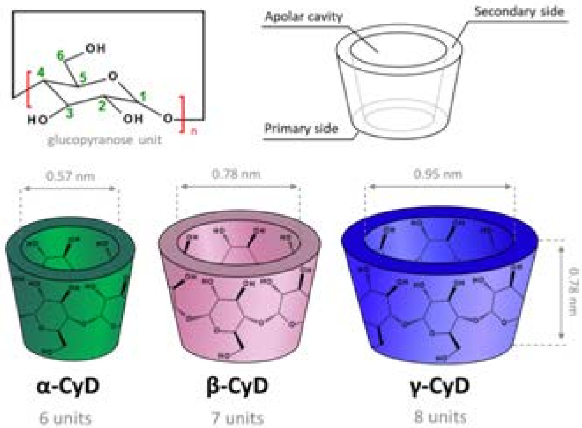
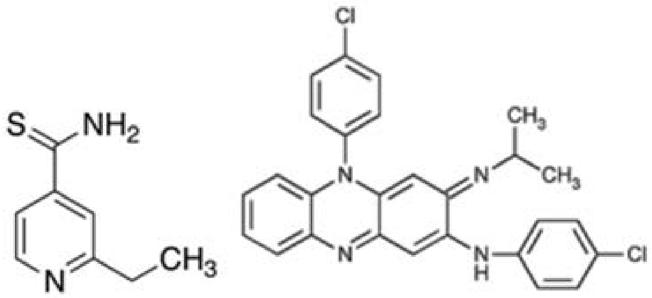
Cyclodextrins (CyDs) are water soluble, biocompatible cyclic oligosaccharides, made of α-D-glucopyranose units joined by α(1-4) linkages. They received considerable attention as carriers/solubilizers for drugs thanks to their ability to host lipophilic guests in their hydrophobic cavity. Various CyD-based nanoassemblies, loading drugs *via* non covalent interactions have been proposed as delivery platforms and some have been considered for preclinical studies. Water soluble CyD polymers can be prepared using crosslinking method based on polycondensation in the presence of a bifunctional agent, like citric acid, or epichlorohydrin. With epichlorohydrin a CyD content up to 70% w/w can be obtained for the water soluble polymers. Most interesting, CyD polymers are able to associate drugs much more efficiently than the monomeric CyD, to enhance the aqueous solubility of several guests and to incorporate two or more drugs or therapeutic agents contemporarily. They have been considered for the delivery of antibiotics and antitumorals and for the implementation of multimodal therapy. We will report on the successful loading in a polymeric βCyD nanoparticle (NP) of the second-line tuberculosis drug Ethionamide together with a synthetic booster using a green approach and reaching high amount of dissolved drug.[1,2] The NP loading both drug and booster revealed suitable for pulmonary spray application. Next, we will discuss encapsulation of Clofazimine, a riminophenazine derivative, known as antileprosy drug. It is known to be active against a wide spectrum of Gram-positive including Mycobacteria, Staphylococci, Streptococci, Enterococci and Listeria as well as MDR resistant strains. As Clofazimine is highly lipophilic, it tends to be deposited predominantly in fat tissues. During the last decade investigations, also in the field of nanotechnology, focused on alternative routes for improved CLZ delivery. We successfully loaded CLZ in sulfobutylether βCyD polymers using a green method and obtained promising results against *Staphylococcus Epidermidis*, a microbe often found in hospital context.[3]



Cartoon of α, β, and γCyD



Structural formula of Ethionamide (left) and Clofazimine (right)

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5′,8-Cyclopurines As Biomarkers Of DNA Damage Induced By HO. Radicals: Chemical, Analytical, Biological, And Diagnostic Aspects

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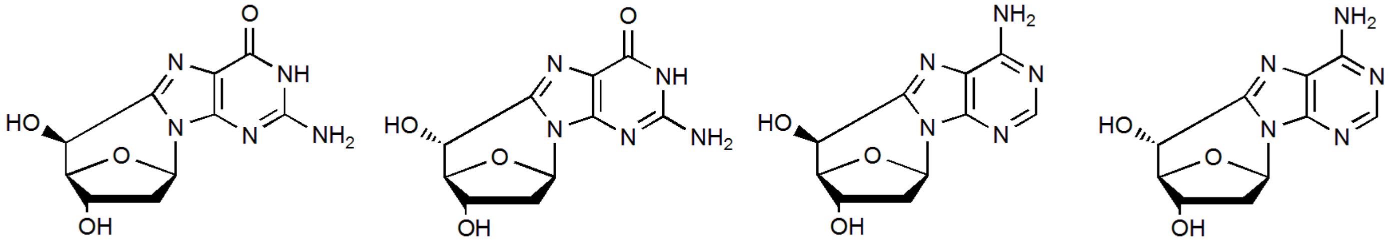
DNA damage caused by free-radicals includes a large variety of base and sugar lesions leading to DNA breaks and DNA-protein cross-links. Among free radicals, the diffusible hydroxyl radicals ($HO^{\bullet}$) are key oxidant species responsible to react with DNA either by hydrogen abstraction from 2-deoxyribose units or by addition to the base moieties.

Our research group is involved in the study of chemical, analytical, biological, and diagnostic aspects of free-radical DNA damage. We individuated the mechanistic key steps and intermediates of the hydroxyl radical ($HO^{\bullet}$) attack to DNA purine nucleotides: C5' radicals are formed, followed by an internal cyclization giving 5',8-cyclo-2'-deoxyadenosine (cdA) and 5',8-cyclo-2'-deoxyguanosine (cdG) identified as products, in two possible diastereomeric forms, 5'*R* and 5'*S* (Fig.1) [1,2]

The biological impact of purine 5',8-cyclo-2'-deoxynucleosides (cPu) is due to their presence in mammalian cellular DNA in vivo as tandem-type lesions, since they involve a concomitant damage to the base and to the sugar moieties, exclusively repaired by the Nucleotide Excision Repair pathway (NER) with low efficiency in comparison with other bulky DNA lesions [3].



(5'S)-5',8-cdG **(5'*R*)-5',8-cdG** **(5'S)-5',8-cdA** **(5'*R*)-5',8-cdA**

The structures of 5',8-cyclo-2'-deoxyguanosine (cdG) and5',8-cyclo-2'-deoxyadenosine (cdA) in their 5'R and 5'S diastereomeric forms.

Nowadays these lesions are used as radical stress biomarkers of DNA damage, they are better markers than other oxidatively generated DNA lesions, thanks to their specific mechanism of formation and their chemical stability during work-up, thus avoiding artifacts.

We addressed our research with a multidisciplinary approach spanning from synthesis to cell biology with important results in:

(i)Synthetic and analytical protocols for the availability and characterization of the diastereoisomeric 5′*S*- and 5′*R*-cPu lesions, also as isotopic labelled references;

(ii) Physical-chemical studies on specific oligonucleotide models as: MD simulations, NMR, Melting Temperature;

(iii) Biological and Clinical studies for the investigation of the relationships between the levels of lesions and human health, disease, and aging is a matter of investigation.

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Revisiting Pyrazolones As Proteasome Activators With Neuroprotective Activity

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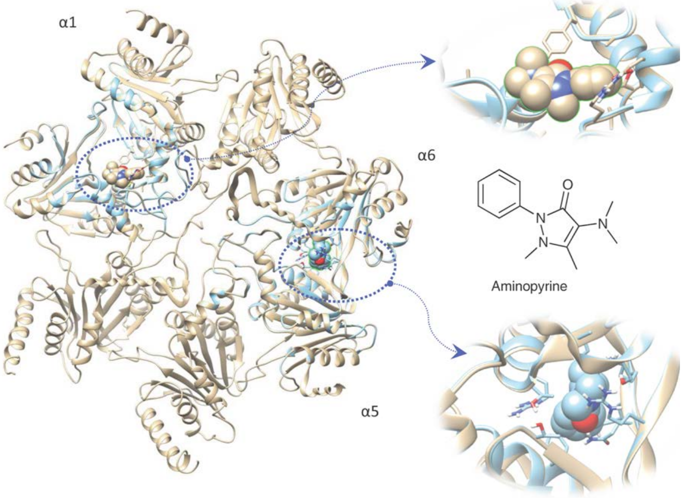
The proteasome is a 700 kDa multi-subunit proteolytic complex responsible for the hydrolysis of many cytosolic protein substrates.[1,2] Evidence is mounting that proteasome failure is normally associated with neurotoxic protein accumulation in the early stage of Alzheimer's Diseases (AD).[3] Hence proteasome activation is increasingly attracting attention as a promising target in the search of effective AD therapies. However, the search of exogenous small molecules proteasome activators is a challenging and poorly explored field.

Pyrazolones are a well-known class of pyrazole hetero-cycles harboring many attractive pharmacological properties and extensively investigated for more than a century. Antipyrine, synthesized in 1883 by Ludwig Knorr, is considered the very first synthetic painkiller drug, and metamizole (Novalgin), developed a few years later, is likely the strongest antipyretic drug known.

Inspired by recent reports showing that some pyrazolones may rescue proteasome activity in mice and attracted by the possibility to repurpose "old" medicines and thus de-risk the drug development process, we scrutinized a small library of drugs by assaying their capacity to augment proteasome activity in tube tests, *in vitro* and *in vivo*. Tube tests showed that aminopyrine activates proteasome through binding the α-ring surfaces and influencing its gating dynamics. Docking studies coupled with STD-NMR experiments showed that H-bonds and π-π stacking interactions between active pyrazolones and the enzyme play a key role in stabilizing the drug-target complex. Aminopyrine exhibits neurotrophic properties and protect differentiated human neuroblastoma SH-SY5Y cells from β-amyloid (Aβ) toxicity. Preliminary experiments performed using 3×Tg-AD mice evidenced a slight dose-dependent rescue of grip strength.

Our results point to aminopyrine as a neuroprotective proteasome activator and we hope that they could inspire chemists to develop new strategies in discovering and optimizing drug candidates for the treatment of chronic neurodegenerative conditions.



Top view of the 20S proteasome "gate". Circled in blue are evidenced two binding poses of amynopirine

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Spectroscopic And *in Silico* Studies On The Interaction Of Substituted-Pyrazolo[1,2-a] Benzo[1,2,3,4]Tetrazine-3-One Derivatives With C-myc And Tel22

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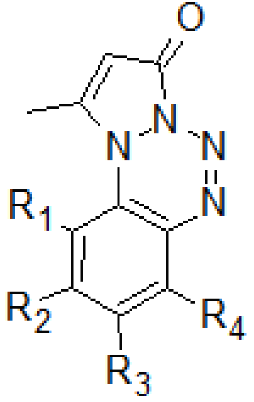
As extension of previous results reached on the pyrazolo[1,2-a]benzo[1,2,3,4]tetrazin-3-one derivatives (PBTs) endowed with anticancer potential, we focused our research interest to new emerging and challenging biological targets involved in carcinogenic process. More precisely to gene promoter related to the oncoprotein c-myc as well as Tel22. C-myc is overexpressed in a large number of cancer and related binders are potential anticancer drugs because they target a promoter quadruplex present upstream of the proto-oncogene myc, down-regulating its expression. Indeed, one of the possible mechanisms underlying the antiproliferative activity of anticancer drugs is precisely based on the induction of quadruplex structure in c-myc, with consequent blockage of oncogene expression. Analogously, telomeric DNA binders inhibit the ability found in most human cancer cells to indefinitely replicate becoming immortal, as they prevent the hybridization of the telomerase RNA template onto the primer. Therefore, the discovery of new molecular entity able to tune the binding or the stabilization of the G4 quadruplex represents a current therapeutically approach for anticancer diseases [1].

A preliminary NCI screening on variously substituted pyrazolo[1,2-a] benzo[1,2,3,4]tetrazin-3-one derivatives (PBTs) against a panel of 60 tumor cell lines, evidenced a promising anti-proliferative activity in the mM and sub–mM range. Depending on the position and nature of the substituents, several derivatives targeted selectively specific tumor cells or in other cases more than ones. These attractive results, for this tricycle scaffold, biologically unexplored so far, prompted us to move to new optimized structures followed by evaluation on apoptosis induction and cell cycle perturbation [2]. Once assessed their anticancer potential, on PBTs further deeper studies became necessary, in order to get insights on their mechanism of action. Thus, more specific biological targets, such as duplex DNA and topoisomerase(II) catalytic cycle, were approached, including *in silico* support [3]. Here, extending the research on other recently recognized anticancer targets, we planned to evaluate the effects of PBTs on c-myc and Tel22 by mean of circular dichroism (CD) and related melting experiments. In support, molecular dynamics (MD) and docking techniques permitted us to gain additional insights on the observed effects. The outcomes will be showed with more details at poster session.

Investigated PBTs



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Smart Peptide Nucleic Acids (PNAs) Probes For Nucleic Acid Based Biomarkers Detection

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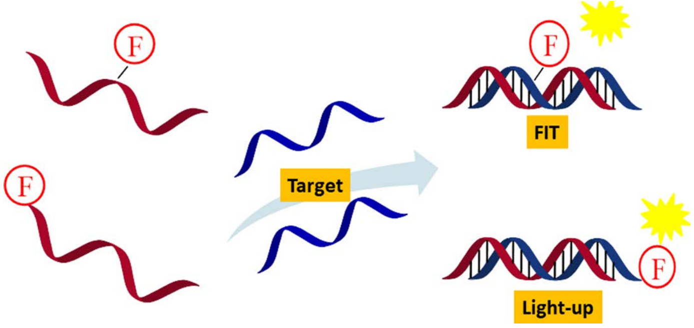
Fluorogenic oligonucleotide probes are invaluable molecular tools to detect, localize and quantify nucleic acids (NA) with a high sensitivity and accuracy.[1] These probes bind to complementary NA via Watson–Crick H-bonding, producing a fluorescence response which allows to discriminate target-bound from target unbound molecules. Among these, single labelled Peptide Nucleic Acids[2] (PNA) based probes (Fig. 1) are very attractive for their easy design and synthesis, impressive performance in terms of specificity, very fast hybridization kinetics, and high signal-to-background ratio regardless of the salt concentration. Additionally, the wash-free detection of target nucleic acids is possible since PNA probes can be labelled with environment sensitive fluorophores.



Schematic representation of FIT and light up probes; red strand PNA, blue strand RNA

MiRNAs[3] are a recently discovered class of non-coding RNAs that play key roles in the regulation of gene expression. Acting at post-transcriptional level, these appealing molecules may fine-tune the expression of almost 30% of all mammalian protein-encoding genes. Besides their regulatory roles, miRNA have emerged as significant biomarkers being deregulated in several diseases. In particular, detection of levels of miRNAs in biological fluids (blood, plasma *etc*) can be employed for early disease diagnosis, to predict prognosis and response to therapy. A group of miRNAs (miRNA-449a, miRNA-492, miRNA-21, miR-486)[3b] deregulated in celiac disease (CD) have been selected for our proof of concept study. We focused on CD since for this disease an early and non-invasive diagnosis methodology is required. The smart probes we realized using peptide nucleic acids (PNAs),[2] a DNA/RNA mimic, which possess enhanced affinity and excellent specificity towards natural nucleic acids, resistance to enzymatic degradation and an extensive range of salt tolerance.[3] The detection of miRNAs was obtained through light up probes, using thiazole orange (TO) as fluorescent tag. PNA based probes were synthesized by solid phase peptide (SPPS) using commercially available Fmoc/Bhoc monomers; exploiting a synthetic protocol developed in our laboratory. Hybridization properties and structural characterization of the PNA probes in complex with the target miRNAs, were obtained by UV, CD and fluorescence spectroscopy. TO-PNA based probes showed great promises for rapid and convenient recognition of specific RNA biomarkers and could represent an emerging forefront technology.

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Tissue Engineering: 3D Printing vs Mold Casting Technology

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Due to its avascular nature and low mitotic activity, cartilage has poor intrinsic capacity to repair. Any cartilage loss or damage can lead to mobility reduction and pain, until arriving to disabling conditions and chronical diseases. Different options are available to treat the symptoms but a resolutive approach has still to be found, despite multiple attempts have been tried.

In response to this need, we aimed to design, evaluate and compare 3D printed and 3D mold casted gelatin-based scaffolds for chondral regeneration, starting from the slurry composition and concentration, moving to 3D printing and mold casting parameters definition until arriving to the final products geometry and properties evaluation. Then, the two different technology were compared. With this we would like to validate the 3D printing technique as tool to develop customized biomimetic scaffolds for chondral regeneration with improved mechanical performances, suitable to repair even large cartilage defects.

Rheology tests were performed to provide the starting information on the slurry behaviour at the liquid state (45°C). Electronic (ESEM) microscopy allowed to determine the success of the mold casting process and directional lyophilization used to obtain an aligned porosity, comparable to the ones of the 3D printed scaffold. The success of the 3D printing process in the scaffolds' realization was instead evaluated through optical microscopy, due to the macro dimensions of the mesh. The porosity tests gave an idea about the total and macro porosity of the realized materials, that was estimated to be around 99% for both the scaffolds types the first, and almost the double for the 3D printed ones the second. A swelling rate of nearly 10 times for the 3D printed scaffolds and of approximately 8 times for the mold casted ones was recorded, providing a good index of the liquid retention capability (e.g. cells growth medium) of the materials. The degradation test at 7 and 21 days showed a good and similar degradation rate of both the materials and its fitness with following possible cell test in physiological environment. Lastly, with DMA, the Young's modulus values were recorded and used to determine the possible suitability of the materials for the thought role.

In conclusions, two different materials for chondral regeneration, differing in the technology with which they were created, were developed, tested and compared. They both showed a promising behaviour, in terms of physicochemical and mechanical properties, with some relevant differences that can be exploited to answer different needs in the engineering of this peculiar tissue. In future, a synergy deriving from the combination of these two different technologies, like a multilayer, could be further investigated to get the best from both. Moreover, different functionalization approaches with biomolecules will be employed to improve the biomimicking and biocompatibility of the developed materials.

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Covalent Functionalization Of A Biomineralized Hybrid Scaffold For Bone Regeneration With Alginate, As Mimetic Of Hyaluronic Acid

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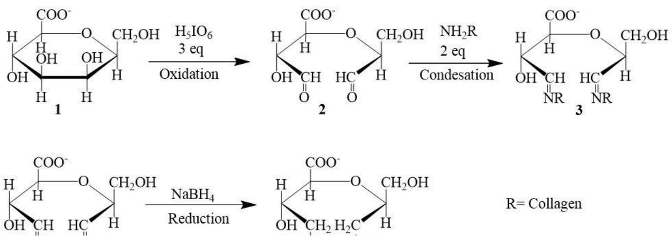
The bio-inspired assembling and mineralization process is a method to apply the concepts of organ-morphicity in the production of biomimetic bones through chemical or biological manipulation, as scaffolds obtained by co-precipitation of hydroxyapatite doped with Mg ions (Mg-HA) and type I collagen (Coll) in a bio-inspired way. (1) To take another step towards the mimesis of bone tissue, this study focuses on the development of MgHA/Coll hybrid scaffolds plugged covalently with oxidized alginate (MgHA/Coll/Alg), a biocompatible molecule, used in biomaterials designs and analog of hyaluronic acid, a component of this connective tissue.



Details of the reaction of functionalization of Collagen with Alginate through oxidation with periodate.

The alginate is oxidized (1 eq) through periodate (3 eq) in water medium, details of the chemical reaction are reported in Fig.1. The Schiff reagent, to perform the chemical test for aldehyde detection, and the periodate consumption, monitored by UV-VIS spectroscopy, are employed to follow the progress of oxidized reaction. The oxidized and purified alginate is then mixed with MgHA/Coll hybrid hydrogel, developed through a biomineralization process, where the mineral phase is nucleated on collagen fibers with a ratio of 30/70wt%. To generate a more stable bond, a reduction of the imino group is performed by treatment with sodium borohydride, then the hydrogel is freeze-dried to obtain a porous scaffold. The final materials and the reaction intermediates are characterized with infrared spectroscopy (FTIR), X-ray diffraction (XRD) and gel permeation chromatography (GPC).

The procedure to perform this coupling is the oxidation of alginate, it leads to the carbohydrate ring opening and the formation of two aldehyde groups (Alg-Ald) (2). GPC, through the principle of size exclusion, allows to measure the polymers molecular weight, and from the comparison between the molecular weight of the alginate and the oxidized alginate, allows to state the formation of the aldehyde. Alg-Ald is highly reactive with amine groups of collagen and through a condensation reaction generate immines, which are then reduced and further stabilized as amines. FTIR analyses detect in the fingerprint area a typical peak of alginate revealed also in the functionalized MgHA/Coll/Alg scaffold. XRD analyses demonstrate the preservation of the mineral apatitic phase also post-functionalization reactions.

This preliminary protocol and future studies to plug biopolymer to collagen, opens up toward large scenarios. In addition to the bone tissue regeneration these highly biomimetic matrices open the way to other important application. The niche of stem cells is formed by collagen and hyaluronic acid and through this method can be predictive to build 3D tumor model. 3D cell culture models are becoming increasingly important for the study of cancer biology because these models recapitulate the in vivo cell situation better than standard monolayer cultures, such as developmental dynamics and tumor progression.

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Peptide Conjugates For Neuroprotection And Amyloid Detection

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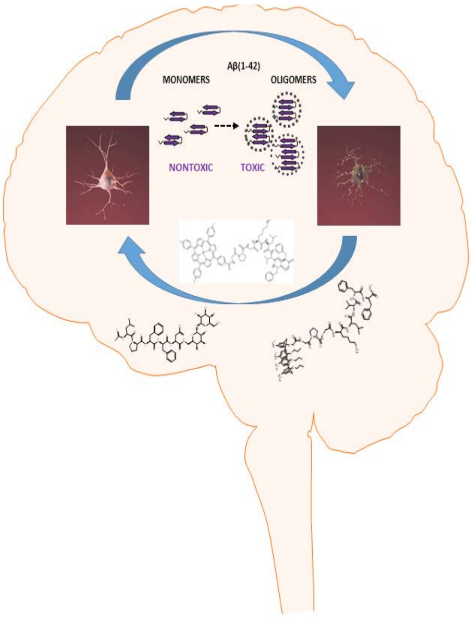
In the extensive and controversial literature dealing with Alzheimer's disease (AD), a predominant idea refers to the crucial role of Amyloid-β peptides (Aβ) in the pathogenesis of the disease. AD has been proving to be extraordinarily refractory to any attempt aimed at halting or slowing the progression of the disease. Current approved drugs provide some relief of the AD symptoms, but do not contrast the causes of disease neither delay its progression. Therefore, the identification of pharmacologically effective targets is urgently needed for AD. Moreover, if Aβ monomers are crucial for the survival of neurons,[1] the selective targeting of cytotoxic oligomers is fundamental for the development of effective therapeutic strategies against AD. Bio-conjugate peptides play an important role in several fields of biomolecular and medicinal chemistry. In particular, peptide-based epitopes with covalently attached other moieties able to explicate additional or complementary functions, including Brain Blood Barrier permeation, metal chelation or aggregates disassembling, targeted imaging and treatment, hold a promising potential for applications in AD. In our laboratory, we have been synthesizing a variety of small peptides bio-conjugates differing by the peptide epitope or the conjugated scaffold.[2,3]

A range of molecular details as well as biological effects have been listed with these systems, all of them accounting for the observed neuroprotection against the toxic insult induced by Aβ aggregation in primary cortical neurons. A detailed structural or mechanistic picture on how these inhibitors can really work is still in progress in our lab. In addition, by changing the typology of the conjugated moiety to the peptide sequence, novel supramolecular systems can be obtained. In this communication an overview of the design principles of the peptide conjugates, their neuroprotective activity and their capability in detecting Aβ peptide in solution are described in terms of potential use of these compounds as theranostic agents and for the targeted drug delivery.



Neuroprotective Peptide Conjugates

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Biohybrid Membrane Systems As Reliable Tools In Neuroscience

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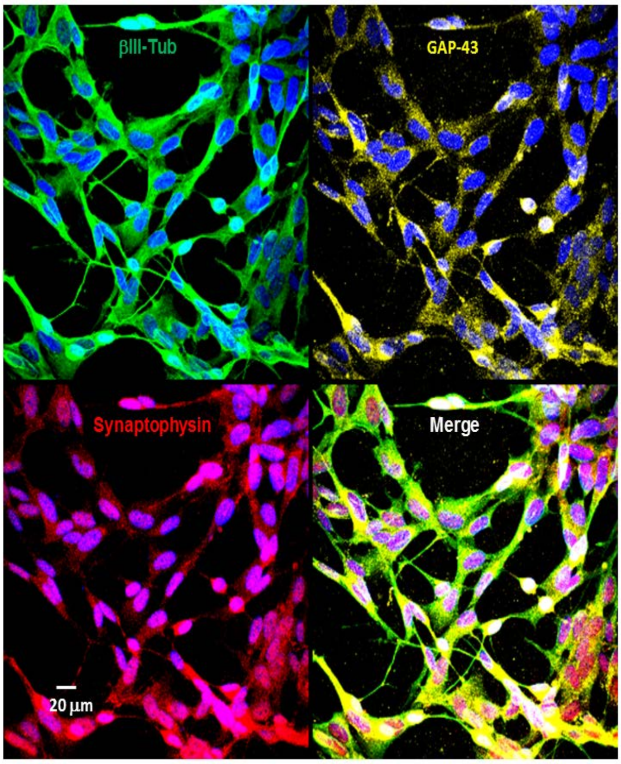
Within the scenario of neuronal tissue engineering membrane-based strategies pursued the realization of sophisticated devices by recapitulating an *in-vivo* like environment in which cells could restore their complex architecture. The reconstruction of a functional neuronal construct, is mainly influenced by the intrinsic membrane properties which can be tuned to better simulate the tissue district of interest. Polymeric membranes act as instructive biomaterials, where key elements as the structural, physico-chemical, mechanical and selective transport properties, are able to drive neurite outgrowth favouring branching and network connectivity. Thanks to the satisfaction of this fundamental issues, membranes are able to promote the in vitro creation of neuronal functional analogues allowing cutting edge investigation in neuroscience [1]. The overall strategy relies on the design and development of microporous polymeric membranes, where the synergistic combination of peculiar membrane features (geometry, configuration) and a constantly perfused cell surrounding, by means of a bioreactor,r give rise to a permissive and balanced microenvironment within which both tissue reconstruction and cell behavior control take place. Indeed, the selective permeability of the membranes and the optimized fluid dynamic conditions created by the membrane bioreactor provide a 3D low-shear stress environment fully controlled at molecular level with enhanced diffusion of nutrients and waste removal, that successfully boost neuronal-like tissue formation.

This kind of membrane platform represents reliable in vitro tools which can be used for a two-pronged approach in order to study brain-related issues in normal and pathological states. A membrane device has been used to test the capacity of neuronal cells to react to topographical stimuli by directing their orientation and polarization according to a definite path. Their use as modelling disease platform represents another proficient application of the in vitro membrane systems: by mimicking the disease development it was possible to gain new insights on neural differentiation, neuroprotection and reinnervation processes mediated by different natural molecules in neurodegeneration and neuroinflammation [2]. On the basis of this considerations it will be highlighted the multifunctional role of biohybrid membrane systems in neuronal tissue engineering as versatile in vitro platforms.



Confocal laser micrographs of differentiated neurons

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The Size-Threshold Dogma Of Nanoparticle Renal Filtration Questioned: Renal Clearance Of 11 Nm Zwitterionic SPIONs

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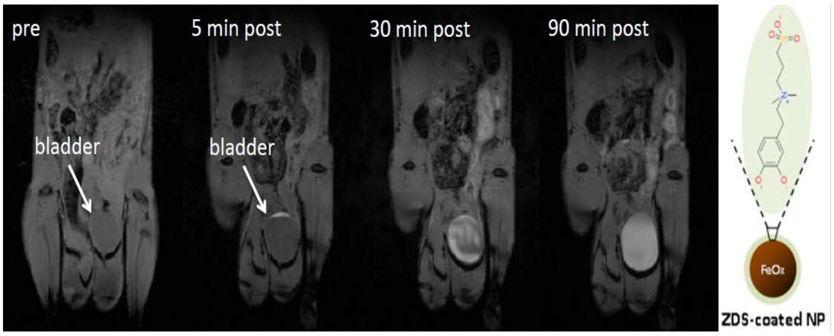
Renal clearance of nanoparticles (NPs) substantially reduces the NP toxicity by preventing NP accumulation in the body. Using QDs, it was established that only NPs smaller than 5.5 nm are cleared through the kidneys, [1] a size threshold (ST) similar to the accepted 6-nm limit for proteins. Many subsequent reports showed renal clearance of NPs < 5.5 nm and the NP ST dogma has been long held as valid. [2]

In the development of bio-compatible magnetic NPs, we carried out a systematic study of ferrite NPs coated by short (zwitter)ionic molecules. We designed the NPs as variations of reference NPs (11-nm magnetite NPs coated with a zwitterionic sulfobetaine, ZDS) [3] in size (3 to 22 nm), core composition (MFe_2O_4), and coating (DS, caffeic acid, coryneine chloride).

All NP types are immunologically safe as they do not elicit not interfere with the innate immune/inflammatory reaction. The *in-vitro* internalization of the NPs by BV2 cells is low and only depends on size. We investigated the *in-vivo* bio-distribution by MRI monitoring of mice IV injected with ZDS-coated magnetite NPs (SPIONs) having small (D_{TEM} = 3.2±0.4 nm; D_H = 9±1 nm) and medium (D_{TEM} = 10.7±0.6 nm; D_H = 13±1 nm) core size. Both SPIONs quickly filter through the kidneys and gather in the bladder (Figure). SPIONs with DH = 9-13 nm are surprisingly cleared by renal excretion even though their D_H is much larger than the 5.5-nm ST.

These results question the NP ST dogma. Indeed, recent results showed that the existence of a universal ST for renal filtration can be a misconception. A functional study showed that the ST depends on the chemical nature of the filtrate (Protein=7.5 nm / Ficoll=9.2 nm / Dextran=11 nm). Thus, SPIONs may have a higher ST than QDs. Structural studies showed that, in each layer of the renal glomerular barrier, the pore size is larger and more broadly distributed than previously thought (endothelium: 50-100 nm, basal membrane: 3-15 nm; podocyte diaphragm: 14-30 nm) so that many pores are large enough for NPs with DH ≈ 10 nm to pass through. Thus, present knowledge of the kidney ultrastructure and function is not in contrast with the renal clearance of SPIONs with $D_H \approx 10$ nm.



T_2-weighted MR images of a mouse IV injected with zwitterionic SPIONs (DH = 13 nm). SPIONs are filtered through the kidneys and collected in the bladder*

Renal filterability of zwitterionic SPIONs with D_H up to 13 nm broadens the pathway to effective theranostic systems based on SPIONs since renally-clearable, medium-sized SPIONs display higher T_2 relaxivity, SAR, and response to external magnetic fields than ultrasmall SPIONs.

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Acknowledgement:

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Engineered Membrane Systems For Advanced Organotypic Tissues

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The design of a biomaterial that promote cell colonization and tissue regeneration represents a critical aspect and the major challenge in tissue engineering and regenerative medicine. Design approaches aim to reproduce or mimic the *in-vivo* 3D microenvironment, recapitulating the natural niches for hosting cells and promoting cell-cell and cell-matrix interactions, which are essential in the maintenance of cell polarity and differentiated functions. Polymeric micro- and nano-structured membranes provide physical support, mechanical stimuli and biochemical cues able to modulate and affect the cell fate [1]. Moreover, porous semipermeable membranes allow the compartmentalization and the physical separation of cells, ensuring in the meantime their communication by the selective mass transfer of the secreted paracrine factors [2]. In this work, two innovative culture strategies, by using engineered membrane systems for cell compartmentalization and colonization will be presented.

The first one deals with the creation of a vascularized 3D liver microtissue by co-culturing human primary hepatocytes and endothelial cells in a hollow fiber (HF) membrane system. Poly(Ɛ-caprolactone) (PCL) HF membranes were employed for the formation of a liver tissue on the extracapillary surface, and for the compartmentalization of endothelial cells in the lumen. Owing to their intrinsic geometry, the HF membranes provided a wide surface area for the adhesion and growth of cells in a small volume and in a 3D architecture, favoring cell interactions, hepatocyte polarity and endothelial capillary-like structure formation. Moreover, the heterotypic co-culture improved the hepatocytes viability and functional integrity in comparison to homotypic systems, maintaining the stable hepatic human phenotype for prolonged period, which is strictly required for therapeutic purpose and for preclinical drug testing.

The second strategy was to create 3D membrane scaffolds with a double porosity as niches for human mesenchymal stem cells (hMSC). Double porous blended membranes of PCL and chitosan consist of macrovoids easily accessible for the invasion and proliferation of the cells, and interconnected micropores for the mass transfer of nutrients, oxygen and growth factors between the macrovoids and throughout the scaffolds [3]. The scaffolds created a permissive environment for hMSC adhesion and invasion and ensured an adequate diffusive mass transfer of nutrients and metabolites, which are essential for the long-term maintenance of cell viability and functions. These properties make the membranes suitable to open new possibility for stem cell based tissue engineering.

Ultimately, both the engineered membrane systems can provide selective cell co-culture models for different tissues where cells can adhere on the surface and simultaneously can be compartmentalized or entrapped in macrovoids, ensuring the biochemical cross-talk, which is necessary for recapitulating physiological functions.

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Hexadecenoic Fatty Acid Isomers In Lipidomic Research: Synthetic, Analytical Biochemical And Diagnostic Aspects

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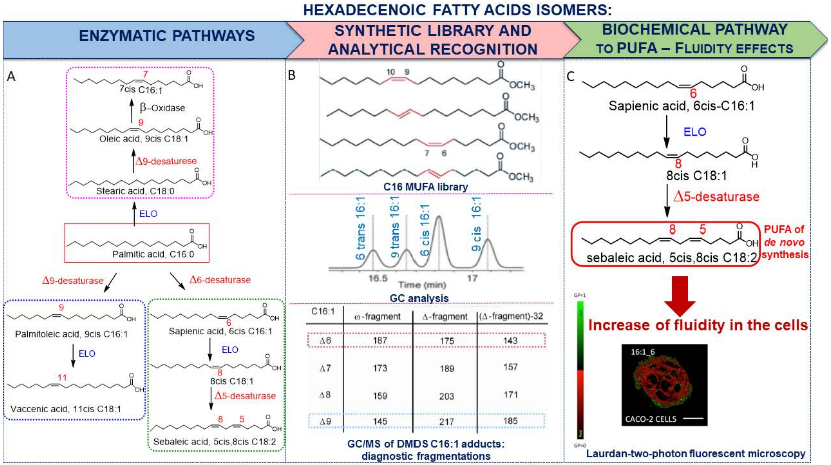
Monounsaturated Fatty Acids (MUFA) are formed from Saturated Fatty acids (SFA) by desaturase enzymes which work regio- and stereo-specifically, so that the double bond is created with the cis geometry and at fixed positions along the hydrocarbon chain. The usual position in MUFAs is delta-9, with oleic acid (9*cis*-18:1) as the major product by SCD-1 enzymatic activity, whereas a minor product is palmitoleic acid (9*cis*-C16:1) (Figure 1A). The SFA-MUFA pathway is necessary for cell replication in order to biosynthesize membrane phospholipids, and its involvement in health conditions (pregnancy) and diseases (cancer, obesity) is emerging. We recently investigated the C16 MUFA structures, building-up the molecular library of positional and geometrical isomers, establishing their synthesis and GC/MS analytical characterization (with unambiguous assignment of the double bond position) of 9*cis* and 9*trans* isomers together with 6*cis*-C16:1 (sapienic acid) and 6*trans*-C16:1 (Figure 1B) [1]. Interestingly, sapienic acid derives from palmitic acid transformation by desaturase enzyme FADS2 (delta 6) (see Figure 1A). Therefore, our library allows for distinguishing the biochemical partition of palmitic acid between SCD-1 and FADS2 enzymatic pathways (Figure 1A). Having the C16:1 MUFA library in our hands, we reported for the first time sapienic acid as component of human lipoprotein phospholipids, triglycerides and cholesteryl esters [1]. We applied this determination to the erythrocyte membrane lipidome profile and to the plasma cholesteryl esters of control and morbidly obese subjects, showing the diagnostic value of the C16 MUFA family [2]. Recently, we deepen the metabolic fate of sapienic acid in cancer cells to envisage new aspects of the SFA-MUFA pathway for the cancer cell survival. Using a colon cancer cell line (Caco-2) and performing membrane lipidomic analysis during sapienic acid supplementation, in comparison with palmitoleic acid, we discovered a previously unknown metabolism, shown in Figure 1C, leading to the omega-10 fatty acids 8*cis*-C18:1, and 5*cis*,8*cis*-C18:2 (sebaleic acid). They are incorporated in membrane phospholipids and in lipid droplets, producing an increase of fluidity evaluated by two-photon fluorescent microscopy (Figure 1C) [3]. It worth nothing that 5*cis*,8*cis*-C18:2 is a polyunsaturated fatty acid (PUFA) which is *de novo* synthesized by the cells, whereas PUFAs are essential fatty acids, only assumed by the diet. Further work is in progress for assessing the importance of n-10 fatty acid analysis in cancer diagnostics.



C16:1	ω-fragment	Δ-fragment	(Δ-fragment)-32
Δ6	187	175	143
Δ7	173	189	157
Δ8	159	203	171
Δ9	145	217	185

Description of (A) enzymatic pathways , (B)synthetic library and analytical determination of hexadecenoic fatty acids, C) Biochemical transformation of sapienic acid to PUFA determined in CACO-2 cells.

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Innovative Interfaces And Devices To Probe And Sense Non Neuronal Brain Cells

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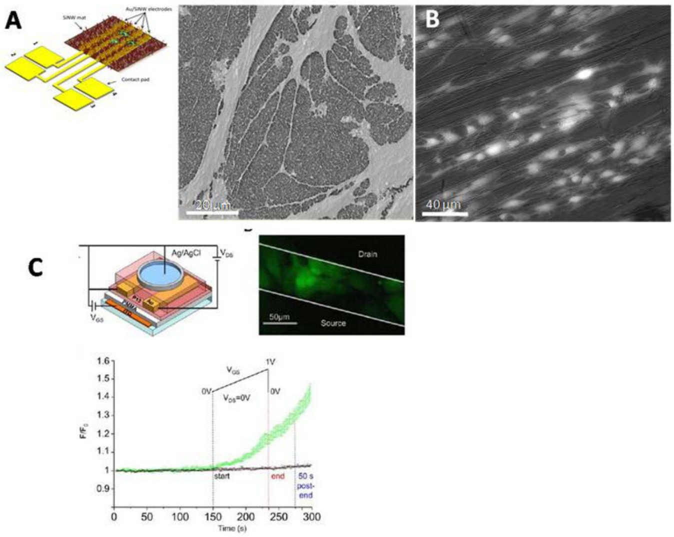
Among the brain cells, astrocytes are the most numerous cells in the central nervous system (CNS). In the past 30 years, the scientists shifted the neurocentric vision from a classical interpretation of non-excitable glial cells as mere neurons supports to key players for the brain functions. Astrocytes ion channels and water channels, named aquaporins, are crucial in the maintenance of cerebral homeostasis as well as in the modulation of synaptic activity. Besides, experimental studies demonstrate the causal role of astrocytes in acute neuropathologies and chronic disease.

Now a day, despite the importance of astrocytes in the CNS, neural engineering is, yet, largely focused on probing and sensing tools targeting neuronal cell functionalities. In this context, we discuss our results on the study of astrocytes/hybrid and polymeric material interaction and organic bioelectronic devices, cause we consider essential for the engineering biosensor and bioelectronic to target astrocytes as a potential alternative therapeutic approach for the treatment of neurological conditions and for the study of brain communication processes.

In particular, we developed glial nanostructured interfaces, such as silicon nanowires, polycaprolactone, silk and hydrotalcites driving the morphological and functional differentiation of astrocytes *in vitro*. Moreover, we validate astrocytes biosensing exploiting bioelectronic and biophotonic materials and using a set of electronic organic bioelectronic device and photonic real-time approaches to trigger, control and record calcium signaling, ionic conductance and water permeability of astrocytes. It is, indeed, the astrogliotic reactivity the major cause of failure of implant performance over long term *in vivo*.

Our results focus on the importance of "cutting-edge" technologies for the basic understanding of brain mechanisms and physiological and pathological processes.



A)Scheme of AuSiNWs device and SEM images of astrocytes plated on AuSiNWs interface B) FDA cell plated on polymeric PCL interface C) Scheme of CaImg experiments performed on O-CST device

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A.I. Borrachero-Conejo, **E. Saracino**, M. Natali, F. Prescimone, S. Karges, S. Bonetti, G. P. Nicchia, F. Formaggio, M. Caprini, R. Zamboni, F. Mercuri, S. Toffanin, M. Muccini, and V. Benfenati, "Electrical stimulation by an organic transistor architecture induces calcium signalling in non-excitable brain cells", Advanced Healthcare Materials, doi: 10.1002/adhm.201801139, (2018).

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Decoding Dynamic Actin Waves Of Ion And Water Membrane Channels In Primary Rodent Astrocytes

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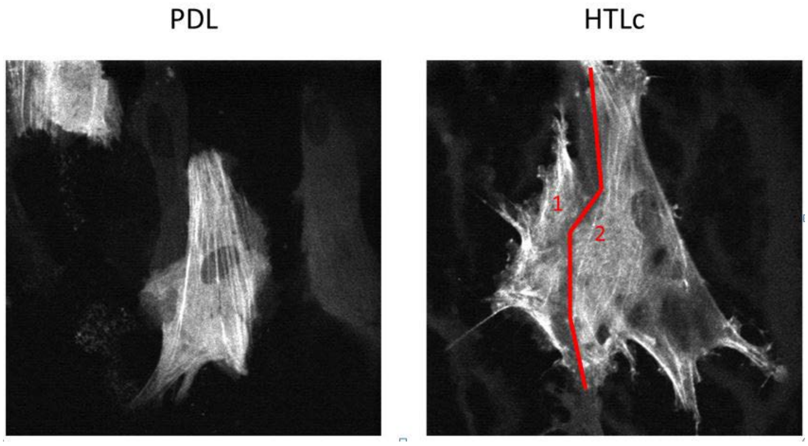
It is known that astrocytes have a crucial role in maintaining homeostasis in the human brain. Notably, a molecular and functional interplay between ion channels, water channel aquaporin 4 (AQP4), and calcium signalling has been established and is mainly localized to the endfeet of astrocytes. Moreover, the role of actin remodelling is essential to these homeostatic processes. However, many studies have relied on imaging static actin fixed samples of astrocytes. Besides, *in vitro* primary astrocytes display a flat, polygonal shape and do not have the morphological, structural, or functional features of *in vivo*. To overcome this limitation, our previous work has validated nanostructured surfaces, such as silicon-nanowires (Au/SiNw), polycaprolactone (PCL) electrospun nanofibers, and hydrotalcite nanoparticles films (HTlc) as novel glial 2D and 3D interfaces that enable *in vitro* astrocytes to grow and differentiate into an *in vivo*-like state by responding to substrate topography. In the present work, we study actin dynamics in primary cultures of neocortical rodent astrocytes cultured on standard poly-D-lysine coated glass and on the mentioned nanostructured surfaces to understand astrocytic responses to the mechanical environment and to investigate on reliable results on in vivo-like astrocytic processes. We provide on the ability of the actin cytoskeleton in astrocytes to change dynamically in response to different substrate topography, which has not before been studied.

Actin observation was preceded by transduction with actin-GFP at 48 h prior to timelapse confocal imaging. Possible variation in actin dynamics were also analyzed in response to a "triggering" solution, such as high potassium extracellular medium or hypotonic solutions, compared to a standard external medium. One of the main purpose of understanding is how the cytoskeleton responds to changes in the ionic environment. Our work also focus on the importance of AQP4 in regulating astrocytic responses. Our results reveal a new understanding of the role of actin in the mechanisms underpinning astrocyte homeostatic function at multiple length scales.



Actin-GFP transduced astrocytes grown on PDL and HTLc. PDL-astrocytes show typical in vitro polygonal shape (left), HTLc-astrocytes show an in vivo like morphology (right).

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Assessment Of The Toxicity Of Metal Oxide Nanoparticles On The Basis Of Fundamental Physical-Chemical Parameters

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Due to their sizes, nanoparticles can penetrate into biological systems easily; anticipating their harmful interactions at the cellular level makes it possible to safeguard workers, consumers, and the environment effectively. Decades of research have identified key properties of nanomaterials that induce adverse responses, and this evidence suggests that the toxicity of a nanoparticle can be inferred from its abiotic behavior. Experimental physical-chemical characterization of nanoparticles, however, is complex and time consuming, and the absence of any standardized method has generated controversial results. We show how known adverse modes of action of nanoparticles arise from fundamental physical-chemical parameters that don't need any experimental quantification. We show that cytotoxicity of metal oxides in different types of in-vitro systems can be foreseen on the basis of the values of oxidation number (Z) and ionic potential (IP) of the cation, and surface reducibility (SR), and redox reactivity (RR) of the oxide. Importantly, the values of these fundamental physical-chemical parameters can be easily deduced from the chemical formula of the nanoparticle with the help of a periodic table. Combining these parameters in a naïve Bayes classifier, a robust probabilistic model that can be run on a pocket calculator, makes it possible to determine the most probable level of toxicity of a nanoparticle given its composition. Results indicate that the probability that nano-oxides exhibit very high cytotoxicity ($EC_{50} < 10^{-3}$ mol·L^{-1}) decreases with increasing oxidation number Z of the cation; high values of Z, however, may become unstable and activate adverse redox processes; in contrast, stable, redox-inert reducible oxides tend to be, probabilistically, less toxic than oxidizable ones. The simplicity of our approach, which exploits concepts and tools of materials chemistry, enables different actors involved in risk assessment of nanoparticles to formulate realistic hypothesis about the toxicity of nanoparticles even before they are actually synthesized.

MADIA: MAgnetic DIagnostic Assay For Neurodegenerative Disease

The MADIA consortium

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Istituto per lo Studio dei Materiali Nanostrutturati (ISMN)

MADIA aims at realizing a versatile and cheap diagnostic device based on PHE (Planar Hall Effect) sensors, microfluidic devices, ultra-small Magnetic Nanoparticels (MNPs) and advanced bio-chemical functionalization methods for early and ultra-sensitive in-vitro detection of biomarker trustfully.

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Polydopamine Synthesis And Processing Strategies To Design Nature-Inspired Platforms

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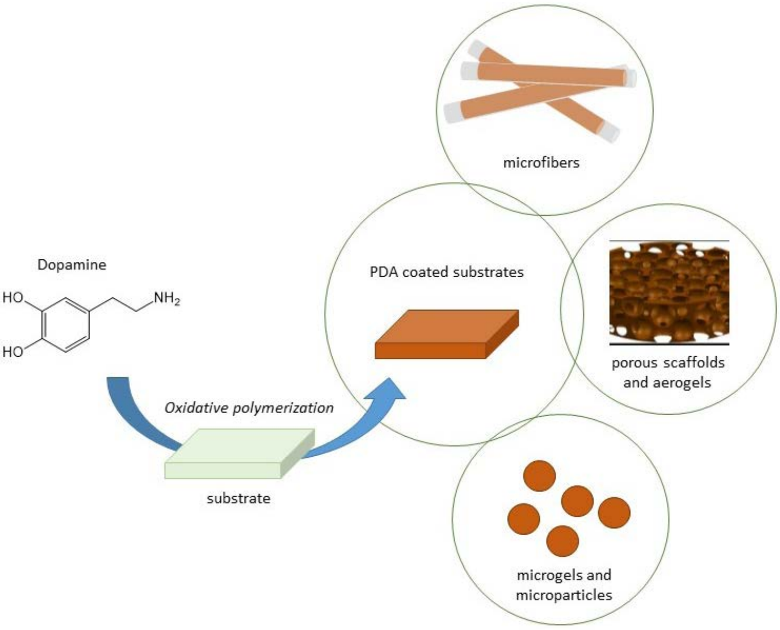
In recent years, polydopamine (PDA) have attracted much attention and it is considered one of the most versatile organic polymer coating for all types of materials [1]. PDA is a dopamine derived synthetic eumelanin polymer able to easily adhere to different substrates, due to the availability of copious functional groups also suitable for covalently immobilizing biomolecules and anchoring reactive species and ions, coordinating metals etc. [2]. PDA could be spontaneously deposit by the self-polymerization of dopamine (DA) under mild and versatile conditions which can be modulated to tune size, shape and morphology of thin films.

All these peculiar properties make this bioinspired polymer suitable for several biomedical applications such as biosensing, bioimaging, drug delivery, antibacterial nanomedicine and tissue engineering. Being biocompatible and cell affinitive, PDA has been successfully used for surface modification to influence in vitro cell activities [3].

In order to develop bio-functionalized systems, PDA was proposed as coating of biomaterials (i.e., polyesters, polysaccharides) differently processed in the form of microgels, sub-micrometric fibres, porous foams and aerogels. We demonstrated that polymerization/oxidation reactions can be properly optimized to guide PDA self-assembly in order to control surface properties, and ultimately, influence cell materials interactions.



Schematic illustration of polydopamine (PDA) coating of differently processed substrates

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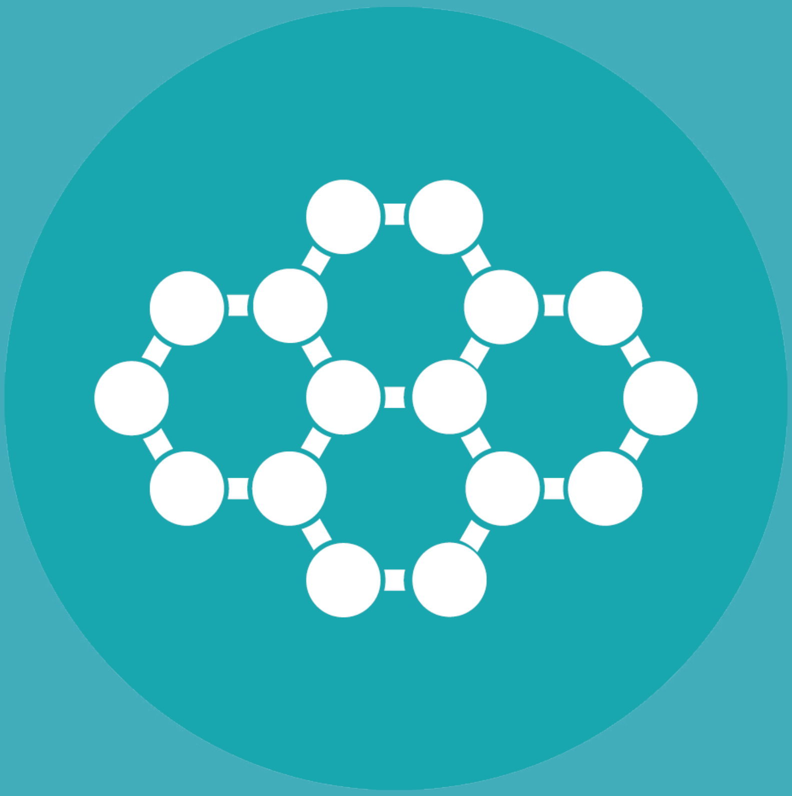
ADVANCED MATERIALS



POSTER COMMUNICATION

Advanced X-ray Characterization Of Hierarchical Systems: From Biotissues To Electronic Devices

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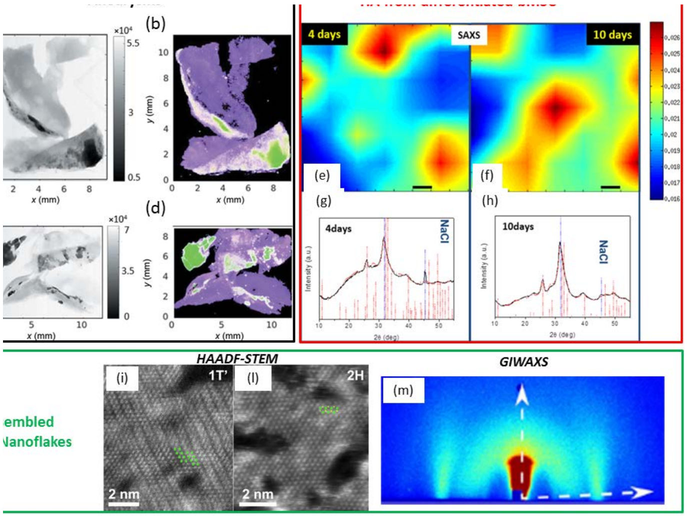
Label-free Multiscale X-ray Imaging can be performed by Table-Top equipment, exploiting both Absorption (usually referred to as X-ray Transmission Microscopy "XTM") and Scattering contrast. X-ray scattering techniques can provide a large amount of structural and morphological information, both at the atomic and nano-scale, and are thus particularly suited to study composite/nanostructured materials. The crystalline components are mainly studied by Wide Angle X-ray Scattering (WAXS), providing information on the crystallinity and crystalline phases, as well as on possible texture. The nanoscale structure/morphology can be assessed based on the Small Angle X-ray Scattering (SAXS) signal, and related to the possible crystallinity through combined SAXS/WAXS mapping. SAXS/WAXS/XT Microscopy is particularly suited to study biological tissues (or any structured material) with nano and/or atomic scale periodicity, such as calcified healthy or pathological tissues [1]. In the biomedical field, this approach allows for example to study mineralized bio-scaffolds, or reveal osteogenic differentiation of stem cells through the analysis of nanocrystalline differentiation products [2].

The availability of high brilliance X-ray micro-sources for laboratory equipment allows nowadays to perform the aforesaid advanced X-ray characterization, in both transmission and reflection geometries, in the home laboratory, being such X-ray sources considered as "synchrotron-class". Moreover, suitable data treatment can further enhance the performances of the experimental equipment, returning in several cases results comparable to those obtained at a synchrotron beamline. A in-house developed package (SUNBIM) for the collection and analysis of X-ray microscopies with absorption and/or diffraction contrast, as well as data reduction for transmission and reflection geometries is freely available at http://www.ba.ic.cnr.it/softwareic/sunbimweb/, and constantly updated. The synchrotron-class micro-source combined with the SAXS/WAXS system installed at IC-Bari (XMI-L@b) has been successfully applied to the study of free-standing bio- and composite materials, as well as to polymer nanofibers for optoelectronic devices. Moreover, it has been successfully applied in grazing incidence reflection geometry (GISAXS/GIWAXS) for the study of several nanostructured films for advanced electronic applications, in particular based on 2D nanocrystals [3].



XTM and μWAXS: Abdominal (a,b) and Popliteal (c,d) Aneurisms. (e, f) μSAXS; (g,h) WAXS: HA from differentiated bMSCs. 2D-WS_2: HAADF-STEM (i,l); GIWAXS (m).

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Poly(Lactic Acid)/Silica Plasticized Nanocomposites

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Poly (lactic acid) (PLA) is a biodegradable, bio-based polymer increasingly used in a wide range of applications, from biomedicine to food packaging. Besides its interesting mechanical properties and good transparency, PLA suffers a high stiffness and a low tensile/impact toughness, thereby limiting its potential in some applications. The addition of plasticizers has proved an effective route for the realization of PLA based blends with tailored thermo-mechanical properties [1], in particular in terms of increased elongation at break and toughness. However, the beneficial effects of plasticizers are often coupled with a large decrease in stiffness and strength and with a progressive deterioration of properties with time, due to the occurrence of phase separation.

The final properties of polymer/plasticizer blends are defined by composition, preparation procedure adopted, miscibility of the components and storage conditions. The addition of a third component into the plasticized matrix, with the realization of composites or nanocomposites, can be an effective strategy to modulate the response of the polymeric materials, inducing an interplay between the different components that can influence the evolution of properties with time [2]. In this contribution, the realization and testing of PLA-based nanocomposites containing fumed silica and different plasticizers will be illustrated and discussed. A pre-mixing step of plasticizers with silica particles was implemented to optimize the dispersion of the particles. Thermo-mechanical properties and morphology of the realized materials have been investigated as a function of composition and aging time and the recorded evolution was compared to the results obtained on unfilled blends.

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Material Development Dedicated To Enhancing Microstructural And Mechanical Properties Of Aluminum Alloys Manufactured By Additive Manufacturing

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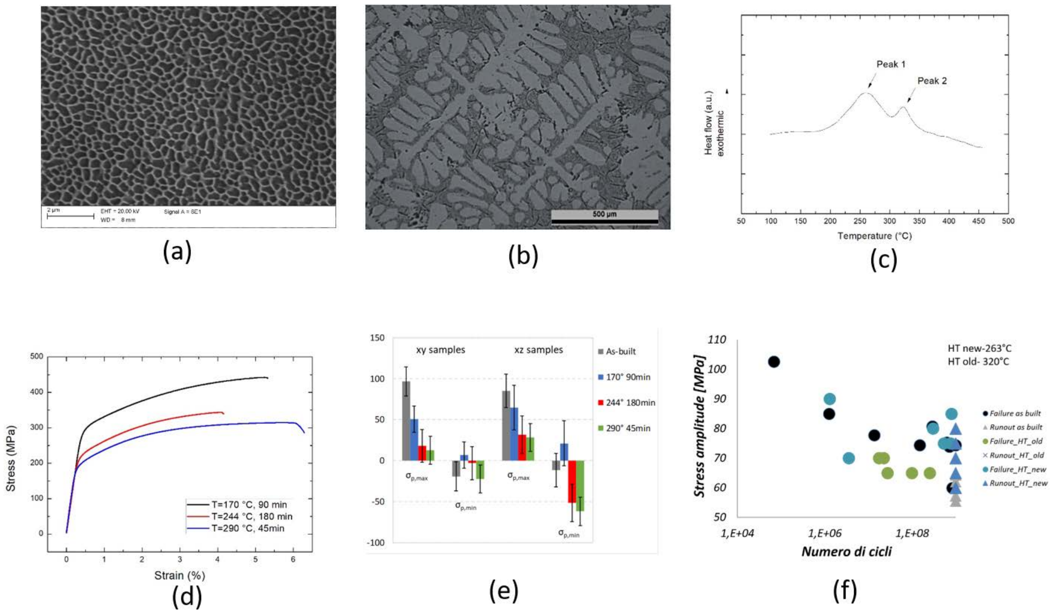
Selective Laser Melting (SLM), belonging to the family of additive manufacturing techniques, is based on locally melting and solidifying small volumes of powder. The consequent rapid cooling rates induce deep microstructural differences with respect to conventionally produced parts, as shown in Figure a-b. Therefore, the modification of the chemical composition of the powder can be taken into account for improving its process-ability, avoiding the formation of defects during the solidification of the alloy.

Moreover, precipitation phenomena are also modified deeply in terms of thermodynamic and kinetic behavior, consequently the thermal treatments usually applied to cast aluminum alloys shall be modified in order to be adapted to the peculiar properties of the SLM built parts [1-2].

The present work recollects the achievements obtained in the last few years in investigating the process-ability of some Aluminum alloys, like AlSi10Mg, AlSi9Cu3 and A205, and the obtained microstructures in the view of proposing dedicated thermal treatments for additive manufactured Aluminum alloys. It is shown how differential scanning calorimetry (DSC) can be used for the thermodynamic and kinetic investigation (see Figure c), identifying the characteristic temperatures at which the microstructure is modified. Therefore, the effect of the thermal treatments on the microstructural changes and mechanical properties (see Figure d-e-f), like tensile and compression behavior, fatigue response and identification of the corresponding residual stresses, is discussed. It was found that heat treatments, performed at temperatures indicated by DSC analysis, can improve the fatigue response of Al alloys, produced by additive manufacturing, with respect to the one associated to traditional heat treatments [3].



(a) (b) (c)

(d) (e) (f)

Microstructure produced by SLM (a) and casting (b); DSC scan (c), tensile curves (d), residual stresses (e) and fatigue curves (f) of SLMed AlSi10Mg alloy.

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Structural Characterization Of Polysaccharides_based Cryogels And Potential Application As Carriers Of Active Molecules: A Case Study Through NMR Spectroscopy

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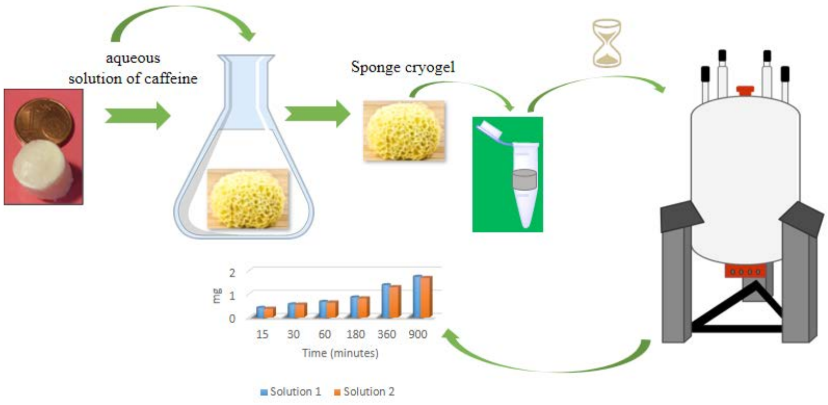
Polysaccharides (PS's) are natural and environmentally friendly polymers that have been used as starting materials for the production of the "new generation" of biobased materials because biocompatible, biodegradable, and nontoxic.[1] In the present study, **PS**_based materials, (from starch and polygalactomannans) were obtained after enzymatic modification, with the Laccase/(2,2,6,6-tetramethylpiperidin-1-yl)oxyl TEMPO system, in aqueous solution. The structural characterization of the modified polysaccharides by solution NMR spectroscopy showed partial conversion of the primary hydroxyl groups versus aldehyde and carboxyl groups, and successive creation of hemiacetal and ester bonds able to generate, upon lyophilisation, stable cryogels.[2,3] The presence of pores of dimensions ranging from 200 nm to few microns, evidenced by Scanning Electron (SEM) Microscopy, supports their potential use for tuning the absorption/release of active molecules. Therefore, **PS**_based cryogels were loaded with caffeine, as model molecule, and release profiles were determined by proton NMR studies during time. Results demonstrated that synthesized cryogels are good candidates to act as drug carriers due to their stability and prolonged residence times of loaded molecules.

Experimental scheme illustrating the procedure for sorption/desorption of caffeine and for the release profile's construction.



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SiO_2@Polydopamine Nanoparticles As Multifunctional Filler For An Aeronautical Epoxy Resin

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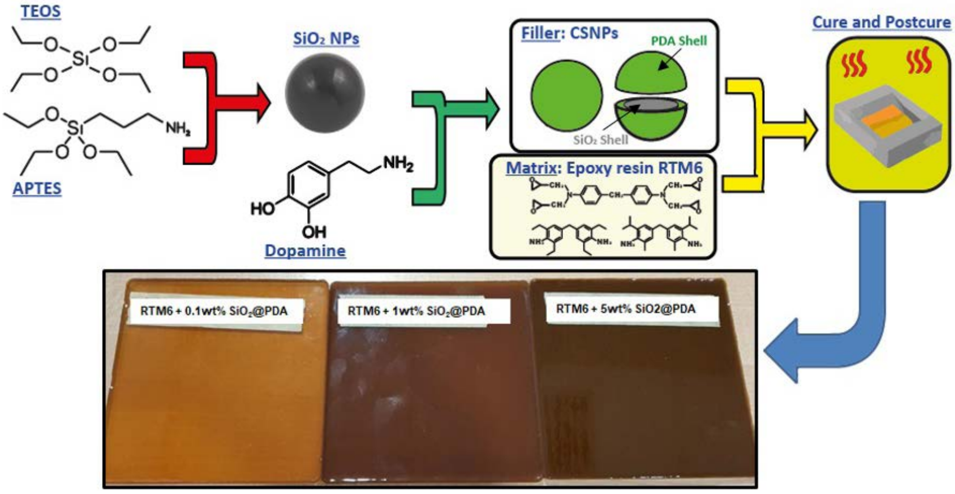
The demonstrated benefits of composite materials compared to metals have led to the recent trend of increased use of the former on primary structures: low specific weight, high mechanical properties and high corrosion resistance are just some of the valuable properties characterizing composite materials. At the same time, several drawbacks of these materials prohibit their use to the extent where their full potential could be exploited. For example, in structural applications in the fields of transport or civil building, high standards of stability and durability are required [1]. Although epoxy resins are widely employed as matrix in high performance composites for aerospace applications, their full potential is not tapped because their intrinsic brittleness; the improvement of epoxy matrix fracture toughness is therefore a critical issue for designing high performance composite elements or structures. The main method employed to increase the their fracture toughness performances is to load them with different filler typologies, such as inorganic particles, thermoplastic particles or combinations thereof. In this work, an aeronautical grade epoxy resin (RTM6) has been loaded with SiO_2@Polydopamine Core/Shell Nanoparticles (CSNPs). The CSNPs were synthesized through a modified single step method [2], based on the nucleation and growth of SiO_2 NPs followed by the growth of a thin polydopamine (PDA) shell around the silica surface. Nanoparticles have been characterized through different methods, such as TEM, FTIR and TGA, which have confirmed the polymeric shell formation: in particular, TEM observations have revealed that CSNPs are ~250 nm in size, with a 15 nm PDA shell. Nanocomposites with different CSNPs contents (0.1, 1 and 5wt%) were manufactured and characterized, with particular attention to the thermal stability and fracture toughness properties. Results have demonstrated that CSNPs effectively improve the fracture toughness performances, in term of critical stress intensity factor (KIC) and critical strain energy release rate (GIC), with a maximum increase compared to the neat matrix of 60% and 139%, respectively.

Schematic illustration of SiO2@PDA synthesis and composites preparation at three different concentration;



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Solid State NMR Spectroscopy: A Multiscale “Lens” For Understanding Complex Materials

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Complexity is an intrinsic feature typical of the most attractive innovative materials in many different research and application fields, as chemistry, optoelectronics, energy, recycling, medicine. Complexity arises from the coexistence of different chemical components, interfaces and phases, as well as from structural disorder and/or heterogeneity. Complexity often hinders a detailed characterization of advanced materials, which, on the other hand, is crucial for understanding the functional performances and orienting the design and optimization of innovative materials. Solid State NMR spectroscopy (SSNMR) is an extremely powerful technique, which can effectively bridge this gap. Indeed, it can be applied to substantially every kind of soft and hard material and, by exploiting many nuclear probes and properties, it allows structural and dynamic properties to be characterized on very wide spatial (0.1-100 nm) and frequency (Hz-GHz) scales [1]. In this contribution I will show case studies of advanced materials characterized in the ICCOM-CNR/UNIPI joint lab [2], which, with the acquisition within the year of a last generation SSNMR spectrometer, will be the largest Italian laboratory for the study of materials by SSNMR. Hopefully this contribution will further increase the opportunity for the DSCTM community of taking advantage of this technique.

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Phosphorene And Black Phosphorus: The ^{31}P NMR View

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Black phosphorus and phosphorene are attracting a large interest in the last years because of their great potential in many application fields [1]. In spite of this, the use of ^{31}P NMR spectroscopy for characterizing these materials has been very limited so far. By exploiting Magic Angle Spinning (MAS) NMR experiments we have characterized for the first time the ^{31}P-^{31}P homonuclear dipolar couplings and the ^{31}P shielding interactions, responsible for the NMR properties of black phosphorus (bP) and of its few-layer exfoliated form (fl-bP). It has been possible to identify the network of ^{31}P nuclei more strongly dipolarly coupled and quantify their effective coupling. Moreover, with the support of DFT calculations, the ^{31}P chemical shif tensors have been fully determined, highlighting two kinds of magnetically nonequivalent ^{31}P nuclei [2]. ^{31}P MAS NMR experiments have been successfully applied to fl-bP derived materials both in suspension and in solid polymeric matrices, obtaining interesting information on the state, modifications and interactions of fl-bP with polymers and functionalizing agents, opening the way to a more extensive NMR application to phosphorene based innovative materials for improving their structural knowledge and control [3].

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Luminescent 1D-Zigzag Lanthanoids Coordination Chains As Color-Coded Thermometer

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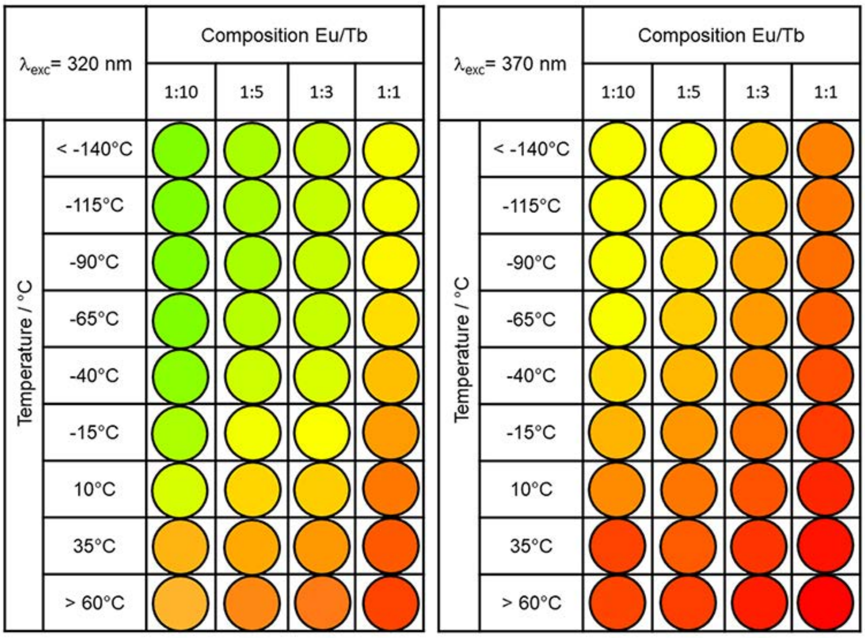
In last years, Lanthanoids-based Coordination Polymers (LCPs) have been increasingly employed as ratiometric self-calibrated luminescent thermometers due to lanthanoids unique luminescent properties. However, the rational design of LCPs is an intriguing challenge still far from be rationalized and hampered by the high coordination number of these ions and their lability. Recently, we developed a convenient and high-yield synthesis of luminescent mono-dimensional CPs based on lanthanoid β-diketonate complexes as nodes and 4,4'-bipyridine (bipy) as unique connector.



Examples of emission color-coding for temperature determination

We exploited the composition (Eu/Tb molar ratios) and temperature dependent emission colour of $[Eu(HFA)_3(bipy)]\cdot C_7H_8$ and $[Tb(HFA)_3(bipy)]\cdot C_7H_8$ (HFA= hexafluoroacetilacetonate) mixtures to develop a Color-Coded Thermometer (CCT) working down to liquid nitrogen temperature and able to distinguish temperature intervals in the order of 20 °C.

Structural Characterization Of Halide Perovskites By X-ray Measurements And Advanced Analysis

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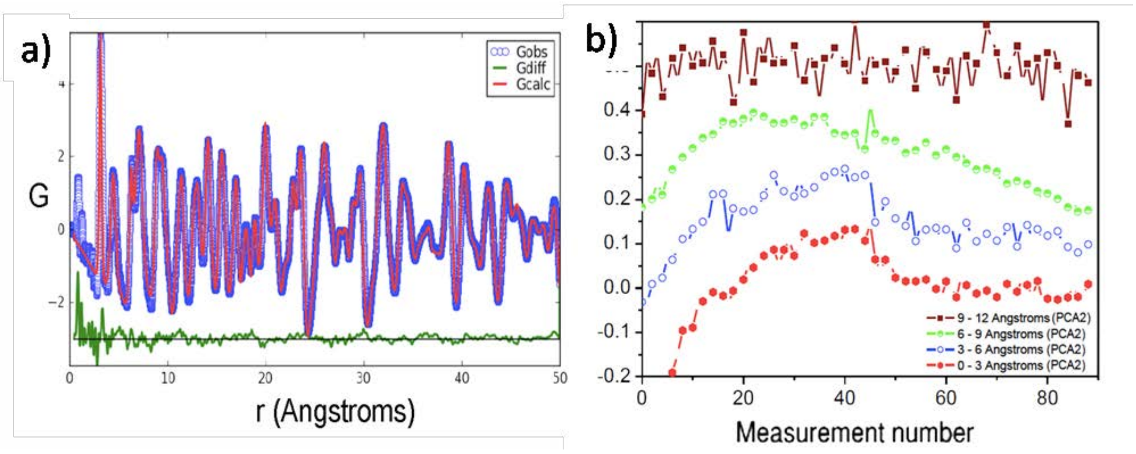
The advent of new-generation X-ray sources as well as more sensitive and fast detectors discloses the possibility of deeper static and dynamic structural investigations. X-ray powder diffraction (XPD) and pair distribution function (PDF) measurements are sensitive to long and short-range order, which can be modelled by fitting procedures. Subtle structural changes induced in situ by varying external parameters (temperature, light) can be also detected by processing efficiently multiple measurements. In this case, the traditional approach to fit each measurement independently can be coupled with the new approach to apply multivariate methods such as Principal Component Analysis and Phase Sensitive Detection to the whole dataset [1]. Single and multiple XPD and PDF measurements have been here analysed for the high-sensitivity structural characterization of halide perovskites. We have investigated the role played by cyclodextrins (CD) to generate a hybrid perovskite-soft material, demonstrating that the interaction between CDs and perovskite precursors leads to the formation of a supramolecular organic–inorganic hybrid framework that modifies solution chemistry and properties of the perovskite film [2]. The multivariate analysis approach has been applied to in situ experiments to reveal under illumination the reversible generation of paramagnetic Pb_3+ defects in $CH_3NH_3PbI_3$ perovskite [3] (Figure 1), and to get new insights into its tetragonal-to-cubic phase transition under temperature changes.

Fit of the PDF profile (a) and scores obtained by PCA applied to the PDF data matrix in slices of 3 Å, for increasing interatomic distances (b).



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Synthesis Of Oxide Nanopowders With Controlled Size And Morphology For Application As Materials For Photonics And Energy Storage

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Nanomaterials find application and extensive usage in many fields for their outstanding functional *(e.g.* electrical, optical, catalytic) properties and are becoming increasingly important in energy conversion and storage. The performance of devices in these fields strongly depends on the availability of starting materials with controlled size and morphology. Wet chemistry methods, such as hydrothermal or solvothermal syntheses, allow the production of highly monodisperse nanoparticles, with controlled size and morphology, or particles with engineered surfaces, through either functionalisation or the formation of core-shell particles.

Nanocrystals with controlled shapes can be used for many applications. Due to their nonlinear properties, for example, $LiNbO_3$ nanocubes act as novel efficient resonant nanostructures for the near ultraviolet range [1]. Starting from nanoparticles with highly controlled size, nanostructured advanced functional ceramics can be prepared through unconventional sintering techniques, such as spark plasma sintering. The properties of nanostructured materials, which strongly depend on their grain size, are largely investigated also to understand the fundamental limits of device miniaturisation, as in the case of barium titanate [2], a material largely used in multilayer ceramic capacitors. The controlled sintering of core-shell particles leads to functional polycrystalline materials with locally graded structure, showing strongly modified dielectric properties [3]. High *k* nanoparticles can be embedded in a polymer matrix for the fabrication of composite films with high breakdown field and high permittivity for energy storage. Depending on the embedded particle system and surface modification, devices with tailored properties can be obtained.

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$BaM_xTi_{1-x}O_3$ (M = Zr, Ce) Ceramics: Structure-Property Relationships And Comparison With Other Homovalent-Substituted Systems

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The high relative dielectric constant (εr = 2000-5000) and low losses (≈1%) of ferroelectric barium titanate, $BaTiO_3$, has made it the most widely used dielectric ceramic material in the electronic industry for the fabrication of multilayer ceramic capacitors, which are used in most electronic circuits, with an annual production of 2000 billion of devices. Owing to the strong temperature dependence of the dielectric constant, $BaTiO_3$ cannot be used in pure form, but its properties have to be properly modified by the incorporation of suitable dopants.

Pure $BaTiO_3$ has 4 crystallographic variants, depending on the temperature. The substitution of Ti^{4+} (r = 0.605 Å) with a homovalent ion in $BaTiO_3$ ceramics, with formation of $BaM_xTi_{1-x}O_3$ (M = Sn, Hf, Zr, Ce) solid solutions, modifies the polar order, with increasing x, from conventional ferroelectric to a so-called relaxor behaviour for high substitution levels via a diffuse transition. Irrespective of M, with increasing x the three phase transitions merge at a tricritical point (x_p, T_p), TCP, the so-called pinched transition, where the four polymorphs coexist. For $x > x_p$, the system then directly transforms from the ferroelectric R phase to the C paraelectric phase with a diffuse transition.

$BaMxTi_{1-x}O_3$ solid solutions have gained large attention for applications. In fact, they show properties such as a very high ($1\text{-}2\cdot10^4$) and stable dielectric constant around room temperature, large dielectric tunability and improved piezoelectric activity, of potential interest for a number of applications, such as, respectively, high permittivity dielectrics, microwave devices for telecommunications, and lead-free piezoelectric sensors, actuators and energy harvester. Recently it was also theoretically predicted and experimentally observed for M = Sn, Hf, Zr, that for specific compositions corresponding to the coexistence of different phases, such as the one close to the TCP, $BaM_xTi_{1-x}O_3$ develops a large electrocaloric response, that could be used in cooling devices.

We present an extensive investigation of $BaM_xTi_{1-x}O_3$ (M = Zr, Ce) over a broad range of compositions, combining macroscopic property measurements and average structure information (electric properties, DSC analysis and high resolution XRD) with the local structure analysis (PDF analysis and Raman spectroscopy). Among the four M ions, Ce^{4+} substitution is the less studied, although it is the largest ion and thus a model system to study the effect of strain on the onset of relaxor behaviour. By comparing our results with the available literature, some general conclusions can be drawn on the origin of relaxor behaviour for the $BaM_xTi_{1-x}O_3$ system. In fact, the compositions corresponding to the tricritical point and the ferroelectric-to-relaxor crossover in $BaM_xTi_{1-x}O_3$ are nearly independent on M, suggesting that, irrespective of the M^{4+} radius, a critical number of Ti-O-Ti bonds has to be broken before a new "state" is established.

Macromolecular Dyes By Chromophore-Initiated Ring Opening Polymerization Of L-lactide

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A lot of research is focusing on improving physico-chemical and mechanical features of PLA, but less efforts are made to study and expand its optical activity in the UV-visible region. Since its general characteristics make PLA particularly useful for fibers, packaging and similar applications, UV-barrier capabilitie and aesthetic appearance are topic issues with a strong influence on the performances of products and appeal. Considering the difficulties in dying PLA-fibers and the possible loss by evaporation or leaching of low molecular weight dyes mixed with the polymer matrix, the immobilization of the chromophores onto the polymer matrix can be a valuable alternative to produce a stable and homogeneously dyed PLA films or fibers. In this paper the use of chromophores as initiators in the ring opening polymerization (ROP) of L-lactide catalyzed by stannous octoate was proposed. The so obtained end-functionalized polylactides may be considered "macromolecular dyes" that can be used "as synthesized" or can be blended with other polymers. In this study, the ROP of L-lactide catalyzed by stannous octoate was carried out in bulk in the presence of three chromophores: 9-fluorenyl-methanol (FM), 9H-carbazol-ethanol (CA) and 2-[4-(2-chloro-4-nitrophenylazo)-N-ethylphenylamino]ethanol (Disperse Red 13, DR). FM and CA absorb in the UVa and UVb region and emit by fluorescence in the range between 300 and 400 nm, whereas DR is a commercially available dye with absorption maximum at about 480 nm in the visible portion of the electromagnetic spectrum. Different initiator/lactide ratios were used for each chromophore in order to keep low the MWs of the products, to facilitate their characterization and to emphasize the relation between initiator and polymer properties. The obtained materials were structurally characterized by FT-IR, ^{1}H-NMR and SEC; their thermal properties were studied by DSC and their photophysical features were determined by UV-Vis spectroscopy and fluorescence emission and compared to those of the free chromophores.

Some selected macromolecular dyes were mixed to high molecular weight PLA with the aim to obtain "dyed PLA" films. For comparison high molecular weight PLA was melt mixed also with the free chromophores. The films were analyzed by UV-Vis spectroscopy and florescence emission and it was demonstrated that the photophysical properties of the macromolecular dyes were transferred to the PLA films. Moreover, by migration tests carried out suspending the PLA films containing the macromolecular dyes or the free chromophores in aqueous/ethanol solution, it was observed that the low molecular weight chromophores are lost by migration whereas macromolecular dyes are not released.

Humidity-Responsive Fluorescent Polymer Nanocomposites

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In recent years, much effort has been devoted to extend applications of commodity plastics through mixing and blending with different additives. In this context, polymer nanocomposites prepared by dispersion of functional nanostructured substrates are of great interest due to the possibility to combine improvements in mechanical properties, heat resistance, flammability, gas permeability, with functional properties, which are transferred from the filler to the polymer composite [1,2]. Intercalation of guest species into layered inorganic solids is a method for producing ordered inorganic-organic assemblies with unique micro-structure controlled by host-guest and guest-guest interactions. Functional hybrid materials obtained by intercalation of specific active species between inorganic layers can be in principle dispersed into a polymer matrix thus obtaining multifunctional polymer nanocomposites.

In this work, fluorescent layered double hydroxides (LDHs) were prepared by anion exchange and calcination-rehydration methods. In particular, the co-intercalation of fluorescein and alkyl sulfate anions was used as an effective strategy for preventing the aggregation of the dye reducing intermolecular quenching and obtaining hybrid LDHs that are fluorescent even in the solid state. Later, fluorescent poly(lactic acid) (PLA) and linear low density polyethylene (LDPE) nanocomposites containing 5 wt.% of fluorescein-modified LDHs were prepared by solution mixing. These materials showed thermal properties similar to those of the neat polymers and morphology depending on the level of dispersion of the inorganic layers. A blue shifted emission (20-25 nm) with respect to the corresponding co-intercalated LDHs was found for both types of nanocomposites with a more pronounced effect for PLA-based samples, revealing a further destruction of dye aggregates due to the dispersion and distribution of the hybrid into the polymer matrix. Fluorescence emission spectra of PLA and LDPE-based composites were registered for dried films and for films exposed to relative humidity of 99%. Interestingly, it was observed an enhanced fluorescence emission by increasing humidity due to the equilibrium between the dianionic and monoanionic fluorescein forms. Even if the effect was generally more marked for LDPE nanocomposites than for PLA based samples, results suggest the possible use of both materials as ON/OFF humidity indicators [3].

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Eco-Composites Based On Biodegradable Polyester: Chemical Modification And Plasma Treatment Of Hemp Fiber Reinforcement

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For over a decade, the interest in using natural fibers (NFs) as a reinforcement in polymer composite materials has increased for both environmental and economic reasons, i.e. biodegradability, renewability, low density, easy-processing, and challenging dynamic-mechanical properties.

Among NFs, hemp fibers (HFs) possess some of the best mechanical properties and, apart textile applications of bast fibers, up to now the short fibers (secondary products of hemp processing) are mainly used for building insulation and fabrication of composite materials based on synthetic plastics for automotive interior.

As a consequence, the development of fully compostable eco-composite materials based on biodegradable or compostable bioplastics and low value HFs has attracted particular interest. Nevertheless, the hydrophilic nature of NFs, mainly due to the presence of hydroxyl groups on their surface, generally results into poor adhesion with polymer matrices, typically hydrophobic, leading to composite materials with low mechanical performance.

Within this framework, in recent years we have undertaken a study aimed at improving the adhesion between NFs (such as wool and hemp) and various polymeric matrices, exploring different compatibilization strategies. The present contribution focus on eco-composites based on a commercial bio-polyester, namely poly(1,4-butylene adipate-co-terephthalate) (PBAT) and high amounts of raw HFs. To promote the adhesion between the polyester matrix and the fibrous reinforcement, the fiber surface was treated with suitable coupling agents. Two different experimental strategies were explored: i) chemical modification of HFs by using PBAT macrocyclic oligomers (MCOs) as the coupling agent [1]; and ii) plasma treatment through a novel soft plasma jet device (developed by Nadir SrL) contemporary able to activate the fiber surface and deposit on it reactive monomers, such as methyl methacrylate (MMA), (3-aminopropyl)triethoxysilane (APTES), and (3-glycidyloxypropyl)trimethoxysilane (GLYMO) [2].

Unmodified and surface modified fibers were characterized and compared in terms of thermal behavior and morphological features. Long-fiber eco-composites were then prepared by a suitable compression molding procedure and characterized by thermal, morphological and dynamic-mechanical analysis.

Experimental evidences indicated that surface of HFs was successfully modified with all the coupling agents investigated. The composites containing fibers surface-modified with MCOs or plasma-treated in presence of APTES showed the best HF/PBAT adhesion, which resulted in enhanced dynamic-mechanical performance.

The overall results gathered so far validate these compatibilization strategies for the preparation of eco-friendly composite materials based on a biodegradable polyester matrix reinforced with high amounts of low cost fibres arising from hemp manufacturing by-products.

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Nanocatalyst Onto Unconventional Substrates For Wastewater Treatment: A New Coating Approach

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The exponential increase of human activities causes harmful consequences for the environment. In this context, water resources are gaining increasing attentions due to the occurrence of emerging pollutants including dyes, pharmaceutical and personal care products (PPCP), endocrine disruptors, pathogens; for this type of pollutants traditional methods show limited performances. The interest of the scientific community has been focusing on alternative methods as the Advanced Oxidation Processes (AOPs). [1] Among AOPs, TiO_2-based photocatalysis has recently emerged as a promising water treatment. In particular, nanosized TiO_2 demonstrated improved performances with respect to its bulk counterpart, thanks to its extremely high surface-to-volume ratio which can greatly increases the density of active sites available for adsorption and catalysis. In addition, the size-dependent band gap of nanosized semiconductors allows tuning the red-ox potentials to achieve selective photochemical reactions. The use of nanostructured photocatalysts requires their immobilization onto solid surfaces.[2] Here two deposition techniques were investigated, namely doctor blade method and a purposely developed dip coating procedure (referred to as "inverted dip coating"), to coat glass with TiO_2 nanoparticles (NPs) and successively the more performing method was used to coat an unconventional substrate, a stainless steel mesh. To this end, a batch of TiO_2 NPs was synthesized by adapting a reported approach, specifically selected for its scalability.[3] UV-Vis absorption spectroscopy, X-ray diffraction analysis and TEM microscopy were used to characterized the obtained product. TiO_2 NPs-based coatings were obtained by means of the *doctor blade* technique and the inverted dip coating method, from isopropanol suspensions of TiO_2 NPs, at increasing concentration, from 6.5% up to 26% by weight. The morphology of the resulting coatings was investigated by SEM analysis and allowed to detect significant differences in morphology by comparing the coatings fabricated by using the two deposition techniques. The photocatalytic activity of the prepared coating was assessed by monitoring the decolouration of a model target molecule, Methylene Blue (MB), in aqueous solution under UV light irradiation. The TiO_2 NPs were then deposited on stainless steel mesh by using isopropanol suspensions at 6,5% and 13% by weight. TiO_2 NPs content. Also, the films deposited onto the stainless steel meshes were thoroughly investigated by SEM microscopy and their photoactivity was evaluated. The experimental results indicate that the coatings obtained by inverted dip coating method at 13% TiO_2 NPs onto stainless steel mesh result to be the most promising for future real application, in terms of film quality and photocatalytic performance.

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Protective Coatings via Advanced Magnetron Sputtering Techniques

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Ta-Al-N, TiB$_2$ and V-N films were deposited via High Power Impulse Magnetron Sputtering (HiPIMS), which is an advanced PVD technology that combines magnetron sputtering with pulsed power concepts. Applying high power pulses, large fractions of sputtered atoms and gas particles are ionized leading to high-density coatings with enhanced adhesion, often improved toughness and reduced columnar structure.

Ta-Al-N is very promising for different technological applications due to its enhanced hardness and thermal stability, noteworthy high temperature oxidation resistance and toughness. Ta-Al-N layers were deposited on Si coupons via reactive HiPIMS from a TaAl target. Working pressure, N$_2$/(Ar+N$_2$) ratio, power, temperature and frequency were kept constant. Conversely, the applied substrate bias voltage was varied from 0 to -100 V and the pulse length was changed over the range 25 - 200 µs. Then, the authors reduced N2 percentage during sputtering from 50 to 5 % in an effort to improve wear resistance. Concerning Ta-Al-N, reducing the N$_2$ amount, a low nitrogen quantity was detected into the coating and also a very small Al at. % was measured. Indeed, the variation in transport behavior and ionization fraction of different species led to a deviation of Ta/Al ratio as compared to the target source. Moreover, microstructure varied and mechanical properties improved (H from ~27 to >30 GPa).

TiB2 is a viable alternative material due to its high strength, melting point and conductivity. Moreover, it offers superior hardness, elastic modulus and abrasive wear resistance and, due to its low wettability, TiB2 is suited to coat cutting tools for non-ferrous alloys. TiB2 coatings were grown on Si and TiAl6V4 alloy substrates by both conventional DC magnetron sputtering and HiPIMS technologies using a stoichiometric compound target. This study was focused on investigating the influence of substrate temperature (RT – 400 °C) and frequency (250 - 1500 Hz) on the resulting microstructure and mechanical properties. HiPIMS TiB2 samples had hexagonal phase, with a marked (001) orientation. The highest hardness values were over 35 GPa. Therefore, HiPIMS was effective in producing TiB$_2$ specimens with increased hardness, elastic modulus, elastic strain to failure and resistance to plastic deformation.

Finally, a wear resistant TiB$_2$/V-N multi-layer system was obtained combining reactive and non-reactive HiPIMS modes: TiB$_2$ is the hard phase, V-N the lubricating one. Indeed, using a multi-layer architecture it is possible to achieve synergistic properties by constructive interactions between the constituent phases of the single layers. The authors are studying the influence of the process parameters on the relative thicknesses of the two different films, on the total thickness of the multy-layer and, consequently, on the overall performance of the coating.

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Iron/Cobalt Perovskite-Type Mixed Oxides Prepared By Solution Combustion Synthesis: Tuning The Structural Properties For Application As Electrocatalysts

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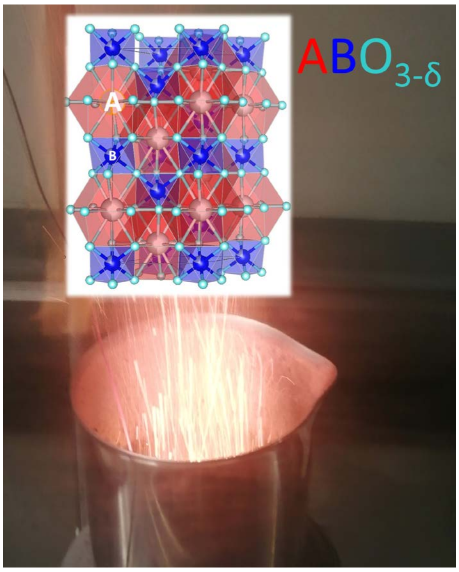
Mixed oxides with perovskite-type structure are an important class of compounds for energy and environmental applications. The essential formula of the perovskite-type structure is $ABO_{3-\delta}$, where A-site cations have much larger ionic radius than B-site ones and δ is the oxygen deficiency. $ABO_{3-\delta}$ perovskite-type structure can be easily doped at both A and B-sites, with single or multiple doping/co-doping [1]. The versatility in the structure of these compounds corresponds in a versatility in their properties and applications. In particular, iron/cobalt-containing perovskites are the most studied ones as electrocatalysts for solid oxide fuel cells and metal-air batteries and they are gradually replacing the metal-based formulations [2].

Doping may affect both the unit cell dimension and the oxidation state of the B-site cation/s. For stronger doping, also the structure can be modified. A change in the oxygen content (δ) plays as well an important role in the perovskite structure. Oxygen content can be controlled by synthesis and/or processing conditions. From this point of view, solution combustion synthesis (SCS) [3] has special advantages over other synthetic methodologies, since a conspicuous number of parameters can be controlled, in order to optimize the perovskite oxygen content and thus the structural properties. In addition, SCS is particularly effective in the energy/cost/time-saving production of pure multicomponent mixed oxides without any phase segregation.

In this presentation, the structural properties of three iron/cobalt perovskite-type electrocatalysts are tuned by changing two important fuel-related solution combustion synthesis parameters, the fuel-type and the reducers-to-oxidizers ratio. Measurable structural parameters are phase purity and composition, phase structure and cell volume, crystal size and microstrain. They can be accurately determined by Rietveld refinement of high-resolution X-ray diffraction patterns at various chemical compositions, synthesis and processing parameters. The starting structures and all their structural information are selected from ICDD database PDF4+. The special relevance of all these structural parameters in the electrocatalytic reactions at bifunctional electrodes of rechargeable metal air batteries and at cathodes of intermediate-temperature solid oxide fuel cells is also highlighted.



A drawing of the $ABO_{3-\delta}$ perovskite-type structure and a picture of a typical combustion process

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Innovative Surface Treatments Of Synthetic Fabrics For The Mitigation Of Microplastic Pollution

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Microplastics have been recently identified as one of the most concerning new class of pollutants, extensively found in various environments. They have been defined as plastic fragments smaller than 5 mm, coming from several sources. The most unexpected source of microplastic pollution is certainly the washing processes of synthetic textiles, that was estimated as a major contributor to the emission of microplastics into global oceans. Due to the mechanical and chemical stresses that fabrics undergo during a washing process in a laundry machine, microfibres detach from the yarn and, through the wastewater, end up in the marine environment. Sampling of marine sediments showed that polyester, acrylic, polypropylene, and polyamide fibres contaminate shores on a global-scale. Their impact on marine flora and fauna is unpredictable and quite dangerous since they can adsorb organic pollutants and be ingested by marine organisms, potentially reaching the human food web.

In this work, innovative surface treatments of synthetic fabrics were developed to mitigate the release of microplastics during their washing. The aim was to create a protective coating on the fabric surface, which can protect clothes during washing processes, then reducing the amount of microfibres released. Instead of using conventional synthetic textile auxiliaries, these treatments involve the usage of alternative polymers, selected for their biocompatibility and eco-sustainability.

Two different strategies were explored to develop such surface treatments on polyamide 6.6. fabrics. The first one is based on the application of pectin, a natural polysaccharide, that was chemically modified by reaction with glycidyl methacrylate (GMA), whose vinylic groups were exploited to graft pectin on the surface of the polyamide fabric.[1] The second treatment is based on the application of an electrofluidodynamic (EFD) method to deposit on the fabric a countinuous layer made of biodegradable polymers from biosources – i.e., polylactic acid (PLA) and polybutylene succinate adipate (PBSA).[2,3] The treated fabrics underwent different analysis to evaluate the coating morphology and possible changes to fabric properties. Among the tecniques used there are scanning electron microscopy (SEM), attenuated total reflectance (ATR) Fourier Transform InfraRed (FT-IR) spectroscopy and thermogravimetric analysis (TGA). Finally, washing tests were performed to evaluate the effectiveness of the finishing treatments in mitigating the release of microplastics during the washing of fabric and the outcomes revealed that all treatments decreased of more than 80% the release of microfibres with respect to untreated fabrics.

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Laser-Induced Emission Of TiO_2 Nanoparticles In Flame Spray Synthesis

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Flame spray pyrolysis (FSP) is considered a powerful method for a massive production of oxide nanoparticles with specific and tailored properties, thanks to the possibility to change flame experimental conditions. Being particle properties often related to surface-to-volume ratio, the characterization of these nanoparticles in terms of particle size is of primary importance. Therefore, it can be particularly attractive to develop a diagnostic tool able to follow nanoparticle size during the formation and growth in the flame synthesis.

Laser-induced incandescence technique is widely used to provide such information. This diagnostic is usually applied to measure the concentration of carbon nanoparticles. The technique is essentially based on heating the nanoparticles by using a nanosecond pulsed high energy laser and collecting the resulting thermal radiation. By knowing the optical properties of these nanoparticles, it is possible to retrieve the heating temperature, here called incandescence. Moreover, the peak of the incandescence signal is related to the particle concentration, while the signal decay rate to the particles size. In fact, smaller particles cool down faster than the larger ones. Aim of this work is to investigate the applicability of the technique to TiO_2 nanoparticles in the flame spray synthesis.

The flame under analysis exhibits a whitish luminous emission due the occurrence of significantly high flame temperature. Thus, performing incandescence measurements in such reactor is particularly challenging. Moreover, fluorescence emission from titania nanoparticles can strongly influence the incandescence as well. Preliminary time-resolved spectral laser-induced incandescence measurements are first carried out on TiO_2 nanoparticles deposited on a filter changing the laser energy density. Then, in order to investigate the thermal spectral features of these nanoparticles, spectral measurements are carried out on the flame spray at different heights above the burner and changing the acquisition delay time. To retrieve information about the incandescence temperature, nanoparticles optical properties are measured as obtained in the particular experimental condition under analysis.

The analysis proves the applicability and the challenges in using this diagnostic tool in flame spray synthesis.

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Microstructure And Mechanical Behaviour Of Inconel 718 Manufactured By Additive Manufacturing

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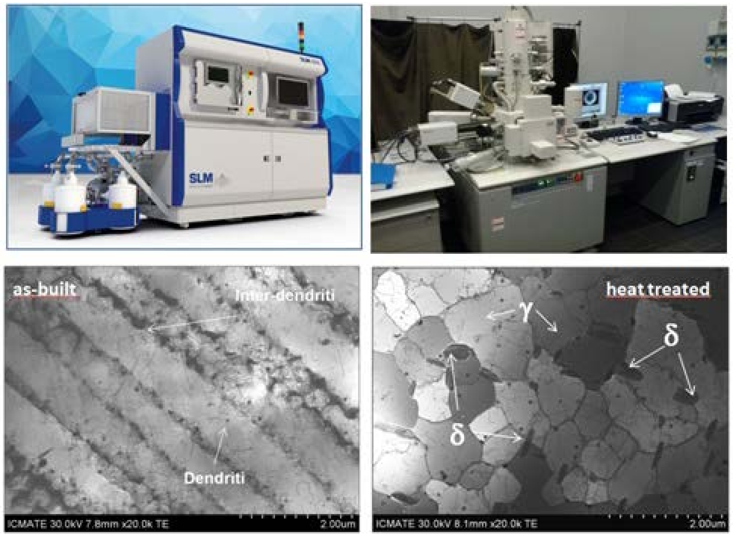
In the industrial field of metal materials production, advanced manufacturing processes represent challenging processing where the laser process induces peculiar microstructures by rapid cooling. In particular, Selective Laser Melting (SLM), belonging to the family of additive manufacturing techniques, is based on locally melting and solidifying small volumes of powder. The consequent rapid cooling rates induce deep microstructural differences with respect to conventionally produced parts, promoting significant and crucial modifications of the mechanical properties of the wrought materials. Therefore, in order to verify the suitability of the semi-finished/final products on the foreseen heat treatments and/or work conditions, the analysis of the micro-structural features and their evolution depending on the process parameters is fundamental, in particular about Inconel 718 super-alloy. For this reason microstructural analysis was developed by high resolution scanning electron microscopy (HR-SEM) and scanning transmission electron microscopy (STEM), on samples of Inconel 718 at the as-built state and post-heat treatment state. The results highlighted the presence of embrittling phases in inter-dendritic regions and high dislocation density on the as-built sample, whilst a very fine grain structure with reinforcing precipitates (γ'' and δ) and low dislocation density was observed on the heat-treated sample. In addition tensile tests at room temperature and at high temperature (650°C) were performed to assess the mechanical resistance of the material.



Instrumentation and results on the microstructural analysis of Inconel 718 produced by Selective Laser metling (SLM)

Keywords: superalloy, additive manufacturing, microstructure, mechanical behaviour

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Role Of Ligands In The Post Synthetic Treatment Of $CsPbBr_3$: Shape And Phase Evolution Of Colloidal Nanocrystals

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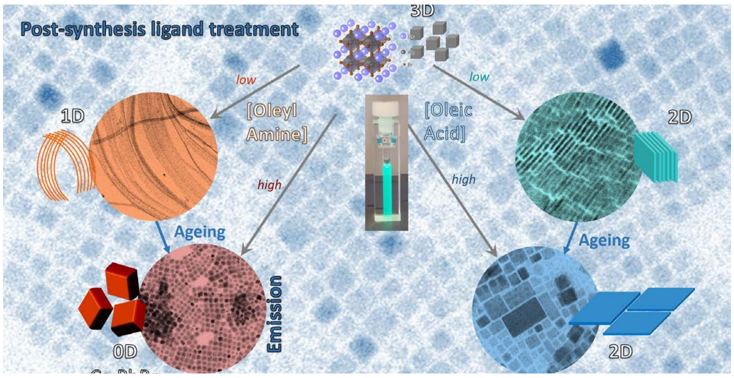
All-inorganic lead halide perovskite materials have attracted significant attention in the context of photovoltaic and optoelectronic applications and efforts have been devoted to the fabrication of colloidally stable versions of these materials. Cesium Lead Halide Bromide ($CsPbBr_3$) colloidal nanocrystals (NCs), in particular, exhibits bright, size and shape-tunable photoluminescence in the blue-green region of the visible spectrum, that is usually not easily accessible with conventional quantum dots. The surface chemistry of colloidal $CsPbBr_3$ nanocrystals is decisive in determining the stability and the final morphology of this class of materials, characterized by ionic structure and a high defect tolerance factor. Here, the high sensitivity of purified colloidal nanocubes of $CsPbBr_3$ to diverse environmental condition (solvent dilution, ageing, ligands post synthetic treatment) in ambient atmosphere is investigated by means of a comprehensive morphological (electron microscopy), structural (θ /2 θ X-ray diffraction (XRD) and grazing incidence wide angle scattering (GIWAXS)), and spectroscopic chemical (1H nuclear magnetic resonance (NMR), nuclear Overhauser effect spectroscopy (NOESY), absorption and emission spectroscopy) characterization. The aging and solvent dilution contribute to modify the nanocrystal morphology, due to a modification of the ligand dynamic. Moreover, we establish the ability of aliphatic carboxylic acids and alkyl amines ligands to induce, even in a post preparative process at room temperature, structural, morphological and spectroscopic variations. Upon post synthesis alkyl amine addition, in particular of oleyl amine and octyl amine, the highly green emitting $CsPbBr_3$ nanocubes effectively turn into one-dimensional (1D) thin tetragonal nanowires or lead halide deficient rhombohedral zero-dimensional (0D) Cs4PbBr6 structures with a complete loss of fluorescence. The addition of an alkyl carboxylic acid, as oleic and nonanoic acid, produces the transformation of nanocubes into still emitting orthorombic two-dimensional (2D) nanoplates. The acid/base equilibrium between the native and added ligands, the adsorbed/free ligands dynamic in solution and the ligand solubility in non-polar solvent contribute to render $CsPbBr_3$ particularly sensitive to environmental and processing conditions and, therefore prone to undergo to structural, morphological and, hence spectroscopic, transformations.



Phase and shape evolution of $CsPbBr_3$ colloidal nanocrystals upon post synthetic ligand treatment

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Application Of Innovative Antimicrobial And Self-Cleaning Membranes For Water Treatment In The Vicinaqua Lake Basin

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The research activity was devoted to the development of a new class of antimicrobial and self-cleaning membranes to be used in the membrane bioreactor (MBR) system, within the VicInAqua project (GA 689427, period 2016-2019) funded by European Union's H2020 Framework Programme. The project involved a consortium of 11 partners (7 from European countries and 4 from African countries) for making a novel sustainable, efficient and robust solution for water sanitation in Lake Victoria Basin (Kenya). During the project, a small-scale technical membrane bioreactor (MBR) was integrated into a domestic wastewater treatment system producing clean water to be used in aquaculture and agriculture.

The MBR run on renewable energies (solar panels) and on a real-time sensor system for water management based on wireless network. The novel MBR membranes, with both antimicrobial and antifouling properties, were developed by exploiting the technology of polymerisable bicontinuous microemulsions (PBMs) that CNR-ITM developed during the past years [1-3]. In particular, during the project a new series of surfactants belonging to the class of quaternary ammonium salts were synthesized and investigated as antimicrobial compounds. The antimicrobial effect of the carbon chain length of these molecules towards different Gram+, Gram- and yeasts strains was studied in order to identify the best molecule to be incorporated into the PBM membranes. Moreover, a new chemo-mechanical strategy able to actively counteract fouling was developed [3]. A self-cleaning PBM membrane was produced by exploiting the catalytic activity of tetra-ruthenium polyoxometalates (Ru_4POMs) when exposed to H_2O_2. The catalysts, suitably functionalized in order to be chemically entrapped in the membrane matrix, were dispersed in a polymerisable bicontinuous microemulsion (PBM) that was polymerized as coating on the surface of polyethersulfone (PES) commercial membranes. Once chemically stimulated, the catalysts started to release O_2 bubbles through the dismutation reaction of H_2O_2. The nascent bubbles acted as a propulsive force able to mechanically displace the foulant particles located at membrane surface. The new proposed approach demonstrated to be particularly effective towards the displacement of irreversible fouling on membranes surfaces which is the most recalcitrant to be removed by conventional cleaning procedures and it is usually the main responsible for membrane performance and life-time reduction.

Picture from the pilot site built up in Kisumu (Kenya) within the VicInAqua Project

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Ultrapermeable Polymers Of Intrinsic Microporosity That Redefine The State-Of-The-Art For CO_2 Capture

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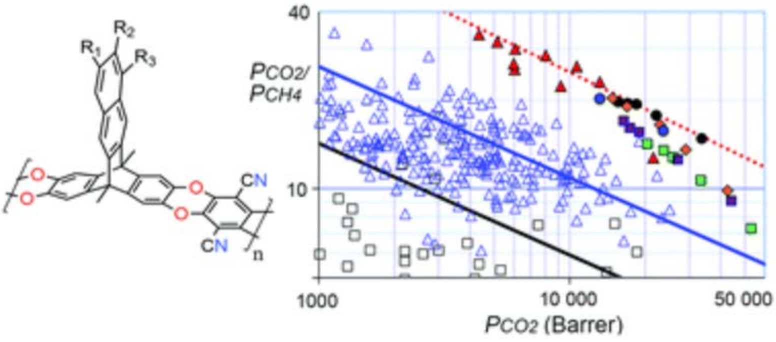
Polymers of Intrinsic Microporosity (PIMs) combine the desirable processability of polymers, with a significant degree of microporosity generated from the inefficient packing of their rigid and contorted macromolecular structures. They are attracting attention for a number of industrial gas separation applications, such as oxygen or nitrogen separation from air (i.e. separation O_2/N_2) or natural gas treatment and biogas upgrading (i.e. separation CO_2/CH_4). However, a further enhancement of the polymer transport properties is desirable to be cost effective in comparison with the traditional separation technology, currently applied for CO_2 capture or removal.

In this work, we report a series of benzotriptycene-based PIMs showing outstanding CO_2/CH4 and CO_2/N_2 permselectivity properties **[1]**, due to the inefficient packing of their 2D polymeric chains which results in large interconnected pores that enhance gas permeability. These benzotriptycene-based PIMs demonstrate ultrapermeability (PCO2>20000 Barrer) and interesting selectivity, and their combination allows the introduction of a new upper bound to define the current state-of-the-art for CO_2 membrane separation processes (Figure 1).

Their gas transport properties will be discussed in terms of permeability, diffusivity and solubility on freshly methanol treated and aged samples. The effect of the temperature on the transport properties will be also discussed. Particular attention will be paid to the relative contribution of diffusivity coefficients with the analysis of the size-selectivity in terms of entropic and energetic selectivity **[2]**, and as a function of the effective diameter of the penetrant gas **[3]**. The latter analysis demonstrates that the diffusivity of light gases through PIMs shows that smaller H_2 and He gas molecules have a transport mechanism that is similar to that of porous materials, whereas larger gas molecules, CH_4, N_2, O_2 and CO_2, show activated transport similar to that of conventional dense polymers. A typical and *defining* feature of PIMs, which differentiates their properties from other high free volume polymers, glassy polymers and rubbers, is the change in slope of the plot of the diffusion coefficient as a function of the gas diameter, with a stronger size-selective trend for the larger gas molecules than for He and H_2.



Molecular structure of the ultrapermeable PIMs and their gas permeability data on the Robeson plot for the CO_2/CH_4 gas pair, including the proposed upper bound.

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Acknowledgement:

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Accurate Chemical Analysis Of Oxygenated Graphene-Based Materials Using X-ray Photoelectron Spectroscopy

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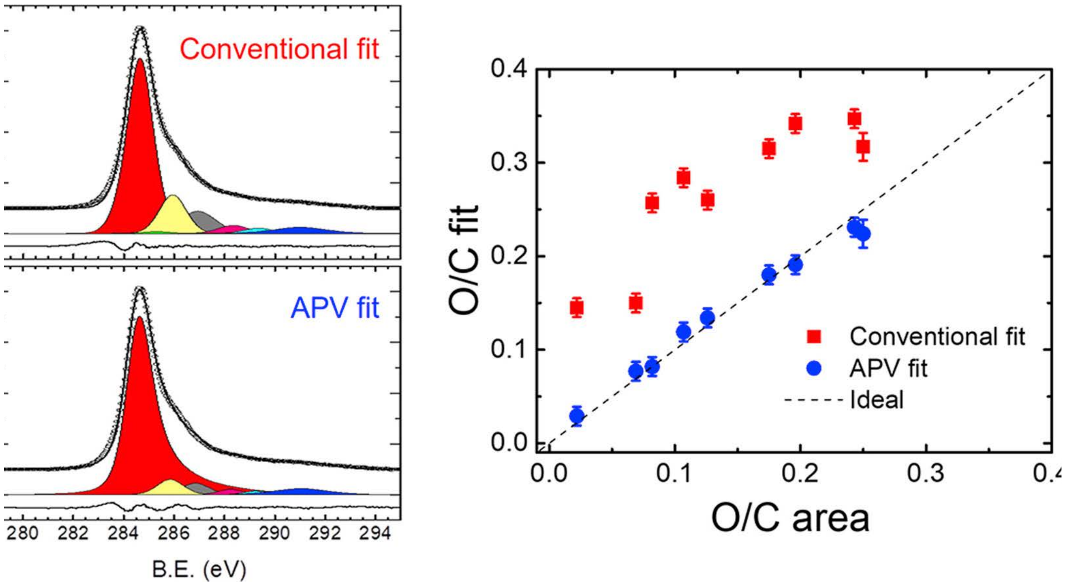
A simple, fast and general protocol for quantitative analysis of X ray photoelectron spectroscopy (XPS) data provides accurate estimations of chemical species in graphene and related materials (GRMs) [1]. XPS data are commonly used to estimate the quality of and defects in graphene and graphene oxide (GO)[2], by comparing carbon and oxygen 1s XPS peaks, obtaining an O/C ratio. This approach, however, cannot be used in the presence of extraneous oxygen contamination.

The protocol, based on quantitative line-shape analysis of C 1s signals, uses asymmetric pseudo-Voigt line-shapes (APV), in contrast to Gaussian-based approaches conventionally used in fitting XPS spectra, thus allowing better accuracy in quantifying C 1s contributions from graphitic carbon (sp2), defects (sp3 carbon), carbons bonded to hydroxyl and epoxy groups, and from carbonyl and carboxyl groups. The APV protocol was evaluated on GRMs with O/C ratios ranging from 0.02 to 0.30 with film thicknesses from monolayers to bulk-like (>30 nm) layers and also applied to previously published data, showing better results compared to those from conventional XPS fitting protocols [3]. Based uniquely on C 1s data, the APV protocol can quantify O/C ratio and the presence of specific functional groups in GRMs even on SiOx, substrates, or in samples containing water.



Correlation: O/C_{fit} vs O/C_{area}. Values obtained from analysis of XPS data using the conventional symmetric model and the APV fit developed here.

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Acknowledgement:

The research leading to these results received funding from the European Union Horizon 2020 research and innovation programme under GrapheneCore2 785219. The XPS instrument was purchased with financial support from the Emilia-Romagna (Italy) regional project POR FES 2007-2013.

Selective Homopolymerization Of Cyclohexene Oxide In Presence Of CO_2 Catalyzed By Hexafluorophosphate Salts

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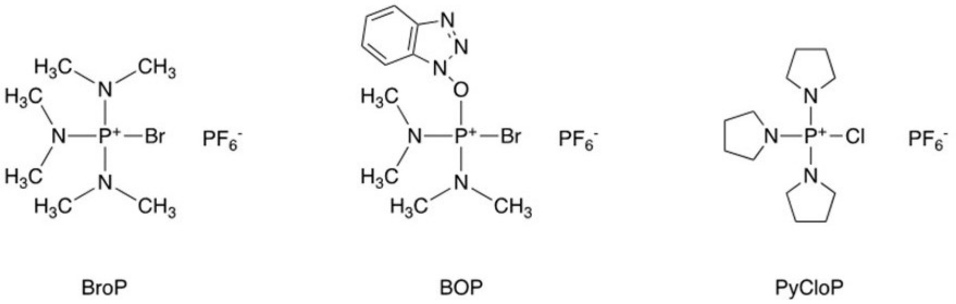
In the last forty years, CO_2 has become the subject of study as a carbon source, being a non-toxic, renewable and easily available resource in large quantities and high purity. It has largely been shown that one of the ways to use carbon dioxide is in the alternating copolymerization with epoxides. Depending on the epoxide used, the resulting materials are compatible with a wide variety of applications such as ceramic binders, adhesives, coatings and packaging materials.
In the frame of the research of novel cocatalysts for epoxide/CO_2 copolymerization, recently it was shown that organic quaternary phosphonium salts can be used as novel cocatalyst in conjunction with chromium salen complexes. Highly efficient formation of polycarbonate with narrow distribution and molecular weights comparable or superior to those obtained with the well-known bis(triphenylphosphine)iminium (PPN+) salts was achieved with these salts. Nonetheless, the most common anions are usually Cl^-, N_3^-, Br-, or OAc while hexafluorophosphate anions, largely used as highly efficient coupling agents for peptides, are commonly regarded as poorly coordinating ligands unable (or hardly able) to activate the catalyst in the coupling of epoxide with CO_2. Notwithstanding their substantial inability to bind a five-coordinated metal center to give rise to the octahedral molecule active in the epoxide ring opening, the phosphonium hexafluorophosphates tested and shown in Figure 1 are able to initiate and carry on the homopolymerization of CHO to PCHO in almost every experimental condition.
Several experiments, performed both in presence or absence of a metal Salen-type catalyst and/or under pressure, selectively led to the unique formation of pure polyether with molecular weight up to 10.000 g/mol and selectivity higher than 97% over the cyclic by-product, with similar properties despite the different used cations, with the cation-bound halide being reasonably disregarded as initiator.



BroP BOP PyCloP

Quaternary phosphonium hexafluorophosphates tested

Such a behavior was not observed when propylene oxide was used as a monomer: a very modest catalytic activity in the copolymerization of PO and CO_2 to poly(propylene carbonate) was detected, the conversion of propylene oxide did not exceed 20% , low selectivities with a medium-to-high content of ether linkage, ranging from 50% to 60% have been observed.
FTIR/ATR, 1H-NMR, SEC and DSC studies on the afforded homopolymers were accomplished.

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Stability And Unexpected Surface Chemical Reactivity Of $PtSn_4$ Crystals

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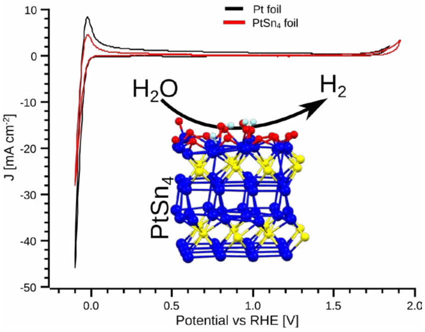
Catalysis and electrocatalysis are key research fields for overcome the challenging tasks owing to the increasing impact of human activities on the environment. Despite the excellent performances of platinum (Pt) in many catalytic reactions, the high cost (>30 US $/g) and the restricted availability of Pt make unavoidable the quest of economic and Earth-abundant potential alternatives. One possible solution is to reduce Pt content by using Pt-based alloys. Among Pt-based alloys, recently PtSn4 has attracted considerable interest due to its exotic electronic structure [1,2]. A recent work has indicated that PtSn4 has an outstanding performance in hydrogen evolution reaction (HER) in alkaline media with a strong similarity with the case of Pt [2].

Here we report the results of density functional theory modeling, surface-science experiments and electrochemical tests, that assess its suitability for catalysis and electrocatalysis. In particular we studied the chemical reactivity of the PtSn4 surface toward CO, H_2O, O_2 molecules at room temperature and, moreover, its stability in air. Furthermore, the use of PtSn4 as electrode in hydrogen evolution reaction and oxygen evolution reaction provides results strongly resembling values for Pt (Tafel slope of 86 mV dec^{-1}). Modeling of hydrogen evolution reaction demonstrates that the process contain two steps (Volmer and Tafel reaction) and the energy barrier of the latter decreases with surface oxidation to values similar to that of Pt(111).

In the end, we identified the pivotal role of the tin-oxide skin formed upon surface oxidation in air in the unexpectedly performances of $PtSn_4$ in HER, which represent an absolutely innovative catalytic mechanism with unexplored capabilities.



Scheme 1. Modeling of the PtSn4 surface terminated with an oxidized tin layer. The electrochemical behavior unexpectedly appears very similar to the Pt(111) in acidic environment.

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Technological Challenges In The Production Of Asymmetric Ceramic Membranes For Hydrogen Separation

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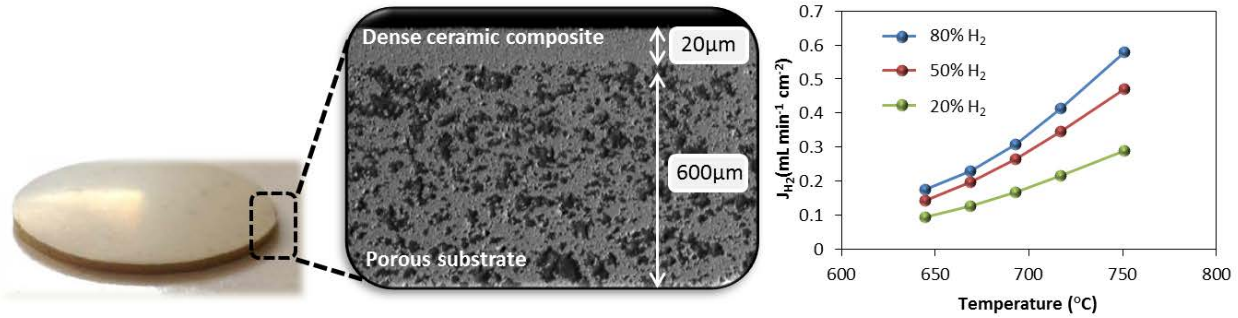
Considering the limited fossil fuel reserves and the environmental concerns, a transition to a sustainable and cleaner "hydrogen economy" is vital. On a short-term period, the intensification and optimization of hydrogen-based technologies that make use of fossil fuel as feedstock, could rapidly boost this revolution. However the main product obtained by these processes is syngas, therefore the separation step is mandatory to obtain pure H_2.

In this context, mixed proton and electron conductor ceramic composites are among the most promising materials for hydrogen separation membrane technology especially if designed in an asymmetrical configuration (thin membrane supported onto a thicker porous substrate)[1]. However a precise processing optimization is needed in order to effectively obtain planar and crack free asymmetrical membranes with suitable microstructure and composition without affecting their hydrogen separation efficiency[2,3].

This work highlights for the first time the most critical issues linked to the tape casting process used to obtain $BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-\delta}$ - $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (BCZY-GDC) asymmetrical membranes for H_2 separation. The critical role of the co-firing process, sintering aid and atmosphere was critically investigated. The optimization of the production strategy allowed to obtain asymmetric membranes constituted by a dense 20 µm-thick ceramic-ceramic composite layer supported by a porous (36 %) 750 µm-thick BCZY-GDC substrate. The asymmetric membranes here reported showed H_2 fluxes (0.47 mL min^{-1} cm^{-2} at 750°C, feeding the 50% of H_2 in He) among the highest obtained for an all-ceramic membrane (Figure 1).



BCZY-GDC asymmetrical membrane: microstructure and H_2 flux (mL min^{-1} cm^{-2}) as a function of temperature and H_2 partial pressure

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Laser Heating For Tuning The Optical Properties Of Flame Soot

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The concept of circular economy is promoting a renewed interest in soot that from polluting and unwanted material can turn into a resource [1-3]. However, the use of flame-generated soot as an innovative and useful material requires careful control of its physicochemical properties. In this work we explore the possibility to tailor the optical properties of flame-soot by in-line irradiation with a high-power laser.

Soot particles are generated by a quenched diffusion flame and irradiated by a 1064 nm short laser pulse. Wavelength-resolved extinction measurements in the visible range are used to follow the transformation in the optical properties by varying the laser energy density. A significant variation of the extinction coefficient of the irradiated particles compared to the extinction coefficient of the pristine ones is observed. In particular, a stronger slope of the extinction coefficient for the irradiated nanoparticles is detected in the blue region.

Raman spectroscopy and X-Ray diffraction analysis emphasize differences in the particles nanostructure. At very high laser fluence laser irradiation seems to promote the formation of onion-like carbon structure. Also, the aggregate structure is affected by laser irradiation as shown by particle size distribution measurements.

The results indicate that laser irradiation affects soot physicochemical properties in a complex way. Both soot nanostructure and optical properties are strongly dependent on the laser energy density when irradiated by a laser source. Therefore, the tunable laser-irradiation process is a promising tool for producing tailored carbon nanoparticles from flame soot. Also this process is potentially of enormous technological importance as the tuning of the particle optical properties can be performed continuously and rapidly.

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Acknowledgement:

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In-situ Synchrotron XRD Analyses For The Structural Investigations Of $BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-\delta}$-Doped Ceria Composite Under H_2 Atmosphere

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Nowadays, dense ceramic membrane based on Gd-doped ceria- $BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-\delta}$ composite has potential applications as H_2 separation membrane at T > 600°C, thanks to an acceptable H_2 flux and good chemical stability under CO_2- and H_2S-containing atmospheres. [1, 2] This membrane selectively separates H_2 by incorporating it into the crystal structure of its constituents as charge protonic defects and electrons/holes that are transported to the opposite side of the membrane under a H_2 partial pressure gradient.

However, the long-term stability at high temperatures and in H_2 atmospheres is a critical issue due to some possible undesired effects such as cation diffusions, crystal structure alterations or formation of insulating species that may significantly affect the performances of the membrane. A better understanding of the complex phenomena involved during the H_2-separation is limited because of the scarcity of suitable *in-situ* techniques to probe these issues. Indeed, the testing conditions used for *ex-situ* XRD and SEM-EDS investigations are not descriptive of the system in working conditions.

To study these phenomena from the structural point of view, we have performed a systematic investigation of the crystal structure stability of $BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-\delta}$-$Ce_{0.85}Gd_{0.15}O_{2-\delta}$ (BCZ20Y15-GDC15) composite material by *in-situ* synchrotron radiation X-ray diffraction analyses at DESY Synchrotron (Beamline P.02.1 at PETRA III, Hamburg). The apparatus used for the analyses was an *in house* made cell developed from Helmholtz Zentrum Geesthacht for investigations under reducing and humid conditions. Data were collected under H2 atmosphere from room temperature to 800°C both in dry and H2O-saturated conditions. [3]

No chemical interaction between the BCZ20Y15 and GDC15 phases occurred in the composite, thus demonstrating its excellent chemical stability under operating conditions. The BCZ20Y15 phase displayed some phase transitions, under both dry and wet H_2: i.e., it showed an orthorhombic *Imma* structure from room temperature to 100°C, trigonal *R-3c* up to 700°C and cubic *Pm-3m* up to 800°C. Conversely, the GDC15 phase did not display any phase transition, remaining in a cubic *Fm-3m* structure under all tested conditions. Moreover, a *synergistic effect* of the BCZ20Y15 and GDC15 phases in the volume expansion of the composite was revealed: indeed, BCZ20Y15 and GDC15 lattice expansion rates tend to approach each other in the composite under reducing conditions. This *synergistic effect* is very important for the mechanical performances of BCZ20Y15-GDC15 composite. The similar expansion rate observed for BCZ20Y15 and GDC15 may reduce the strain and prevent failure of this ceramic membrane under operating conditions.

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Acknowledgement:

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Fiber Reinforced Composites For Aerospace And High Temperature Applications: A Sustainable Route Using Inorganic Polymers

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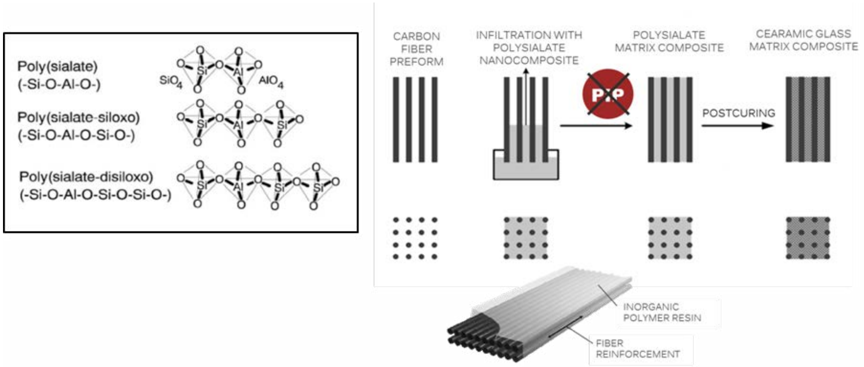
In key sectors as the automotive and aerospace industry, the need to develop new materials able to combine lightness, mechanical strength and fire protection, together with an easy and sustainable processability, has becoming an important challenge to face. Current research efforts in the FRP sector, indeed, are increasingly dealing with reducing the emissions of volatile organic compounds from organic resins, and limiting the energy demand and the environmental impact of the manufacturing process, without affecting the overall performances of the materials.

In this framework, with the aim to ensure an optimal balance between performances, sustainability and costs, and allow for a viable industrial scale-up and distribution, an innovative fiber reinforced composite material based on an inorganic polymer matrix has been designed [1]. Such composite material shows properties and characteristics halfway between traditional FRPs and CMCs, and is particularly suitable to produce highly engineered structures through a simple, sustainable and low cost process. The hazard-free aqueous based matrix ensures the compliance with the most strict environmental legislations and codes of practice, granting at the same time the possibility of working with the same equipment and within the same process conditions of traditional FRPs. Moreover, thanks to its easily tunable nanostructured matrix, it can be specifically customized and used for structural applications in the aeronautic, naval, rail field, replacing the most common materials as Inconel or Titanium superplastic alloy. Innovative architectures based on such reinforced composite with nanometric inclusions enable the creation of complex geometry structures with almost fully customizable properties, which can be further adjusted by additional post impregnation and/or postcuring steps, depending on the desired final properties.

Compared to conventional materials, such composite can grant no-smoke emissions and boast a high temperature resistance (up to 1200 °C), coupled with a low thermal expansion and a very low thermal conductivity, and good mechanical properties (up to 200 MPa for tensile strength). Moreover, lightness and low life cycle costs make it a valid technological solution, especially when fire proofness and high working temperatures are requested, allowing to save up to 30% in weight respect to all the conventional materials.



Classification of polysialates inorganic polymers and their use in the process of impregnation of carbon fiber preforms with vacuum bagging technology

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Selective Laser Melting Of NiTi Alloys

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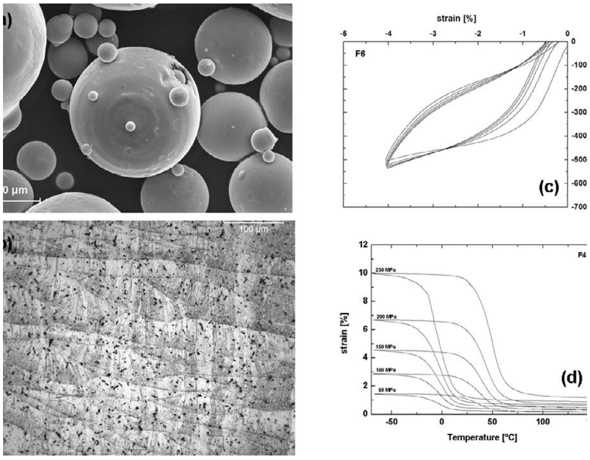
Near-equiatomic NiTi is known for the ability to gain high deformations when subject to a thermal cycle under load (shape memory effect) or during a loading/unloading cycle at constant temperature (pseudoelasticity). The resulting mechanical work may be exploited in practical applications as actuators and sensors. Lightness, compactness, noiseless and thermo-mechanical cyclic stability are the leading characteristics of NiTi-based devices. However, the poor workability by means of conventional processing techniques limits the use of NiTi. The high ductility and the high degree of work hardening of NiTi alloys during cutting lead to difficult processing and poor workpiece quality. Therefore, in most applications the NiTi component is designed out from the same semifinished product (sheet, strip, wire, tube, bar) and its final geometry is simple and it is often in the form of wire, spring or tape [1].

Selective laser melting (SLM) is an additive production process that uses a laser beam source to selectively melt metal micrometric powder, layer by layer and following a 3D CAD model. It allows producing three dimensional objects of even complex geometry, limiting the use of tools and overcoming the problems related to traditional technologies. As a first consequence, the possibility to produce near-net-shape components has expanded the field of applications of NiTi.

In this work, on the base of previous results [2], an optimized set of process parameters was selected to deepen the variation of the microstructure, the phase transformation temperatures and the mechanical response of NiTi parts produced by SLM, starting from a 55.2wt% Ni NiTi powder. After the production process, it was detected the depletion of Ni in the as-built parts which caused an overall increasing of the phase transformation temperatures. All NiTi families present a shape memory response at room temperature. It is shown that the resulting material may exhibit distinct damping and strain recovery responses correlated with the used SLM parameters. Moreover, differences in thermal and mechanical behavior were also observed between samples with same process parameters highlighting the effect on of phase transformation temperature of part growing direction and position on the building platform.



Sem image of the NiTi micrometric powder (a), optical microscope observation of the NiTi as-build part (b), stress-strain (c) and strain recovery (d) responses.

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Polymer Blending And In Situ Polymerization Approaches For 2D Black Phosphorus Polymeric Materials

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Black phosphorus (bP) has been extensively investigated for both electronic and photonic applications. However, the difficulty in engineering large scale exfoliation procedures and the intrinsic instability of exfoliated bP towards both moisture and air has so far overshadowed its possible applications. Here, polymer-based hybrid materials containing dispersed black phosphorus nanoflakes (bPn) are prepared, and their structural characteristics analysed and compared, to evaluate the bP dispersion degree and the effectiveness of bPn interfacial interactions with polymer chains aimed at their environmental stabilization. In particular, the polymethyl methacrylate (PMMA) passivation results particularly effective for the hybrid material prepared by polymerization in-situ of MMA, after the direct liquid phase exfoliation in the monomer (without solvent and by operating in ambient conditions). The procedure yields hybrids where the bPn, even if with a gradient of dispersion (size of aggregates), preserve their chemical structure from oxidation, even after UV exposure.

The feasibility of this methodology, capable of efficiently exfoliating bP while protecting its structure, is verified using different vinyl monomers: styrene (S) and N-vinylpyrrolidone (NVP) and even by building PS-block-PMMA copolymers. In addition the dispersion of the bPn in mixtures of partially miscible polymers (PS / PMMA, P3HT / PMMA) was carried out with the target to confine the sheets of bP at the interface or in a specific phase to modulate the properties of electronic transport by exploiting the morphological properties of the final product generated by the different solubility in specific solvent. A selected hybrid is used to design a device without the need of a glove box in any stage of the fabrication, where the nanoflakes show resistance and mobility comparable with electronic-grade liquid phase exfoliated bP. This result proves that the methodology here realized provides hybrid materials as suitable platforms for devices fabrication in the field of optoelectronics.

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Textile Fabrics Dyeing To Confer Halochromic Properties

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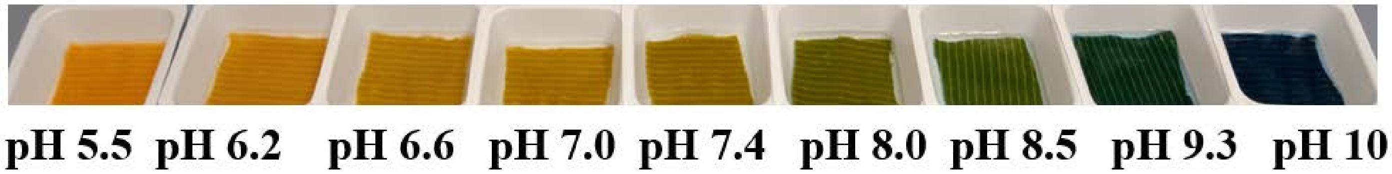
Recent literature reported an increasing number of papers related to pH-sensitive materials because of their broad range of applications as sensors systems [1,2]. Among these materials, textiles with halochromic properties are having a significant attention due to their flexibility, mechanical properties, lightweight and washability. These properties allow to produce wearable pH sensitive devices, that might be employed in a wide range of applications [3], like for example in wound dressing to indicate the progress of wound healing; or in water filtration as well as in agriculture to monitor the pH of soil. Finally, a color-changing textile can have an interest in house applications including curtains, tablecloths, and bed linen. The manuscript shows the possibility to dye textile fabrics with halochromic dyes. Five different halochromic dyes were tested:Bromocresol Purple, *m*-Cresol Purple, Chlorophenol Red, Curcumin and Bromothymol Blue. The dyeing recipe was applied on a multifibers textile fabrics composed of wool, acrylic, polyester, polyamide 6.6, cotton and acetate, to test the affinity of different fibers for the dyes. The dyes were solubilized in a water solution and the dyeing bath was heated at 100°C for 40 min. Washing and light fastness of the dyed fabrics were evaluated, as well as color changing at different pH. Some fibers, polyamide 6.6 and wool in particular, showed a good fastness of the dye and halochromic properties. Bromothymol Blue was selected to dye polyamide 6.6 and cotton fabrics. Cotton required a mordant application step before the dyeing. Both cotton and polyamide 6.6 evidenced good halochromic properties in a pH range from 4 to 10. Cotton fabrics exhibited an immediate color changing; polyamide 6.6 changed color after few minutes, and the color transition was faster as temperature increased. On the other hand, cotton fabrics showed a poor light and washing fastness, while polyamide 6.6 evidenced a good dyes fastness. Figure 1 reports the results of the halochromic test on cotton fabrics.



results of the halochromic test performed on cotton fabrics dyed with bromothymol blue

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Guidelines To Design And Understand Eu(III)-Based Luminescent Thermometers And A Model To Predict Their Behaviour

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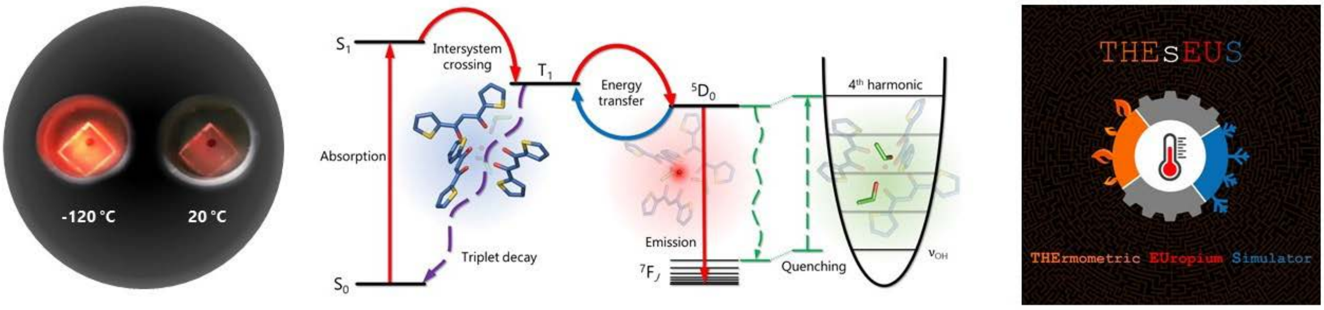
Non-invasive precise thermometers working at the nanoscale with high spatial resolution, where the conventional methods are ineffective, have emerged over the last years as a field of paramount importance for the developing of advanced materials. Lanthanide (Ln) based luminescent thermometers exploit the peculiar Ln luminescence properties to sense and map the temperature through a non-invasive approach reaching sub-micrometric spatial resolutions and impressive temperature resolutions, *i.e.* the smallest temperature variation that can be revealed, up to the order of milli-Kelvin. Hence, such materials are particular valuable for a wide range of applications ranging from material science and engineering to nanomedicine [1].



Understanding and predicting the behavior of Eu(III) molecular thermometers

A new model [2] to describe the temperature dependence of Eu(III) based molecular thermometers (MTs) is here presented and used to draw some general guidelines to design new Eu(III) MTs. In the model, non-radiative deactivation channels are described by thermally activated energy transfer processes and can be included in a modular way. This model takes into account the energy differences between the various excited states, modulated by fixed, one-size-fits-all parameters and one single variable parameter to weigh the contributions of the two main deactivation channels. The model has been developed and tested on a library of Eu(III) based complexes of general formula EuL_3A_2, where L is a β-diketone with different polycyclic aromatic hydrocarbon (PAH) substituents in order to fine tuning its triplet energies, and A is an ancillary ligand that in turn can be a quencher molecule (EtOH) or a not-quenching system (TPPO). The model proved to be very effective in describing the interplay between triplet and vibronic deactivation channels. It predicts the thermometric response both reproducing trends and ranges of applicability of the tested molecular thermometers. Finally, we developed a MATLAB based standalone application named THEsEUS (THErmometric EUropium Simulator) that implements the discussed model [2].

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Novel Isoprene Polymers With An Alternating Cis-1,4/3,4 Structure: Synthesis, Characterization And Properties

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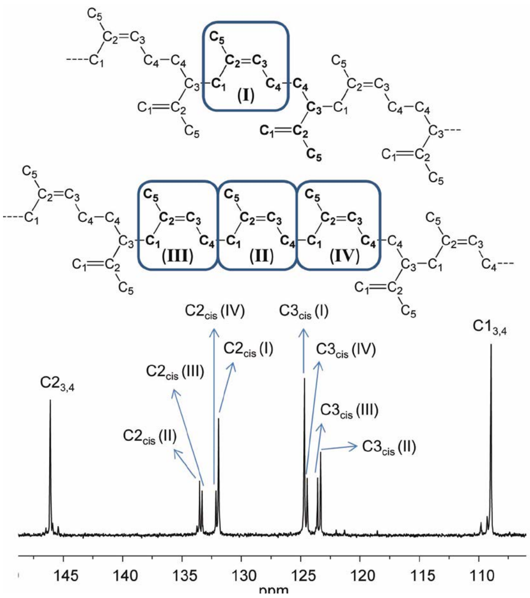
The stereospecific polymerization of isoprene can give polymers having different structure and properties [1]. A *cis*-1,4 polymer with a very high cis content (≥98%), very similar to natural rubber, can be obtained with catalysts based on neodymium (*e.g.*, TIBAO/$NdCl_3$·L, being L = bis-imine and TIBAO = tetra-isobutylaluminoxane) and titanium (*e.g.*, $TiCl_4/AlEt_3$); a highly *trans*-1,4 polymer was prepared with vanadium catalysts (*e.g.*, $V(acac)_3$-MAO); 3,4 iso- and syndiotactic polymers were instead synthesized with catalysts based on silylene-linked cyclopentadienyl-phosphido rare earth metal alkyl complexes and on $Fe(bipyridyl)_2Cl_2$ complexes, respectively. *Trans*-1,4 and 3,4 iso- and syndiotactic polymers are crystalline, while the *cis* polymer is amorphous, exhibiting the typical elastomeric properties making it extremely useful for the production of truck tires. Very recently a 1,2 enriched polyisoprene was obtained with catalysts based on cobalt complexes carrying aminophosphoryl fused (PN^3) ligands.



^{13}*C NMR of a predominantly alternating cis-1,4/3,4 polyisoprene obtained with iron-based catalysts.*

Our recent years research activity, which was particularly focused on the polymerization of conjugated dienes with catalysts based on transition metal and lanthanide organometallic complexes having a well-defined structure [2], has now allowed us to synthesize a novel isoprene polymer showing a particular structure not reported yet. We synthesized and characterized several types of cobalt phosphine complexes and imino-pyridyl iron complexes, and successively we used them, in combination with methylaluminoxane, for the polymerization of isoprene. By varying the nature of the ligands on the metal atom, we were able to synthesize perfectly alternating *cis*-1,4/3,4 polyisoprenes or predominantly alternating *cis*-1,4/3,4 polymers in which however some *cis*-14 sequences of different lengths are present along the polymer chain, as indicated by the NMR analysis (Figura 1).

This result was quite interesting since, depending on the catalyst structure, it was possible to obtain crystalline polymers or amorphous polymers with tunable transition glass temperature in a large range of temperatures.

These features make these novel polymers of potential interest in the automotive field for the preparation of elastomeric tire compounds.

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Process Optimization To Produce An Austempered Ductile Iron With High Microstructure Stability

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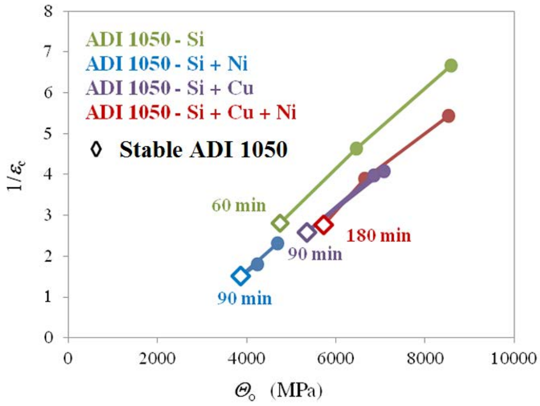
Commercial Austempered Ductile Irons (ADIs) are produced through a multi-step heat treating of conventional ductile irons (DIs), usually with minor addition (e.g. Ni, Cu). The heat treatment sequence consists of austenitization at high temperatures followed by austempering, i.e. quenching to the temperature range 250-400°C and then tempering for a proper time. ADIs peculiar microstructure (ausferrite) is characterized by nodular graphite, Widmanstätten ferrite and metastable high carbon austenite, which provides elevated mechanical properties with outstanding ductility [1]. Thanks to these properties, ADIs can be an economical substitute for steel in several structural applications (e.g. in the automotive industry). The stability of the metastable austenite is a key factor for ADIs' mechanical applications, since loading during service may induce a martensitic transformation which would cause the appearance of hard and detrimental phases.

During austempering a two-stage transformation occurs: in stage I, when austenite is quenched from austenitization temperature into salt bath ferrite and high carbon austenite appear; in stage II, which takes place for longer soaking time in salt bath, austenite partially decomposes into ferrite and ε' carbides, causing detrimental brittleness. The best combination of mechanical properties (tensile strength and ductility) is achieved after the completion of the first reaction but before the onset of the second one.

However, the proper austempering time depends on several factors, like the chemical composition, austenitization temperature and time, and microstructure resulted from solidification [2]. Strain hardening analysis of tensile flow curves, based on dislocation-density-related constitutive equations, of ADIs at different times during austempering transformation has been proved [3] to be a useful tool to define the proper austempering time. In this work, ADIs with Ni, Cu and Ni+Cu additions were analysed after different austempering times in order to assess their microstructural evolution.

This work is done in the framework of a two years project named POPADI, funded by the Italian MAECI and the Polish Foreign Department that aims at finding the proper process conditions and Ni content for producing ADIs with the best compromise between strength and ductility, with the best austenite stability.



Strain hardening parameters for the ADIs tested in the present work as a function of austempering time.

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Ionic Liquid Crystals And Their Potential Applications In Membranes

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Ionic Liquid Crystals (ILCs) are mesophases, that is materials exhibiting thermotropic Liquid Crystal (LC) behavior, entirely composed of ions. From the molecular point of view, they share many structural features with Ionic Liquids (ILs), isotropic fluids made of ions and liquid around room temperature. Several examples of ILs often based on organic nitrogen salts, such as imidazolium, ammonium, pyridinium, have been reported. Common counter-anions are halides, tetrafluoroborate, hexafluorophosphate, triflate, bistriflimide among others. When the alkyl chain of the cation exceeds a certain length (that is the number of carbon atoms in the chain is above a minimum value), micro-segregation between the ionic parts and the hydrophobic chain drives the formation of layered phases. Besides the crystal phase, in many cases a mesophase of smectic type is observed.

Applications of ILCs have been demonstrated in a number of cases. In particular, when charge or mass transfer occurs within a medium or within an electrolyte, ILCs show an improved performance compared to analogous systems having no mesophase in similar operating conditions. Thus, ILCs have been tested, for example, as electrolytes in dye sensitized solar cells and ion batteries. The main drawback is, however, the relatively high viscosity of these systems.

The main research line of our group is the study, both from an experimental and a computational point of view, of ILCs and their properties, with the aim of using them as fillers in polymeric membranes in order to obtain stimuli-responsive materials. In this presentation we will highlight some recent experimental and computational results obtained.

We have synthesized and characterized several types of viologen based ILCs: symmetric and non-symmetric monomers, dimers, and polyfluoroalkyl systems. The stability of the smectic A phase has been investigated and we have observed a significant dependence of the phase behavior on the molecular structure of the cation. A prototype of a reversible electrochromic device has been also realized using the polyfluorinated samples that exhibit a stable smectic phase at room temperature [1].

In parallel, we have conducted Molecular Dynamics simulations of ILCs, using either fully atomistic Force Fields or Coarse-Grained versions at various levels of coarsening. Atomistic simulations have been used to interpret experimental data obtained from ordered NMR spectroscopy and 129-Xe diffusion NMR. Coarse-grained simulations have been used to understand the basic features that promote and stabilize ILC phases over crystal and isotropic liquid systems [2].

Finally, we will show some preliminary results concerning dense polymeric membranes filled with ILCs as well as porous membranes where a viologen ILCs has been used as co-surfactant during the production stage to improve the membrane structure [3].

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Colloidal Nanocrystal/ Dye Coupled Systems For Energy And Charge Transfer Processes

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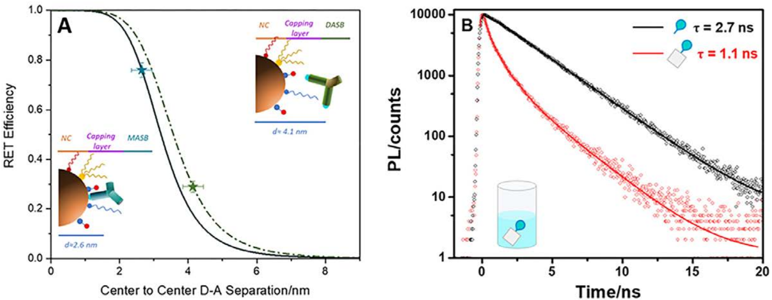
The urgent demand for low-cost green clean energy has stimulated the research for new materials for energy storage and conversion. Colloidal semiconductor nanocrystals (NCs) were demonstrated as promising materials for light harvesting applications [1], while nanostructured titanium dioxide (TiO_2) has been successfully exploited in electrodes for photovoltaics. In particular, NCs with controlled size and shape, coupled and/or functionalized with suitable organic chromophores demonstrated efficient energy transfer (ET) and charge transfer (CT) processes [2]. Understanding the events occurring at organic/inorganic interfaces in both ET and CT processes is crucial for the direct application of the developed materials in real devices.

In this work, CdSe NCs of selected size, synthesized by hot-injection methods, were coupled with organic chromophores, based on boron-dipyrromethene (BODIPY) dye, properly functionalized with amino groups to improve their affinity with NC surface. The spectroscopic investigations on such hybrid nanosystems in solution revealed a FRET process occurring between the NCs (donor) to the conjugated dye. A comparative study was performed, to evaluate the effect of the substitution extent at the BODIPY rings on the ability of the two dyes to effectively support the ET process. Experimental results show that the mono-functionalization with an amino-styryl group both provides an improved spectral overlap between the NCs emission and dye absorption and a shorter donor-acceptor separation distance, resulting in higher FRET efficiency with respect to the hybrid based on the bi-functionalized dye. A remarkable increase of the FRET efficiency was obtained for the coupled nanosystems deposited on substrate, with respect to the layered thin films of NCs and dye, indicating a favourable influence of the reduced interparticle separation [3].

In addition, TiO_2 NCs and a Zn phthalocyanine functionalized with carboxylic acid groups (PcTC) were selected to investigate CT processes, due to proper band alignment. The hybrid composite was prepared in solution and in solid state, by exploiting both simple physisorption and effective chemical bond formation after activation of the carboxylic acid functionalities. The quenching of the dye fluorescence suggested the emergence of CT (Figure 1B). In particular, in the solution-phase nano-hybrids, CT efficiency and stability were sensitive to the nature of the solvent, as well as to the preparation strategy.



A) Theoretical (line) and experimental (star) E_{FRET} for mono (blue) and di-amino (green) modified dye/NCs; B) PL decays of the dye (black) and of the hybrid TiO_2/dye (red)

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Chromophores For Sensing And Optoelectronic Applications

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Multifunctional π-electron systems based on porphyrin and BODIPY (BD) chromophores are widely studied in synthetic chemistry and material science in virtue of their fascinating photophysical properties which are strictly dependent on the chemical functionalization of the molecular backbone. They are versatile tools for manifold applications such as artificial light harvesting systems, chemical sensors for the detection of contaminants in solution and the synthesis of hybrid materials. On these bases, here we report a variety of novel systems properly synthesized to achieve specific goals. In particular, opportunely functionalized BD have been exploited to build organic/inorganic hybrid materials. The proper choice of the substituents on the BD allowed to improve the efficiency of the Forster type energy transfer processes by interaction with CdSe Quantum Dots. Supramolecular architectures based on BD with moieties able to give complementary hydrogen bondings have been conveniently synthesized to investigate the role and the mechanism of long- lived quantum coherence phenomenon in electronic energy transfer (EET). To the best of our knowledge, no examples of supramolecular systems have been so far investigated to this aim[1]. Despite many reports dealing with the use of porphyrin or BD systems, their subunits, i.e. dipyrrins, are only rarely used for photometric metal detection. Indeed, this class of molecules possesses useful photophysical properties and high affinity constants towards a variety of metal ions making them excellent candidates for achieving new fast, cheap and sensitive chemical sensors through their optical feedback. For all the investigated systems, a detailed spectroscopic characterization has been carried out using a combination of UV/Vis absorption, static and time- resolved fluorescence emission, and NMR techniques. Furthermore, pyrene derivatives with different functional substituent groups (i.e. ionic liquids and boronic groups) have been used for the design of supramolecular adducts with porphyrins and a 2D materials as phosphorene[2,3], respectively.

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Novel Hydrophobic/Hydrophilic Coated Membranes For Water Treatment Using Perfluoropolyether (PFPE) Compounds As Surface Modifier

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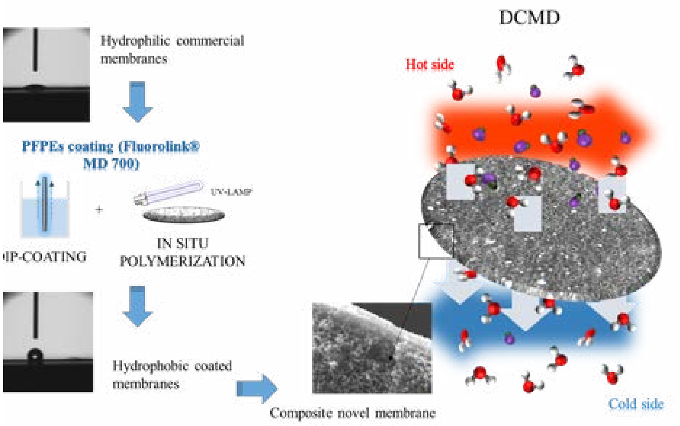
Recently, most studies focus the attention to the preparation of tailored membranes in order to improve their performance. In fact, near the commonly preparation techniques, now the attention was focalized to the preparation of tailored membranes via coating technique, in order to produce high-performance membranes [1]. There are several methods used, such as solution coating or polymerization reaction. Hydrophilization and hydrophobization of membrane surface are the most commonly modification, that embrace different fields from the control of fouling to membrane distillation (MD). In this scenario, Solvay Specialty Polymers S.p.A., developed a novel class of Flurolink® perfluoropolyether (PFPE) compounds UV-curable as surface modifier [2]. Hydrophobic or super hydrophobic and oleophobic coated membranes can be easily prepared using hydrophilic cheaper membranes as supporting material, via dip-coating and UV in situ polymerization Fluorolink® MD700 PFPE UV cross-linkable, was used as coating material on two different hydrophilic commercial membranes, polyamide (PA) and polyethersulfone (PES) at three different pore size (0.1, 0.22 and 0.45 µm). Initially the influence of starting material (PA-PES) was studied in terms of water/oil repellence. All covered membranes were characterized in terms of surface morphology (SEM and AFM), porosity and pore size, water liquid entry pressure (LEPw) and mechanical tests. The formation of a thin hydrophobic layer on the hydrophilic commercial membranes, make the membranes suitable for the membrane distillation process. Coating stability on membrane surface was then evaluated during time using salty solution NaCl 0.6 M, typical feed in desalination treatment and chemicals cleaning agents (KMnO4 0.1 wt.%, Hypochlorite NaClO pH 4.25, HCl pH 2.5, NaOH pH 11.5). Membranes performance were finally tested in DCMD configuration, using deionized water and salty solution 0.6M (NaCl), as feed. An highest value of permeate flux until 22 kg/m2h was obtained and concerning the tests with salty solution, a final salt rejections of about 99.95% after 158h of test was obtained for the best selected membrane [3].



Schematic procedure of Fluorolink®MD700 coated membranes preparation and characterization

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Heating And Antibacterial Textiles By Polypyrrole Coating

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Polypyrrole (PPy) is a conjugated polymer that shows excellent electrical conductivity, as well as antibacterial properties. The electrical conductivity is an intrinsic property of PPy because of its conjugated chemical structure. Moreover, the bioactivity is likely due to the presence of positive charges along the backbone chain able to open the membrane cell of bacteria [1,2].

PPy can be deposited to textiles by a direct chemical deposition [2] to produce heating fabrics. However, the separation between polymer synthesis and fabric coating would lead to benefits in terms of productivity, evenness, cost, wastewater and chemicals usage. This process is useful in particular for antibacterial textiles that requires low amount of coating to be effective.

In this work, chemical synthesis of PPy was carried out following two methods: 1) in presence of the fabrics in the polymerization bath in order to produce heating fabrics with high amount of PPy; 2) without a textile substrate in order to produce a PPy dispersion in water suitable for a following deposition on fabrics by ultrasound or spraying.

Method 1. Fabrics were cut to 20 x 20 cm and plunged in a 0.18 M solution of ferric sulphate (liquor ratio 50:1), then the monomer was added under stirring to a concentration of 0.06 M. The samples were pulled out from the polymerization bath after 4 h, rinsed in cold water, gently squeezed, and dried overnight at room temperature. Then, the samples were stored in a conditioned laboratory at 20°C and 65% RH at least 24 h before tests.

Method 2. PPy was synthetized in presence of poly(styrene sulphate) in order to produce stable water dispersions of PPy nanoparticles. PPy was deposited on fabrics by an ultrasound-assisted deposition process or a spraying coating plant [3].

The heating fabrics (PPy amount 27 % wt.), produced with the Method 1, showed excellent electrical properties (voltage: 9 V, electrical current: 108 mA, electrical resistance: 83 ohm, average surface temperature increase: 3.4°C).

Antibacterial tests were carried out according to ISO 20743 against *Staphylococcus aureus* and *Escherichia coli* on fabrics produced with the Method 2 at different PPy amount. The fabrics with the higher amount of PPy (3.7 % wt.) showed excellent antibacterial properties (~100% of efficacy) against both bacteria.

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Various Applications Of Electrospun Keratin-Based Nanofibers

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Keratin is a biocompatible and biodegradable protein as main component of wool and animal hair fibers. Keratin-based materials support fibroblasts and osteoblasts growth. Keratin has been extracted by sulphitolysis, a green method (not harmful chemicals) with a yield of 38-45%. Keratin has been electrospun into nanofibers from solutions of formic acid or from water for three different applications:

1) Production of electrospun keratin nanofiber membranes for air and water treatment. Keratin electrospun nanofibers have been successfully fabricated and coated with nylon woven fabric and characterized in terms of morphology, pore size, surface properties, pore size and performance, as water and air permeability. The results of nanofibers characterization suggest their potentiality in different applications including the removal of micron size and suspended solid particles such as flocs, bacteria, etc. in both water and wastewater treatment, adsorption of heavy metal and organic compounds, ion adsorption and also for air/gas filtration [1].

2) For dental implants application, a new technology based on mechanically produced nanogrooves (0.1–0.2 μm) and keratin nanofibers deposited by electrospinning has been proposed in order to obtain titanium surfaces able to drive gingival fibroblasts alignment and proliferation without increasing bacterial adhesion. The morphological signal exerted by uniaxially aligned keratin fibres was clearly predominant with respect to those of surface topography, thus leading to increased cells proliferation on the surfaces with nanofibers, disregarding the presence of the surfaces grooves [2, 3].

3) Production of composite nanofibers consist of keratin and other polymer. In the bilateral collaboration project between CNR and NRC Egypt for "Multi-jet Electrospinning of Renewable Biopolymers-based composites", keratin and sericin proteins were electrospun for the production of active nanofiber membranes. Keratin was extracted from wool fibers by sulfitolysis. Sericin was extracted from raw natural silk simply using hot water. The purified keratin or sericin was mixed with PEO or PVA to obtain electro-spinnable solutions. The solutions were electrospun into nanofibers by using a multi-nozzle electrospinning plant and a nozzle-less electrospinning plant.

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Multilayers Of Carbodithioate And Sulfide-Linked CdSe Nanocrystals: Progressive Increasing Of Exciton Delocalization

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Semiconductor nanocrystals (NCs) are challenging materials to be exploited in devices like light emitting diodes, solar cells and photodetectors, because of their unique electronic, magnetic and optical properties. Typically such devices require that the NCs should be both distinct particles that exhibit quantum confinement of the charge carriers and strongly coupled to the neighbouring particles when they are assembled into a film. In fact, quantum confinement allows the electronic properties to be tuned with the size, while electronic coupling facilitates charge transport in the device.

Unfortunately, such goals are difficult to achieve because of the very poor inter-particles contacts caused by linkers between NCs[1]. In fact, though much effort has been devoted in optimizing molecular core conductivity, there have been relatively few attempts at designing optimal anchoring groups to semiconducting nanocrystals. In a previous work we found that multilayered hybrid films realized by the alternation of CdSe-NCs and bi-functionalized linkers bearing dithiocarbamate moiety with ethylene or phenylene as spacers, have shown promising photoconductive properties[2], which were supported by photo-excited carrier dynamic experiments combined with theoretical calculations[3]. These latter studies show that the dithiocarbamate anchoring group causes the hybridization of the molecular HOMO state with the CdSe-NCs layers, which may favor the delocalization of the charge carriers through the layers. According to these encouraging results, other linkers bearing sulfur-based anchoring groups were taken into account.

In the present work tetrathioterephtalate (TTTP) and sulfide (S) dianions were reacted with (hexadecylamine/stearate)-capped CdSe nanocrystals (4.5 nm diameter) to form multilayers on ITO glass via layer-by-layer alternation. The study provides the determination of the electronic properties of the linkers by means of both UV-vis and electrochemical analyses. Linkers coordination to CdSe-NCs surface was investigated in bulk by FTIR analyses and in monolayers by UV-vis and electrochemical determinations. 10-multilayered film formation was monitored with UV-vis spectroscopy and it was observed a decrease of the energy of the optical band-gap (ΔE_{gn}) which depends linearly with the inverse of the number of layers (*n*). The change of NCs packing during multilayers build-up causes progressive increase of exciton delocalization. The effect was modeled and discussed in the light of the photoluminescence and photoconductive properties of the multilayers. Comparison with the previously investigated ethylene or phenylene bis-dithiocarbamate dianions has been performed.

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Influence Of Silanized Hollow Glass Microspheres On Thermal, Rheological And Mechanical Properties Of Poly(ε-Caprolactone) Composites For Rotational Molding

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In this work we report on the thermal, rheological and mechanical properties of composites prepared by mixing hollow glass microspheres (HGM), as such or surface modified by treatment with (3-aminopropyl) triethoxysilane (APTES) [1], with poly(ε-caprolactone) (PCL). The silanization treatment implies a good dispersion of filler within the matrix and an enhanced filler-polymer adhesion as testified by scanning electron microscope observations [2].

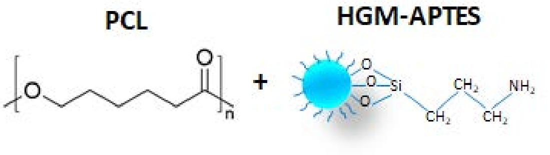
The crystallization of PCL/HGM composites at different filler concentrations (from 10 to 25 wt%) was investigated by differential scanning calorimetry under isothermal and dynamic conditions. The results showed that the HGM acted as nucleating agent, as confirmed by a remarkable reduction of the crystallization time. This effect was observed as a function of the HGM amount in the composites. Moreover, the silanization of glass microspheres enabled even faster crystallization rates.

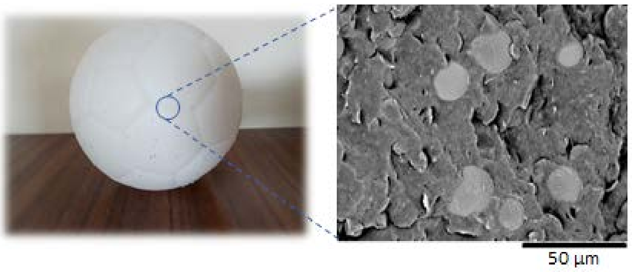
The effect of HGM on the thermal stability and degradation of the composites was studied by thermo-gravimetric experiments. The presence of HGM as such leads to an increase in the thermal stability of the composites compared to neat PCL. Conversely, the composites filled with silanized HGM show a decrease of thermo-oxidative stability because of the presence of less stable APTES anchored onto HGM surface.

Reinforcing PCL with HGM involved an increase in both storage modulus and complex viscosity as observed through rheological tests. A pseudo solid-like behavior, characterized by a plateau of storage modulus at low frequencies, in the presence of 20 wt% silanized HGM highlighted a stronger filler-matrix interactions.

The addition of HGM also affected the mechanical properties. Tensile tests showed a high increase of Young's modulus and a decrease of elongation at break with a consequent reduction of ductility for all composites compared to neat PCL. Nevertheless, the composites filled with the modified HGM, characterized by an increase of the tensile strength, pointed out the important role played by the silane in improving the filler-matrix adhesion. This is a remarkable result, considering that the addition of 20 wt% HGM implies a decrease of density by about 23% compared to neat PCL.

Finally, PCL/HGM composites were firstly proven to be successfully processed by rotational molding, both at laboratory and industrial scale.





Rotomolded prototype based on PCL and 10 wt% silanized HGM and SEM micrograph of the composite

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Nanoindentation And Tribological Tests – Suitable Tools For Design And Research On Thin Films

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The use of thin, hard coatings in tribological applications requests a fully understand of the relationships between the intrinsic properties of the coating/substrate system and its tribological performance. For satisfactory mechanical and chemical stability in operation, some properties are essential, i.e. elastic modulus, hardness, interfacial adhesion, fracture toughness, corrosion resistance. Since in most applications the behaviour of a film is given by the synergistic action of different properties, they must therefore be characterized as a whole. Data on wear resistance, adhesion and toughness can be obtained by tribology, microindentation and scratch tests, together with a simultaneous characterization of corrosion and wear behaviour that is crucial for coatings operating in harsh conditions. Mechanical properties measurements at nanoscale can be carried out by nanoindentation, thanks to fast, simple and economical operation, without any surface preparation.

Such combined and multilevel characterization is possible at ICMATE-CNR, where a cutting-edge laboratory for the mechanical-tribological studies is operating. The coupling of nanoindentation and tribology leads to an in-depth knowledge of the mechanisms regulating the behaviour of materials in relative motion conditions between contact surfaces and operating in chemically aggressive environments.

A tracking shot of examples, taken from the recent scientific activities, illustrates the potential of this set of techniques, used in a synergistic way.

Al-Ti-N based protective coatings, for high temperature applications within the aeronautic sector, protect structural materials against hot oxidation. They were subjected to highly stressing thermal cycles up to 950°C, to investigate the formation of a protective oxide scale and underwent wear tests before and after heat treatments. Al-rich layers for nuclear applications were corrosion tested in stagnant Pb and later investigated tribologically [1]. Mo-N based films deposited onto commercial pistons for the automotive sector were tribologically studied in both dry and lubricated conditions up to 100°C [2]. Ta-N and Ta-Al-N based coatings for high temperature protection purposes, were analysed by means of both tribological tests and nanoindentation, to correlate functional properties with microstructure and chemical nature. V-N, Ti-B and multilayer Ti-B/V-N systems are currently studied as smart adaptive materials for anti-wear applications in mutable operating conditions and as hard protective coatings for cutting tools of non-ferrous alloys.

Finally TiO_2 coatings for dental implant application, were studied by tribocorrosion to evaluate the tribological and chemical behavior of material in artificial saliva [3].

Beside these case studies, also nanofluids for lubrication and ceramic membranes for H_2 separation were investigated tribologically and mechanically at the nanoscale.

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COMPUTATIONAL MODELING

POSTER COMMUNICATION

Computational Approaches To Prebiotic Chemistry

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Computational approaches are nowadays a full, self-standing branch of chemistry, both for their quantum-based ("*ab initio*") accuracy, and for its multi-scale extent. Nowadays it has become possible to simulate – *in silico* – a series of possible circumstances giving rise to the onset of prebiotically relevant molecules from very simple precursors. In particular, among the many possible reaction pathways underlying the onset of life on Earth, we report a couple of representative attempts to simulate the main mechanisms of the basis of the synthesis of amino acids and simple sugars. We thus report on the first *ab initio* computer simulations, based on quantum physics and a fully atomistic approach of Miller-like experiments in condensed phase showing that glycine spontaneously forms from mixtures of simple molecules once an electric field is switched on [1]. Then we present how intense electric fields are able to trigger the synthesis of (D)-erythrose – the direct ribose precursor – from ubiquitous molecules such as glycolaldehyde and water, without the assistance of any catalyst or template [2]. Finally, the multi-scale shock-compression technique (MSST), when combined with *ab initio* molecular dynamics, is able to simulate intense shock waves propagating through relatively small numerical samples. Based on this technique, we simulated the collision between interstellar dust grains composed of H_2 and HNCO [3], and demonstrated that a plethora of prebiotically significant species spontaneously arises.

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Shwachman-Diamond Syndrome, A Rare Disease But Common Problems To Deal With It: A Multi Approach Strategy

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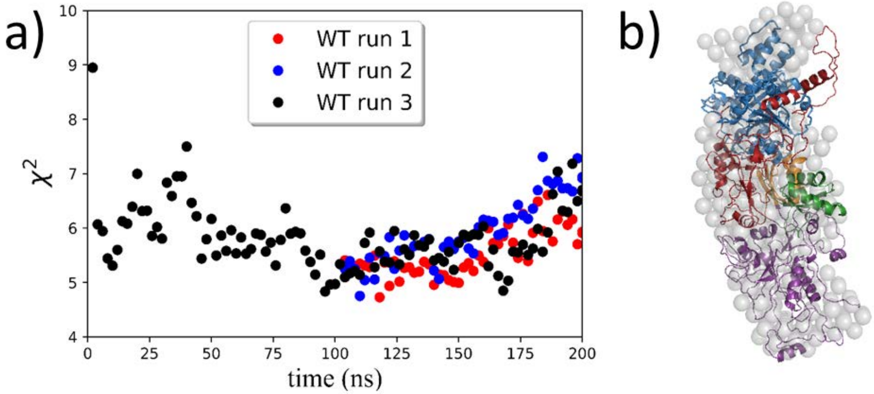
The Shwachman-Diamond Syndrome (SDS) is a disorder arising from mutations in the genes encoding for the Shwachman-Bodian-Diamond Syndrome (SBDS) protein [1] and the GTPase known as Elongation Factor Like-1 (EFL1) [2]. Together, these proteins remove the anti-associationfactor eIF6 from the surface of the pre-60S ribosomal subunit to promote the formation of mature ribosomes. SBDS missense mutations can either destabilize the protein fold or affect surface epitopes. The molecular alterations resulting from the latter remain largely unknown, although some evidence suggest that binding to EFL1 may be affected. We further explored the effect of these SBDS mutations on the interaction with EFL1 [3], and showed that all tested mutations disrupted the binding to EFL1. Binding was either severely weakened or almost abolished, depending on the assessed mutation. In higher eukaryotes, SBDS is essential for development, and lack of the protein results in early lethality. The existence of patients whose only source of SBDS consists of that with surface missense mutations highlights the importance of the interaction with EFL1 for their function. Additionally, we studied [3] the interaction mechanism of the proteins in solution and demonstrated that binding consists of two independent and cooperative events, with domains 2–3 of SBDS directing the initial interaction with EFL1, followed by docking of domain 1. In solution, both proteins exhibited large flexibility and consisted of an ensemble of conformations, as demonstrated by Small Angle X-ray Scattering (SAXS) experiments [3]. Molecular Dynamics simulations on human EFL1 (wilt type form and mutants) have be performed in the presence of explicit solvent in physiological ionic concentrations in order to shed light on the conformational effect of the loss-of-function EFL1 mutations. The obtained data were combined with further experimental test by SAXS in order to assess the robustness of the employed molecular model.



EFL1 protein a) Fitting MD frames (three different runs) with SAXS experimental data b) superposition of averaged MD model with SAXS low-resolution model.

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Ab initio Spectroscopy Of Water Under Electric Field

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Whereas a broad literature exists on the spectroscopy of water in disparate conditions, infrared (IR) and Raman spectra of water subjected to electric fields have never extensively been investigated so far. Based on *ab initio* molecular dynamics simulations, here we present IR and Raman spectra of bulk liquid water under the effect of static electric fields beneath the molecular dissociation threshold (i.e., up to 0.30 V A^{-1}) [1]. A contraction of the entire frequency range is recorded upon increasing the field intensity both in the IR and in the Raman spectra. Whilst the OH stretching band is progressively shifted toward lower frequencies - indicating a field-induced strengthening of the H-bond network - all the other bands are up-shifted by the field [2]. The order-maker action of the field emerges also from the increase of the water tetrahedral order. The kosmotropic effects carried by the field render the water structure more and more “ice like” as the field strength is increased.

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CHEMISTRY FOR CULTURAL HERITAGE

POSTER COMMUNICATION

The INTERFACE Project: Conservation Of Painted Metal Artefacts

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During the last decades conservation science became of upmost importance in the field of cultural heritage conservation. So far, many studies have been conducted on artworks made of single materials (e.g. painting, stone, metal), but a growing interest is rising about the characterisation and conservation of composite artefacts. The INTERFACE (paINTed mEtal aRteFActs ConsErvation) project, funded by the European Union's Horizon 2020 research and innova¬tion programme under the Marie Skłodowska-Curie Action, is focused on composite artworks made of linseed oil paints on copper and iron/low carbon steel plates. Indeed, the use of metals as 'canvas' has been poorly investigated, even though many masterpieces were created using this particular technique (Figure 1).

Guido Reni - The coronation of the Virgin, The National Gallery, London

Rembrandt – Selfportrait, National Museum, Stockholm

Peter Paul Rubens - The Judgement of Paris, Academy of Fine Arts, Vienna

Diego Velazqes- Portrait of the Count-Duke of Olivares, Royal Palace, Madrid

Important artists produced masterpieces using oil paint on metal that are now preserved in foremost European museums

The aim of the INTERFACE project is to fill this gap of scientific information by achieving two main objectives:

1. The characterisation of the degradation mechanisms, with particular attention to the processes occurring at the paint-metal interface (e.g. the formation of metal soaps due to the interaction between the fatty acids of the binder and the metal substrate);

2. The development of a conservation methodology that considers the differences between the two materials and formulates a product that will act both as consolidant for the painting and as corrosion inhibitor for the metal substrate.

The project is pursuing its objectives by studying artificial samples aged by cycles of T, RU and UV light as well as analysing real artefacts thanks to collaborations with Italian national museums.

This study presents preliminary results of the project.

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This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement N° 796291 (INTERFACE - paINTed mEtal aRteFActs ConsErvation)

Influence Of External Electric Fields On Raman Spectra Of Indigo: An *Ab initio* Study

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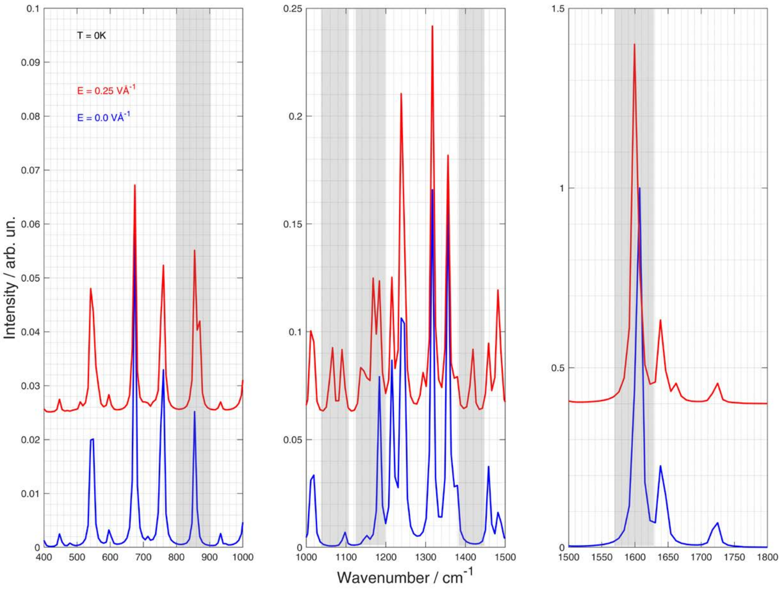
Indigo ($C_{16}H_{10}N_2O_2$) is one of the most common and antique natural pigment, characterized by an intense blue colour. It has been extensively studied by means of IR and Raman spectroscopy, in particular in dyed textile and artworks. Raman spectroscopy, specifically, is a widely used non-destructive technique for the detection and identification of pigments in the cultural heritage field. Nevertheless, organic dyes show an intense fluorescence which can hinder the Raman spectral features. From this point of view, surface enhanced Raman spectroscopy (SERS) can be adopted to overcome this issue. When adsorbed on a nanostructured metallic surface (e.g., Ag or Au), indeed, molecules show a strong enhancement of the Raman scattering cross section beside a drastic quenching of the fluorescence signal. The enhancement is attributed either to the electromagnetic (EM) or to the (chemical) charge transfer between adsorbates and metals. EM mechanism is due to the strong amplification of the local electromagnetic field near the nanostructured metal surface associated with the excitation of surface plasmonic resonances (SPR) of the nanostructure. Both mechanisms can lead to a modification of the spectral features of the Raman spectrum so that the SERS spectrum is rather different from the corresponding conventional one. In this work we investigate the influence of an external electric field (E) on the Raman spectrum of an indigo molecule by *ab initio* molecular dynamics simulations. As long as the intensity of the external electric field is increased up to 0.25 V Å^{-1} several changes in the Raman spectra are observed with respect to the zero-field case. Simulations were performed in the gas phase at T=300 K and at T=0 K. Observed spectral changes depend both on the field intensity and on the applied field direction with respect to indigo molecular axes. Concerning those simulations, it was observed that, at T=300 K, the indigo molecule has the tendency to re-orient its major axis along the E direction, while in the case at T=0 K, differences in the Raman spectra were observed when the E field was oriented along the major molecular axis.



Raman spectra computed at T=0 K, in the absence (blue line) and under (red line) electric field oriented along the major axis of the indigo molecule. Gray shaded areas highlight spectra differences.

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