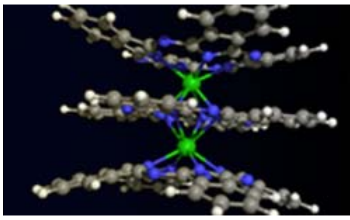

ICON²-2015

International conference on
« Novel nanomaterial: engineering and properties »
9th to 11th of September 2015
Synchrotron SOLEIL

*****

ABSTRACTS BOOKLET

*****

Summary

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Welcome

In the last years, intensive research activity has been devoted in the field of nanomaterials to significantly improve knowledge on their preparation, characterization, properties and potential applications. **ICON^2** is an interdisciplinary conference which aims at facilitating discussions and scientific interactions on chemistry, biomaterials, functional polymers, energy storage and conversion materials, nano materials, ceramics, metals, and other novel materials. The conference is divided into three sessions. The first session is dedicated to time resolved experiments. Laser-pump-synchrotron-probe based spectroscopy and related techniques (X-FEL, HHG, 2PPE) at time scales ranging from millisecond to femtosecond are the main focus of this session. The second session is focused on the engineering and characterization of organic, inorganic and hybrid nanomaterials. The third session deals with nanomaterials for energy conversion and storage.

The objective of this conference is to bring together students and researchers in a collaborative environment to present and discuss issues related to nanomaterial engineering and characterisation as well as their potential applications. It provides a platform for people working in this field to share their respective knowledge and experiences and to develop new ideas to improve nanomaterial technology.

ICON² is organized by the Synchrotron SOLEIL and the CEA Saclay and is held at **Synchrotron Soleil** in the immediate vicinity of the CEA on **September 9th-11th, 2015.**

Bienvenue

Au cours des dernières années, une intensive activité de recherche a porté sur le domaine des nanomatériaux conduisant à une amélioration considérable et des découvertes dans le domaine des nouveaux matériaux, pour leur préparation, leur caractérisation, leurs propriétés et leurs applications. **ICON²** est une Conférence interdisciplinaire ayant pour but de faciliter les discussions et les interactions scientifiques sur la chimie, les biomatériaux, les polymères fonctionnels, les matériaux de transformation et de stockage de l'énergie, les nano matériaux, les matériaux céramiques, les matériaux métalliques et les autres nouveaux matériaux. La conférence est divisée en trois sessions. La première session est dédiée aux expériences résolues en temps. Elle sera centrée sur les techniques de spectroscopie pompes/sondes laser/rayonnement synchrotron et les techniques connexes (X-FEL, HHG, 2PPE) à des 'échelles de temps allant de la milliseconde à la femtoseconde. La deuxième session portera sur l'ingénierie et la caractérisation de nanomatériaux inorganiques et hybrides. La troisième session concernera les nanomatériaux pour la conversion et le stockage de l'énergie.

L'objectif de cette conférence est de réunir étudiants et chercheurs dans un environnement collaboratif pour présenter et discuter des questions relatives à l'ingénierie des nanomatériaux et leur caractérisation. Elle fournit une plate-forme permettant aux personnes travaillant dans ce domaine de partager leurs connaissances respectives et leurs expériences afin de développer de nouvelles idées et améliorer la technologie des nanomatériaux.

Icon², organisée par le Synchrotron SOLEIL et le CEA Saclay, se tient au **Synchrotron Soleil** à proximité immédiate du CEA du **9 au 11 septembre 2015.**

International Conference on Novel nanomaterial: Engineering and properties
ICON² - 2015

Synchrotron SOLEIL - L'orme des Merisiers
Saint-Aubin, France

09th-11th of September 2015

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International Conference on Novel nanomaterial:
Engineering and properties
ICON² - 2015

Synchrotron SOLEIL - L'orme des Merisiers
Saint-Aubin, France
09th-11th of September 2015

Programme

Wednesday, September 9th

08:30 - 09:30	Registration & Welcome coffee
09:30 - 09:40	Welcome word, Paul Morin, Director of Research, Synchrotron SOLEIL

SESSION I

Chairpersons: M. Silly – F. Silly

09:40 - 10:20	Dynamics at surfaces, studied by VUV-soft X-ray chronospectroscopy ***Iwao Matsuda –*** *Institute for Solid State Physics - University of Tokyo, Japan*
10:20 - 10:35	Photo-induced phase transition between charge density wave states in 1T-TaS$_2$ ***Claire Laulhé –*** *Synchrotron SOLEIL, Saint-Aubin, France*
10:35 - 11:00	Ultrafast magnetization dynamics by time resolved XMCD ***Christine Boeglin –*** *CNRS - IPCMS – Strasbourg, France*
11:00 - 11:25	*Coffee break*
11:25 - 12:05	Unraveling how electronic and spin structures control macroscopic properties of manganite ultra-thin films ***Andrivo Rusydi –*** *Singapore Synchrotron Light Source, Singapore*
12:05 - 12:20	Spin-state switching of spin-crossover nanomaterials ***Marie-Laure Boillot*** *– ICMMO, Orsay, France*
12:20 - 12:45	Probing ultrafast magnetization dynamics on the nanometer length scale by coherent X-ray diffraction at XFELs ***Jan Lüning –*** *Laboratoire de Chimie Physique-Matière et Rayonnement, Paris, France*
12:45 - 13:00	X-ray absorption study of iron and cobalt clathrochelates for application in proton exchange membrane water electrolysers ***Pierre Millet*** *– ICMMO/Eriée, Orsay, France*
13:00 - 14:00	*Lunch*

SESSION II

Chairpersons: S. Campidelli – R. Cornut

14:30 - 14:25	Synthesis, encapsulation, and templating of polymers mediated by metal-organic frameworks ***Takashi Uemura –*** *Department of Synthetic Chemistry and Biological Chemistry - Kyoto University, Japan*

14:25 - 14:50	Chromophore confinement into single-walled carbon nanotubes : Supramolecular organization and physical interactions ***Laurent Alvarez –*** *Laboratoire Charles Coulomb, Université de Montpellier, France*
14:50 - 15:15	One-dimensional self-assembly of semiconductor nanorods ***Takuya Nakashima –*** *Graduate school of Materials Science, Nara Institute of Science and Technology, Japan*
15:15 - 15:30	Effect of supramolecular organization of porphyrin molecules to optimize energy transfer to single wall carbon nanotubes ***Geraud Delport –*** *Laboratoire Aimé Cotton, Orsay, France*
15:30 - 16:00	*Coffee break*
16:00 - 16:25	Structurally defined graphene nanoribbons: Bottom-up solution synthesis and characterizations ***Akimitsu Narita –*** *Max Planck Institute for Polymer Research, Germany*
16:25 - 16:50	Ultrafast studies of non equilibrium electronic states in complex materials ***Marino Marsi –*** *Laboratoire de Physique des Solides, Orsay, France*
16:50 - 17:15	Control of sequence and chain topology for vinyl polymers ***Makoto Ouchi –*** *Department of Polymer Chemistry, Kyoto University, Japan*
17:15 - 17:40	Theoretical characterisation of STM images of assemblies of flat organic molecules in surface ***Manuela Mura –*** *School of Mathematics and Physics, University of Lincoln, United Kingdom*
17:40 - 17:55	Engineering two-dimensional hybrid NaCl-organic coordinated nanoarchitectures on metal surface ***David Peyrot –*** *CEA Saclay, Gif-sur-Yvette, France*
18:15 -	*Transfer to Paris*
21:00 -	*Dinner conference*

Thursday, September 10th

SESSION III

Chairpersons: M. Silly – X. Sun – M. Marsi

09:00 - 09:40	Unravelling the mysteries of solar nanocells: surface and interface chemistry in quantum dots ***Wendy R. Flavell –*** *The Photon Science Institute - University of Manchester, United Kingdom*
09:40 - 09:55	Molar mass versus polymer solar cell performance: Highlighting the role of homocouplings ***Tim Vangerven –*** *Institute for Materials Research (IMO-IMOMEC), Hasselt University, Diepenbeek, Belgium*
09:55 - 10:20	Supramolecular preorganization of monomers for the growth of carbon nitride materials ***Menny Shalom –*** *Max Planck Institute of Colloids and Interfaces, Germany*
10:20 - 10:35	Tailoring nanoscale morphologies in high-efficiency polymer-fullerene bulk heterojunction solar cells ***Pierre Beaujuge –*** *King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia*

10:35 - 11:00	*Coffee break*
11:00 - 11:40	Non-noble metal electrocatalysts for hydrogen economy ***Bruno Jousselme –*** *CEA Saclay, Gif-sur-Yvette, France*
11:40 - 11:55	Polyoxometalates-based hybrids as covalently anchored homogeneous catalysts ***Richard Villanneau –*** *Institut Parisien de Chimie Moléculaire, Paris, France*
11:55 - 12:20	Nanostructures material for energy conversion: Synergic effects between carbon nanotubes and metal oxides ***Giovanni Valenti –*** *Department of Chemistry «Giacomo Ciamician», University of Bologna, Italy*
12:20 - 12:35	Iron sulfide nanoparticles as cathode catalyst for PEM electrolyzers : Towards a mechanism for hydrogen evolution reaction ***Marion Giraud –*** *Laboratoire ITODYS, Paris, France*
12:35 - 12:50	Optimization of nanometric epitaxial hematite films for solar water splitting by oxygen vacancy engineering ***Maxime Rioult –*** *CEA Saclay, Gif-sur-Yvette, France*
13:00 - 14:00	*Lunch*
14:00 - 14:25	Bioinspired multifunctional coatings for advanced structural metals/alloys ***Masanobu Naito –*** *National Institute for Materials Science, Japan*
14:25 - 14:40	Implementation of hybrid nano-emitters coupling fluorophores and plasmonics nano-particles ***Céline Molinaro*** *– CEA Saclay, Gif-sur-Yvette, France*
14:40 - 14:55	Characterization of CVD graphene: Work function modulation and its opportunities for heterojunctions ***Mohamed Boutchich*** *– GeePs, Gif-sur-Yvette, France*
14:55 - 15:10	Analysis and functionalization of graphene oxide with electrochemical microscopy ***Renaud Cornut –*** *CEA Saclay, Gif-sur-Yvette, France*
15:10 - 15:25	Synthesis of 14C-labeled graphene ***Nathalie Fresneau –*** *CEA Saclay, Gif-sur-Yvette, France*
15:25 - 15:45	*Coffee break*
15:45 - 17:40	SOLEIL beamline visits & Poster Session

Friday, September 11th

SESSION IV

Chairpersons: M. Mura – H. Magnan

09:00 - 09:25	Mesostructured materials via the sol-gel process for energy conversion and storage ***Christel Laberty-Robert –*** *Laboratoire de Chimie de la Matière Condensée, Paris, France*
09:25 - 09:50	A double-strand approach to biomimetic multiporphyrin architectures ***Mitsuhiko Morisue –*** *Kyoto Institute of Technology, Kyoto, Japan*
09:50 - 10:05	Stability of supported lead nanoparticles: Five-fold twinned pyramids versus single crystals ***Lise Serrier-Garcia –*** *Institut des Nanosciences de Paris, Paris, France*

10:05 - 10:35	*Coffee break*
10:35 - 11:00	Stimuli responsive supramolecular materials through host and guest interactions ***Yoshinori Takashima –*** *Department of macromolecular science, Osaka University, Japan*
11:00 - 11:15	Supramolecular chiral nanoarchitectures and chiral phase transitin induced by the selective assembly of barbituric acide derivative enantiomers ***Xianan Sun –*** *Laboratoire ITODYS, Paris, France*
11:15 - 11:30	XPS of isolated nanoparticles ***Olivier Sublemontier –*** *CEA Saclay, Gif-sur-Yvette, France*
11:30 - 11:45	Hot carrier relaxation in photoexcited GaAs: The role of the electron-phonon coupling ***Jelena Sjakste –*** *Laboratoire des Solides Irradiés, Palaiseau, France*
11:45 - 12:20	Closing session Best student oral presentation award
12:20 - 13:45	*Lunch*
13:45	*Departure*

ABSTRACTS

Wednesday, September 9th, 2015

SESSIONS I & II

ICON^2 - 2015

Wednesday, September 9th

SESSION I

Chairpersons: M. Silly – F. Silly

KN-01	Dynamics at surfaces, studied by VUV-soft X-ray chronospectroscopy *I. Matsuda*
OC-01	Photo-induced phase transition between charge density wave states in 1T-TaS$_2$ *C. Laulhé*
IT-01	Ultrafast magnetization dynamics by time resolved XMCD *C. Boeglin*
KN-02	Unraveling how electronic and spin structures control macroscopic properties of manganite ultra-thin films *A. Rusydi*
OC-02	Spin-state switching of spin-crossover nanomaterials *M.L. Boillot*
IT-02	Probing ultrafast magnetization dynamics on the nanometer length scale by coherent X-ray diffraction at XFELs *J. Lüning*
OC-03	X-ray absorption study of iron and cobalt clathrochelates for application in proton exchange membrane water electrolysers *P. Millet*

SESSION II

Chairpersons: S. Campidelli – R. Cornut

IT-03	Synthesis, encapsulation, and templating of polymers mediated by metal-organic frameworks *T. Uemura*
IT-04	Chromophore confinement into single-walled carbon nanotubes : Supramolecular organization and physical interactions *L. Alvarez*
IT-05	One-dimensional self-assembly of semiconductor nanorods *T. Nakashima*
OC-04	Effect of supramolecular organization of porphyrin molecules to optimize energy transfer to single wall carbon nanotubes *G. Delport*
IT-06	Structurally defined graphene nanoribbons: Bottom-up solution synthesis and characterizations *A. Narita*

IT-07	Ultrafast studies of non equilibrium electronic states in complex materials *M. Marsi*
IT-08	Control of sequence and chain topology for vinyl polymers *M. Ouchi*
IT-09	Theoretical characterisation of STM images of assemblies of flat organic molecules in surface *M. Mura*
OC-05	Engineering two-dimensional hybrid NaCl-organic coordinated nanoarchitectures on metal surface *D. Peyrot*

Dynamics at Surfaces, Studied by VUV-soft X-ray Chronospectroscopy

I. Matsuda

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ABSTRACT

Dynamics of carriers, spins, or molecules at surfaces has been interesting issues in surface science and the researches have been significant in sustainable energy technology, *i.e.* solar cell and photocatalysis. Spectroscopies using VUV-Soft X-rays (VUV-SX) have been powerful experimental tools to probe electronic states or chemical species of a sample *directly* and the time-resolved measurements further allow us to chase the dynamical phenomena in *real time*. The experiments nowadays have been carried out with various types of VUV-SX sources, such as synchrotron radiation, high-harmonic generation (HHG) laser, and free electron laser. Since characteristics of these sources are distinctive from each other, researchers need to choose the appropriate ones for their time-resolved measurements [1]. In this presentation, I would like to introduce our researches of surface dynamics and to discuss roles of VUV-SX chronospectroscopy for investigating novel nanomaterials.

We developed time-resolved core-level photoemission spectroscopy system using high-brilliant synchrotron radiation at SPring-8 BL07LSU [2]. By the pump-probe method using a femtosecond-pulse laser, we have studied dynamics of the photo-excited carriers on various semiconductor surfaces of Si [3,4], TiO_2[5] and ZnO[6] after generation of the surface photovoltage. With systematic results on atomically controlled surfaces, I would like to discuss process of the electron-hole recombination at a surface and its relation to the other dynamical phenomena such as photocatalysis.

Recently, we have succeeded in directly observing hot carrier distribution in the Dirac band of a monolayer graphene by femtoseconds-time- and angle-resolved photoemission measurements using HHG laser [7]. The internal energy dissipation was found to be specific to the Dirac band and indicated possible existence of the cascade carrier multiplication that is important in the future opto-electronic devices.

At the summary of the talk, chronology of the photocarrier at a surface is overviewed together with systematic comparisons of the dynamics models for analyzing the experimental results and for designing the novel nanomatrials.

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Photo-induced Phase Transition Between Charge Density Wave States in 1T-TaS$_2$

C. Laulhé[1,2], T. Huber[3], G. Lantz[4], L. Cario[5], B. Corraze[5], E. Janod[5],
A. Ferrer[3,6], S.O. Mariager[6], S. Grübel[6], J.A. Johnson[6], J. Rittmann[6],
L. Huber[3], A. Lübcke[6], M. Kubli[3], M. Savoini[3], V. Esposito[6], G. Ingold[6],
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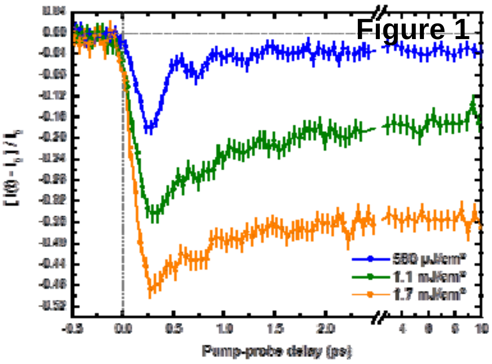
ABSTRACT

1T-TaS$_2$ is a lamellar compound formed by sheets of edge-linked TaS$_6$ octahedra. Within each sheet, the Ta-atoms form a hexagonal lattice which presents a series of structural modulations as the temperature decreases. The unmodulated structure observed at highest temperatures undergoes a first transition below 543 K with the formation of an incommensurate (I) Charge Density Wave (CDW), which further evolves into a nearly commensurate (NC) CDW below 353 K, and a commensurate (C) CDW below 183 K.

We will report on the photo-induced structural dynamics in the NC phase of 1T-TaS$_2$, on timescales ranging from fs to µs:



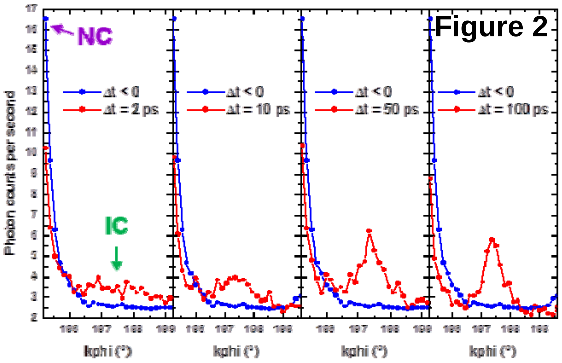


Figure 1 shows the time-evolution of the diffracted intensity at a NC satellite position of reciprocal space, for laser fluences ranging from 0.25 to 1.70 mJ/cm². At all fluences studied, a drop of diffracted intensity is observed, followed by a partial recovery within 3 ps.

Figure 2 shows diffracted intensity profiles on the line that joins the NC and I satellite peak positions, for various pump-probe delays at a fluence of 2.2 mJ/cm². The region shown is centered on the I satellite peak position, and only the base of the NC satellite peak is visible. One can observe that the reduction of intensity on the NC satellite peak is accompanied by an increase of diffuse scattering, which progressively condenses into a narrow satellite peak characteristic of a photo-induced I phase. Our measurements thus provide a unique view on the dynamics of a 1st order phase transition on its characteristic timescale.

Ultrafast Magnetization Dynamics by Time Resolved XMCD

C. Boeglin

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ABSTRACT

Ultrafast processes involving the electrons and spins are important issues for both fundamental science and for the applications, in order to optimize both, the recording speed and densities, down to the picosecond time and nanometer length scales. Application of ultrashort Infra-Red (IR) laser pulses allows ultimately the manipulation of the local magnetization in magnetic films. The important time scales are below one picosecond down to the femtosecond scale. In order to understand the change of the initial magnetic or structural state, induced by IR laser pulses, it is essential to describe the individual and fundamental processes taking place during the first hundred femtoseconds. Since the first observation of laser induced spin dynamics [1] performed by time resolved magneto-optics, the mechanisms responsible for the femtosecond demagnetization have been widely debated, but no consensus could be found until today.

Recently, time-resolved X-ray Magnetic Circular Dichroism (XMCD) using synchrotron facilities and X-ray free electron sources have provided femtosecond time resolution and thus new information concerning femtosecond demagnetization dynamics. The XMCD spectroscopy is an element-specific tool which can be used to study ultrafast magnetization, electronic or structural dynamics with chemical resolution. Whereas at high X-ray energies (E ~20 keV) the dynamics of the crystalline structure and phase transitions can be described, at soft X-ray energies (E ~1eV) it is now possible to measure the dynamics of the spin and orbital magnetic moments with a high temporal resolution (100 fs) [2-5].

One of the recent results using the new potential of the XMCD technic, show that right after the IR laser excitation, interatomic transfer of angular moment takes place at the femtosecond scale, whereas the global demagnetization proceeds, illustrating one of the most efficient way of conservation of angular moment, during the loss of magnetization in the system. Recently, the coherence of the polarized X-ray beam is used to observe the dynamics of magnetic domains, focussing on the reversible or irreversible domain transformations in single pump-probe experiments for example [6].

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Unraveling how Electronic and Spin Structures Control Macroscopic Properties of Manganite Ultra-thin Films

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ABSTRACT

Perovskite manganites exhibit fascinating transport and magnetic properties, essential for fundamental research and applications. With the development of thin film technologies, more exotic properties have been observed in doped-manganites over a wide range of temperature. Unraveling the interplay of spin, charge and orbital degrees of freedom that drives exotic, macroscopic properties is therefore crucial for the understanding of strongly correlated electron systems. Here, using a combination of transport, spectroscopic ellipsometry, X-ray absorption spectroscopy and X-ray magnetic circular dichroism, we observe two concomitant electronic and magnetic phases (insulating paramagnetic phase for T~195 K and insulating cantedferromagnetic for T~140 K) with an intermediate metal-like state in ultra-thin $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) film on $DyScO_3$ substrate. Surprisingly, the O2p-Mn3d hybridization strength reduces with decreasing temperature, driving the system more insulating and ferromagnetic. The Jahn–Teller effect weakens markedly within the intermediate temperature range, making the system more metal-like. We also apply this comprehensive method to a LSMO film on $SrTiO_3$ substrate for comparison. Here, we find strong electron-electron and electron-hole interactions manifested in Wannier-like exciton and high-energy resonant excitons in $SrTiO_3$ also influences the properties of manganites ultrathin films. Our study reveals that the interplay of the O2p-Mn3d hybridization, the dynamic Jahn–Teller splitting, and strong interplay between the substrate and manganite controls the macroscopic transport and magnetic properties in ultra-thin manganites.

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Spin-state Switching of Spin-crossover Nanomaterials

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ABSTRACT

Spin-crossover (SCO) compounds form a class of switchable and bistable magnetic materials exhibiting abrupt changes of spin multiplicity of the metal ion under the effect of physical and chemical stimuli. In such solids, the change of volume related to SCO produces highly cooperative transformations resulting from the spreading of elastic strains. Potential technological interests as sensor, switch or memory derive from their cooperative and hysteretic behaviors. For the high-density information storage, one key issue is the preservation of a bistable regime at nanoscale. Recent developments in nanochemistry have been made possible the elaboration and processing of SCO nano-objects, the investigation of their size-dependent properties for gaining control over SCO-based functionalities in advanced nanomaterials.[1]

We focus here on few examples of SCO materials of molecular nature, prepared as nano- or microparticles with a solvent-assisted approach.[2] Beside the disappearance of bistability and the smoothening of thermal SCO, the size reduction of solids considerably improves the efficiency and selectivity of their photoswitching. This has been exploited for dynamical investigations of the electronic spin-state switching following photo-excitation of two prototypical Fe(II) and Fe(III) compounds.[3] Evidences for ultrafast inter-system crossing and coherent oscillations in the photo-induced high-spin state have been provided.

Moreover, studies conducted with microparticles dispersed in polymers, molecular liquids or oils have revealed a complex SCO behavior ranging from smooth, fully reversible processes to apparent hysteretic ones.[4] The investigation of the latter with the First-order reversal curves (FORC) approach and a mean-field model supports an analysis based on physisorption, volume-dependent effects between particles and matrices and thus, suggests in line with a few recent reports of hysteresis re-opening at nanoscale,[1] the possibility to tune the properties of size-reduced materials via size, interface, coating and nature of compounds.

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Probing Ultrafast Magnetization Dynamics on the Nanometer Length Scale by Coherent X-ray Diffraction at XFELs

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ABSTRACT

Since the discovery of the ultrafast demagnetization phenomenon by E. Beaurepaire and colleagues in 1996 [1], the field of femtomagnetism has developed to an active research area. Initial experiments relied mostly on all-optical pump-probe techniques, which raised concerns about optical artifacts affecting the measurement. Since these limitations can be overcome by X-ray based techniques, the advent of sources providing femtosecond short X-ray pulses was awaited for by the interested community. In addition to accessing the complete electronic structure, X-ray techniques offer additional advantages. First of all, this is their shorter wavelength, which matches naturally the nanometer length scales expected to be of relevance in ultrafast magnetization dynamics. Furthermore, X-ray techniques provide via the accessible core electron absorption resonances element sensitivity and offer a wide variety of magnetic dichroism effects exploitable as contrast mechanism, for example, in scattering experiments. This allows probing of the magnetization dynamics of individual components of complex, heterogeneous materials on the nanometer length scale.

These expectations were indeed fulfilled by the first experiments (e.g., Ref. [2,3]) realized at the femtosecond pulsed tunable X-ray sources emerging since the mid 2000's (BESSY femtoslicing facility and HHG sources). With the advent of X-ray free electron lasers emitting in the XUV and soft X-ray photon energy range, however, unprecedented experimental capabilities became available. In this talk I will review how we [4,5,6] (and others, e.g., Ref. [7]) have exploited the high intensity, the femtosecond short duration and the high degree of coherence of the XFEL pulses to obtain novel insight into the mechanisms underlying ultrafast magnetization dynamics. In particular, I will show how the combined nanometer spatial and femtosecond temporal resolution enabled us to obtain experimental evidence for the occurrence of spin transport by the hot, polarized valence electrons, a phenomenon modeled theoretically in 2010 by Battiatio and co-workers [8].

In the context of condensed matter experiments, the high peak fluence of XFEL pulses raises concerns about sample modification and other experimental artifacts hindering the aimed for characterization of a material's property. A discussion of experimental observations and our current understanding of such phenomena [5,9] will conclude the presentation.

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X-ray Absorption Study of Iron and Cobalt Clathrochelates for Application in Proton Exchange Membrane Water Electrolysers

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ABSTRACT

Polymer Electrolyte Membrane (PEM) water electrolysis is considered as a key technology for the large scale implementation of hydrogen as an alternative energy carrier. In a PEM water electrolysis cell, a proton-conducting polymer is used as electrolyte. The acidity is such that only platinum-group metals (Pt at the cathode and IrO_2 at the anode) are used as electrocatalysts [1]. More recently, it has been shown that transition-metal molecular complexes such as clathrochelates can be implemented in PEM water electrolyzers to replace platinum at the cathode for the hydrogen evolution reaction (HER) [2,3]. Clathrochelates (Figure 1) form a vast and rich family of organo-metallic complexes that are electro-active with regard to the HER. By selecting the appropriate radicals at the periphery (Figure 2), it is possible to tune the redox properties of the metal active center in order to make the catalyst more efficient with regard to the reaction of interest.

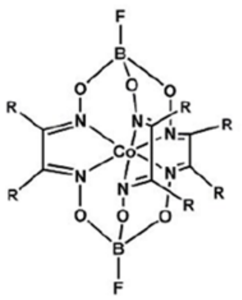

Fig. 1 : *general structure of Co clathrochelates*

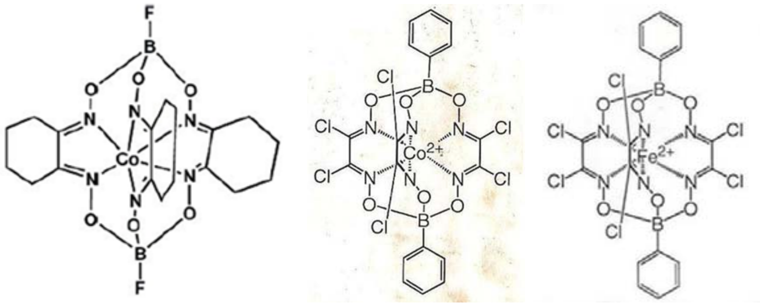

Fig. 2 *: some substituted cobalt and iron clathrochelates used for the HER.*

The purpose of the work reported here is to describe the local structure of cobalt and iron clathrochelates in various states and environments (in solution, in different oxidation states, adsorbed at the surface of carbonaceous substrates, in contact with polymer electrolyte). Problems related to the surface functionalization of these complexes at the surface of appropriate carbonaceous substrates and their implementation in PEM water electrolysis cells will also be discussed.

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Synthesis, Encapsulation, and Templating of Polymers Mediated by Metal-organic Frameworks

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ABSTRACT

Metal-Organic Frameworks (MOFs) prepared by self-assembly of metal ions and organic ligands have attracted much attention because of their wide applications in gas storage, molecular recognition, and catalysis. The characteristic features of MOFs are highly regular channel structures, controllable channel sizes approximating molecular dimensions, and designable surface functionality. Use of their regulated and tunable channels for a field of polymerization can allow multi-level controls of the resulting polymer structures.[1] In addition, construction of nanocomposites between MOFs and polymers will provide unprecedented material platforms to accomplish many nanoscale functions.[1]

Controlled radical polymerization of vinyl monomers can be attained in MOF nanochannels, showing many remarkable effects of pore size, shape, and functionality on the structures and alignment of the resulting polymers.[2] For example, stereo- and regioregularity of polymers could be systematically changed depending on the pore structure.[2a-d] Controlled uniaxial alignment of vinyl polymer chains was achieved by host-guest cross-polymerization.[2e] A variety of polymerization reactions can be also catalyzed in functionalized MOFs.[3] For example, MOFs with specific basic sites accelerated stereo- and monomer-selective polymerization of substituted acetylenes.[3a] Oxidative polymerizations of pyrrole within 2D and 3D MOFs containing redox-active sites gave polypyrroles whose orientations were directly related to the original host templates.[3b,c] Use of MOFs as removable templates was a promising method for the preparation of morphological polymer particles as well as the mixing of immiscible polymer pairs at the molecular level.[4]

Polymers confined in nanochannels of MOFs have distinctly different properties to those in the bulk state because of the formation of specific polymer assemblies and conformations. For example, incorporation of poly(ethylene glycol) (PEG) into MOFs enabled observation of thermal transitions of only a few chain assemblies.[5] Confinement of photoconductive polymers, such as poly(vinyl carbazole) and polysilane in one-dimensional channels of MOFs led to increase in their conductivity because of the specific conformational changes.[6] Fluorescent oligomers accommodated in a flexible MOF showed conformational variations concurrently with the host structural change during gas adsorption, which is a key for fluorescent detection of gases.[7] We also developed new autonomous chemical motors by integrating MOFs and self-assembling peptides.[8]

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Chromophore Confinement into Single-walled Carbon Nanotubes : Supramolecular Organization and Physical Interactions

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ABSTRACT

1D hybrid nano-systems are elaborated with photo-active pi-conjugated molecules (quathertiophene and phathlocyanine) encapsulated into the hollow core of single-walled carbon nanotubes. We evidence that the supramolecular organizations of confined oligothiophenes (from 1 to 3 chains into a nanotube section) depend on the nanocontainer size[1]. The physical interactions can switch from molecule-molecule to molecule-nanotube interactions depending on the tube diameter. In addition, permanent and photo-induced electron transfers are evidenced from the confined molecules to the nanotubes.

The supramolecular organization of MPc molecules is shown to be a 1D-phase for which the angle between the molecule ring and the nanotubes axis is close to 32°. Confined MPc molecules display Raman spectra hardly altered with respect to the bulk phase, suggesting a rather weak interaction with the tubes[2].

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One-dimensional Self-assembly of Semiconductor Nanorods

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ABSTRACT

The last decade has witnessed tremendous developments in the controlled synthesis of semiconductor nanocrystals (NCs) with tailored shapes, compositions and properties.[1] Along with such developments, interest in the self-assembly of NCs has been emerging because of (i) the desire to mimic life systems such as protein assemblies and their functions and (ii) the ability to build nanostructures with collective and enhanced properties. One-dimensional (1D) self-assemblies of nanocrystals are of particular interest because of their vectorial properties as well as polymer-like properties characterized by their topology and dynamics.[2] Here, we report a simple methodology to gain elongated 1D-assemblies of semiconductor nanorods (NRs) through end-to-end attachment.[3]

CdSe NRs synthesized in a hot mixture of alkylphosphonic acids and trioctylphosphine oxide (TOPO) were subjected to the ligand exchange with short-chained water soluble thiols with an ionic group. The weaker binding of ionic thiolate ligands to the ends of NRs compared to the side face causes the frequent desorption of ligands to make the ends unpassivated which are intrinsically hydrophobic. The amphiphilic NRs with the hydrophilic-side and hydrophobic-end faces self-assembled in an end-to-end manner facilitated by the hydrophobic effect between the ends (Fig. 1). The self-assembly was also applied to CdS NRs with a wurtzite structure, which further led to co-assemblies of CdS NRs with CdSe NRs to give multiblock heteronanowires.

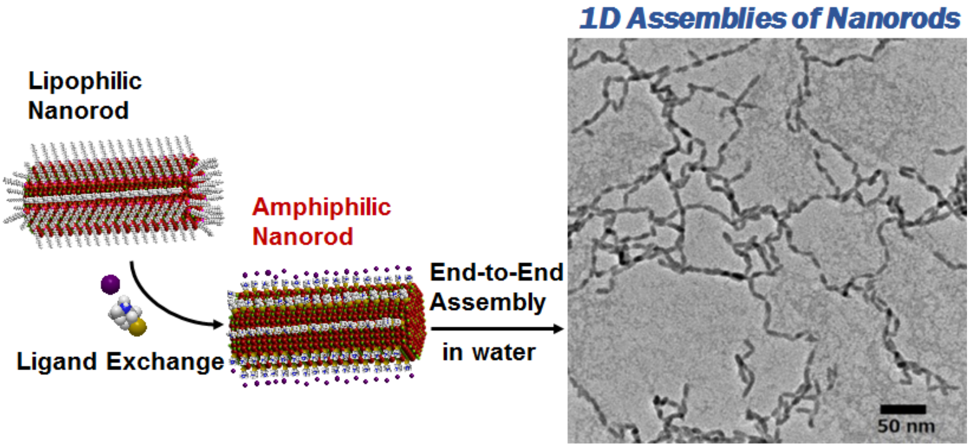

Fig. 1 Ligand-exchange mediated self-assembly of CdSe NRs.

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Effect of Supramolecular Organization of Porphyrin Molecules to Optimize Energy Transfer to Single Wall Carbon Nanotubes

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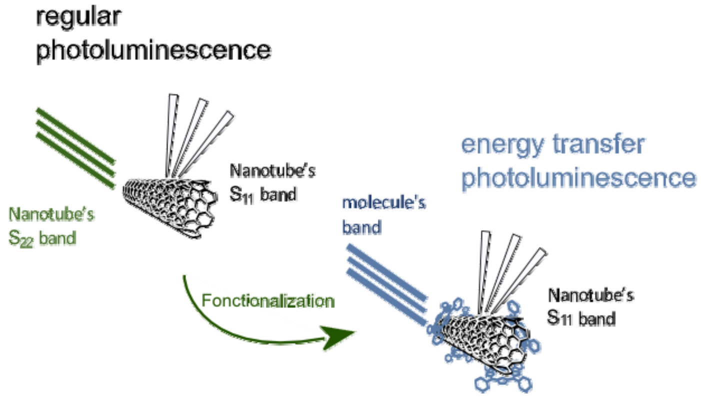
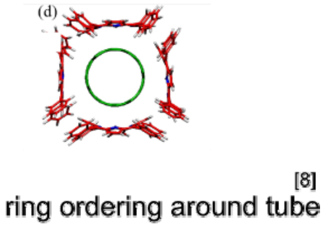
ABSTRACT

The delocalized π-electronic system of carbon nanotubes allows them to link non-covalently to organic molecules such as porphyrins. This weak interaction preserves most of the nanotubes intrinsic properties, and induces new functionalities [1, 2], such as strong energy transfer from the molecule to the nanotube. While numerous classical dyes have been stacked onto nanotubes [3, 4, 5, 6], the coupling process is not fully understood as its efficiency seems to vary strongly upon small chemical changes [6,7].

In this work, we will use tetraphenylporphyrin as a chemical model to investigate the influence of organization of the molecules around the tube. We will show how the supramolecular arrangement plays a role in the efficiency of the energy transfer process. In particular, we will highlight the role of the phenyl groups of the porphyrin in the stabilization of the compound, in good agreement with recent calculations [8].





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Structurally Defined Graphene Nanoribbons: Bottom-up Solution Synthesis and Characterizations

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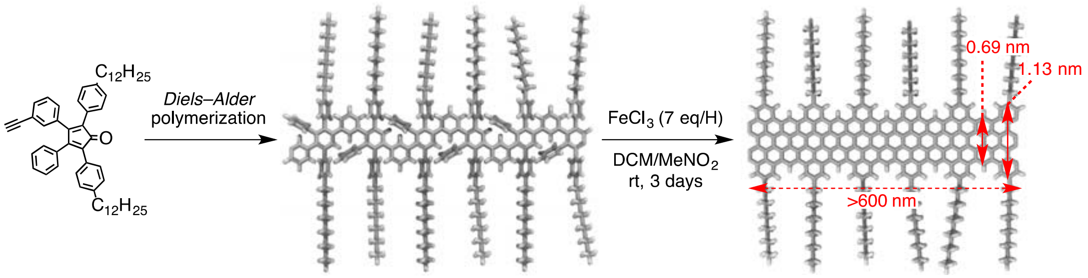
ABSTRACT

In contrast to the zero-bandgap graphene, laterally confined graphene nanoribbons (GNRs) possess open bandgaps while preserving the high charge-carrier mobilities, making them promising materials for future electronic devices. The properties of the GNRs critically depend on their chemical structures such as the width and the edge configuration. Precise structural control is therefore essential to reproducibly obtain GNRs with desired (opto-)electronic properties, which, however, cannot be achieved by the predominant "top-down" fabrication methods. In our group, we have developed a "bottom-up" approach for the synthesis of atomically precise GNRs, which can be performed "in solution" by the conventional synthetic chemistry as well as "on surface" using the modern techniques in physics.[1] By changing the monomer design, a great variety of GNRs can be obtained with different widths and edge structures, allowing for fine-tuning of their electronic properties.

Especially, GNRs extending over 600 nm have been achieved by the solution synthesis, employing AB-type Diels–Alder polymerization.[2] The GNRs with a large optical bandgap of 1.9 eV were comprehensively characterized by a combination of spectroscopic techniques and scanning probe microscopy. THz photoconductivity measurements revealed excellent semiconducting properties of thus synthesized GNRs with estimated intrinsic mobility in the range of 150–15,000 $cm^2 \cdot V^{-1} \cdot s^{-1}$.[2,3] Moreover, the long GNRs showed remarkable liquid-phase processability, which enabled fabrication of working transistor devices on isolated GNR strands.[4,5] Through the lateral extension of the GNR structure with the width from ~1 to ~2 nm, the optical bandgap could be lowered from 1.9 eV down to 1.2 eV, featuring broad optical absorption extending into the near-infrared region.[6] These results suggested a high potential of such GNRs in nanoelectronic and optoelectronic applications.



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Ultrafast Studies of Non Equilibrium Electronic States in Complex Materials

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ABSTRACT

The development of femtosecond light sources opened new perspectives in terms of manipulating the properties of condensed matter over ultrafast time scales. On one hand, these perspectives represent a novel approach to explore the properties of complex materials, alternative and complementary to more traditional experimental techniques; on the other hand, they disclosed the possibility of changing the properties of matter using light pulses, and of creating transient electronic and structural phases that cannot be reached changing conventional thermodynamic parameters like pressure, temperature or chemical doping.

Among the various experimental approaches to this kind of studies, time and angle resolved photoelectron spectroscopy can provide an important contribution, thanks to its unique capabilities of direct visualisation of transient electronic states in reciprocal space. Selected examples will be discussed to illustrate the possibilities of ultrafast spectroscopy in the study of prototype systems like Mott compounds or topological insulators.

Control of Sequence and Chain Topology for Vinyl Polymers

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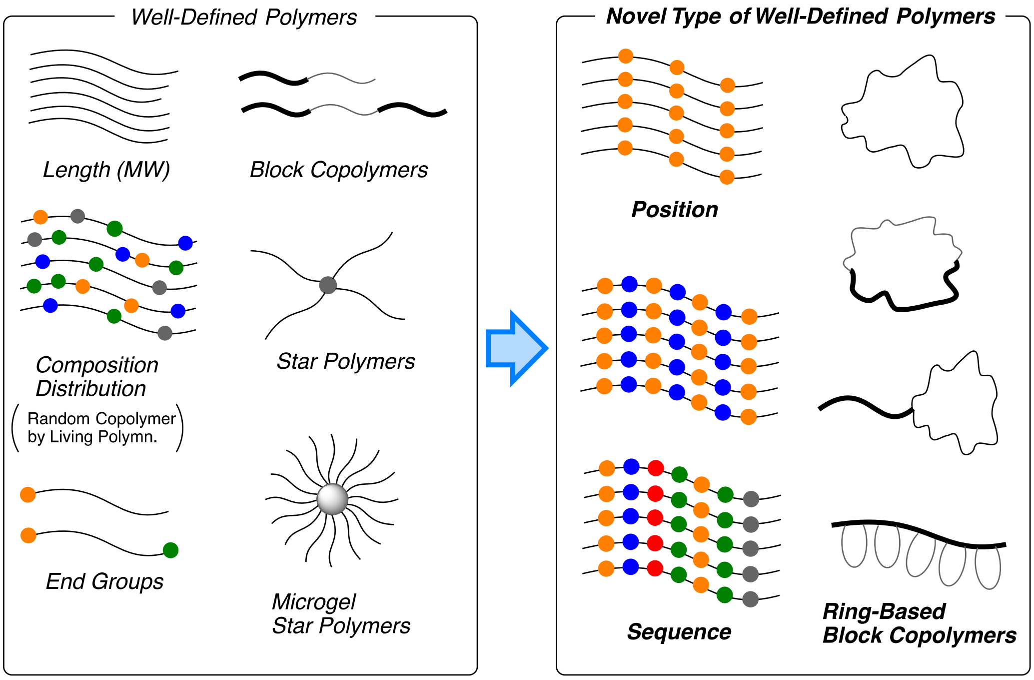
ABSTRACT

Biopolymers such as DNA and proteins are expressing their functions based on sequence and position of functional groups in the pendant groups as well as shape (topology) of the main chain. These structural factors should be essence for “macromolecules” to express smart functions by coordinating variety of functional groups.

On the other hand, for synthetic polymers, control of the chain length and terminal groups is now possible using living polymerizations, but that of topology and sequence is still extremely difficult. Our efforts have been directed to creative design of molecules (i.e., initiators and monomers) for polymerizations to control of sequence and topology, leading to construction of new type of well-defined polymers.



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Theoretical Characterisation of STM Images of Assemblies of Flat Organic Molecules in Surface

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ABSTRACT

The phenomenon of self-assembly of atomic and molecular superstructures on crystal surfaces has attracted an increasing interest in nanotechnology. Self-organised nano-templates where the self-assembled monolayer traps other molecules with selected functional properties, can be used as building blocks for larger nanoscale structures. These superstructures can form chiral domains ranging from 1D chains to 2D monolayers. In particular, there have been many scanning tunneling microscopy (STM)studies of self-assembly of flat organic molecules on the Au(111).

STM images of these networks do not reveal the exact details of the intermolecular bonding and process of network growth. It is therefore the task of theory to determine the exact atomic structure of these networks. We present a theoretical study of self-assembly of molecular networks based on different molecules by using a systematic approach to build molecular superstructures and investigating the surface influence in the assembly of the molecules. The energies of these structures are calculated using the density-functional theory SIESTA code. The theoretically predicted monolayer structures are in very good agreement with the results of STM measurements.

We also investigate the nature of interaction of the molecules and superstructures with the gold substrate and analyse the diffusion of the
networks with the Au(111) surface.

Engineering Two-dimensional Hybrid NaCl-organic Coordinated Nanoarchitectures on Metal Surface

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ABSTRACT

Engineering novel atomic and molecular nanostructures on surfaces is a challenge in nanosciences. Several interactions such as metal-organic or hydrogen bonding[1] have been used so far to drive the formation of such nanostructures. Ionic bonding is another interaction that has a great potential since the strength of an ionic bond can be ten times higher than H-bond interactions.

Here, we report the selective engineering of two dimensional self-assembled PTCDI-NaCl nanoarchitectures[2]. For the first time, hybrid ionic-organic nanoarchitectures were observed by Scanning Tunneling Microscopy at room temperature resolving both individual NaCl dimers and PTCDI molecules. PTCDI molecules appear to selectively interact with individual NaCl dimers. Co-deposition of PTCDI and NaCl on Au(111) surface leads to the formation a flower like structure (Fig 1A). After moderate post annealing, a new 2-D porous hybrid nanoarchitecture with rectangular pores was observed (Fig 1B). PTCDI and NaCl appear to form PTCDI..NaCl...PTCDI sticks in this structure. After annealing at higher temperature, a new chain-structure was also observed (Fig 1D). Detailed analysis reveals that NaCl-dimers selectively interact with molecular NH group (Fig 1C). The PTCDI···NaCl-dimer binding also appears to be highly directional. Hybrid molecular-ionic self-assembly can be a promising alternative to metal-coordinated and multicomponent organic nanostructures to engineer novel nanoarchitectures on surfaces.

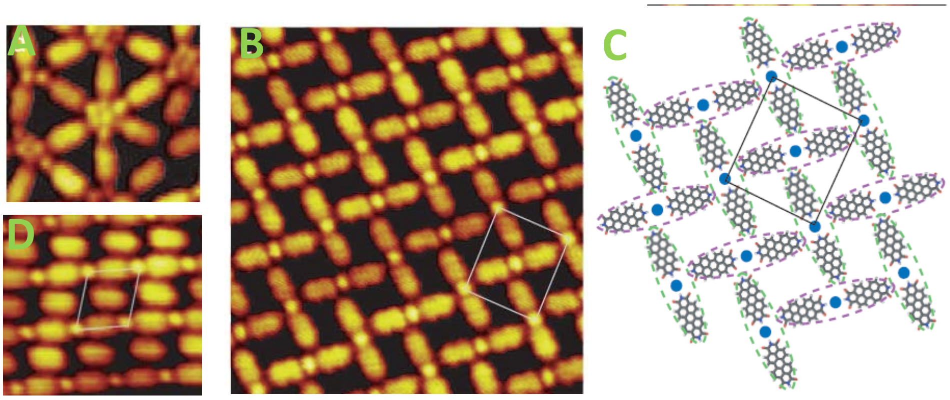

Figure 1

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ABSTRACTS

Thursday, September 10th, 2015

SESSION III

ICON^2 - 2015

Thursday, September 10th

SESSION III

Chairpersons: M. Silly – X. Sun – M. Marsi

KN-03	Unravelling the mysteries of solar nanocells: surface and interface chemistry in quantum dots *W.R. Flavell*
OC-06	Molar mass versus polymer solar cell performance: Highlighting the role of homocouplings *T. Vangerven*
IT-10	Supramolecular preorganization of monomers for the growth of carbon nitride materials *M. Shalom*
OC-07	Tailoring nanoscale morphologies in high-efficiency polymer-fullerene bulk heterojunction solar cells *P. Beaujuge*
KN-04	Non-noble metal electrocatalysts for hydrogen economy *B. Jousselme*
OC-08	Polyoxometalates-based hybrids as covalently anchored homogeneous catalysts *R. Villanneau*
IT-11	Nanostructures material for energy conversion: Synergic effects between carbon nanotubes and metal oxides *G. Valenti*
OC-09	Iron sulfide nanoparticles as cathode catalyst for PEM electrolyzers : Towards a mechanism for hydrogen evolution reaction *M. Giraud*
OC-10	Optimization of nanometric epitaxial hematite films for solar water splitting by oxygen vacancy engineering *M. Rioult*
IT-12	Bioinspired multifunctional coatings for advanced structural metals/alloys *M. Naito*
OC-11	Implementation of hybrid nano-emitters coupling fluorophores and plasmonics nano-particles *C. Molinaro*
OC-12	Characterization of CVD graphene: Work function modulation and its opportunities for heterojunctions *M. Boutchich*
OC-13	Analysis and functionalization of graphene oxide with electrochemical microscopy *R. Cornut*
OC-14	Synthesis of 14C-labeled graphene *N. Fresneau*

Unravelling the Mysteries of Solar Nanocells Surface and Interface Chemistry in Quantum Dots

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ABSTRACT

There is an urgent requirement to make better use of the 120,000 TW of power provided by the Sun, by using it to generate power, or by using its energy directly to make useful chemical feedstocks. At the University of Manchester, we are working to develop next generation solar nanodevices, that could be used for microgeneration. Core components of our prototype devices are colloidal semiconductor quantum dots (QDs) that harvest the incident light, creating an electron-hole pair (exciton), and n-type and p-type conductors that separate the charge. Issues of key importance are the energy level line-up between the QDs and the surrounding components of the cell[1], and the influence of the surface properties of the QD on charge separation into the device and carrier multiplication in the QD[2-4]. I will show how a combination of synchrotron radiation (SR) and laser spectroscopies may be used to investigate the surface chemical composition, surface ageing and 'core-shell' structure of the colloidal QDs[1,5,6], the energy level-line-up and the charge dynamics in photovoltaics[7,8,9] (the latter using laser - SR pump-probe spectroscopy). I will also illustrate the use of ultrafast transient absorption spectroscopy to investigate the phenomenon of carrier multiplication in QDs[1,10].

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Molar Mass versus Polymer Solar Cell Performance: Highlighting the Role of Homocouplings

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ABSTRACT

Although a strong link between the molar mass of conjugated polymers and the performance of the resulting polymer:fullerene bulk heterojunction organic solar cells has been established on numerous occasions, a clear understanding of the origin of this connection is still lacking. Moreover, the usual description of molar mass and polydispersity does not include the shape of the polymer distribution, although this can have a significant effect on the device properties. In this work, the effect of molar mass distribution on photovoltaic performance is investigated using a combination of structural and electro-optical techniques for the state-of-the-art low bandgap copolymer PTB7. Some of the studied commercial PTB7 batches exhibit a bimodal distribution, of which the low molar mass fraction contains multiple homocoupled oligomer species, as identified by MALDI-TOF analysis. This combination of low molar mass and homocoupling drastically reduces device performance, from 7.0 to 2.7%. High molar mass batches show improved charge carrier transport and extraction with much lower apparent recombination orders, as well as a more homogeneous surface morphology. These results emphasize the important effect of molar mass distributions and homocoupling defects on the operation of conjugated polymers in photovoltaic devices.[1]

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Supramolecular Preorganization of Monomers for the Growth of Carbon Nitride Materials

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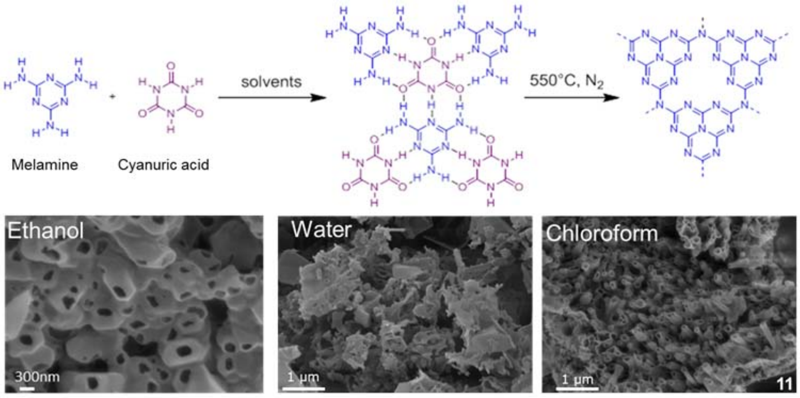
ABSTRACT

Carbon nitride (C_3N_4) has appeared to be a good metal-free catalyst in many energy related applications. C_3N_4 materials demonstrated high activity in heterogeneous catalysis, photocatalysis, oxygen reduction reactions, and more. C_3N_4 synthesis usually involves the thermal condensation of organic molecules which contain nitrogen and carbon atoms, and results in lowly organized C_3N_4 textures with small grain sizes. Moreover, because of the nature of the synthesis, the resulting C_3N_4 possesses low surface area, low conductivity, and poor electronic properties. In addition, for photoelectrochemical applications such as solar cells and water electrosplitting, a direct connection between C_3N_4 and the conductive materials must be established. Consequently, it is essential to find a new and simple synthetic pathway to grow C_3N_4 in its powder form and on different substrates.

Here we show a new synthetic method which are based on supramolecular chemistry approach to synthesize well-defined structures of C_3N_4 such as hollow boxes, spheres, tubes and spherical macroscopic assemblies with the possibility to control their photophysical and photocatalytic properties. The use of supramolecular chemistry provides a great opportunity for the synthesis of nanostructured materials without any further templating techniques. The supramolecular approach includes the use of non-covalent interactions such as hydrogen bonding to form order between building blocks for the desired synthesis. The structure of the final products can be controlled by choosing the appropriate monomers and solvents for the synthesis. Moreover, using the supramolecular approach we were able to grow highly ordered carbon nitride structures on different substrates both in solid state and liquid-based growth. Thanks to the new deposition methods we were able to show, for the first time, that C_3N_4 can act as efficient electrocatalyst for water splitting and as an absorber in solar cells.



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Tailoring Nanoscale Morphologies in High-efficiency Polymer-fullerene Bulk Heterojunction Solar Cells

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ABSTRACT

A number of recent studies point to the importance of solution and thin-film ordering effects in π-conjugated polymers for bulk heterojunction (BHJ) solar cells with fullerene acceptors such as PCBM. In many instances, π–aggregation governs the self-assembly of the polymer donor – a key aspect that can ultimately impact nanoscale thin-film morphology and the phase-separation pattern of the BHJ.[1] Significant differences in phase-separation patterns are known to influence BHJ solar cell performance, and in order to curb these effects, small-molecule processing additives, such as 1-chloronaphthalene (CN) and 1,8-diiodooctane (DIO), are now commonly used in the optimization of high-efficiency polymer-PCBM BHJ solar cells. In poly(benzo[1,2-*b*:4,5-*b'*]dithiophene–thieno[3,4-*c*]pyrrole-4,6-dione) (PBDTTPD) and wide-bandgap analogs blended with PCBM,[2-11] the formation of π–aggregates in solution and in thin-films depends upon i) the combination of side-chain substituents and ii) the functional groups appended to the main chain, and the use of processing additives can be critical in the optimization of the BHJ morphologies. Furthering our understanding of how the main chain substitution pattern mediates the interplay between polymer donor and fullerene acceptor is a critical step as we look to continue improving BHJ solar cell efficiencies.

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Non-noble Metal Electrocatalysts for Hydrogen Economy

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ABSTRACT

Electrolysers and Fuel cells are important devices for the development of sustainable energy conversion and storage and have the potential to revolutionize the way we power our Society, offering cleaner, more efficient alternatives to the combustion of gasoline and other fossil fuels. However, the viability of an economy based on hydrogen is related to the development of catalysts without scarce, expensive noble platinum group metals catalysts ((PGM) Pt, Ir and Ru) as presently used. Thus one of the objectives of the LICSEN group with collaborators is to develop new, cheap, efficient and stable catalysts based on carbon nanotubes for cathodes and anodes of fuel cells and electrolysers.

In a first part of the presentation, the catalytic activity for both the production and the uptake of hydrogen of nickel-based bio-inspired catalysts covalently bound on carbon nanotubes[1,2] will be presented. This extremely stable material operates in highly acidic environment and is compatible with the Nafion® membranes. Moreover, they are highly selective with the substrate unlike platinum nanoparticles which are irreversibly polluted by gases or organic traces. The development of this new material represents a new stage in the race for the improvement of the hydrogen solution for energy.

In a second part, new materials for oxygen reduction reaction (ORR)[3] still based on modified carbon nanotubes will be discussed. These catalysts were synthesized either in soft conditions using a new functionalization process[4] or by heat treatment of a mixture of carbon nanotubes, a nitrogen precursor and with or without a non-noble metal catalyst.[5,6] ORR activities studied by electrochemistry show really good performances for N-enriched carbon nanotubes in basic condition but in acidic condition, catalysts present still a high overpotential with a number of electrons involved below four.

Recently, Nickel molecular H_2 oxidation catalysts and noble metal-free O_2-reducing materials were combined, to fabricate a noble metal-free PEMFC, with an 0.74 V open circuit voltage and a 23 μW cm^{-2} output power under technologically relevant conditions.[7]

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Polyoxometalates-based Hybrids as Covalently Anchored Homogeneous Catalysts

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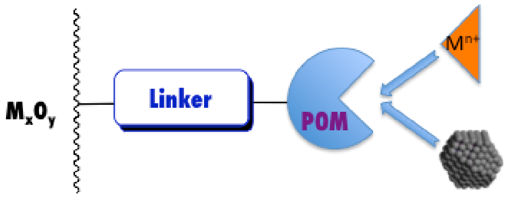
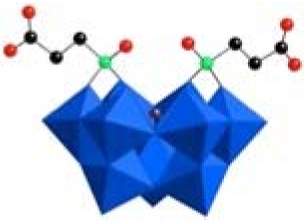
ABSTRACT

Catalysis is considered as one of the pillars of Green Chemistry.[1] In the field of oxidation reactions, there is a constant search for catalytic processes using O_2 that could substitute to conventional oxidants (CrO_3, MnO_4^-, HNO_3) used at a laboratory or industrial scales and affording stoichiometric amounts of non-valuable by-products. In fine chemistry, cleaner oxidation pathways are usually based on homogeneous transition metal (TM)-centered catalysts. The principal limitations to their use are linked to separation problems: loss of (often expensive) active centers and contamination of the reaction products by metal traces, incompatible with pharmacological applications. Heterogenization of "soluble" catalysts onto mesoporous supports then constitutes an elegant solution, since it may allow the chemist to combine the activity and selectivity of the homogeneous catalyst with the ease of recovery of the heterogeneous one.[2] The bridge between homogeneous and heterogeneous approaches can also be built through the use of magnetic core@shell nanoparticles (NPs), with large relative surface area.[3] These NPs are based on a magnetic maghemite core and an external silica shell. Due to the presence of the magnetic core, the recycling of the catalyst is then facilitated.



In both systems, the efficiency of the supported molecular catalysts (on an extended oxide or a NP) is linked to the optimization of both the dispersion and the accessibility of the active sites on the support. We thus developed a project based on the elaboration of catalytic materials functionalized with nucleophilic hybrid polyoxometalates (POMs, *i.e.* TM oxoanion nanosized clusters).[4] The anchorage to functionalized mesoporous oxides/magnetic core@shell NPs of vacant POMs hybrids[5] (also able to bind transition metal active centers) have been investigated in the field of anchored homogeneous catalysts for mild oxidation reactions. In this context, several POMs-functionalized materials have been obtained through the covalent grafting of POMs onto the wall of the supports. The nanostructuration of POMs in the different materials have been evaluated by HR-TEM (microtome cuttings) and correlated to their catalytic activity in a model reaction, the cyclooctene epoxidation reaction.



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Nanostructures Material for Energy Conversion: Synergic Effects between Carbon Nanotubes and Metal Oxides

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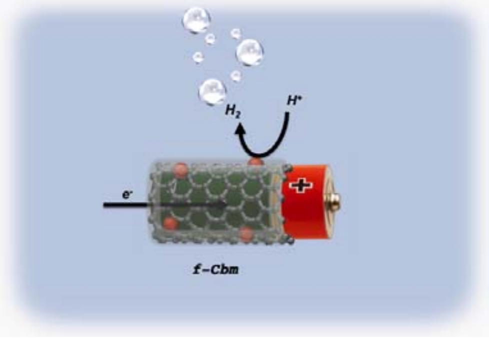
ABSTRACT

The growing need for energy on global scale and the realization that the so called oil-based economy cannot sustain our world anymore, prompted researchers to find new ways to "power" the planet.[1] In particular a lot of efforts have been done in the field of chemical energy conversion, that remains very challenging because of the requirement for higher efficiencies.[2] The splitting of water to high energy chemical fuels is one of the most attractive and pursued alternatives; among the major issues there is the need to find catalytic systems that are able to boost the overall reaction efficiently and durably.[3]

In this context our group recently focused the attention on the study of catalytic systems for the oxygen evolution reaction (OER).[4] Our last efforts have been done in the development of new C-based nanocomposites that combine the unique properties of multiwall carbon nanotubes (MWCNTs), metal oxides (TiO_2 and CeO_2) and Pd nanoparticles (Pd NPs).[5] The nanocomposites MWNT@Pd/TiO_2 and MWNT@Pd/CeO_2 have been designed and evaluated as electrocatalyst for the reaction of hydrogen evolution (HER) and for the CO_2 reduction, respectively.

Both systems exhibit very good performances and efficiencies, showing physical and chemical properties that differ to those expected from the simple sum of the individual building blocks. Due to these synergic effects, we shed light on the role of the MWCNTs in terms of their influence on the electronic properties of the two semiconductors (e.g. presence of surface states and different doping levels), resulting in better electrocatalytic activities.



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Iron Sulfide Nanoparticles as Cathode Catalyst for PEM Electrolyzers: Towards a Mechanism for Hydrogen Evolution Reaction

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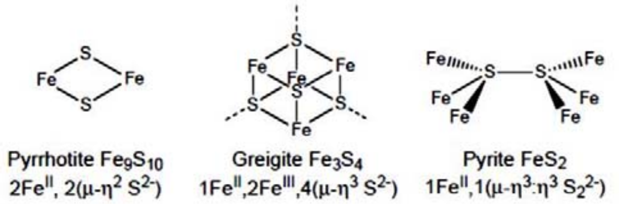
ABSTRACT

Recently, heterogeneous electrocatalysts, in the form of electrodeposited bulk material or nanoparticles, based on molybdenum sulfide, colbalt sulfide, cobalt phosphate, iron or nickel phosphide, and alloys of nickel-molybdenum have been reported for their high activity toward hydrogen evolution reaction (HER) in acidic or neutral water at relatively low overpotentials[1]. Given the ubiquity of iron sulphide minerals in nature, and the presence of iron sulfide clusters in hydrogenase enzymes, we decided to investigate iron sulfide as a new material for HER.



Pyrrhotite Fe_9S_{10}
$2Fe^{II}, 2(\mu\text{-}\eta^2\ S^{2-})$

Greigite Fe_3S_4
$1Fe^{II}, 2Fe^{III}, 4(\mu\text{-}\eta^3\ S^{2-})$

Pyrite FeS_2
$1Fe^{II}, 1(\mu\text{-}\eta^3{:}\eta^3\ S_2^{2-})$

Figure 1: *Iron and Sulfur formal oxidation states.*

In order to decipher the influence of iron and sulfur oxidation states, and crystal structure on the catalysis of the HER, we have synthesized FeS nanoparticles of different stoichiometry: pyrrhotite Fe_9S_{10}, greigite Fe_3S_4 and pyrite FeS_2, using soft chemistry routes, and tested *ex-situ* and *in-situ* for HER. The nanoparticles crystalline structure and morphology were characterized by XRD and SEM and TEM, respectively. Mössbauer spectroscopy was used to probe the iron oxidation and magnetic states in each material.

For FeS nanoparticles-Nafion coated glassy carbon electrodes, overpotentials between 200 and 300 mV were observed, and long-duration (6 days) controlled-potential electrolysis were performed to assess the durability and robustness of the materials. Quantitative (≥0.99) Faradic yield for molecular hydrogen evolution was confirmed by gas chromatography analysis as well as volumetric measurements[2]. EXAFS and XANES spectra were recorded in an electrochemical cell on Nafion or phosphonated-polymer films loaded with pyrite and pyrrhotite catalysts at both the Fe and S K-edges, to follow the evolution of the materials structure during the HER. The prepared FeS nanoparticles were also tested as cathode catalysts in membrane-electrode assembly in an electrolyzer (anode: IrO_2, 5 cm^2, T=80 to 120°C, P=2 bars). Pyrite was found to be the most active compared with greigite and pyrrhotite, and showed a 400mV overpotential at 2 A cm^{-2} compared to standard Pt/C and stability over 100 h.

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Optimization of Nanometric Epitaxial Hematite Films for Solar Water Splitting by Oxygen Vacancy Engineering

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ABSTRACT

Using hydrogen as an energy carrier for solar energy storage and/or fuel alternative to oil is very appealing, especially as it can be cleanly produced by solar water splitting (solar-assisted water oxido-reduction). Hematite (α-Fe_2O_3) is one of the most promising photo-anodes materials (for water oxidation), given its quasi ideal band-gap for this application, stability, abundance and low cost [1]. Unfortunately, hematite is limited by weak transport properties (low conductivity and low hole diffusion length *ca.* 2-4 nm).

Oxygen stoichiometry is a key parameter for the optimization of hematite photoanodes. Indeed oxygen vacancies are expected to act as donor dopants in hematite [2], increasing the overall carrier concentration and therefore the conductivity. However the induced partial iron reduction from Fe^{3+} to Fe^{2+} may be detrimental through structural modifications or the presence of electronic states within the band gap [3], favoring the recombination of photo-generated charges and hence lowering the water splitting performances [2]. The investigation of these concomitants phenomena is a tricky issue to tackle. The use of single crystalline films, providing a very good control of the materials properties (structure, stoichiometry) is an elegant way to conduct properly this kind of study.

In this work we studied single crystalline hematite films of nanometric thickness elaborated by atomic oxygen plasma molecular beam epitaxy. Oxygen vacancies were introduced in the films upon annealing in an ultra-high vacuum environment, with relatively low temperatures (200-450°C range). X-ray Photoelectron Spectroscopy (XPS), Extended X-ray Absorption Fine Structure (EXAFS) and photocurrent results are presented. We were able to correlate the photo-electrochemical performances to structural changes due to iron cations reduction, unravelling the origin of an optimal annealing temperature.

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Bioinspired Multifunctional Coatings for Advanced Structural Metals/Alloys

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ABSTRACT

Structural metals/alloys are inevitable part of our daily life and numerous industrial applications. One key issue of using such materials is to maintain their structural/functional integrity and appearance from external hazards. There are several methods such as chromate passivation, electrochemical plating, anodizing, and coatings to overcome these shortcomings. Generally, in those cases a protection layer forms on the metal surface, which consists of several tens to hundreds of μm in thickness. On the other hand, during last few decades a huge demand has emerged in materials science/technology for compact size, weight and sophisticated devices/tools. These trends have led to a significant advance in the field of nano- materials/technology, resulting in new innovations with structural metals/alloys. Considering reduced metal backbone dimensions and weight, protection layer has to be more sophisticated and thin, possibly below sub-micron level, with adequate performance and versatility. Therefore, it is need of hour to develop ultrathin, versatile, ecofriendly, and easy coating technique for state-of-the-art structural architectures.

At present, we demonstrate an efficient and versatile coatings technique inspired by an underwater bioadhesion mechanism[1]. Many marine organisms survive under harsh deepsea condition and they do it by a unique adhesive foot, which contains mainly catechol and amine units. By mimicking this natural phenomenon, we prepared a wide-range of synthetic polymers and macromolecules for practical applications in diverse fields including anticorrosion, antifouling, adhesive, and smart coatings of metals/alloys. Our study revealed that a simple combination of anchoring catechol moieties and hydrophobic alkyl chains led to an efficient and versatile coating method.

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Implementation of Hybrid Nano-emitters Coupling Fluorophores and Plasmonics Nano-particles

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ABSTRACT

Due to reduced plasmon damping [1], gold nanorods (GNR) are known to exhibit highly localized electromagnetic field enhancement effects leading to quite attractive nano-antenna properties and making GNR interesting objects for various applications: photovoltaics [2], biology [3] and in the creation of smaller light sources such as nanolasers [4]. Indeed, new hybrid nano-sources can be implemented by using the huge enhancement field induced by the GNR to enhance the emission of fluorophore close to the GNR. We report here our recent studies aiming at optimizing the coupling of fluorescent polymer to a GNR.

In a first step, the field enhancement properties of different GNR were investigated at the single particle level using two-photon luminescence (TPL). TPL is indeed directly linked to the local density of electromagnetic states (LDOS) and thus constitute a relevant tool to probe the local hotspots on nanostructures [5]. For this purpose, an inverted microscope set-up associated to a femtosecond Ti-sapphire laser excitation (Tsunami, Spectra Physics, 770nm < λ< 930nm) and coupled to an Atomic Force Microscope (NanoWizard III, JPK) was used. This experiment allows us to perform correlated TPL and topography measurements in single GNR immobilized on ITO covered glass substrates. GNR display two localized surface plasmon resonances: λ^{T}_{LSP} around 520 nm and λ^{L}_{LSP} between 750 and 850 nm associated to their transversal and longitudinal size, respectively. We have been focusing on two different colloidal GNR exhibiting the same aspect ratio of 4 but having a different volume ($40x10x10nm^3$ and $29x6x6nm^3$). We analyzed their TPL to determine their field enhancement properties. A statistical study on more than 20 GNR for each batches has been performed to find out the GNR with the best enhancement factor. The GNR $40x10x10nm^3$ presented an enhancement factor of 34 twice as big as the one presented by the GNR $29x6x6nm^3$.

As a next step, a method to couple a fluorescent system (a polyphenylene vinylene (PPV) derivative) to the previously immobilized GNRs was then studied: the so-called layer-by-layer technique was more particularly investigated, bilayers of polysterenesulfonate (PSS) and pollyallylamine hydrochloride (PAH) being used as spacers. The main point of this coupling is to avoid quenching by controlling the distance between the GNR and the fluorophore. With the layer-by-layer technique we were able to manage precisely this distance. Previous studies done in the laboratory using this technique demonstrated a gain of a factor of 2 on the global intensity [6]. This gain is really small compared to the enhancement ratio of the GNR itself. We will discuss this result and the effect of the quenching from the ITO substrate which is currently used to immobilize GNRs. Experiments are now in progress towards optimized hybrid nano-emitters.

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Characterization of CVD Graphene: Work Function Modulation and its Opportunities for Heterojunctions

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ABSTRACT

We are concerned with the engineering of heterogeneous two-dimensional layered materials, including semi metallic graphene and semiconducting transition metal dichalcogenides (LTMDs). These new materials present a valuable opportunity to produce tunable electronic and optoelectronic systems e.g. photovoltaics[1] or nanoelectronic functions such as nonvolatile memory applications[2,3]. A judicious design of such heterostructures requires the precise determination of the band offsets and work function among other electronic properties. One question that arises is whether we could engineer adjustable band offsets using combined graphene and 2D analogues system in order to replace typical semiconductor such as silicon and gallium arsenide. At this sub-nm scale, advanced characterization must be coupled to steady state techniques.

INVESTIGATIONS ON CVD GRAPHENE

GeePS and ANTARES have initiated a collaboration to investigate various combination of material at synchrotron Soleil. So far, we have focused on CVD graphene samples. These samples presented peculiar flower-shaped structures composed of trilayer. We have observed Moiré patterns by TEM. However, using nano-ARPES[4] we have been able to evidence that the patterns actually form between the copper substrate and the first monolayer graphene and not between graphene multilayers as initially thought. Moreover, on the same CVD graphene samples, we demonstrated a large modulation of the work function by in situ Rb reversible doping up to 1eV. This magnitude is in itself very much interesting to adjust injection barrier for electrode for instance. Yet, the striking feature observed is that the Rb preferably deposit onto CVD/Cu Moiré. As a result, a variation of work function of several meV is possible within the nm range. Such a modulation opens a route to engineer the carrier injection with doped CVD graphene for various applications particularly photovoltaic heterojunctions among other devices.

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Analysis and Functionalization of Graphene Oxide with Electrochemical Microscopy

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ABSTRACT

Graphene and graphene analogues such as graphene oxide (GO) or reduced-GO (r-GO) are attracting increasing attention from the scientific community.[1] These materials have outstanding properties, so that many potential applications in the fields of electronics, sensors, catalysis and energy storage are being considered. GO combines several advantages such as availability in large quantity, low cost and easy processability. However, contrary to graphene, GO is electronically insulating and has to be reduced into a conductive material, r-GO.

In a recent work[2] we introduced a new localized functionalization method of GO deposited on a silicon oxide surface based on its reduction at the local scale thanks to scanning electrochemical microscopy (SECM): the reducer is generated at the microelectrode, that is moved close to the substrate. The recovery of electronic conductivity upon reduction enables the selective electrochemical functionalization of patterns.

Besides, we introduced a new method to evaluate at a local scale the conductivity of r-GO layers with SECM.[3] In addition we show how images of individual and interconnected flakes directly reveal the signature of the contact resistance between flakes in a non-contact and substrate-independent way.[4] Quantitative evaluation of the parameters is achieved with the support of numerical simulations to interpret the experimental results.

Overall, these works illustrate the high potential and versatility of SECM to investigate and functionalize 2D materials.

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Synthesis of ^{14}C-labeled Graphene

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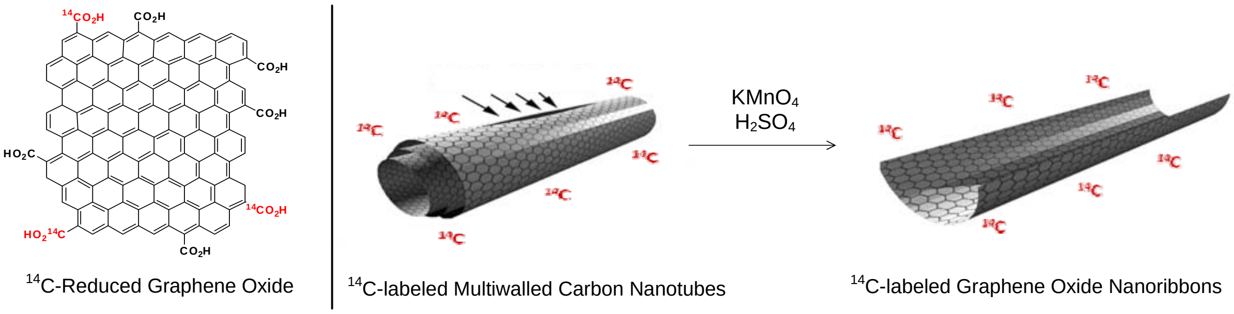
ABSTRACT

Graphene is a monolayer of *sp*^{2} hybridized carbon atoms arranged into a two-dimensional (2D) honeycomb lattice. Today, graphene is the most attractive nanomaterial because of its exceptional electronic, thermal and mechanical properties.[1] These capacities have made graphene ideal for diverse applications in many technological fields such as nanocomposite materials, batteries or supercapacitors.[2] Accordingly, as graphene will represent a source of exposure to population, the impact on health and environment have to be studied.

One way to answer this issue is to achieve tissue distribution and metabolism studies of this nanoparticle. In this framework, the aim of the project is to develop chemical synthesis of ^{14}C-labeled graphene and its ^{14}C-labeled derivatives. In view of graphene synthesis described in the literature, we have developed two labelling strategies: Labelling of reduced graphene oxide by multi-step synthesis[3] and unzipping of ^{14}C-carbon nanotubes by oxidative treatment[4] (Figure 1). Here, we will present the development of those two labelling studies.



^{14}C-Reduced Graphene Oxide

^{14}C-labeled Multiwalled Carbon Nanotubes

^{14}C-labeled Graphene Oxide Nanoribbons

Figure 1 – Graphene labelling strategies

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ABSTRACTS

Friday, September 11th, 2015

SESSION IV

ICON^2 - 2015

Friday, September 11th

SESSION IV

Chairpersons: M. Mura – H. Magnan

IT-13	Mesostructured materials via the sol-gel process for energy conversion and storage *C. Laberty-Robert*
IT-14	A double-strand approach to biomimetic multiporphyrin architectures *M. Morisue*
OC-15	Stability of supported lead nanoparticles: Five-fold twinned pyramids versus single crystals *L. Serrier-Garcia*
IT-15	Stimuli responsive supramolecular materials through host and guest interactions *Y. Takashima*
OC-16	Supramolecular chiral nanoarchitectures and chiral phase transitin induced by the selective assembly of barbituric acide derivative enantiomers *X. Sun*
OC-17	XPS of isolated nanoparticles *O. Sublemontier*
OC-18	Hot carrier relaxation in photoexcited GaAs: The role of the electron-phonon coupling *J. Sjakste*

Mesostructured Materials via the Sol-gel Process for Energy Conversion and Storage

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ABSTRACT

Sol-gel chemistry coupled with processing technologies including dip-coating, electrospinning, spray-coating, etc…allows the synthesis of materials with various compositions, structures as well as different shapes. All these attributes facilitate their integration into electrochemical devices as either electrodes or solid-electrolyte. In this presentation, we will explore different synthetic approaches that allow either the fabrication of nanostructured electrodes for energy conversion device. For μ−SOFC, we have developed the sol□gel chemistry with dip□coating for fabricating nanostructured electrodes. One of the main difficulties is to maintain in these electrodes good ionic and electronic conductivities as well as efficient gas diffusion. To achieve it, we investigated by impedance spectroscopy the in situ anode formation. In particular, we defined the experimental conditions including T and time that gives rise to percolated Ni network into thin film mesostructured ionic network.

We have extended this method to the synthesis of light sensible electrodes for both water splitting and photo-battery application. We will discuss the interest of the nanostructure for these technologies.

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A Double-strand Approach to Biomimetic Multiporphyrin Architectures

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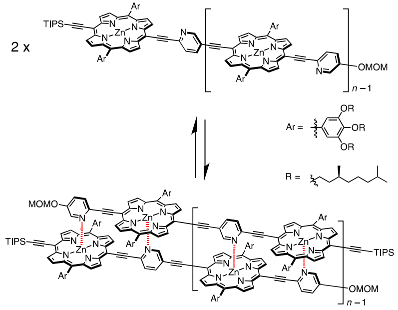
ABSTRACT

A shape-programmable bottom-up nanotechnology is now emerging as the state-of-the-art methodology to manipulate nanomaterials with molecular scale precision over a size regime beyond the micrometer length scale, as exemplified by DNA-nanotechnology. Stiff rod-like double-stranded structure is key in shape-programming molecular architectures. Inspired by the DNA-nanotechnology, oligomeric porphyrin array with an alternating pyridyl–zinc-porphyrin sequence was designed to assemble the double-strand through self-complementary pyridyl-to-zinc coordination bonds by the aid of *π*-stack (Scheme 1). The double-stranded porphyrin arrays formed with exceptionally high stability constants, and the selectivity attained self-sorting molecular assembly even when porphyrin arrays with different length were mixed.

The double-stranded porphyrin array was applied for supramolecular polymerization based on the shape-persistence of the double-strand unit with high stability constant in toluene. Supramolecular array was extended enough to obey the Beer's law even at very dilute conditions less than 0.1 mM, suggesting ignorable terminal effect in electronic absorption spectra. Cryogenic transmission electron micrograph (cryo-TEM) revealed that giant multiporphyrin array was stretched over a micrometer length.

Moreover, the double-stranded porphyrin array provided *π*-electron network through a successive slipped-cofacial stack of the porphyrin planes. The *π*-stacked conformation is close reminiscence of that in bacterial light-harvesting antenna complex, and therefore the double-strand porphyrin array is powerful building unit for sophisticated hierarchical molecular architectures aiming at artificial photosynthetic model. For instance, the supramolecular polymer extended stacked *π*-system, and the absorption and emission bands were penetrated into the near-infrared (NIR) wavelength region in thin film prepared by simple spin-cast method. The solid-state NIR photoluminescence drew sharp contrast to general energy-gap law. The double-strand approach is thus privileged methodology toward biomimetic artificial photosynthesis.

Scheme 1. Double-strand formation of porphyrin array (n = 1–3).



$$\frac{d[F_1]}{d\omega_2} = S\Delta m_2 \cos\alpha, \quad \frac{d[F_1]}{d\omega_3} = S\Delta m_3 \cos\alpha.$$

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Stability of Supported Lead Nanoparticles: Five-fold Twinned Pyramids versus Single Crystals

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ABSTRACT

Many metals adopt a face-centered cubic structure in their bulk form, but they often exhibit important structural and morphological deviations when confined to nanoscale or interacting with the environment. We investigated the growth of lead nanoislands on silicon(111) in ultrahigh vacuum for different evaporation conditions: temperature, flux, annealing time, and source or surface condition. Unexpected Pb icosahedral nanoparticles of a very large, up to 100 nm, size have been revealed to grow on Si(111) substrate. We probed the coexistence between these 5-fold twinned Pb pyramids and expected face-centered cubic (fcc) Pb single crystals in situ by Scanning Tunneling Microscopy (STM) and ex situ by Scanning Electron Microscopy (SEM). We found that the growth of the Pb icosahedral particles only occurs when very high Pb diffusion conditions are met, with a high quality of the silicon surface and a purified lead source. Moreover, we observed that the icosahedral pyramids are more stable than fcc single crystals upon ripening at room temperature.

This work is supported by French ANR Project Electrovortex and University Pierre and Marie Curie Grant Emergence.

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Stimuli Responsive Supramolecular Materials through Host and Guest Interactions

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ABSTRACT

In biological system, there are some attractive functions such as enzymatic reactions, muscle motion, and self-healing properties. Inspired by these functions, many supramolecular chemists engage the creation of supramolecular complexes reminescent of biological functions. We have focused on the creation of supramolecular materials reminescence of the muscle motion, self-organization of cell and self-healing properties through host-guest interactions (Fig. 1). We employ cyclodextrin (CD) as a host molecule. This presentation demonstrates supramolecular actuators and self-healing materials.

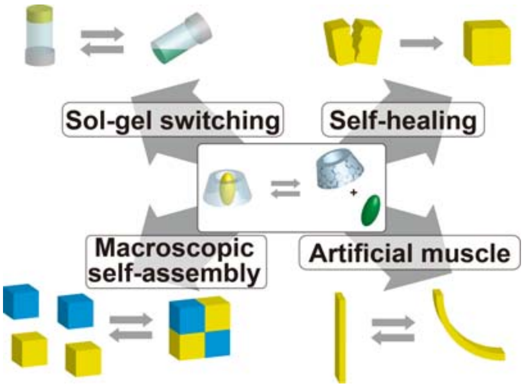

Figure 1. Conceptual scheme of our studies.

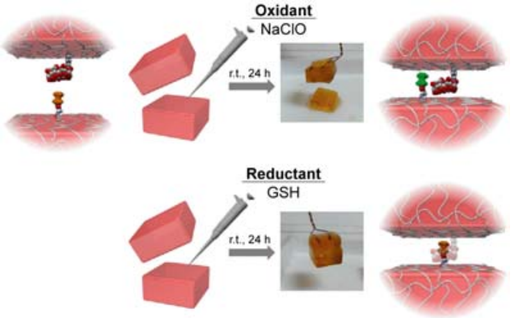

Figure 2. Redox-responsive healing experiment of the pAA-6βCD/pAA-Fc hydrogel using oxidizing/reducing agents.

A photoresponsive supramolecular hydrogel with αCD as a host molecule and an azobenzene (Azo) derivative as a guest and photoresponsive molecule exhibits reversible macroscopic deformations in both size and shape when irradiated by ultraviolet (UV) at λ = 365 nm or visible light (Vis) at λ = 430 nm. The deformation of the supramolecular hydrogel depends on the incident direction. A light-driven supramolecular actuator with αCD and Azo stems from the formation and dissociation of an inclusion complex by UV or Vis light irradiation.[1]

We have investigated two approaches to prepare self-healing materials. First method is a supramolecular materials using poly(acrylic acid) modified with cyclodextrins (pAA-CDs) as a host polymer and pAA with ferrocene (pAA-Fc) as a guest polymer (Fig. 2).[2] Second method is the radical copolymerization of βCD and adamantane (Ad) monomers to give supramolecular hydrogels in water without crosslinkers. The supramolecular hydrogels formed by host-guest interactions exhibits self-healing properties to reach 99% of the initial gel's strength.[3-5]

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Supramolecular Chiral Self-assemblies and Chiral Phase Transition from Barbituric Acide Derivatives

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ABSTRACT

Barbituric acid derivatives are prochiral molecules, i.e. they are chiral upon adsorption on surfaces. Scanning tunneling microscopy reveals that barbituric acid derivatives self-assemble into two different chiral supramolecular architectures at the solid-liquid interface on graphite.

The first structure is a chiral supramolecular guest-host architecture. The host-nanoarchitecture is a porous network which is having a sophisticated wavy shape pattern. Paired guest molecules are nested insides the cavities of the host structure. The wavy patterns of the nanoarchitecture are formed from alternative appearance of left- and right-handed chiral building blocks which makes the network heterochiral [1]. The chiral guest-host architecture can be transformed in a second close packed structure. The second structure is a chiral structure with almost linear stripes. It is composed of either left-handed or right-handed enantiomeric domains. Both of the two structures are racemic.

The two functional chiral nanoarchitectures and their chiral phase transition are the results of 2D chiral amplification from single enantiomers to organizational hetero/homo chiral supramolecular self-assembly.

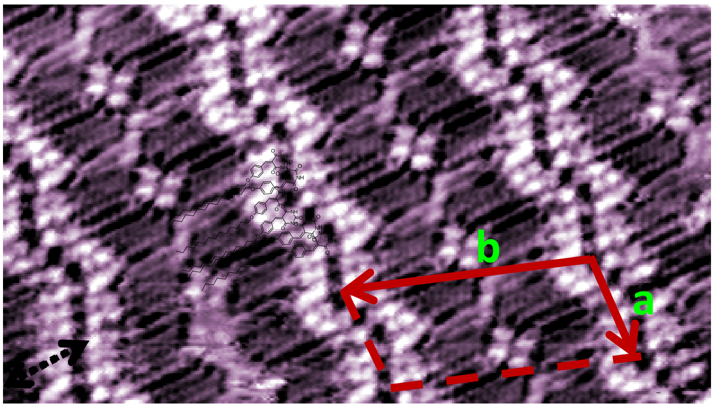

Figure: STM observed wavy-shape supramolecular guest-host architecture.

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XPS of Isolated Nanoparticles

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ABSTRACT

X-ray photoelectron spectroscopy (XPS) is a very efficient and still progressing surface analysis technique.[1] It has been demonstrated to be a unique tool for characterizing the surface[2] and bulk[3] chemical structure of nanoparticles. However, XPS on supported nano-objects faces drawbacks due to their interaction with substrates[4] and sample charging effects, which often lead to uncertainty in the interpretation of measurements.[3] Here we investigate the feasibility and relevance of high resolution Synchrotron Radiation XPS (SR-XPS) analysis of isolated nanoparticles.

The principle of the experiment is to cross a beam of isolated nanoparticles with synchrotron radiation under high vacuum conditions, so that the interaction between a particle and the soft x-rays is well defined both spatially and temporally. An Aerodynamic Lens System (ADLS) produces a focused, continuously renewable nanoparticle beam under vacuum from an aerosol stream at atmospheric pressure. This is achieved by carrying the nano-aerosol flow through a 200 µm limiting entrance orifice followed by a series of four chambers separated by diaphragms. It is part of a dedicated multipurpose source chamber available at the PLEIADES beam-line at the French national synchrotron radiation facility SOLEIL.[5] The nanoparticle beam passes entirely through a 1.5 mm diameter skimmer and emerges into a high vacuum region before crossing the soft x-ray beam. The pressure in the interaction chamber is maintained at around 10^{-6} mbar.

Several examples on different objects of study will be given, including the Si/SiO_2 interface on isolated silicon nanocrystals[6] and water adsorption on TiO_2 nanoparticles[7]. Thanks to the high surface sensitivity, the core level spectra reveal the chemical structure of the particle surfaces at the atomic scale. The continuous refreshment of the sample upon analysis avoids charging effects, thus allowing high accuracy in absolute kinetic energies determination. The technique should be applicable to a large range of nano-objects.

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Hot Carrier Relaxation in Photoexcited GaAs: The Role of the Electron-phonon Coupling

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ABSTRACT

Electron scattering by phonons is one of the major processes that determine the transport characteristics and relaxation dynamics in semiconductor-based devices. Indeed, carrier lifetimes are mainly limited by impurity and phonon scattering. For the hot electrons in a semiconductor such as GaAs, the electron-phonon scattering time is surprisingly fast, of the same order of magnitude as the interaction between free carriers[1].

Although density functional theory (DFT) -based computational methods for the calculation of the electron-phonon coupling matrix elements in metals exist since the late nineties, DFT-based calculations of the electron-phonon coupling in semiconductors started much more recently. These calculations allowed us to successfully predict the scattering times related to electron-phonon coupling in several semiconductors, as well as in bismuth[2,3,4]. Very recently, we have developed a new computational method for the calculation of the electron-phonon coupling in polar materials. This method is based on the interpolation of the electron-phonon matrix elements in Wannier representation[5]. This method allowed us to successfully interpret, in collaboration, the dynamics of hot electron relaxation in bulk GaAs, in excellent agreement with time- and angle- resolved photoemission experiment by the group of K. Tanimura (University of Osaka, Japan). The measured, and calculated, electron-phonon scattering times turned out to be surprisingly fast, of the order of a few tens of femtoseconds. Moreover, we have demonstrated, for the relaxation of hot carriers in GaAs, the existence of two distinct relaxation regimes, one related with the momentum, and the other with energy relaxation. We have demonstrated that both regimes are almost entirely ruled by the electron-phonon interaction. [6]

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POSTER SESSION

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PO-02	Development of new functionalization methods of carbon nanotubes and graphene *S. Campidelli*
PO-03	Doped twisted graphene bilayers studied by scanning tunneling spectroscopy *V. Cherkez*
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PO-17	Organic based photovoltaics: Challenges *T. Vangerven*
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PO-19	First principles calculations of $Bi_2Al_4O_9$: Equation of states and elastic properties *E. Zahedi*
PO-20	Density Functional Study on Electronic and Photocatalytic Properties of Orthorhombic $Bi_2M_4O_9$ ($M=Al^{3+}$, Ga^{3+}) *E. Zahedi*
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Characterization of Epitaxial $BaTiO_3$ / $CoFe_2O_4$ Multiferroic Heterostructures using Synchrotron Radiation

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ABSTRACT

Multiferroic materials have found many applications in the field of spintronics[1,2]. Among them, ferrimagnetic $CoFe_2O_4$ spinel thin layers on ferroelectric $BaTiO_3$ constitute a well referenced system for the study of magnetic states upon multiferroic coupling[3]. An indirect magneto-electric coupling is expected to arise in such systems through strain, the spinel being magnetostrictive and the perovskite having piezoelectric properties. In this study we focused on the evolution of the structural, electric and magnetic properties of such samples with different thin film thicknesses, *i.e.* with an interfacial strain evolution.

For the purpose of this study we prepared 18 samples of CoFe2O4 / BaTiO3 thin layered samples, combining 3 thicknesses of $BaTiO_3$ (7 to 21 nm) layers with 6 thicknesses of $CoFe_2O_4$ (2.2 to 15 nm) layers. Such samples were obtained by molecular beam epitaxy with high control of deposition time, crystallinity and stoichiometry[4,5].

The lattice parameters of those films were determined by synchrotron-based Grazing Incidence X-Ray Diffraction, alongside with the direction of constraint in the reciprocal lattice.

The stability of the ferroelectricity in such samples was characterized using PiezeoForce Microscopy to polarize the surface of samples with an applied bias. The voltage necessary to write a pattern depends on the film thickness. The temperature stability was investigated using Low-Energy Electron Microscopy. As expected from thin films[6], the Curie temperature obtained was much higher than for bulk $BaTiO_3$.

X-ray Magnetic Dichroism (linear and circular) was used to correlate the evolution of those parameters with magnetic properties. Significant modifications of the strain in the lattice parameters indeed induced an evolution of the M_R / M_S ratio (M_R magnetic remanent moment, M_S saturation moment), as well as of the $L_{2,3}$ transition signal of Co in the ferrite.

This link between magnetic, electric and structural properties strongly suggests the possibility for magneto-electric coupling.

Moreover, magnetic and electric properties are highlighted at room temperatures, result of high interest for potential spintronics applications.

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Development of New Functionalization Methods of Carbon Nanotubes and Graphene

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ABSTRACT

The fabrication of tailor-made functional hybrid materials that preserves and combines the properties of their building blocks is a central issue of nanosciences. In particular, the development of efficient techniques for the functionalization of carbon-based nanomaterials (carbon nanotubes and graphene) preserving their exceptional quality, while robustly enriching their functionalities is highly desirable.

Here, I will describe the general approach that we developed in our group for functionalizing nanotubes and graphene. This method is based on the templated-polymerization of organic molecules around nanotubes or graphene; it combines most advantages of both covalent and non-covalent methods without their principal drawbacks.[1] This approach permits to obtain hybrid materials exhibiting high stability while preserving the integrity of the π-conjugated system responsible for their optical and electrical properties. The functional nanotube hybrids were tested as electrocatalysts for the oxygen reduction reaction (ORR) in a series of electrochemical measurements in acidic conditions. Compared to similar systems in which monomeric porphyrins are simply physisorbed, the nanotube hybrib showed a higher activity, a higher current density, a lower overpotential and a four electrons reaction pathway.[2]

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Doped Twisted Graphene Bilayers Studied by Scanning Tunneling Spectroscopy

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ABSTRACT

Twisted graphene bilayers (tBL) form a class of 2D materials whose electronic structure can be controlled by a geometric parameter, namely by the rotation angle θ between the graphene layers [1-4]. For twist angles θ > 1-2° the tBL's low energy band structure can be considered as a superposition of the Dirac cones of the individual graphene planes. Coupling between planes results in the opening of partial gaps on the Dirac cones. Associated logarithmic divergences in the density of states (DOS) called van Hove singularities (vHs) appears within ~ 1 eV from the Fermi level E_F. For undoped bilayer the vHs energies are almost symmetric with respect to the E_F and decrease with θ. Unusual magneto-transport [5] and optical [6] properties, as well as the appearance of many body instabilities [7], have been predicted for the doped tBL, when the Fermi level is brought in the vicinity of the vHs. These predictions have motivated us to study in a direct experimental way the influence of the doping on the low energy electronic structure of the twisted graphene layers, to determine for instance at which angle the vHs crosses E_F for a given charge.

We present an analysis by Scanning Tunneling Microscopy (STM) and Spectroscopy (STS), complemented by tight binding calculations, of the density of states of electron doped tBL in a wide range of angles (1.5° < θ < 15°) [8]. We have investigated the electronic structure of twisted bilayers doped by charge transfer from the 6H-SiC (carbon face) substrate. Spectroscopic studies [9] have revealed that the doping level is in the 10^{12} cm^{-2} range. The charge density is larger for the plane closest to the substrate and decreases for the next layer. This results in a different electric potential on each graphene plane [10], which shifts the electronic energy levels (e.g. the Dirac points) of the layers accordingly. Analyzing 17 independent tBL we find by STS that the vHs crosses the Fermi level for θ ≈ 3°, with no change in the vHs splitting compared to the neutral case [4]. The layer dependent doping results in a difference in the electrical potentials of the two layers of the order of 0.1 V at most, as deduced from a simple model supported by experimental observations.

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Gold Nanoparticle Defects Probed by Unified SAXS/WAXS/XRD Analysis

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ABSTRACT

Shape and size are known to determine a nanoparticle's properties. Internal crystal structure (i.e. particle defects and symmetry) is just as critical since it directly impacts catalytic efficiency, plasmon resonance, and orients anisotropic growth of metallic nanoparticles. Hence its control cannot be ignored any longer in today's research and applications in nanotechnology. Here we present a reliable measurement combining all these three aspects. The unified small angle, wide angle X-ray scattering, and diffraction measurement (SAXS/WAXS/XRD) coupled with molecular dynamics, allows simultaneous determination of nanoparticles' shape, size and defects at the atomic scale [1].

Model gold particles are synthetized in organic solution using mild conditions [2]. As several stable structures exist [3], a mixture of monocrystalline and flawed particles is usually obtained (Figure 1a and b).

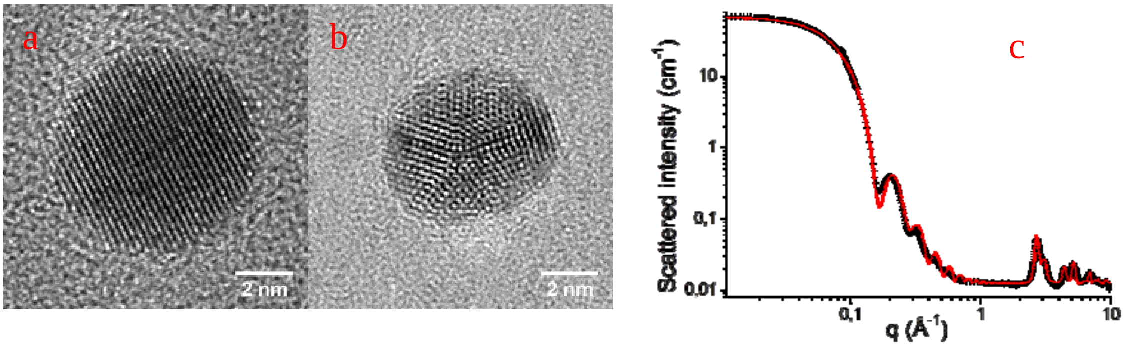

Figure 1: TEM of monocrystalline (a) and flawed (b) particles. (c) SAXS/WAXS/XRD unified diagram.

Using molecular dynamics [4], TOh, Dh and Ih gold particles are calculated. A model combining these particles is fitted to the X-ray total scattering diagrams (SAXS/WAXS/XRD) (Figure 1c). External shape, size and concentration being constrained by the SAXS pattern, the internal structures were described by quantitative numbers. Particles are found to be mainly flawed, with a majority of icosahedra. A complementary analysis is obtained in direct space, using Pair Distribution Functions (PDF).

This methodology is not limited to metallic nanoparticles and could be applied as well to oxides, alloys and hybrid particles.

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Two-dimensional Graphene Based Insulator

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ABSTRACT

Graphene is the most potential candidate for next-generation nanoelectronic because its outstanding properties[1]. To build a graphene-based field effect transistor (FET), graphene-on-insulator are typically used to investigate the carrier transport properties in the earlier stage[2]. However, graphene-on-insulator structure is not realistic device architectures. To be compatible with standard CMOS and IC processes, a top-gated graphene device is necessary. However, the conventional dielectric deposition techniques usually result in defective graphene or low-quality insulator[3]. Here, a graphene based dielectric, fluorographene, with 3eV bandgap and G$\Omega/\square$ resistance is employed in gFET as the gate insulator. The insulating capabilities were seriously evaluated in metal-insulator-metal capacitor structure for qualifying typical dielectric parameters. As a result, fluorographene exhibits awesome performance as a dielectric in terms of high breakdown electric field up to 12MV/cm, stable thermal stability up to 400^{o}C and low-frequency dependent capacitance ranging in 20-100kHz. Ultimately, one-step formation of multilayer fluorographene for few layer stacking graphene sheets was established so as to reduce randomly formed leakage path. A whole graphene-based FET is eventually fabricated with typical CVD-graphene mobility.

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Solution Processed Perovskite Solar Cells

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ABSTRACT

In recent years, hybrid perovskite ($CH_3NH_3PbI_{3\text{-}X}Cl_X$) solar cells have been studied steadily due to their potential properties: high power conversion efficiency, low-cost processing and possibility to produce large area.[1] The hybrid perovskite film has a crystalline structure. Many different solvents are being developed and gradually adopted for high performance inorganic-organic hybrid perovskite solar cells.[2] The conditions of annealing and spin coating have a decisive effect on the crystallinity of perovskite film which is used as active layer. In this study, inverted-type perovskite solar cells were fabricated by solution process at low temperature. PEDOT:PSS and $PC_{60}BM$ are used as hole transport layer (HTL) and electron transport layer (ETL), respectively. The size of active area is 0.28cm^2. A power conversion efficiency (PCE) of 9.93% is obtained with a current density (Jsc) of 16.1mA/cm^2. Electrical measurements (Transmission Line Method (TLM), Steady State Photo-carrier Grating (SSPG), Impedance Spectroscopy (IS)) will support our study on electrical transport mechanisms in this perovskite film correlated to crystal morphologies.

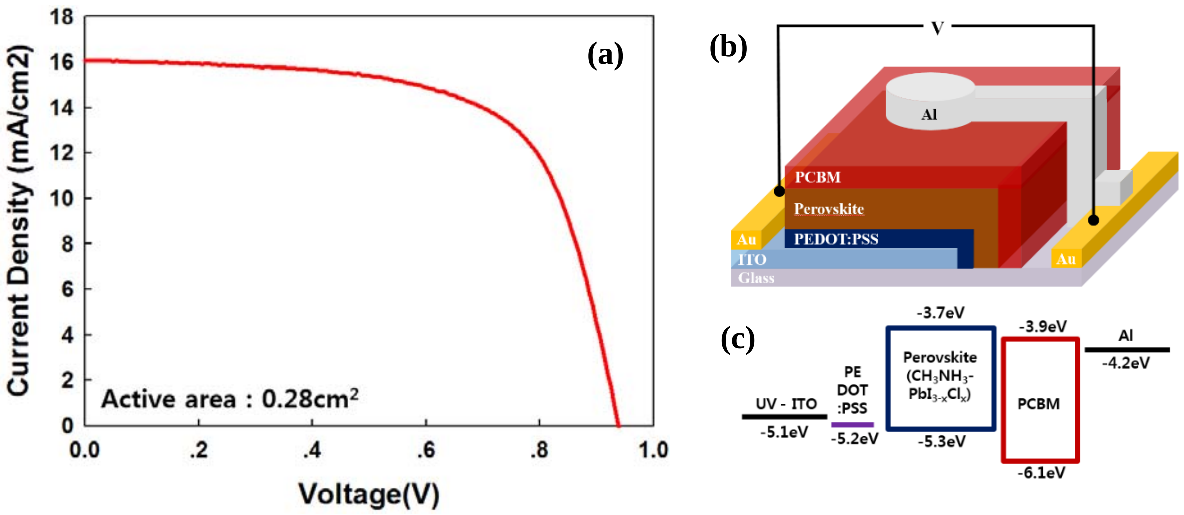

Figure 1 (a) J-V curve in different wiping conditions, **(b)** Full device structure, **(c)** Energy band-diagram of solar cells device in this study

Solar cells Parameters	Jsc (mA/cm^2)	Voc (V)	FF (%)	PCE (%)
Value	16.1	0.94	66	9.93

Table1. Basic parameters of perovskite solar cells in this study

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Silica Vitrimer Nanocomposites

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ABSTRACT

One of the current challenges of numerous industries such as aeronautics or automotive industries is to replace metals with lighter materials presenting similar mechanical properties. Composites based on thermosetting resins are currently widely used. However, once the resin is cured, it is impossible to reshape or repair them. Finding alternative systems has become a necessity and one possible solution could be provided by vitrimer based composites.

Vitrimers[1,2], a new class of polymer materials, are made of molecular networks that can rearrange their topology by catalyzed exchange reactions without altering the number of links between their atoms. These materials are insoluble and exhibit dimensional stability of thermosets; yet at high temperatures when exchange reactions are fast they can flow like thermoplastics. Even more importantly, these networks show Arrhenius-like gradual viscosity variations. Their topology can be quenched and the material behaves as a solid even above a classical glass transition. Depending on the chemistry chosen, vitrimers at room temperature can resemble either hard or soft elastic solids.

Our goal is to investigate the effects of dispersing colloidal particles on mechanical properties of vitrimers such as fracture resistance, elastic modulus, abrasion resistance, etc. This study focuses on reinforcing a soft vitrimer network by nano-sized silica fillers. The polymer matrix is an epoxy network undergoing catalyzed transesterification reactions and behaves like an elastomer at room temperature. In this poster, we present the synthesis and the functionalization of silica fillers, the processes and the characterization of their dispersions in the soft vitrimer matrix, and the mechanical properties of the so obtained nanocomposites.

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Modification of Surfaces and Materials XPS: A Suitable Technique

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ABSTRACT

X-ray Photoelectrons Spectroscopy is a technique usually used for studying surfaces, interfaces and materials in our laboratory.

We present some examples of XPS characterizations performed in the context of our laboratory studies:

- Reduction graphene oxide
- Interface in a device for organic solar cells
- Evidence of chemical graft for biological applications

Internal Field Tailoring of Ferroelectric Photoelectrodes for Efficient Solar Water Splitting

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ABSTRACT

Efficient semiconducting photoelectrodes able to produce hydrogen as a solar fuel by solar water splitting are an important milestone in renewable energy harvesting. Ferroelectric oxide semiconductors are photoactive and exhibit a self-polarization state, acting as a permanent internal electric field. This is of prime interest for tuning the photogenerated charges separation and transport, as it was pointed out for the perovskite photovoltaics breakthrough [1]. This additional degree of freedom has high potential for optimization of photoelectrodes [2,3]. Barium titanate perovskite ($BaTiO_3$) is one of the best candidates considering its high remnant polarization and its stability. However, very little is known about the correlation between the polarization state, the electronic structure (work function, band bending and positions) and the water splitting performances. To tackle these questions, we studied nanometric $BaTiO_3$ epitaxial thin films poled in different remnant polarization states. The electronic structure of the films was investigated by X-ray photoelectron spectroscopy (XPS) and microscopy (X-PEEM), using synchrotron radiation. Photoelectrochemical measurements show a significant increase of the photocurrent by a factor larger than 2 when the $BaTiO_3$ film is downward polarized. These findings are understood as resulting from the presence of an internal electric field which favors the separation of photo-generated charges.

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Polyoxometalates-Based Hybrid Magnetic Nanocatalysts

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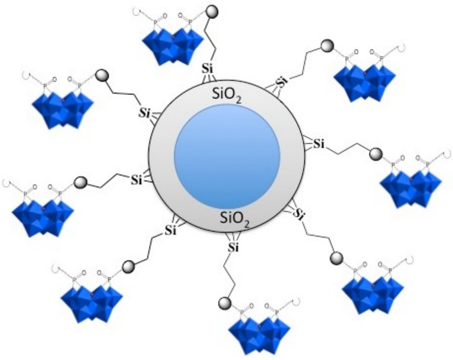
ABSTRACT

In the present project, we developed the elaboration of new hybrid nanomaterials based on the covalent association of vacant organophosphonyle polyoxometalates (POMs, *i.e.* d^0 transition metal oxoclusters)[1] and functionalized core@shell magnetic nanoparticles. In comparison with conventional separation methods, more facile, fast and efficient separation of the catalyst at the end of the reaction cycle can be obtained using magnetic separation. Moreover the use of magnetically recoverable supports can be considered as an eco-friendly approach,[2] since it minimizes the use of auxiliary substances and energy for achieving catalyst recovery.[3]

As major class of advanced core@shell materials, magnetic nanospheres with magnetically responsive cores and functionalized shells have been paid increasing attention, especially in the fields of biomedicine or biology. These materials were obtained by embedding maghemite nanoparticles (γ- Fe_2O_3, typically with mean physical diameter of 7 nm) in a fluorescent silica shell. In a second time, the silica surface was twice functionalized with polyethyleneglycol chains to enhance colloidal stability and with $-NH_2$ terminal organic chains in order to allow post-functionalization. In the chosen strategy, lacunary POM hybrids[5] and their supporting nanoparticles partners present complementary organic functions in order to favor their covalent association with an adequate coupling agent. The catalytic activities of the systems that were developed were evaluated in the frame of mild oxidation processes. Alkene (cyclooctene, cyclohexene or pinene) epoxidation with H_2O_2 as the oxidant were thus performed in organic solvents and in water.



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Understanding Ions to Crystal Transformation via Intermediate State(s): $YbVO_4$ Nanoparticles

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ABSTRACT

Basically, physical properties of any materials, in particular, nanoparticles are strongly depending on their structure and morphology it takes. Controlling structure and morphology of inorganic nanoparticles would inherently modify/engineer the physical properties of system studies and in turn their potential applications, which are typically ranging from sensors to drug release. Until recent times, formation of nanoparticles from supersaturated solutions are solely considered to be a single step process, via nucleation and growth phase, which is generally predicted by classical nucleation theory (CNT). This assumption has been strongly challenged by nanoparticles produced through multi-step nucleation process. In this route, ions to crystal transformations are believed to occur through one or more intermediate states and possibly touted as pre-nucleation clusters, liquid-liquid phase separation, and amorphous phase. Having said all, monitoring intermediate phases and concomitant transition to crystals are highly challenging due to fast kinetics/reaction times of pathway/final products.

To understand/control such mechanism, in this work, synthesis of $YbVO_4$ nanoparticles was studied for their well-known applications and morphology induced physical properties. Series of $YbVO_4$ nanoparticles were prepared using co-precipitation technique by upon mixing of an aqueous solution of ytterbium and vanadate salts, optionally with added sodium carbonate. By varying the concentration of initial reactants, we successfully controlled the final structure of YbVO4 nanoparticles either to 40 nm single crystals or 40 nm poly-crystals made up of 2 nm primary grains. To investigate the evolution of reaction times and pathway of these final nanoparticles, stopped-flow and peristaltic set-ups were employed in coupling with x-ray absorption fine structure (XAFS) and wide angle x-ray scattering (WAXS).

Using these set-ups, amorphous to crystalline nanoparticles transformation was tracked. From XAFS analysis, first shell (Yb-O) local ordering around Yb^{3+} ion was evaluated using Debye-Waller factor, which is found to varying from ~0.008 to 0.002 $Å^2$ for amorphous and nanoparticles phase, respectively. Furthermore, formation of nanoparticles through aggregation of amorphous domain was captured using WAXS.

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Silicene Functionalization

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ABSTRACT

Silicene and germanene, which have attracted enormous interest since publication in 2012 of the epitaxial synthesis of the archetype 3 × 3 reconstructed monolayer silicene phase coinciding with a 4 × 4 supercell on a silver (111) substrate [1], are emergent novel artificial two-dimensional (2D) materials that might rival graphene for logic applications in electronics [2]. Single layer germanene, predicted to be a robust 2D topological insulator at nearly room temperature, has been later grown on a gold substrate [3], next on an aluminum one with just one phase [4]. Strikingly, the first monolayer silicene Field Effect Transistors with ambipolar characteristics have been already fabricated [5]. Multilayer silicene, which is self-protected in ambient air, has been further synthesized on a silver template. Synchrotron radiation photoelectron spectroscopy results acquired at the SOLEIL facility demonstrate that it hosts Dirac fermions with a Fermi velocity about one-third of that of free standing graphene [6].

Ordered hydrogenation of monolayer silicene has been achieved recently in Beijing [7], next at the PIIM Lab in Marseille, with complimentary High Resolution Electron Energy Loss spectroscopy results [8]. Instead, hydrogenation of multilayer silicene leads to an etching process.

My talk will summarize these advances and draw perspectives for future research and potential applications.

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Engineering 2d Porous Organic Nanoarchitectures Taking Advantage of Star-shaped Molecule Self-assembly

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ABSTRACT

Engineering complex two-dimensional (2D) porous organic nanoarchitectures is the focus of recent research interest. Molecular self-assembly offers a unique direction for the fabrication of two-dimensional organic nanoarchitectures. These structures can be tailored at the nanometer scale by exploiting intermolecular interactions. Star-shape molecules [1] are archetypal molecular building block to create porous structures. However strong inter-molecular bindings are required to stabilize organic open networks and to thus prevent the formation of close-packed structures [1].

We used scanning tunnelling microscopy (STM) to investigate the formation of hydrogen and halogen-bonded organic nanoarchitectures at the liquid-solid interface. We observe in the case of 1,3,5-triphenylbenzene star-shaped molecules, that the nature of peripherical substituent is a key parameter driving molecular self-assembly. Various porous nanoarchitectures can be engineered changing the substituent and the solvent [1-3]. In the case of 2,8,14-tripropyloxy-5,11,17-triazatrinaphthylene derivatives, we modified the nature of the bay substituants to selectively create porous and guest-host structures [4]. Salen derivatives with benzoic acid have a non-symmetrical star shape. We show that we can tailor the structure of salen self-assembled nanoarchitectures and engineer compact as well as porous structures by changing the nature of the substituants close to the molecular central metal atom [5,6].

These examples show that the wise selection of molecular design as well as substituent nature and position allow us to prevent close-packed molecular assembly and engineer porous two-dimensional nanoarchitectures on surfaces.

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Localized Electronic States Induced by Intermolecular Coupling at the Interface between 2d Self-assembled PTCDI Nanoarchitectures and Gold Surface

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ABSTRACT

Controlling the formation of organized structure at the nanometer scale is essential to develop the next generation of organic devices. Perylene imides are promising organic building blocks for photovoltaic application due to their semiconducting nature, and their thermal and photo-stability. The efficiency of organic photovoltaic device is usually very low. One origin of this limitation is usually attributed to organic film defects. The device performances are often improved after annealing the organic layer. Annealing is often used to reduce disorder in the organic layer. However annealing can also have major influence on molecular long-range organization, which in turn can have new electronic properties.

We investigate temperature-dependent PTCDI two-dimensional self-assembly on Au(111) in ultra high vacuum using scanning tunneling microscopy. STM images show that molecules self-assemble into a hydrogen-bonded canted nanoarchitecture at room temperature [1]. After 50°C post-annealing, PTCDI molecules self-assemble into new double and triple-chain structures. STM images recorded at different bias reveal strong electronic coupling between side-by-side molecules. This electronic coupling strongly affects molecular contrast as well as molecular shape in the STM images [2]. These observations show that post-annealing can be used not only to modify the structure of the perylene-based nanoarchitectures, as it is usually expected, but also to create new localized electronic states in the organic layer. This observation is of huge interest to engineer new perylene diimide-based nanoarchitectures having specific electronic properties for application in organic devices.

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Charge Carrier Lifetime Measurement by Means of Laser Pump/ Synchrotron Radiation Probe Time Resolved X-ray Photoemission Spectroscopy

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ABSTRACT

Charge carrier lifetime in inorganic and organic semiconductors plays a key role in devices performances. In inorganic semiconductors, minority carrier lifetime has shown to directly determine the efficiency of devices as solar cell.[1] Many parameters as doping level, surface states, adsorbates influence the minority carrier lifetime. Surface photovoltage studied by means of soft X ray core level photoemission spectroscopy is an attractive measurement approach, nondestructive contactless combined to the chemical sensitivity of the technique. Recent paper has shown interest of Laser pump/X-ray photoemission spectroscopy to study transient surface photovoltage. [2]

The soft X-ray beamline TEMPO at Synchrotron Soleil (France) is dedicated to time resolved experiments and especially designed to perform pump-probe experiments ranging from seconds to sub-picoseconds time scales. [3] The photon energy range from 50 to 1500 eV is covered by two undulators with a variable polarization (linear to circular). The energy range is well suited to probe organic compounds (C, N, O), various semiconductors (Si, Ge), transition metals and rare earth atoms. The high photon flux is coupled to the excellent energy resolution of the SCIENTA SES 2002 electron energy analyzer. A new fast delay line detector [4] coupled a high energy resolution Scienta SES 2002 electron analyser allow to measure the dynamics of excited states by means of photoelectron spectroscopy. On our experimental station, we can study electronic properties by tuning the X-ray photon energy to selectively probe chemical species.

We will present experimental setup and first measurements in charge carrier lifetime determination using laser pump/Synchrotron radiation probe time resolved X-ray photoemission spectroscopy applied to organic and inorganic semiconductors.

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Deactivation of Poly(o-aminophenol) Film Electrodes by Storage without use in the Supporting Electrolyte Solution and its Comparison with other Deactivation Processes. A Study Employing EIS

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ABSTRACT

The effect of storage time without use (STWU) in the supporting electrolyte solution on the charge-transport parameters of poly(*o*-aminophenol) (POAP) film electrodes was studied employing electrochemical impedance spectroscopy (EIS). STWU causes a decrease in the charge transport rate of the polymer. This effect is herein called deactivation. Impedance diagrams of both nondeactivated and deactivated films in contact with a solution containing the *p*-benzoquinone/hydroquinone redox couple were interpreted on the basis of a model formulated for homogeneous conducting polymers where the bathing electrolyte contains a redox pair that provides the possibility for electrons to leak from the film surface. Dependences of diffusion coefficients for electron (D_e) and ion (D_i) transport and interfacial resistances related to ion ($R_i^{f|s}$) and electron ($R_{m|f}$, $R_e^{f|s}$) transfer across the polymer/solution and metal/polymer interfaces, respectively, on the degree of deactivation (θ_d) of the polymer were obtained. These dependences were compared with those obtained in previous work for POAP films deactivated by employing other procedures, such as, high positive potential limits (HPPL), soaking in a ferric ion solution (SFeIS) and prolonged potential cycling (PPC).

Keywords: poly(*o*-aminophenol); deactivation; storage time; electrochemical impedance spectroscopy; charge-transport parameters.

Organic Based Photovoltaics: Challenges

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ABSTRACT

Organic based and printable solar cells are considered worldwide as promising emerging technologies for next generation photovoltaic energy conversion with unique differentiating characteristics compared to traditional solar cells such as printability, flexibility, novel aesthetical and design possibilities (colors, semi-transparency, shape,..), better response under diffuse and indoor lighting,.. This emerging class of solar cells faces the following 3 major challenges:

- Further increase of efficiency
- Development of robust, economically efficient and green production processes
- Increase of lifetime

In this contribution an overview will be given of recent activities within Hasselt University to address these challenges through a better understanding of the underlying electro-optical, morphological and photovoltaic properties and through the exploration of novel material systems.[1-4] The main focus of the contribution lies on the influence of the molar mass distribution of the donor polymer as well as the variation of side chains as these parameters influence the efficiency and lifetime drastically.

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Polarization-tilt Coupling Studies on Ferroelectric Liquid Crystal Gel Forming

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ABSTRACT

Nanoropes are twisted structures formed by hierarchical self-assembly, which is a hallmark of biological materials. Carbon nanotubes are known to form nanoropes from twisted individual strands which would not only offer higher load transfer, but also make the configuration structurally much more stable than untwisted raft-like bundles[1]. More recently the self-assembly of a sequence-specific bioinspired peptoid copolymer has been demonstrated to be resulting in monodisperse superhelices thereby forming nanorope structures[2].

We have been able to realize a nanorope structure from the composite of a ferroelectric liquid crystal mixture (forming Smectic C* phase) with a simple organic gelating agent[3].The creation of such a structure is argued (from AFM imaging) to be due to an interesting feature termed 'chirality transfer' or 'chiral imprinting'[4] from the ferroelectric liquid crystal (FLC) to the gel strands. Upon gelation -a phenomenon in which the molecules of the gelating agent combine to form a gel network (in this case nanorope structure) and confines the liquid crystal medium (*Fig.1-a*), the system becomes mechanically strong which is shown by a large increase in the elastic moduli.

For the SmC* phase, the tilt and polarization are identified as the primary and secondary order parameters respectively. The influence of gelation on the magnitude of the tilt angle appears to be dependent on the probe employed: there is no change in the values obtained by X-ray diffraction (θ_{xray}), which looks at the projection of the entire molecular length onto the layer normal. In contrast, the value from the electrooptic method (θ_{opt}) wherein the molecular-core is responsible for the results, diminishes with gelator concentration (*Fig.1-b*). The latter feature is copied by the magnitude of the polarization also.

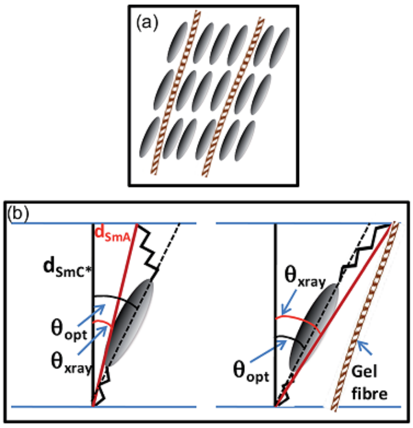

Fig.1

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First Principles Calculations of $Bi_2Al_4O_9$: Equation of States and Elastic Properties

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ABSTRACT

Mullite-type orthorhombic $Bi_2Al_4O_9$ with the space group *Pbam* is crystalline oxide material which represent interesting properties such as photo-luminescence with green-yellow and red emission bands, thermal/chemical/radiation stability, and oxygen ionic conductivity, especially if a portion of the Bi^{3+} ions is replaced by twofold charged cations like Sr^{2+}, Ca^{2+}, and Ba^{2+}[1,2]. The pressure dependencies (0 - 30 GPa) of structural properties, stability, mechanical properties, mechanical anisotropic, linear compressibility, Debye temperature, minimum thermal conductivity and thermal expansion coefficient of the orthorhombic $Bi_2Al_4O_9$ have been studied using density functional theory framework with the plane wave pseudo-potential in the frame of the generalized gradient approximation proposed by Perdew, Burke, Ernzerhof (PBE) [3]. First, crystal structures of orthorhombic $Bi_2Al_4O_9$ has been optimized using BFGS algorithm [4]. The equilibrium lattice constants is in excellent agreement with the experimental data. The maximum and minimum deviation of lattice parameters are 1.97% and 0.28%, respectively. These results show that the computational method and parameters used in this work are reasonable. The tetrahedral AlO4 (Td) and octahedral AlO6 (Oh) are distorted in which the center of gravity is deviated from the position of the Al^{3+} ion.

The bulk modulus (105 GPa) and its pressure derivatives (4.4) are extracted through the third-order Birch-Murnaghan (3BM) equation of state which are close to experimental values 122 Gpa and 4.9, respectively. The obtained elastic stiffness constants(C_{ij}) of the orthorhombic $Bi_2Al_4O_9$ under studied external hydrostatic pressures satisfy that the stability criteria are fulfilled, which indicate that this material is stable under hydrostatic pressures up to 30 GPa. By increasing in the external hydrostatic pressure from 0 - 30 GPa bulk modulus (Reuss) of the orthorhombic $Bi_2Al_4O_9$ increases from 115.92 to 250.42 GPa and its compressibility decreases from 0.0086 to 0.0039 GPa^{-1}. The bulk modulus from 3BM equation of state is very close to the bulk modulus from elastic stiffness constants at ambient pressure. Also, their trend show that the structure at higher pressures is harder and stiffer than ambient pressure. Isotropic degree of bulk modulus and Young's modulus at (1 0 0), (0 1 0) and (0 0 1) crystal planes are considered by plotting three-dimensional dependencies of the bulk modulus and Young's modulus as a function of direction and its planar contours.

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Density Functional Study on Electronic and Photocatalytic Properties of Orthorhombic $Bi_2M_4O_9$ ($M=Al^{3+}$, Ga^{3+})

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ABSTRACT

$Bi_2M_4O_9$ ($M=Al^{3+}$, Ga^{3+}, Fe^{3+}) are materials with high potentials for the use as electrolytes in solid oxide fuel cells (SOFCs), scintillating detectors, spintronic devices, photocatalyst, semiconductor gas sensors and gas-separation membranes [1,2]. The whole structure of $Bi_2M_4O_9$ are characterized by the linear Zweier single chains of edge-sharing MO_6 octahedral which are connected together via M_2O_7 diortho-groups formed by corner-sharing MO_4 tetrahedral [3,4]. The electronic, optical, and photocatalytic properties of mullite-type orthorhombic $Bi_2M_4O_9$ ($M=Al^{3+}$, Ga^{3+}) have been elucidated using the density functional theory (DFT) method with the plane wave pseudo-potential in the frame of the generalized gradient approximation (GGA) proposed by Perdew,Burke,Ernzerhof (PBE) [5] as implemented in CASTEP code. $Bi_2Al_4O_9$ and $Bi_2Ga_4O_9$ are direct and indirect band gap semiconductors with electronic band gaps 2.71 and 2.88 eV, respectively. The effective masses of electrons and holes are obtained by parabola fitting of the band dispersions of $Bi_2Al_4O_9$ and $Bi_2Ga_4O_9$ in along [1 0 0], [0 1 0], and [0 0 1] directions near the band extremes. Smaller effective mass of electrons compared to holes is due to more dispersion feature of conduction bands, implying that the photo-generated electrons migrate rapidly. The composition of the calculated electronic bands were assigned using the total, site- and *l*-projected density of states (DOS) diagrams. Also, chemical bonding feature in each band structure region were examined in detail using projected electronic wave function (PEWF). Mulliken bond population analysis and iconicity index values confirm that Bi-O bonds in both studied crystals have ionic nature more than 92%. On the other hand the M-O bonds ($M=Al^{3+}$, Ga^{3+}) in tetrahedral MO_4 (Td) are stronger and more covalent respect to octahedral MO_6 (Oh). Energy loss spectrums $L(\omega)$ of $Bi_2Al_4O_9$ and $Bi_2Ga_4O_9$ show that the plasmon energies appear at 11.44 and 10.99 eV, respectively, indicating they are shiny (reflective) in the visible range. Both $Bi_2Al_4O_9$ and $Bi_2Ga_4O_9$ have strong activity for oxidation of H_2O to active species O_2, H_2O_2, and O_3 which are able to oxide or decompose organic pollutants and dye molecules.

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DFT Study on Electronic, Optical and Photocatalytic Properties of Three-layer Perovskite Dion-Jacobson $CsBa_2M_3O_{10}$ (M = Ta, Nb)

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ABSTRACT

Three-layer perovskite Dion-Jacobson (DJ) phase has a general formula $A'[A_{n-1}B_nO_{3n+1}]$, where *A'* is monovalent alkali metal ion, *A* is divalent alkaline earth metal ion, and *B* is tetravalent or pentavalent transition metal ion [1]. They have various interesting physical and chemical properties, such as ionic conductivity due to ion exchange of alkali ions with molten salts or under acidic conditions, dielectricity, superconductivity, luminescence, photocatalytic activity, magnetism, and giant magneto-resistivity [1,2]. The electronic, optical, and photocatalytic properties of three-layer perovskite Dion-Jacobson phase $CsBa_2M_3O_{10}$ (M = Ta, Nb) have been studied with the plane wave pseudo-potential using the density functional theory (DFT) method considering the exchange-correlation function within the generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE) [3]. $CsBa_2Ta_3O_{10}$ and $CsBa_2Nb_3O_{10}$ are indirect band gap semiconductors with different type of M–O bonds from pure covalent to pure ionic. Symmetry of the MO_6 octahedra in $CsBa_2Ta_3O_{10}$ and $CsBa_2Nb_3O_{10}$ is reduced from O_h point group to centrosymmetric (D_{4h}) and non-centrosymmetric (C_{4v}) point groups, leading to generation of local internal fields, promoting the separation of electron-hole pairs in the very initial process of photo-oxidation, and improving photocatalytic activity. The population iconicity index [4] indicated that there are different percentages of covalence nature in the M–O bonds from pure covalent to pure ionic. Site and angular projected density of states for $CsBa_2M_3O_{10}$ showed that the valence and conduction bands are made mainly of O and M orbitals; therefore, the presence of dipole moment at the MO_6 octahedra will play an important role in separating charges. $CsBa_2Ta_3O_{10}$ and $CsBa_2Nb_3O_{10}$ are UV-light-responsive photocatalysts with plasmon energies 13.16 and 12.07 eV, respectively, which can oxidize/decompose organic pollutants. Moreover, they are good candidates for photocatalytic hydrogen generation from water splitting.

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Adsorption of NO and CO Molecules on Oxygen Doped Zigzag Boron Nitride Nanotube (7,0) via DFT

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ABSTRACT

An air pollutant is a substance in the air that can have adverse effects on humans and the ecosystem. The increase in the atmospheric pollution caused by some gases such as nitrogen monoxide (NO) and carbon monoxide (CO) is a global problem. Several studies on the interaction of nanotube, graphene and nanoparticles with NO and CO have been reported in the past [1-4]. The initial geometry of boron nitride nanotube (7,0) with tube length 14 Å was adopted. Then three nitrogen atoms are replaced by O atoms to produce boroxol ring. Adsorption of NO and CO gases on the external surface of oxygen doped zigzag boron nitride nanotube with different orientation of NO and CO molecules are investigated using density functional theory at the B3LYP/6-31G* level. The stabilities of wave functions for all studied structures were verified by using STABLE keyword. Total electronic energies were corrected by addition of geometrical counterpoise (gCP) and dispersion (D3) energies [5] to correct the intramolecular basis set superposition error (BSSE) and the London dispersion interaction energy, respectively. Values of adsorption energies indicated that adsorption of NO and CO on the boroxol ring is chemisorption. NBO [6] charge transfer between adsorbent and gases, total (TDOS), partial (PDOS) and overlap population density of states (OPDOS) in terms of Mulliken population analysis [7] are studied in detail. Also, nature of interactions are investigated using Quantum theory of atoms in molecules (QTAIM) [8] and molecular electrostatic potential (MEP). The calculated results suggest that the oxygen doped zigzag boron nitride nanotube is an ideal material for elimination and filtering of NO and CO molecules.

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