VI WORKSHOP NAZIONALE AICIng

Molecules and materials: Chemistry for Engineering

Roma, 22 e 23 giugno 2015

Sala del Chiostro di San Pietro in Vincoli

AICIng

Associazione Italiana di Chimica per Ingegneria

ATTI DEL CONVEGNO

AICIng

Associazione Italiana di Chimica per Ingegneria

VI workshop nazionale AICIng

Molecules and Materials: Chemistry for Engineering

Roma, 22-23 giugno 2015

Chiostro di San Pietro in Vincoli

Programma e libro degli Abstract

EdiSES

COMITATO ORGANIZZATORE E SCIENTIFICO

Prof. Marta Feroci – Sapienza Università di Roma

Dott.ssa Isabella Chiarotto – Sapienza Università di Roma

Dott. Stefano Vecchio – Sapienza Università di Roma

Prof. Alessandra D'Epifanio – Università di Roma Tor Vergata

Dott.ssa Barbara Mecheri – Università di Roma Tor Vergata

Dott. Francesco Basoli – Università di Roma Tor Vergata

Prof. Giovanni Sotgiu – Università di Roma TRE

Prof. Monica Orsini – Università di Roma TRE

Dott. Luca Tortora – Università di Roma TRE

Dott. Alberto Rainer – Università Campus Bio-Medico di Roma

EdiSES

ISBN 9788879598774

I NOSTRI SPONSOR

Platinum Sponsor	Gold Sponsor	Silver Sponsor	Bronze Sponsor
GAMBETTI- Vacuum Technology and Related Solutions	EDISES Edizioni Scientifiche ed Universitarie	ASSING	LEICA MICROSYSTEM
	GILSON S.A.S.	METTLER TOLEDO S.p.A	MICRO LAB EQUIPMENT s.r.l.
	NIKON INSTRUMENTS EUROPE B.V.		ZEISS Italia

PLATINUM SPONSOR

GOLD SPONSOR

SILVER SPONSOR

BRONZE SPONSOR

PROGRAMMA SCIENTIFICO

Lunedì 22 giugno 2015

8:30-9:00	**Registrazione** presso Chiostro San Pietro in Vincoli, Facoltà di Ingegneria
9:00-9:30	**Benvenuto**: Prof. **Fabrizio Vestroni** *Preside della Facoltà di Ingegneria Civile e Industriale (Sapienza Università di Roma)* Prof. **Luigi Palumbo** *Direttore del Dipartimento di Scienze di Base e Applicate per l'Ingegneria, SBAI (Sapienza Università di Roma)* Prof.ssa **Silvia Licoccia** *Delegato del Rettore alla Ricerca Scientifica di Ateneo (Roma Tor Vergata)* Prof. **Eugenio Guglielmelli** *Prorettore alla Ricerca (Università Campus Bio-Medico di Roma)* Prof. **Paolo Atzeni** *Direttore del Dipartimento di Ingegneria (Università Roma Tre)*
9:30-10:15	**Conferenza Plenaria** Prof. **Francesco Paolucci:** *Nano Carbon-based Electrocatalytic Composites for the Artificial Leaf*
Sessione Biomateriali: *Chairperson* Alberto Rainer	
10.15-10.30	**Flavia Bollino**: *Sol-gel synthesis of SiO_2·CaO·P_2O_5 glasses: influence of the heat treatment on their bioactivity and biocompatibility*
10.30-10.45	**Marco Costantini**: *Microfluidic Foaming as an Effective Tool to Augment the Control over Scaffold Microarchitecture*
10.45-11.00	**Valerio Graziani**: *Doped, mechanically reinforced calcium phosphate cements for bone tissue engineering*
11.00-11.30	Coffee Break
Sessione Green Chemistry: *Chairperson* Isabella Chiarotto	
11.30-11.45	**Alberto Zeffiro**: *Sugar Production for bioethanol from alfalfa stems. Results, and comparative study with application of lignocellulolytic activities of novel fungal species.*
11.45-12.00	**Francesca Chiara Carrozza**: *Evaluation and development of biomass conversion processes for the chemical valorization of lignin*
12.00-12.15	**Anna Scarlino**: *Removal of 4-nitrophenol and arsenic(V) from tap water by combined heterogeneous photo-Fenton and coagulation processes*
12.15-12.30	**Emanuela Mastronardo***: Synthesis of Carbon Based Heat Storage Materials via Deposition-Precipitation Method*
12.30-12.45	**Bianca Gumina***: Hydrogenolysis and APR of biomass derived sorbitol and glycerol under mild reaction conditions promoted by Pd/Fe catalyst*

12.45-13.00	**Luciana Minieri:** *Hybrid ZrO_2-acetylacetonate gel-derived material as catalyst for pullutants removal*
13.00-14.30	Pranzo Libero
Sessione DSSC: *Chairperson* Francesco Basoli	
14.30-14.45	**Giuseppina Anna Corrente**: *Effect of different donor groups on dsscs performance.*
14.45-15.00	**Nicola Sangiorgi:** *Influence of anions on transparency of electro-polymerized polypyrrole counter electrode for Dye-Sensitized Solar Cells*
Sessione poster: *Chairperson* Barbara Mecheri	
15.00-16.30	**Presentazioni Flash su Poster**
16.30-17.00	Tea Break
17.00-18.00	**Sessione Poster**
20.00	Cena Sociale

Martedì 23 giugno 2015

Sessione Sintesi e Catalisi: *Chairperson* Giovanni Sotgiu	
9.00-9.15	**Marianna Fazio:** *Nanotubes mediated synthesis of zeolite SAPO-34*
9.15-9.30	**Marianna Bellardita:** *H_2 and value added chemicals from photocatalytic conversion of glucose*
9.30-9.45	**Alberto Olivo:** *A sustainable approach for visible light active titania photocatalysts for NOx abatement*
9.45-10.00	**Mario Luigi Naitana:** *Amphiphilic Corroles for Novel Supramolecular Sensing Material*
Sessione Materiali e Tecniche di Caratterizzazione: *Chairperson* Luca Tortora	
10.00-10.15	**Mario Maggio:** *Exfoliation and Intercalation of Graphite Oxide*
10.15-10.30	**Marco Urbini:** *Chemical analysis of hydroxides and carbonates species in perovskite films by ToF-SIMS and PCA*
10.30-10.45	**Silvia Della Marta:** *Development of nanostructured substrates for quantitative analysis with Surface-Enhanced Raman Spectroscopy (SERS)*
Sessione Elettrochimica e Superfici : *Chairperson* Alessandra D'Epifanio	
10.45-11.00	**Gabriele Tarquini:** *Synthesis and characterization of $LiNi_{0.5}Mn_{1.5}O_4$. High potential cathode material for Lithium ion batteries*
11.00-11.30	Coffee Break
11.30-11.45	**Emanuela Giudo***: Development of hybrid sol-gel based films for cellulose wearable sensors*
11.45-12.00	**Maurizio Fiorini:** *Trasformazioni chimiche e microstrutturali del fosfato di litio ferro in elettrodi per batterie trattati con laser pulsato*
12.00-12.15	**José Augusto Berrocal:** *Monodisperse block copolymer-type architectures for carbon nanotubes deposition on surfaces*
12.15-12.30	**Enrico Negro:** *Oxygen reduction reaction carbon-nitride based nano-electrocatalysts for proton-exchange membrane fuel cells*
12.30-13.00	**Premiazione e chiusura lavori**: Prof. Salvatore Failla (*Presidente AICIng*), Prof.ssa Marta Feroci
13.00-14.30	Pranzo Libero
15.00-17.00	**Visita guidata Basilica di San Pietro in Vincoli e Basilica di San Clemente**

SESSIONE POSTER

- P01 **Acocella**, Maria Rosaria — Dual Role of Graphite Oxide Nanofiller in Epoxy and Polyester resins
- P02 **Ambrogi**, Veronica — Release of Coumarin-6 from UV responsive polyamide nanocapsules
- P03 **Argentino**, Chiara — Nanomaterials and nanotechnologies for restoration of deteriorated parchment and leather
- P04 **Basoli**, Francesco — Infiltrated $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ based cells fed with biogas
- P05 **Biocca**, Paola — Characterization of triterpenes by ToF-SIMS and Chemometrics
- P06 **Blanco**, Ignazio — The influence of POSS molecular structure on the thermal properties of POSS/PS nanocompsites
- P07 **Bloise**, Ermelinda — Cardanol-based nanovesicles as potential "multifunctional-green" tools for tumor treatment
- P08 **Boaretto**, Aldrei — Nanomaterials for restoration of damaged plaster surfaces: case of studies
- P09 **Borrazzo**, Cristian — Sputtering of PolyMethylMethacrylate (PMMA) with bismuth cluster ions: Monte Carlo simulation study
- P10 **Branchi**, Mario — Composite membrane based on sulfonated poly ether ether ketone and functionalized oxides for direct methanol fuel cell
- P11 **Chiarotto**, Isabella — Stability and reactivity of electrogenerated 1-butyl-3-methylimidazol-2-ylidene in the presence of acids in DMF solution
- P12 **Concolato**, Sofia — Functionalization of Polycaprolactone Surfaces with Lactose-Modified Chitosan: a Secondary Ion Mass Spectrometry Study
- P13 **Dell'Era**, Alessandro — Structural, spectroscopic and thermal characterization of bioactive silicate gel-glasses
- P14 **Dispenza**, Clelia — Radiation synthesis of nanogels as therapeutic agent vectors
- P15 **Eddahaoui**, Khadija — Sol-gel auto combustion synthesis of spinel ferrites nano-particle $CoM_xFe_{2-x}O_4$ (M = Ni, Cu, Mn and Ca) and $SrM_xFe_{2-x}O_4$ (M= Ni, Cu): structural characterization and photocatalytic activity
- P16 **Espro**, Claudia — Solid acid catalysts for citrus wastes depolymerisation via direct hydrolysis

- P17 **Failla**, Salvatore — Synthesis, X Ray Structure and aggregation properties of a Zinc(II) salen Schiff-Base complex derived from cis-1,2-cycloexanediamine
- P18 **Falcinelli**, Stefano — Bioactive compounds on Lodoicea Maldivica fruits: Their determination by CG-MS
- P19 **Fiorini**, Maurizio — Preparazione e caratterizzazione di compounds a base di poli(lattide) con ritardanti di fiamma “halogen free”
- P20 **Fiorini**, Maurizio — Saldatura laser di film polimerici sottili per applicazioni nel packaging
- P21 **Giannitelli**, Sara M — A novel Pluronic/Alginate scaffold for 3D liver cell culture
- P22 **Gori**, Manuele — A novel model of nonalcoholic fatty liver disease in a 3D liver-on-chip device
- P23 **Iannaci**, Alessandro — Platinum free catalysts for microbial fuel cell application
- P24 **Iannazzo**, Daniela — Carbon nanostructured materials as drug delivery systems for antiviral agents
- P25 **Luciani**, Giuseppina — TiO2 mediated photocatalytic polymerization of DHICA: a new straightforward synthetic strategy to hybrid materials
- P26 **Marcì**, Giuseppe — Confronto tra attività catalitica e fotocatalitica dell’eteropoliacido di Keggin $H_3PW_{12}O_{40}$ supportato su ossidi o su nanotubi di carbonio
- P27 **Mattiello**, Leonardo — New Low Bandgap Oligothiophene Donors for Organic Photovoltaics
- P28 **Mozetic**, Pamela — Release of N-acylethanolamines by biomaterials of clinical relevance
- P29 **Narzi**, Daniele — Electron, proton and water transfer along the catalytic cycle of the Photosystem II
- P30 **Natali Sora**, Isabella — Photocatalytic degradation of micropollutants under visible light irradiation
- P31 **Piperopoulos**, Elpida — Synthesis of high surface area CNTs by CCVD
- P32 **Raggio**, Michele — Synthesis of chromophore modified graphene
- P33 **Ronchin**, Lucio — Nuovi materiali self-healing per l'edilizia
- P34 **Rosi**, Marzio — CO_2^{2+}, N_2O^{2+}, $C_2H_2^{2+}$ molecular dications formation and their Coulomb explosion with subsequent fragment ions escaping from planetary atmospheres

- P35 **Sabbatella**, Gianfranco — Probing exogenous-induced intracellular acidification: the effects of the incubation time
- P36 **Sabbatella**, Gianfranco — Synthesis of spiropyran for gold and silver nanoparticles functionalization
- P37 **Sarno**, Caterina — Ni-γ Al_2O_3 catalysts supported on cordierite monoliths for the dry reforming of methane
- P38 **Sileno**, Ilaria — Analogues of Neostigmine as Potential Acetilcholinesterase Inhibitors
- P39 **Sisti**, Laura — Utilizzo di idrotalciti organo-modificate per la preparazione di biocompositi
- P40 **Turco**, Rosa — Methylesters epoxidation catalyzed by novel niobium oxide based materials
- P41 **Vavasori**, Andrea — Synthesis of Light-Emitting Polymers via Heck coupling reactions
- P42 **Vecchiocattivi**, Franco — How the reactivity depends on the angular approach between reagents: stereo-dynamics of Penning ionization involving hydrogenated molecules
- P43 **Volpi**, Francesca — Engineered Graphene with enzymes for restoration of polychrome paintings on canvas or plaster surfaces
- P44 **Guidoni**, Leonardo — Molecular Simulations of Novel Materials for Energy Research

COMUNICAZIONI ORALI

NanoCarbon-based Electrocatalytic Composites for the Artificial Leaf

Giovanni Valenti, Alessandro Boni, Stefania Rapino, Massimo Marcaccio, Matteo Iurlo, and Francesco Paolucci

[1]*Department of Chemistry "G. Ciamician" University of Bologna, INSTM and IENI-CNR Associated Unit, Via Selmi 2, 40126 Bologna, Italy*

Email: Francesco.paolucci@unibo.it

Nature uses H_2O and CO_2, small and ubiquitous molecules, as pristine building blocks, for the construction of higher molecular complexity, enabling human survival during our daily life. Mastering of H_2O and CO_2 bond-re-organization to produce O_2 and carbohydrates is accomplished through very efficient and specialized photocatalytic pathways, evolved over thousands of millennia, together with the organization of multi-scale materials and functional architectures for solar power storage.

Although seemingly simple, the water splitting reaction ($2H_2O = 2H_2 + O_2$) is a slow, four-electron process with high energy barrier (1.23 eV). Although precious-metal are able to catalyze this reaction, the exchange-current densities, a measure of the kinetics of the electrochemical reaction, are very low, so that large amounts of the precious metal are required to achieve a high enough area for rates to be sufficient. Loss of metal surface area due to sintering is also a problem. Therefore, it is important to develop materials that exhibit low overpotentials and long-term stability, while making efficient use of scarce materials.

We recently demonstrated that the electrocatalytic properties of Pd or Pt nanoparticles and Ru nanoclusters can be dramatically enhanced when placed in a nano-architecture, prepared by self-assembly of multi-wall carbon nanotubes (MWCNTs) and either titanium dioxide, ceria or polyoxometalate shells. These nanostructured catalysts exhibit much higher turn-over frequencies and improved long-term stability compared to traditional catalysts due to efficient electron-hole separation and charge funneling that takes place at the interfaces between the component building blocks.

Sol-gel synthesis of SiO_2·CaO·P_2O_5 glasses: influence of the heat treatment on their bioactivity and biocompatibility

Flavia Bollino[1], Rosa Angela Renella[1], Ferdinando Papale[1], Michelina Catauro[1]

[1] Department of Industrial and Information Engineering, Second University of Naples, Via Roma 29
Email: flavia.bollino@unina2.it

Bioactive glasses based on SiO_2·CaO·P_2O_5 constitute a promising class of bioactive materials proposed for bone repair and substitution [1].
In the present work, SiO_2·CaO·P_2O_5 bioactive glasses have been synthesized via sol-gel and the influence of the Ca/P molar ratio and of the heat treatment on their biological properties has been investigated. Two gels with different Ca/P molar ratios (Ca/P = 3 and 6) have been prepared. The obtained gels have to heat-treated at 120°C, 600°C and 1000°C. The bioactivity of the glasses has been evaluated by soaking the samples in a simulated body fluid. FTIR spectroscopy and SEM microscopy allowed to detect the presence of an hydroxyapatite (HA) layer on the surface of the samples after 7, 14 and 21 days of exposure. In order to confirm the obtained results, after the samples had been removed from SBF after 7 days, the solution was analyzed by inductively coupled plasma atomic emission spectrometer (ICPE) for the estimation of the amount of Ca^{2+} and P released from the materials, respectively. Moreover, the biocompatibility of the obtained glasses has been assessed by means of WST-8 assay using the NIH 3T3 murine fibroblast cells. It has been shown that both Ca/P molar ratio and heat-treatment have a significant influence on the biological properties of the materials. The presence of Ca^{2+} induces the HA nucleation. The sample with the higher calcium content and heat-treated at 600°C, has been found to be the most bioactive and biocompatible. The heating at 120°C showed to be insufficient for the removal of the toxic synthesis residues. FTIR and ionic chromatography (IC) proved that NO_3^- ions are released from the materials, which induce cell death. The heating at 1000°C causes the formation of wollastonite and pseudowollastonite crystalline phases, which dissolve in SBF hampering ionic exchanges and, thus, HA nucleation. Moreover, the FTIR spectra proves that a carbonate HA is formed on the surfaces of the sample heated at 600°C and 1000°C. EDX analysis of the biomineral globules recorded a Ca/P molar ratio < 1.67, confirming that calcium deficient HA precipitate [2].

References

[1] A. Balamurugan, G. Balossier, S. Kannan, J. Michel, A.H.S. Rebelo, J.M.F. Ferreira, Acta Biomater. **2007**, 3, 255-62.
[2] J. Barralet, S. Best, W. Bonfield, J. Biomed. Mater. Res. **1998**, 41, 79-86.

Microfluidic Foaming as an Effective Tool to Augment the Control over Scaffold Microarchitecture

M. Costantini[1], C. Colosi[1], P. Mozetic[2], A. Tosato[1], A. Rainer[2], M. Trombetta[2], J. Jaroszewicz[3], W. Święszkowski[3], M. Dentini[1], A. Barbetta[1]

[1] Department of Chemistry, Sapienza University of Rome, 00185 Rome, Italy.
[2] Tissue Engineering Lab, Università Campus Bio-Medico di Roma, 00128 Rome, Italy
[3] Warsaw University of Technology, Faculty of Materials Science and Engineering, 02507 Warsaw, Poland

Email: marco.costantini@uniroma1.it

In the design of tissue engineering scaffolds, morphological parameters such as pore size, shape and interconnectivity, as well as transport properties should be tailored in order to meet the requirements posed by the culture of a specific cell type. In this work, we demonstrate that a regular and ordered scaffold morphology is a fundamental property, since it helps achieving both a higher and more homogeneous cell population within the scaffold.
Two different technological approaches were used, both of which are based upon the gas-in-liquid foam templating method. Following the first approach, foam was obtained by insufflating argon in a solution of alginate and a surfactant under stirring. In the second one, foam was generated inside a flow-focusing microfluidic chip under highly controlled and reproducible conditions.
As a result, in the former case the derived scaffold (GF) was characterized by polydispersed pores and interconnects, while in the latter (μFL) the porous structure was highly regular both with respect to the spatial arrangement of pores and interconnects and their monodispersity. Cell seeding under perfusion on the two scaffolds show that cell population inside μFL was quantitatively higher and more homogeneously distributed than GF. These results were validated by simulation of local flow velocity inside the scaffolds that show that μFL is more permeable than GF.

References

[1] Colosi, C.; Costantini, M.; Barbetta, A.; Pecci, R.; Bedini, R.; Dentini M. Morphological Comparison of PVA Scaffolds Obtained by Gas Foaming and Microfluidic Foaming Techniques. Langmuir 2013, 29, 82−91.

Doped, mechanically reinforced calcium phosphate cements for bone tissue engineering

Valerio Graziani[1,2], Marco Fosca[1], Marco Ortenzi[1], Vladimir S. Komlev[3], Ruggero Caminiti[4], Julietta V. Rau[1]

[1] Istituto di Struttura della Materia (ISM-CNR), Via del Fosso del Cavaliere 100, 00133 Rome, Italy
[2] Dipartimento di Scienze di Base e Applicate per l'Ingegneria, Università di Roma "La Sapienza", Via A. Scarpa 14-00161 Roma, Italy
[3] A.A. Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, Leninsky prospect 49, 119991 Moscow, Russia
[4] Dipartimento di Chimica, Universita di Roma "La Sapienza", Piazzale Aldo Moro, 5-00185 Rome, Italy

Email: valerio.graziani@ism.cnr.it

Calcium phosphate based cement (CPC) materials are currently among the most favoured synthetic bone tissue substitutes, used to repair and reconstruct small bone and teeth defects and non-load bearing fractures. Due to their chemical similarity to the mineral phase of natural tissue, they are suitable candidates for this purpose. However, bulk calcium phosphate materials are known to be brittle, and the proposed up to now new cement formulations lack for the required mechanical properties, which ideally should be similar to those of the host bone. Among the key mechanical properties, their compressive strength must be significantly improved.

A cement system usually is composed of one/several components powder and a hardening liquid. After mixing of these components, their interaction takes place, followed by the hardening process. Our previous investigations demonstrated that the CPC hardening mechanism is much more complex than expected, since an anomalous micro- and macroscopic behaviour of a CPC was registered by means of an Energy Dispersive X-Ray Diffraction (EDXRD) technique, supplemented by the standard compressive strength measurements [1-3]. The EDXRD method is most suitable for real-time monitoring of the CPC hardening process *in situ*, allowing to follow such processes as: amorphousinto-crystalline conversion (i.e. the primary and secondary crystallization); chemical reaction andphase transformations (new phases and intermediate products). Furthermore, a diffraction 3D map can be obtained: a sequence of diffraction patterns, collected as a function of the scattering parameter and of time.

Our goal was to develop CPCs for implant use in bone tissue engineering, being the purpose twofold: (1) to provide the antibacterial properties to a CPC based on ß-tricalcium phosphate by introducing Ag+ and Zn2+ ions, and (2) to enhance the mechanical characteristics of the cements. For this latter task, SWCNT and MWCNT additions are under investigation, since a very recent literature [4] reports the results indicating much increased compressive strength of CPC-MWCNT systems,

being able to promote the osteogenic differentiation of osteoblasts, and to serve as promising bone repairing graft material.
Furthermore, during the *in situ* time-resolved high-energy diffraction monitoring of the hardening process of a number of CPC based bone cement compositions it is expected to deepen the knowledge on their hardening mechanism. The obtained results will be used to develop the materials science paradigm «composition-structure-property», which in our case can be detailed as chemical and phase composition of the initial systems – macro/micro/nanostructure of material - functional properties to maintain and promote osteogenesis. The actuality of the project is based on the modern medical requirements in novel materials for traumatology and orthopaedics and on the necessity to decrease the rehabilitation time and to increase the life quality of post-operation patients. The expected results will contribute to the development of new biomedical technologies devoted to the replacement and reconstruction of the damaged human bone tissue.

References

[1] A. Generosi, J.V. Rau, V.S. Komlev, et al. *J. Phys. Chem. B,* 2010, *114(2),* 973-79.
[2] M. Fosca, V.S. Komlev, A.Yu Fedotov, R. Caminiti, J.V. Rau, *ACS Appl. Mater. Interf.,* 2012, *4(11),* 6202-10.
[3] J.V. Rau, M. Fosca, V.S. Komlev, et al. *ACS Cryst. Growth & Design,* 2010, *10,* 3824-34.
[4] G. Ahn et al. *Tissue Engineer. Regen. Med.,* 2011, *8(4),* 390.

Sugar Production for bioethanol from alfalfa stems. Results, and comparative study with application of lignocellulolytic activities of novel fungal species.

Alberto Zeffiro[1], Daniele Dondi[1], Roberto Paolo Marconi[1], Marco Malagodi[2], Carolina Girometta[3], Antonio Bentivoglio[1],Simone Lazzaroni[1], Elena Savino[3], Erick Nielsen[4], Armando Buttafava[1]

[1] Dipartimento di Chimica, UNIPV, Viale Taramelli 12, 27100 Pavia (IT)

[2] Laboratorio Arvedi di Diagnostica non Invasiva, UNIPV, Via Bell'Aspa 3, 26100 Cremona (IT)

[3] Dipartimento di Scienze della Terra e dell'Ambiente, Sezione Orto Botanico, UNIPV, Via S. Epifanio 14, 27100 Pavia (IT)

[4)] Dipartimento di Biologia e Biotecnologie, UNIPV, Via Ferrata 9, 27100 Pavia (IT)

Email: alberto.zeffiro@unipv.it

Bioethanol production from non-food lignocellulosic material is one of the most important topics in the field of biofuel production. We report on experiments with a treatment for the production of fermentable sugars from the fibrous parts of alfalfa (Medicago sativa L.), a widely used forage plant.

Fibers are mainly present in the stems, which can easily be separated from leaves by mechanical means [1]. In fact, leaves and stems differ in composition: on a dry weight basis, total alfalfa herbage contains 18–22% protein with the leaves containing 26–30% protein and stems only 10–12%. Our study regards a process divided into the following steps: fungi treatment, microwave hydrolysis and enzymatic hydrolysis with a mixture of cellulase and β–glucosidase leading to the final production of fermentable sugars. This process was followed by a detailed HPLC analysis for the detection of sugars, oligomers but also by-products (furfural, hydroxymethylfurfural and acids) that could affect fermentation. Scanning electron microscopy (SEM) was used for a visual characterization of the material throughout all these steps, and TGA to quantify cellulose and lignin content [2].

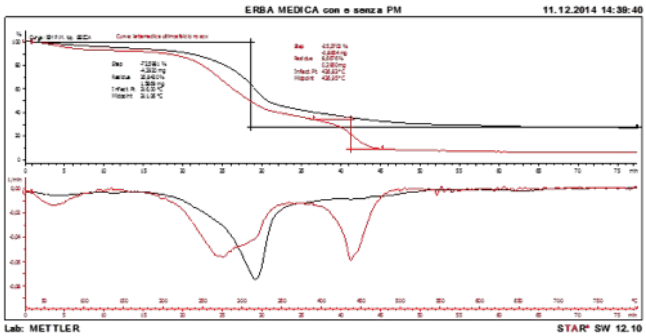


Figure 1. TGA on alfalfa with and without Perenniporia Meridionalis.

Fungi treatment improves the production of fermentable sugar yield obtained from hydrolysis. This could be related to the removal of lignin and thus a major exposure of cellulose fibers. In fact the degradation activity of these cultures on lignin was already documented on poplar wood[3].

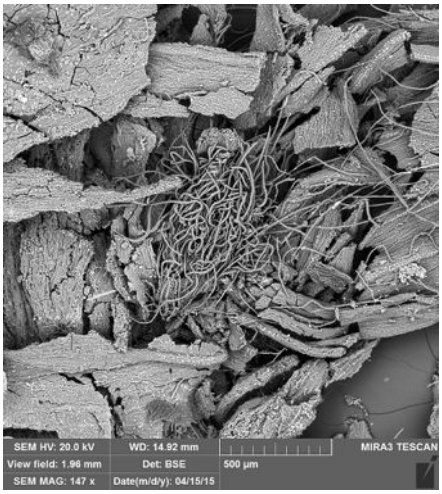


Figure 2. Lenzites Warnieri applied on alfalfa stems.

References

[1] Arinze EA, Schoenau GJ, Sokhansanj S, Adapa P; Aerodynamic separation and fractional drying of alfalfa leaves and stems - A review and new concept. **2003** Drying Technol 21: 1669–1698

[2] Structural modification of Alfalfa Stems During Hot Water and Enzymatic Hydrolysis for Sugar Production; D Dondi, A Zeffiro, P Nola, A Facchini, P Arcioni, M Malagodi, M Licchelli, E Nielsen, A Buttafava, Cellulose, **2015**, In press. Doi 10.1007/s10570-015-0580-8

[3] E Doria, E Altobelli, C Girometta, E Nielsen, T Zhang, E Savino; Evaluation of lignocellulolytic activities of ten fungal species able to degrade poplar wood; International Biodeterioration & Biodegradation **2014** 94 160-166

Evaluation and development of Biomass conversion processes for the chemical valorization of lignin

C.F. Carrozza[1], A. Citterio[1], R. Sebastiano[1]

[1] Department of Chemistry, Materials, and Chemical Engineering "G. Natta", Politenico di Milano, Via Luigi Mancinelli 7, 20133 Milano, Italy.

Email: chiarafrancesca.carrozza@polimi.it

Through the integration of green chemistry into biorefineries and the use of low environmental impact technologies, future sustainable production chains of biofuels and high value chemicals from biomass could quickly forecast. Despite the fact that a massive amount of lignin is obtained from the biorefineries, the use of lignin in real industrial processes is far to be obtained. While lignin is currently primarily used as a source of energy, approaches to develop lignin conversion into high-value co-products are progressively investigated. Using lignin for value added applications would allow us to make better use of biomass and make biorefining more economically attractive [1].

Conversion of lignin to low-molecular-weight aromatic/phenolic compounds offers a promising route for the high-value application of lignin. Development of selective and robust catalytic processes specifically designed for lignin conversion must be a core effort in a biorefinery program [2].

Thus a catalytic fragmentation-hydrogenolysis process for depolymerizing native lignin into aromatic products in alcoholic solvents has been studied in the attempt to preserve the side chain tri-carbon atoms. The dissolution capacity of different solvents towards lignin was studied and it was found that lignin can be solubilize in 1,2-propanendiol with a yield of about 80%. The product distribution was obtained by GC-MS analysis and it was found that native lignin can be fragmented a soluble lignin fragment and into smaller aromatic species which are under investigation for potential recovering. Furthermore catalytic oxidation processes for biorefinery lignin in batch reactor have also been investigated for the assessment of the potential of this polymer in the oxidative conversion to aromatic chemicals, including the three phenolic aldehydes vanillin, syringaldehyde, p-hydroxybenzaldehyde [3]. Through the variation of reaction parameters, results were obtained on the reactivity of the raw material and in particular on the production profiles of the compounds. The control of successive oxidations has emerged as one of the most critical aspects to deeply consider. Milder conditions of pressure and temperature (P = 3 bar, T = 130 °C) compared to those experienced initially (P = 10 bar, T = 150 °C) proved to be more adequate for the preservation of the products.

References

[1] Zakzeski, J., Bruijnincx, P. C., Jongerius, A. L., Weckhuysen, B. M., *Chem.Rev.* **2010**, *110*, 3552.
[2] Song, Q., wang, F., Cai, J., *Energy Environ. Sci.*, **2013**, 6. 994.
[3] Pinto, P. C. R., Costa, C. E., Rodrigues, A. E., *Ind. Eng. Chem. Res.* **2011**, 50, 741–748.

Removal of 4-nitrophenol and arsenic(V) from tap water by combined heterogeneous photo-Fenton and coagulation processes

Anna Scarlino[*1], Iolanda Pio[1], Giuseppe Mele[1], Domenico Santoro[2], Giuseppe Vasapollo[1]*

[1] Department of Engineering for Innovation, University of Salento, Via Arnesano, 73100 Lecce, Italy
[2] Department of Chemical and Biochemical Engineering, University of Western Ontario, London, ON N6A 5B9, Canada

anna.scarlino@unisalento.it

Photo-Fenton and coagulation processes are considered to be good cost-effective methods for water and wastewater treatment and the possibility to combine these two different technologies able to remove simultaneously Arsenic and organic contaminants has become of great interest.
Thus, the aim of this research is to investigate the possible combination of photo-Fenton heterogeneous process followed by coagulation/flocculation process to remove toxic contaminants from tap water. So, new porphyrin/Fe-Loaded TiO_2 composites prepared by us, were used as heterogeneous photo-Fenton catalysts for the degradation of 4-nitrophenol (4-NP) and aluminum polychloride was employed to remove As(V) from tap water.
4-NP and As(V), were chosen as probe reactions in laboratory batch experiments.
Fe-loaded TiO_2 powder, previously prepared and described in our previous work [1], was impregnated with functionalized metal-free porphyrin and Cu(II)-porphyrin by using a wet impregnation method similarly to what already reported in the literature [2]. These two new photocatalysts were characterized by XRD, EDX and SEM techniques.
A 300 W UV-visible lamp (SANOLUX HRC) with emission wavelength range from 300-900 nm and radiant flux of 340 W/m^2 was used. The experiments were performed in 500 mL glass vessel equipped with magnetic stirrer 300 mL of 4-NP ($[C_0]$ = 20 mgL^{-1}) tap water solution was spiked at different arsenic (V) concentrations of 25, 50, 100 µg/L. The solution recovered after photo-Fenton treatment was added with aluminum polychloride ($[C_0]$ =150 µL/L) for the subsequent coagulation/flocculation process. Experimental results showed that in the heterogeneous photo-Fenton treatment (by using 1%Fe-TiO_2 and CuPp-1%Fe-TiO_2) were efficient for the removal of 4-NP in presence of As at different initials As concentrations. In fact, 4-NP disappeared completely within 45 minutes of irradiation time in tap water.
Figure 1 reports the results obtained in the case of 4-NP photo-degradation test by using one of the most effective photo-catalyst (CuPp-1%Fe-TiO_2) employed in this work.

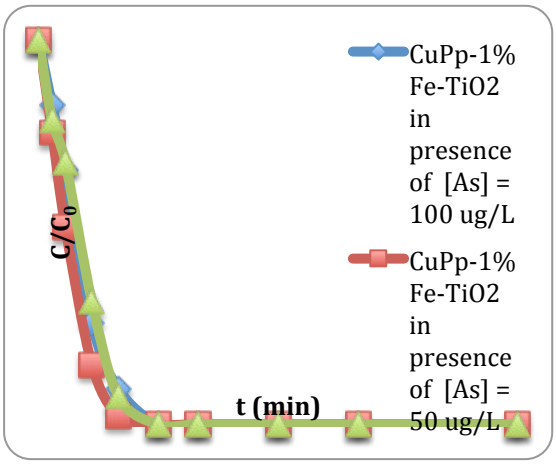


Fig.1 Degradation of 4-NP as a function of irradiation time in presence of different concentrations of arsenic (V) .

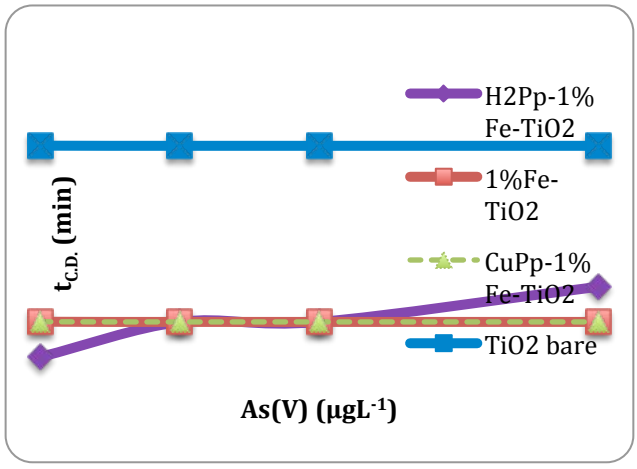


Fig.2 Complete degradation of 4-NP *vs* different initial concentrations of As(V).

Starting arsenic concentration (µg/L)	As(V) removal efficiency (%)	$[As(V)]_{R.C.}$
100	77	23 μgL^{-1}
50	87	6,5 μgL^{-1}
25	77	5,8 μgL^{-1}

Table1. As removal efficiency at different initial arsenic concentrations 100 μgL^{-1}- 25 μgL^{-1}.

Figure 2 shows that the presence of arsenic(V) doesn't influence the photocatalytic activities in both case of bare TiO_2 and porphyrin/Fe-loaded TiO_2 composites, with the exception of the case in which it is used for H_2Pp-1%Fe-TiO_2. Moreover, we have noted that when photo-catalysts are superficially modified these resulted more efficient than the bare TiO_2.

Table 1 shows the removal of As(V) at different initial concentration (100 µg/L to 25 µg/L) in the coagulation process. Interestingly, starting from the initial concentration of arsenic (V) of 25 and 50 µg/L the residual concentration of As doesn't exceed the required WHO limits in drinking water [3].

References

[1] B. Zhao, G. Mele, I. Pio, J. Li, L. Palmisano, and G. Vasapollo, *Journal of Hazardous Materials*, **2010**, *1*, 569-574.

[2] G. Mele, R. Del Sole, G. Vasapollo, E. Garcia-Lopez, L. Palmisano, M. Schiavello, *Journal of Catalysis*, **2003**, 217, 334.

[3] Guidelines for drinking-water quality, fourth edition, World Health Organization **2011.**

Synthesis of Carbon Based Heat Storage Materials via Deposition-Precipitation Method

Emanuela Mastronardo[1], Lucio Bonaccorsi[1], Yukitaka Kato[2], Elpida Piperopoulos[1], Candida Milone[1]

[1] *Department of Electronic Engineering, Chemistry and Industrial Engineering, University of Messina, Messina, 98166, Italy*

[2] *Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, Tokyo, 152-8550, Japan*

Email: emastronardo@unime.it

The $MgO/H_2O/Mg(OH)_2$ Chemical Heat Pump (CHP) [1] is a promising technology for the recovery of industrial low-grade waste heat. Novel heat storage materials made of magnesium hydroxide ($Mg(OH)_2$) and a carbonaceous support (EG - exfoliated graphite or CNTs - carbon nanotubes) were synthesized via a Deposition-Precipitation method to improve the heat transfer properties of the storage medium (Fig. 1). The compatibility between the two phases is improved by the electrostatic interaction promoted by the different point of zero charge of the materials in solution. The heat storage and output capacities of the obtained hybrid materials were evaluated by thermogravimetric analysis which simulates the CHP cycle and compared with that of pure $Mg(OH)_2$.

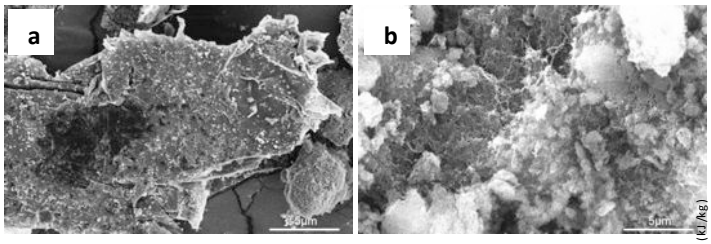


Figure 1. SEM images of (a) EG-$Mg(OH)_2$ and (b) CNTs-$Mg(OH)_2$

The developed hybrid materials showed higher storage capacity and higher heat output rate with respect to pure $Mg(OH)_2$ (Fig. 2). The CNTs based hybrid sample (CNTs-$Mg(OH)_2$) exhibited the highest stored heat values and heat output rate: it can respond immediately in case of energy demand releasing most part of stored heat in ~10 minutes.

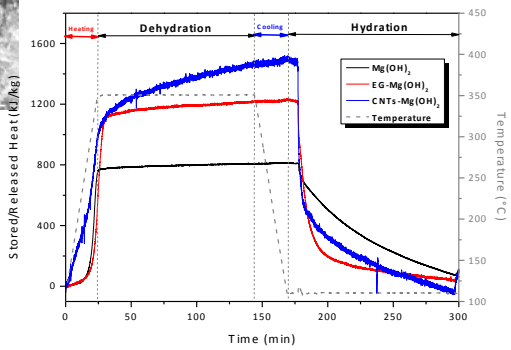


Figure 2. CHP cyclic experiment.

References

[1] Y. Kato, F. Takahashi, A. Watanabe, Y. Yoshizawa, *Appl. Therm. Eng.*,**2001**, 21, 1067-1081.

Hydrogenolysis and APR of biomass derived sorbitol and glycerol under mild reaction conditions promoted by Pd/Fe catalyst

Bianca Gumina[1], Alessandro Vinci[2], Claudia Espro[1], Francesco Mauriello[2], Signorino Galvagno[1] and Rosario Pietropaolo[2]

[1] Department of Electronic Engineering, Chemistry and Industrial Engineering, University of Messina, Contrada di Dio – 98166 Messina, Italy
[2] Department of Civil, Energy, Environmental and Materials Engineering, Mediterranea University of Reggio Calabria, Feo di Vito – 89122 Reggio Calabria, Italy

Email: bianca.gumina@unime.it

Sorbitol and glycerol are in the "Top 10" of most relevant building blocks derived from biomass [1]. Among several catalytic processes for upgrading biomass derived compounds, hydrogenolysis and aqueous phase reforming (APR) are two fundamental approaches because of their great potential linking current technologies up to bio-refineries [2].
In particular sorbitol and glycerol hydrogenolysis involves the production of 1,2-propanediol (1,2-PDO), 1-propanol (1-PO) and ethylene glycol (EG), fundamental intermediates for chemical production [3]. Furthermore aqueous phase reforming is a well known process that allows to produce hydrogen and alkanes [4].
The catalytic testing of these two processes were performed in a batch reactor under mild conditions, using water as solvent and a coprecipitated palladium on iron oxide (Pd/Fe) catalyst. The coprecipitation ensures a strong interaction between palladium and iron, leading to formation of bimetallic ensambles which allows to obtain superior performances in both hydrogenolysis and APR [2].
The main aims of our work are:

- to test the distribution of products obtainable with the coprecipitated Pd/Fe catalyst in hydrogenolysis reaction;
- to explore the production of alkanes and H_2 under APR conditions;
- to present a comparative study on the hydrogenolysis and APR of C_3-C_6 polyols.

References

[1] (1a) M. Besson, P. Gallezot, C. Pinel, *Chem Rev.*,**2014**, *114*, 1827-1870; (1b) J.J.Bozell, G.R. Petersen, *Green Chem.*, **2010**, *12*, 539-554.
[2] F. Mauriello, H. Ariga, M.G. Musolino,R. Pietropaolo,S. Takakusagi,K. Asakura, *Appl. Catal. B*,**2015**, *166-167*, 121-131.
[3] A.M. Ruppert, K. Weinberg, R. Palkovits, *Angew. Chem. Int. Ed.*,**2012**, *51*, 2564-2601.
[4] R.D. Cortright, R.R. Davda, J.A. Dumesic, *Nature*,**2002**, *418*, 964-967.

Hybrid ZrO_2-acetylacetonate gel-derived material as catalyst for pullutants removal

Luciana Minieri[1], F. Sannino[2], P. Pernice[1], D. Pirozzi[1], C. Imparato[1], G. D'Errico[3], G. Vitiello[1], A. Aronne[1]

[1] Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università di Napoli Federico II, Piazzale Tecchio, 80 - 80125 Napoli
[2] Dipartimento di Agraria e CERMANU, Università di Napoli Federico II, Via Università 100 – 8055 Portici, Napoli
[3] Dipartimento di Scienze Chimiche, Complesso Universitario Monte Sant'Angelo, Via Cintia, I - 80126 Napoli

Email: luciana.minieri2@unina.it

Among the technologies that involve the use of inorganic catalysts to the removal of pollutants, advanced oxidation processes have been widely used for the wastewaters treatment over the last few decades. Recently, a particular attention has been focused on the combined use of oxidants and photocatalysts. In particular, ZrO_2 is one of the most considered semiconducting oxide used for environmental applications to decompose pollutants under UV-irradiation. Nevertheless, ZrO_2 presents a large band gap (5.0 eV), which limits the possibility to capture the sunlight that contains prevalently visible and near-infrared radiation. This represents a strong limitation to wide applications. To overcome these drawbacks, different approaches have been explored in order to reduce the optical band gap between conduction band and valence band of the semiconducting ZrO_2 oxide. The conjugation of an organic ligand to the inorganic matrix is one of the most promising approach to reduce the band gap, improving the catalyst activity. In this study, hybrid gel-derived ZrO_2-based materials have been synthesized using the acetylacetonate as organic ligand. These catalysts have shown a very high remediation activity toward four different phenoxy herbicides from aqueous solution. Experimental results have shown that ZrO_2–acetylacetonate hybrid material behaved like a heterogeneous catalyst, acting as radicals initiator without any light irradiation at 30°C. Free radicals were formed by an intramolecular acac-to-metal electron transfer mechanism giving on the solid surface the equilibrium between Zr(IV)-acac and Zr(III)-acac• complexes, from which reactive oxygen species are produced in the presence of molecular O_2. Therefore, this material allows extending the frontiers of ZrO_2 application to pollutants degradation as its functionality does not require any activation procedure neither thermal nor light.

References

[1] F. Sannino, P. Pernice, L. Minieri, G. A. Camandona, A. Aronne, D. Pirozzi, *ACS Appl. Mater. Interfaces,* **2015,** *7*, 256–263.

Effect of different donor groups on DSSCs performance

Giuseppina Anna Corrente[1,4], Agostina Lina Capodilupo[2], Luisa De Marco[1], Giuseppe Gigli[1,2,3] and Giuseppe Ciccarella [2,4]

[1] Center for Biomolecular Nanotechnologies (CBN) Fondazione Istituto Italiano di Tecnologia (IIT), Via Barsanti 1, Arnesano, 73010, Italy
[2] Istituto di Nanotecnologia CNR-Nanotec, via Arnesano 16, 73100 Lecce, Italy
[3] Dipartimento di Matematica e Fisica "Ennio De Giorgi", Università del Salento, Via Monteroni, 73100, Lecce, Italy
[4] Dipartimento di Ingegneria dell'Innovazione, Università del Salento, Via Monteroni, 73100, Lecce, Italy

Email: giuseppinaanna.corrente@studenti.unisalento.it

Dye-sensitized solar cells (DSSCs) have attracted considerable attention in scientific research and practical applications. These devices show high conversion of sunlight to electricity and low-cost production. The organic sensitizing plays a significant role in DSSCs, because its light-harvesting ability determines the upper limit of the conversion efficiency. The dye produces the primary steps of photon absorption and subsequent electron transfer process. Organic sensitizers for DSSCs are mainly classified as metal-containing and metal-free dyes. Compared to the first class, metal-free sensitizers have advantages such as low cost and structural design flexibility. By a careful molecular design, photovoltaic performance of DSSCs can be widely improved. [1-3] We have designed and synthesized three novel organic dyes containing a 2D-π-A system (Fig. 1): two arylamines as the donor moieties, a dibenzofulvene linked with two thiophene rings as the p-bridge and the cyanoacrylic group as the acceptor unit. Two alkoxy chains of different length have been introduced in *p*-position of the aryl rings of donor units in order to modulate the properties of the organic dye and then the performance of the solar cells.

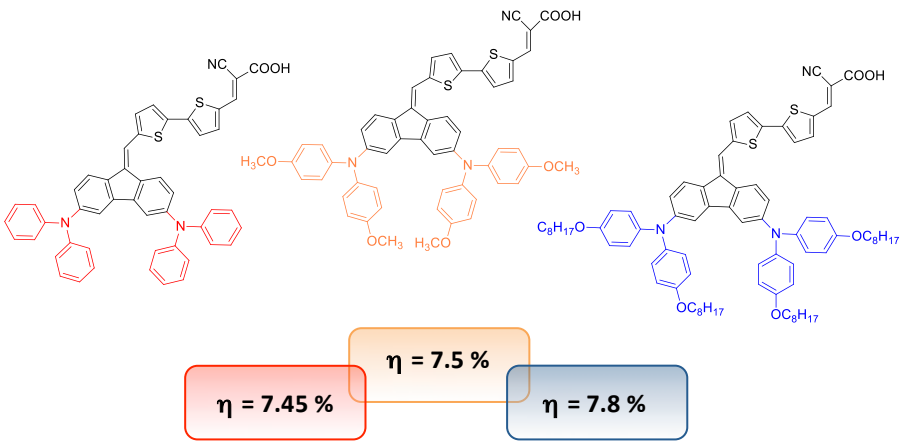


Fig.1: Dye's structures and photovoltaic performances

References

[1] A-L. Capodilupo, L. De Marco, E. Fabiano, R. Giannuzzi, A. Scrascia, Cl. Clarlucci, G. A. Corrente, M. P. Cipolla, G. Gigli and G. Ciccarella, *J. Mater. Chem. A,* **2014***, 2,* 14181-88.

[2] A. Scrascia, L. De Marco, S. Laricchia, R. A. Picca, C. Carlucci, E. Fabiano, A. L. Capodilupo, F. Della Sala, G. Gigli and G. Ciccarella*, J. Mater. Chem. A*, **2013**, *1*, 11909.

[3] A. Scrascia, M. Pastore, L. Yin, R. A. Picca, M. Manca, Y.-C. Guo, F. De Angelis, F. Della Sala, R. Cingolani, G. Gigli and G. Ciccarella, *Current Organic Chemistry*, **2011**, *19*, 3535.

Influence of anions on transparency of electro-polymerized polypyrrole counter electrode for Dye-Sensitized Solar Cells

Nicola Sangiorgi[1,2], Riccardo Bendoni[1,2], Alex Sangiorgi[1,3], Alessandra Sanson[1]

[1] CNR-ISTEC, Via Granarolo 64, 48018 Faenza, Italy, phone +390546699743
[2] Department of Chemical Science and Technology, University of Rome "Tor Vergata", via della Ricerca Scientifica 1, 00133 Rome, Italy
[3] University of Parma: Department of Chemistry, Parco Area delle Scienze 23/A, 43124 Parma, Italy

Email: nicola.sangiorgi@istec.cnr.it

The aim of the present work was the preparation and characterization of a counter-electrode based on one of the most appealing alternative to Platinum, polypyrrole (PPy). Moreover, the influence of each doping anions on the transmittance and electrochemical properties of the PPy film was studied. The counter-electrode was prepared by electrochemical polymerization considering different anions: Potassium Chloride (Cl^-), Lithium Perchlorate (ClO_4^-), Sulfuric Acid (SO_4^{2-}) and Sodium-dodecylbenzensulfonate (DBS^-). The electro polymerization was carried out in a three electrochemical cell with the FTO substrate as the working electrode. The polymerization was performed at 1 V vs SCE in an aqueous solution containing different concentration of doping anions (0,2 M low concentration and 0,5 M high concentration). The morphology of the PPy films was analyzed by FE-SEM whereas the transmittance was determined by a spectrophotometer. The electro-catalytic activity on iodide/triiodide redox couple was studied by cyclic and linear voltammetry. Finally, the counter-electrode based on PPy film doped with different anions were tested in a real DSCs system, and J-V curves and Incident Photon-to-electrical-Conversion Efficiency (IPCE) analyses were done. The PPy film doped with Cl^- anion and obtained with high dopant concentration possess the highest transmittance while the PPy doped with BDS^- shows the highest catalytic activity. These trends can be explained by the microstructure (small particles) and porosity of the polymer surface. When the light reachs the dye cell from counter-electrode side, the final efficiency was influenced also by the counter-electrode/electrolyte interface. These results explain the influence of doping anions on the transparency and electrochemical properties of the PPy film and confirming the good potentialities of the developed material and process in the specific DSCs application that required a transparent counter electrode.

Nanotubes mediated synthesis of zeolite SAPO-34

Marianna Fazio, S. Abdul Rahim, Lucio Bonaccorsi, Signorino Galvagno, Candida Milone

Dipartimento di Ingegneria Elettronica, Chimica e Ingegneria Industriale, Università di Messina, Contrada di Dio 98166 Messina, Italia

Email: faziom@unime.it

In the last years, the interest of many researchers focused on the reduction of the zeolite crystals size and on its emerging applications both in catalysis than in separation processes [1, 2].
In this frame, the purpose of this study is the optimization of the synthesis method previously proposed, in order to obtain crystals of SAPO-34 of smaller and homogeneous size.
Recently, it has been successfully presented a new method of synthesis of zeolites, using carbon nanotubes as nanoreactors.
Due to the particular configuration assumed by the templating agent upon interaction with the CNTs, the available space where the formation reaction of zeolites can take place is very small. Therefore, the nucleation of the SAPO-34 crystals, rather than growth, has been favored by supersaturation of the precursors that occurs within the bungles of nanotubes, also leading to the formation of particles smaller than 1 μm (Figure 1).

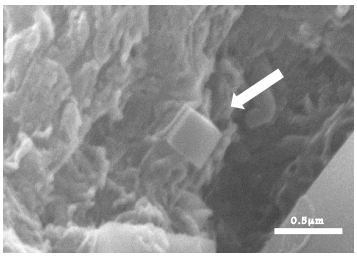


Figure 1. SEM image of the synthesized sample.

The size distribution obtained is still very wide. In order to further inhibit the growth of the crystallites, the hydrothermal synthesis will be performed for a shorter time and in some cases even with the assistance of the microwaves.

References

[1] .H. Van Heyden, S. Mintova, T. Bein, Chem. Mater. 2008, 20, 2956-2963
[2] M. Dargahi, H. Kazemian, M. Soltanieh, S. Rohani, M. Hosseinpour, Particuology 9 (2011) 452-457.

H_2 and value added chemicals from photocatalytic conversion of glucose

Bellardita Marianna, Elisa García-López, Giuseppe Marcì, Leonardo Palmisano

"Schiavello-Grillone" Photocatalysis Group, Dipartimento di Energia, Ingegneria dell'informazione, e modelli Matematici (DEIM), Università degli Studi di Palermo, Viale delle Scienze Ed. 6, 90128, Palermo. Italy.

Email: marianna.bellardita@unipa.it

Glucose, as biomass model, is an attractive renewable source for H_2 and valuable chemicals production. Conventional technologies used for this purpose as steam reforming, biochemical processes, thermal catalysis, pyrolysis, require severe reaction conditions and/or the use of expensive and toxic oxidants. In this context, heterogeneous photocatalysis can be also considered as an effective alternative because it can be carried out under mild experimental conditions and by using green solvents.

Commercial (P25), home prepared (HPR) TiO_2 and Pt-TiO_2 samples have been used for aerobic (in the presence of air) and anaerobic (bubbling N_2) aqueous glucose conversion. The runs were carried out at room temperature and ambient pressure in a 800 mL Pyrex reactor irradiated in the UV region with an immersed 125 W medium pressure Hg lamp. The initial aqueous glucose concentration was 1 mM and the runs were carried out at natural pH.

The distribution of the products strictly depended on the type of photocalyst both in the presence and absence of air but Pt resulted essential for the production of H_2 as hydrogen was not detected by using naked TiO_2 photocatalysts. The main products were arabinose and formic acid. Erythrose was also found in the presence of HPR and HPR-Pt0.5.

References

[1] R.Chong, J. Li, Y. Ma, B. Zhang, H. Han, C. Li, *J. Catal.*, **2014**, *314*, 101-108.

A sustainable approach for visible light active titania photocatalysts for NO_x abatement

Alberto Olivo[1], Michela Signoretto[1], Valentina Trevisan[1], Elena Ghedini[1], Giuseppe Cruciani[2]

[1] Dept. of Molecular Sciences and Nanosystems, Ca' Foscari University Venice and Consortium INSTM, RU of Venice, Dorsoduro 2137, 30123 Venice, Italy
[2] Dept. of Physics and Earth Sciences, Ferrara University, via G. Saragat 1, 44121 Ferrara, Italy

Email: alberto.olivo@unive.it

Recently, many efforts have been addressed to reduce environmental pollution from undesirable compounds, such as NO_x, that are harmful to men and environment, by means of photocatalytic processes. Among common photocatalysts, titanium dioxide (TiO_2) is a viable option but the relatively wide band-gap (3.2 eV) restricts the potential applications because this parameter restricts titania's effectiveness in NO_x abatement using solar light. Non-metal doping has been extensively studied to increase titania photoactivity under visible light irradiation[1]. Nitrogen and carbon are the most commonly used non metal dopants: their traditional sources are inorganic and organic molecules[2,3] that usually cannot be considered environmentally sustainable. Considering this critical issue, attention has been shifted to natural compounds containing carbon and nitrogen as well. Chitosan, a natural polyglucosamine, is an appealing alternative to traditional dopants for its availability, sustainability and eco-friendliness.

The goal of this work to synthesise an innovative C-N co-doped titania photocatalyst using chitosan as carbon and nitrogen source for NO_x abatement in gas phase under visible light at atmospheric pressure and room temperature. All the samples have been tested in NO oxidation in gas phase under visible light. These C-N co-doped titania photocatalysts has proven to be as effective as the best commercial sample in NO oxidation under visible light even at low irradiances, proving their high photoactivity in non-optimal conditions.

This is a very promising result that meets well to the requirement of this research: finding an innovative synthesis for C-N co-doped titania photocatalysts. This green and inexpensive synthesis has been optimized to obtain a stable and efficient photocatalytic system with the co-presence of both the dopants.

References

[1] M. Signoretto, E. Ghedini, V. Trevisan, C.L. Bianchi, M. Ongaro, G. Cruciani, *Appl. Catal. B: Environm*,**2010**, 95, 130-136.
[2] V. Trevisan, M. Signoretto, F. Pinna, G. Cruciani, G. Cerrato, *Chem. Today*,**2012**, 30, 25-28.
[3] V. Trevisan, A. Olivo, F. Pinna, M. Signoretto, F. Vindigni, G. Cerrato, C.L. Bianchi, *Appl. Catal. B: Environm*,**2014**, 319, 61-70.

Amphiphilic Corroles for Novel Supramolecular Sensing Material

Mario Luigi Naitana, Sara Nardis, Roberto Paolesse

Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, 00133 Roma, Italy
Email: naitana@scienze.uniroma2.it

The quality of a good sensor has to face the 3 "S" challenge: sensitivity, selectivity, and stability. Up to now, the research has worked to better solve these problems on different edges such as releasing novel sensing material, controlling the sensor structures, improving data analytical method, measurement and fabrication techniques.
In the last decade, the development of nano-science and technology has allowed, as reported in literature, an increasing in the number of suitable nanostructured materials including tubes, rods, belts and wires. All these nanostructures represent potential and powerful platforms for a broad range of sensors[1]. In particular, supramolecular nanomaterials with well-defined shapes and dimensions, based on an organized self-assembling/aggregation of macrocyclic chromophores, have attracted a large interest for their potential applications in photodynamic therapy, nonlinear optics, and as artificial light harvesting systems that mimic natural photosynthetic receptors (DSSC). In particular, porphyrinoids represent a highly attractive molecular class due to their unique optical and electronic properties and their chemical versatility, able to offer the possibility to drive the self-assembled molecular aggregation to ordered geometrical structures[2].
Porphyrinoids aggregation, established by non-covalent interactions, changes remarkably the optical and electronic properties of the molecular aggregates with the respect to those shows by single subunits.
5,10,15,20-Tetrakis(4-sulfonatophenyl)porphyrin (TSPP) is, perhaps, one of the most studied synthetic porphyrins due to its peculiar ability to self-assemble forming extended J-aggregates which exhibit interesting nonlinear and optoelectronic properties mainly related to their peculiar structures[3], that can be tunable depending on the aggregation protocol.
In this work we turn on the spotlight on a novel sulfonated tetrapyrrolic macrocycle able to express a peculiar supramolecular behaviour with the potential to fulfil the request for an optimal "3S" sensing material.

References

[1] X-J. Huang, Y-K. Choi, *Sens. Actuators B,* **2006**, *122,* 659-71.
[2] F. Dini, E. Martinelli, G. Pomarico, R. Paolesse, D. Monti, D. Filippini, A. D'Amico, I. Lundstrom, C. Di Natale, *Nanotechnology,* **2008**, *20, 1-8.*
[3] M.A. Castriciano, A. Carbone, A. Saccà, M.G. Donato, N. Micali, A Romeo, G. De Luca, L.M. Scolaro, *J. Mat. Chem., 20, 2882-86.*

Exfoliation and Intercalation of Graphite Oxide

Mario Maggio, Maria Rosaria Acocella, Marco Mauro, Gaetano Guerra

Department of Chemistry and Biology and INSTM Research Unit, Università di Salerno, 84084 Fisciano (SA)

E-mail: mariomaggiochem@gmail.com

The first part of the contribution will describe the ability of graphite oxide (GO) aqueous suspensions to form robust and resilient GO paper is largely improved by basification of the suspension prior of processing. In particular, casting procedures, which are generally unsuitable for production of GO paper[1], become suitable for the case of basified GO (b-GO) suspensions, leading to flexible free-standing papers. Thermal treatments of b-GO paper easily produce graphene oxide paper, i.e. paper with exfoliated GO (eGO), while thermal treatments of GO paper lead to mixed GO, eGO and graphite components. Differently from usual GO and eGO papers, papers from b-GO suspensions exhibit remarkable resistance to solvents as well as to acids and bases, even in aqueous solutions.

The second part of the contribution will be devoted to highly ordered graphite oxide intercalation compounds (GOIC)[2] and fully disordered graphite oxide exfoliated compounds (GOEC) have been obtained, for quaternary phosphonium salts. X-ray diffraction patterns of both GOIC and GOEC maintain the 100 and 110 reflections of GO, clearly indicating the maintenance of in plane GO order. For GOICs, few 00l reflections (with l up to 3) appear, indicating an increase with respect to GO of crystalline order as well as an increase of spacing between GO layers from 0.84 nm up to 1.40 nm. GOIC and GOEC have been compared for their kinetics of release in aqueous solutions of a phosphonium ion, being a known antibacterial agent. GOICs exhibit pH sensitive cation release, with zero order kinetics, which could be helpful for applications requiring triggered and constant supply of active ions.[3]

References

[1] Ruoff *et al*. *Nature* **2007**, Vol 448.
[2] Mauro, M.; Maggio, M.; Cipolletti, V.; Galimberti, M.; Longo, P.; Guerra, G. *Carbon* **2013**, *61*, 395.
[3] Mauro, M.; Maggio, M.; Antonelli, A.; Acocella, M.R.; Guerra, G.*Chem. Mater* **2015**, *27*, 1590.

Chemical analysis of hydroxides and carbonates species in perovskite films by ToF-SIMS and PCA

Marco Urbini[1,2], Jean-Marc Tulliani[3], Marta Maria Natile[4], Pierre Bonville[5], Isabella Natali Sora[6] and Luca Tortora[1]

[1] Department of Mathematics and Physics & INFN, Surface Analysis Laboratory, University of Rome "Roma Tre", via della Vasca Navale 84, 00146 Rome, Italy
[2] Department of Industrial Engineering, University of Rome "Tor Vergata", via del Politecnico 1, 00133 Rome, Italy
[3] INSTM R.U. PoliTO, Politecnico di Torino, Dipartimento di Scienza Applicata e Tecnologia, Corso Duca degli Abruzzi 24, 10129 Torino, Italy
[4] CNR-IENI, INSTM and Dipartimento di Scienze Chimiche, Università di Padova, via F. Marzolo 1,35131 Padova, Italy
[5] Commissariat à l'Energie Atomique, Centre d'Etudes de Saclay, 91191 Gif-sur-Yvette, France
[6] INSTM R.U. and Università di Bergamo, Dipartimento di Ingegneria, Viale Marconi 5, 24044 Dalmine (BG), Italy

Corresponding Author: luca.tortora@uniroma3.it

Monitoring and controlling environmental humidity are receiving ever wider attention, mainly for domestic comfort and various industrial processes. Recently, lanthanum strontium copper orthoferrites (LSFC) have been proposed as sensing components in chemical sensors for humidity detection. The presence of copper inside the orthoferrite structure increases the performance of the sensor. Indeed, compared to orthoferrite without Cu-addition, the presence of copper has allowed to obtain a low relative humidity (RH) values detection (15% RH) instead of 65-70% RH. Although the LSFC-based humidity sensors showed several promising properties and a good reproducibility between several measurements, they suffered a loss of sensitivity when ageing. However, the sensing activity of the perovskite film may be re-activated after a thermal treatment at 900 °C for 2 h[1].

The sensing films studied here have been obtained from nanosized powders of lanthanum strontium copper orthoferrites $La_{0.80}Sr_{0.20}Fe_{0.95}Cu_{0.05}O_{3-w}$ (LSFC05) and $La_{0.80}Sr_{0.20}Fe_{0.90}Cu_{0.10}O_{3-w}$ (LSFC10), prepared by citrate auto-combustion of dry gel obtained from a solution of the corresponding nitrates in citric acid solution.

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a well established technique for surface chemical analysis, giving three different kind of chemical information: mass spectra, chemical map and depth-profiling. The use of ToF-SIMS in *dynamic mode* allows to obtain high mass resolution (until 10000 M/ΔM), sub-micrometer lateral resolution and high depth resolution (<1nm).

The aim of this work was to investigate the causes of the loss of sensitivity after one year. In particular, we focused the attention on the distribution and the chemical nature of metal carbonates and carbonate ions.

Finally, we have applied principal component analysis (PCA) to ToF-SIMS depth profiling data in order to obtain the correlation between signals originated from carbonates and hydroxides species as a function of the depth profile.

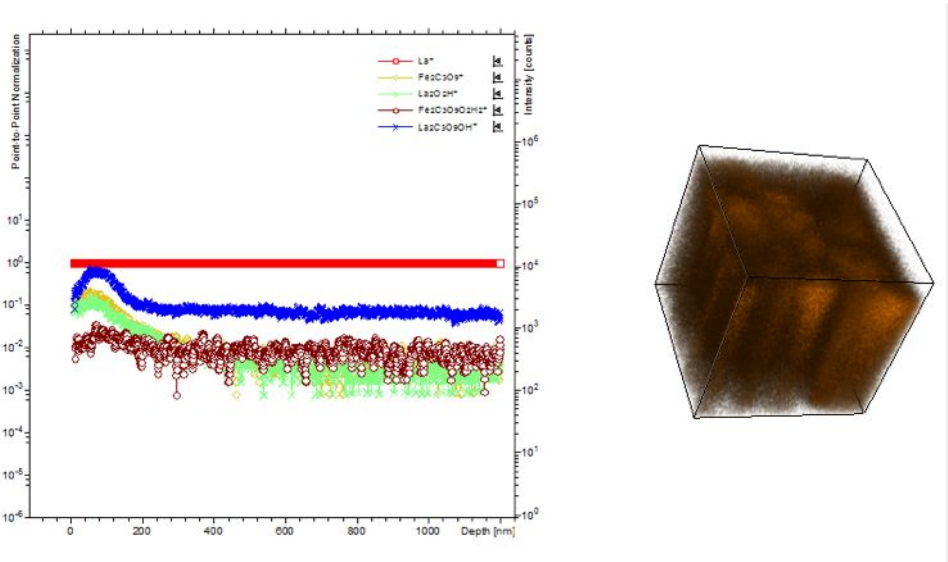


Figure 1 Depth profiling of carbonates and hydroxides species of Lanthanum and Iron using 500eV Cs^+ for sputtering. The intensities have been normalized to Lanthanum ion signal (left). 3D reconstruction of carbonate ion (CO_3^-) (right).

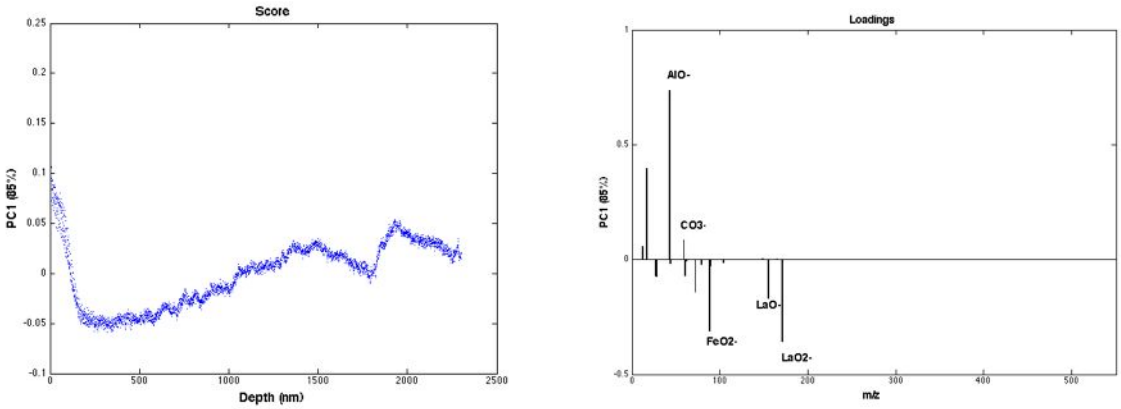


Figure 2 Scores (left) and Loadings (right) from PC1 of the negative ion depth profiles.

References

[1] J-M. Tulliani, M. Borgna, I. Grigioni, I. Natali Sora *Ceramics International*, **2013**, *39*, 4923-27.

Development of nanostructured substrates for quantitative analysis with Surface-Enhanced Raman Spectroscopy (SERS)

S. Dalla Marta[1], A. Bonifacio[1], V. Sergo[1]

[1] Engineering and Architecture Department , University of Trieste, via Valerio 6/A - Trieste, Italy.

silvia.dallamarta@phd.units.it

In the latest years, the use of Surface-Enhanced Raman Spectroscopy with solid substrates for nanoplasmonic sensing has been considerably growing[1]. The signal enhancement due to nanostructured materials as gold and silver nanoparticles (Au and Ag NPs), coupled with the specificity of Raman spectra, makes SERS highly sensitive to the presence in solution of specific molecules in low concentration[2]. The efficiency and rapidity of SERS measurements, together with the availability of portable instruments, make this approach extremely attractive for applications were a quick response is needed on the spot, as the monitoring of the anticancer drugs in biofluids of patients undergoing chemotherapy.
We developed SERS substrates upon immobilizing Au or Ag NPs on common filter paper. These substrates were found to be repeatable and homogeneous, allowing a quantitative analysis with a variation on the integrated Raman band area below 15%. However, especially for non-resonant molecules present in a complex matrix as biofluids, higher sensitivity and specificity are needed. For this purpose a supramolecular host guest approach, in order to increase the affinity of the anticancer drugs for the metallic surface, is presented[3]. The functionalization of the NPs surface with a host molecule able to trap a guest in solution through weak interactions, allows the SERS detection of the guest in a complex matrix as well, leading a platform for a quantification of the anticancer drugs in biofluids.

Acknowledgements: This work is carried within the framework of a scientific collaboration with the National Cancer Institute (C.R.O.) in Aviano (PN), Italy.

References

[1] L. Polavarapu, L. Marzan, *Phys. Chem. Chem. Phys.*, **2013**, *15*, 5288-5300.
[2] B. Sharma, R.R. Frontiera, A. Henry, E. Ringe, R.P. Van Duyne, *SERS: Materials, applications, and the future*, *MaterialsToday*, **2012**, 15, 1-2.
[3] S. Kasera, F. Biedermann, J. J. Baumberg, O. A. Scherman, S. Mahajan, *Nano Lett.*, **2012**, 12, 5924–5928.

Synthesis and characterization of $LiNi_{0.5}Mn_{1.5}O_4$. High potential cathode material for Lithium ion batteries

Gabriele Tarquini[1], Mauro Pasquali[1], Pier Paolo Prosini[2]

[1]Università degli studi di Roma "La Sapienza"
[2]ENEA C.R. Casaccia, , Via Anguillarese 301, Rome 00060, Italy

Email: gabriele.tarquini@uniroma1.it

The increasing demands on high energy and high power Li-ion batteries for hybrid electric vehicle and power tools lead the researchers to investigate the high-voltage material[1].

The Mn and Ni oxides are used as new generation cathode materials in lithium ion batteries. $LiNi_{0.5}Mn_{1.5}O_4$ spinels have high average discharge voltage (around 4.7 V vs. Li+/Li couple), fast Li+ diffusion within the three-dimensional structure, low cost and environmental friendliness. For these reason have been regarded as one of the most promising candidates for high power and high energy cathode materials[2].

Spinel compound $LiNi_{0.5}Mn_{1.5}O_4$ with high capacity and high rate capability was synthesized at 800 ^{0}C by solid-state reaction

The effects of the time of calcination on the physical properties and electrochemical performance of the products were investigated. Samples were characterized by thermal gravimetric analysis(TGA), scanning electron microscopy(SEM), X-ray diffractometry(XRD), charge-discharge tests. Scanning electron microscopy(SEM) image shows that as time increase, the crystallinity of the samples is improved, and their grain sizes are obviously increased Fig. (1-2). It is found that $LiNi_{0.5}Mn_{1.5}O_4$ calcined at 800 ^{0}C for different time exhibit a typical cubic spinel structure with a space group of *Fd*3*m* with different amount of Mn^{3+} ions, degree of structural ordering and micro-morphologies[3]. These differences involve different electrochemical performance of the material.

Electrochemical tests demonstrate that the sample obtained possesses high capacity and excellent rate capability. However the performance of the samples are variable in terms of specific capacity, decreases with decreasing of the calcination time (from 5 to 1 h), passing from 130 to 118 mAh/g. Overall the samples present good electrochemical performances in term of cyclabilty also at different discharge rate Fig. (3). This result is important for future applications in electrochemical storage systems.

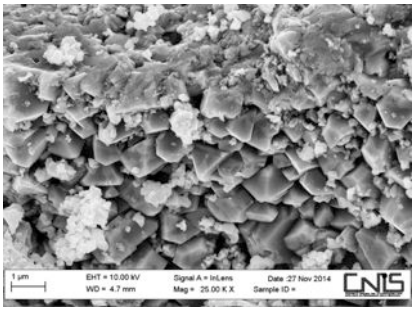


Fig. 1 $LiNi_{0.5}Mn_{1.5}O_4$ after 5 h of calcination

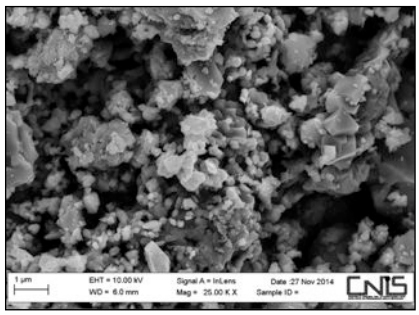


Fig. 2 $LiNi_{0.5}Mn_{1.5}O_4$ after 1 h of calcination

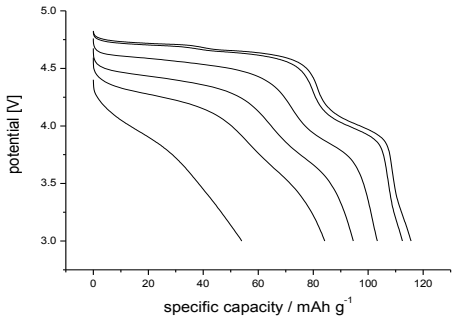


Fig 3 potential trends vs specific capacity at different discharge rate(C/10, C/5, C, 2C, 3C e 5C)

References

[1] Jung Han Lee, Kwang Joo Kim, *Electrochimica Acta*, 137 **(2014)** 169–174
[2] Guiyang Liu, Yannan Li, Baosen Wang, *Int. J. Electrochem. Sci.*, 10 **(2015)** 3124 – 3135
[3] Liping Wang, Hong Li, Xuejie Huang , Emmanuel Baudrin, *Solid State Ionics* 193 **(2011)** 32–38

Development of hybrid sol-gel based films for cellulose wearable sensors

Emanuela Guido[1], Claudio Colleoni[1], Maria Rosaria Plutino[2], Giuseppe Rosace[1]

[1] Department of Engineering and Applied Science, University of Bergamo, viale Marconi 5, 24044, Dalmine (BG), Italy
[2] Institute for the Study of Nanostructured Materials, ISMN – CNR, O.U: Palermo, Messina, Italy; c/o Department of Chemical Science, University of Messina,Viale F. Stagno d'Alcontres 31, Vill. S. Agata, 98166 Messina, Italy

Email: emanuela.guido@unibg.it

In the last years a remarkable growth in the textile industry for engineering applications has been observed. Recently, there have been many efforts to increase textile "intelligence", i.e. capabilities to sense and react to the environment, obtaining smart fabrics. Smart textiles can assume a growing interest as colorimetric sensors, that are capable to change their color with a change of external stimuli. The pH is one of the key parameters that can be used for the detection of acidic or alkaline values for environmental pollution monitoring or for medical tests [1]. The sol-gel method was employed in this work to produce dye-doped thin films with the same experimental procedures already adopted by the authors in previous researches [2,3]. Hybrid halochromic sensor coatings were realized immobilizing Nitrazine Yellow onto cotton fabrics via the epoxy group of 3-glycidoxypropyltrimethoxysilane silica precursor in the presence of BF_3 [4]. The smart textiles were prepared by padding on cotton fabrics the sols synthetized with three different BF_3 percentages. The halochromic behaviour of the textile fabrics treated with hybrid films showed that the pH-sensitive properties of the NY remained after covalent immobilization by the hybrid matrix on the textile surface. Changes in reflectance intensity associated with the protonation–deprotonation process on dedicated instrumentation attached to the halochromic fabric were monitored. The smart fabric, associated to its color electronics sensor, can be easily embedded into various types of portable systems. In the future different organic sensors immobilized onto textile fabric via sol-gel could be used to develop a portable device able to monitor simultaneously a variety of gas, temperature and ions in dangerous environments.

References

[1] L. Van der Schueren, K. De Clerck, *Tex. Res. J.*, **2010**, 80, 590–603.
[2] L. Van der Schueren, K. De Clerck, G. Brancatelli, G. Rosace, E. Van Damme, W. De Vos, *Sens. Actuators B: Chem.* **2012**, 162, 27–34.
[3] M. Caldara, C. Colleoni, E. Guido, V. Re, G. Rosace, *Sens. Actuators B: Chem.*, **2012**, *171/172*, 1013–1021.
[4] E. Guido, C. Colleoni, K. De Clerck, M.R. Plutino, G. Rosace, *Sens. Actuators B: Chem.*, **2014**, 203, 213–222.

Trasformazioni chimiche e microstrutturali del fosfato di litio ferro in elettrodi per batterie trattati con laser pulsato

Maurizio Fiorini[1], Adrian H. Lutey[2], Alessandro Fortunato[2], Alessandro Ascari[2]

[1] DICAM, Università di Bologna, via Terracini 28 40131 Bologna, Italy
[2] DIN, Università di Bologna, via Terracini 24 40131 Bologna, Italy

Email: maurizio.fiorini@unibo.it

Il fosfato di litio ferro (LFP) rappresenta uno materiali più promettenti per la produzione di anodi per batterie al litio [1] grazie ad una elevata densità di energia, una vita utile prolungata, una maggiore sicurezza e migliore compatibilità ambientale rispetto ad altri materiali per elettrodi [2-4,]. I precursori per la produzione di LFP sono abbondanti e economici, tuttavia i costi di produzione degli anodi da assemblare nelle batterie restano abbastanza elevati, principalmente a causa del costo degli utensili impiegati nelle operazioni di taglio degli elettrodi. Tali utensili sono soggetti ad usura rapida e quindi richiedono molta manutenzione per la loro affilatura e frequenti sostituzioni. Il taglio laser è una tecnologia già applicata in molti settori della lavorazione di precisione di leghe metalliche e può quindi rappresentare un'alternativa al taglio tradizionale anche per gli elettrodi per batterie al litio [5-7].

In questa comunicazione sono descritti i risultati di due diverse serie di esperimenti. In una prima serie di prove, anodo (costituito da una lamina di alluminio ricoperta con LFP) e catodo (lamina di rame ricoperta di grafite) sono stati esposti al fascio di un laser pulsato (lunghezza d'onda 1064 nm, impulsi di durata variabile tra 4 e 200 ns) per realizzate incisioni di profondità crescente, fino ad arrivare al taglio completo della lamina composita. Grazie alla microscopia Raman è stato possibile studiare le trasformazioni strutturali subite dalla fase attiva di LFP nella zona interessata dal fascio laser e in quella adiacente (zona termicamente influenzata, HAZ). In una seconda serie di prove, gli stessi elettrodi sono stati tagliati con un laser industriale, a velocità di lavorazione di 1 m/s, ovvero valori compatibili con le esigenze di un processo di taglio industriale.

Nelle due serie di esperimenti condotti in condizioni molto diverse tra loro, è stato osservato che la HAZ è limitata a poche decine di micron dalla linea descritta dal fascio laser. Con la microscopia Raman è stato possibile individuare le principali trasformazioni chimiche subite dal LFP, in particolare l'ossidazione del Fe(II) a Fe(III) e la formazione di una diversa fase solida contenente fosfato di Li e Fe [8].

Le prove di taglio con il laser industriale hanno dimostrato che questa tecnologia può competere con la più tradizionale tecnica di taglio meccanico [9].

References

[1] A. Padhi, K. Nanjundaswamy, J. Goodenough Journal of the Electrochemical Society 144 (4) (1997) 1188-1194.
[2] M. Takahashi, S. Tobishina, K. Takei, Y. Sakurai Journal of Power Sources 97-98 (2001) 508-511.
[3] S-Y. Chung. J. Bloking, Y-M. Chiang Nature Materials 1 (2002) 123-128.
[4] B. Scrosati, J. Garche Journal of Power Sources 195 (9) (2010) 2419-2430.
[5] M. Luetke, V. Francke, A. Techel, T. Himmer, U. Klotzbach,. A. Wetzig, E. beyer Physics Procedia 12B (2011) 286-291.
[6] D. Lee, R. Patwa, H. Herfurth, J. Mazumeder Journal of Power Sources 210 (2012) 327-338.
[7] D. Lee, R. Patwa, H. Herfurth, J. Mazumeder Journal of Power Sources 240 (2013) 368-380.
[8] A. Lutey, M. Fiorini, A. Fortunato, A. Ascari, Applied Surface Science322 (2014) 85-94.
[9] A. Lutey, M. Fiorini, A. Fortunato, S. Carmignato Applied Physics A (2015) DOI 10.1007/s00339-015-9083-6

Monodisperse block copolymer-type architectures for carbon nanotubes deposition on surfaces

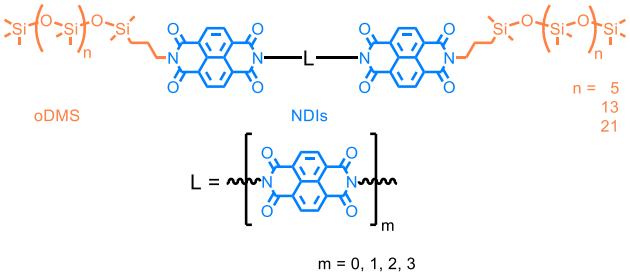
José Augusto Berrocal[1], Bas de Waal[1], Miguel Garcia-Iglesias[1], E. W. Meijer[1]

[1] Institute for Complex Molecular Systems, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, the Netherlands

Email: j.berrocal@tue.nl

The search for silicone alternatives has become a major theme in the scientific world towards the fulfillment of Moore's Law. Single Walled Carbon Nanotubes[1] (SWCNs) have been identified as potential candidates for their promising, yet not fully explored, properties. SWCNs insolublity and high tendency to bundle result in tedious synthesis and purification and extremely challenging preparation of devices. Few succesfull strategies deriving from the combination of supramolecular chemistry and physical confinement on patterned substrates have been reported so far.[2] However, either the extent of the alignment or SWCN density on wafers was poor, leading to poor device performance.

In our approach to address the problem, we merge concepts from supramolecular chemistry and microphase separation of block copolymers.[3] These notions are chemically translated into ABA block monodisperse macromolecular architectures of oligodimethysiloxane (oDMS) and naphthalenediimides (NDIs), SWCN-binding moieties.[4] The self assembly of such structures on silicon wafers can lead to the formation of a device substrate to supramolecularly control SWCN deposition. As an alternative strategy, exfoliation of SWCNs (induced by NDIs) followed by deposition on a silicon substrate will be investigated. Preliminary results for the synthesis of the monodisperse macromolecular architectures will be presented in this communication.



References

[1] A. Javey, *ACS Nano*, **2008**, *2*, 1329-335.

[2] H. Park, A. Afzali, S.-J. Han, G. S. Tulevski, A. D. Franklin, J. Tersoff, J. B. Hannon, W. Haensch, *Nat. Nanotechnology*, **2012**, *7*, 787–91.

[3] F. S. Bates, G. H. Fredrickson, *Annu. Rev. Phys. Chem.*, **1990**, *41*, 525–27.

[4] Z. Hu, G. Dan Pantoş, N. Kuganathan, R. L. Arrowsmith, R. M. J. Jacobs, G. Kociok-Köhn, J. O'Byrne, K. Jurkschat, P. Burgos, R. M. Tyrrell, S. W. Botchway, J. K. M. Sanders, S. Pascu, *Adv. Funct. Mat.*, **2012**, *22*, 503-18.

Oxygen reduction reaction carbon-nitride based nano-electrocatalysts for proton-exchange membrane fuel cells

Enrico Negro[1], Vito Di Noto[1], Keti Vezzù[2]

[1] Department of Chemical Sciences, University of Padova, Via Marzolo 1, 35131 Padova (PD), Italy
[2] Veneto Nanotech S.C.p.a., Via San Crispino 106, I-35129 Padova (PD), Italy

Email: enrico.negro@unipd.it

The oxygen reduction reaction (ORR) is one of the fundamental electrochemical processes involved in the operation of fuel cells (FCs). The ORR is a very sluggish process and bottlenecks the performance of FCs working at T < 250°C, *e.g.* proton-exchange membrane fuel cells (PEMFCs). The latter systems are of a high scientific and technological relevance for their exceptional energy conversion efficiency, remarkable power density and environment-friendly operation. To achieve a performance level compatible with the applications, PEMFCs must mount suitable ORR electrocatalyts (ECs). Typical state-of-the-art ORR ECs for application in PEMFCs comprise Pt nanocrystals supported on active carbons with a large surface area. The performance and durability of these ECs is still insufficient; furthermore, the high loading of Pt raises the costs to unacceptable levels.
One approach to address the above issues consists in the development of carbon nitride (CN)-based ECs. These systems are characterized by a porous conductive CN support, coordinating the metal alloy nanoparticles bearing the ORR active sites in *"nitrogen coordination nests"*. This contribution overviews the development of this family of ECs [1]. Early unsupported materials were studied to identify the best preparation route and the chemical composition yielding the best ORR performance. A major breakthrough was achieved by devising *"core-shell"* CN-based ECs; in these systems, the CN *"shell"* embedding the ORR active sites is supported on a conductive carbonaceous *"core"*. It was shown that the morphology of the *"core"* plays a crucial role to modulate the performance of the CN-based EC. The performance in the ORR of the best *"core-shell"* CN-based ECs is outstanding. With respect to the reference ECs, the intrinsic ORR activity is no less than twice larger (>300 mA/cm^2_{Pt} at 0.9 V *vs. ca.* 150 mA/cm^2_{Pt} of the reference) [2], while the Pt loading to achieve 1 kW or power is as little as *ca.* 1/3 (0.3 g_{Pt}/kW *vs.* 1.1 g_{Pt}/kW of the reference) [3].

References

[1] V. Di Noto, E. Negro, Electrochim. Acta, 2010, **55**, 7564-74.
[2] E. Negro, S. Polizzi, K. Vezzù, L. Toniolo, G. Cavinato, V. Di Noto, *Int. J. Hydrogen Energy*, **2014**, *39*, 2828-41.
[3] V. Di Noto, E. Negro, *Fuel Cells*, **2010**, *10*, 234-44.

COMUNICAZIONI POSTER

Dual Role of Graphite Oxide Nanofiller in Epoxy and Polyester resins

Maria Rosaria Acocella, Mario Maggio, Gaetano Guerra

Dipartimento di Chimica e Biologia, Università di Salerno, Via Giovanni Paolo II, 84084-Fisciano (SA)

Email: macocella@unisa.it

Nanocomposites with carbon-based fillers have been widely investigated due to unique properties derived from the extended interface between the polymer matrix and the filler. In particular, many studies have been focused on GO reinforced nanocomposites showing relevant improvements of physical and mechanical properties. Recently we reported the dual role of graphite oxide (GO) in epoxy resin thermosets exerted as catalyst on the reaction between the epoxy and amine groups of the resin, which leads to higher crosslinking density in milder conditions, and as filler for the nanocomposite.[1]

A dual role of graphite oxide was also found for polyester resins. In fact, GO is effective to promote the polymerization reaction from the starting monomers, like diethyl fumarate and ethylene glicole, to give prepolymers suitable for the subsequent curing step. The chemical functionalization of GO during the polymerization assures a better dispersion reducing the possible nanofiller aggregation.

References

[1]. M. Mauro, M. R. Acocella, C. Esposito Corcione, A. Maffezzoli, G.Guerra *Polymer* **2014,***55*, 5612-5615

Release of Coumarin-6 from UV responsive polyamide nanocapsules

Veronica Ambrogi[1], Cosimo Carfagna[2], Pierfrancesco Cerruti[2], Marta Giamberini[3], Valentina Marturano[1,2], Bartosz Tylkowski[3]

[1]Department of Chemistry, Materials and Engineering, University of Naples "Federico II", Piazzale Tecchio 80, 80125 Napoli, Italy
[2]Institute for Polymers, Composites and Biomaterials (IPCB-CNR), via Campi Flegrei 34, 80078 Pozzuoli (Na), Italy
[3]University Rovira i Virgili, Department of Chemical Engineering, Av.Paisos Catalans 26, 43007 Tarragona, Spain

Email: ambrogi@unina.it

In this work, interfacial polymerization in miniemulsion method [1] was used to synthesize nanosized capsules based on a lightly cross-linked polyamide containing azobenzene moieties in the main chain. The obtained nanocapsules were loaded with a fluorescent probe molecule, Coumarin-6, dissolved in toluene. Diameters of the nanocapsules were in the 100-900 nm range, depending on the selected emulsion conditions. The morphology and shape of the samples were observed by TEM and SEM analysis while the emulsion droplets and nanocapsules size was measured by DLS.
Under continuous UV (365nm) irradiation the capsules were able to release the encapsulated probe molecule. At this specific wavelength E-Z photoisomerization of azobenzene is triggered [2], resulting in a massive rearrangement of the polymeric shell, from a "closed" conformation to a more "open" one. Variation in diameter of the nanocapsules with the time of UV irradiation was detected through DLS analysis. 10-30% growth was observed, depending on the sample. The kinetics of release of Coumarin-6 was followed by spectrofluorimetry in ethanol. In absence of irradiation, the fluorescence intensity appeared to be constant over time, while it increased when the sample was irradiated with UV light.

References

[1] K. Landfester, *Angew. Chem. Int. Ed.*, **2009**, 48, 4488-4507
[2] A. Natansohn, P.Rochon, *Chem. Rev.* **2002**, 102, 4139-4175

Nanomaterials and nanotechnologies for restoration of deteriorated parchment and leather

Chiara Argentino[1], Aldrei Boaretto[2,3], Simonetta Antonaroli[3], and Federica Valentini[3]

[1]ICRCPAL-Istituto Centrale per il Restauro e la Conservazione del Patrimonio Archivistico e Librario Via Milano (Roma)
[2] CAPES foundation, Ministry of Education of Brazil, Brasilia -DF 70040-020 (Brazil)
[3] Chemistry Department Tor Vergata University, via della Ricerca Scientifica 1, 00133 Rome (Italy)

Email: chiara.argentino@beniculturali.it

Parchment and leather samples present several damages and deterioration phenomena, related to the physical-chemical reactions of the inner materials with the environmental pollutants, induced and catalyzed by light (i.e.; photochemical reaction mechanisms). In addition, biochemical degradation processes could be also involved and a synergism of all events could be responsible for the *red rot* phenomena.
Several traditional treatments [1] have been investigated during the past years but they present several problems as yellowing, aging and modification of the optical and mechanical properties of parchment and leather support. For this purpose, in this work, new technologies based on nanomaterials will be presented and discussed, especially that based on the nanocollagen. Best results are obtained by using the new technology on the parchment affected by the red rot event. An analytical and systemic evaluation of the efficiency of the new nanocollagen based treatment is performed comparing it with that exhibited by using the traditional/conventional restoration methodology [1], widely applied on deteriorated parchment.

References

[1] Luca Richard De Bella, et al., *Capitolato Speciale Tecnico Tipo*,**2005**.

Infiltrated $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ based cells fed with biogas

F. Basoli[1], I. Luisetto[2], F. Zurlo[1], S. Licoccia[1] and E. Di Bartolomeo[1]

[1] Dept. of Chemical Science and Technologies, University of Rome Tor Vergata, Via della Ricerca Scientifica, 00133 Rome, Italy
[2] Dept. of Science, University of Roma Tre, via della Vasca Navale, 00146 Rome, Italy

Email: francesco.basoli@uniroma2.it

The main drawback of $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) as electrolyte for solid oxide fuel cells is its chemical reactivity across the interface with anodic layer when fired at high-temperatures. To overcome this problem it is possible to use at two steps procedure: a high temperature step for the half cell fabrication and a lower temperature step for the infiltration of metallic catalyst.

$La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) based porous/dense structures were optimized for infiltration of different metal catalysts [1]. A concentrate solution of metal salts (Ni, Co, Cu and their 1:1 mixtures) was used for the infiltration process. $La_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}O_{3-\delta}$ was used as cathode.

The reduction behavior of the different catalysts was examined by H_2-TPR techniques. Ex-situ catalyst activity measurement was used for the initial catalyst screening. The electrochemical measurements were performed in the temperature range between 650 and 750°C both in H_2 and biogas.

The catalytic activity for CH_4 and CO_2 conversion followed the order Ni~Ni-Co>Co>Ni-Cu>>Co-Cu. Co is known to lower the carbon deposition in different ways such as decreasing the particle size of metallic alloy and thanks to its low affinity toward carbon, though its main drawback is the low catalytic activity in comparison with Ni [2]. Adding Co to Ni slightly decreased the overall catalytic activity, thus Ni-Co alloys could effectively couple the high activity of Ni with the high carbon and sintering resistance of Co yielding higher performing catalysts. The catalysts selectivity of different catalysts for the dry reforming reaction increased with temperature both for Ni and Ni-Co. Stability tests were also performed on both Ni and Ni-Co impregnated powders, conversions in both methane and carbon dioxide were stable in Ni-Co without sign of conversion decrease, showing promising performance for bio-gas internal reforming.

Electrochemical measurements were performed on both Ni and Ni-Co infiltrated cells, the amount of the infiltrated phase being the same. Measurements were performed both in H_2 and CH_4 and results compared. The maximum power density at 750°C in 100 cm^3min^{-1} of H_2 was 813 mw/cm^2 and in 60 cm^3min^{-1} of CH_4 and 40 cm^3min^{-1} of CO_2 was 446 mw/cm^2 for the Ni infiltrated cell (electrolyte thickness 13-15 μm). Similar performance were obtained for slightly thicker electrolyte (17-19 μm) Ni-Co based cell (max power density 654 mw/cm^2 in H_2 and 425 mw/cm^2 in

60 cm^3min^{-1} of CH_4 and 40 cm^3min^{-1} of CO_2) confirming the results of the catalytic investigation on the corresponding infiltrated LSGM powders: the catalytic activity of Ni-Co infiltrated anodes is comparable to that of Ni infiltrated anodes.
LSGM based cell infiltrated with different metal catalysts were fabricated and tested. The electrochemical tests in biogas showed promising results that confirm the catalytic investigation.

Acknowledgments

Thanks to the Italian Ministry for Education, University and Research (PRIN-2010-2011-Prot.2010KHLKFC

References

[1] Z. Salehi, F. Basoli, A. Sanson, E. Mercadelli, S. Licoccia, E. Di Bartolomeo, *Ceramics International*, **2014**, *40*, 16455-16463.
[2] S. McIntosh, R. J. Gorte, *Chem. Rev.*, **2004**, *104*, 4845-4865.

Characterization of Triterpenes by ToF-SIMS and Chemometrics

Paola Biocca[1,2], Luca Tortora[1], Giovanni Sotgiu[2] , Francesco de Notaristefani[1], Marcella Ioele[3]

[1]Laboratorio di Analisi delle Superfici, Dipartimento di Matematica e Fisica & INFN, Università Roma Tre via della Vasca Navale 84, 00146 Roma
[2]Dipartimento di Ingegneria & INFN, Università Roma Tre, via Vito Volterra 62 00146 Roma
[3] Istituto Superiore per la Conservazione ed il Restauro, via di San Michele 23 00153 Roma

Email: paola.biocca@uniroma3.it

Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) technique coupled to Multivariate Statistics such as Principal Component Analysis (PCA) can be a powerful tool to identify and localize the fragmentation of a complex blend of triterpenes such as dammar resin. This characteristic makes the techniques particularly useful in all fields: from biomedical studies to cultural heritage[1].
The potential of triterpenes belonging to the lupane, oleanane or ursane group, to treat cancer by different modes of action are showed in several papers. Pentacyclic triterpenes are also the principal component of natural resins, used like varnishes in pictorical trade. In this work the analysis of high-resolution mass spectra of aged dammar resin is presented. In addition four pure triterpenes, lupan series (lupeol and lupenone) and oleanan-type (oleanolic and ursolic acid), were characterized in order to evaluate the characteristic peaks. Principal Component Analysis (PCA) is the most commonly unsupervised multivariate statistical technique used for ToF-SIMS analysis. PCA has been used to identify similarities and differences in ToF-SIMS spectra and classify spectra into groups by reducing the multidimensionality of the mass spectra. The study of distribution fragments of the components in the resin has allowed to identify the marker peaks in the dammar spectra with the use of chemometrics statistic analysis.

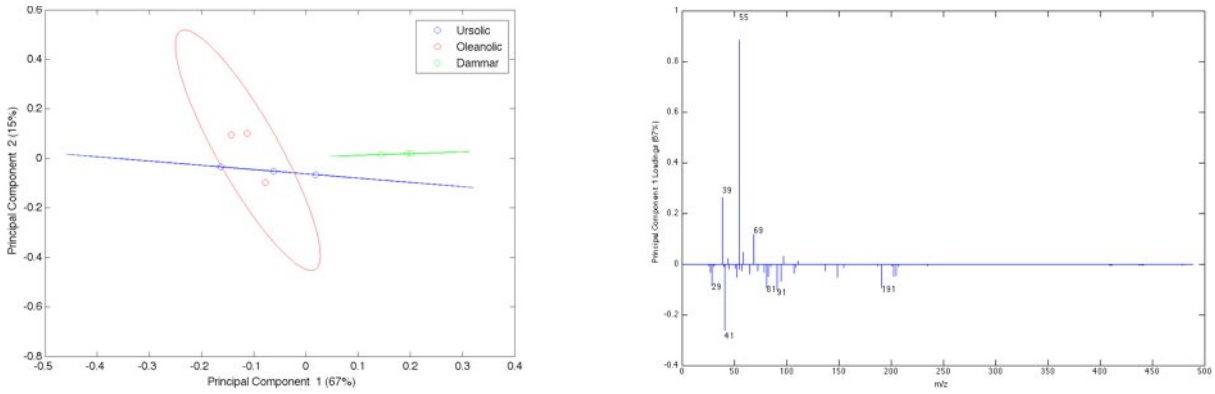


Figure 1: Scores (left) and loadings (right) plot from PC1 of the positive ion mass spectra. Tof SIMS data have been normalized by sum of peaks and mean centered before PCA.

References

[1] L. Tortora, F. De Notaristefani, M. Ioele, *Surf. Interface Anal*,2014, 46, 807-811.

The influence of POSS molecular structure on the thermal properties of POSS/PS nanocomposites

Ignazio Blanco[1], P. Bottino[2], M.A. Chiacchio[2]

[1]Department of Industrial Engineering, University of Catania, Via S. Sofia 64, 95125 Catania, Italy
[2]Department of Pharmaceutical Sciences, University of Catania, Via S. Sofia 64, 95125 Catania, Italy

Email: iblanco@dii.unict.it

Polyhedral oligomeric silsesquioxanes (POSSs) are hybrid inorganic/organic compounds that have assumed considerable importance owing to their excellent thermal, mechanical, optical and electrical properties[1] and use as fillers in the production of polymer nanocomposites.[2] The most used POSSs for this purpose have molecular formula $(RSiO_{1.5})_8$ and is thus formed by an inorganic Si_8O_{12} nanostructured skeleton surrounded by eight same or different organic groups (Fig. 1).

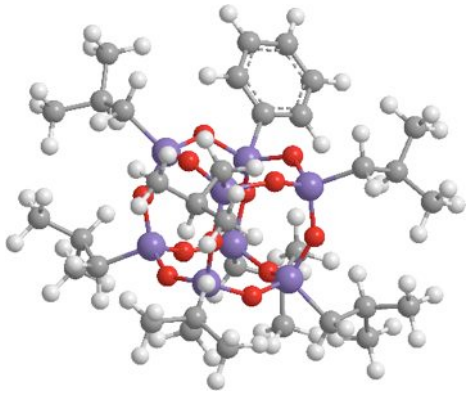


Figure 1. Molecular structure of a mono chloro phenyl isobutyl POSS

The research in this field, which also engaged our group, has been directed towards the synthesis of new POSSs showing good compatibility with polymers and, at the same time, high thermal stability. Recently we investigated the influence of POSS microstructure on the properties of the corresponding POSS/Polystyrene (PS) nanocomposites and we found that their comprehensive thermal behaviour is strictly dependent by the structures of the different POSSs used as reinforcement.[3-5]

References

[1] R.H. Baney, M. Itoh, S. Sakakibara, T. Suzuki, *Chem. Rev.*, **1995**, *95*, 1409-1430.
[2] I. Blanco, L. Abate, F.A. Bottino, P. Bottino, *Polym. Degrad. Stab.*, **2012**, *97*, 849-855.
[3] I. Blanco, F.A. Bottino, P. Bottino, *Polym. Compos.*, **2012**, *33*, 1903-1910.
[4] I. Blanco, L. Abate, F.A. Bottino, *J. Therm. Anal. Calorim.*, **2013**, 116, 5-13.
[5] I. Blanco, L. Abate, F.A. Bottino et al., *J. Compos. Mat.*, **2015**, doi: 10.1177/0021998314549616

Cardanol-based nanovesicles as potential "multifunctional-green" tools for tumor treatment

Ermelinda Bloise[1], Giuseppe Mele[1], Mergola Lucia[1], Barbara Piccinni [2], Tiziano Verri[2], Diego Lomonaco[3], Selma E. Mazzetto[3], Mohamed Behalo[4]*

[1]Department of Engineering for Innovation, University of Salento, via Arnesano, Lecce, Italy
[2]Department of Biological and Environmental Sciences and Technologies, University of Salento, via Monteroni, Lecce, Italy
[3]Organic and Inorganic Chemistry Department, Federal University of Ceara, C.P. 6120, 60455-760 Fortaleza (Brazil)
[4]Chemistry Department, Faculty of Science, Benha University, Benha (Egypt)

Email: ermelinda.bloise@unisalento.it

This work aims to prepare and test novel "green" multifunctional anticancer tools by nanocarrier technology. In particular, the preparation of vesicular nanodispersions, using cardanol (CA) as main component, by a new sustainable organic solvent-free method, to vehicle bioactive molecules. CA is a natural and renewable organic raw material with antioxidant properties [1], a potential anticancer [2] and antimicrobial activity [3,4], obtained by vacuum distillation of Cashew Nut Shell Liquid (CSNL). The "green vesicles" were loaded with lipophilic or hydrophilic bioactive compounds, in which a high percentage or the entire system is derived from renewable "functional" molecules.
The first example of CA-nanovesicles having an embedded lipophilic porphyrin was obtained [5] (CA-CH-H_2Pp). Afterwards, CA-nanovesicles have been used to encapsulate chlorogenic acids (CQAs) [6], a class of natural phenolic compounds extracted from two different rowanberries (*Sorbus Americana* and *Vaccinium* sp.) by an efficient and environmentally friendly process using water (CA-CH-*S. Americana* and CA-CH-*Vaccinium* sp.). At last, CA-nanovesicles were loaded with four of lipophilic 1,4-disubstituted phthalazine derivatives series which have already shown a potent cytotoxic effect against MCF-7 cells [7]. Figure 1 shows the TEM analysis of various nanovesicles.

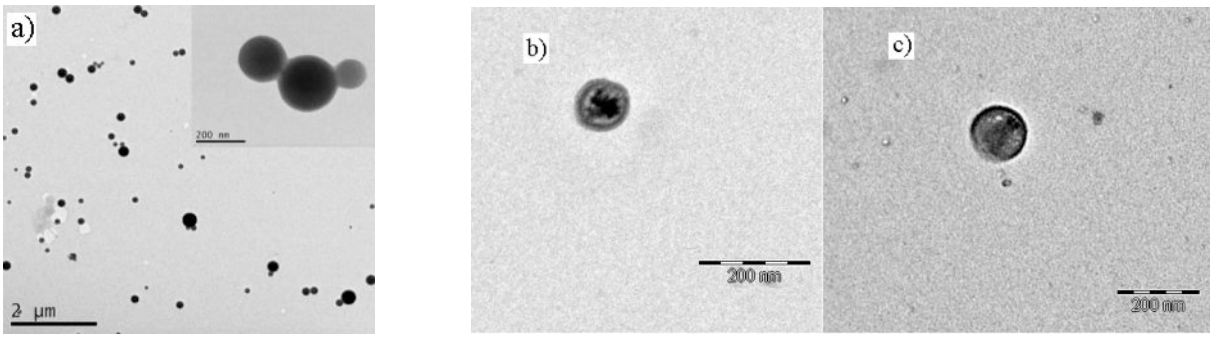


Fig. 1: Transmission electron micrographs of CA-based vesicles embedded with: a) lipophilic porphyrin-cardanol hybrid; b) *Sorbus Americana* hydrophilic extract; c) *Vaccinium* sp. extract extract.

Preliminary biological tests on some of these nanovesicles were carried out on culture cell lines to studies their cytotoxicity effects.

In particular, *in vitro* citotoxicity of CA-CH-H_2Pp and CA-CH (blank sample) against 3T3 mouse fibroblast, human colon cancer CaCo2, breast cancer MCF7 cells has been examined. The exposure of all cell lines to CA-CH-H_2Pp and CA-CH vesicular nanodispersions ([CA] range 35-5 µg/ml; 0, 24, 48, 72 hours) has resulted in a dose-dependent inhibition of cell growth determined by MTT assay, as showed in figure 2.

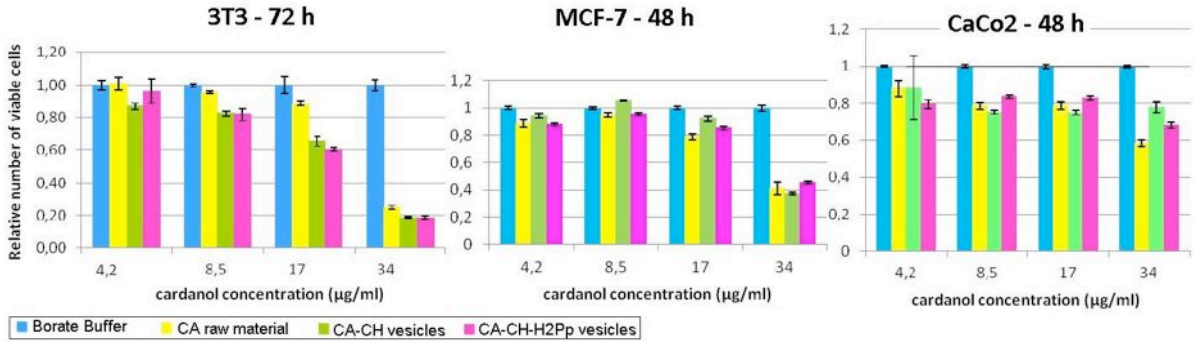


Fig. 2: MTT assay conducted on 3T3, MCF-7 and CaCo2 cell lines treated with borate buffer, CA, CA-CH vesicles (blank sample) and CA-CH-H_2Pp vesicles.

Antioxidant, DNA protective and cytotoxic activity of CA-nanovesicles embedded with phthalazine derivatives(CA-PHTs) are currently under investigation. Preliminary results on unloaded vesicles CA-CH shown that CA itself confers moderate antioxidant and cytotoxic effects to the system making it an innovative potential "multifunctional-green" nanocarrier.

References

[1] M. T. S.Trevisan; B. Pfundstein; R. Haubner; G. Wurtele; B. Spiegelhalder; H. Bartsch; R. W. Owen. *Food Chem. Toxicol.*, 44, 188−197, (2006).
[2] D. Teerasripreechal; P. Phuwapraisirisan; S. Puthong; K. Kimura; M. Okuyama; H. Mori; A. Kimura; C. Chanchao. *BMC Compl. Altern. Med.*, 12, 27, (2012).
[3] P. Boonsai, P. Phuwapraisirisan, C. Chanchao. *Int. J. Med. Sci.* 11, 327-336 (2014).
[4] C. Celis, A. García, G. Sequeda, G. Mendez, R. Torrenegra.Emir. *J. Food Agric.* 23, 249-257 (2011).
[5] E. Bloise; L. Carbone; G. Colafemmina; L. D'Accolti; S.E. Mazzetto; G. Vasapollo; G. Mele. *Molecules*, 17, 12252-61 (2012).
[6] E. Bloise; M. Becerra-Herrera; G. Mele; A. Sayago; L. Carbone; L. D'Accolti; S.E. Mazzetto; G. Vasapollo. *ACS Sustainable Chem. Eng.*, 2, 1299-1304 (2014).
[7] A. F. Wasfy; A. Abdelmaboud Aly; M. S. Behalo; Nora Sobhi Mohamed. *Der Pharma Chemica*, 5(2), 82-96, (2013).

Nanomaterials for restoration of damaged plaster surfaces: case of studies

A. Boaretto[1,2], S. Antonaroli[2] and F. Valentini[2]

[1] CAPES foundation, Ministry of Education of Brazil, Brasilia -DF 70040-020 (Brazil)
[2] Chemistry Department Tor Vergata University, via della Ricerca Scientifica 1, 00133 Rome (Italy)

Email: aldreibrt@gmail.com

Recently, Nanomaterials and Nanotechnologies are applied also to the restoration and conservation of Cultural Heritage and artwork surfaces. The reasons for this seem to be related to the excellent chemical-physical properties of nanostructured materials, as: the large surface nominal area, the possibility to modify the "surface chemistry" in order to obtain selective nano-platforms, high electrical conductivity, high mechanical and thermal stability, biocompatibility towards the "end-users" (as restorers and conservators) and eco-sustainability toward environment. In particular the case of study, reported in this work, concerns the new bio-mineral synthesis approach for the $CaCO_3$ nanoparticle production and their subsequent characterization. The analytical application was performed on the damaged plaster surfaces of the "*Palazzo Lancia*", located on Largo Argentina (Rome, Italy). *Palazzo Lancia* is a Roman Renaissance Palace (*1400-1450*) and it presents several deterioration problems especially on the plaster surfaces. The consolidation strategy has been performed by using the conventional methodologies, widely reported in literature [1] and then the new treatments based on the $CaCO_3$ nanoparticles (synthesized by the bio-mineral approach [2]) has been also applied for comparison. The efficiency of the new treatments results highly significant and promising for the restoration of Cultural Heritage, representing a valid alternative to the traditional/conventional treatments.

References

[1] Capitolato Speciale d'appalto, MINISTERO PER I BENI E LE ATTIVITÀ CULTURALI
[2] A. Boaretto, F. Valentini, D. Gazzoli, et al., *European Journal of Science and Theology*,**2015**, *submitted*.

Sputtering of PolyMethylMethacrylate (PMMA) with Bismuth Cluster Ions: Monte Carlo Simulation Study

Cristian Borrazzo[1,2], Marco Urbini[2,3], Matteo Galasso[2], Andrea Fabbri[2] and Luca Tortora[2]

[1] Department of Molecular Medicine, University of Rome "Sapienza", via Regina Elena 5, 00161 Rome, Italy
[2] Department of Mathematics and Physics & INFN, Surface Analysis Laboratory University of Rome "Roma Tre", via della vasca navale 84, 00146 Rome, Italy
[3] Department of Industrial Engineering, University of Rome "Tor Vergata", via del politecnico 1, 00133 Rome, Italy

Email: c.borrazzo@gmail.com

Cluster Time-of-Flight secondary ion mass spectrometry (ToF-SIMS) has played a critical role in the characterization of polymeric and biological materials over the last decade, providing elemental and molecular surface chemical information.
The introduction of polyatomic sources such as Bi^+, Bi_3^+, Bi_3^{++} and Bi_5^{++} has allowed to obtain greater yield of secondary ion signal from high molecular weight as opposed to more conventional atomic beams.
The advantage of cluster ToF-SIMS compared to classic atomic beams is the localized surface fragmentation with rapid sputter removal rates, resulting in a system at equilibrium, where the damage created is rapidly removed before it can accumulate.
High accuracy is achieved with Monte Carlo (MC) methods that can take into account nuclear processes in addition to the classic electromagnetic interactions.
However, these are not standard implemented MC in research system today due to the need of high computing power. The simulation toolkit GEANT4 [1] is a promising MC tool, because all physical processes are implemented. Nevertheless, it still has to be validated for energy regions where secondary ion mass spectrometry is applied. In this energy region, some nuclear cross sections are insufficiently known, leading to the need of new measurements.
Aim of the simulation is modeling and investigating the abundance of the most frequent reaction channels occurring from inelastic interaction with the target material by focusing a primary Bi+ ion beam of 30 keV on a target. The simulation plays a key role to assess the physical processes that influence ToF-SIMS measurements. Furthermore, the simulation can investigate the effects of target thickness, different detector systems and geometries on measured variables. The results of this study have been compared with ToF-SIMS measurements and have been found discrepancy between data and model of the order of a few percent, confirming the validity of the simulations. We have also developed a reconstruction

algorithm whose aim was to estimate the kinematic variables necessary for the fragmentation identification and full event reconstruction. The algorithm has been verified with MC data. Several preparatory analyses are actually addressed to the analysis of the two most important reaction channels. Cut sequences are developed with the aid of MC truth to ensure a high level of purity of the reaction signal.

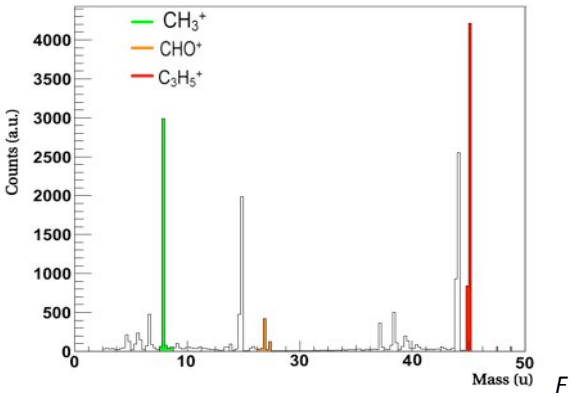


Figure 1: Simulation of Static spectra from the surface of PMMA.

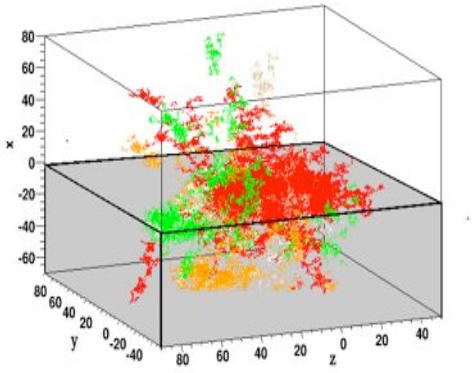


Figure 2: Simulation localized surface fragmentation of PMMA PolyMethylMethacrylate.

Reference

[1] Agostinelli, Sea, et al. "GEANT4—a simulation toolkit." *Nuclear instruments and methods in physics research section A: Accelerators, Spectrometers, Detectors and Associated Equipment* 506.3 (2003): 250-303.

Composite membrane based on sulfonated poly ether ether ketone and functionalized oxides for direct methanol fuel cell

Mario Branchi[1], Alessandra D'Epifanio[1], Catia de Bonis[1], Barbara Mecheri[1], Maria Assunta Navarra[2] and Silvia Licoccia[1]

[1] Department of Chemical Science and Technology, University of Rome Tor Vergata, Via della Ricerca Scientifica, 00133 Rome, Italy
[2] Chemistry Department, University of Rome Sapienza, P.le Aldo Moro 5, 00185 Rome, Italy

Email: mario.branchi@uniroma2.it

In the wide field of fuel cell, direct methanol fuel cells (DMFCs) are the most suited in the sector of portable applications with low power density required. DMFCs don't suffer of storage problems because methanol is easy to transport and has a high energy density. However methanol crossover is well known to be one of the major problems blocking the wide commercialization of DMFCs [1].
Nowadays, Nafion is the most used polymer electrolyte in DMFCs due to its high thermal stability and its good mechanical strength, but it suffers of a high crossover to the methanol reducing the cell efficiency. An interesting alternative to the Nafion are the membranes made of the sulfonated polyetheretherketone (SPEEK) that are less expensive. These electrolytes show lower methanol permeability with respect to the Nafion but suffer from lower proton conductivity because their microstructure consists of narrower channels with a wide ramification making resistance to the diffusion of methanol and water [2]. One way to improve the membrane conductivity and to decrease the methanol permeability is the modification of existing ionomer by the preparation of composite membranes with inorganic fillers. On the other hand, one of the main limitations to obtain high-performance composite membranes is due to the difficulty to achieve a homogenous dispersion of the filler in the matrix for its spontaneous agglomeration and clustering.
In this work, TiO_2 and Al_2O_3 are the base inorganic fillers chosen to enhance the composite membrane performances. TiO_2 nanoparticles were opportunely functionalized on the surfaces with an organic group to increase their acidity and compatibility in the SPEEK matrix (fig.1) [3]. Furthermore, Al_2O_3 nanoparticles were prepared and sulfated on surface to enhance their acidic sites (fig.2).
To obtain a better homogeneity of the composite membranes, a spray deposition method was used instead of the traditional casting.
Key properties of the hybrid membranes were studied in terms of water uptake (WU), ionic exchange capacity (IEC) and conductivity measurements. Functionality of the composite membranes were tested in fuel cell system. Polarization and

power density curves as well as in-situ electrochemical impedance spectroscopy measurements were performed to evaluate the effect of temperature and pressure on the cell performances.

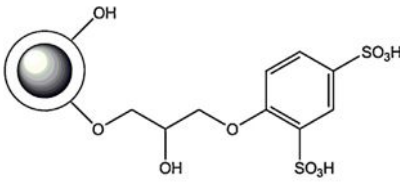


Fig.1 Structure of functionalized TiO_2

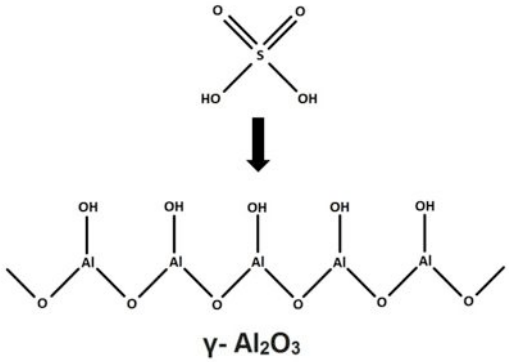


Fig.2 Sulfatation of γ- Al_2O_3.

References

[1] V. Neburchilov, J. Martin, H. Wang, J. Zhang, *J. Power Sources* **2007**, *169*, 221-238.
[2] K. D. Kreuer, *J. Membr. Sci.* **2001**, *185*, 29-39.
[3] C. de Bonis, D. Cozzi, B. Mecheri, A. D'Epifanio, A. Rainer, D. De Porcellinis, S. Licoccia, *Electrochim. Acta* **2014**, *147*, 418–425.

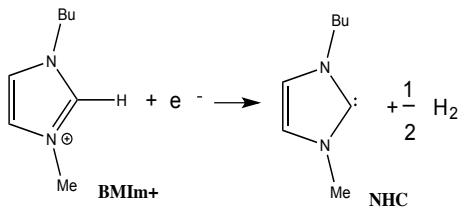
Stability and reactivity of electrogenerated 1-butyl-3-methylimidazol-2-ylidene in the presence of acids in DMF solution.

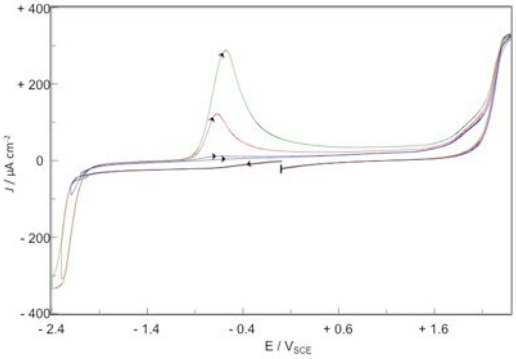
Isabella Chiarotto[1], Marta Feroci[1], Achille Inesi [2]

[1] Dept. SBAI, Sapienza University of Rome, via Castro Laurenziano, 7, 00161 Rome, Italy
[2] via Antelao, 9 00141 Rome, Italy

Email: isabella.chiarotto@uniroma1.it

N-Heterocyclic carbenes (NHCs) are a new generation of organocatalysts and represent a significant alternative to organometallic catalysts as regards cost and environmental impact. The very extensive utilization of NHCs in catalyzed syntheses carried out in organic solvents spurred us to investigate the stability of NHCs in organic solvents, according to the assumption that the NHC lifetime might be affected by several factor: the nature of the solvent and of anion of the parent imidazolium salt. Also, the reactivity and the life-time of NHC vs an acidic substrate can be interesting. In fact, its basicity may promote a proton-exchange with an acid substrate present in the reaction mixture, thus decreasing NHC concentration and affecting its efficiency as organocatalyst. Therefore, a careful analysis of the effective presence of NHC in solutions containing acid substrates is advisable. In order to study the proton-exchange equilibrium of a NHC with organic acids of different strength, we take 1-butyl-3-methylimidazol-2-ylidene as model carbene. As carbene can be obtained by cathodic reduction of the corresponding cation $BMIm^+$ in BMImX-DMF solutions, we analyse the reactivity of NHC both at the electrode surface, generating NHC by voltammetry, and in the bulk of solution, generating NHC by electrolyses [1]





The effectiveness of a proton-exchange between electrogenerated NHC and acid substrates HA can be verified by comparing the voltammetric curves of BMImX-DMF solutions recorded in the absence and in the presence of HA. We will consider three organic acids with pKa smaller than $BMIm^+$ (pKa in DMSO: 22): acetic acid (pKa 12.3) 2,6-dimethylphenol (pKa 16.0), and diethyl malonate (pKa 16.4). The utilization of electrogenerated NHC in base-induced organic synthesis will be discussed.

References

[1] I. Chiarotto, M. Feroci, G. Forte, M. Orsini, A. Inesi, *Chem. ElectroChem,* **2014**, *1*, 1525-1530;
M. Feroci, I. Chiarotto, F. D'Anna, G. Forte, R. Noto, A. Inesi *Electrochimica Acta,* **2015,** *153*,122-129.

Functionalization of Polycaprolactone Surfaces with Lactose-Modified Chitosan: a Secondary Ion Mass Spectrometry Study

Sofia Concolato[1,2], Pamela Mozetic[3], Sara Maria Giannitelli[3], Alberto Rainer[3], Marcella Trombetta[3], Monica Orsini[2] and Luca Tortora[1]

[1]Department of Physics and Mathematics, Surface Analysis Laboratory & INFN, University of Rome "Roma Tre", Via della Vasca Navale 84, 00146 Rome, Italy;
[2]Dipartimento di ingegneria, Università di Roma TRE, Via Vito Volterra 62, 00146, Roma
[3]Tissue engineering Unit, "Università Campus Bio-Medico di Roma", via Alvaro del Portillo 21, 00128 Roma, Italy

Email: sofia.concolato@uniroma3.it

Polycaprolactone (PCL) is an absorbable biopolymer of the polyester family, which is finding an increasing number of biomedical applications for bone, cartilage, ligament, and tendon regeneration [1].
With the aim to improve cell response to the biomaterial, PCL bioactivity can be augmented by surface modification treatments, including grafting of bioactive molecules. In this framework, surface functionalization of PCL with lactose-modified chitosan (Chitlac) represents a potential strategy to improve adhesion, proliferation, and ECM synthesis of different cell phenotypes, including chondrocytes [2].
In this work, two different strategies for PCL surface modification were investigated with the aim to increase the amount of free carboxyl groups as a handle for Chitlac grafting: oxygen plasma irradiation and mild alkaline hydrolysis. After activation, Chitlac (synthesized according to [2]) was grafted on PCL surface using EDC/NHS coupling. Additionally, Chitlac was physisorbed onto PCL specimens to be used as a control.
Surface analyses were performed by time-of-flight static secondary ion mass spectrometry (ToF-SIMS), which allows detecting many surface molecular fragments with high mass resolution and obtaining the related chemical maps [3]. Spectra were recorded both in positive and negative polarity, in order to investigate the peaks proper to PCL substrate and grafted Chitlac, and ionic abundances were studied using univariate analysis. In particular, CN^- and $C_6H_{11}O_3^-$ fragments were associated to Chitlac and PCL backbone, respectively.
Our preliminary results confirm that both PCL activation techniques were effective in increasing the yield of Chitlac immobilization with respect to physisorption.

References

[1] M.A. Woodruff, D.W. Hutmacher, *Progress in Polymer Science*,**2010**, 35, 1217-1256
[2] I. Donati, S. Stredanska, G. Silvestrini, A. Vetere, P. Marcon, E. Marsich, P. Mozetic, A. Gamini, S. Paoletti, F. Vittur, *Biomaterials* **2005**,6,987-998
[3] A. M. Belu, D. J. Graham, D. G. Castner, *Biomaterials*, **2003,** 24, 21:3635-3653

Structural, spectroscopic and thermal characterization of bioactive silicate gel-glasses

Stefano Vecchio Ciprioti[1], *Michelina Catauro*[2], *Alessandro Dell'Era*[3]

[1] Dipartimento S.B.A.I., Sapienza Università di Roma, Via del Castro Laurenziano 7, I-00161 Roma, Italy
[2] Dipartimento di Ingegneria Industriale e dell'Informazione,
Seconda Università di Napoli, Via Roma 21, I-81031 Aversa, Italy
[3] Dipartimento di Meccanica ed Energetica, Università di Roma G. Marconi,
Via Plinio 44, I-00193 Roma, Italy
Email: stefano.vecchio@uniroma1.it

Periodontitis is one of the most common diseases in humans, affecting in its most severe form, approximately 10–15% of the world population [1]. It is characterized by progressive destruction of the tooth-supporting apparatus (*periodontium*), which consists of two soft (gingival and periodontal ligaments) and two hard (alveolar bone and cementum) tissues. Both alveolar bone and cementum are highly calcified tissues consisting mainly of *hydroxyapatite* ($Ca_5(PO_4)_3(OH)$).
In the last years, among the most innovative bioactive materials, those belonging to the class of CaO-SiO_2-P_2O_5 gel-glasses (prepared by the sol-gel method), attracted increasing interest for their capability in bone repair and substitution [2]. Their bioactivity is expressed by the possibility to replace degraded bones, due to the formation of an apatite layer on their surface with composition and structure equivalent to the mineral phase of bone [3], but with improved mechanical properties. Since according to previous studies [4] the optimal glass composition for periodontal tissue replacement was found to contain 30 mol% CaO and 70 mol% SiO_2, this starting material was used to prepare two series of ternary systems with low but different content of both P_2O_5 and Ag_2O, respectively. The materials investigated were characterized using X-ray diffraction (on fresh and calcined samples), FTIR spectroscopy and simultaneous thermogravimetry/differential thermal analysis (TG/DTA). This multi-technique approach revealed the degree of amorphization (on fresh samples) and the possible presence of crystalline phases on thermally treated samples, the strength and length of the Si-O bonds, able to produce after the thermal treatment modified oxides, which increase the number of non-bridging oxygen atoms and, finally, to study their thermal behavior by analyzing all the physical (i.e. crystallization) and chemical processes occurring during heating up to 1200°C.

References

[1] P.M. Preshaw, A.L. Alba, D. Herrera, S. Jepsen, A. Konstantinidis, K. Makrilakis, et al., *Diabetologia*,**2012**, *55*, 21-31.
[2] W. Vogel,W. Holand, *J. Non-Cryst. Solids*,**1990**, 123, 349-353.
[3] L.L. Hench, *J. Am. Ceram. Soc.*,**1991**, 74, 1487-1510.
[4] S. Midha, T.B. Kim, W. Van Den Bergh, P.D. Lee, J.R. Jones, C.A. Mitchell. Acta Biomater., **2013**, 9, 9169-9182.

Radiation synthesis of nanogels as therapeutic agent vectors

C. Dispenza[1,2], M.A. Sabatino[1], L.A. Ditta[1], A. Ajovalasit, G. Spadaro[1]

[1] *Dipartimento di Ingegneria Chimica, Gestionale, Informatica, Meccanica, Università degli Studi di Palermo, Edificio 6, Viale delle Scienze 90128 Palermo, Italy.*
[2] *CNR-Istituto di Biofisica U.O.S. di Palermo, via Ugo La Malfa 153 90146, Palermo, Italy.*

Email: clelia.dispenza@unipa.it

Nanogels (NGs) are physically or chemically crosslinked polymer networks and are promising candidates in the development of therapeutic agent vectors. In fact, thanks to their tunable size and properties, they offer unique advantages, including a large and flexible surface for multivalent bio-conjugation, an internal 3D aqueous environment for incorporation and protection of (bio)molecular drugs, stimuli-responsiveness to achieve temporal and/or site control of the release function and biocompatibility.

In order to develop effective NGs-based biomedical devices an inexpensive, robust and versatile synthetic methodology is required. In this perspective, we have produced NGs with high yields and through-puts by pulsed electron-beam irradiation. In particular, using an industrial electron accelerator, carboxyl functionalized NGs from a dilute aqueous solutions of poly(N-vinyl pyrrolidone) (PVP), and acrylic acid as functional monomer have been produced. This process allows simultaneous polymer cross-linking and monomer grafting. Moreover, depending on the value of the total irradiation dose, also the sterilization of the irradiated material can be obtained. Since organic solvents, toxic initiators or catalysts and surfactants are not required, this procedure can be defined as an eco-friendly and clean one.

Crosslinked nanoparticles with multi-armed surfaces, and size, crosslinking density, and surface electric charge density controlled, have been generated. Nanogels produced have been proven to be hemocompatible and not cytotoxic or genotoxic at the cellular level.

NGs have been decorated with fluorescent probes, proteins and anti-MiR. Thanks to the use of fluorescent variants, it has been argued that NGs showed a good affinity for cells, as they rapidly and quantitatively bypass the cellular compartments, accumulating in specific cell portions for the first hours, and being completely released from the cells in the next 24 hours. Moreover, it has been proven that the proteins and anti-MiR, once conjugated, maintain their biological activity giving rise to targeting features toward specific cell types.

References

[1] C. Dispenza, M.A. Sabatino, N. Grimaldi, G. Spadaro, D. Bulone, M.L. Bondì, G. Adamo, S. Rigogliuso, *Chem. Eng. trans.*, **2012**, 27, 229-234.
[2] M.A. Sabatino, D. Bulone, M. Veres, A. Spinella, G. Spadaro, C. Dispenza, *Polymer*, **2013**, 54 (1), 54-64.
[3] C. Dispenza, M.A. Sabatino, N. Grimaldi, D. Bulone, M.L. Bondi, M.P. Casaletto, S. Rigogliuso, G. Adamo, G. Ghersi, *Biomacromolecules,* **2012**, 13, 1805-1817.
[4] N. Grimaldi, M.A. Sabatino, G. Przybytniak, I. Kaluska, M.L. Bondì, D. Bulone, S. Alessi, G. Spadaro, C. Dispenza, *Rad. Phys. Chem.*, **2014,** 94, 76-79.
[5] S. Rigogliuso, M.A. Sabatino, G. Adamo, N. Grimaldi, C.Dispenza, G. Ghersi, *Chem. Eng. trans.* **2012**, 27, 247-252.

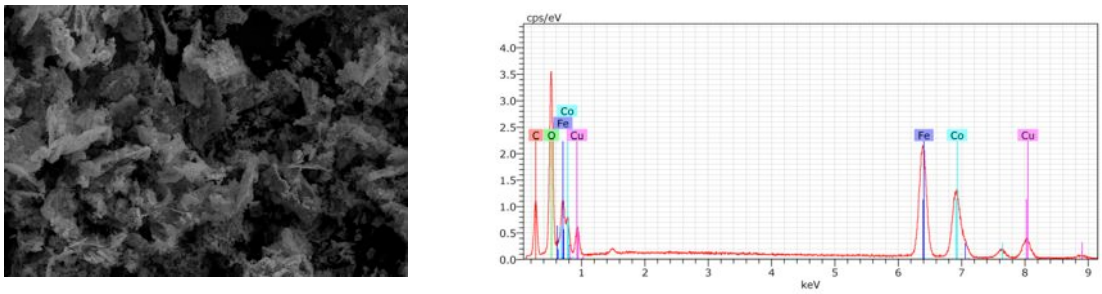
Sol-gel auto combustion synthesis of spinel ferrites nano-particle $CoM_xFe_{2-x}O_4$ (M = Ni, Cu, Mn and Ca) and $SrM_xFe_{2-x}O_4$ (M = Ni, Cu): structural characterization and photocatalytic activity

Khadija Eddahaoui[1,2], Alberto De Riccardis[1], Giuseppe Mele[1], Said Benmokhtar[2], Rachid Essehli[3], M. A. Deyab[4]

[1] Department of Engineering for Innovation of University of Salento, via Arnesano 73100, Lecce, Italy
[2] University Hassan II of Casablanca, Faculty of Sciences Ben M'sik, Laboratory of Chemistry and Physics of Materials, Department of Chemistry, Casablanca, Marocco.
[3] Qatar Environment and Energy Research Institute (QEERI) Bg CP4, Qatar Foundation, Doha, Qatar.
[4] Egyptian Petroleum Research Institute (EPRI), PO Box 11727, Nasr City, Cairo, Egypt.

Email: khadija_eddahaoui@yahoo.fr

Synthesis and characterization of spinel ferrites nano-particle CoM_xFe_2-xO_4 (M = Ni, Cu, Mn and Ca) and SrM_xFe_2-xO_4 (M = Ni, Cu) by sol-gel auto combustion method for photocatalytic degradation of 4-nitrophenol under UV-Visible light irradiation in aqueous dispersions in the presence of H_2O_2 is here reported.
Spinel ferrites are well known as one of the most important scientific and industrial materials by virtue of their electrical and magnetic properties [1].Their application range from electronic devices to photocatalysis [2–4].
In this view the catalytic activity of the entire ferrite composition was studied in 4-nitrophenol (4-NP) degradation reactions.
Full characterization of material (XRD, SEM, EDAX,IR, UV-Vis and Raman spectroscopies) is also reported. Selected results have been in Figure 1.



(A)

Fig. 1. SEM image and EDAX spectrum of (A) CoCu0.5Fe1.5O4.
The SEM image and EDAX spectrum of CoCu0.5 Fe1.5O4 have been reported in Figure 1.

The photocatalytic activity decreases in following order: $CoCu_{0.5}Fe_{1.5}O_4$>$SrCu_{0.5}Fe_{1.5}O_4$>$SrNi_{0.5}Fe_{1.5}O_4$>$CoMn_{0.5}Fe_{1.5}O_4$>$CoNi_{0.5}Fe_{1.5}O_4$ showing that the most efficient $CoCu_{0.5}Fe_{1.5}O_4$ is able to completely degrade 4-NP in 33 min.

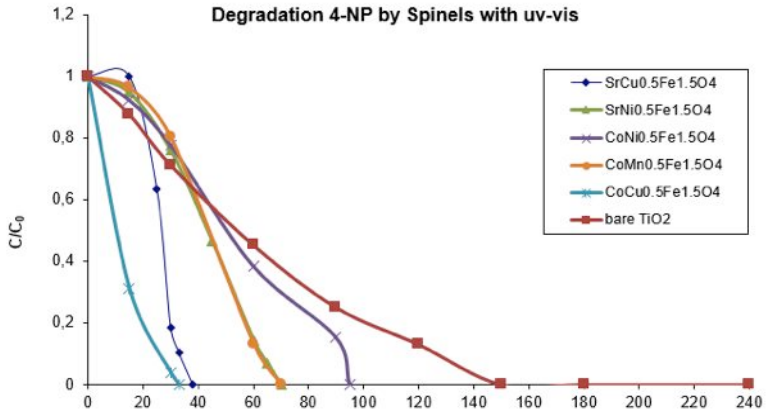


Fig.3 Degradation of 4-NP as a function of irradiation time in the presence of different photocatalysts, with H_2O_2 and air bubbling. Experimental conditions: [4-NP] = 20 mgL-1, catalyst amount: 0.08 gL-1; reaction volume= 300 mL; lamp: UV-vis lamp SANOLUX, 300 W

In conclusion, we have demonstrated as combined H_2O_2/ spinel ferrites nano-particle based processes can be applied as effective catalysts for degradation of organic pollutants in aqueous solution such as industrial wastewater and polluted water resources.

References

[1] A.Goldman, Modern FerriteTechnology, second ed., Springer, Pittsburgh,2006.
[2] M.A. Gabal, S.S. Ata-Allah, Mater. Chem. Phys. 85 (2004) 104–112.
[3] Y. Chen, J.E. Snyder, C.R. Schwichtenberh, K.W. Dennis, R.W. Mc-Callum, D.C.Jiles, IEEE Trans. Magn. 35 (1999) 3652–3654.
[4] Y. Chen, J.E. Snyder, K.W. Dennis, R.W. McCallum, D.C. Jiles, J. Appl. Phys. 87(2000) 5789-5800.

Solid acid catalysts for citrus wastes depolymerisation via direct hydrolysis.

C. Espro, B. Gumina, M. Fazio, D. Iannazzo, A. Pistone, S. Galvagno

Department of Electronic Engineering, Chemistry and Industrial Engineering, University of Messina, Contrada di Dio - 98166 Messina, Italy

Email: espro@unime.it

World production of citrus fruits has experienced continuous growth in recent decades. Brazil, Mediterranean countries (particularly Spain and Italy), United States and China represent more than two-thirds of global production of citrus fruits which is over 88 million tons per year [1]. Oranges constitute the bulk of citrus fruit production, and a large portion of this production is addressed to the industrial extraction of citrus juice, which leads to huge amounts of residues, including peel, segment membranes and other by-products considered as citrus wastes (CWs). The citrus processing residues are rich in both soluble and insoluble carbohydrates, which make them an attractive potential feedstock for biological conversion into value added products, by preliminary chemical or enzymatic hydrolysis and subsequent biological conversion. Cellulose is a key component of citrus waste, whose conversion by hydrolysis of the β-1,4 glycosidic bonds into useful sugars (saccharides) is of interest as a means of producing cellulosic ethanol fuel and a variety of industrially important chemicals [2-3]. Therefore, the aim of this work is to develop an efficient green orange peels depolymerisation process, based on the direct cellulose hydrolysis on solid acid catalysts, under mild conditions. Preliminary results on the performance evaluation of various commercial and non commercial solid acid catalysts will be outlined. The citrus wastes depolymerisation via direct catalytic hydrolysis, under mild condition (P, 1 atm; T, 80-120°C), leads to the formation of high added values saccharides (glucose, fructose, sucrose), and soluble organic acids. The influence of reaction parameters on the activity and selectivity towards the formation of high added value products, will be presented. A preliminary account of the physical-chemical and morphological properties of titled catalytic materials, determined by means of SEM, TEM, XRD, BET and TGA techniques will be reported.

References

[1] S.V. de Vyver, J. Geboers, P. A. Jacobs and B. F. Sels, *ChemCatChem*,**2011**, *3*, 82-94.
[2] I. Choi, Y. Lee, S.K. Khanal, B. J. Park, H.J. Bae, *Appl. Energy*, **2015**, *140*, 65-74
[3] G. Santi, S. Crognale, A. D'Annibale, M. Petruccioli, M. Ruzzi, R. Valentini, M. Moresi, *Biomass and Bioenergy*, **2014**, *61*,146-156

Synthesis, X Ray Structure and aggregation properties of a Zinc(II) salen Schiff-Base complex derived from *cis*-1,2-cycloexanediamine

Giuseppe Consiglio[1], Ivan Pietro Oliveri[2], Francesco Punzo[3], Santo Di Bella[2] and *Salvatore Failla[1]*

[1] *Dipartimento di Ingegneria Industriale, Università di Catania, I-95125 Catania, Italy.*

E-mail: sfailla@dmfci.unict.it

[2] *Dipartimento di Scienze Chimiche, Università di Catania, I-95125 Catania, Italy.*

E-mail: sdibella@unict.it

[3] *Dipartimento di Scienze del Farmaco, Sezione Chimica, Università di Catania, I-95125 Catania, Italy*

Tetracoordinated Zn^{II} Schiff-base complexes are Lewis acidic species that saturate their coordination sphere by coordinating a large variety of Lewis bases with formation of monomeric species, or in their absence, can be stabilized through intermolecular Zn···O axial coordination involving Lewis basic atoms of the ligand framework with formation of aggregated systems.[1,2] Alternatively, the appropriate design of ligands possessing flexible Lewis donor atoms as side substituents, suitable to axially coordinated the Zn^{II} atom of another molecular unit, allows the achievement of new tailored Zn^{II} supramolecular architectures.[3] For the amphiphilic bis(salicylaldiminato)Zn^{II} Schiff-base complexes having conjugated diamine bridge, the degree of aggregation is influenced by nature of the bridging diamine and concentration of the solution.[1,2]

This contribution explores the effect of the bridging diamine upon the aggregation properties of the title complex, both in the solid state and in solution. The X-ray structure shows the presence of a densely packed dimer in the solid state which pentacoordinates two Zn atoms involved in a μ-phenoxo bridge. Detailed studies in solution, through ^{1}H NMR, DOSY NMR, and optical spectroscopic investigations, indicate the typical aggregation/deaggregation behaviour on switching from non-coordinating to coordinating solvents, in relation to the Lewis acidic character of such Zn^{II} complex.

References

[1] G. Consiglio, S. Failla, P. Finocchiaro, I. P. Oliveri, R. Purrello, S. Di Bella, *Inorg. Chem.*, **49**, 5134-5142, (2010).

[2] G. Consiglio, S. Failla, P. Finocchiaro, I. P. Oliveri, S. Di Bella, *Dalton Trans.*, **41**, 387-395, (2012).

[3] I. P. Oliveri, S. Failla, G. Malandrino, S. Di Bella, *New J. Chem.*, **35**, 2826-2831, (2011).

Bioactive compounds on Lodoicea Maldivica fruits: Their determination by CG-MS

Stefano Falcinelli[1,2], Marzio Rosi[1], Federico Giorgini[2], Martino Giorgini[2], Marta Bettoni[2], Bartolomeo Sebastiani[3], Franco Vecchiocattivi[1]

[1]Dipartimento di Ingegneria Civile ed Ambientale, Università di Perugia, 06125 PERUGIA, ITALY
[2]Vis Medicatrix Naturae S.r.l., 50034 MARRADI (FI), ITALY
[3]Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, 06123 PERUGIA, ITALY

Email: stefano.falcinelli@unipg.it

The Lodoicea Maldivica, commonly named “Coco de mer” or “Double Coco-Nut”, is a native palm of the Seychelles islands in the Indian Ocean. The about 4000 palms of the “Coco de mer” are protected and despite the importance of the site, the local government allows to sold with high price all hundreds of coco-nuts picked every year, e.g. 701 nuts in 2003 [1]. These palms are considered as the last witness of the old continent “Gondwana”, formed by Africa, Madagascar and India, which 65 millions of years ago split into a number of lands leaving Seychelles alone. The dried “Coco de mer” kernel is exported in various parts of the world, especially the Middle East and China, where it has been used for centuries in traditional medicine and in “ayurvedics”, both as an aphrodisiac and for rejuvenating cosmetic creams and to treat other pathologies such as coughs. Despite the characteristics mentioned above, it has never been studied from a chemical point of view. The analytical study here presented intends to fill this gap with particular attention to highlight the healthy and food safety use of the fruit, and the possible presence of chemical compounds interesting from a nutritional and pharmacological point of view. The analysis was performed by GC-MS technique to determine phytosterol and fatty acid composition profiles in internal and external pulp. Total phytosterol content was almost constant in both kernel coco-nut (24.6 μg/g for the external and 22.5 μg/g for the internal portion). The fatty acid pattern has been determined. The composition was characterized by seven saturated acids ranged from C14:0 (myristic) to C20:0 (arachidic) and two monounsaturated acids, the palmitoleic (C16:1, ω7) and the oleic (C18:1, ω9). Palmitic acid (C16:0) was the predominant one with contribution of about 49% followed by pentadecanoic, stearic (C18:0) and myristic acids (C14:0) in all two examined kernel parts.

References

[1] S. Falcinelli, M. Giorgini, B. Sebastiani, *Applied Engineering Sciences, Ed. By Wei Deng - Taylor & Francis Group, London,* **2015**, *Chapter 19,* 99-104. ISBN: 978-1-138-02649-0

Preparazione e caratterizzazione di compounds a base di poli(lattide) con ritardanti di fiamma "halogen free"

Maurizio Fiorini[1,2], Stefano Oradei[1], Raffaele Morelli[2],

[1]DICAM, Università di Bologna, via Terracini 28 40131 Bologna, Italy
[2]CIRI MAM, Università di Bologna, via Terracini 28, 40131 Bologna, Italy

Email: maurizio.fiorini@unibo.it

Il poli(lattide) (PLA) rappresenta oggi il polimero ottenuto da fonti rinnovabili con le maggiori prospettive di sviluppo in numerosi settori industriali [1, 2]. IBM ha che entro la fine del 2014 verrà commercializzata una nuova linea di server in cui alcuni pannelli esterni sono stampati con leghe policarbonato/PLA con ritardanti di fiamma[2]. Pertanto, lo sviluppo di formulazioni a base di PLA contenenti ritardanti di fiamma "halogen free" rappresenta un tema di ricerca interessante e attuale, anche se complesso.
Questo contributo descrive la preparazione e caratterizzazione di formulazioni a base di poli(lattide) contenenti ritardanti di fiamma intumescenti "halogen free" [3,4]. Compounds a base di PLA (Ingeo 4043D di Natureworks e altri gradi prodotti da Sulzer) sono stati prodotti con un estrusore bivite Coperion ZSK-18. Per le diverse formulazioni intumescenti sono stati impiegati alcuni tipi di polifosfato d'ammonio combinato con polioli quali il pentaeritritolo (PER, un componente utilizzato in diversi studi già descritti in letteratura [4], che quindi è stato usato da noi come riferimento). In alternativa al PER sono stati inseriti la glicerina e oligomeri del PLA. In alcune formulazioni è stato anche aggiunto un derivato della melammina come agente espandente. I campioni per le diverse prove di caratterizzazione sono stati stampati a iniezione con una pressa Negri Bossi VE70-240. I risultati dei tests di Limiting Oxygen Index, Glow wire temperature, rating secondo UL-94 e delle proprietà meccaniche a trazione sono discussi in relazione alla composizione dei compounds.

References

[1] AIM, Workshop su "Opportunità applicative del PLA: Problematiche e Aspettative" Alessandria, 25 febbraio 2014.
[2] Innovation Takes Roots, Orlando (USA), 17-19 febbraio 2014.
[3] C. Reti, M. Casetta, S. Duquesne, S. Burbigot e R. Delobel, *Polym. Adv. Technol.* 19, 628 (2008)
[4] S. Burbigot, G. Fontaine, *Polym. Chem.*, 1, 1413 (2010)

Saldatura laser di film polimerici sottili per applicazioni nel packaging

Maurizio Fiorini[1], Giampaolo Campana[2], Raffaele Morelli[3], Nunziante Pagano[3]

[1]DICAM, Università di Bologna, via Terracini 28 40131 Bologna, Italy
[1]DIN, Università di Bologna, via Terracini 24 40131 Bologna, Italy
[3]CIRI MAM, Università di Bologna, via Terracini 28, 40131 Bologna, Italy

Email: maurizio.fiorini@unibo.it

L'industria dell'imballaggio impiega su larga scala film polimerici di spessore inferiore a 100 micron. La saldatura di film di spessore così sottile richiede un controllo molto preciso di diversi parametri di processo e dell'omogeneità dei materiali. La saldatura con lama calda oppure a radiofrequenza e la giunzione con un solvente opportuno sono esempi di tecnologie più tradizionali, largamente diffuse nel settore dell'imballaggio.
La saldatura laser è una tecnologia già largamente diffusa nella giunzione di acciai al carbonio, basso-legati ad alta resistenza e inox [1]. Inoltre viene applicata a leghe di alluminio, magnesio e di titanio [2]. Più di recente è stata adattata alla saldatura di componenti in materiali polimerici per l'industria automobilistica (sensori per airbag, quadri per contachilometri, etc.) e sensori per l'industria elettronica [1]. Tale tecnologia è investigata ed ha trovato le prime applicazioni anche per la saldatura di materiali dissimili dove, in particolare per i metalli dissimili, consente di limitare i difetti qualitativi tipici dei processi tradizionali [3] oppure consente di realizzare processi innovativi, come nel caso della saldatura di metalli con polimeri [4]. In questa comunicazione, film sottili preparati a partire da poli(lattide) sono stati saldati assieme e su film di alluminio, usando come sorgente un laser a stato solido. La resistenza delle saldature è stata misurata mediante prove a trazione con un dinamometro Instron 5966. Il materiale lungo il cordone di saldatura e nelle zone immediatamente ai lati è stato esaminato mediante cistoscopia FTIR e Raman. Nel caso della giunzione film su film, sono state realizzate giunzioni con cloroformio, un buon solvente per il poli(lattide) allo scopo di avere un benchmark di riferimento realizzato con una tecnica tradizionale.

References

[1] Rolf Klein, "Laser Welding of Plastics", Wiley-VCH Verlag, 2012.
[2] T. Luijendijk, Welding of dissimilar aluminium alloys, Journal of Materials Processing Technology, 103, p. 29-35, 2000.
[3] Xiu-Bo Liua, Ming Panga, Zhen-Guo Zhangb, Wei-Jian Ninga, Cai- Yun Zhenga, Gang Yua, Characteristics of deep penetration laser welding of dissimilar metal Ni-based cast superalloy K418 and alloy steel 42CrMo, Optics and Lasers in Engineering, Vol.45, p. 929-934, 2007.
[4] S. Katayama, Y. Kawahito, Y. Niwa, S. Kubota, Laser-assisted metal and plastic joining. In Proc. of the 5th LANE 2007 Conference, Erlangen, September 2007, pages 41–51, 2007.

A novel Pluronic/Alginate scaffold for 3D liver cell culture

Sara Maria Giannitelli, Manuele Gori, Pamela Mozetic, Marcella Trombetta, Alberto Rainer

Department of Engineering, Tissue Engineering Lab, Università Campus Bio-Medico di Roma, via Alvaro del Portillo 21, 00128 Rome, Italy

Email: a.rainer@unicampus.it

Background: One of the major obstacles to the diffusion of additive manufacturing (AM) in tissue engineering has long been represented by the limited set of available biomaterials that could be directly processed. In this regard, processing of hydrogels represents a main challenge in view of soft tissue engineering applications. Furthermore, direct manufacturing of tissue precursors with a cell density similar to native tissue has the potential to overcome the extensive *in vitro* culture required for conventional cell-seeded scaffolds. Aim of this study was the investigation of hepatic metabolism in a novel composite 3D scaffold, which better approximates the *in vivo* liver conditions compared to a conventional cell culture system.

Methods: Pluronic/alginate scaffolds were fabricated by pressure-assisted deposition using a custom designed AM equipment [1]. A pluronic/alginate solution (20 wt% PF127, 2 wt% sodium alginate in diluted DMEM) was loaded into a gel dispensing syringe at 4 °C. The syringe was then heated to 37 °C, leading to gelation, and gel was extruded through a 250 µm nozzle at a pressure of 1.2 bar. Squared scaffolds were obtained by depositing layers of fibers laminated in a 0°/90° pattern. Scaffolds were briefly exposed to a sterile 25 mM $CaCl_2$ aq. solution to induce alginate crosslinking. Mechanical properties were assessed by unconfined compression tests. Scaffold degradation was measured in terms of weight loss following incubation in PBS. Similarly, cell-laden constructs were prepared by suspending HepG2 cells, a human hepatoblastoma cell line that retains many characteristics of normal differentiated hepatocytes [2], at a concentration of $2x10^6$ cells/mL into ice-cold polymer solution. Afterwards, the gel was extruded at 37 °C using the previously described equipment. Cell morphology and distribution within the scaffold were assessed by immunofluorescence staining. After 24h, cell viability was determined by Trypan Blue and Vybrant cytotoxicity assay. Proliferation of HepG2 cells on the AM-scaffold, in comparison with a 2D culture plate, was investigated by MTT (3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyl tetrazolium bromide) assay at selected time points (i.e., 1, 4, 7 days). To study the liver-specific functions of the HepG2 cells embedded into the scaffold, secreted albumin and urea levels were determined through specific ELISA assays.

Results: 3D structures with controlled architectures were successfully manufactured starting from a pluronic/alginate system, in which pluronic F127 conferred thermo-sensitive properties, while alginate endowed the formation of a strong gel upon exposure to bivalent cations in aqueous solution. This positive combination led to constructs with precisely defined microarchitectures and enhanced stability. Embedded HepG2 cells survived the deposition process, homogeneously spread inside the gel phase, and showed albumin and urea production during the culture period.
Conclusions: Our cell-laden scaffold provides optimal conditions for hepatic cell proliferation as well as a suitable microenvironment for liver-specific metabolic functions. In light of the obtained results, the proposed 3D culture system may represent a novel human hepatic model for drug screening and toxicological studies.

References
[1] A. Rainer, S.M. Giannitelli et al. Ann Biomed. Eng, **2012**, 40, 966-975.
[2] N.B. Javitt,FASEB J., **1990**, 4, 161-168.

A novel model of nonalcoholic fatty liver disease in a 3D liver-on-chip device

Manuele Gori[1], Maria Chiara Simonelli[1], Luca Businaro[2], Marcella Trombetta[1], Alberto Rainer[1,2]

[1]Department of Engineering, Tissue Engineering Lab, Università Campus Bio-Medico di Roma, via Alvaro del Portillo 21, 00128 Rome, Italy
[2]Institute for Photonics and Nanotechnologies, National Research Council (CNR), Rome, Italy

Email: a.rainer@unicampus.it

Background: Nonalcoholic fatty liver disease (NAFLD) is a chronic liver disease, ranging from simple steatosis to nonalcoholic steatohepatitis (NASH), which may progress to cirrhosis, leading eventually to hepatocellular carcinoma (HCC). HCC ranks as the third highest cause of cancer-related death globally, requiring an early diagnosis of NAFLD as a potential risk factor [1,2]. However, the molecular mechanisms underlying NAFLD are still under investigation. So far, many *in vitro* studies on NAFLD have been hampered by the limitations of 2D culture systems, in which cells rapidly lose tissue-specific functions. The present liver-on-chip approach aims at filling the gap between conventional *in vitro* models, often scarcely predictive of an *in vivo* condition, and animal models that are potentially biased by their xenogeneic nature.
Materials & Methods: Microfluidic devices were fabricated by soft-lithography, starting from a photolithographically-obtained SU-8 master that was used as a mold for replicas in polydimethylsiloxane (PDMS), and seeded with HepG2 cells, a human hepatoblastoma cell line that retains many characteristics of normal differentiated hepatocytes [3]. Cells were cultured in 3D under microfluidic perfusion, through a system of parallel micrometric channels that mimic the endothelial-parenchymal interface, allowing the necessary diffusion of nutrients [4]. A continuous flow of medium (flow rate of 18,3 uL/day), supplemented with a mixture of Free Fatty Acids (FFAs), namely Palmitic and Oleic acid at a final concentration of 1mM, was provided for different time-points in culture. Controls were represented by on-chip and 2D adherent cultures in plain medium. Intracellular lipid accumulation was measured using AdipoRed assay (Lonza). Cell viability was evaluated using LIVE/DEAD assay (Life Technologies), and oxidative stress by analyzing intracellular ROS levels through 2',7'-dichlorodihydrofluorescein diacetate (H_2DCFDA, Life Technologies).
Results: Our preliminary data show that the FFA treatment produced a marked intracellular lipid accumulation, different cytotoxic effects and ROS levels compared to 2D controls. Overall, the liver-on-chip system provides a more suitable culture microenvironment than traditional 2D cultures, thereby representing a

better and more reliable model, close to the liver pathophysiology *in vivo*, for investigating NAFLD pathogenesis.

Discussion: The liver-on-chip approach constitutes a paradigm shift for developing robust 3D *in vitro* models, representative of *in vivo* liver metabolic disorders, to unveil the molecular basis of NAFLD. In a long-term perspective, liver-on-chip implementation may boost the evaluation of therapeutic effects, selection of tailored treatments and novel therapeutic targets in both NAFLD and other metabolic disorders. This work will be extremely relevant to build a bridge between liver studies and micro-technologies, providing a starting point in genome- or proteome-scale analysis in the framework of metabolic diseases.

Acknowledgements:
Dr. Gori is supported by a "Fondazione Umberto Veronesi" fellowship.

References:

[1] P. Angulo, N Engl J Med., **2002**, 346, 1221-31.
[2] B.Q. Starley, C.J. Calcagno, S.A. Harrison, Hepatology, **2010**, 51, 1820-32.
[3] N.B. Javitt, FASEB J., **1990**, 4, 161-168.
[4] P.J. Lee, P.J. Hung, L.P. Lee, Biotechnol. Bioeng., **2007**, 97, 1340-46.

Platinum free catalysts for Microbial fuel cell application

Alessandro Iannaci[1], Barbara Mecheri[1], Silvia Licoccia[1] and Alessandra D'Epifanio[1]

[1]Dip. Scienze e tecnologie Chimiche Università degli studi di Roma "Tor Vergata", Via della Ricerca Scientifica 00133- Rome, Italy

email: alessandro.iannaci@uniroma2.it

Microbial fuel cell (MFC) is an innovative technology based on the ability of bacteria found on waste to digest organic matter through a cascade of redox reactions, producing electricity with the use of different kind of organic sources such as domestic wastewater as fuel, and reducing also problems linked to their disposal. The MFC performance is greatly affected by the cathode side [1], where oxygen is the most popular cathodic electron acceptor due to its charge-free nature and high redox potential characteristic. The use of platinum (Pt) as catalyst for the oxygen reduction reaction (ORR) significantly contributes to device cost, thus representing one obstacle to the commercial development of MFCs.Also, it is well known that Pt can be easily poisoned by several contaminating agents, reducing cathode lifetime. To overcome those problems, we employed two different strategies in order to realize Pt free cathodes based on novel and cheap ORR active materials: Zirconium oxide (ZrO_2) and Iron phthalocyanine (FePc). The ZrO_2 have been mixed with carbon Vulcan (C) at different compositions by mechanical milling whereas, FePc have been mixed with Polyindole (PID) and C and multiwalled carbon nanotubes (CNTs) in methanol solvent (FePc/PID/C and FePc/PID/CNTs). The obtained samples were characterized by Scanning Electron Microscopy and Energy Dispersive X – Ray Spectroscopy (SEM-EDS), BET surface area and cyclic voltammetry (CV). Preliminary investigation allowed to select the most performing mixtures of those two catalytic families: C/ZrO_2 (90/10 and 75/25 wt./wt.) and FePc/PID/CNTs (nominal ratio FePc:(PID+Carbon) 1:1 wt/wt) that were be assembled as cathodes in a single chamber air breathing cathode MFC prototype. Polarization and coulombic efficiency data showed an improved performance in the case of MFC assembled with both C/ZrO_2 based cathodes compared with bare C. In case of FePc/PID/CNTs electrochemical performance are comparable with commercial Pt/C based catalyst. FePc/PID/CNTs cathode achieved a maximum power density of 799 ± 41 mWm^{-2} and a current density of 3480 ± 83 mAm^{-2} that are higher respect to Pt/C one (646 ± 25 mWm^{-2} and 3011 ± 84 mAm^{-2}, respectively). The long-term MFC operation conducted for 700 h indicated a stable performance of FePc/PID/CNTs cathode, demonstrating its potential ability to substitute Pt catalyst for ORR in MFCs.

References

[1] M.T. Nguyen, B. Mecheri, A. D'Epifanio, T.P. Sciarria, F. Adani, S. Licoccia, *Int. J. Hydrogen Energ.*, **2014**, *39*, 6462-69.

Carbon nanostructured materials as drug delivery systems for antiviral agents

D. Iannazzo[1], A. Pistone[1], C. Espro[1], S. Ferro[2], L. De Luca[2], A.M. Monforte[2], S. Galvagno[1]

[1] Department of Electronic Engineering, Chemistry and Industrial Engineering, University of Messina, Contrada di Dio - 98166 Messina, Italy
[2] Department of Pharmaceutical Sciences and Health Products, University of Messina, Viale Annunziata, I-98168 Messina, Italy

Email: diannazzo@unime.it

The use of nanomaterials in medicine raises high expectations for human health and nanotechnology is already contributing to the development of new drugs, biologics, and medical devices [1]. The materials based drugs at the “nano” scale possess physicochemical properties distinct from those of bulk materials or single molecules or atoms, which critically may influence their interaction with the biological systems. Among the different classes of nanomaterials the carbon allotropes, fullerenes, carbon nanotubes (CNT) and more recently, carbon nanodots and their functionalized derivatives have attracted particular attention in antiviral therapy. In order to prove their in vitro ability to form strong interactions with viral enzymes and to act as HIV inhibitors, we have studied the antiviral activity of highly hydrophilic and dispersible carboxylated multi-walled CNT that exerted by the same nanomaterial bearing antiretroviral drugs and hydrophilic functionalities [2]. From this study, the physicochemical properties of these nanomaterials, namely hydrophilicity and dispersibility, emerged as the most relevant features able to control the antiviral activity. The presence of free carboxylic groups inducing a better water dispersibility of the nanomaterial, necessary for biological applications, seems to be relevant for the interaction with biological counterparts by means of electrostatic or hydrogen bonds. So, preliminary investigations have been also performed on the development of a new class of highly dispersible and hydrophilic carbon nanomaterials, such as carbon nanodots [3]. Because of their excellent water solubility and the possibility to be revealed in a biological medium, these materials have been investigated as drug delivery systems for non nucleoside reverse transcriptase inhibitors.

References

[1] S. Marchesan, M. Prato, *ACS Med Chem Lett* **2013**, *4*, 147–149.
[2] D. Iannazzo, A. Pistone, S. Galvagno, S. Ferro, L. De Luca et al, *Carbon*, **2015**, *82*, 548–561.
[3] H. Li, Z. Kang, Y. Liu, S.T. Lee, *J. Mater Chem* **2012**, *22*, 24230-53.

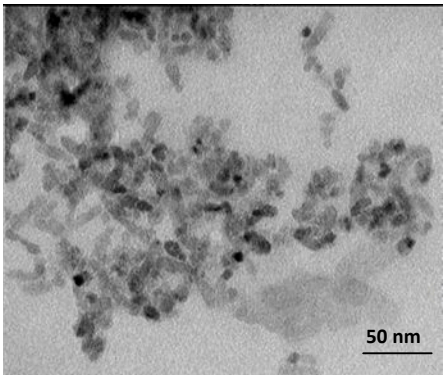
TiO_2 mediated photocatalytic polymerization of DHICA: a new straightforward synthetic strategy to hybrid materials

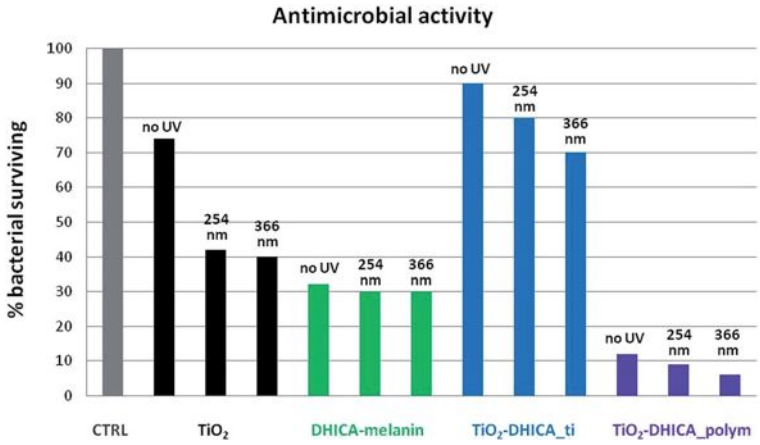
Giuseppina Luciani[1], Giuseppe Vitiello[1], Brigida Silvestri[1], Aniello Costantini[1], Francesco Branda[1], Alessandro Pezzella[2]

[1] Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, DICMAPI, Università di Napoli Federico II, p.le V. Tecchio 80, 80125 Napoli
[2] Dipartimento di Scienze Chimiche, Università di Napoli Federico II, via Cintia 4, 80126 Napoli

Email: luciani@unina.it

Organo-inorganic hybrids, made by coupling inorganic phases to organic molecules, not only combine the often dissimilar characteristics of inorganic and organic components into one material, but often show unique and peculiar properties. This provides the opportunity to invent a huge set of new multifunctional materials with a wide range of applications in the fields of energy, health and electronics. In this continuous look for organo-inorganic pairings eumelanins and more generally melanin-like materials offer a noteworthy prospect for the development of novel hybrid functional materials inspired to biologically active natural products. Melanins show very intriguing properties such as high immunogenicity, protection against UV-radiation as well as intrinsic antimicrobial activity. Eumelanins can be produced in vitro by oxidative polymerization of indoles such as 5,6 dihydroxyindole-2-carboxylic acid (DHICA). Titanium dioxide (TiO_2) is an inexpensive, environmentally friendly, nontoxic material, as well as high performance catalyst in photo-oxidative processes. This TiO_2 property has been actually exploited to catalyze DHICA polymerization by oxidative reactions; ultimately leading to hybrid TiO_2-DHICA nanostructures, through in-situ hydrothermal synthesis [1,2]. Physico-chemical characterization through Electron Paramagnetic Resonance (EPR) spectroscopy, X-ray diffraction (XRD), TEM microscopy, BET porosimetry, proved that both organic and inorganic phases strongly affect each other during in-situ formation, as far as it concerns both morphology and microstructure, conferring unique biocide properties to the resulting nanomaterials, even under visible under visible light irradiation. The proposed straightforward synthetic approach settles a new role for the inorganic phase, as an active agent in promoting formation of hybrid nanosystems and driving structure of the organic component, opening new perspectives in the design of multifunctional materials.





References

[1] G. Vitiello, A. Pezzella, A. Zanfardino,M. Varcamonti,B. Silvestri,A. Costantini,F. Branda and G. Luciani, J. Mater. Chem B, **2015**, **3**, 2808-15

[2] A. Pezzella, L. Capelli, A. Costantini, G. Luciani, F. Tescione, B. Silvestri, G. Vitiello, F. Branda, *Mater. Sci. Engin. C*, **2013**, 33, 347-55.

Confronto tra attività catalitica e fotocatalitica dell'eteropoliacido di Keggin $H_3PW_{12}O_{40}$ supportato su ossidi o su nanotubi di carbonio

Giuseppe Marcì, Elisa García-López, Marianna Bellardita, Francesca Rita Pomilla, Leonardo Palmisano, Aleksandra Kirpsza, Anna Micek-Ilnicka

"Schiavello-Grillone" Photocatalysis Group, Dipartimento di Energia, Ingegneria dell'informazione, e modelli Matematici (DEIM), Università degli Studi di Palermo, Viale delle Scienze Ed. 6, 90128, Palermo. Italy.

giuseppe.marci@unipa.it

In questo contributo viene riportato lo studio della reazione sia catalitica sia fotocatalitica di disidratazione del 2-propanolo effettuata utilizzando l'eteropoliacido di Keggin $H_3PW_{12}O_{40}$ supportato su vari ossidi metallici o su nanotubi di carbonio. Questi materiali binari sono stati preparati per impregnazione o attraverso un trattamento solvotermico utilizzando sia supporti commerciali: SiO_2 (Mallinckrodt), TiO_2 (Evonik P25) e nanotubi di carbonio (Sunnano) che supporti preparati solvotermicamente nel nostro laboratorio: SiO_2, TiO_2 o ZrO_2. Tutti i materiali sono stati caratterizzati mediante diffrazione dei raggi X (XRD), microscopia elettronica a scansione (SEM) con microanalisi (EDX), misure di area superficiale specifica e spettroscopia di riflettanza diffusa (DRS). Il mantenimento della struttura dell'anione Keggin è stata confermata in tutti i materiali binari sia mediante spettroscopia FTIR che mediante indagine Raman. La disidratazione (foto)catalitica di 2-propanolo è stata studiata in regime gas-solido sia utilizzando un (foto)reattore che lavora in continuo a pressione atmosferica e 80 °C, sia registrando gli spettri IR (da temperatura ambiente a 150 °C) sulla superficie dei solidi contenenti l'eteropoliacido su cui il 2-propanolo è stato precedentemente adsorbito. Per le reazioni foto-assistite il reattore è stato illuminato con LEDs. I principali prodotti di reazione osservati sono stati propene e diisopropil etere, tuttavia si osservano differenze significative utilizzando i diversi materiali binari. In ogni caso la presenza dell'eteropoliacido è risultata necessaria ai fini della reazione, sia catalitica che fotocatalitica, di disidratazione del 2-propanolo.

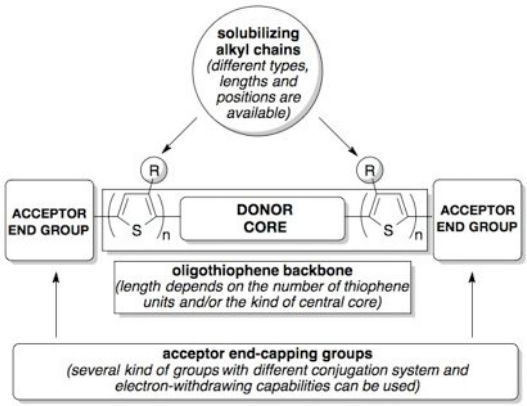
New Low Bandgap Oligothiophene Donors for Organic Photovoltaics

Leonardo Mattiello[1] and Francesca Brunetti[2]

[1]Dept. of Basic and Applied Sciences for Engineering - University of Rome "La Sapienza"
Via del Castro Laurenziano 7 - 00161 Rome Italy
[2]Center for Hybrid and Organic Solar Energy (CHOSE), University of Rome Tor Vergata (UTV), Italy
Via del Politecnico 1 - 00133 Rome Italy

Email: leonardo.mattiello@uniroma1.it

Compared to conjugated polymers, small molecules can offer several intrinsic advantages in organic electronics applications [1,2]. They possess well-defined chemical structures, and purity far higher with relatively simple low-cost syntheses and purification methods. Among small molecules for OPV [3], thiophene oligomers possess extended π- electron delocalization along the backbone and are good hole-transporting materials. In general, dipolar push-pull chromophores with highly polarizable π-electron systems with donor (D) and acceptor (A) groups possess properties that result from the existence of photoinduced intramolecular charge transfers at quite low energies. In Figure is depicted, as an example, one of the possible oligothiophene donor architecture (A-D-A). The Research Team works on the syntheses of novel oligothiophene derivatives with different lengths (in terms of thiophene units), different solubilizing alkyl chains, different endcapping groups with different electron-accepting properties can help to control the tunability of the wavelength range of absorption, and several "core" architectures, in order to achieve the goals of better physico-chemical, optical and electrochemical properties as valuable low bandgap donor materials in Organic Solar Cells [4].



References

[1] K. Mullen, G. Wegner (Editors), Electronic Materials: The Oligomer Approach. Wiley-VCH. ISBN: 978-3-527-61205-5, **2008**, (627 pages).
[2] Oligomeric derivatives of spirobifluorene, their preparation and use. L. Mattiello ; G. Fioravanti; L. Rampazzo; P. Stoessel; E. Breuning. Patent Property of Merck. JP2008506657, **2008**.
[3] A. Mishra, P. Bäuerle, Angew. Chem. Int. Ed., **2012**, *51*, 2020–2067.
[4] Y. Chen, X. Wan, G. Long, Acc. Chem. Res., **2013**, *46*, 2645–2655.

Release of N-acylethanolamines by biomaterials of clinical relevance

Pamela Mozetic[1], Tiziana Bisogno[1,2], Vincenzo Di Marzo[2], Mauro Maccarrone[1,3], Marcella Trombetta[1], Alberto Rainer[1]

[1]Endocannabinoid Research Group, Institute of Biomolecular Chemistry, National Research Council, Pozzuoli, Italy;
[2]Center for Integrated Research, "Università Campus Bio-Medico di Roma", Rome, Italy.
[3]European Center for Brain Research, Santa Lucia Foundation I.R.C.C.S., Rome, Italy.

p.mozetic@unicampus.it

Tissue engineering is considered an attractive field of research, in virtue of its promising potential for recovery and replacement of organ subunits. Targeting tissue regeneration or replacement, a good deal of the literature currently focuses on developing 3D scaffolds using synthetic polymers to reproduce the extracellular matrix (ECM) and provide a good substrate for cell adhesion, proliferation and differentiation. Electrospinning is one of the approaches that allow the fabrication of several synthetic materials into fibrous and porous structures in the micro- and nanometer scale. Moreover, electrospun materials can be functionalized with drugs for localized delivery.
Here, we report the convenient incorporation of N-acyl-ethanolamines (NAEs) into an electrospun polyesther scaffold for their sustained release in vitro.
Scaffolds were prepared starting from a 8 wt% poly(ε-caprolactone) (PCL) solution containing [14C]-AEA (0.1% w/w vs. PCL), that was electrospun at 15 kV onto a grounded target placed at 15 cm, with a feed rate of 1.5 mL/h. Scaffold morphology were characterized by Field Emission Scanning Electron Microscopy (FE-SEM). A time-dependence of AEA release by the scaffold was assessed by measuring the amount of radioactivity associated with the eluates for up to 14 days at 37 °C in PBS. Additionally, FAAH enzymatic assay performed in rat brain membrane preparation confirmed that AEA released by the scaffold was still substrate for its main hydrolytic enzyme.
In conclusion, we report data indicating that electrospun PLC scaffolds might be functionalized with AEA without interfering with its chemical structure and might be a good platform for AEA release. Moreover, the reported data encourage the use of biodegradable electrospun polymers as suitable delivery systems for AEA long-term administration on 3D cultured cells.

Electron, proton and water transfer along the catalytic cycle of the Photosystem II

Daniele Narzi[1], Daniele Bovi[1] and Leonardo Guidoni[1,2]

[1] University of L'Aquila

[2] La Sapienza - University of Rome

Email: daniele.narzi@gmail.com

Water oxidation in photosynthetic organisms occurs through the five intermediate steps S0–S4 of the Kok cycle in the oxygen evolving complex of Photosystem II (PSII). Along the catalytic cycle, four electrons are subsequently removed from the Mn_4CaO_5 core by the nearby tyrosine Tyr-Z, which is in turn oxidized by the chlorophyll special pair P680, the photo-induced primary donor in PSII. Recently, two Mn_4CaO_5 conformations, consistent with the S_2 state (namely, S_2^A and S_2^B models) were suggested to exist[1], perhaps playing a different role within the S_2-to-S_3 transition[2,3]. Here we report multiscale *ab initio* density functional theory plus U simulations revealing that upon such oxidation the relative thermodynamic stability of the two previously proposed geometries is reversed, the S_2^B state becoming the leading conformation. In this latter state a proton coupled electron transfer is spontaneously observed at ~100 *fs* at room temperature dynamics. Upon oxidation, the Mn cluster, which is tightly electronically coupled along dynamics to the Tyr-Z tyrosyl group, releases a proton from the nearby W1 water molecule to the close Asp-61 on the femtosecond timescale, thus undergoing a conformational transition increasing the available space for the subsequent coordination of an additional water molecule. The results can help to rationalize previous spectroscopic experiments and confirm that the water-splitting reaction has to proceed through the S_2^B conformation.

References

[1] D.A. Pantazis, W. Ames, N. Cox, W. Lubitz,F. Neese, *Ang. Chem. Int. Ed.*, **2012**, *51*, 9935–9940
[2] D. Bovi, D. Narzi, L. Guidoni, *Ang. Chem. Int. Ed.*, **2013**, *52*, 11744–11749.
[3] D. Narzi, D. Bovi, L. Guidoni, *Proc. Natl. Acad. Sci. USA*, **2014**, *111*, 8723-8728.

Photocatalytic degradation of micropollutants under visible light irradiation

Isabella Natali Sora and Davide Fumagalli

Università di Bergamo, Dipartimento di Ingegneria e Scienze Applicate, Viale Marconi 5, 24044 Dalmine (BG), Italy

Corresponding Author: Isabella.natali-sora@unibg.it

Many organic wastewater contaminants are not removed by biological degradation treatment in wastewater treatment plants (WWTP), and thus are persistent in WWTP effluents at ng/L to µg/L levels. In particular, large efforts have been made in these last decades to study the amount and potential risks of antibiotics in the environment. Ciprofloxacin (CP) is an antibiotic that belongs to the family of medications known as quinolones. CP is the most prescribed fluoroquinolone in Europe. The discharge into surface waters and in WWTPs of antibiotics may give rise to ecotoxicological effects and antibacterial resistance.

As far as the decontamination issue is concerned, heterogeneous photocatalytic processes are quite eco-friendly in comparison with chemical depollution methods. The objective of this work is to assess the photocatalytic efficiency of $LaFeO_3$ nanopowder to decontaminate water from micropollutants under Visible light irradiation. The optical band-gap energy of $LaFeO_3$ nanopowder is 2.54 eV [1]. The photocatalytic activity was tested on 4-Nitrophenol which is a compound representing an important group of water pollutants and the antibiotic Ciprofloxacin.

The photocatalytic degradation reactions were carried out using a Rayonet reactor equipped with 8 lamps (8 W) emitting in the Visible region. A solution was prepared using 100 mL of distilled water, the initial concentration of 4-Nitrophenol (4-NP) was 1.4 $x10^{-4}$ mol L^{-1}. The initial concentration of H_2O_2 was 0.005 mol L^{-1}. The catalyst powder (0.03 g L^{-1}) was added to the resulting solution in a cylindrical Pyrex. The initial concentrations for the suspension of CP were: 5.0 $x10^{-6}$ mol L^{-1} for CP, 0.0026 mol L^{-1} for H_2O_2, and 0.13 g L^{-1} for $LaFeO_3$. Both suspensions were magnetically stirred for 30 min prior to illumination. Subsequently, irradiation was performed on continuously stirred suspension. The temperature increment during the degradation tests was monitored and it never reached temperature higher than 40°C. The degradation of 4-NP and CP was followed by taking 3 mL of the suspension at regular time intervals, and centrifuged for 10 min to separate the catalyst. Their concentration was calculated according to the variation in absorbance of the irradiated solution.

The degradation efficiency using $LaFeO_3$ in presence of H_2O_2 under Visible light irradiation (6 h) is more than 90% for both compounds, much higher than that with

H_2O_2 under Visible light. For the sake of comparison, the experiments were also carried out under dark, and both 4-NP and CP were not significantly converted.

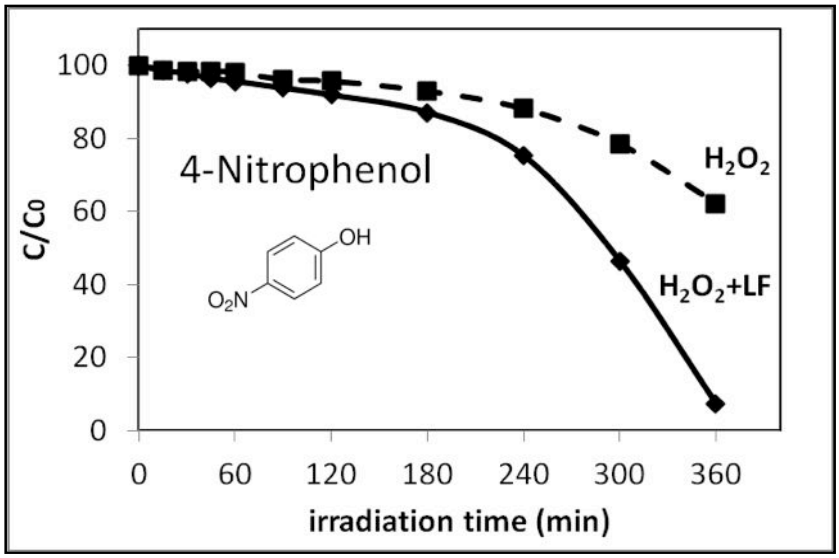


Figure 1 4-Nitrophenol (C_0 =1.4 x10^{-4} mol L^{-1}) degradation in presence of H_2O_2 and LF nanopowder under Visible light irradiation (continuous line), in presence of H_2O_2 under Visible light irradiation (dotted line).

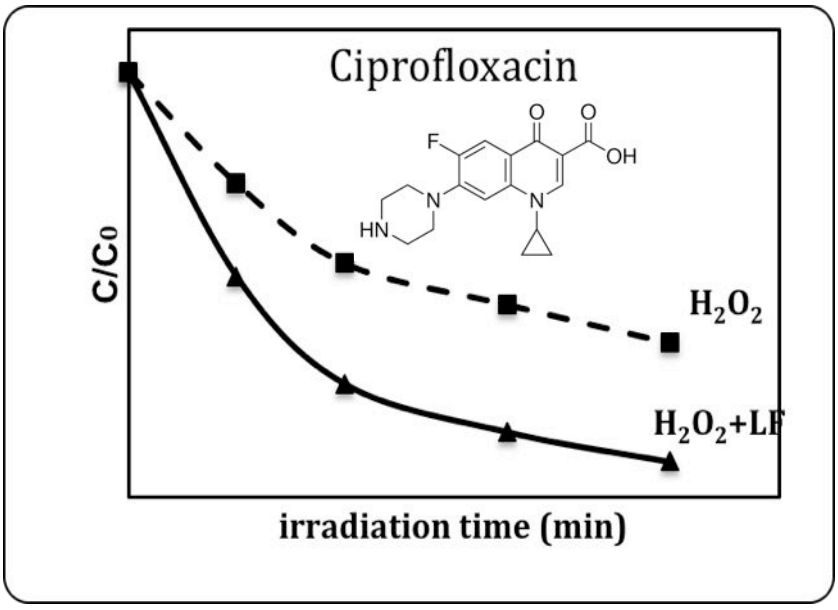


Figure 2 Ciprofloxacin (C_0 = 5.0 x10^{-6} mol L^{-1}) degradation in presence of H_2O_2 and LF nanopowder under Visible light irradiation (continuous line), in presence of H_2O_2 under Visible light irradiation (dotted line).

References

[1] I. Natali Sora, F. Fontana, R. Passalacqua, C. Ampelli, S. Perathoner, G. Centi, F. Parrino, L. Palmisano, *Electrochimica Acta, **2013**, 109, 710-715.*

Synthesis of high surface area CNTs by CCVD

Elpida Piperopoulos[1], Saveria Santangelo[2], Maurizio Lanza[3], Signorino Galvagno[1], Candida Milone[1]

[1] Dip. di Ingegneria Elettronica, Chimica ed Ingegneria Industriale, Messina, 98166, Italy
[2] Dip. di Ingegneria Civile, dell'Energia, dell'Ambiente e dei Materiali, Reggio Calabria, 89122, Italy
[3] Consiglio Nazionale delle Ricerche (CNR), Istituto per i Processi Chimico-Fisici, Messina, 98158, Italy

Email: epiperopoulos@unime.it

Despite the necessity of carbon nanotubes (CNTs) with a high surface area (SA) for different fields of application, up to now, most of the CNTs reported in literature generally have a SA in the range of 100–300 m^2/g. In order to improve the properties of CNTs, post-reaction treatments are usually applied. Among the used methods, modification via KOH activation appears to be the favorite route to improve the CNTs' surface area [1].

In this work high surface area CNTs are synthesized by Catalytic Chemical Vapor Deposition (CCVD) of methane on Cobalt-Molybdenum-Magnesium (CoMoMg) catalysts. Three kinds of catalyst preparation methods are investigated (Sol gel, Wet Impregnation and Wetness impregnation) to compare produced CNTs (SG-CNTs, W-CNTs, WN-CNTs respectively) in terms of yield and morphology. CNT synthesis is carried out using CH_4 (Φ_{CH4}=550 sccm) as carbon source for 30 min. Catalyst structure and CNT morphology, varying catalyst preparation method, are investigated by means of X-Ray analysis, Scanning Electron Microscopy, BET, Thermogravimetric analysis and Raman spectroscopy. High surface area CNTs are obtained directly by synthesis, without resorting to subsequent treatments after reaction. Using different catalyst preparation, obtained CNTs show a sponge-like structure (Fig.1), in which CNT bundles are tightly interconnected by means of catalyst's particles that represent the nodes of a highly porous structure. The surface area of the three samples is higher than the ones reported in literature (Fig.2), especially SG-CNTs report, in addition to a good cristallinity ($I_{G'}/I_D$= 0.86), the highest surface area of 650 m^2/g. These results make the obtained products interesting for different applications.

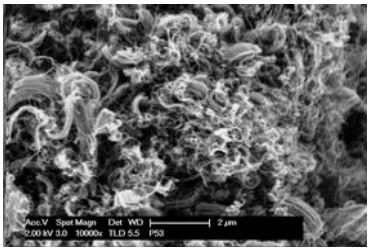


Figure 1. Sponge-like structure of obtained CNTs

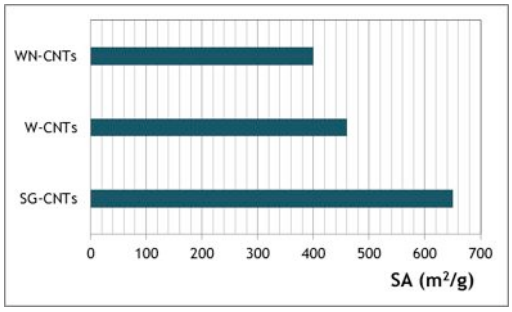


Figure 2. SA of obtained CNTs

References

[1] J.J. Niu, J.N. Wang, Y. Jiang, L.F. Su, J. Ma, *Microporous and Mesoporous Materials*, **2007**, 100, 1-5.

Synthesis *of chromophore modified graphene*

Michele Raggio, Sara Nardis, Mario Luigi Naitana, Alessandra D'Epifanio, Roberto Paolesse

Department of Chemical Science and Technology, University of Rome "Tor Vergata"

Email: michele.raggio@uniroma2.it

Since the first successful exfoliation of single-layer graphene from graphite in 2004 [1], this two-dimensional sp^2-hybridized carbon material has been deeply investigated due to its unique properties ranging from high surface area to high thermal and electronic conductivity. Many efforts have been made to enable this material to be processed by solvent-assisted techniques, like layer-by-layer assembly, spin-coating and filtration, with the aim to use graphene as a versatile material for the fabrication of electrochemical devices such as supercapacitors, fuel cells, drug delivery system, memory devices, transistor devices, biosensors, solar cells, etc. Functionalization with organic functional groups can be performed by covalent and noncovalent modification techniques on both graphene oxide (GO) and reduced graphene oxide (rGO) [2], to prepare processable graphene, preventing agglomeration and facilitating the formation of stable dispersions in organic solvents. This is a crucial move towards nano composite materials and moreover represents a way to introduce new properties that can be combined with those of graphene. For this purpose we studied the interactions of both GO and rGO with a tetrapyrrolic chromophore: different triarylcorroles have been used to covalently functionalize GO or to enhance the solubility of rGO in polar solvents. The acylation reaction on GO allowed to perform the coupling with an amminoarylcorrole through the formation of an amide bond. On the other hand the intermolecular interactions between GO and corrole derivatives bearing polar groups have been investigated. The reduction reaction to obtain rGO was carried out in the presence of such corroles affording an increased dispersibility of graphene in polar solvents. The materials have been characterized through XPS technique, IR and Raman spectroscopy. Several microscopy techniques (AFM, STM, SEM) have been used to analyze GO, rGO and modified graphene on gold substrate.

References

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science*, **2004**, *306*, 666-669.

[2] V. Georgakilas, M. Otyepka, A. B. Bourlinos, V. Chandra, N. Kim,K. C. Kemp, P. Hobza, R. Zboril, K. S. Kim, *Chem. Rev.*, **2012**, *112*, 6156−6214.

Nuovi materiali self-healing per l'edilizia

Antonella Cecchi[2], Evgeny Demenev[1], Cristina de Nardi[2], Giuseppe Quartarone[1], Lucio Ronchin[1] , Federica Sartor[1], Andrea Vavasori[1]

[1] Dipartimento di Scienze Molecolari e Nanosistemi Università Ca' Foscari Venezia
[2] Dipartimento di Architettura Costruzione Conservazione, Università IUAV di Venezia

Email: ronchin@unive.it

Lo studio di nuovi additivi e materiali che in aggiunta alle tradizionali malte da calci idrauliche le rendano intrinsecamente self-healing, cioè capaci di riparare (almeno parzialmente) un danno meccanico subito, è di grande interesse per il consolidamento di strutture storiche. L'auto-riparazione può avvenire sia a livello microscopico che macroscopico e viene avviata da una "fase mobile" che si rende disponibile a seguito di un danno meccanico [1, 2].

L'idea centrale consiste nel creare una malta con una parte della calce "protetta" da uno strato superficiale impermeabile, in grado di renderla inerte durante le fasi di presa e indurimento. Nel momento in cui il materiale subisce una sollecitazione esterna tale da generare l'innesco di una micro-lesione o lesione, lo strato protettivo dei granuli trattati dovrebbe subire una rottura che consentirà di innescare un altro *step* di presa e indurimento a carico del materiale reso "dormiente" dal trattamento. La ricucitura dei lembi fessurativi avverrà per idratazione. La ricerca preliminare che si sta compiendo nei nostri laboratori è relativa allo studio ed alla formazione di diverse tipologie di granuli "protetti" con differenti "shell". Recentemente sono stati osservati risultati interesanti da granuli trattati con $NaHF_2$ in H_2O. La presa della calce trattata è risultata trascurabile e il materilale risulta incoerente e appena agglomerato. Al contrario lo stesso materiale se sottoposto a stress meccanico medianrte macinatura ha mostrato una buona ripresa della presa e dell'indurimento: A livello microscopico mediante analisi EDX e XPS sono state evidenziate formazioni di CaF_2 superficiale che possono spiegare il comportamento macroscopico del materiale. In Fig. 1 è possibile osservare la modifica microstrutturale osservata tra un campione trattato ed uno non trattato.

a **b**

Fig. 1. Immagini SEM di una calce idraulica trattata (a) e non trattata (b)

References

[1] K. Van Balen, Cem. Conc. Res., 2005, 35, 647-657,
[2] T. Ahn, T. Kishi, J. Advan. Concr. Technol. 2010 171-186

CO_2^{2+}, N_2O^{2+}, $C_2H_2^{2+}$ molecular dications formation and their Coulomb explosion with subsequent fragment ions escaping from planetary atmospheres

Stefano Falcinelli[1], Marzio Rosi[1], Fernando Pirani[2], Franco Vecchiocattivi[1]

[1]Dipartimento di Ingegneria Civile ed Ambientale, Università di Perugia, 06125 PERUGIA, ITALY
[2]Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, 06123 PERGIA, ITALY

Email: marzio.rosi@unipg.it

A very important characteristic in the chemistry of molecules interesting for planetary ionospheres is that they interact with the electromagnetic waves: γ, X rays and ultraviolet (UV) light. The dissociative double photoionization processes induced by VUV and EUV photons leading to the production of fragment ions with a high kinetic energy content could give in general an important contribution to the ion species escape from the atmosphere of some planets of the Solar System, like Venus, Mars and Titan. In fact, these processes occur via formation of intermediate molecular dications that can dissociate by Coulomb explosion towards the formations of two ion fragments having a kinetic energy released (KER) of several eV, and therefore much larger than the limiting thermal escape velocity. When CO_2, C_2H_2 and N_2O molecules are ionized using photons with an energy in the range of 30 to 65 eV, molecular fragmentation can be induced, with several two-body dissociation reactions leading to ion final products with high kinetic energy content [1,2]. These ionic species (CO^+, O^+, N_2^+, N^+, NO^+, H^+, C^+, CH^+, CH_2^+ and C_2H^+) are formed by Coulomb explosion of an intermediate molecular dication (CO_2^{2+}, N_2O^{2+} and $C_2H_2^{2+}$, respectively). The fragments are characterized by a translational energy ranging between 1.0 and 5.5 eV (only for H^+, the measured KER reaches the maximum value of 6.0 eV), which is large enough to allow some of them to escape from the atmospheres of Mars and Titan. In the case of O^+, we can conclude that the dissociative double photoionization of CO_2 induced by VUV and EUV photons in the ionosphere of Mars can contribute to explain the observed behavior of the O^+ ion density profile measured by the Viking 1 lander in the upper atmosphere of this planet, compared with the CO_2^{2+} density profile as calculated for the Viking 1 lander and Mariner 6 spacecraft geophysical conditions [1].

References

[1] S. Falcinelli, M. Rosi, P. Candori, F. Vecchiocattivi, J.M. Farrar, F. Pirani, N. Balucani, M. Alagia, R. Richter, S. Stranges *Plan. Space Sci.*, **2014**, *99*, 149-157.
[2] M. Alagia, N. Balucani, P. Candori, S. Falcinelli, F. Pirani, R. Richter, M. Rosi, S. Stranges, F. Vecchiocattivi, *Rend. Fis. Acc. Lincei*, **2013**, *24*, 53-65.

Probing exogenous-induced intracellular acidification: the effects of the incubation time

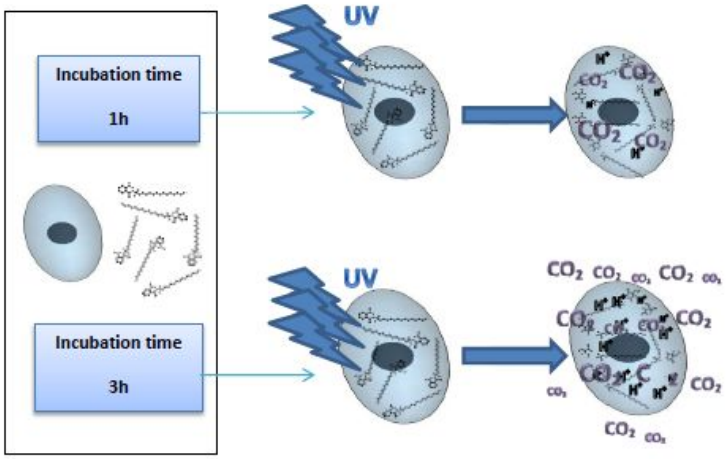
G. Sabbatella[1,2], S. Antonaroli[1], D. Donia[3], V. Orlando[4], S. Biagioni[4], A. Nucara[5,6], M. Carbone[1,7]

[1] Dept. of Chemical Sciences and Technologies, University of Rome Tor Vergata, Rome, Italy
[2] Dept. of Chemistry, University of Rome La Sapienza, Rome, Italy
[3] Dept. Experimental Medicine and Surgery, University of Rome Tor Vergata, Rome, Italy
[4] *Dept. of Biology and Biotechnology "Charles Darwin"* University of Rome La Sapienza, Rome, Italy
[5] Dept. of Physics, University of Rome La Sapienza, Rome, Italy
[6] Center for Life Nano Science, Istituto Italiano di Tecnologia, Rome, Italy
[7] Consorzio Interuniversitario Biostrutture e Biosistemi, Rome, Italy

Email: gianfranco.sabbatella@uniroma1.it

Intracellular pH, plays a pivotal role in cellular processes and is highly regulated in every organelle [1]. The structural stability and function of proteins are tightly associated with pH [2]. Osmotic response, ion transport and membrane polarization are pH-dependent. Furthermore, the cellular uptake of cancer drugs is pH-dependent [3]. A control of the intracellular pH is also a control of the intracellular functions.

It has been shown that proton caged compounds may act as on-command acidification agents by a UV-light switch. Two different proton caged compounds, the 1-(2-nitrophenyl)-ethylhexadecylsulfonate (HDNS) and the disulfanediyldinonane-9,1-diylbis{[1-(2-nitrophenyl)ethoxy]sulfonyl}carbamate (NESS-deca) were probed by infrared spectroscopy, with respect to their acidification capability upon UV irradiation [4, 5].



The responsiveness of cells to the exogenous control of the internal pH may vary as a function of operational parameters. Here we report the different response as a function of the incubation time of HEK-293 cells are incubated with HDNS. In

particular, we demonstrate that an incubation time as long as 3 hours “switches off” the natural intracellular buffer system and provokes an intense intracellular acidification, whereas 1 hour incubation with HDNS provokes an acidification which can still be absorbed by the cells.

References

[1] J.R. Casey, S. Grinstein, J. Orlowski, Nat. Rev. Mol. Cell Biol., 2010, 11, 50–61.
[2] S.W. Englander, L. Mayne, M.M.G.Q. Krishna, Rev. Biophys., 2007, 40, 287-326.
[3] S. Simon, D. Roy, M. Schindler, Proc. Natl. Acad. Sci. U. S. A., 1994, 91, 1128-1132.
[4] M. Carbone, T. Zlateva, L. Quaroni, Biochim. Biophys. Acta, Gen. Subj., 2013, 1830(4) 2989-2993.
[5] G. Sabbatella, S. Antonaroli, M. Diociaiuti, A. Nucara, M. Carbone, New J. Chem., 2015, 39 2489-2496.

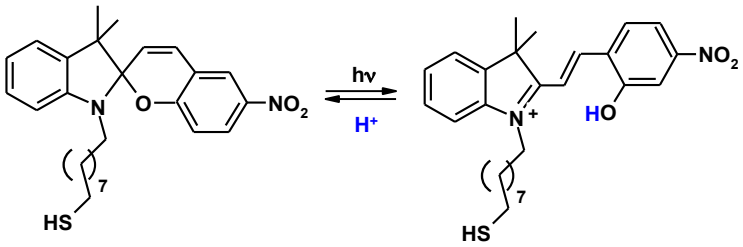
Synthesis of spiropyran for gold and silver nanoparticles functionalization

Marilena Carbone[1,2], Gianfranco Sabbatella[1,3], Simonetta Antonaroli[1], Martin Ashley Case[4], Alessandro Nucara[5]

[1] Dept. of Chemical Science and Technologies, University Tor Vergata, Rome Italy,
[2] Consorzio Interuniversitario Biostrutture e Biosistemi Rome, Italy
[3] Dept. Of Chemistry, University La Sapienza, Rome, Italy,
[4] Johnson & Johnson, Sacramento, USA
[5] Dept. of Physics, University La Sapienza, Rome, Italy

Email: gianfranco.sabbatella@uniroma1.it

The exogenous control of intracellular properties has a fundamental role in medical treatments, such as cancer photodynamic therapy, where photosensitizers [1] are dosed or accumulated into cells and afterwards "turned on" via selective photoexcitation [2]. Furthermore, the association of photosensitizers with gold nanoparticles (AuNPs) enhances the photodynamic effect [3].
The pH regulation has a fundamental role in several intracellular processes [4] and its variation via exogenous compounds is a potential tool for intervening in the intracellular mechanism.
In a recent research we showed both that an exogenous control of pH is possible via purposely synthesized proton caged compounds [5, 6] and that the intracellular acidification in enhanced by the association of AuNPs.
Another class of pH regulating compounds of potential interest for in vitro experiments are spiropyrans and spirooxazines, because of their reversible ring-opening to the corresponding merocyanines with associated proton caption or release, depending on the direction of the following reaction [7].



Here we report the synthesis of the photoacid 1,9-(Mercaptononyl)-3',3'-dimethyl-6'-nitrospiro[2H-1-benzopyran-2,2'-(2H) indole], a variant of spiropyrans, functionalized with a thiol group for further functionalization of gold and silver nanoparticles.

References

[1] M. Ethirajan, Y. Chen, P. Joshi, R.K. Pandey, Chem. Soc. Rev. 2011, 40, 340–362.
[2] R. Bonnett, Chem. Soc. Rev., 1995, 24, 19-33.
[3] Y. Cheng, A.C. Samia, J.D. Meyers, I. Panagopoulos, B. Fei, C. Burda, J. Am. Chem. Soc., 2008, 130, 10643-10647.
[4] J.R. Casey, S. Grinstein, J. Orlowski, , Nat. Rev. Mol. Cell Biol. 2010, 11, 50–61.
[5] M. Carbone, T. Zlateva, L. Quaroni, Biochim. Biophys. Acta, Gen. Subj., 2013, 1830,4, 29892993
[6] G. Sabbatella, S. Antonaroli, M. Diociaiuti, A. Nucara, M. Carbone, New J. Chem., 2015, 39, 2489-2496
[7] Y. Luo, C. Wang, P. Peng, M. Hossain, T. Jiang, W. Fu, Y. Liao, M. Su, J. Mater. Chem. B, 2013, 1, 997-1001

Ni-g Al_2O_3 catalysts supported on cordierite monoliths for the dry reforming of methane

Canterina Sarno[1], Igor Luisetto[2], Simonetta Tuti[2], Francesco Basoli[1], Silvia Licoccia[1], Elisabetta Di Bartolomeo[1]

[1] Department of Chemical Science and Technologies, University of Rome Tor Vergata, Via della Ricerca Scientifica 1, 00133 Rome, Italy
[2] Department of Sciences, University of Rome "Roma Tre", Via della Vasca Navale 79, 00146 Rome, Italy

Email: caterina.sarno@uniroma2.it

The CO_2 reforming of CH_4 (equation 1), also called dry reforming (DRM), has been recently recognized as an efficient way for the CH_4 and CO_2 valorisation [1]. In fact, the produced syn-gas has an H_2/CO ratio equal to one suitable for the synthesis of oxygenated hydrocarbons and synthetic fuels.

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad \Delta H^0_{298K} = 247 kJmol^{-1} \qquad (1)$$

To date its industrial implementation is impeded mainly by the catalyst deactivation and/or the reactor plugging due to carbon deposits formed by the methane cracking Ni-based catalysts are so far the most active catalysts for the DRM, but also highly prone to carbon formation, because, together with the ability to activate the C-H bond, Ni has a high affinity to carbon. The Ni particle size has a strong effect on the carbon tolerance of the catalyst, and generally, particles smaller than 5 nm have low catalytic activity toward the C-H cracking [2, 3]. Therefore, the stabilization of small Ni nanoparticles at high temperatures is a promising way for the lifetime increase [4, 5].

Catalysts deposited on structured supports, such as ceramic or metallic monoliths, have several advantages over conventional packed bed reactors: increase of mass and heat transfer, lower pressure drop, larger surface-to-volume ratio and compact reactor design. Structured supports permit to decrease the particle size of the active metals by using low metal content, maintaining high catalytic performance. Therefore, it is possible to obtain nickel supported catalysts with high resistance toward carbon deposition.

In the present work, several Ni structured catalysts were prepared using commercial cordierite monoliths with 400 cpsi cell density. The g-Al_2O_3 carrier was deposited by reliable wash coating method whereas nickel was deposited by either wet impregnation or controlled adsorption methods. Catalysts were characterized by XRD, FE-SEM, H_2-TPR, BET techniques. The catalytic activity for DRM was evaluated at 1073K during time on stream at different GHSV.

The catalysts layers were well adherent to the cordierite substrates with macropores suitable for gas diffusion. Ni was homogeneously distributed along the

monolith channels forming species in low (Ni-a) and strong (Ni-b) interaction with the g-Al_2O_3 carrier. Preliminary catalytic tests showed that Ni particles obtained by reduction of Ni-a species were active for the DRM reaction with low carbon formation whereas catalysts with large amount of Ni-b deactivated rapidly during time on stream without carbon formation. The effect of Ni interaction and Ni particle size on catalytic activity and on carbon formation is currently under investigation.

References

[1] M.C.J. Bradford, M.A. Vannice, Catalysis Reviews 41 (1999) 1-42.
[2] K.O. Christensen, D. Chen, R. Lødeng, A. Holmen, Applied Catalysis A: General 314 (2006) 9-22.
[3] J.-H. Kim, D.J. Suh, T.-J. Park, K.-L. Kim, Applied Catalysis A: General 197 (2000) 191-200.
[4] K. Mette, S. Kühl, H. Düdder, K. Kähler, A. Tarasov, M. Muhler, M. Behrens, ChemCatChem 6 (2014) 100-104.
[5] Z. Li, L. Mo, Y. Kathiraser, S. Kawi, ACS Catalysis 4 (2014) 1526-1536.

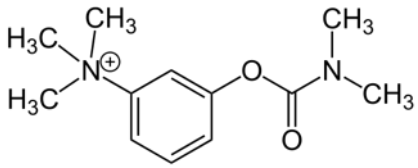
Analogues of Neostigmine as Potential Acetilcholinesterase Inhibitors

Ilaria Sileno[1], *Isabella Chiarotto*[1], *Luigi Ornano*[1], *Daniela De Vita*[2], *Marta Feroci*[1]

[1] Dip. Scienze di Base e Applicate per l'Ingegneria,Sapienza University of Rome,via Castro Laurenziano 7, 00161, Roma, ITALY
[2] Istituto Pasteur-Fondazione Cenci Bolognetti,Dip.Chimica e Tecnologie del Farmaco, Sapienza University of Rome, Piazzale Aldo Moro, 5, 00185 Rome, Italy

marta.feroci@uniroma1.it

Alzheimer disease is a neurological and invalidating pathology of unknown origins in which dementias along with a slow and irreversible degeneration of memory are present, due probably to an accumulation of amyloidal plaques and neurofibrillary tangles [1]. In this pathology a sensible deficit of acetylcholine is present. The acetylcholinesterase enzyme is the target of drugs, called "anti-cholinesterase", which inhibit acetylcholinesterase (AChE), whose action is the hydrolysis of acetylcholine (AcH) into its precursors (choline and acetate ion). Among the inhibitors of AChE, physostigmine and neostigmine are often used. In particolar, these compounds show a carbamate moiety which is hydrolyzed more slowly than the ester group of AcH. The primary effect of these drugs is to increase both level and duration of AcH activity, to attenuate the cognitive symptoms of dementia.



Neostigmine

In our work, we synthesized a short library of analogues of neostigmine compounds using as building block the carbamoyl moiety linked with chain-spacer of three, four or six atoms of carbon to a nitrogen atom. Two aromatic systems are also present in these molecules. Fluorine substituted aromatic groups were preferred because fluorinated groups usually improve the pharmacological activity.
The pharmacological evaluations about this new lead compounds are still in progress.
We tested these compounds on Acetylcholinesterase to determinate their effectiveness as inhibitors.

References

1] M. Pohanka, Int. J. . Mol. Sci., **2014**, *15(6)*, 9809-9825.

Utilizzo di idrotalciti organo-modificate per la preparazione di biocompositi

Laura Sisti, Grazia Totaro, Annamaria Celli

Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali (DICAM). Università di Bologna, Via Terracini 28, 40131 Bologna, Italia

Email:laura.sisti@unibo.it

Il tema della protezione ambientale e la necessità sempre crescente di fornire valide alternative ai prodotti basati sul petrolio hanno determinato un forte interesse nel campo dello sviluppo di polimeri provenienti da fonti naturali e biodegradabili. I poliesteri alifatici rappresentano una classe molto promettente di polimeri cosiddetti eco-friendly ed in base alla composizione presentano un'ampia varietà di proprietà fisiche, meccaniche e di biodegradabilità. La relativa semplicità di sintesi sta inoltre facendo si che questi materiali si stiano imponendo a livello commerciale, tra questi il poli(butilene succinato) (PBS), grazie alla sue proprietà termiche e buone caratteristiche meccaniche sta lentamente entrando nel mercato. Attualmente la ricerca, in vista di un ampliamento delle possibili applicazioni del PBS, sta cercando di migliorare alcuni aspetti delle sue caratteristiche che lo rendono ad esempio poco adatto al packaging rigido. Inoltre il PBS presenta bassa viscosità in fuso e scarse proprietà barriera. Allo scopo di migliorare queste proprietà vengono spesso utilizzati filler inorganici. In questo ambito si inquadra la ricerca sviluppata al DICAM che mette in luce il ruolo positivo delle idrotalciti organo-modificate con molecole derivate da biomassa, per il miglioramento delle proprietà in fuso del PBS.

Le idrotalciti [1,2] sono materiali inorganici naturali costituiti da miscele di idrossidi lamellari contenenti anioni scambiabili nella regione interstrato. Sono utilizzate nei nanocompositi a matrice polimerica poiché presentano notevoli vantaggi quali facilità di sintesi e funzionalizzazione, elevata purezza, cristallinità, possibilità di controllo della dimensione delle particelle, composizione chimica modulabile, in base alle necessità, ed elevata biocompatibilità. Questi vantaggi sono stati sfruttati, nella presente ricerca, per la preparazione di biocompositi attraverso la polimerizzazione *in situ* e la miscelazione in fuso per l'ottenimento di un polimero finale con un peso molecolare maggiore garantendo così alte viscosità in fuso e migliorate capacità di processo del materiale finale.

References

[1] F. Cavani, F. Trifirò, A. VAccari, *Catal. Today*, **1991**, *11*, 173-301.
[2] L. Sisti, G. Totaro, M. Fiorini, A. Celli,C. Coelho, M.Hennous, V.Verney, F. Leroux, *J. Appl. Polym. Sci.*, **2013**, *130*,1931-1940.

Methylesters epoxidation catalyzed by novel niobium oxide based materials

Rosa Turco[1], Martino Di Serio[1], Riccardo Tesser[1], Luciana Minieri[2], Pasquale Pernice[2], Antonio Aronne[2]

[1] Dipartimento di Scienze Chimiche, Università di Napoli, via Cintia, 80126, Napoli, Italia and CIRCC.
[2] Dipartimento di Ingegneria Chimica,dei materiali e delle produzioni industriali Università di Napoli, Piazzale V. Tecchio 80, 80125 Napoli, Italia

Email: rosa.turco@unina.it

The performances of Nb_2O_5-SiO_2 solids, were extensively studied in epoxidation reaction of different olefins with hydrogen peroxide: it was found that the synthesis method and the distribution of surface acid sites strongly affect the catalyst efficiency, because Lewis acid sites promote the epoxidation, but strong Brønsted acid sites promote the reaction of ring epoxide opening by hydrolysis forming diols [1-4].
Epoxidized methyl esters derived by oils are important building blocks for the preparation of chemical intermediates and consumer products, such as plasticizers and stabilizers for PVC, components of lubricants etc.
In this work, Nb_2O_5-SiO_2 materials, with different niobium content, are synthesized by sol-gel method using niobium chloride, $NbCl_5$ and tetraethoxysilane, $Si(OC_2H_5)_4$ (TEOS) and Brij® C10 as surfactant template, in order to control the pore size and surface area. These catalysts are studied in epoxidation of methyl oleate with hydrogen peroxide, and their activity was compared with a similar set of the niobium catalysts, without template.
A higher activity was found for the catalysts synthesized with the addition of the surfactant, as a consequence of more suitable morphological properties.

References

[1] A. Feliczak, K. Walzak, A. Wawrzynczak, I. Novak, *Catal. Today*, **2009**, *140, 23-29.*
[2] C. Tiozzo, C. Bisio, F. Carniato, L. Marchese, A. Gallo, N. Ravasio, R. Psaro, M. Guidotti *Eur. Lipid Sci. Technol.*, **2013**, 115, 86-93.
[3] R. Turco, A. Aronne, P. Carniti, A. Gervasini, L. Minieri, P. Pernice, R. Tesser, R. Vitiello, M. Di Serio, *Catal. Today* **2015**, *in press.*
[4] M. Di Serio, Rosa Turco, P. Pernice, A. Aronne, F. Sannino, E. Santacesaria, *Catal. Today* **2012**,*192, 112-116.*

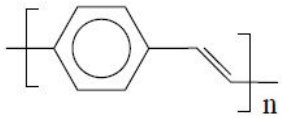
Synthesis of Light-Emitting Polymers via Heck coupling reactions

Andrea Vavasori[1], Chiara Pezzella[1], Lucio Ronchin[2], Giuseppe Quartarone[1], Claudio Tortato[1], Evgeny Demenev[1]

[1]Department of Molecular Sciences and Nanosystems, University Ca' Foscari Venice, Italy

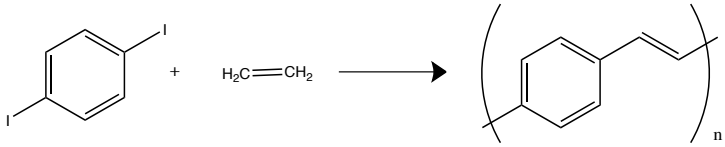
Email: vavasori@unive.it

Conjugated polymers represent a very promising class of organic materials for photonics and electronics, which exhibits a unique combination of optical and electrical properties typical of semiconductors with processing advantages and mechanical features of polymers [1].
Light-emitting devices (LED) were first fabricated from small organic molecule, having the main disadvantage that they can re-crystallize during device operation, leading to poor device stability. The use of conjugated polymers, potentially more stable, in such devices was first realized in the early 1990 [2]. The most efficient polymeric systems are actually based on poly(p-phenylenevinylene) (PPV) films, which emit basically green 1ight. However, there is still a big challenge in obtaining highly efficient blue-light-emitting devices.



Poly(p-phenylenevinylene) (PPV)

Among the several methods reported for the synthesis of PPV, the Heck coupling between an organic halide and an olefin, giving a carbon-carbon double bond, shows to have a great potential.
In the present paper we reported on the palladium catalyzed synthesis of PPV starting from p-di-iodobenzene and an olefin.



The reaction conditions of the Heck reaction has been optimized leading to light-emitting PVB of different colour (Figure 1).

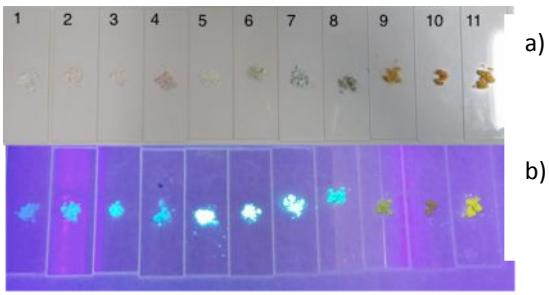


Figure 1 – Photoluminescence of different PVB polymers a) visible, b) UV a 240 nm

References

[1] Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; MacKay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B., *Nature*, **1990**, *347*, 539**1990.**

[2] Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Santos, D. A.; Bredas, J. L.; Lõgdlund, M.; Salameck, W. R. *Nature* **1999**, 397, 121.

How the reactivity depends on the angular approach between reagents: stereo-dynamics of Penning ionization involving hydrogenated molecules

Stefano Falcinelli[1], Marzio Rosi[1], Alessio Bartocci[2], Fernando Pirani[2], Franco Vecchiocattivi[1]

[1]Dipartimento di Ingegneria Civile ed Ambientale, Università di Perugia, 06125 PERUGIA, ITALY
[2]Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, 06123 PERGIA, ITALY

Email: franco.vecchiocattivi@unipg.it

Gas phase chemiionization processes of water, hydrogen sulfide, and ammonia molecules, induced by excited metastable noble gas atoms (Ng^*), known as Penning ionizations, play an important role in several phenomena occurring in low energy ionized plasmas, electric discharges, planetary atmospheres, and interstellar environments [1,2]. In the present contribution we report on ammonia molecules ionized by collisions with neon and helium metastable atoms. The investigation has been carried out by analyzing the total ionization cross section as a function of the collision energy for different approaching angles between Ng* and NH_3 reagents, as well as the energy of emitted electron spectra. For such advanced analysis we have exploited a semiclassical treatment of the collision dynamics together with potential energy surfaces whose formulation, given in terms of fundamental physical properties of the involved partners, is provided in an analytical form, useful to represent the system in the whole space of configurations. Therefore, such a potential formulation appears suitable for quantitative molecular dynamics calculations that allow to control the angle of approach between the reagent particles, and therefore to perform a detailed stereo-dynamical study of Penning ionization reactions. The final results obtained from this investigation show the evidence that ionization process is controlled by the competition between the formation of a hydrogen bond like complex, when the rare gas excited atom approaches the molecules towards the hydrogen atom side, and the formation of a halogen bond like complex, when the approach occurs towards the lone pair side. In the latter configuration the ionization is stimulated by a pronounced electron exchange probability between a filled orbital of the molecule and the inner shell hole of the ionic core of Ng^* atom.

References

[1] S. Falcinelli, F. Pirani, F. Vecchiocattivi, *Atmosphere*, **2015**, *6*, 299-317.
[2] S. Falcinelli, M. Rosi, P. Candori, F. Vecchiocattivi, J.M. Farrar, F. Pirani, N. Balucani, M. Alagia, R. Richter, S. Stranges *Plan. Space Sci.*, **2014**, *99*, 149-157.

Engineered Graphene with enzymes for restoration of polychrome paintings on canvas or plaster surfaces

Francesca Volpi[1], Aldrei Boaretto[2,3], Simonetta Antonaroli[3], and Federica Valentini[3]

[1] Università di Bologna – Sede di Ravenna Centro interdipartimentale di ricerca per le scienze ambientali (CIRSA) Laboratorio diagnostico di microchimica e microscopia dei beni culturali (M2ADL) Via Guaccimanni 42 48100 RAVENNA (Italy)
[2] CAPES foundation, Ministry of Education of Brazil, Brasilia -DF 70040-020 (Brazil)
[3] Chemistry Department Tor Vergata University, via della Ricerca Scientifica 1, 00133 Rome (Italy)

Email: aldreibrt@gmail.com

Graphene exhibits excellent chemical-physical, biochemical and mechanical features, very useful for analytical applications in several fields. Recently, in our laboratories in Tor Vergata University, graphene has been engineered with enzymes and other molecular systems in order to obtain nanocomposites, selective for restoration of artworks. In this paper we present a case of study where engineered graphene with lipase enzymes have been successfully applied for the cleaning and restoration of the polychrome paintings (located on mobile canvas and/or wall paintings). The goal to achieve is the efficient removal of the oily polymer resins used during previous restoration events. It is very well known [1] that the oily polymeric resins cause problems of yellowing due to the interaction with the light, which induces reactions polymer chain (mainly oxidative reaction mechanisms, responsible for the phenomena of aging of the supports). Good performances have been observed after the engineered graphene based treatments, if compared with the conventional methodologies (widely used for the polychrome paintings, [2]) and this new approach could be very promising for restoration of paintings, also considering the biocompatibility of graphene oxide derivatives (a useful property especially for the "*end-users*"). In addition, graphene and graphene derivatives represent "eco-friendly" nanomaterials, smart for environment.

References

[1] Patrick Dietemann, Catherine Higgitt, Moritz Kalin, Michael J. Edelmann, Richard Knochenmuss, Renato Zenobi,*Journal of Cultural Heritage*,**2009**, *10*, 30-40.
[2] https://www.getty.edu/conservation/publications_resources/pdf_publications/pdf/2nd_silkroad6.pdf

Molecular Simulations of Novel Materials for Energy Research

Leonardo Guidoni

Università degli Studi dell'Aquila, Dipartimento di Scienze Fisiche e Chimiche, L'Aquila, Italy

Email: Leonardo.guidoni@univaq.it

Several synthetic catalysts, containing different transition-matal-oxo cores have been recently proposed, but earth-abundant Fe, Ni, Mn, Co amorphous oxides likely represent the most promising route towards technologically relevant and low cost photo-electrolytic cells. [1] A thorough understanding of water oxidation promoted by these amorphous transition-metal oxides requires detailed insight in the atomistic texture and in the electronic properties of the catalysts. In combination with x-ray absorption spectroscopy measurements, computer simulations can provide important atomic-level structural information that may help to design structural models of the catalysts. In the present contribution we will use quantum chemistry and first principles molecular dynamics to investigate the structural and catalytic properties of cluster models of different water splitting catalysts. For the cobalt-based catalyst (CoCat) in explicit water solution, we have provided insights into the pathways for oxygen evolution by identifying the formation of Co(IV)-oxyl species as the driving ingredient for the activation of the catalytic mechanism. [2] For the manganese-based catalyst, in collaboration with H. Dau and I. Zaharieva, we have carried out accurate DFT simulations comparing the obtained results with the XAFS measurement collected, thus revealing the details of the structural motifs of the catalytic sites. [3] Comparison between these results and those obtained for the catalytic core of the natural water-splitting enzyme (Photosystem II) [4] suggests differences and similarities between the inorganic and the biological catalysts.

References

[1] M.W. Kanan et al., Science 321 (2008) 1072. D.Nocera, *Acc.Chem.Res.* 45, **2012**, 767. M. Risch et al. *Chem. Comm.* 47, **2011**, 11912. A. Bergmann et al. En. & *Env. Sci.* 6, **2013**, 2745. J. Suntivich et al. *Science* 334, **2011** 1383.
[2] G. Mattioli, P. Giannozzi, A. Amore Bonapasta, L. Guidoni, *J.A.C.S.* 135, **2013**, 15353.
[3] G. Mattioli, I. Zaharieva, H. Dau, L. Guidoni, *in preparation*
[4] D.Narzi, D.Bovi, L.Guidoni, *P.N.A.S.* 111, **2014**, 8723.

LISTA DEI PARTECIPANTI

Acocella Maria Rosaria
Ambrogi Veronica
Argentino Chiara
Basoli Francesco
Bellardita Marianna
Berionni Berna Beatrice
Berrocal José Augusto
Biocca Paola
Blanco Ignazio
Bloise Ermelinda
Boaretto Aldrei
Bollino Flavia
Bonifacio Alois
Borrazzo Cristian
Branchi Mario
Carrozza Chiara Francesca
Chiarotto Isabella
Cicione Claudia
Concolato Sofia
Corrente Giuseppina Anna
Costantini Marco
D'Epifanio Alessandra
Dalla Marta Silvia
De Bonis Catia
Dell'Era Alessandro
Dispenza Clelia
Eddahaoui Khadija
Espro Claudia
Failla Salvatore
Falcinelli Stefano
Fazio Marianna
Feroci Marta
Fiorini Maurizio
Giannitelli Sara M
Gori Manuele
Graziani Valerio
Guido Emanuela
Guidoni Leonardo
Gumina Bianca
Iannaci Alessandro
Iannazzo Daniela
Licoccia Silvia
Luciani Giuseppina
Luisetto Igor
Maggio Mario
Mandoj Federica
Marcì Giuseppe
Mastronardo Emanuela
Mattiello Leonardo
Mecheri Barbara
Minieri Luciana
Mozetic Pamela
Naitana Mario
Nardis Sara
Narzi Daniele
Natali Sora Isabella
Negro Enrico
Olivo Alberto
Ornano Luigi
Orsini Monica
Palmisano Leonardo
Paolesse Roberto
Pasquali Mauro
Piperopoulos Elpida
Pomarico Giuseppe
Raggio Michele
Rainer Alberto
Rau Julietta V.
Ronchin Lucio
Rosace Giuseppe
Rosi Marzio
Sabbatella Gianfranco
Sangorgi Nicola
Sarno Caterina
Scarlino Anna
Sileno Ilaria
Sisti Laura
Sotgiu Giovanni
Spadaro Giuseppe
Stefanelli Manuela
Stipa Pierluigi
Tarquini Gabriele
Tortora Luca
Trombetta Marcella
Turco Rosa
Urbini Marco
Vavasori Andrea
Vecchio Ciprioti Stefano
Vecchiocattivi Franco
Volpi Francesca
Zeffiro Alberto

LISTA DEGLI AUTORI

A

Acocella M. R. O16; P1
Ajovalasit A. P14
Ambrogi V. P2
Antonaroli S. P3; P8; P35; P36; P43
Argentino C. P3
Aronne A. O9; P40
Ascari A. O21

B

Barbetta A. O2
Bartocci A. P42
Basoli F. P4; P37
Behalo M. P7
Bellardita M. O13; P26
Bendoni R. O11
Benmokhtar S. P15
Bentivoglio B. O4
Berrocal J. A. O22
Bettoni M. P18
Biagioni S. P35
Biocca P. P5
Bisogno T. P28
Blanco I. P6
Bloise E. P7
Boaretto A. P3; P8; P43
Bollino F. O1
Bonaccorsi L. O7; O12
Bonifacio A. O18
Bonville P O17
Borrazzo C. P9
Bottino A. P6
Bovi D. P29
Branchi M. P10
Branda F. P25
Brunetti F. P27
Businaro L. P22
Buttafava A. O4

C

Caminiti R. O3
Campana G. P20
Capodilupo A. L. O10
Carbone M. P35; P36
Carfagna C. P2
Carrozza C. F. O5
Case M. A. P36
Catauro M. O1; P13
Cecchi A. P33
Celli A. P39
Cerruti P. P2
Chiacchio M. A. P6
Chiarotto I. P11; P38
Ciccarella G. O10
Citterio A. O5
Colleoni C. O20
Colosi C. O2
Concolato S. P12
Consiglio G. P17
Corrente G. A. O10
Costantini A. P25
Costantini M. O2
Cruciani G. O14

D

D'Errico G. O9
D'Epifanio A. P10; P23; P32
Dalla Marta S. O18
de Bonis C. P10
De Luca L. P24
De Marco L. O10
de Nardi C. P33
de Notaristefani F. P5
De Riccardis A. P15
De Vita D. P38
de Waal S. O22
Dell'Era A. P13
Demenev E. P33; P41
Dentini M. O2
Deyab M. A. P15
Di Bartolomeo E. P4; P37
Di Bella S. P17
Di Marzo V. P28
Di Noto V. O23
Di Serio M. P40
Dispenza C. P14
Ditta L. A. P14
Dondi D. O4
Donia D. P35

E

Eddahaoui K. P15
Espro C. O8; P16; P24
Essehli P. P15

F

Fabbri A. P9
Failla S. P17
Falcinelli S. P18; P34; P42
Fazio M. O12; P16
Feroci M. P11; P38
Ferro S. P24
Fiorini M. O21; P19; P20
Fontana F. P30
Fortunato A. O21
Fosca M. O3
Fumagalli D. P30

G

Galasso M. P9
Galvagno S. O8; O12; P16; P24; P31
Garcia-Iglesias M. O22
García-López E. O13; P26
Ghedini E. O14
Giamberini M. P2
Giannitelli S. M. P12; P21
Gigli G. O10
Giorgini F. P18
Giorgini M. P18
Girometta C. O4
Gori M. P21; P22
Graziani V. O3
Guerra G. O16; P1
Guido E. O20
Guidoni L. P29; P44
Gumina B. O8; P16

I

Iannaci A. P23
Iannazzo D. P16; P24
Imparato C. O9
Inesi A. P11
Ioele M. P5

J

Jaroszewicz J. O2

K

Kato Y O7
Kirpsza A. P26
Komlev V. S. O3

L

Lanza M. P31
Lazzaroni S. O4
Licoccia S. P4; P10; P23; P37
Lomonaco D. P7
Luciani G. P25
Luisetto I. P4; P37
Lutey A. H. O21

M

Maccarrone M. P28
Maggio M. O16; P1
Malagodi M. O4
Marcì G. O13; P26
Marconi R. P. O4
Marturano V. P2
Mastronardo E. O7
Mattiello L. P27
Mauriello F. O8
Mauro M. O16
Mazzetto S. E. P7
Mecheri B. P10; P23
Meijer M. O22
Mele G. O6; P7; P15
Mergola L. P7
Micek-Ilnicka A. P26
Milone C. O7; O12; P31
Minieri L. O9; P40
Monforte A. M. P24
Morelli R. P19; P20
Mozetic P. O2; P12; P21; P28

N

Naitana M. L. O15; P32
Nardis S. O15; P32

Narzi D. P29
Natali Sora I. O17; P30
Natile M. M. O17
Navarra M. A. P10
Negro E. O23
Nielsen E. O4
Nucara A. P35; P36

O

Oliveri I. P. P17
Olivo A. O14
Oradei S. P19
Orlando V. P35
Ornano L. P38
Orsini M. P12
Ortenzi O. O3

P

Pagano N. P20
Palmisano L. O13; P26
Paolesse R. O15; P32
Papale F. O1
Pasquali M. O19
Pernice P. O9; P40
Pezzella A. P25
Pezzella C. P41
Piccinni B. P7
Pietropaolo R. O8
Pio I. O6
Piperopoulos E. O7; P31
Pirani F. P34; P42
Pirozzi D. O9
Pistone A. P16; P24
Plutino M. R. O20
Pomilla F. R. P26
Prosini P. P. O19
Punzo F. P17

Q

Quartarone G. P33; P41

R

Raggio M. P32
Rahim S. A. O12
Rainer A. O2; P12; P21; P22; P28
Rau J. V. O3
Renella R. A. O1
Ronchin L. P33; P41
Rosace G. O20
Rosi M. P18; P34; P42

S

Sabatino M. A. P14
Sabbatella G. P35; P36
Sangiorgi A. O11
Sangiorgi N. O11
Sannino F. O9
Sanson A. O11
Santangelo S, P31
Santoro D. O6
Sarno C. P37
Sartor F. P33
Savino E. O4
Scarlino A. O6
Sebastiani B. P18
Sebastiano R. O5
Sergo V. O18
Signoretto M. O14
Sileno I. P38
Silvestri B. P25
Simonelli M. C. P22
Sisti L. P39
Sotgiu G. P5
Spadaro G. P14
Święszkowski W. O2

T

Tarquini G. O19
Tesser R. P40
Tortato C. P41
Tortora L. O17; P5; P9; P12
Tosato A. O2
Totaro G. P39
Trevisan V. O14
Trombetta M. O2; P12; P21; P22; P28
Tulliani J.-M. O17
Turco R. P40
Tuti S. P37
Tylkowski B. P2

U

Urbini M. O17; P9

V

Valentini F. P3; P8; P43
Vasapollo G. O6
Vavasori A. P33; P41
Vecchio Ciprioti S. P13
Vecchiocattivi F. P18; P34; P42
Verri T. P7
Vezzù K. O23
Vinci A. O8
Vitiello G. O9; P25
Volpi F. P43

Z

Zeffiro A. O4
Zurlo F. P4

INDICE

Comitato Organizzatore e Scientifico..... 3
Lista Sponsor..... 4
Programma Scientifico..... 6
Lista Poster..... 9
Comunicazioni Orali.....12
Comunicazioni Poster.....44
Lista Partecipanti.....104
Lista Autori..... 105