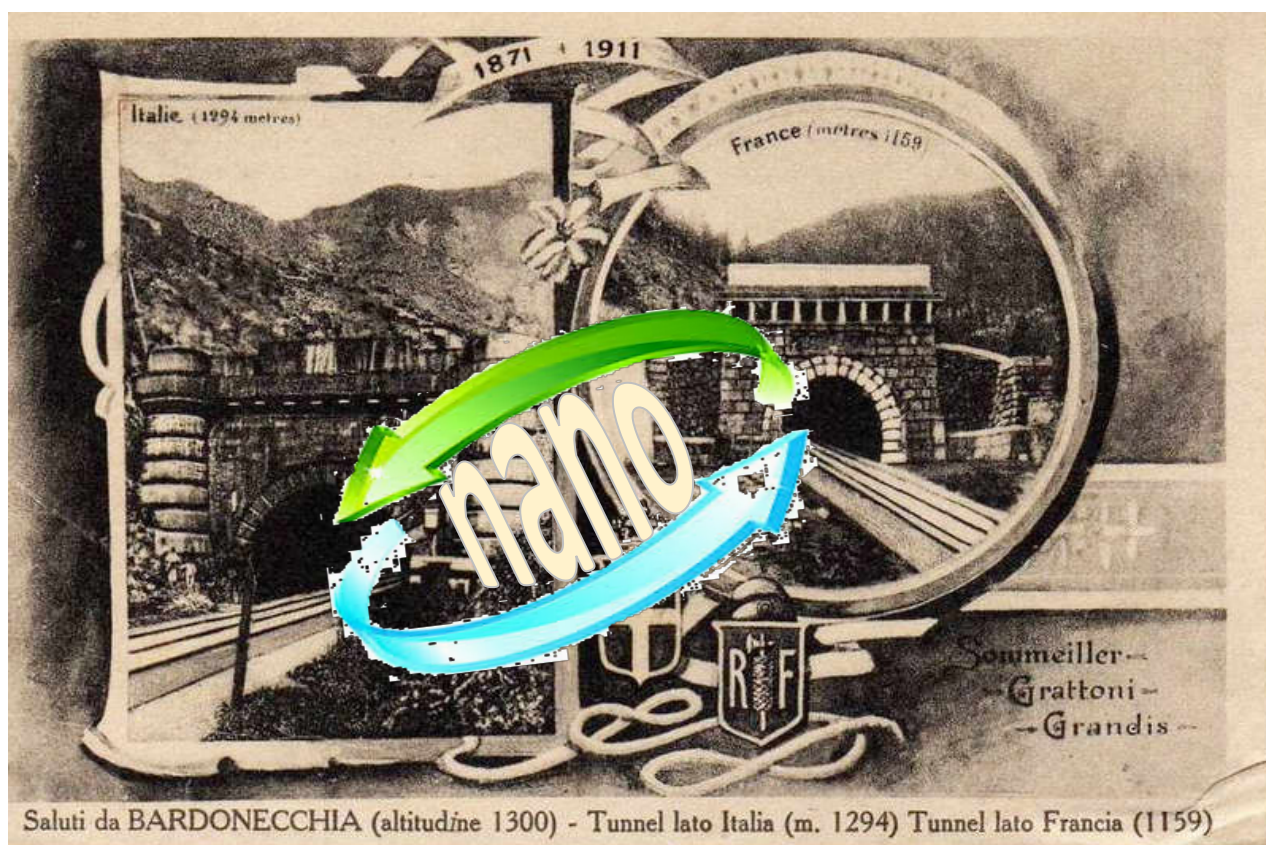




Sezione Piemonte
Valle d'Aosta

Provence-Alpes-
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Seconde Giornate Italo-Francesi di Nanoscienze
2èmes Journées Italo-Françaises de Nanosciences



**Bardonecchia - Villaggio Olimpico
Italia-Italie**

Benvenute e benvenuti!

Care colleghi, cari colleghi,

eccoci alla seconda edizione delle Giornate Italo-Francesi di Nanoscienze, con un passaggio dal sole della costa francese del Mediterraneo alla neve del versante italiano delle Alpi. Come prima cosa, grazie a tutti e a tutte per aver accettato l'invito a partecipare, e per l'elevata qualità dei contributi con cui avete deciso di presentare a questo incontro. I vari argomenti trattati hanno permesso di organizzare un programma ricco e vivace, che prende in considerazione un numero considerevole delle problematiche scientifiche di maggior rilievo ed attualità nel campo delle nanoscienze. Siamo sicuri che sarà occasione di scambi di idee, approfondimenti, e magari di nascita di nuove collaborazioni. Sperando di rinnovare il successo della prima edizione a Porquerolles, ci auguriamo che anche queste giornate a Bardonecchia possano essere un piccolo, ma significativo contributo delle nostre Sezioni della Società Chimica Italiana e dalla Société Française de Chimie allo sviluppo di una comunità scientifica, ed in particolare chimica, europea. Buon lavoro!

Gianmario Martra

Presidente della
Sezione Piemonte Valle
d'Aosta

Bienvenues et bienvenus!

Chers collègues,

Bienvenue au Village Olympique de Bardonecchia. Nous vous souhaitons des journées agréables et fructueuses. Après la mer à Porquerolles en 2015, la montagne en 2018 ...

Merci à Gianmario Martra et aux collègues italiens pour l'organisation de cette édition.

Complétant les Journées Franco-italiennes de Chimie, qui sont désormais une tradition bien établie dans notre communauté de chimistes des régions Piémont-Val d'Aoste, Ligurie et Provence-Alpes-Côte d'Azur, ces deuxièmes Journées Franco-italiennes de Nanosciences ouvrent une nouvelle page de la collaboration entre nos sections régionales de la Società Chimica Italiana et de la Société Chimique de France. Comme pour la précédente édition, toutes les présentations se font sur invitation.

Comme Monsieur Jourdain faisait de la prose sans le savoir, les chimistes font du "nano" depuis toujours, sans s'en prévaloir. Vive la Chimie Nano!

Philippe Knauth

Ex-Président,
Section Régionale
Provence-Alpes-Côte d'Azur

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31.01-2.02 2018
Bardonecchia - Villaggio Olimpico
Italia-Italie

Programma-Programme

PL X = plenary n. X; OX = orale/oral n. X

mercoledì/mercredi 31/01/18		
15.00	<i>Accoglienza dei partecipanti/ Accueil des participants</i>	
16.00-16.15	<i>apertura/ouverture (G. Martra, P. Knauth)</i>	
16.15-17.15	PL 1. B. Kuchta: "Computational study of structural properties of nano-porous materials. A research program in the Erasmus Mundus Master «Chemical Nanoengineering»	p. 1
<hr/>		
17.15-17.35	<i>pausa caffè/pause café</i>	
<i>Chairpersons: A. Ferrari, D. Grosso</i>		
Session 1: an overview of nanoscience on both sides of Alps		
17.35-17.55	O1. M.L. Di Vona: "Nano-composite ion exchange membranes"	p. 2
17.55-18.15	O2. S. Bodoardo: "Post lithium-ion batteries. Nanostructures to enhance electrochemical performance"	p. 3
18.15-18.35	O3. L.-M. Raimundo: "Highly versatile organic dielectric for ion detection up to the femtomole in field effect transistor sensors"	p. 5
18.35-18.55	O4. S. Arpicco: "Strategies and challenges for efficient active targeting"	p. 6
<hr/>		
19.00-20.00	<i>check-in</i>	
20.00	<i>cena/diner</i>	

giovedì/jeudi 01/02/18

mattino/matin

Chairpersons: L. Firlej, M. Minella

8:30-9:30 **PL2. M. Laus:** "Deterministic doping in semiconductors via self-limited grafting to reactions" **p. 8**

Session 2: nanofabrication

9.30-9.50 **O5. P. Knauth:** "Electrodeposition of ionomer membranes for miniaturized energy storage and conversion devices" **p. 9**

9.50-10.10 **O6. A.M. Ferrari:** "Ab initio simulation of ZnO/La(Sr)MnO₃ heterojunctions: insights into their structural and electronic properties" **p. 10**

10.10-10.30 **O7. D. Grosso:** "Nano/micro structured TiO₂ coatings prepared by high throughput top-down/bottom-up methods, and recent applications" **p. 11**

10.30-10.50 **O8. O. Chuzel:** "Catalytic Scanning Probe Nanolithography (CSPL). A promising strategy for chemically constructive nanolithography" **p. 12**

10.50-11.10

pausa caffè/pause café

Chairpersons: G. Cerrato, F. Fagès

Session 3: nano&light

11.10-11.30 **O9. F. Sordello:** "Improved photocatalysis on ordered macroporous materials" **p. 13**

11.30-11.50 **O10. L. Santinacci:** "Water photooxidation onto ALD-covered porous silicon electrode" **p. 14**

11.50-12.10 **O11. M.C. Paganini:** "New photoactive materials based on transition metal oxides doped with rare earth metal ions" **p. 15**

12.10-12.30 **O12. O. Margeat:** "Metal oxide nanocrystals for solution-processed interfacial layers in organic solar cells" **p. 16**

12.30-12.50 **O13. E. Boccaleri:** "Properties and application of 3D hybrid nanomaterials: polyhedral oligomeric silsesquioxanes" **p. 18**

13.00

pranzo/déjeuner

giovedì/jeudi 01/02/18

pomeriggio/après-midi

Chairpersons: S. Visentin, Y. Blache

14.30-15.30 **PL3. Y. Coquerel:** "A synthetic journey from anticancer drug to chiral nanographenes" **p. 20**

Session 4: nano&molecules

15.30-15.50 **O14. N. Barbero:** "Functional organic compounds in nanostructured materials: synthesis and characterization" **p. 21**

15.50-16.10 **O15. F. Fages:** "Curcuminoid-borondifluoride dyes for photonic nanomaterials" **p. 22**

16.10-16.30 **O16. K. Martina:** "Covalent functionalization of carbon based nanomaterials by 1,3 dipolar cycloaddition" **p. 23**

16.30-16.50 *pausa caffè/pause café*

Chairpersons: B. Bonelli, D. Gigmès

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16.50-17.10 **O17. Y. Blache:** "Towards bioinspired anti-biofilm strategies: a green solution to reduce environmental impact of antifouling coatings" **p. 25**

17.10-17.30 **O18. R. Cavalli:** "Polymer-shelled nanobubbles: a novel multifunctional delivery tool" **p. 26**

17.30-17.50 **O19. T. Trimaille:** "Polylactide based reactive copolymer micelles: a versatile nanoplatform for bio-related applications" **p. 27**

17.50-18.10 **O20. F. Carniato:** "Exploring mesoporous silica nanoparticles as multimodal imaging and theranostic probes" **p. 28**

18.10-18.30 **O21. N. Guigo:** "Nanocomposites from biobased furanic polymers" **p. 29**

18.30-18.50 **O22. S. Visentin:** "«Imaging» the future: a nanostructured matrices assessment to study drug distribution in solid tumor tissue by mass spectrometry" **p. 30**

19.45

*cena in chalet di montagna
diner en chalet à la montagne*

venerdì/vendredi 02/02/18

mattino/matin

Chairpersons: K. Martina, L. Santinacci

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9.30-9.50 **O23. L. Pasquini:** "Mechanically stable nanofibrous sPEEK/AQUIVION® composite membranes for fuel cell applications" **p. 33**

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10.10-10.30 **O25. T. Djenizian:** "Titania nanotubes based electrodes for Li-ion batteries" **p. 36**

10.30-10.50

pausa caffè/pause café

Chairpersons: N. Barbero, Y. Coquerel

Session 7: nano for the quality of life: safety & energy

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11.30-11.50 **O27. D. Gigmès:** "Synthesis of single-ion BAB triblock copolymers as efficient electrolytes for lithium metal battery" **p. 38**

11.50-12.10 **O28. M. Baricco:** "Complex hydrides: from hydrogen storage to solid electrolytes" **p. 39**

12.10-12.30 **O29. L. Firlej:** "How dense is the gas confined in nanopores?" **p. 40**

12.30-12.50 **O30. A.M. Rossi:** "Surface enhanced Raman scattering strategies for trace contaminants detection" **p. 41**

12.50-13.00

conclusione/conclusion (V. Maurino, P. Knauth)

13.00

pranzo/déjeuner

Pomeriggio: partenza, o permanenza privata al Villaggio Olimpico

Après-midi: départ, ou séjour pour le fin de semaine

Seconde Giornate Italo-Francesi di Nanoscienze
2èmes Journées Italo-Françaises de Nanosciences

ABSTRACTS

ERASMUS MUNDUS MASTER “CHEMICAL NANOENGINEERING”

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ABSTRACT

Erasmus Mundus Joint Master in "Chemical Nano-Engineering" [1] is a two year, Master Program which provides a broad multidisciplinary education in the emerging domain of nano-engineering with strong specialization in chemistry and modeling of nano-objects. The graduated students will have a double competence, experimental and numerical, in design, synthesis and applications of nano-systems. The Erasmus Mundus Joint Master Degree in "Chemical Nano-Engineering" is offered by the Consortium of three Universities [2] : Aix-Marseille University in France, Wroclaw University of Science and Technology in Poland and University of Roma Tor Vergata in Italy. They are providing an excellent environment for Nano-Engineering studies and opportunities for students to participate in research projects conducted by world-class researchers. Upon the completion of the two-year cycle, successful students will be awarded a Joint Master degree. In addition, the CNE consortium furnishes a joint degree-supplement providing a description of the nature and level of the program followed. The language of the CNE Master is English. The consortium offers an innovative and integrated program, based on a jointly developed curriculum and composed of lectures fully recognized by all consortium partners. The first semester is in Marseille, at Aix-Marseille University, where the students learn the basics and fundamental background of chemistry, then they study more engineering at Wroclaw University of Science and Technology and applications of complex nano-systems at University of Rome Tor Vergata. The program is focused on the methodology of bottom-up designing nano-systems and using modeling to design chemical synthesis at the nano-scale. The traditional materials science courses have been adapted for the presentation of the macro towards nano evolutions of materials properties.

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[2] <https://chimie-sciences.univ-amu.fr/chemical-nanoengineering>

COMPUTATIONAL STUDY OF STRUCTURAL PROPERTIES OF NANO-POROUS MATERIALS

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ABSTRACT

ZIFs are porous materials composed of tetrahedrally coordinated metal centers connected by imidazolate linkers. These materials have recently attracted scientific attention due to many possible applications such as gas storage gas storage and gas or liquid separation. Some of the materials from ZIF group possesses particularly interesting vibrational properties such as gate-opening mechanism in ZIF-8 [1] and ZIF-7 [2] (hence, they are referred as flexible ZIFs). ZIF-8 was previously studied with experimental and computational methods and it has been shown that the low-energy vibrations ($<100\text{ cm}^{-1}$) are responsible for the deformation processes such as gate-opening.

Our research was extended to other structures with the same SOD topology but (i) different metal ions in metallic centers (B and Li or Cu at the tetrahedrally coordinated positions, Co, Cd), (ii) different functionalization of imidazolate ring ($-\text{H}$, $-\text{NO}_2$, $-\text{H}$, $-\text{NH}_2$, $-\text{CHO}$) and (iii) different geometry (ZIF-7 and ZIF-9). We used density-functional theory in conjunction with the finite displacement method to predict the normal modes and visualize vibrations of the lattice. Results were used to determine how changes in composition or geometry affect the presence and frequency of the mode related to the gate opening mechanism. We show that there are several particularly interesting modes – one which is a symmetric distortion of the framework leading to opening of the pore (IR inactive due to its high symmetry) and a collection of IR active modes which might be related to asymmetric gate-opening. We claim that the frequency of the IR inactive “gate opening” mode is caused by the interactions between the linkers, therefore depending on attraction/repulsion between the attached functional groups. In contrast, the frequencies (and hence energies) of the IR active modes are sensitive and proportional to the mass of the linker.

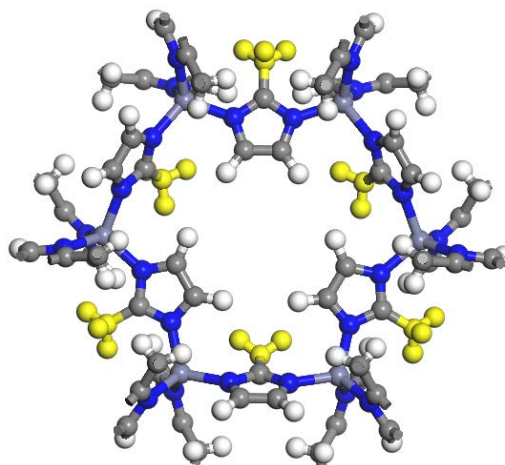


Figure 1. Part of the structure of ZIF-8 with highlighted methyl groups - possible substitution sites.

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NANO-COMPOSITE ION EXCHANGE MEMBRANES

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ABSTRACT

The research aspect is the most important background of the Erasmus Mundus Joint Master Degree Chemical Nano-Engineering (CNE). The idea of the CNE program was born during the common meetings with the research partners as an amplification factor of the existing active common research programs. These programs have been developed in the last 10 years and include the research in the domain of nano-porous materials for energy carriers (H₂, CH₄) as well as nano-technologies for new electrochemistry energy technologies. An international associated laboratory (L.I.A. LIME) of CNRS, Aix Marseille University and University of Rome Tor Vergata on nanostructured membranes for electrochemical energy devices was signed in 2015.

The main topics of LIME are: 1) Proton conducting ionomers. They are materials of choice for fuel cells and water electrolysis. The properties can be improved by innovative thermal treatments for annealing and cross-linking the macromolecules [1]. 2) Cation conducting ionomers. Various cations can be introduced by ion exchange or chemical reaction (e.g. with butyl-Li). The ionomers can be used as separators for rechargeable batteries (in anhydrous state) or for aqueous metal batteries. 3) Hydroxide conducting ionomers. The most common anion exchange membranes (AEM) contain quaternary ammonium groups. The basic operating conditions allow using non-noble electrocatalysts for the oxygen reduction reaction and thus an important cost reduction for alkaline fuel cells and water electrolyzers [2]. 4) Anion conducting ionomers. They can be prepared by ion exchange from hydroxide conducting ionomers or by innovative synthesis by reaction of acids with basic groups (e.g. sulfonamides). Such ionomers are especially useful for redox flow batteries, where the cation permeability must be minimized. 5) Amphoteric ionomers. Acidic and basic groups coexist in a single macromolecule: the type and value of the ionic conductivity depends on the pH of its environment. This versatility and the low ionic permeability are very useful for technologies requiring low ion permeability.

Different strategies have been developed to improve the AEM performances. Among them hybrid organic-inorganic materials show many interesting features: they have the capacity to combine the functionality of organic compounds with the stability of inorganic materials [3,4]. Class I hybrids (or composites) are obtained dispersing inorganic components (generally oxides) in a polymeric matrix. The composites are generally obtained mixing preformed nanoparticles or forming nanoparticles via in situ sol-gel routes. The different nature of the filler can vary the structure of the nano-phase separated channels leading to well-connected ionic domains and the optimization of the microstructure. The results are a stabilization of the polymeric phase and a decrease of fuel crossover. However, a decrease of the conductivity is generally observed due to the presence of a second phase. In this presentation an overview of the different composite exchange membranes will be given.

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POST LITHIUM-ION BATTERIES. NANOSTRUCTURES TO ENHANCE ELECTROCHEMICAL PERFORMANCE

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ABSTRACT

Typical Li ion technologies cannot meet the high-energy demands for systems such as smart grids and electrical transportation, as their energy density is practically limited to 300 W h kg⁻¹[1, 2].

New technologies, such as Lithium Sulphur (Li-S) and Lithium Air (Li-Air) batteries emerged as a prospective solution to the issue due to their remarkably high specific energy value (2600 W h kg⁻¹ for Sulphur and 11500 Whkg⁻¹ for Oxygen), that is respectively > 5 and 10 times to the available Li ion technology [2-4]. Li-S cells are much closer to the market while the roadmap of the Li-Air technology is predicted to be extended to a 20 years window.

The reversible electrochemical conversion of sulphur (S₈) into Li₂S through a series of lithium polysulphides (LiPS) results in a high-energy Li-S system. However, insulating nature of both sulphur (S₈) and Li₂S, and solubility of intermediate LiPS severely hamper the capacity retention and high rate capabilities. Herein, a facile and scalable synthesis approach is reported to yield conductive Magnéli Phase Ti_nO_{2n-1} decorated carbon matrices to host sulphur for long life Li-S batteries.

The longevity, greater capacity retention and higher Coulombic efficiency of as prepared sulphur cathodes can be attributed to both physical confinement and chemical bonding of LiPS. The experimental characterizations are evident of strong Magnéli Phase Ti_nO_{2n-1} interaction with LiPS assisted by rise in local concentration of LiPS owing to the absorptivity of carbon matrix. These cathodes allowed working at low electrolyte to sulphur (E/S) ratio to target high gravimetric and volumetric capacities in comparison to their highly porous carbon counterparts. The assembled cells from as obtained cathodes exhibited the initial discharge capacity of 1100 mA h g⁻¹ at 0.1 C and maintained its reversible capacity to 520 mA h g⁻¹ at 0.2 C for more than 500 cycles. The loss in capacity is recorded less than 0.06% per cycle for 1000 cycles with Coulombic efficiency close to 99% even at 1 C [5].

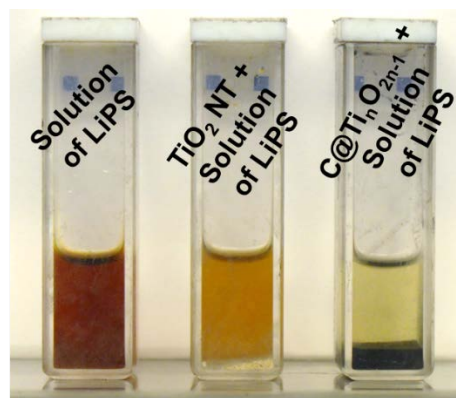


Fig. 1 Experimental illustration of LiPS adsorption onto Magnéli Phases Ti_nO_{2n-1} NPs loaded carbon matrix, in solution.

Li-Air cells are using the very high voltage of Oxygen reduction reaction. Several major issues are responsible for the limited actual capacity and cycle ability of Li-Air. In principal, the stability of the electrolyte solvent [6,7] and the precipitation of lithium oxides discharge products inside the cathode pore structure during cell discharge. The high recharge potentials needed to decompose the insulating lithium peroxide and the parasitic products formed from the electrolyte decomposition result in energy losses for achieving a reversible electrochemical process [8]. Catalysts are needed to facilitate the decomposition reaction of Li_2O_2 , which is the main reaction product.

Mesoporous carbon nanofibres doped with palladium nanoparticles (Pd CNFs) are synthesized by electrospinning with subsequent thermal treatment processes and used as electro-catalysts at the oxygen cathode of Li-O_2 batteries. FESEM images show that the spherical Pd nanoparticles (NPs) are homogeneously dispersed on the surface of CNFs and X-ray diffraction (XRD) measurements display a fcc structure of Pd. The surface area of the nanocomposite CNFs is greatly increased with the incorporation of the metal NPs up to $600 \text{ m}^2 \text{ g}^{-1}$ and the presence of the metal promotes graphitization of the carbon.

Addition of the *N*-[(aminoethyl)aminopropyl]trimethoxysilane additive in the precursor solution for electrospinning allows the reduction of the Pd NPs particles size, preserving the highly mesoporous *N*-doped large surface area and graphitic-nitrogen groups of the carbon nanofibres. Incorporating with a Pd/CNFs catalysed cathode, the Li-O_2 battery shows a very low voltage gap of 0.48 V vs. Li^+/Li between the terminal discharge and charge voltages, as the recharge occurs at a potential underneath 4.0 V vs. Li^+/Li for about 90 cycles at the curtailed capacity of 200 mA h g^{-1} . The low recharge voltage can relieve parasitic reactions due to the decomposition of electrolyte and favour a longer cycle life [9].

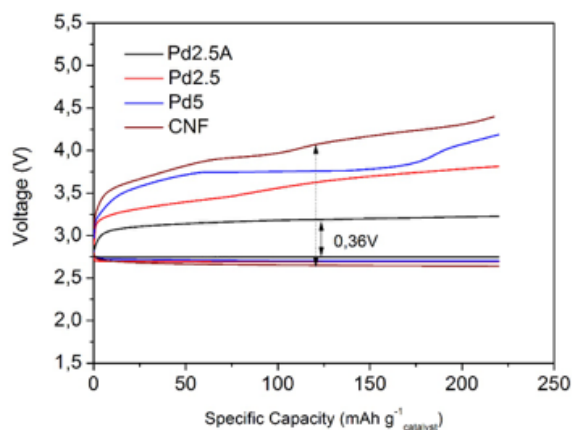


Fig. 2 Galvanostatic discharge and charge of the Li-O_2 cells at the curtailed capacity of 200 mA h g^{-1} at the applied current of $20 \text{ mA g}_{\text{cathode}}^{-1}$ with cathodes: Pd2.5A (black line), Pd2.5 (red line), Pd5 (blue line), CNF (green line) and the GDL (pink line). The voltage vs. capacity plot refers to the 1st cycle.

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HIGHLY VERSATILE ORGANIC DIELECTRIC FOR ION DETECTION UP TO THE FEMTOMOLE IN FIELD EFFECT TRANSISTOR SENSORS

Ahmad Kenaan,^a Volkan Kilic,^a Tin Phan Nguy,^b Frédéric Brunel,^a Sébastien Lamant,^a Matthieu Petit,^a Yutaka Wakayama,^b Anne M. Charrier,^a Jean-Manuel Raimundo^a

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ABSTRACT

The recent advanced developments in sensors and wireless-communications devices enabled the design of miniature, cost-effective, and smart physiological sensor. However, despite high progress in these domains there is still a crucial interest and demand on the development of new specific and selective sensors towards various kind of analytes associated to a good stability, selectivity and reproducibility.

To this aim we have recently developed an innovative MOS-type field effect transistor for the electrical detection of metal ions implicated in biological processes. Sensitivity of sensor strongly depends on the value of the electric field change created across the dielectric that's why the thickness of the insulator constitutes a key parameter that is crucial to optimize. We present herein an original platform constituted of an engineered lipid monolayer that is used both as the active sensitive layer and as ultra-thin gate dielectric in field effect transistor sensors. Lipid derivatives have been selected due to their known intrinsic properties such as natural barrier to ions/molecules, high electrical resistance, a low thickness and their ease to be chemically modified.

We will present herein specific sensing assays demonstrating the effectiveness of the new developed device associated to a wide linear detection range and a limit of detection up to the femtomole, sensitivity up to 90 mV/decade and a linear response over more than 8 decades.[1] In addition, chemical modifications have been performed in order to make this dielectric sufficiently stable to endure high electric fields affording a device associated with a direct dielectric breakdown occurring at ~30MV/cm, that is much higher than for a silicon oxide layer of similar thickness.[2] Full organic devices are now foreseen with the replacement of the inorganic semi-conductor by organic analogues and preliminary results will be given.

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STRATEGIES AND CHALLENGES FOR EFFICIENT ACTIVE TARGETING

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ABSTRACT

The side effects of drugs used in the therapy of some diseases, like cancer, would be reduced by introducing them selectively into those cells or tissues where their action is required.

Ideally, a drug designed for clinical use should have a high therapeutic index, which is the ratio of the drug's efficacy (therapeutic effect) to its toxicity (side effects). A drug with low therapeutic index but high activity should be delivered in a higher concentration to the target cells (thereby increasing efficacy) and away from non-target cells (thereby reducing toxicity). This delivery approach, called drug targeting, provides a mean of increasing the therapeutic index of the drugs and achieving more effective therapy, with possible economic benefit.

Many different systems have been explored to target antineoplastic agents selectively to cancer cells or tissues. One of the more general approaches is to link a carrier molecule, such as a protein, polysaccharide, natural or synthetic macromolecule, lectin or an antibody, by a covalent bond to an active moiety, such as an antitumoral drug or a cytotoxic protein [1].

In searching for the ideal carrier, it is tempting to look for systems which can intrinsically 'recognise' the target. Monoclonal antibodies have been shown to increase cytotoxicity and specificity in targeting antitumour drugs or toxins towards malignant cells [2]. Glycoproteins are another category of macromolecules, that, depending on their charge and carbohydrate structure, are specifically recognised by certain tissues and cell groups within these tissues [3]. Moreover, hormones, lectins and transferrin can be used as carrier molecules with receptor-mediated uptake.

Many biologically active molecules have been delivered in the form of covalent conjugates with water-soluble, biodegradable polymers or natural macromolecules. The modification of drugs by conjugation with polymers has been investigated for a variety of purposes.

A useful alternative approach to target antineoplastic drugs to tumour cells has been to use vesicular or particulate systems, such as liposomes, nanoparticles, microparticles for regional therapy or cells (erythrocytes, leukocytes, hepatocytes, platelets), to improve the drug concentration at the target by altering both tissue distribution and the drug's pharmacokinetic constant. Among vesicular particulates, liposomes have also been successfully used in clinical medicine for their ability to deliver drugs to the target cell or tissue, decreasing toxic side effects and also drug dosage [4]. With the so-called classic liposomes, recognition of the specific cell or tissue depends mostly on a passive targeting mechanism, which is given by the bulk structural character of the carrier, such as its hydrophilicity or hydrophobicity, charge density, membrane fluidity or vesicles size. The most important drawback of this type of liposome is the very rapid elimination from the blood by the cells of the mononuclear phagocytic system (MPS). This prevents most of the administered liposomes from reaching their target site. The development of long-circulation liposomes ("stealth" liposomes), obtained by coating the lipid bilayer with polyethylene glycol, has renewed interest in liposome delivery systems. These liposomes leak from the tumour vasculature to reach the tumour cells, exploiting the enhanced vascular permeability, limited recovery via post capillary venules and lack of lymphatic system. Nevertheless, it has been shown that stealth liposomes also tend to be located in the tumour extracellular compartment, but are not fully

taken up by tumour cells.

To further enhance the cytotoxic effect, selective delivery of drugs to target cells can be achieved by conjugating lipid vesicles to various targeting ligands, such as antibodies, lectins, peptide hormones or growth factors. In this way, the conjugated liposomes are potentially able to bind a specific receptor on target cell membranes, triggering their own internalisation by the mechanism of endocytosis. This is followed by the enzymatic digestion of the liposomes in the intracellular compartment (endosome, phagosome or acidosome), accompanied by the intracellular distribution of liposomal components to the cytosol.

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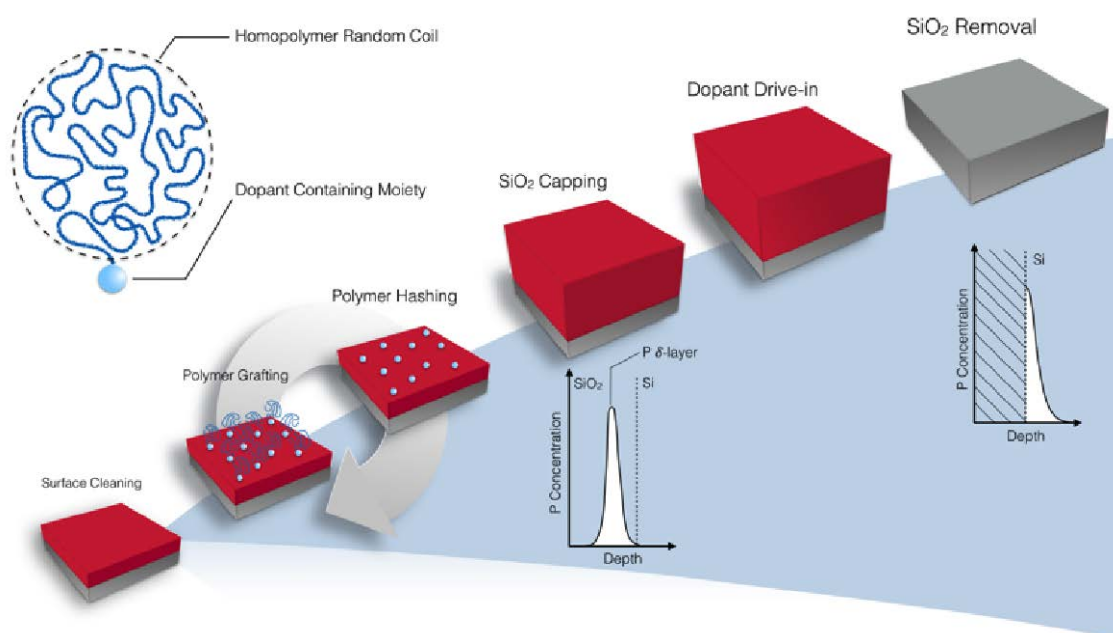
DETERMINISTIC DOPING IN SEMICONDUCTORS VIA SELF-LIMITED GRAFTING TO REACTIONS

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ABSTRACT

An effective bottom-up technology, illustrated in Scheme 1, for precisely controlling the amount of dopant atoms tethered on silicon substrates is presented.



Scheme 1. Schematic workflow of the doping process.

Monodisperse polystyrene and poly(methyl methacrylate) polymers end-terminated with a hydroxyl containing moiety were synthesized[1] by ARGET-ATRP with different molar mass and narrow size distribution and subsequently reacted with diethyl chlorophosphate leading to the diethylphosphate (DPP) end-capped moiety[2]. The polymers were spin coated and subsequently end-grafted onto non-deglazed silicon substrates. P atoms were bonded to the surface during the grafting reaction and their surface density was set by the polymer molar mass, according to the self-limiting nature of the "grafting to" reaction. Repeated cycles of polymer grafting followed by plasma hashing led to a stepwise increase in the dose of P atoms grafted to the silicon surface. P injection in the silicon substrate was promoted and precisely controlled by high temperature thermal treatments. Sheet resistance measurements demonstrated effective doping of Si substrate. Lithographic masks prepared by block-copolymer based technology[3] were employed to control at the nanoscale the lateral confinement of the dopant atoms.

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ELECTRODEPOSITION OF IONOMER MEMBRANES FOR MINIATURIZED ENERGY STORAGE AND CONVERSION DEVICES

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ABSTRACT

Electrochemical synthesis is a powerful tool for the preparation of conformal, thin solid electrolyte membranes directly on the electrodes, particularly with complex shapes, such as nanotubes, nanowires etc.

Such separators should present the highest possible conductivity by the electrochemically active ions, negligible electronic conductivity combined with high chemical and mechanical stability.

These requirements drive our development work: we use aromatic polymers, given their excellent mechanical properties (large stiffness and strength), which are decisive for a high durability of the separators and the devices. Single-ion conductivity is assured by grafting the counter-ions on the polymer chain (ionomers).

The talk will present examples of electrodeposition of ionomer membranes and report structural, microstructural and electrical properties of the ionomers, including relevant applications, such as Li batteries.

1. Cation-conducting membranes

We synthesized several ionomers containing grafted sulfonate groups. These ionomers (including poly(styrene sulfonate), PSS) can be used for proton exchange membrane fuel cells and Li batteries [1-3].

2. Anion-conducting membranes

These ionomers contain quaternary ammonium as fixed cationic groups. They can be applied for example in anion exchange membrane fuel cells or solid-state water electrolyzers [4].

Thin ionomers separators are a valuable asset for the realization of micropower devices, especially microbatteries and microfuel cells. Furthermore, anodic and cathodic deposition conditions were explored, which opens perspectives for the realization of deposits on various semiconducting substrates and simultaneous or sequential co-deposition with noble or non-noble metals for the realization of catalytic electrodes for example.

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AB INITIO SIMULATION OF ZnO/La(Sr)MnO₃ HETEROJUNCTIONS: INSIGHTS INTO THEIR STRUCTURAL AND ELECTRONIC PROPERTIES

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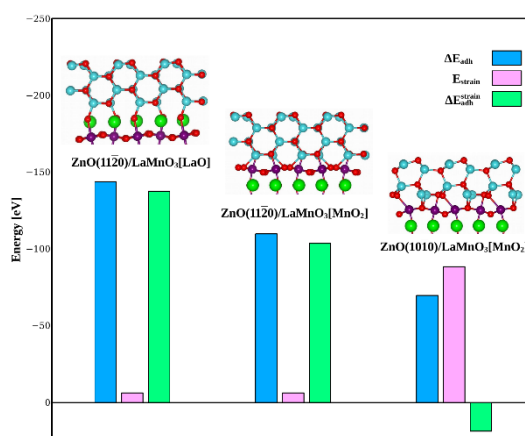
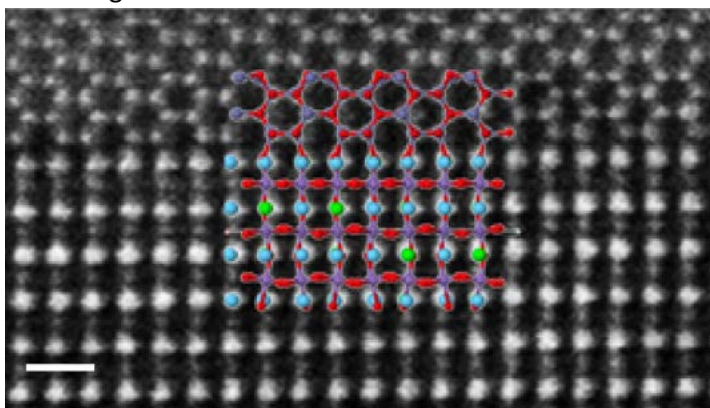
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ABSTRACT

Layered oxide heterostructures show interesting properties that encompass those of the standalone moieties, hence a detailed understanding of the interface is key to the development and use of such materials. In this work, we have performed quantum-chemical ab initio calculations to give a complex description of structural and electronic properties of epitaxial growth ZnO/LaMnO₃ (ZnO/LMO) interfaces.

The Crystal code [1], that uses a local (Gaussian) basis set, is used to design and characterize ZnO/LMO heterostructures including (11-20) and (10-10) non-polar overlayers of ZnO on LMO(001), support from simpler formulation to hybrid functionals of density-functional-theory (DFT). The applied structural models and coincidence cells are described and illustrated in details. We discuss the impact of different termination of LMO through stability (computed strain and adhesion energies), structural and electronic properties (density of states and 3D charge density differences). The ZnO(11-20) overlayer shows the less structural distortion and the most stable configuration with LaO termination of LMO [2].

Following the results of this work the most stable interface has been also studied through a combined



experimental/theoretical approach for Sr doped LMO La_{0.7}Sr_{0.3}MnO₃/ZnO (LSMO/ZnO) heterostructures. These interfaces exhibit extremely interesting electronic properties making them promising candidates for novel oxide p-n junctions, with multifunctional features. The ab initio predictions agree well with experimental high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images and confirm the validity of the suggested structural model [3].

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NANO/MICRO-STRUCTURED TiO₂ COATINGS PREPARED BY HIGH THROUGHPUT TOP-DOWN/BOTTOM-UP METHODS, AND RECENT APPLICATIONS

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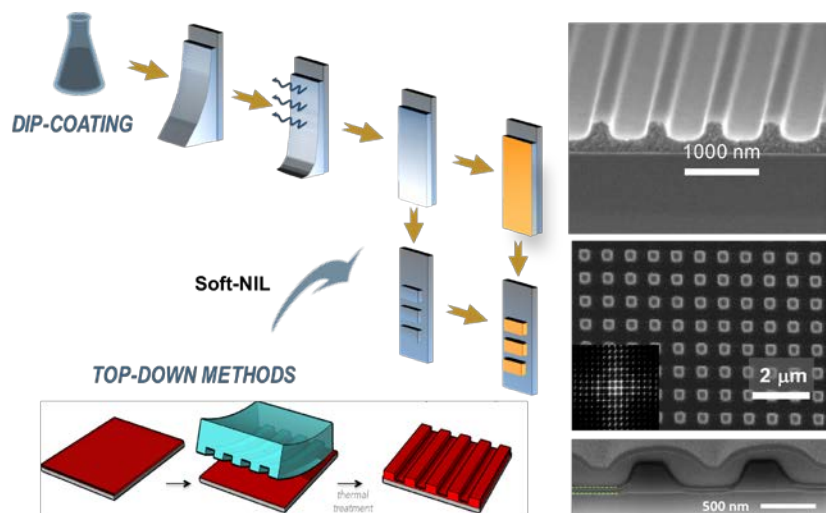
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ABSTRACT

Complex hierarchical nano structures can be achieved when combining chemical advanced bottom-up strategies, such as self-assembly and sol-gel chemistry, together with liquid solution processing. Amongst them, dip-coating is an extremely versatile tool to prepare thin nanostructured and mesoporous metal oxide films from liquid solutions and has been used for many decades without taking advantage of its whole potentiality. [1,2] This communication reports on the recent progresses performed in nanostructured sol-gel TiO₂ coatings, and their combinations with conventional “top-down” micro(nano) fabrication technologies such as Soft-NIL, to construct even more complex morphologies with multi scales features and motifs. [3] [4] Recent implementations in surface wetting, and photonics will be presented. [5]

Fig. Strategy applied to elaborate patterned surfaces using combined sol-gel process and soft-Nano-Imprint-Lithography. SEM images of structured obtained by this strategy.



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CATALYTIC SCANNING PROBE NANOLITHOGRAPHY (CSPL) A PROMISING STRATEGY FOR CHEMICALLY CONSTRUCTIVE NANOLITHOGRAPHY

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ABSTRACT

Scanning probe (STM and AFM) nanolithography belongs to the most important methods for creation of nanoobjects on the surface with sub-100 nm resolution. It is generally based on the direct diffusion transfer (Dip-Pen nanolithography) and mechanic or electrical destruction of the surface. Limited reports on the AFM catalyzed chemical surface modification was achieved using AFM probes coated with metals (Pd and Pt-azide hydrogenation^[1] and alkene hydrosilylation^[2]), metal oxides (Cu₂O, alkyne-azide “click” reaction^[3]) and absorbed metal nanoparticles (Pd NPs, Suzuki and Heck cross-coupling^[4]). We report herein the first use of the AFM tip with immobilized homogeneous catalyst for spatially controlled epoxidation of the surface terminal alkene groups (Figure 1).^[5,6]

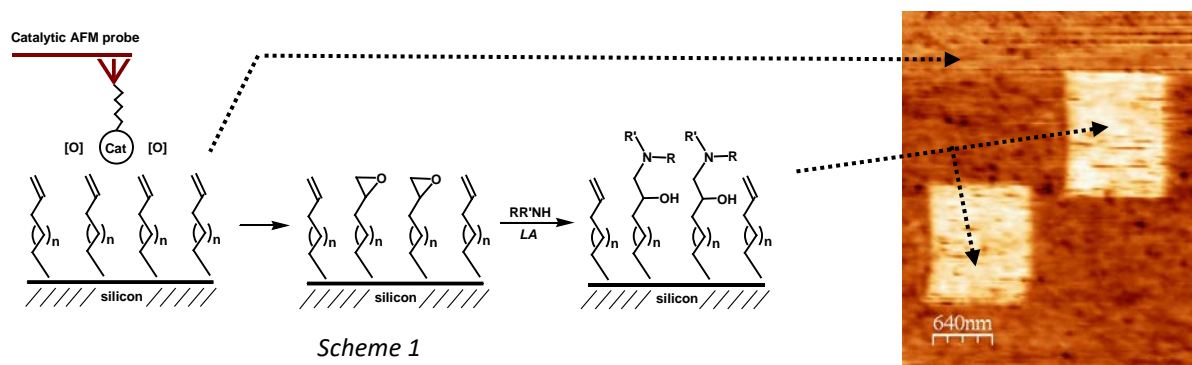


Figure 1. AFM topography image of the surface after local epoxidation of two 1 μm squares on the alkene terminated SAM followed by the reaction of the epoxide groups with secondary amine

The reaction was carried out in the solution of the epoxidation agent by the direct contact of catalytic AFM probe with alkenyltrichlorosilane SAM on silicon within the appropriate force range (Scheme 1). After treatment of resulting surface with a secondary amine in the presence of a Lewis acid, AFM imaging revealed the positive surface topographic change roughly corresponding to the length of amine molecule in the epoxidized area only thus indicating the formation of aminoalcohol domains on the alkene SAM. The concept used in this work could be attractive for the controlled 3D fabrication of various types of nanodevices.

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IMPROVED PHOTOCATALYSIS ON ORDERED MACROPOROUS MATERIALS

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ABSTRACT

In photocatalysis a redox reaction is accelerated thanks to the ability of a semiconductor of absorbing light, generating charge carriers, separating and transferring them to species in the gas or liquid phase. The main losses of the photocatalytic process are the recombination of the photogenerated charge carriers and the limited light absorption of the semiconductors employed, such as TiO₂ [1]. We concentrated our attention on this latter aspect, and, in particular, on the role of three-dimensional structuration in the improvement of light absorption. We fabricated TiO₂ inverse opals and TiO₂ macroporous materials with disordered arrangement of the pores in the space and we measured the photocatalytic activity of these materials in the degradation of phenol. We found that the inverse opal displayed greater activity than the macroporous powder and the crushed powder, which had lost its structural order, when the irradiation wavelength was properly tuned to fall at the edges of the photonic band-gap. Conversely, the materials behaved very similarly when the irradiation wavelength lay outside the photonic stop band [2]. With this procedure we were able to isolate the contribution of 3D structuration in increasing the light absorption compared with improved mass transfer and increased specific surface area, which are also improved with 3D structuration. In summary, slow photons play a huge role in the improvement of the photocatalytic activity. Porosity and specific surface area have only a minor influence on the photocatalytic activity of TiO₂ inverse opals, because they cannot explain alone the observed phenol degradation rates.

Moving from these experimental evidences, the optical and photoelectrochemical behavior of TiO₂ inverse opals and TiO₂ disordered macroporous materials were investigated by means of UV-Vis spectroscopy, cyclic voltammetry, chronopotentiometry and electrochemical impedance spectroscopy [3]. These techniques confirmed the better absorption of light of TiO₂ inverse opals, due to the slow light phenomenon. TiO₂ inverse opals and TiO₂ disordered macroporous structures are shown to have the same recombination rate of photogenerated charge carriers, but TiO₂ inverse opals are characterized by a better reactivity of photoelectrons towards O₂. This property can also contribute to the improvement of the photocatalytic activity observed by several groups [4, 5].

This increased reactivity of photoelectrons could be exploited in the photocatalytic reforming of organic compounds to yield H₂. Again, to discriminate the effects of slow photons, the hydrogen photoproduction experiments were carried out at two different wavelengths, at 365 nm where the effect of slow photons is maximized, and at 254 nm where it is negligible. TiO₂ inverse opals present increased photocatalytic production of H₂ compared with TiO₂ macroporous structures with disordered arrangement of the pores. The resulting hydrogen production rates also highlight the importance of the polymer template employed in the synthesis of the TiO₂ powders. Indeed, the polymeric template determines the crystalline phase of the resulting TiO₂ material and, as a consequence, affects its catalytic performances [6].

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WATER PHOTOOXIDATION ONTO ALD-COVERED POROUS SILICON ELECTRODE

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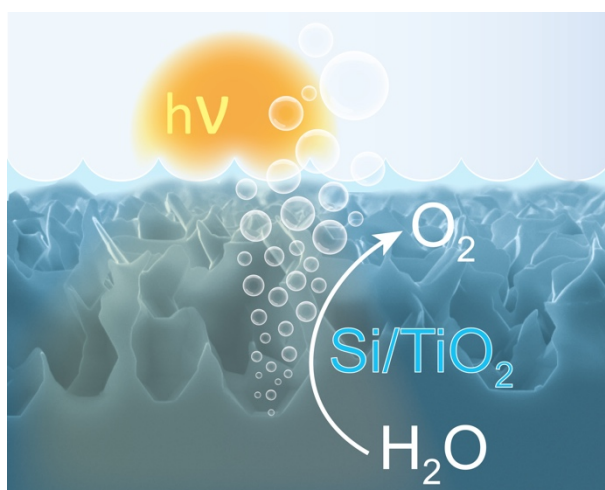
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ABSTRACT

The sunlight's intermittent nature is one of the issues limiting widespread harvesting of solar energy for power infrastructures. A leading approach is to store as chemical fuels the energy produced by this discontinuous renewable energy source [1]. The development of photoelectrochemical cells (PECs) used to produce H₂ and O₂ from water photo-splitting has, therefore, attracted a great deal of interest. Although the concept has been initially demonstrated on TiO₂ [2], Si has become a highly appealing material for such target because it is an abundant and cheap element and also because its energy band structure is well suited for the absorption of the solar radiations. Conversely, silicon is not stable under the water photo-splitting conditions and it exhibits a high reflectance.

In this contribution, we report a rapid, inexpensive two-step method for structuring n-type (100) Si surfaces with micron-sized cavities, the process is based on the photoelectrochemical etching (PEE) of the Si surface and its subsequent alkaline etching. This method produces a layer of random macropores over a large area, which renders the Si surfaces antireflective over the visible spectrum. We demonstrate that such surfaces can be conformably coated by anatase TiO₂ layers by atomic layer deposition (ALD) and that they can be used as stable photoanodes producing enhanced photocurrents under simulated sunlight with respect to their planar counterparts. These TiO₂-protected Si microstructured surfaces were highly stable in strongly alkaline solutions and were used as photoanode for several hours under simulated sunlight. Such photoanodes surfaces showed 50 % photocurrent enhancements and ~400 mV negative shift of onset potential without any co-catalysts, demonstrating their high potential for solar energy conversion applications [3].



Artistic view of the structured and functionalized photoelectrode (from [3]).

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New Photoactive Materials Based on Transition Metal Oxides Doped with Rare Earth Metal Ions

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ABSTRACT

The applications of visible light in photocatalytic reactions is the challenge for scientists in the next years. Since 1972 when the seminal paper of Fujishima and Honda has been published, TiO₂ played a crucial role among photocatalysts. New generations of photocatalysts have been prepared and tested since the beginning of this century. The aim is to go beyond titanium dioxide and was initially a prediction proposed by N. Serpone and A. Emeline^{1,2}. This was based on the idea of a wide band gap semiconductor (hence with excellent flat band potentials) containing extra electronic levels at intermediate energy in the band gap capable of allowing the transition of electrons from the VB to the CB with a double excitation. With the present contribution, we intended to test the photoactivity of this novel family of materials investigating both zirconium dioxide and zinc oxide doped with lanthanide ions, at various quantitative levels. Firstly, we synthesized and fully characterized via XRD, Diffuse Reflectance UV-Vis and BET the new materials. Secondly we investigated their photoactivity through EPR spectroscopy, generating charge carriers and monitoring their reactivity. This was done in order to verify the potentiality of the novel systems in photocatalytic reactions under low energy photons (i.e. in the absence of UV components) that is essential for future applications under true solar light. In our study we synthesized ZrO₂ and ZnO doped with various Rare Earth (RE= Ce, Pr, Er) ions (0.5-1-5 wt%) and with different techniques. Encouraging results have been obtained especially with the samples containing Ce ions. The photoformation of both electrons and holes under irradiation with visible light ($\lambda > 420\text{nm}$) has been monitored via EPR. The results show an interesting photocatalytic activity of all Ce containing materials. The introduction of new electronic states in high band gap semiconductors like ZrO₂, realized by doping with rare earth elements like Ce and other lanthanides, leads to new photocatalysts able to absorb some portions of visible light, and to perform, in this way, a classic electron-hole separation. The same photoactivity can be observed with Ce doped ZnO but the electronic structure, in this case, is completely different. The optimal composition for the two different families of photocatalysts was individuated. Photocatalytic activity results, rigorously obtained under visible light irradiation. The doping with cerium of ZrO₂ (0.5wt%) and ZnO (1wt%) lead to the formation of catalysts that showed the highest value of activity. The materials here described can be assumed to well describe the third generation catalysts theorized by Emeline and Serpone^{1,2}.

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METAL OXIDE NANOCRYSTALS FOR SOLUTION-PROCESSED INTERFACIAL LAYERS IN ORGANIC SOLAR CELLS

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ABSTRACT

Polymer solar cells (PSCs) have attracted high attention over the last decade due to their unique advantages of low-cost production, environmental sustainability, mechanical flexibility and light weight. Interfacial layers (IL) that sandwich the active layer (**Figure 1**) are important parts of high efficient organic solar cells as they provide efficient charge carrier extraction towards the electrodes avoiding hereby losses such as non-ohmic contact, charge carrier recombination and exciton quenching at the interfaces.[1] In the past, solution-processed materials such as metal oxides have been successfully introduced as hole and electron blocking layers for organic solar cells. Especially, ZnO based electron extraction layers are nowadays one of the most promising IL candidate leading to efficiencies above 11% in single junction devices.[2] Beside their electronic properties, such metal oxide layers introduce so-called optical spacer (OSP) effects that modify the light distribution inside the solar cell.[3] We could previously demonstrate that optimization of optical, morphological and electronic properties of nanocrystal-based ZnO IL (**Figure 2**) is necessary to reach high efficiencies in PSCs.[4] Although metal-oxide-based IL are applied to organic solar cells for a decade, their low conductivity limited their thickness to tenth of nanometers and thus limited their compatibility with robust solution processing, i.e. industrial developments.

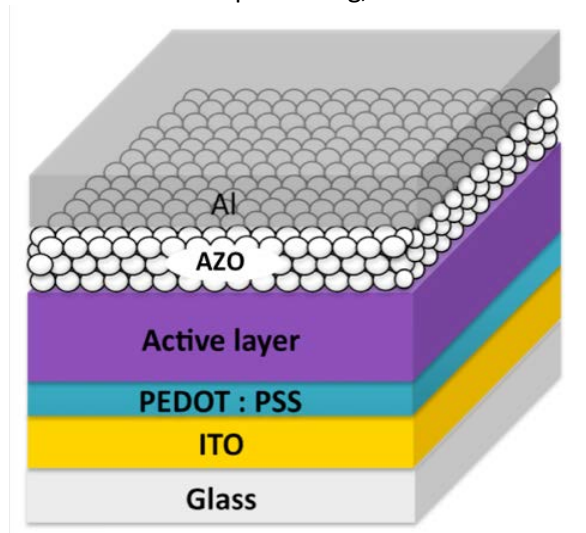


Figure 1: Regular device structure of a PSC using metal oxide nanocrystals as electron extraction layer.

As electron extraction layer, the case of aluminum-doped ZnO (AZO) nanocrystals is presented, allowing for fabricating solar cells using thick optical spacers with low temperature processing. The synthesis and detailed analysis of AZO nanocrystals are reported, followed by the elaboration of cluster-free nanocrystal solutions in alcohol based solvent. These AZO nanocrystals are processed into thick highly conductive IL with very low film roughness at low temperature and are thus compatible with processing of highly

efficient polymer solar cells using normal device structures. In order to demonstrate the potential of AZO-based optical spacers for robust solar cell processing using thick layers, we focused on processing of PTB7:PC₇₀BM blend layers with thicknesses up to 210 nm. We could show that AZO-based optical spacers with thickness up to 100 nm lead to solar cells with conversion efficiency up to 7.6% when combined with photoactive layer of 200 nm thickness, both enhancing strongly the robustness of device processing. More importantly, we could show for the first time that the AZO-based optical spacers allow color tuning of organic solar cells over a large range by varying the thicknesses of both optical spacer and polymer blends, opening new opportunities for the use of optical spacer in organic photovoltaic.[5]

As hole extraction layer, recent studies using nickel oxide (NiOx) nanocrystals are presented (**Figure 2**), showing promising results as replacement of PEDOT:PSS in inverted device structures.

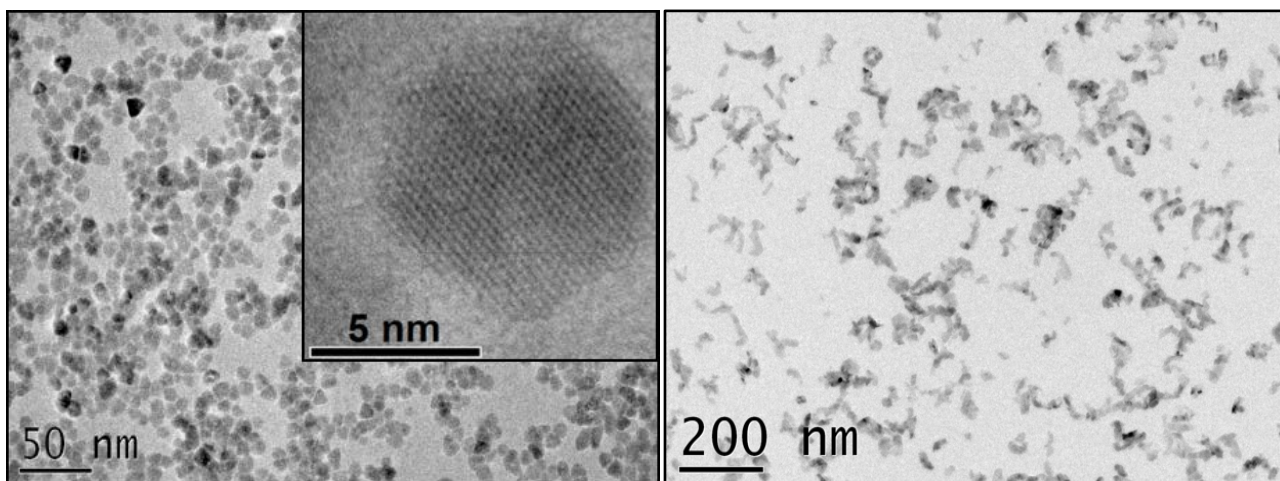


Figure 2: TEM pictures of aluminum-doped ZnO nanocrystals (left) and nickel oxide nanocrystals (right).

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PROPERTIES AND APPLICATION OF 3D HYBRID NANOMATERIALS: POLYHEDRAL OLIGOMERIC SILSESQUIOXANES

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ABSTRACT

Polyhedral oligomeric silsesquioxanes (POSS) are a class of condensed three dimensional oligomeric organosiliceous compounds with the cage framework having different geometries and symmetries. As a general feature, the molecular structure of these compounds consists of silicon atoms bonded to one- and-a-half oxygen (“sesqui-”) and hydrocarbon (“-ane”) moieties (herein denoted as R), leading to (RSiO_{1.5}) bond units.

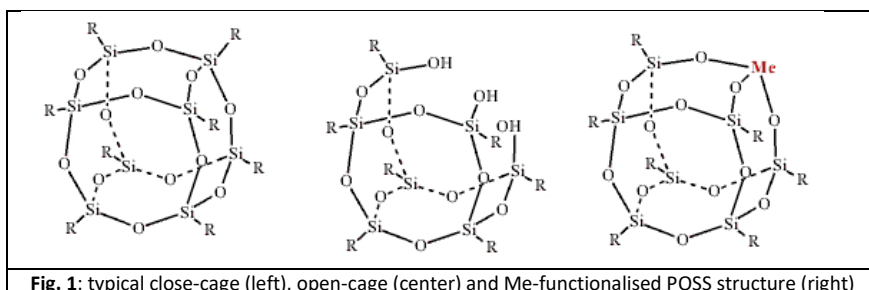
The most common materials are cubic systems, with general formula R₈Si₈O₁₂.^[1] These compounds show valuable unique features as materials for nanotechnological uses, thanks to their 3D cage nanostructure, the bottom-up preparation affording high homogeneity and purity, and highly versatile chemical properties (R groups can be essentially chosen on the basis of the wide range of organosilanes).

For these reasons, they are addressed as smart hybrid materials, coupling at best the features of inorganic and organic compounds, and providing the relevant perspective, for nanoscience, of the possibility to design and reproducibly tailor specific functional features.

POSS have attracted growing interest in the last decade as 3D nanomaterials, finding applications in several fields, spanning from catalysis, to bio-medical and diagnostic uses, to the preparation of nanocomposite materials with improved physico-chemical features ^[2].

Besides fully condensed polyhedral silsesquioxanes that are generally identified with a cubic R₈Si₈O₁₂ structure, open-corner POSS compounds, structurally related to cubic systems where a Si vertex is removed leaving incompletely condensed silanol groups (with general formula R₇Si₇O₉(OH)₃), seem to be currently more interesting, because of their capability to link different functionalities through the reaction with specific organosilane and heteroelement precursors.

In particular, partially condensed POSS can react with a large variety of metal centres (in the form of alkoxides or chlorides), thus affording a completely condensed metal-silsesquioxane species (M-POSS).^[3] The “Periodic Table of metal-containing POSS” already covers numerous chemical elements spanning from alkali metals to transition and lanthanide ions and the chemistry of these solids continues to be an area of vigorous research activity.



In this work, an overview of the experimental activity carried on in our group will be provided, based on the development and optimisation of synthetic methods to produce M-POSS, the ways to understand and describe their features, and some relevant application of POSS and M-POSS.

Two main classes of M-POSS will be shown: on one side, molecular materials containing metal centres with different functional roles (i.e. catalysis, luminescence), on the other side, hierarchical structures containing M-POSS as functional modifiers.

M-POSS can be prepared using corner capping reaction in solution, employing essentially mild conditions and relatively short times of reactions [4]. The follow up of the reaction and the characterisation of the products make use of FT-IR spectroscopy, Raman spectroscopy, Solid State NMR, X-ray diffraction and X-ray photoelectron spectroscopy. The reaction conditions allow the control of the final structure of the M-POSS, as typically, monomer-dimer equilibria can be present.

This method has been applied to produce Ti, V, Al, Eu-POSS derivatives, and explored for their properties in the field nanocomposites and fire retardancy of polymers and catalysis in several fields. [5-6]

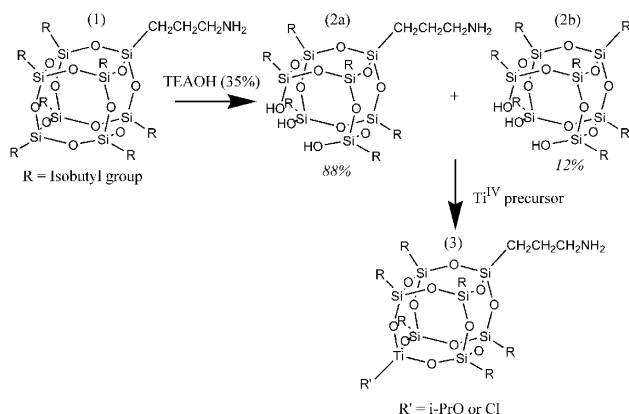


Fig. 2: synthesis of difunctional M-POSS

These materials have been also employed to develop multifunctional systems, via subsequent corner-opening and capping procedures. [7] These materials can thus be employed as functional modifiers for different hosting structures using different anchoring interactions, as ionic exchange or chemical grafting.

Their use in fully synthetic clay-like materials as saponite and its use as multifunctional additive for polystyrene, and as chemically bound modifier onto mesoporous silicas as supported catalyst for epoxidation reactions were investigated. [8-9]

Lanthanide-containing POSS (Ln-POSS) have been prepared using Eu^{3+} , since luminescent features of this ion can be bridged with a high thermal and mechanical stability.

A detailed investigation of the physico-chemical properties of the Eu(III)-POSS was carried on by NMR applied to ^{13}C and ^{29}Si nuclei, FT-IR and MALDI-TOF analyses, providing information on the reaction steps and on the nature of the final product. Results indicate that the Eu^{3+} ion caps the POSS unit by the dangling oxygen groups of the open corner and expands its coordination sphere by linking solvent molecules from the reaction medium.

From the optical point of view, interesting luminescent properties were found: Eu(III)-POSS has proved a quantum efficiency of ca. 14%, in agreement with parent samples based on silica matrices, and high photostability to photobleaching. [6]

As well, thanks to their molecular and hybrid nature, POSS and M-POSS are suitable for the dispersion in organic environment as for instance polymeric matrices.

Application of these materials in polymer-based nanocomposites highlight their relevant potential as functional additives operating at nanoscale level.

Examples on the application of POSS in PVC systems, and M-POSS in PP matrices, and their effect in the thermal behavior and stability will be shown.

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A SYNTHETIC JOURNEY FROM PACLITAXEL ANTICANCER DRUG TO CHIRAL NANOGRAPHENES

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ABSTRACT

As a synthetic chemist addicted to molecular chirality, I have been involved in the syntheses of many chiral and structurally complex molecules ranging from naturally occurring anticancer drugs to nanographenes. Curved polyaromatic hydrocarbons (PAHs) with extended π -systems are of great interest in organic chemistry and materials science, especially in research on nanographenes, nanoribbons, and distorted graphene sheets with peculiar topology.^[1] Accordingly, a rapidly increasing number of large, nonplanar, and molecularly defined PAHs have been designed and synthesized in the past decade. However, the ultimate challenge in this field is probably to exploit chirality as a parameter to fine-tune and to fully exalt organic materials properties, such as their physical, supramolecular, photophysical, conductive, chiroptical, molecular recognition, and switching properties.^[2] Helicenes are typical units that can be used to induce chirality in PAHs.^[3] Recently, a new series of nonplanar PAHs have received great attention: the multiple helicenes, that are PAHs containing two or more helicene moieties.^[4] In this lecture, we will discuss how progresses in synthesis now enable the relatively simple construction of some helicene-based chiral nanographenes with unique properties.^[5]

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FUNCTIONAL ORGANIC COMPOUNDS IN NANOSTRUCTURED MATERIALS: SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

Nanoscience is a central thread in fundamental research, and it is becoming an important part of present and future technology. Advances in nanoscience and nanotechnology have led to the development of functional materials in recent years, which have found applications ranging from biomedical to environmental engineering and energy storage as well as garnered interests in fundamental science.

Among these functional nanomaterials are carbon nanotubes (CNTs), graphene, fullerenes, nanoparticles, metal organic nanomaterials, self-assembled and supramolecular nanostructures, and their derivatives to name a few. Their unique physico-chemical properties such as catalytic, dielectric, optical and mechanical give rise to their distinctive applications in sensors, drug delivery, proteomics and biomolecular electronics. In particular, their biological applications have furthered fundamental understanding of biomolecular systems such as vesicles, viruses and cells as well as stimulated the design of nanomaterials with biological functions.

In this context we will present some examples of functional organic nanomaterials useful for hi-tech applications that were recently developed in our laboratories. Particular attention will be held on the design and synthesis of dyes [1] and surfactants [2] with specific photochemical and physico-chemical properties related to a wide range of applications, from optoelectronics, such as Dye-sensitized Solar Cells (DSCs), [3] or light emitting cells (LEC), [4] to biomedical applications as photodynamic therapy (PDT), [5] and hybrid organic-inorganic materials for imaging [6] and drug delivery. [7]

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CURCUMINOID-BORONDIFLUORIDE DYES FOR PHOTONIC NANOMATERIALS

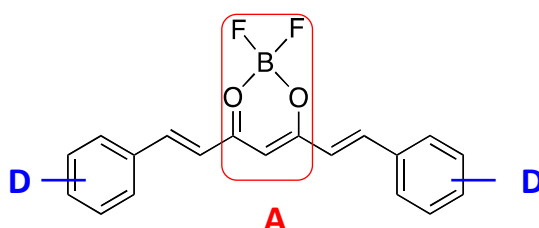
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ABSTRACT

Borondifluoride complexes of 1,7-bis(aryl)-1,6-heptadiene-3,5-dione derivatives, the so-called curcuminoids, represent a versatile class of donor-acceptor-donor dyes. The synthesis of those compounds is extremely simple and cost effective.[1]



Chemical structure of the curcuminoids-BF₂ dyes featuring lateral electron donor (D) groups and the electron acceptor (A) dioxaborinine unit.

Depending on the nature of the D groups, they display far red to near infrared (NIR) fluorescence emission properties in solution and in the solid state using one- and two-photon absorption. Using the fats precipitation method, we prepared fluorescent organic nanoparticles that were shown to enable the fluorescent labeling of living cells using NIR-to-NIR imaging.[2,3]

Amazingly, those dyes are thermally-assisted fluorescent and show high efficiency NIR electroluminescence and amplified spontaneous emission.[4,5] Moreover, in combination with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) acceptor, triphenyl amine-containing derivatives were shown to act as efficient donor materials in solution-processed bulk heterojunction organic solar cells (OSCs).³ Power conversion efficiencies above 4 % have been achieved and best-performing OSCs exhibit high open circuit voltage (V_{oc}) over 1.0 V.[6]

This presentation will focus on photophysical properties of some borondifluoride complexes of curcuminoids and show the potential of this class of D-A-D dyes as versatile molecular scaffolds on which to base the design of functional nanomaterials for (opto)electronic organic devices

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COVALENT FUNCTIONALIZATIONS OF CARBON BASED NANOMATERIALS BY 1,3 DIPOLAR CYCLOADDITION

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ABSTRACT

Carbon-based nanomaterials have peculiar physical and chemical properties and their unique structure make them truly promising systems. In particular, the scientific community was inspired by graphene, a simple two-dimensional sheet of graphite with nano-size dimension, because of its large potential in different fields, from materials chemistry to drug delivery, imaging and therapy.[1]

Within the family of carbon nanomaterials, nanodiamonds are an emerging class which possess a unique set of chemical and physical properties and they also were applied for a variety of biological applications in the fields of drug delivery, tissue engineering, and bioimaging. Many efforts have been made for the functionalization of graphene and nanodiamond in both covalent and noncovalent fashion.[2]

Based on our previous experience in the covalent functionalization under non-conventional conditions of SWCNTs and rGO, we focus our attention on the environmentally friendly decoration of rGO and nanodiamonds.[3-5] Three different procedures based on 1,3-dipolar cycloaddition of azomethine ylides, nitrile oxide, and nitrones have been exploited with the aim to optimize the synthetic procedure.

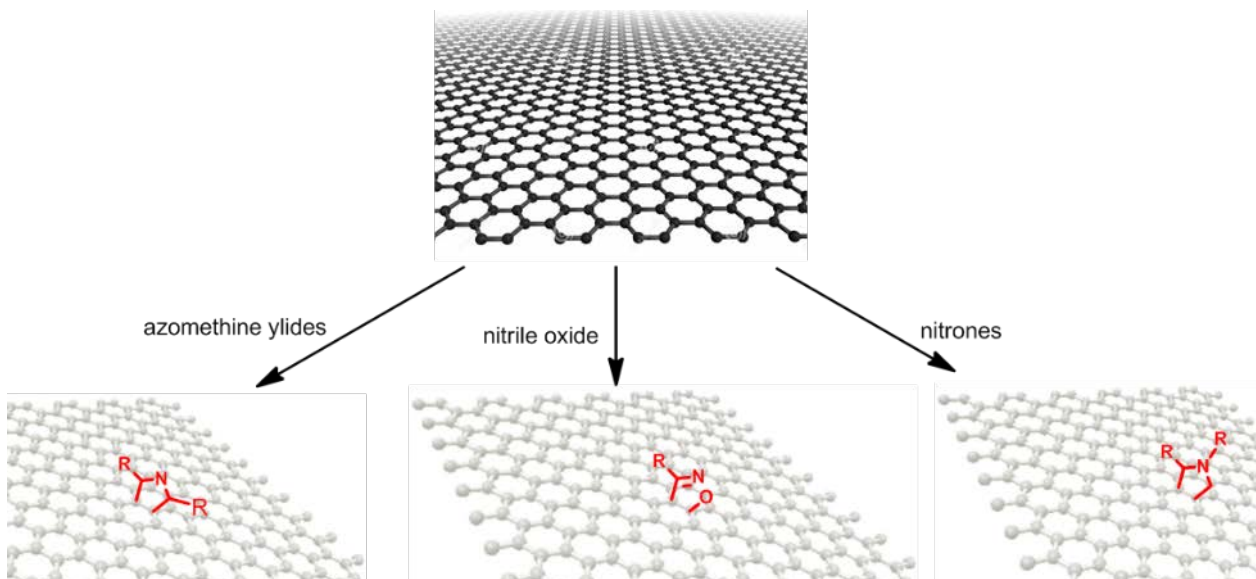


Figure 1. Schematic representation of covalent derivatization of RGO and nanodiamonds via 1,3-dipolar cycloaddition of azomethine ylides, nitrile oxide, and nitrones

In order to reach an accurate evaluation of the grafting efficiency, a series of Fmoc protected intermediates were prepared. Aliphatic and aromatic azomethine ylides, nitrile oxide and nitrones N-Fmoc protected derivatives were employed in 1,3-dipolar cycloaddition with rGO and nanodiamonds and the reaction was optimized under conventional and non-conventional conditions. Dibenzofulvene–piperidine adduct was quantified by UV spectroscopy quantification after Fmoc deprotection to evaluate the degree of surface

derivatization by No-dis and the data were compared with TGA profile. IR, and Raman spectroscopy were employed in order to confirm the structure of the appended derivative.

The investigation afforded to three synthetic pathways with reaction temperature in a range from 130 °C in presence of azomethynylide to r.t. when the nitrile oxide was reacted. The functionalization degree measured was almost 20 percent in all cases of rGO grafting while nanodiamonds gave about 10% of derivatization. TGA and Fmoc UV data were in accordance.

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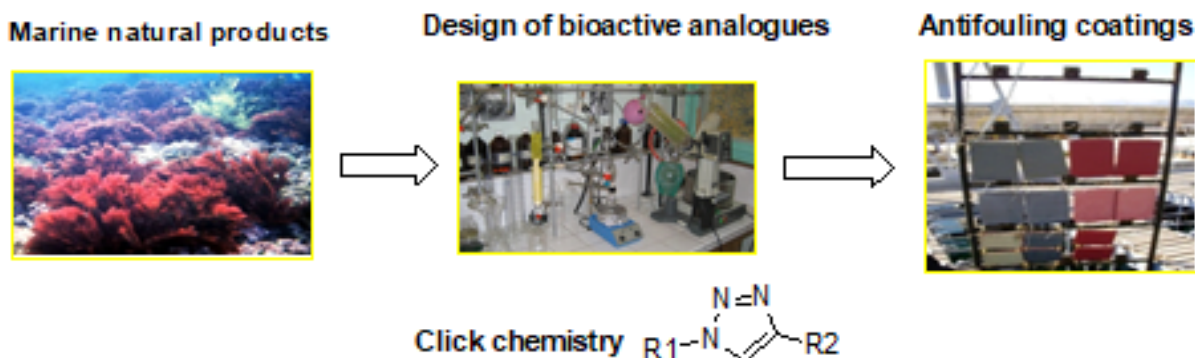
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TOWARDS BIOINSPIRED ANTI-BIOFILM STRATEGIES: A GREEN SOLUTION TO REDUCE ENVIRONMENTAL IMPACT OF ANTIFOULING COATINGS

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ABSTRACT

Marine biofouling is an invasive phenomenon causing large and significant economic and ecological problems, and it is highly undesired for man-made structures submerged in water such as on shipping, aquaculture and offshore petroleum industry. In order to eradicate this phenomenon, antifouling coatings which contain toxic biocides (in particular metal-based paints) are used and are found to adversely affect the environment due to the collateral damage inflicted on the marine ecosystem and non-target species. This observation has motivated investment in the research of potential “environmentally-friendly” antifouling compounds from natural origin. Although such molecules do not guarantee their non-toxicity, they come with the advantage that they have been selected during evolution to the highest specificity, highest efficiency and might be potential nontoxic fouling inhibitors. However, these natural products are only obtained in small quantities, are not stable over time and are not often compatible with polymers coatings. Therefore, their use on a large scale appears to be difficult to achieve. These factors led the scientific community to consider biomimetic approaches by synthesis of analogues maintaining natural frameworks, allowing the development of low-cost, competitive solutions to be placed on the market. In this context, we have developed an efficient strategy to generate marine alkaloids analogues associated with a biological screening allowing us to design potent inhibitors of biofilm formation in marine environment. This methodology led us to select some potent anti-biofilm leads exhibiting low toxicity when compared to standard biocides such as TBTO or ZINEB, or standard antibiotic ampicillin. Finally, these researches result in original solutions to reduce environmental impact of the use of biocides in antifouling coatings.



POLYMER-SHELLED NANOBUBBLES: A NOVEL MULTIFUNCTIONAL DELIVERY TOOL

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ABSTRACT

Polymer shelled nanobubbles (NBs) are spherical core/shell nanostructures filled by a gas or a vaporizable compound (i.e. perfluorocarbons) with sizes in the nanometer order of magnitude. In particular, the NB architecture consists of three domains: inner core, interface and external polymer shell. The design of this nanostructured system is challenging because there are several stability issues to take into account. Formulation criteria comprise various strategies in order to stabilise nanobubbles, including chemical composition, the presence of surfactants at the interface, reduction of the Laplace pressure differences, limitation of gas diffusion [1]. The addition of co-surfactants, besides surfactant or polymer stabilisers, can be exploited to finely modulate interfacial properties and sizes. Finally, the shell composition can deeply affect the bubble dynamic and bubble lifespan, influencing the gas exchange from the core to the external medium. Indeed, shell thickness and elasticity determine nanobubble stability. The polymeric shell is also an important feature of the nanostructure because permits to increase the drug loading and the shell functionalization with specific target ligands.

Among various applications, nanobubbles have shown promising results as innovative nanocarriers. Indeed, their small sizes allow the possibility of extravasation from the blood vessels into the surrounding tissues. Moreover, they might accumulate within tumour tissues via either the Enhanced Permeability and Retention (EPR) effect or through active targeting, i.e. by binding of antibodies on bubble surface.

They have gained an increasing attention for drug delivery, because they can be loaded with gases, drugs and genes for targeted release [2-3]. Different technological approaches have been proposed to associate molecules within the bubble structures. The versatile structure of nanobubbles can be exploited for co-delivery of two different drugs for either combination therapy or theranostic purposes.

NBs are suitable nanocarriers to be combined with physical external stimuli (ultrasound and shock waves) to control the rate of drug delivery and to target specific site in the body obtaining a physically-triggered intracellular drug release. An additional advantage of this US-targeted strategy is the possibility of visualising the delivery and release of the loaded compound by means of real-time echography imaging.

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POLYLACTIDE BASED REACTIVE COPOLYMER MICELLES: A VERSATILE NANOPLATFORM FOR BIO-RELATED APPLICATIONS

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Polymeric micelles represent highly attractive nano-objects for drug/vaccine delivery and diagnostics. Particularly, biocompatible polylactide-*b*-polyethylene glycol (PLA-*b*-PEG) block copolymer micelles have been extensively explored, due to PLA biodegradability and PEG antifouling character [1]. However, PEG, as a polyether, presents poor ability for biofunctionalization with molecules of interest (e.g. targeting agents), still limiting micelle performances. Moreover, PEG has recently raised toxicity and hypersensitivity concerns [2], urging the need of safer alternatives.

In this context, we developed a block copolymer platform based on a PLA block and a hydrophilic block made of *N*-vinylpyrrolidone/*N*-acryloxysuccinimide (NVP/NAS) copolymer, through combination of ring-opening polymerization (ROP) and SG1 nitroxide mediated polymerization (NMP). While the NVP units bring stealth properties similar to PEG, the reactive *N*-succinimidyl ester moieties of the NAS units along the backbone can be used for biomolecule coupling (Figure 1). We have demonstrated that the PLA-*b*-P(NAS-co-NVP) based micelles could be highly functionalized with various biomolecules of interest (sugars, peptide/proteins) for inducing high affinity with specific targets [3].

The potential of this micelle platform was further explored in a vaccine context, using an encapsulated immunostimulatory drug (imiquimod) and a surface coupled HIV-1 p24 protein antigen (Figure 1). The encapsulated imiquimod was found to induce much higher stimulation of the dendritic cells, a key player in immune responses, than the free analog, as shown by flow cytometry [4]. Preliminary in vivo HIV-1 immunization studies in mice showed that p24-coupled micelles induced an intensity and quality of the antibody response as high as those observed for gold standard adjuvants (alum, MF59).

Furthermore, the p24 antigen coupled at the micelle surface induced a strongly improved recognition by anti-p24 antibodies, as attested by ELISA immunoassays [5]. These results demonstrate the relevance and potential of our micelle platform not only for vaccine delivery, but also for improving sensitivity of bioassays, in a diagnostic context.

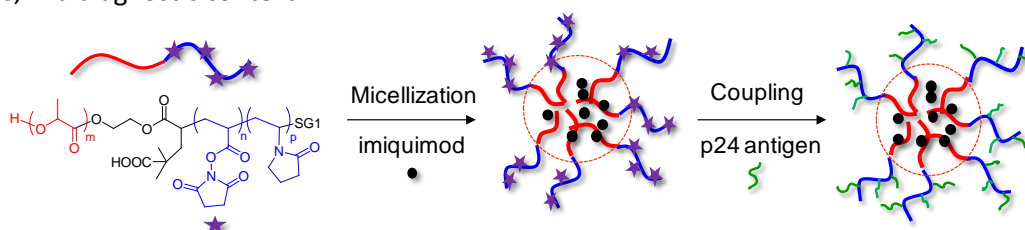


Figure 1 – Schematic view of the functional PLA-P(NAS-co-NVP) micelle nanopatform.

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EXPLORING MESOPOROUS SILICA NANOPARTICLES AS MULTIMODAL IMAGING AND THERANOSTIC PROBES

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ABSTRACT

The ability of mesoporous silica nanoparticles (MSNs) to act as platform for carrying both imaging probes and drugs has greatly increased their use as diagnostic and theranostic probes. In our group, we investigated in detail the chemical role of the porous support on the magnetic properties of different Gd^{III}-chelates immobilized on nanosized MSNs¹⁻² as well as the possibility to act as high sensitivity Chemical Exchange Saturation Transfer (CEST) probes.³ Very high relaxivities per Gd and per particle were found, in particular when the Gd-chelates are anchored on the outer surface of MSNs.⁴ On the other hand, the interaction between Ln-chelates and silanol groups on the MSNs surface allowed to obtain CEST effect with excellent sensitivity in the μM range. Drug loading on Gd-based MSNs and release in physiological conditions was also tested showing that mutual interactions between the drug, Gd-chelates and the silica surface determine the effectiveness of the final theranostic system.⁵ Furthermore, a strong and unexpected enhancement of photoacoustic effect was found by confinement of Indocyanine Green inside MSNs' mesopores widening the application of such probes also by Photoacoustic Imaging.⁶ Finally, functionalized MSNs were exploited through a bioorthogonal approach to target the membrane monosaccharide sialic acid residues as relevant biomarkers of metastatic activity of tumors. Thus, the functionalization of the drug loaded MSNs with a strained cyclooctyne derivative allowed the nanoparticle to selectively react in vitro and in vivo via Cu-free click chemistry to a previously locally inoculated azide-containing sugar.

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NANOCOMPOSITES FROM BIOBASED FURANIC POLYMERS**Nathanaël Guigo**

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In the biorefinery processes, carbohydrates can be transformed into various building blocks via catalytic or enzymatic pathways. In particular, 5-hydroxymethylfurfural (HMF) and furfural are two platform chemicals which can be obtained from the dehydration of C6 and C5 sugars. They can be further converted into furanic derivatives such as 2,5-furandicarboxylic acid (FDCA) or furfuryl alcohol (FA) which are well-known precursors for the elaboration of bio-based polymers.

This presentation aims at highlighting the preparation and characterization of novel smart furanic nanocomposites. The poly(ethylene 2,5-furandicarboxylate) (PEF) emergence as high performance engineering thermoplastic capable of multiple applications is getting realistic since it possesses greatly improved barrier properties and attractive thermal and mechanical properties compared to its terephthalic analogue, poly(ethylene terephthalate).[1] Various PEF nanocomposites were prepared and they exhibit faster crystallization rate and improved degradation properties.[2]

On the other hand, polyfurfuryl alcohol which is a thermoset matrix prepared from the acid-catalyzed polymerization of FA has been successfully used for the development of high performance biobased nanocomposites.[3] Recently, nanosilica clusters were synthesized via precipitated silica process and were dispersed in FA under sonication. [4] The nanosilica clusters clearly promote the FA polymerization at lower temperatures thus avoiding the autocatalytic activation of the acidic initiator. Moreover, lower energetic barriers are obtained for the final stage of polymerization due to nanoconfinement effects. Finally, the multi-frequency analysis of PFA and PFA/silica glass transition highlighted the frequency dependence of T_g for both materials. It was concluded that the presence of silica nanoclusters leads to higher energetic barrier for the PFA cooperative chains motions due to their specific rearrangement in the polymer matrix during the polymerization process.

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**“IMAGING” THE FUTURE: A NANOSTRUCTURED MATRICES ASSESSMENT TO
STUDY DRUG DISTRIBUTION IN SOLID TUMOR TISSUES
BY MASS SPECTROMETRY**

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ABSTRACT

The imaging of drugs inside tissues is pivotal in oncology to assess whether a drug reaches all cells in an adequate enough concentration to eradicate the tumor [1]. Matrix-Assisted Laser Desorption Ionization Mass Spectrometry Imaging (MALDI-MSI) is one of the most promising imaging techniques that enables the simultaneous visualization of multiple compounds inside tissues [2]. The choice of a suitable matrix constitutes a critical aspect during the development of a MALDI-MSI protocol since the matrix ionization efficiency changes depending on the analyte structure and its physico-chemical properties. **The objective of this study is the improvement of the MALDI-MSI technique in the field of pharmacology; developing specifically designed nanostructured surfaces that allow the imaging of different drugs with high sensitivity and reproducibility.** Among several nanomaterials, we tested the behavior of gold and titanium nanoparticles, and halloysites and carbon nanotubes as possible matrices. All nanomaterials were firstly screened by co-spotting them with drugs on a MALDI plate, evaluating the drug signal intensity and the signal-to-noise ratio. The best performing matrices were tested on control tumor slices, and were spotted with drugs to check the ion suppression effect of the biological matrix. Finally; the best nanomaterials were employed in a preliminary drug distribution study inside tumors from treated mice.

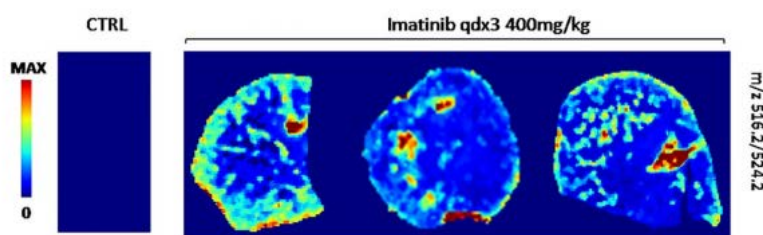


Figure 1: Mass spectrometry imaging visualization of imatinib distribution and of m/z 560.5 ion signal distribution,

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CARBON BASED AND GRAPHENE ANALOGUES HYBRID NANOCOMPOSITES

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ABSTRACT

In recent years the nanoscience field and then the nanotechnologies have experienced a rapid growth, since the realization of new devices coming from nanoscale materials gave access to improved and innovative functionalities (i.e. electrical, optical, mechanical, thermal, catalytic, etc.). As a matter of fact, after assembling the nanometer-scale units in an ordered structure, it is possible to exploit the obtained physical/chemical properties in an optimized manner [1].

Carbon-based materials with different dimensionality, including single and multi-wall carbon nanotubes, graphene and graphene oxide, graphene nanoplatelets and graphite have attracted increasing attention due to their unique electrical conductivity, structural regularity, chemical inertness, biocompatibility, mechanical and thermal stabilities [2].

In the majority of cases, such properties can be better exhibited, if nanocarbons are confined in another phase (i.e., polymers, biomolecules, etc.) or combined with other systems, completely different in terms of composition, nature and properties, to form multifunctional hybrid and/or composite architectures, able to produce novel, unprecedented physical and chemical properties, or to increase the efficiency of the solar energy conversion, photocatalytic environmental remediation, sustainable fine chemistry thus creating new opportunities for device concepts and applications [3].

In particular, as regards the polymers, the peculiar properties such as resistance to chemical corrosion, simplicity of manufacturing and production, low density and lightweight, can be associated with the mechanical and electrical properties of the nanocarbon conducting fillers [4-7].

Besides nanocarbons, prominent candidates for heterostructures and hybrid combinations belong to the family of semiconducting inorganic systems, such as nanostructured oxides (i.e. TiO₂, SiO₂, ZnO, SnO₂, MnO₂, Co₃O₄, Fe₃O₄, NiO, Cu₂O, etc.) and transition metal dichalcogenides (TMDs, i.e., MoS₂, WS₂, CdS, CdSe, CdTe, PbS, ZnS, ZnSe), which are grown on carbon nanotubes, on graphene nanosheets and graphene derivatives via different synthetic approaches [8,9].

The interest of the scientific community in transition metal dichalcogenides can be considered a natural development of the study of graphene, that is becoming a cutting-edge material that opens up new horizons to a whole new variety of possibilities. It is known that the optical and electronic properties of 2D materials are different from their respective 3D structures due to confinement of electrons, but also due to the absence of interlayer interactions, that, despite being generally quite weak, play an important role in determining the band structure. Some other changes in properties, such as mechanical and chemical response, are mainly due to geometry effects and to the high (even infinite in the thinnest materials) surface-bulk ratio [3].

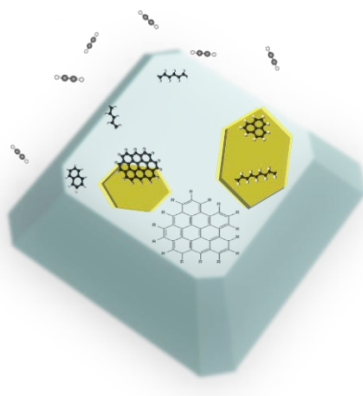
Among the semiconductors of the MeX₂ type, great attention is devoted to MoS₂, because of its electronic, optical and catalytic properties. Depending on the application fields, two main MoS₂ structures can be considered: regular and large-area MoS₂ monolayers, having direct band gap and small clusters, quantum dots or "patches" (often defective) made by few-layer MoS₂ of reduced size, which can have enhanced photoluminescence, photocatalytic and electrochemical efficiencies [10]. Moreover, it should be noticed that due to the quick recombination of photo-generated charge carriers in MoS₂, its photocatalytic efficiency has to be further improved. According to this, graphene, acting as an excellent electron-acceptor/transport material, is able to decrease the photo-generated electron-hole recombination, thus improving the light adsorption [11]. The favourable optical properties of MoS₂ have been exploited even to increase the visible light absorption ability of TiO₂. In fact TiO₂, although

characterized by excellent photocatalytic properties, has an absorption edge, that falls in the UV region (~390 nm), which involves only the 3% of the sunlight spectrum without absorption in the visible region. Notwithstanding, feasible strategies may be adopted in harvesting the visible solar light, including non-metal and metal doping, quantum dots firmly anchored at the surface of the semiconductor or the formation of hybrid interfaces based on 2D materials (i.e., graphene, transition metal dichalcogenides). Hence, due to its absorption in the visible and UV range, MoS₂ was found to be of great interest to perform TiO₂/MoS₂ hybrid materials [12-14].

Taking into account the aforementioned points and considering the peculiar properties of nanocomposites made by organic and inorganic materials a few examples are listed and discussed in this contribution:

- i) TiO₂-graphene hybrid nanocomposites, made by the top-down approach, (dispersion of exfoliated graphene oxide, GO, on TiO₂ nanoparticles) or by the bottom-up approach, (polycyclic aromatic hydrocarbons (PAH) from acetylene interacting on TiO₂ surface [15])
- ii) reduced GO/MoS₂ composites (rGO/MoS₂), (small and crystalline rGO particles, decorating the surface of more extended MoS₂ platelets) [16]
- iii) hybrid materials, made by TiO₂/titanates sensitized with exfoliated MoS₂ or nanoMoS₂ [12-14].

Lastly, a case study concerning the building up of carbon-based domains (black structures) on MoS₂ few layers platelets (green-yellow), which in turn are bottom-up grown on TiO₂ surfaces (light-blue), as shown in scheme, will be also discussed [14].



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MECHANICALLY STABLE NANOFIBROUS sPEEK/AQUIVION® COMPOSITE MEMBRANES FOR FUEL CELLS APPLICATIONS

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ABSTRACT

The development of the ionomer membrane is crucial for the reliability and high volume commercialization of proton exchange membrane fuel cells (PEMFCs) [1]. Perfluorosulfonic acids (PFSA) including Nafion® and Aquivion® are the most widely utilized ionomers because of their outstanding proton conductivity. However, the dramatic decrease of the latter at low humidity, the relatively high gas permeability, and the deficient membrane stabilities are major drawbacks for the long-term fuel cell operation [2]. Among the various approaches to stabilize proton exchange membranes and to improve their properties for fuel cell application, the development of composite nanostructured systems comprising electrospun nonwoven mats is emerging as a promising strategy [3-5].

The work presented here [6] describes the preparation of membranes comprising a sulfonated polyetheretherketone (sPEEK) nanofibrous reinforcement in a short-side-chain PFSA Aquivion® matrix.

The sulfonation of PEEK was studied as a function of synthesis procedure, time and temperature to determine and optimize the degree of sulfonation (DS). The sPEEK electrospun mats were realized with different DS and the highly sulfonated mat was subject to a thermal treatment of crosslinking [7,8] in order to stabilize the polymer otherwise soluble in water. In all cases, the morphology of the membrane shows a homogenous dispersion of the nanofibers throughout the entire membrane section, with an open web structure.

An improvement in the mechanical tensile strength compared to the pristine Aquivion® membrane is observed ascribed to the high stiffness of the nanofibrous morphology of the sPEEK electrospun mat. Above all a significant increase in the mechanical properties is obtained in the case of the crosslinked mat. In this case the membrane demonstrated also a limited area and volume swelling, lower than the pristine membrane and of the reinforced membranes with non-crosslinked mat, by maintaining a similar water uptake. Finally, the proton conductivity values of the sPEEK/Aquivion® composites are lower than that of non-reinforced membrane, due to the relatively low conductivity of sPEEK. However, the advantages in terms of mechanical and swelling properties are remarkable. The incorporation of sPEEK nanofibrous mats seems thus promising for the stabilization of Aquivion® and in general of perfluorosulfonated ionomer membranes.

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PHOTO-ACTIVATED DEGRADATION OF TARTRAZINE BY H₂O₂ AS CATALYZED BY BOTH BARE AND FE-DOPED METHYL-IMOGOLITE NANOTUBES

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ABSTRACT

The photo-catalytic degradation of tartrazine (TRZ, a widely employed food dye) in heterogeneous phase is investigated in the presence of H₂O₂ and imogolite-like materials. Those are nanotubes (NTs) of methyl-imogolite (MeIMO [1]), a hybrid organic/inorganic material with chemical composition (OH)₃Al₂O₃SiCH₃. MeIMO occurs as single-walled NTs with an inner surface lined by Si-CH₃ groups [1], and an outer surface analogous to an aluminum oxo-hydroxide where the isomorphic substitution of Al³⁺ ions by Fe³⁺ ions is possible.

EXPERIMENTAL

MeIMO was obtained by a literature procedure [1]. Fe-doped MeIMO was prepared by ionic exchange of preformed NTs with two Fe contents, *i.e.* 0.70 wt.% (Fe-0.025-MeIMO) and 1.4 wt.% (Fe-0.050-MeIMO). The materials were characterized by X-rays diffraction; N₂ isotherms at 77 K; Diffuse Reflectance UV-Vis spectroscopy; electrophoretic mobility. TRZ degradation tests were carried out on 160 ml aqueous solution of TRZ (purity grade > 99.0%; initial concentration = 40 ppm; initial pH = 6.4) in a stainless-steel sealed batch photoreactor designed by some of us [2]

RESULTS

Table 1

Sample	MeIMO	Fe-0.025-MeIMO	Fe-0.050-MeIMO
Nominal composition	(OH) ₃ Al ₂ O ₃ SiCH ₃	(OH) ₃ Al _{1.975} Fe _{0.025} O ₃ SiCH ₃	(OH) ₃ Al _{1.950} Fe _{0.050} O ₃ SiCH ₃
wt% Fe	0	0.70	1.4
d₁₀₀ (nm, ±0.01)	2.58	2.61	2.68
a (nm)^a	2.97	3.01	3.10
BET SSA (m² g⁻¹)	557	617	565
NL-DFT SSA (m² g⁻¹)	476	525	475
Microporous area/SSA % (m² g⁻¹)^b	55	53	48
Microporous Vol. (cm³ g⁻¹)^c	0.12	0.11	0.10
Total Pore Vol. (cm³ g⁻¹)^d	0.29	0.33	0.33
PZC	8.6	8.7	6.4

(a) As calculated by assuming a hexagonal packing of NTs according to the equation: $a = 2d_{100}/\sqrt{3}$

(b) Percentage ratio [(Microporous SSA)/(Total SSA)] as calculated from NL-DFT cumulative surface area curves

(c) As calculated by applying the *t*-plot

(d) Point of Zero Charge (PZC) as obtained by ζ-potential measurements.

Table 1 gathers the most relevant features of the studied materials, as obtained by X-ray powders Diffraction, N₂ isotherms at 77 K and electrophoretic mobility measurement. Details on composition and synthesis procedure are also reported. As a whole, before thermal collapse NTs are obtained, which form bundles of nearly hexagonal symmetry in the powder. The presence of Fe does not alter much samples morphology. Concerning the surface charge, electrophoretic mobility measurements show a limited effect of Fe on the PZC.

DR-UV-Vis spectroscopy shows that doping with Fe results in a decrease of the band gap energy (E_g) of bare MeIMO (an insulator with $E_g = 4.9$ eV) to $E_g = 2.4$ eV with both Fe-0.025-MeIMO and Fe-1.4-MeIMO,.

At low Fe content (*i.e.* 0.70 wt. % Fe), isomorphic substitution of Al³⁺ by Fe³⁺ is the main process occurring during ionic exchange, leading to a material containing isolated Fe³⁺ sites within the nanotube structure, able to provide total discoloration and mineralization of tartrazine after 3 h under UV irradiation, when a catalyst concentration of 0.25 g L⁻¹ is used. At higher Fe content (*i.e.* 1.4 wt. % Fe) the higher amount of Fe oxo-hydroxide clusters, likely located at the outer surface of nanotubes, has a detrimental effect on tartrazine mineralization. This is due to both a lower photo-Fenton activity of the clusters with respect to isolated Fe³⁺ species and their ability to catalyze the (undesired) decomposition of H₂O₂ to oxygen and water.

Interestingly, bare MeIMO is also active towards tartrazine removal in the presence of H₂O₂: under UV light almost 90 % Total Organic Carbon (TOC) is removed within 3 h due to the formation of reactive Al-OOH groups (after reaction of H₂O₂ with the outer surface of nanotubes), which under UV irradiation promptly release HO· radicals able to attack the dye.

With Fe-0.70-MeIMO, photo-Fenton reaction occurs due to the presence of Fe³⁺ species enhancing the TOC removal, which is equal to 100 % after 3 h. Conversely, the presence of some Fe oxo-hydroxide clusters at the outer surface of Fe-1.4-MeIMO NTs lowers the photo-Fenton activity as far as the TOC removal is concerned.

CONCLUSIONS

Fe-doping of methyl-imogolite has been obtained by ionic exchange of preformed nanotubes. Such process led to enhanced properties towards the photo-Fenton oxidation of tartrazine, an important pollutant of both wastewater and groundwater, as the moiety is a common food dye recalcitrant to biodegradation [3]. Photo-degradation tests show that both bare and Fe-doped MeIMO efficiently remove TRZ from aqueous mixtures, although through different mechanisms.

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TITANIA NANOTUBES BASED ELECTRODES FOR LI-ION BATTERIES

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ABSTRACT

Lithium-ion batteries (LIBs) are widely used to power portable devices, microelectronics, vehicles, etc. With many advantages such as high surface area and improved charge transport, self-supported 3-D nanostructured metal oxides such as titania nanotubes (TiO_2 nts) are promising electrode materials for LIBs and their impact is particularly significant when considering the miniaturization of energy storage systems and the development of 3D microbatteries.

This talk will review the concept and fabrication of all-solid-state Li-ion microbatteries using TiO_2 nts based based electrodes [1-7]. Effects of material selection and processing on the performance and reliability are presented as a means to develop conceptual guidelines to understand and improve microbattery designs. Fundamentals such as electrode reactions, lithium ion diffusion and the conformal electrodeposition mechanism of polymer electrolytes onto the nanostructured electrodes will be presented. The fabrication of a full 3D microcells showing high electrochemical performance will be presented and the development of the next generation of 3D microbatteries will be discussed.

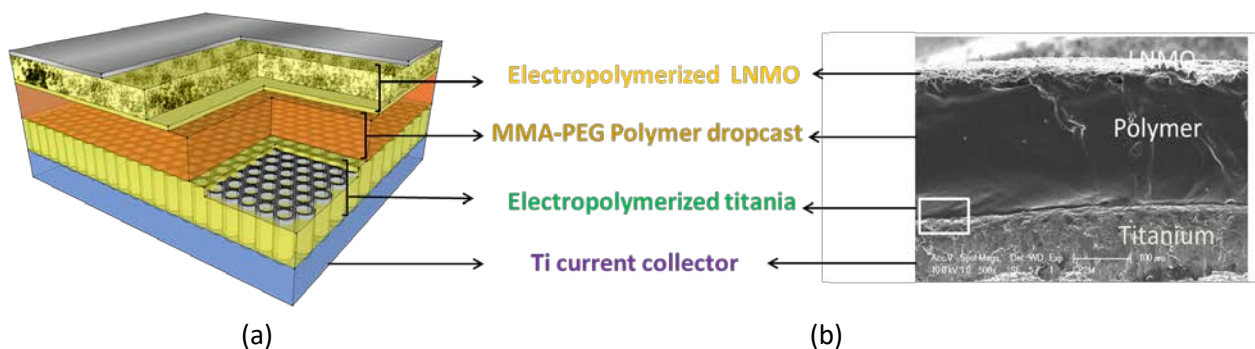


Fig. 1. (a) Schematic representation and (b) cross-sectional SEM image of a thin film microbattery.

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Novel active sorbents based on layered materials for the decontamination of hazardous chemical warfare agents

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ABSTRACT

The oxidative abatement of toxic chemical warfare agents is conventionally achieved via stoichiometric reactions based on the use of strong oxidants with high environmental impact and/or via thermal degradation. In this work, synthetic and natural clays able to promote selective oxidation reactions to transform toxic chemical warfare agents (CWA) in non-noxious products with reduced environmental impact are proposed.

A Nb(V)-containing saponite clay, obtained by introducing in the framework of saponite clay Nb(V) was identified as potential catalyst for the CWA oxidative abatement.

The synthesis method was modified to allow the insertion of Nb(V) ions within the inorganic framework of the clay, thus obtaining a bifunctional catalyst with strong oxidizing properties (due to the presence of Nb(V) centres) and acid character (due to Brønsted acid sites of the saponite clay)[1]. XANES, FTIR and DR-UV-Vis spectroscopy provided information about the chemical nature and the delocalization of Nb(V) sites and allowed to study the redox properties of the catalysts. The catalytic properties of these solids were evaluated at room temperature in the oxidative degradation, with H₂O₂, of (2-chloroethyl)ethyl sulfide (CEES), an organic compound whose chemical structure and reactivity is similar to that of sulfur

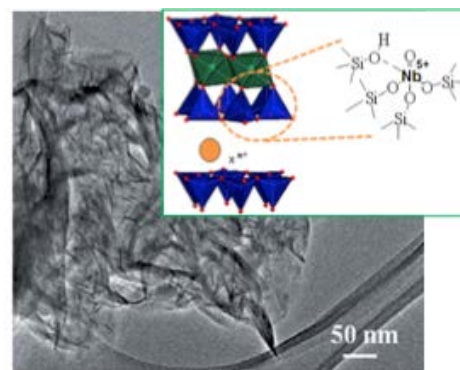


Fig. 1 HR-TEM image of synthetic Nb-saponite

mustard but with reduced toxicity. Nb-SAP sample is able to transform selectively 80% of CEES in less than 8 h. Moreover, tests performed on the real blistering agent (2, 2'-dichlorodiethyl)sulfide, sulfur mustard, HD agent) showed that the catalysts has a good activity also on the live CWA, under stringent conditions, being able to decompose more than 90% of the sulfide in *ca.* 50 hours.

Besides synthetic clays, a catalyst based on commercial bentonite from natural origin (containing at least 80 wt% of montmorillonite clay) was prepared and tested for the oxidation of CWA [2].

The bentonite from natural origin was modified by introducing iron species and acid sites in the interlayer space, aiming to obtain a sorbent with strong catalytic oxidising and hydrolytic properties. The catalytic performance of these materials was evaluated in the oxidative abatement of (2-chloroethyl)ethyl sulfide (CEES), in the presence of aqueous hydrogen peroxide as an oxidant. A new decontamination formulation was, moreover, proposed and obtained by mixing sodium perborate, as a solid oxidant, to iron-bentonite catalysts. Solid-phase decontamination tests, performed on a cotton textile support contaminated with organosulfide and organophosphonate simulant agents revealed the good activity of the solid formulation, especially in the in situ detoxification of blistering agents. Tests carried out on HD agent, showed that, thanks to the co-presence of the iron-based clay together with the solid oxidant component, a good decontamination of the test surface from the real warfare agent could be achieved (80% contaminant degradation, under ambient conditions, in 24 h).

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SYNTHESIS OF SINGLE-ION BAB TRIBLOCK COPOLYMERS AS EFFICIENT ELECTROLYTES FOR LITHIUM METAL BATTERY

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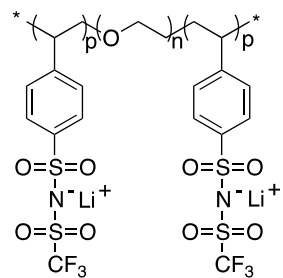
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ABSTRACT

The development of alternative transportation modes such as electric or hybrid vehicles, has become a key need for a sustainable long term development¹. In this context, the increase of energy density for the battery systems is crucial and imposes necessary to explore original strategies for both the active electrode materials and electrolyte^{2,3}. Among the different systems, battery technology based on a lithium metal anode would be particularly attractive notably in combination with Li-S and Li-air systems⁴. Unfortunately, the use of lithium metal associated with liquid electrolyte, led to safety problems due to a possible irregular metallic lithium electrodeposits during the recharge. In some cases, this phenomenon could result in dendrite formation responsible for dramatic explosion hazards. The use of a solid polymer electrolyte (SPE), could solve most of the safety issues encounter with liquid electrolyte. However, the development of SPE has been hampered by two hurdles i/ the inability to design a SPE that exhibits both a high ionic conductivity and good mechanical properties and ii/ during battery operation, the motions of lithium ions carry only a small fraction of the overall ionic current which leads to the formation of strong concentration gradient resulting in undesired effects like favored dendritic growth⁵ and limited energy density especially when power increases.

In recent years, increasing research efforts have been focused on SPE made from block copolymers such BAB, where A represents an ionic conductor typically poly(ethylene oxide) (PEO) block and B a polymer providing the mechanical strength. Indeed, thank to their ability to self-assemble at the nano-scale, block copolymers represent a unique class of materials allowing the combination of different properties in a single material. The main advantage of the block copolymers is based on the covalent attachment of two different polymers, thus avoiding the unwanted macrophase separation when the blocks are immiscible.

Recently we demonstrated that BAB triblock copolymers consisting in an A block of a linear poly(ethylene oxide) (PEO) as a template for lithium ion conduction, and a B block consisting of poly(4-styrene sulfonyl(trifluoromethylsulfonyl)imide) lithium salt exhibited remarkable properties⁶ as SPE. In this lecture, we will present our latest results^{7,8} in the field of SPE and and more particularly the influence of the nature of the external anionic block on the performances of the prepared polymer as electrolytes for lithium metal batteries.



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COMPLEX HYDRIDES: FROM HYDRIGEN STORAGE TO SOLID ELECTROLYTES

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ABSTRACT

Hydrides are investigated for various energy storage applications. Solid state hydrogen storage based on hydrides has been investigated in recent years with the goal to improve hydrogen gravimetric density and to match thermodynamic requirements necessary for dehydrogenation reactions with an equilibrium close to ambient conditions. Metal hydrides show fast hydrogen sorption kinetics and high volumetric density, but suffer from a low gravimetric density.

Complex hydrides [1] are interesting for hydrogen storage because of their light weight and their high number of hydrogen atoms per metal atom. Complex hydrides exhibits Li superionic conduction and they have been suggested as solid-state electrolyte for Li-ion batteries [2]. In this work, examples of studies on complex hydrides for different applications will be provided.

For hydrogen storage materials, thermodynamic properties and phase diagrams have to be known in details. Results of assessments of thermodynamic properties for complex hydrides (e.g. LiBH_4 [3], $\text{Mg}(\text{BH}_4)_2$ [4]) will be reported. Experimental data can vary significantly depending on experimental conditions, because several metastable products can be formed during dehydrogenation reactions [5]. Combining ab-initio calculations and experimental investigations, possible dehydrogenation paths were outlined [4,5].

By mixing different hydrides, it is possible to tailor the hydrogen sorption processes. Examples will be provided for eutectic mixtures of borohydrides (e.g LiBH_4 - NaBH_4 [6]) and for equimolar combinations in the LiBH_4 - NaBH_4 - KBH_4 - $\text{Mg}(\text{BH}_4)_2$ - $\text{Ca}(\text{BH}_4)_2$ system.

On the basis of hydrogen sorption properties, applications of a solid state hydrogen tank based on complex hydrides coupled with a HT-PEM fuel cell will be shown [7].

Due to a structural transition at around 390 K from orthorhombic-to-hexagonal structure, LiBH_4 shows an ionic conductivity up to $10^{-3} \text{ S} \cdot \text{cm}^{-1}$. The combination of different complex hydrides provides the stabilization of the high conducting phase or the development of new crystal structures, characterized by open channels for fast Li-ion mobility. Examples will be provided for $\text{Li}_4(\text{NH}_2)_3(\text{BH}_4)$, $\text{Li}_2(\text{NH}_2)(\text{BH}_4)$ and $\text{Li}_5(\text{BH}_4)_3\text{NH}$ compounds [8,9].

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HOW DENSE IS THE GAS CONFINED IN NANOPORES?

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ABSTRACT

The properties of nano-objects differ from those of their macroscopic analogs, and any system of nanometric size shows characteristics that strongly depend on its size and geometric form. It is mainly because the major part of atoms (or molecules) of nano-volume are located at the object surface and their cohesive energy is smaller than for the atoms in the bulk. As a consequence, the density of the nanoobjects is not homogeneous, and may decrease close to the object boundary.

Here we show that when a fluid is confined in nano-volume, delimited by non-interacting pore walls, its density is on average smaller than the bulk density. The heterogeneous distribution of fluid density results from the nano-confinement, and progressively weakens when the pore size increases: it disappears for pores larger than 5 nm. On the other side, the fluid density approaches the ideal gas values in the limit of very small pores. This effect results from nanoconfinement only and have to be distinguished from the well know heterogeneity of density of fluids **adsorbed** in nanopores, driven by the difference between the strength of fluid-fluid and fluid-pore wall interactions.

The reported observation has non-trivial influence on experimental evaluation of excess/total amount of fluid adsorbed in nanopores, as these two quantities are calculated assuming the known – and homogeneous – bulk density of gas in the pore. Additionally, the gas density in the pores depends on the definition of the pore volume which is neither straightforward nor unique. We analyze this phenomenon on an example of two gases: H₂, CH₄, the two intensively studied energy vectors, confined in model slit-shaped infinite nanopores. For H₂, the distributions of densities of gas confined in adsorbing and not adsorbing pores are compared and commented.

SURFACE ENHANCED RAMAN SCATTERING STRATEGIES FOR TRACE CONTAMINANTS DETECTION

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ABSTRACT

Compared with the conventional analytical techniques, Raman spectroscopy allows fast detection times, high selectivity due to the Raman fingerprint of molecules and minimal or no preliminary treatment of the sample. Moreover, the sensitivity of the normal Raman technique can be increased by several orders of magnitude in SERS analysis due to the enhancement of the Raman scattering of molecules absorbed onto, or microscopically close to, a suitable plasmonically active surface, such as roughened nanostructured metal surface, or metal colloids (1). For all these reasons SERS represents a good candidate in food control analysis. Different SERS approaches were already reported on the detection of various classes of pesticides in real-food matrices. In case of solid matrices, different methods to recover pesticides from the surface were used and the detection was subsequently performed using solid surface-based substrates (2, 3). In situ detection of pesticides in fruits was also demonstrated using different types of metal nanoparticles (NPs) (4, 5) which were spread as “smart dust” over the surface that has to be probed. However, even if these SERS substrates demonstrated to achieve a very high sensitivity in the detection of chemical contaminants, they usually suffer from lack of reproducibility and inconsistent performance when spot-to-spot tests are conducted, leading to problems in the quantification process. Therefore, standardized SERS tool with a good compromise between sensitivity and reproducibility of analysis are needed to provide reliable analytical methods in the detection of food contaminants. The scope of this work is to compare different nanostructured systems to provide a reproducible Surface Enhanced Raman Scattering effect. Several innovative approaches were tested using different probe molecules, such as melamine, cumarin and pyrimethanil, which were selected as representative test materials for a wide class of food contaminants. SERS active surfaces ranging from solid substrates, flexible metal coated silicon nanopillars, and liquid suspensions of spheroidal gold nanoparticles were fabricated and tested in order to compare their efficiency in the detection of the above cited contaminants.

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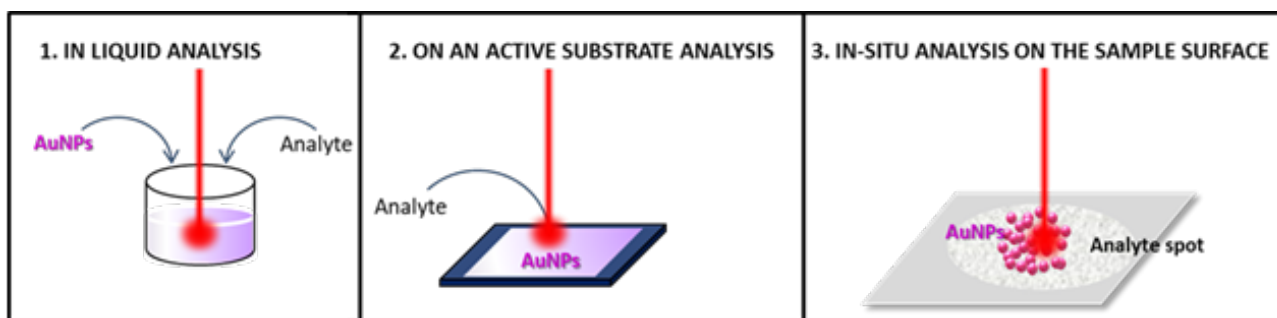


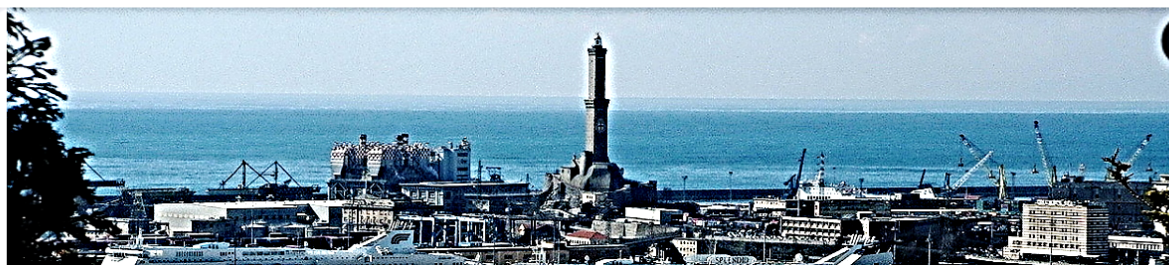
Figure 1: Schematic representation of three different analytical approaches for SERS analysis. a) In liquid analysis, based on mixing the metal colloid with the test solution containing the analyte, the SERS spectrum is collected in liquid medium; b) extraction of the analyte from the matrix and deposition on a SERS active surface, the SERS spectrum is collected on a solid SERS substrate; c) deposition of gold nanoparticles directly on the contaminated surface, the SERS spectrum is collected in-situ.

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