

**ICON<sup>2</sup> - 2017**

International Conference on « Novel Nanomaterial : engineering and properties »  
18<sup>th</sup> to 20<sup>th</sup> of October 2017 - CEA - Synchrotron SOLEIL

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## **ABSTRACTS BOOKLET**


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### **Summary**

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- Conference Committees
- General Program
- Abstracts
  - ✓ Wednesday, October 18<sup>th</sup>  
Sessions I & II
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Sessions III & IV
  - ✓ Friday, October 20<sup>th</sup>  
Session V
- Poster Session

Sponsors:





## ICON<sup>2</sup> - 2017

International Conference on « Novel Nanomaterial : engineering and properties »  
18<sup>th</sup> to 20<sup>th</sup> of October 2017 - CEA - Synchrotron SOLEIL

### **Welcome**

During the last years intensive research activity in the field of nanomaterials lead to tremendous improvement and discoveries in the fields of novel materials including their preparation, characterization, properties and applications.

ICON<sup>2</sup> is an interdisciplinary conference with the aim of facilitating discussions and scientific interactions on fine chemistry, biomaterials, functional polymers, energy storage and conversion materials, nano materials, ceramic materials, metallic materials, and other novel materials.

A session is dedicated to time resolved experiments and especially laser pump / synchrotron based spectroscopy and related techniques (X-FEL, HHG, 2PPE) at time scale ranging from millisecond to femtosecond to promote this growing research field.

The objective of this conference is to bring together students, experts, scientists and researchers in a collaborative environment to present and discuss issues relating to nanomaterial engineering and characterization as well as nanomaterial 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.

### **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.

ICON<sup>2</sup> 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 est 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 porte 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.

**International Conference on Novel nanomaterial:  
Engineering and properties  
ICON<sup>2</sup> - 2017**

**INSTN – CEA Saclay  
&  
Synchrotron SOLEIL - L'orme des Merisiers  
Saint-Aubin, France**

**18<sup>th</sup>-20<sup>th</sup> of October 2017**

**COMMITTEES**

**Scientific committee**

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Mathieu SILLY  
Stéphane CAMPIDELLI

CEA  
Synchrotron SOLEIL  
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Saint-Aubin, France  
18<sup>th</sup>-20<sup>th</sup> of October 2017**

**Programme**

**Wednesday, October 18<sup>th</sup>**

**INSTN –CEA Saclay**

09:00 - 09:30 Registration & Welcome coffee

09:30 - 09:50 Welcome word, Jean Daillant, Director of Synchrotron SOLEIL  
Welcome word, Martine Soyer Director of CEA

**SESSION I**

09:50 - 10:30 Foldable and unfoldable supramolecular fibers  
**Shiki Yagai** - Chiba University, Japan

10:30 - 10:55 Femto-magnetism and electron transport at core-excited organic molecule/graphene interfaces  
**Guido Fratesi** - Università degli Studi di Milano, Italy

10:55 - 11:20 Coffee break

11:20 - 11:35 Strain field mapping of a 120 nm single gold nanocrystal supported on TiO<sub>2</sub> provided by Bragg coherent diffraction imaging during in situ CO oxidation reaction  
**Ana F. Suzana** - Synchrotron SOLEIL, Gif-sur-Yvette, France

11:35 - 11:50 Low-cost nanomaterial for stable HER within full pH range  
**Matias Villalba** - Ecole Polytechnique, Palaiseau, France

11:50 - 12:05 Rational design of size selected bimetallic nanocatalysts: Chemical routes  
**Alter Zakhtser** - Sorbonne Universités, LCPMR, Paris, France

12:05 - 12:20 Polyoxometalates-based hybrids for homogeneous supported catalysis  
**Richard Villanneau** - IPCM, Paris, France

12:20 - 12:35 ZnO thin films on Pt (111), an inverse oxide/metal nanocatalyst: Fabrication and characterizations with STM, LEED and STS  
**Hang Liu** - Sorbonne Universités, LCPMR, Paris, France

12:35 - 12:50 Influence of the oxygen deposition pressure on the electronic states of Ti in TiO<sub>2</sub> anatase thin films  
**Benoit Gobaut** - Synchrotron SOLEIL, Gif-sur-Yvette, France

12:50 - 13:05 Exploring the hydrogen interaction with Pd clusters confined within MIL-101 (Cr) pores  
**Abdelmalek Malouche** - ICM Paris-Est, Thiais, France

13:05 - 14:20 Lunch

## SESSION II

- 14:20 - 15:00 What material science is needed for ubiquitous solar cells?  
**Jean-François Guillemoles** - IRDEP, UMR EDF-CNRS-ENSCP 7174, Chatou, France
- 15:00 – 15:15 Photoemission studies of band bending in PbS colloidal quantum dot films for next generation solar cells  
**Pip C.J. Clark** - University of Manchester, UK
- 15:15 - 15:30 Dynamics in HgTe 2D nanocrystals  
**Emmanuel Lhuillier** - Institut des NanoSciences de Paris, France
- 15:30 - 15:45 Autocatalyzed growth of GaAs nanowires on silicon: Study of the catalyst  
**Louise Fouquat** - Synchrotron SOLEIL, Gif-sur-Yvette, France
- 15:45 - 16:15 Coffee break
- 16:15 - 16:40 Self-assembly of semiconductor nanocrystals with an amphiphilic surface pattern  
**Takuya Nakashima** - Nara Institute of Science and Technology, Japan
- 16:40 - 17:05 Two-dimensional colloidal nanostructures: Synthesis and electrical transport  
**Christian Klinke** - Swansea University, UK
- 17:05 - 17:30 GaAs heterostructured nanowires grown by molecular beam epitaxy  
**José Penuelas** - Institut des Nanotechnologies de Lyon, Ecully, France
- 17:30 - 17:45 "Mixed-thiols" functionalized Au and AgNPs: A close look at the atomic structure and chemico-physical properties by SR-XPS  
**Laura Carlini** - Università degli Studi Roma Tre, Italy

**Thursday, October 19<sup>th</sup>**

## Synchrotron SOLEIL – Saint-Aubin

### SESSION III

- 09:30 - 10:10 The 2D transition metal dichalcogenide interface  
**Andrew T.S. Wee** - National University of Singapore, Singapore
- 10:10 - 10:35 A monolayer of MoS<sub>2</sub> on Au(111) as a decoupling layer for single molecules  
**Christian Lotze** - Freie Universität Berlin, Germany
- 10:35 - 11:00 Intrinsically patterned two-dimensional materials for selective adsorption of molecules and nanoclusters  
**Shixuan Du** - Chinese Academy of Sciences, Beijing, China
- 11:00 - 11:25 Tailoring carbon-based nanostructures via on-surface synthesis  
**Dingyong Zhong** - Sun Yat-sen University, Guangzhou, China
- 11:25 - 11:50 Coffee break
- 11:50 - 12:15 Introduction to SOLEIL storage ring upgrade  
**Marie-Agnès Tordeux** - Synchrotron SOLEIL, Gif-sur-Yvette, France
- 12:15 - 12:40 Overview of VUV- soft X-ray free electron lasers  
**Marie-Emmanuelle Couprie** - Synchrotron SOLEIL, Gif-sur-Yvette, France
- 12:40 - 13:05 Coherent collective modes studied with time-resolved photoelectron diffraction  
**Matthias Hengsberger** - University of Zurich, Switzerland
- 13:05 - 14:00 Lunch

## SESSION IV

- 14:00 - 14:40 Single molecule magnets grafted on surfaces and explored by Xmcid  
**Philippe Sainctavit** – IMPMC, Paris, France
- 14:40 - 14:55 Time resolved X-ray holographic imaging of magnetic domains at the SEXTANTS beamline of the SOLEIL Synchrotron  
**Horia Popescu** - Synchrotron SOLEIL, Gif-sur-Yvette, France
- 14:55 - 15:20 State of the art of laser produced XUV sources with picosecond and femtosecond time resolution: High harmonic generation and soft X-ray lasers  
**Sophie Kazamias** – LPGP, Université Paris sud, Orsay, France
- 15:20 - 15:35 High-order harmonics at MHz for photoelectron spectroscopy on correlated electron pairs in solids  
**Cheng-Tien Chiang** - Max-Planck-Institut für Mikrostrukturphysik, Halle, Germany
- 15:35 - 17:00 Coffee break and Poster Session
- 17:00 Transfer to Paris Musée d'Orsay

## Friday, October 20<sup>th</sup>

### SESSION V

- 09:30 - 09:55 Ultrathin films of TiOx on Au(111)  
**Martin R. Castell** - University of Oxford, UK
- 09:55 - 10:10 Multi-scale phase transitions of ditopic ligands on surface  
**Xiaonan Sun** – ITODYS, Paris, France
- 10:10 - 10:35 Invited Talk  
**Anthoula Papageorgiou** - Technische Universität München, Garching, Germany
- 10:35 - 10:50  $\beta$ -lactoglobulin unfolding and heat-aggregation at Atomist Scale: How NMR Associated with SAXS Reveal Protein Structures at Atomist Scale  
**Paulo Peixoto** - INRA, Laboratoire UMET/CNRS, Villeneuve d'Ascq, France
- 10:50 - 11:15 Coffee break
- 11:15 - 11:40 Invited Talk  
**Karl Heinz Ernst** – EMPA, Dübendorf, Switzerland
- 11:40 - 12:05 Coherent quantum phenomena in ultimate 2D superconductors: A STM study  
**Dimitri Roditchev** – ESPCI, Paris, France
- 12:05-12 :20 Super periodicity induced band gap opening in epitaxial graphene buffer layer  
**Maya N. Nair** - Synchrotron SOLEIL, Gif-sur-Yvette, France
- 12:20 - 12:35 Electronic structure of long range ordered on surface synthesized polymeric networks  
**Yannick Fagot-Revurat** - Institut Jean Lamour, Nancy, France
- 12:35 - 13:00 Closing session  
Best student oral presentation award
- 13:00 - 14:00 Lunch
- 14:00 Departure

# **ABSTRACTS**

**Wednesday, October 18<sup>th</sup>, 2017**

**SESSIONS I & II**

# ICON<sup>2</sup> - 2017

Wednesday, October 18<sup>th</sup>

## SESSION I

- KN-01 Foldable and unfoldable supramolecular fibers  
*S. Yagai*
- IT-01 Femto-magnetism and electron transport at core-excited organic molecule/graphene interfaces  
*G. Fratesi*
- OC-01 Strain field mapping of a 120 nm single gold nanocrystal supported on TiO<sub>2</sub> provided by Bragg coherent diffraction imaging during in situ CO oxidation reaction  
*A.F. Suzana*
- OC-02 Low-cost nanomaterial for stable HER within full pH range  
*M. Villalba*
- OC-03 Rational design of size selected bimetallic nanocatalysts: Chemical routes  
*A. Zakhiser*
- OC-04 Polyoxometalates-based hybrids for homogeneous supported catalysis  
*R. Villanneau*
- OC-05 ZnO thin films on Pt (111), an inverse oxide/metal nanocatalyst: Fabrication and characterizations with STM, LEED and STS  
*H. Liu*
- OC-06 Influence of the oxygen deposition pressure on the electronic states of Ti in TiO<sub>2</sub> anatase thin films  
*B. Gobaut*
- OC-07 Exploring the hydrogen interaction with Pd clusters confined within MIL-101 (Cr) pores  
*A. Malouche*

## SESSION II

- KN-02 What material science is needed for ubiquitous solar cells?  
*J-F. Guillemoles*
- OC-08 Photoemission studies of band bending in PbS colloidal quantum dot films for next generation solar cells  
*P.C.J. Clark*
- OC-09 Dynamics in HgTe 2D nanocrystals  
*E. Lhuillier*
- OC-10 Autocatalyzed growth of GaAs nanowires on silicon: Study of the catalyst  
*L. Fouquat*
- IT-02 Self-assembly of semiconductor nanocrystals with an amphiphilic surface pattern  
*T. Nakashima*



- IT-03 Two-dimensional colloidal nanostructures: Synthesis and electrical transport  
*C. Klink*
- IT-04 GaAs heterostructured nanowires grown by molecular beam epitaxy  
*J. Penuelas*
- OC-11 "Mixed-thiols" functionalized Au and AgNPs: A close look at the atomic structure and chemico-physical properties by SR-XPS  
*L. Carlini*

# Foldable and Unfoldable Supramolecular Fibers

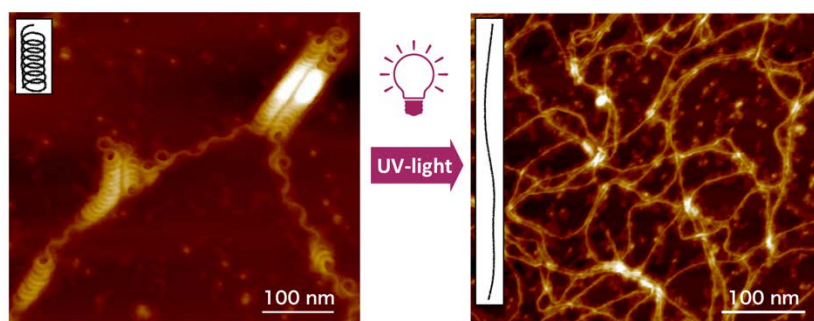
S. Yagai

Graduate School of Engineering, Chiba University  
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## ABSTRACT

Higher-order conformations furnish a range of critical functionalities to one-dimensional polymers not only in biological systems (e.g., protein folding) but also in our daily life (functional polymers). One-dimensionally elongated molecular aggregates known as supramolecular polymers are emerging nanoscale materials with promising applications[1]. However, to compete over covalent counterparts as well as naturally occurring polymers (polypeptides and DNA), development of supramolecular polymers with well-defined higher-order conformations are desired. To address this issue, we have exploited a previously reported hydrogen-bonded cyclic hexamer of barbiturated naphthalene that polymerizes noncovalently into circular supramolecular fibers denoted as "nanoring".[2] The shape persistency of the nanoring along with its uniformity of diameter (ca. 14 nm) implies that a "spontaneous curvature" would occur by high degree of internal order within the continuous stacking of hexamers. In order to extend this system to "supramolecular polymers with well-defined higher-order structures", we synthesized several new compounds based on the molecular design of the naphthalene monomer and succeeded in obtaining outstanding supramolecular systems whose higher order structures could be manipulated by external stimuli.

For examples, we introduced azobenzene chromophore to the parent molecule. By changing the polymerization condition in nonpolar solvent, this new molecule form helically coiled supramolecular polymers. Because the spontaneous curvature of the main chain can be destroyed by UV irradiation through the photoisomerization of the azobenzene unit, we realized unprecedented level of conformation change (unfolding) of supramolecular polymers by external light, which has been visualized by AFM observation for the dried samples (see the figure).[3] The occurrence of this unfolding in solution state has also been confirmed by SAXS measurements.



*Nature Commun.* **2017**, *8*, 15254

## REFERENCES

- [1] T. Aida, E. W. Meijer, S. I. Stupp, *Science* **2012**, 813.
- [2] S. Yagai et al., *Angew. Chem. Int. Ed.* **2008**, *47*, 4691; *J. Am. Chem. Soc.* **2009**, *131*, 5402; *Angew. Chem. Int. Ed.* **2012**, *51*, 6643; *J. Am. Chem. Soc.* **2012**, *134*, 18205; *Nature Commun.* **2015**, *6*, 8936; *Angew. Chem. Int. Ed.* **2016**, *55*, 9890.
- [3] S. Yagai et al., *Nature Commun.* **2017**, *8*, 15254.

# Femto-magnetism and Electron Transport at Core-excited Organic Molecule/Graphene Interfaces

G. Fratesi

*Dipartimento di Fisica, Università degli Studi di Milano, via Celoria 16, I-20133 Milano, Italy*

## ABSTRACT

We investigate by ab initio theoretical methods phenomena occurring on the femtosecond time scale as a result of core level excitations in organic molecules adsorbed on graphene. Molecular chemisorption induces a magnetic ground state in graphene, that relaxes towards a non-spin polarized configuration upon the excitation of a molecular core state due to the coupling of the adsorbate energy levels with the graphene mid-gap (defect) ones. Conversely, physisorbed molecules shift from a non-magnetic to a magnetic state [1].

Femtosecond electron transfer times at interfaces can be measured by resonant core-level spectroscopies, where backward transfer (substrate-to-molecule) was also observed following the excitation at the molecule. We describe this phenomenon within a theoretical framework based on density-functional theory (DFT) and a molecular break junction setup [2,3]. The ultrafast transfer ( $\tau=4$ fs) induced by N 1s excitation for bipyridine molecules on epitaxial graphene/Ni(111) [4] is significantly slowed down by the addition of a second layer of graphene [5]. This is rationalized by the transition from the strong hybridization between C and metal states in epitaxial graphene, to a decoupled interface for bilayer graphene where the C layer in contact with the molecule is less hybridized with Ni underneath. The absence of transfer in principle expected by the current approach for molecules on free-standing graphene is a stimulus for further developments.

## REFERENCES

1. A. Ravikumar, A. Baby, H. Lin, G. P. Brivio, and G. Fratesi, *Scientific Reports* **6**, 24603 (2016), doi:[10.1038/srep24603](https://doi.org/10.1038/srep24603).
2. G. Fratesi, C. Motta, M. I. Trioni, G. P. Brivio, and D. Sánchez-Portal, *J. Phys. Chem. C* **118**, 8775 (2014), doi:[10.1021/jp500520k](https://doi.org/10.1021/jp500520k).
3. D. Cvetko, G. Fratesi, G. Kladnik, A. Cossaro, G.P. Brivio, L. Venkataraman, and A. Morgante, *Phys. Chem. Chem. Phys.* **18**, 22140 (2016), doi:[10.1039/c6cp04099c](https://doi.org/10.1039/c6cp04099c).
4. O. Adak, G. Kladnik, G. Bavdek, A. Cossaro, A. Morgante, D. Cvetko, and L. Venkataraman, *Nano Lett.* **15**, 8316, (2015), doi:[10.1021/acs.nanolett.5b03962](https://doi.org/10.1021/acs.nanolett.5b03962).
5. A. Ravikumar, G. Kladnik, M. Müller, A. Cossaro, G. Bavdek, L. Patera, D. Sánchez Portal, L. Venkataraman, A. Morgante, G.P. Brivio, D. Cvetko, and G. Fratesi, *submitted*.

# Strain Field Mapping of a 120 nm Single Gold Nanocrystal Supported on TiO<sub>2</sub> Provided by Bragg Coherent Diffraction Imaging During *in situ* CO Oxidation Reaction

A.F. Suzana<sup>1,2,3</sup>, F. Berenguer<sup>3</sup>, S.H. Pulcinelli<sup>1</sup>, C.V. Santilli<sup>1</sup>,  
A. Rochet<sup>2</sup> and F. Meneau<sup>2</sup>

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<sup>3</sup>Synchrotron SOLEIL, 91192 Saint Aubin, Gif-sur-Yvette, France

## ABSTRACT

Visualization and measurements of defects and surface strain of nanocrystals catalysts is a fundamental to its characterization since these imperfections are usually the catalytic sites for the reaction occurrence. There is an increasing need for strain engineering and consequently for strain measurements in real time under realistic conditions<sup>1</sup>. Determine the strain field using *in operando* conditions is an essential step in the deep understanding of catalytic processes and strain tailored materials. Bragg Coherent Diffractive Imaging (Bragg CDI) is a nondestructive strain-sensitive microscopy technique that records diffracted coherent X-rays in the far-field configuration on a sensitive area detector and uses phase retrieval algorithms to recover the 3D electron density and lattice displacement in nanocrystals<sup>2</sup>. One relevant catalytic reaction is the CO oxidation, which has been extensively studied due to its industrial and environmental relevance once this reaction is used to eliminate this gas from automotive exhausts systems and from the hydrogen gas feed used in fuel cells<sup>3</sup>.

In this work, we apply Bragg CDI in a single 120 nm gold crystal during *in situ* CO oxidation reaction. The  $2\theta$  angle of the (111) Au reflection was scanned in fine increments yielding a series of 2D diffraction patterns to yield a 3D coherent Bragg peak. A dedicated *in situ* cell was used, enabling us to measure the 3D Bragg peaks in three different temperatures: 20, 200 and 400°C under controlled gas flux of CO/O<sub>2</sub>. Using a phase retrieval algorithm, the reciprocal diffraction pattern recorded in the detector area was reverted in a real image, the 3D lattice displacement field recovered and the changes in morphology and surface/internal strain during the reaction occurrence were observed. We imaged it at a real space resolution of 12 nanometers.

## REFERENCES

- (1) Kuo, C.; Lamontagne, L. K.; Brodsky, C. N.; Chou, L.; Zhuang, J.; Sneed, B. T.; Sheehan, M. K.; Tsung, C. The Effect of Lattice Strain on the Catalytic Properties of Pd Nanocrystals. **2013**, 1993–2000.
- (2) Ulvestad, A.; Sasikumar, K.; Kim, J. W.; Harder, R.; Maxey, E.; Clark, J. N.; Narayanan, B.; Deshmukh, S. A.; Ferrier, N.; Mulvaney, P.; *et al.* In Situ 3D Imaging of Catalysis Induced Strain in Gold Nanoparticles. **2016**, 3008-3013.
- (3) Li, D.; Zhu, Y.; Wang, H.; Ding, Y. Nanoporous Gold as an Active Low Temperature Catalyst toward CO Oxidation in Hydrogen-Rich Stream. *Sci. Rep.* **2013**, 3, 30-15.

# Low-cost Nanomaterial for Stable HER within Full pH Range

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<sup>a</sup>Laboratoire ITODYS, Université Paris Diderot.

<sup>b</sup>Laboratoire de Chimie Moléculaire, Ecole Polytechnique, Université Paris-Saclay, Palaiseau.

## ABSTRACT

According to IEO2016 estimations, human demands for fuel energy in transportation are predicted to keep growing at a 1.4% rate per year from 2012 to 2040. On a base of this consumption rate, the fossil fuels will be irreversibly exhausted without a renewable source. Hence, a cleaner, sustainable and economically affordable alternative is needed. One possible solution is hydrogen-based fuel cell<sup>1</sup> which are beginning to be commercially available. However, this requires the facilities for fuel delivery as well as hydrogen massive electrochemical production to avoid the use of steam gas reforming. The requirement of platinum as electrocatalyst for hydrogen evolution reaction (HER) is facing some hardship due to its cost and scarcity. An attractive replacement to platinum would be a group of materials composed of first-row transition metals and chalcogen<sup>2</sup> anion because they are: i) earth-abundant, ii) highly active towards HER and iii) their preparation in a nanometric scale is affordable and scalable for industrial purposes. Herein, we synthesize iron pyrite via polyol method<sup>3</sup>. Its morphology, crystallinity and chemical composition was fully characterized by SEM, XRD and XRF. Figure 1A shows that this material consists of spherical agglomerates of nanometer-sized particles with a pure iron pyrite crystallographic phase. Additionally, an atomic ratio equal to 2.03 between sulfur and iron was determined by XRF. The prepared particles were tested for HER and Figure 1B displays the established HER potential for an applied current density and the open circuit potential at different pH values.

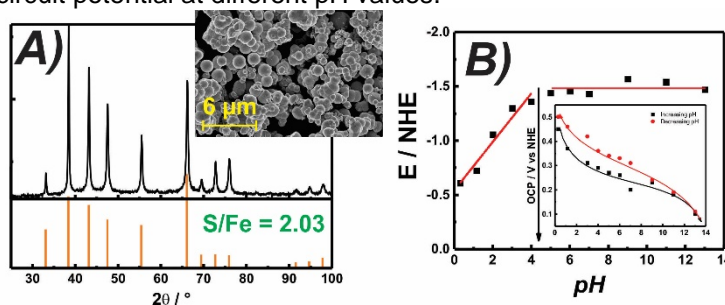


Figure 1. A) FeS<sub>2</sub> diffractogram and SEM image and B) stable potential when the electrode was biased at 10 mA.cm<sup>-2</sup> and OCP of the electrocatalysts during acid-base titration.

An S-shape trend was observed when the film containing FeS<sub>2</sub> was titrated, locating an inflection point between pH 5 and 7. Furthermore, the measured potential under HER conditions increases linearly when the pH increases only below 5. On the other hand, its value remains constant above this point and the potential gradient is close to 900 mV (expected for a fast one-electron reaction).

To conclude, we have selectively produced iron pyrite nanomaterials and this electrocatalysts showed long-life activity (> 24 hs) within a full pH range. It is highly active at low pH and HER potential shows a linear pH-dependency. However, above pH 5, HER requires higher but fairly constant potential thus resembles a pH-independent reaction.

## REFERENCE

1. Kirubakaran, A., et. al., "A Review on Fuel Cell Technologies and Power Electronic Interface." *Renew. Sus. Energ. Rev.* 13, 2430-40, 2009.
2. Zeng, M. et. al., "Recent advances in heterogeneous electrocatalysts for the hydrogen evolution reaction." *J. Mat. Chem. A.*, 29, 2015.
3. Di Giovanni, C. et. al. "Low-Cost Nanostructured Iron Sulfide Electrocatalysts for PEM Water Electrolysis". *ACS Catal.*, 6, 2016.

# Rational Design of Size Selected Bimetallic Nanocatalysts: Chemical Routes

A. Zakhtser<sup>1,2</sup>, A. Naitabdi<sup>2</sup>, C. Salzemann<sup>1</sup>, C. Petit<sup>1</sup>, F. Rochet<sup>2</sup>

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## ABSTRACT

Pt is widely used as a catalyst in the composition of both the anode and cathode of proton exchange membrane fuel cells.<sup>[1]</sup> Nevertheless, widespread practical applications are still hindered by the high cost and instability of Pt, and their rather limited life-time due to deactivation phenomena such as sintering and active sites poisoning. Therefore, new research strategies are emerging in order to address these limitations and produce catalysts with enhanced stability. In this regard, rational design of nanocatalysts with controlled size and composition are being developed.

Recently, Zn has emerged as one of the most prominent element in bimetallic catalysts owing in part to the stability of its ZnO under reducing conditions and, more importantly, to the fact, that CO doesn't adsorb on the surface of ZnO, hence limiting the poisoning effect.<sup>[2]</sup> Additionally, Cu-ZnO is also an important industrial catalyst for methanol synthesis reactions.

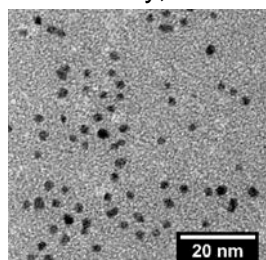


Figure 1. TEM image of Pt-Zn NPs obtained by combining equimolar quantities of metals

Thus, we have synthesized bimetallic NPs with controlled size, shape and composition of two ZnO-based nanoparticles using two methods.

The first one is based on the decomposition at high temperature of metal organic salts in presence of a capping agent (Oleylamine (OAm) f.e.).<sup>[3, 4]</sup> Pt-Zn NPs were generated by simultaneous decomposition of [Pt(acac)<sub>2</sub>\*OAm] and [Zn(acac)<sub>2</sub>\*OAm] complexes which most likely play a crucial role in obtaining of uniform NPs (Fig. 1).

The second method is based on using diblock copolymers which are dissolved in nonpolar solvent, in order to produce reverse micelles. After the adding of metal salts into the solution, metal-loaded micelle spheres are formed (Fig. 2). Subsequently, oxygen plasma treatment lead to complete removal of the micelles. Hence, ZnO-based size-selected with tunable interparticle distance and well-organized NPs into hexagonal arrangement on supports are obtained.

Thus we have shown that with these two chemical methods we can synthesize bimetallic size-controlled NPs with specified composition, shape and morphology.

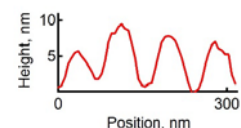
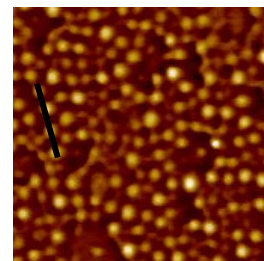


Figure 2. AFM image of reverse micelles containing equimolar quantities of Pt and Zn

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# Polyoxometalates-based Hybrids for Homogeneous Supported Catalysis

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## ABSTRACT

Polyoxometalates (POMs) are nanoscopic clusters consisting of metal ions in their highest oxidation number ( $W^{VI}$ ,  $Mo^{VI}$ ,  $V^V$ ) assembled by  $O^{2-}$  ligands. They have been extensively used as homogeneous acid and oxidation catalysts. Meanwhile, their applications as catalyst supports/ligands for transition metal active species have also been explored. However, homogeneous systems have major limitations related to separation issues: loss of active centers, pollution of products and incompatibility with processes in pharmacology. The covalent immobilization of soluble catalysts on insoluble supports can lead to improved robustness and therefore increased efficiency, as long as the dispersion and accessibility of the active sites on the support are optimized.

Thus, in this work two strategies were chosen for the heterogenization of POMs:

- the use of platforms with large specific area for the anchorage and with porosity ranging from 5 to 20nm, such as structured mesoporous materials (Silica type SBA15)
- the use of core shell nanoparticles, consisting of a magnetic core (maghemite) and a silica shell.<sup>1</sup> The recovery of the catalyst can be easily performed magnetically.

These two supports were functionalized with reactive organic functions allowing them to covalently graft the catalysts.<sup>2</sup> The synthesized materials were tested in a targeted model catalytic reactions (the epoxidation of alkenes with  $H_2O_2$ ).<sup>3</sup> The incorporation of  $La^{3+}$  metal cations is the second step for the elaboration of these materials. Their selective uptake by POMs in the materials was checked in particular by La  $L_{III}$  edge EXAFS spectroscopy.

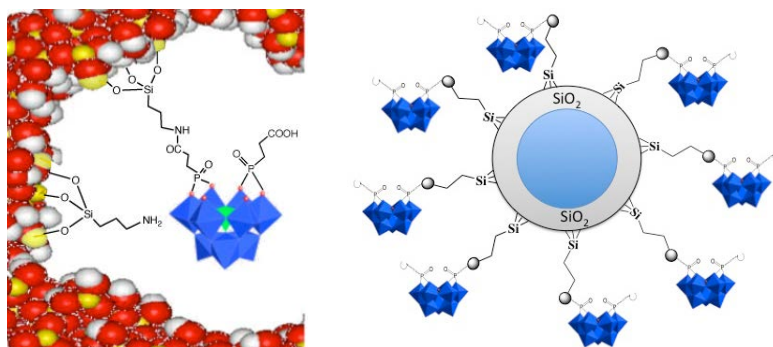


Image 1: POMs grafted on mesoporous silica (left) and magnetic nanoparticles (right).

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# ZnO Thin Films on Pt (111), an Inverse Oxide/Metal Nanocatalyst: Fabrication and Characterizations with STM, LEED and STS

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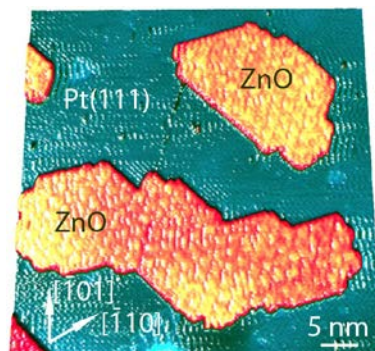
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## ABSTRACT

The inverse oxide/metal catalysts have been shown to exhibit remarkable catalytic performances in the CO oxidation and represent a promising highly active and stable catalytic system.<sup>1,2</sup> Recently, Zn, an affordable metallic material, has emerged as one of the most promising element in heterogeneous catalysis owing to the stability of its ZnO under reducing conditions<sup>3</sup> and its greater “affinity” to oxygen compared with that of Pt. Indeed, ZnO/Pt is active for CO oxidation and promotes catalytic reactions relevant for fuel cells.

In our experiment, well-ordered ZnO thin films, from sub-monolayer (ML) up to 5 ML, have been prepared by electron beam evaporation procedure and oxidized under O<sub>2</sub> on the clean Pt (111) single crystal in ultrahigh vacuum (UHV) chamber equipped with STM and low-energy electron diffraction (LEED). The growth of ZnO films on Pt (111) has been studied by STM. The ZnO islands, at low coverage, appear to be flat with the step height of 2.0 Å, corresponding to one monolayer thick islands. The ZnO film grows seemingly in layer-by-layer mode. When the ZnO film reaches multilayers, the triangular islands are observed on the surface with the size ranging from 7.8 to 32.6 nm<sup>2</sup>, which is a characteristic of the ZnO (0001)-Zn-terminated surface. Thanks to the high-resolution STM, the Moiré structure on the surface have also been observed, which is assigned to a coincident lattice formed at the interface of ZnO and Pt (111). The LEED patterns of the ZnO films obtained correspond to ZnO(5×5)/Pt(6×6) structure. As the ZnO film grows thicker, a set of six spots begins to appear around the ZnO spots, which is in agreement with the Moiré structure observed on the surface of ZnO films. The current-voltage (I-V) measurements on the ZnO films have been performed using scanning tunneling spectroscopy (STS). The significant change in the electronic local density of states (LDOS) of ZnO films, in particular, the onset of the metallic behavior to the n-type semiconducting behavior, is observed with increasing the thickness of the ZnO films.



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# Influence of the Oxygen Deposition Pressure on the Electronic States of Ti in TiO<sub>2</sub> Anatase Thin Films

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## ABSTRACT

TiO<sub>2</sub> has been a long-studied material for its different properties and potential applications ranging from photocatalysis to resistive-switching memory device, photovoltaic or pollutants reduction [1]. But research has for a long time concentrated on the rutile polymorph which is the most stable form of titanium dioxide despite anatase is supposed having better photocatalytic properties. These interesting properties of TiO<sub>2</sub> are strongly related to its electronic properties. In particular the presence of Ti<sup>3+</sup> electronic states, generally related to oxygen vacancies, is often a key parameter in the study of this potential application. Since the development of thin film growth technology, it is now possible to grow TiO<sub>2</sub> anatase films tuning the oxygen content. Previous studies have already addressed the question of the organization of oxygen vacancies within the thickness of the film [2]. On another hand, the surface reconstruction of anatase (001) and the presence of Ti<sup>3+</sup> electronic states in the subsurface region is still a debated question [3, 4].

Here [5], we present a combined study of the electronic and structural properties of anatase TiO<sub>2</sub> (001) thin films grown at different oxygen growth pressure. Resonant photoelectron spectroscopy was used to monitor the evolution of intensity of the Ti<sup>3+</sup> electronic states as a function of the oxygen growth pressure. Hard X-ray photoelectron spectroscopy and transmission electron microscopy were compared to address the structural organization of the defects state within the film and to conclude on the bulk rather than surface character of these defects.

We finally discuss the origin of these defects states and their organization on the surface of TiO<sub>2</sub> anatase.

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# Exploring the Hydrogen Interaction with Pd Clusters Confined within MIL-101 (Cr) Pores

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## ABSTRACT

Due to their high pore volumes and large specific surface areas, MOFs are a very important class of materials for solid-state hydrogen storage.[1] However, MOFs have high hydrogen adsorption capacities only at cryogenic temperature (77K) due to the low enthalpy of adsorption (6 kJ.mol<sup>-1</sup>). One of the possible solutions to enhance the hydrogen storage capacity at ambient temperature is to increase the isosteric heat of adsorption by the insertion of metal nanoparticles and clusters inside the MOFs' nanopores.[2] However, the insertion of the nanoparticles with homogeneous size dispersion is challenging.

Well dispersed 1 nm Pd clusters have been stabilized in MIL-101(Cr) for high metal loading (up to 20 wt.%) using the Double Solvent Method followed by a reduction under H<sub>2</sub> flow at 573K.[3] The MIL-101(Cr) porous structure is kept intact after the metallic clusters insertion within the pores. The Pd clusters contain in average 33 atoms and crystallize in a face centred cubic (*fcc*) system, typical of bulk metal. This was confirmed by *in situ* X-ray absorption spectroscopy (XAS) and HR-TEM. The local structure of Pd clusters was investigated by XAS in transmission mode on the ROCK beam line at SOLEIL synchrotron. Hydrogen sorption properties have been studied by several techniques: H<sub>2</sub> absorption by Pressure-Composition-Isotherms (PCI), hydrogen desorption by Thermal-Desorption-Spectroscopy (TDS) and H<sub>2</sub> absorption in Pd clusters by *in situ* XAS.

From EXAFS refinements, an expansion of the R<sub>Pd-Pd</sub> distances from 2.75 to 2.78 Å ( $\Delta a = 0.03$  Å) under He and H<sub>2</sub> gas, respectively, is noticed at ambient T clearly proving the occurrence of the hydrogen absorption in 1 nm Pd. This expansion is much smaller than bulk Pd ( $\Delta a = 0.1$  Å) forming a hydride phase under the same conditions. Consequently, 1 nm Pd clusters absorb hydrogen forming solid solution instead of a hydride phase, as usually encountered for bulk and Pd nanoparticles down to 2-3 nm. This can be understood by the decrease of the critical temperature of the two-phase region ( $\alpha$ - $\beta$ ) in the Pd-H phase diagram at nanoscale below room temperature.[4] Moreover, the activation energy of desorption of H<sub>2</sub> from hydrogenated 1 nm Pd clusters, as determined by TDS experiments, is almost 2 times lower than bulk. This suggests a change in the rate limiting step during hydrogen desorption.

In conclusion, the present results are very interesting and may open the route to a new material design strategy not only for solid-state hydrogen storage but also for heterogeneous catalysis field, given that Pd-based catalysts are widely used for many chemical reactions involving hydrogen.

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# What Material Science is Needed for Ubiquitous Solar Cells?

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## ABSTRACT

Photovoltaics has become an important part of the energy mix in less than a decade. In this growing industry, progresses on materials and production processes have played an important part to the discovery and mastering of materials, as well as for the development of innovative, cheap and environmentally minded processes: that is, for the achievement of the full potential of the technology.

The presentation will first review the state of the art, with a special emphasis of recent advances.

Some of the many challenges ahead before photovoltaics fulfils one day its promises of clean, abundant and cheap energy will finally be reviewed.

# Photoemission Studies of Band Bending in PbS Colloidal Quantum Dot Films for Next Generation Solar Cells

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## ABSTRACT

Solar cells that incorporate films of PbS colloidal quantum dots (CQDs) have recently reached efficiencies of 13.4 % [1]. A common design uses a film of CQDs, which can have high carrier mobilities [2]. The modification of CQD surfaces, through ligand exchange, allows control over the doping level and type of the film. Using doped CQD films allows for the engineering of band alignment between different CQD films, and CQD and oxide interfaces. This has led to increases in CQD solar cell efficiencies [3]. Still, there remains a question of whether band bending exists at the surface of a CQD film alone, interfaced with vacuum.

We have tested for band bending at the surface of CQD films, in studies aimed at understanding the electronic structure of depleted heterojunction CQD solar cells. First we have used synchrotron-radiation-excited XPS to study the surface photovoltage (SPV) shift in the core levels and valence band of PbS CQD films photoexcited with white light. Unlike bulk semiconductors, there is no obvious mechanism for the creation of surface defect states to cause band bending at the surface. Nevertheless, we are able to observe a significant SPV shift, of the order of up to 70 meV in doped films.

Second we have used time-resolved laser-pump X-ray photoemission-probe spectroscopy at the TEMPO beamline at Synchrotron SOLEIL to study the carrier dynamics within the CQD films as the SPV shift relaxes. This technique has previously given insight into the quantum dot – ZnO heterojunction, commonly found in CQD solar cells [4]. Results from CQD films subjected to different ligand treatments, and different thicknesses are discussed.

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# Dynamics in HgTe 2D Nanocrystals

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## ABSTRACT

Nanocrystals are attracting a lots of interest because of their bright and wavelength tunable light emitting properties. They are actually equally promising for the design of low cost optoelectronic devices and especially in the infrared where current technologies remains expensive. To push the absorption signal of nanocrystal in the near and mid IR narrow band gap material has to be used. In this sense HgTe, as a semimetal is of utmost interest.<sup>1,2,3</sup>

However most of the recent result have been focused on 0D quantum dots for which the optical properties remains generally by the inhomogenous broadening due to the nanoparticle size distribution. Here we rather use 2D nanoplatelets of HgTe, which lacks of roughness in the only confined direction and thus leads to narrow excitonic transition.<sup>4</sup> After a brief introduction to the synthesis of this material and their exceptional optical features, I will rather focus on their transport and electronic properties. We demonstrate that thin film of HgTe nanoplatelets can be made conductive and photoconductive and that the majority carrier can be tuned by changing the capping chemistry.<sup>5</sup> This results are then further confirmed by XPS measurements made on the Tempo beamline of Soleil. In the last part of the talk, I discuss how the photoconductive and photoemission dynamics compared to each other.<sup>5</sup> Our results are quite promising for the design of faster component based on HgTe 2D nanoplatelets.

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# Autocatalyzed Growth of GaAs Nanowires on Silicon: Study of the Catalyst

L. Fouquat<sup>1,2</sup>, X. Guan<sup>1</sup>, J. Penuelas<sup>1</sup>, G. Grenet<sup>1</sup> and M. Silly<sup>2</sup>

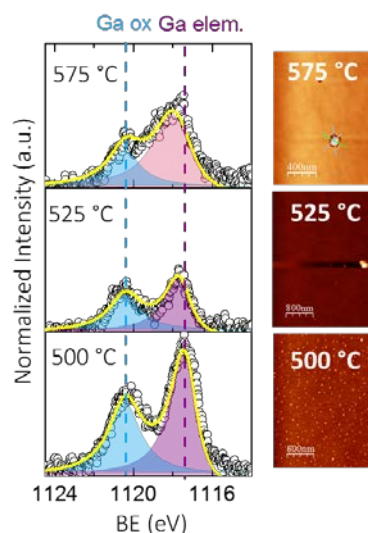
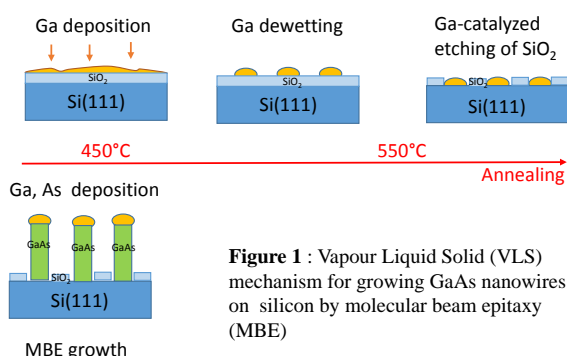
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## ABSTRACT

To obtain good optoelectronic performances, Ga (rather than Au) must be used as catalyst to grow GaAs nanowires on silicon by Vapor-Liquid-Solid (VLS) [1]. It has been found that such an auto-catalyzed growth is better controlled if performed on epitaxial Si substrates rather than on clean Si substrates [2-5].

Using atomic force microscopy and X-ray Photoelectron Spectroscopy (XPS) we have studied the effect of the growth temperature (from 50 °C to 700 °C) on the size and density of Ga droplets. This initial configuration of the Ga droplets is of special interest as it determines NWs dimensions and repartition. The evolution of the Si2p, O1s, and Ga2p core levels as a function of the growth temperature allows for displaying interfacial Ga oxides in association with a dewetting phenomenon. Finally, the mechanism of formation of pinholes catalyzed by droplets in the SiO<sub>2</sub> film is discussed.



**Figure 2:** Ga<sub>2p3/2</sub> core level for 3ML of Ga deposited at 450 °C annealed at 500 °C, 525 °C and 575 °C and the corresponding AFM images

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# Self-assembly of Semiconductor Nanocrystals with an Amphiphilic Surface Pattern

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## ABSTRACT

Site-selective surface modifications on the shape-controlled nanocrystals is a key approach in the programmed self-assembly of inorganic colloidal materials. This study demonstrates a simple methodology to gain self-assemblies of semiconductor nanocrystals with anisotropic shapes through tip-to-tip attachment. Short-chained water-soluble cationic thiols are employed as a surface ligand for CdSe-based nanorod,<sup>1</sup> tetrapods and octapods.<sup>2</sup> Because of the less affinity of arm-tip to the surface ligands compared to the arm-side wall, the tip-surface becomes uncapped to give hydrophobic nature, affording an amphiphilic surface pattern. The amphiphilic tetrapods aggregated into porous agglomerates through tip-to-tip connection in water, while they afforded a hexagonally arranged Kagome-like two-dimensional (2D) assembly by the simple casting of aqueous dispersion with the aid of a convective self-assembly mechanism. A 2D net-like assembly was similarly obtained from amphiphilic octapods. A dissipative particle dynamics simulation using a planar tripod model with an amphiphilic surface pattern reproduced the formation of the Kagome-like assembly in a 2D confined space, demonstrating that the lateral diffusion of nanoparticles and the firm contacts between the hydrophobic tips play crucial roles in the self-assembly.

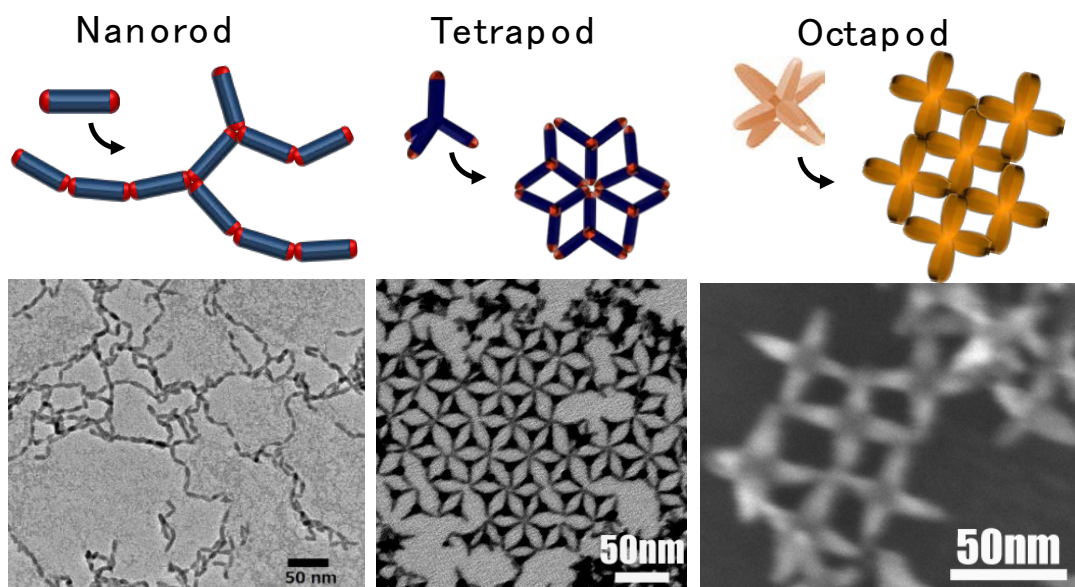


Fig. 1 Self-assembly of semiconductor nanoparticles with an amphiphilic surface pattern.

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# Two-dimensional Colloidal Nanostructures: Synthesis and Electrical Transport

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## ABSTRACT

In my talk I will show that two-dimensional colloidal nanosheets represent very attractive optoelectronic materials. They combine good lateral conductivity with solution-processability and geometry-tunable electronic properties. For example, the formation of ordered and densely packed ligand surface layers of oleic acid on {100} lead sulfide surfaces can drive the normally isotropic growth of colloidal crystals into a two-dimensional oriented attachment of nanocrystals, resulting in PbS nanosheets. The electronic confinement in height allows tuning the effective bandgap of the materials, which make them interesting for optoelectronic applications. Thus, the electrical transport through these materials was analyzed in devices like field-effect transistors and solar cells. It turns out that the electronic confinement allows for an optimization of their performances. Further, I will show that colloidal 2D show interesting spintronic effects.



# GaAs Heterostructured Nanowires Grown by Molecular Beam Epitaxy

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## ABSTRACT

Semiconductor nanowires (NWs) have been intensively studied over the past few years because of their original physical properties. Unlike other systems, NWs offer the possibility to create hetero-epitaxial structures via two different types of material combinations: radial [1] (combining materials around the growth axis of NWs) and axial [2] (combining materials along the NW axis). In both case an accurate control of the interface quality is needed. In this presentation we will present these two kinds of heterostructures, based on GaAs NWs, fabricated by molecular beam epitaxy.

The first heterostructure is made of axial insertion of Wurtzite segment in the Zinc Blende GaAs NWs. The availability of ZB and WZ crystalline structure is of strong importance since they can display different optical and transport properties [3]. We will show that it is possible to control the formation of such structures by tuning the flux of As and Ga during the growth.

The second kind heterostructure consists in core GaAs / shell SrTiO<sub>3</sub> nanowires. In this case the heterogeneity is large, consequently the growth of a functional oxide on III-V semiconductor nanowires is difficult to achieve because it is necessary to avoid undesirable oxidation during the sample transfer or during the functional oxide growth. We propose a capping / decapping technique to obtain GaAs facets free from contamination before the shell growth [4]. Moreover using adapted SrTiO<sub>3</sub> growth condition we obtained crystalline SrTiO<sub>3</sub> on the facets of GaAs allowing the integration of ferroelectric functional oxides such as BaTiO<sub>3</sub>.

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# "Mixed-thiols" Functionalized Au and AgNPs: A Close Look at the Atomic Structure and Chemico-physical Properties by SR-XPS

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## ABSTRACT

In recent years, thiol-functionalized MNPs have been synthesized, characterized and developed to be used in many different fields such as optoelectronics, sensors, catalysis, and biomedicine [1]. Functionalized Au and AgNPs, composed of a metallic core and a ligand shell, show a peculiar optical behavior and provide a very powerful tool for biotechnological applications. Mixtures of ligand molecules can be used to coat the nanoparticles and control shape and size distribution, making them suitable for active purposes in microscopy, nanoelectronics and bioanalysis. In this communication, we present MNPs (Au and Ag) functionalized with mixed organic ligands (DEA and 3MPS), prepared with different metal/thiol stoichiometric ratios. The molecular overlayer has been selected on purpose for the biomedical applications [2,3], as well as to stabilize the nanoparticles. The changes in the stoichiometric ratio between metal and different capping agents can influence the chemical properties of ligands functional groups and the dimension of the functionalized MNPs. Moreover, the biocompatibility of the system depends strictly on the charge and thickness of capping molecules layer. Therefore, the study of the interaction at the interface between the organic ligand and MNPs at atomic level is the first step for the fabrication and developing of very suitable nanomaterials for diagnostic and therapy. The characterization of the nano-systems was carried out by means of Synchrotron Radiation induced X-Ray Photoelectron Spectroscopy (SR-XPS). SR-XPS has been demonstrated to be a unique tool for investigating the nature of the interaction at the capping agent/metal NP interface, as well as the chemical structure and stability of MNPs surface [4,5]. This technique provides information on the local bonding environment of a given species and allows to achieve a deep understanding of the influence of the thiols stoichiometric ratio on the electronic properties and stability of the functionalized MNPs. In conclusion, to answer to the constant demand for more stable and functional NPs, this project provides a deep study concerning the characterization, by means of SR-XPS, of innovative Au and AgNPs, which can act as suitable candidate for drug delivery, for diagnostic or radiosensing applications.

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# **ABSTRACTS**

**Thursday, October 19<sup>th</sup>, 2017**

**SESSION III & IV**

# ICON<sup>2</sup> - 2017

Thursday, October 19<sup>th</sup>

## SESSION III

- KN-03      The 2D transition metal dichalcogenide interface  
*A.T.S. Wee*
- IT-05      A monolayer of MoS<sub>2</sub> on Au(111) as a decoupling layer for single molecules  
*C. Lotze*
- IT-06      Intrinsically patterned two-dimensional materials for selective adsorption of molecules and nanoclusters  
*S. Du*
- IT-07      Tailoring carbon-based nanostructures via on-surface synthesis  
*D. Zhong*
- IT-08      Introduction to SOLEIL storage ring upgrade  
*M-A. Tordeux*
- IT-09      Overview of VUV- soft X-ray free electron lasers  
*M-E. Couprie*
- IT-10      Coherent collective modes studied with time-resolved photoelectron diffraction  
*M. Hengsberger*

## SESSION IV

- KN-04      Single molecule magnets grafted on surfaces and explored by XmcD  
*P. Sainctavit*
- OC-12      Time resolved X-ray holographic imaging of magnetic domains at the SEXTANTS beamline of the SOLEIL Synchrotron  
*H. Popescu*
- IT-11      State of the art of laser produced XUV sources with picosecond and femtosecond time resolution: High harmonic generation and soft X-ray lasers  
*S. Kazamias*
- OC-13      High-order harmonics at MHz for photoelectron spectroscopy on correlated electron pairs in solids  
*C-T. Chiang*

# The 2D Transition Metal Dichalcogenide Interface

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## ABSTRACT

We have previously shown that the electronic properties of graphene can be controllably tuned via molecular functionalization and other surface modifications [1]. In this talk, I will focus on our recent work on semiconducting 2D transition metal dichalcogenides (TMDs) with layer-dependent tunable direct bandgaps, thereby making them suitable for optoelectronic device applications [2-4]. We use high resolution scanning tunneling microscopy/spectroscopy (STM/STS) to study the atomic structure and local electronic properties of 2D MoS<sub>2</sub> and WSe<sub>2</sub> layers on HOPG substrates, and show that the electronic bandgaps can be tuned by strain at grain boundaries and dislocations [5,6]. Using PTEDA as a prototype semiconductor organic molecule, we show that a monolayer TMD can effectively screen an organic-inorganic heterointerface [7]. We demonstrate the fabrication and unravel the electronic properties of a lateral doped/intrinsic heterojunction in 2D WSe<sub>2</sub>, partially covered with a molecular acceptor C<sub>60</sub>F<sub>48</sub> [8].

In the second part of the talk, I will present our recent work on the opening of an inverted optical gap in monolayer MoS<sub>2</sub> on a gold substrate, as predicted by theory [9]. This is attributed to a phase transformation to 1T' MoS<sub>2</sub>, which is triggered by annealing at a specific temperature window. We also demonstrate that gold plasmonic hybrid structures can induce giant photoluminescence enhancement in 2D WSe<sub>2</sub> [10]. Finally, we shed light on how adsorption and desorption of oxygen by monolayer MoS<sub>2</sub> can be employed to modify its electronic and optical properties to suit different applications [11].

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# A Monolayer of MoS<sub>2</sub> on Au(111) as a Decoupling Layer for Single Molecules

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## ABSTRACT

Thiophene based molecules are commonly used for semiconducting devices like solar cells or light emitting diodes. To optimize these, a detailed understanding of the molecules electronic structure and the environmental influence on the latter is of great interest.

Scanning tunneling spectroscopy (STS) allows addressing individual molecules in a precisely known surrounding. However, it bears the drawback that it requires a conductive substrate. Deposition of organic molecules on a metal substrate leads to strong hybridization of the electronic states. Preservation of the molecular character requires the inclusion of thin band-gapped materials.

Here, we present STS experiments performed on 2,5-bis(3-dodecylthiophen-2-yl)thieno[3,2-b]thiophene-*n* (BTTT-*n*; *n*=1,2) molecules adsorbed on a single layer molybdenum disulfide (MoS<sub>2</sub>) on Au(111). We show that it acts as an effective decoupling layer. Differential conductance spectra of the molecules exhibit a multitude of sharp characteristic peaks, which are connected to the highest occupied molecular orbital. We propose that these originate from a surprisingly effective excitation of vibronic [1] resonances by the tunneling electrons.

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# Intrinsically Patterned Two-dimensional Materials for Selective Adsorption of Molecules and Nanoclusters

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## ABSTRACT

Two-dimensional (2D) materials have been studied extensively as monolayers, vertical or lateral heterostructures. To achieve functionalization, monolayers are often patterned using soft lithography and selectively decorated with molecules. Here, the growth of a family of 2D materials that are intrinsically patterned has been demonstrated. A monolayer of PtSe<sub>2</sub> can be grown on a Pt substrate in the form of a triangular pattern of alternating 1T and 1H phases. Moreover, in a monolayer of CuSe grown on a Cu substrate, strain relaxation leads to periodic patterns of triangular nanopores with uniform size. Adsorption of different species at preferred pattern sites is also achieved, demonstrating that these materials can serve as templates for selective self-assembly of molecules or nanoclusters, as well as for the functionalization of the same substrate with two different species.

I thank the cooperation with H.-J. Gao, H. M. Guo, Y. L. Wang, J. C. Lu, Y. Shao, X. Wu, J. B. Pan, L. Gao, S. Y. Zhu, K. Qian, Y. F. Zhang, D. L. Bao, L. F. Li, Y. Q. Wang, Z. L. Liu, J. T. Sun and T. Lei from Institute of Physics, CAS; X. Lin and Y. Y. Zhang from the University of CAS; C. Liu, J. O. Wang and K. Ibrahim from Institute of High Energy Physics, CAS; D. N. Leonard from ORNL; S. T. Pantelides from Vanderbilt University.

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# Tailoring Carbon-based Nanostructures via on-surface Synthesis

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## ABSTRACT

Graphene is one of the promising two-dimensional atomic materials with a zero band gap. However, a finite band gap is needed in order to applying graphene for field-effect transistors with high on-off ratio. Band gap opening has been expected theoretically for laterally confined ribbons of graphene. Here, I will present the experimental approach of the selective and precise growth of subnanometer wide graphene nanoribbons (GNRs). Spatially well-aligned GNRs have been prepared and characterized by scanning tunneling microscopy and direct/inverse photoemission spectroscopy, revealing the existence of a finite band gap for the 7-armchair GNRs. Furthermore, decorating nonhexagonal rings into the honeycomb lattice is an effective way to tailor the electronic structures and magnetic properties of graphene. But nonhexagonal rings are usually energetically unstable compared to the hexagonal counterparts, making it challenging to embed nonhexagonal rings in a controllable manner. I will talk about the on-surface synthesis of GNRs periodically embedded with four- and eight-membered carbon rings. It was found that the nonhexagonal rings as a topological modification dramatically change the electronic properties of the nanoribbons.

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# Introduction to SOLEIL Storage Ring Upgrade

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## ABSTRACT

A new generation of storage-ring based synchrotron light source is going to be developed, in order to promote the realization of a new class of experiments, critically dependent on source brightness and transverse coherence. In that context, SOLEIL as other synchrotron centers, aims to propose an upgrade of the present machine. First steps of this study will be presented, with a specific focus on the time resolved aspects of the present and future source.

# Overview of VUV- Soft X-ray Free Electron Lasers

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## ABSTRACT

More than 50 years after the lasers' discovery, VUV- X light sources are actively developed around the world. Among them, accelerator based light sources have known a wide growth. They rely on emission of synchrotron radiation by accelerated relativistic charged particles. In the case of a Free Electron Laser, the longitudinal coherence is achieved by setting in phase the electrons, thanks to an energy exchange between the electrons and a light wave (the spontaneous emission or an external seed) resulting in bunching and further amplification of the light. After introducing the main historical steps of Free Electron Laser development, the landscape of VUV soft-X ray Free Electron Laser sources will be sketched. These light sources provide short pulses, in the femtosecond range, and extremely high brilliance. The different processes and schemes will be given. Further developments envision paths towards advanced and compact FELs, with flexible characteristics aiming at answering user needs...

# Coherent Collective Modes Studied with Time-resolved Photoelectron Diffraction

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## ABSTRACT

Dynamics in solid surfaces occur on atto-, femto- and picosecond timescales. Angle-resolved photoelectron spectra contain a wealth of information about the electronic and atomic structure in surfaces. When used with pulsed light in a pump-probe setup the dynamics of the atomic and electronic structure can be investigated in great detail.

We will introduce photoelectron diffraction (PED) as a suitable probe for studying structural dynamics in surfaces and in molecular layers. With respect to complementary methods like conventional electron diffraction, PED is only sensitive to local order, i.e. the neighborhood of the emitting atom [1]. In photoelectron diffraction experiments the angular intensity distribution of photoelectrons emitted from well-defined states is recorded as function of emission angle. Similar to holographic imaging, interference of the directly emitted and the scattered electron waves produces a complex pattern from which the atomic environment of the emitter can be reconstructed.

Using the example of molecular layers we will demonstrate how the bonding geometry can be obtained from experimental patterns [2], and that it is possible to observe changes in molecular conformation of only a small fraction of molecules present on the surface [3].

More importantly, well-defined collective modes can be excited using suitable excitation pump pulses either very short with respect to the time of period [4,5] or in resonance with the frequency of the mode [6]. Using the example of coherent phonons in bismuth single crystals we will present how electronic and atomic dynamics can be disentangled and the relative timing between the structural and the electronic excitation can be deduced from the experimental data [5]. At the end an outlook and discussion of forthcoming potential experiments at free-electron laser or high-harmonic sources be given, like e.g. shown in simulations of coherent molecular motion of CO molecules on solid surfaces [6].

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# Single Molecule Magnets Grafted on Surfaces and Explored by Xmcd

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## ABSTRACT

I shall focus on the original properties that are exhibited by molecular magnetic systems when they are grafted on a surface. I shall first present the Single Molecule Magnets (SMM) with their unique property associated to the quantum relaxation of magnetization. Then I shall review how such unusual properties are modified when SMMs are deposited on either a metallic, an insulating or a ferromagnetic surfaces. Emphasis shall be brought to the nature of the magnetic ions with a special attention to the orbit and spin contributions to the magnetization. The main technique of investigation is x-ray magnetic circular dichroism and for which the basic concepts shall be rapidly introduced [1-4].

$$\frac{d[F_1]}{d\omega_2} = SAm_2 \cos \varpi, \quad \frac{d[F_1]}{d\omega_3} = SAm_3 \cos \varpi.$$

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# Time Resolved X-ray Holographic Imaging of Magnetic Domains at the SEXTANTS Beamline of the SOLEIL Synchrotron

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## ABSTRACT

Resonant scattering of polarized coherent x-rays offers the possibility of achieving x-ray imaging with element selectivity and magnetic sensitivity. In particular Fourier transform holography (FTH) is a lensless imaging technique [1] combining high spatial resolution, chemical selectivity and flexible sample environment. It makes use of a holographic mask, consisting of an object aperture and of one or more reference apertures, placed in front of a transparent sample. Holographic imaging relies on the interference between coherent beams scattered by the object and by the references. In the integrated mask/sample approach (where the sample and the holographic mask are deposited on the same silicon nitride membrane), the alignment is easy and the system is not affected by vibrations or drifts. The disadvantage is a complex sample fabrication and, especially, a fixed field of view. Another approach is to prepare the mask and the sample on two separate membranes: this requires precise alignment and stability, but allows for a movable field of view. We have implemented both approaches in our experimental setup. The scattered intensity is collected using a CCD camera equipped with a light-tight Al filter and a movable beam-stop. Magnetic images can be obtained using either circular or linear polarization [2]. In addition to continuous films, we analyzed the magnetic domain structure in laterally confined nano objects. We used normal transmission geometry for imaging out of plane magnetic domains, while the sample was tilted by 30° [3] or 45° [4] for analyzing in-plane domains. Time resolved magnetic imaging was recently performed by RF pumping [5]. The IRMA2 [6] and the COMET [7] experimental stations of the Sextants beamline [8], adapted to coherent diffraction experiments in reflectivity and transmission, are already opened for SOLEIL users.

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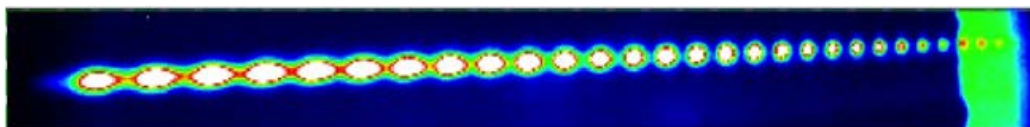
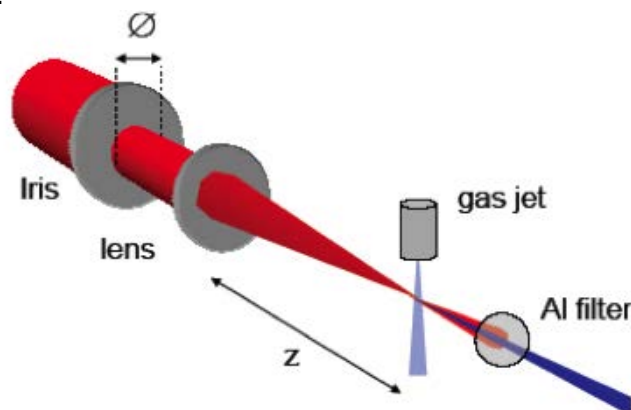
# State of the Art of Laser Produced XUV Sources with Picosecond and Femtosecond Time Resolution: High Harmonic Generation and Soft X-ray Lasers

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## ABSTRACT

An overview will be presented on the XUV source development using intense femtosecond infrared lasers as a tool for the generation of coherent sources in the soft x-ray domain with picosecond and femtosecond duration. After a brief introduction about the physical processes that generate those sources, their performances will be detailed in terms of spectral ranges, number of photons, pulse duration, temporal and spatial coherence, polarization, etc. Examples of pump/probe experiments that can be carried out with such sources will be provided.



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# High-order Harmonics at MHz for Photoelectron Spectroscopy on Correlated Electron Pairs in Solids

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## ABSTRACT

Studying the interaction between electrons in solids has been a main topic for many decades aiming at a deeper understanding of magnetism and superconductivity. With the recent progress of double photoemission (DPE) spectroscopy, emission of correlated electron pairs from solids has been observed using synchrotron as well as laboratory light sources. In this contribution we report a new DPE setup using a laser-based high-order harmonic generation light source at megahertz repetition rates in combination with a pair of time-of-flight spectrometers [1,2].

By using the photon energies of 25 and 32 eV, we discover detailed structures in the energy distribution of electron pairs emitted from Ag(001) and Cu(111) surfaces [3]. In the two-dimensional DPE energy spectra, distinct features with well-defined sum-energies ( $E_{\text{sum}}$ ) of electron pairs can be identified. These features are attributed to the emission of correlated  $sp$ - and  $d$ -electrons as well as to two correlated  $d$ -electrons. Moreover, by comparing the  $E_{\text{sum}}$  spectra with the self-convolution of density of states of electrons in Ag and Cu, we observe a three-fold enhanced emission of  $sp$ - $d$  electron pairs only on Ag. This observation will be discussed in terms of electron correlation.

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# **ABSTRACTS**

**Friday, October 20<sup>th</sup>, 2017**

**SESSION V**



# ICON<sup>2</sup> - 2017

Friday, October 20<sup>th</sup>

## SESSION V

- IT-12      Ultrathin films of TiO<sub>x</sub> on Au(111)  
*M. R. Castell*
- OC-14      Multi-scale phase transitions of ditopic ligands on surface  
*X. Sun*
- IT-13      Invited Talk  
*A. Papageorgiou*
- OC-15       $\beta$ -lactoglobulin unfolding and heat-aggregation at atomist scale: How NMR associated with SAXS reveal protein structures at atomist scale  
*P. Peixoto*
- IT-14      Invited Talk  
*K.H.Ernst*
- IT-15      Coherent quantum phenomena in ultimate 2D superconductors: A STM study  
*D. Roditchev*
- OC-16      Super periodicity induced band gap opening in epitaxial graphene buffer layer  
*M.N. Nair*
- OC-17      Electronic structure of long range ordered on surface synthesized polymeric networks  
*Y. Fagot-Revurat*

## Ultrathin Films of TiO<sub>x</sub> on Au(111)

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### ABSTRACT

There is a great deal of interest in the surfaces of metal oxides because of their broad range of applications in catalysis, microelectronics, and gas sensing. However, oxides that are created as ultrathin films have electronic, optical, magnetic and chemical properties that may be quite different from their bulk crystal counterparts [1]. This is because of the strong interaction between the oxide film and the substrate that it is grown on. Many ultrathin metal oxide films that are only a few atomic layers thick should be considered as 2D hybrid structures - part bulk, part interface, and part surface. This talk introduces ultrathin oxides in general and then concentrates in detail on the work we have carried out on TiO<sub>x</sub> ultrathin films on Au(111) substrates.

Ultra-thin films of TiO<sub>x</sub> were grown on Au(111) by evaporating low coverages of Ti in UHV onto the Au substrates and subsequently annealing the samples in an environment containing oxygen [2]. For certain processing conditions a 2×2 Ti<sub>2</sub>O<sub>3</sub> honeycomb structure is created on the surface. We have studied this structure with STM, LEED, AES, XPS, ARPES and DFT.

Because the Ti<sub>2</sub>O<sub>3</sub> honeycomb structure is a 2×2 overlayer there is the possibility that neighbouring domains are offset with respect to each other. This gives rise to domain boundaries where the usual hexagonal rings are no longer stable. The boundary structures have been studied by STM, which shows that [11-2] and [1-10] oriented boundaries are most common. The structures consist of combinations of rings of 8, 7, 5 and 4 Ti atoms for the different boundaries. DFT has been used to calculate the boundary energies. There is a good fit between the most frequently observed boundary structures seen in STM and the lowest energy structures as determined by DFT.

The honeycomb structure provides a unique environment for the adsorption of ad-species, and in this instance we evaporated Ba atoms on the structure. STM imaging shows that the Ba atoms adsorb individually in the hollow sites of the HC network [3]. Depending on the Ba coverage (x) which ranges from 0 to 2/3, two ordered phases can be identified at x = 1/3 and x = 2/3. A disordered labyrinth-like phase is observed for values of x between 1/3 and 2/3. Theoretical modelling shows that the structural character of these films is driven by the charge transfer that occurs between the electropositive Ba atoms and the electronegative Ti<sub>2</sub>O<sub>3</sub>/Au support. The evolution of the structure of the thin films as a function of Ba coverage can be described using a lattice gas model with first-, second- and third-nearest-neighbour Ba-Ba repulsive interactions, and modeled using Monte Carlo techniques.

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# Multi-scale Phase Transitions of Ditopic Ligands on Surface

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## ABSTRACT

Studies of molecular switches and conformational changes at the single-molecule level by scanning tunneling microscopy (STM) have attracted huge scientific interest due to its potential applications in the fields of molecular electronics, molecular motors and optical devices.

A multi-scale irreversible switching of a ditopic ligands on HOPG surface has been investigated by STM in the solid-liquid interface. The ditopic ligands consist of two coordinating bipyridine entities linked through a central fluorene bridge (bpyFbpy). Molecule bpyFbpy has the ability to switch between various conformations. One possibility is the cis- to trans-like isomerization which has here

been triggered by protonation. A 2D structural phase transition is generated where a gear-chain structure is transformed

into a linear stripe structure due to the isomerization, Figure.1. The gear-chain network is an enantiomerically-mixed structure showing 2D heterochirality. On the contrary, the linear stripe network is an enantiomerically-separated structure showing 2D homochirality. The cis-trans transformation is therefore a heterochiral to homochiral phase transition<sup>1</sup>.

A second kind of ditopic ligands are investigate where the ligand consists of two coordinating terpyridine entities linked through one or two central fluorene bridges (GL-I or GL-II). The two molecules self-organize into two completely different supramolecular organizations even they maintain the same terpyridine terminals. This is due to the selective conformational switching from the ligands isomers to form hydrogen bonds stabilized 2D networks<sup>2</sup>.

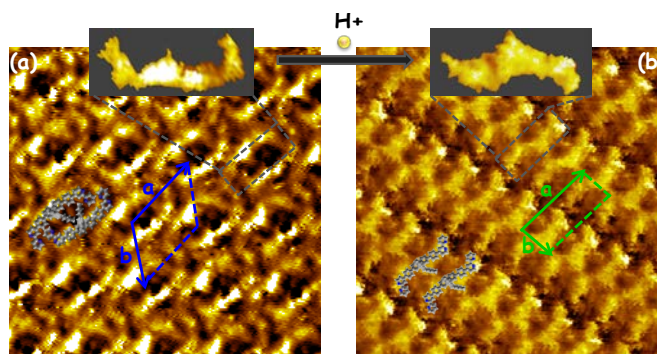


Figure 1 Cis to Trans-like isomerization of **bpyFbpy** molecules observed by STM

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- 2 X. Sun, F. Lafolet, G. Lemerrier, J. C. Lacroix, to be submitted.

# **Invited Talk**

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# $\beta$ -lactoglobulin Unfolding and Heat-aggregation at Atomist Scale: How NMR Associated with SAXS Reveal Protein Structures at Atomist Scale

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## ABSTRACT

In presence of calcium ions, Betalactoglobulin (BLG) form simultaneously different kind of aggregates (spheres microgels, strands...) after heating. However, the molecular mechanism of this process is poorly understood.<sup>1,2</sup> To better understand the aggregation mechanism we have studied the evolution of molecular structure during heating using NMR pulse field gradient technique operating in high field (900 MHz) associated with small angle scattering. The association of these techniques enables us to distinguish molecular conformation of BLG in different states, free and bond to a cluster, in the very first steps of aggregation at some specific physico-chemical conditions. These data show a picture where calcium ions promote aggregation by screening the charges of specific sites in a partially unfold protein. This is one of the first reports showing the impact of calcium ions over BLG conformation at the atomic scale and the specific role of calcium ions in the process. In the discussion we argue that this effect is likely to occurs in wide range of unfold proteins.

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## **Invited Talk**

**K. H. Ernst**

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# Super Periodicity Induced Band Gap Opening in Epitaxial Graphene Buffer Layer

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## ABSTRACT

The joy and pitfall of graphene for nanoelectronics come from its inherent property such as zero bandgap in its electronic structure. Several methods have been proposed to open a bandgap in monolayer graphene [1, 2]. We have recently shown that the precursor growth state of graphene, i.e. a layer with the honeycomb structure of graphene exhibits a bandgap of more than 0.5eV [3], twice the previous value in epitaxial graphene samples [4]. The origin of this bandgap was unclear.

To understand the bandgap opening in buffer, we used different experimental techniques such as scanning tunneling microscope (STM), high-resolution scanning transmission electron microscope (HR-STEM) and angle-resolved photoemission spectroscopy (ARPES). We show that the band structure in the buffer has an electronic periodicity related to the structural periodicity observed in STM and our X-ray diffraction [5]. Our ARPES analysis shows that the bandgap opening is correlated to the super periodicity induced by the substrate. The surface periodicity promotes the folding of the bands in the superperiodic Brillouin zone edges as seen by constant energy cuts in photoemission [6].

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# Electronic Structure of Long Range Ordered on Surface Synthetized Polymeric Networks

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## ABSTRACT

On-surface covalent self-assembly of organic molecules is a very promising bottom-up approach for producing atomically controlled nanostructures. Due to their highly tunable properties, these structures may be used as building blocks in electronic carbon-based molecular devices as shown for graphene nanoribbons (GNRs). We map the electronic structure of an ordered array of poly-para-phenylene (PPP) chains, ascribed to 3-AGNRs, produced by surface-catalyzed dehalogenative polymerization of (1,4)-dibromobenzene on copper (110) [1,2]. The quantization of LUMO states are measured as a function of oligomer length by scanning tunneling spectroscopy (STS), with Fermi level crossings observed in the longest chains. Angle-resolved photoemission spectroscopy (ARPES) reveals a graphene-like quasi one-dimensional HOMO-band as well as a direct HOMO-LUMO gap of 1.15 eV, as the LUMO is partially occupied through adsorption on the surface. Tight-binding modelling and ab initio DFT calculations lead to a full description of the organic band structure, including the dispersion, the gap size and charge transfer mechanisms which drive the system into metallic behaviour [3]. Moreover, changing the organic precursor [4] or the substrate geometry is shown to drive a metal to semiconductor transition. Moreover, we have determined the structure and electronic properties of well-ordered quasi-infinite semiconducting PPP chains grown on Cu vicinal surfaces combining STM/STS, ARPES, Fast-XPS and NEXAFS technics [5].

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# Coherent quantum phenomena in ultimate 2D superconductors: A STM study

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## ABSTRACT

In 1964 V. L. Ginzburg predicted that new superconducting phases could appear in ultrathin films deposited on insulating surfaces. In 2010 superconductivity below 2K was discovered in some crystalline atomic monolayers of Pb grown on atomically clean Si(111) [1,2]. Owing their peculiar electronic properties, these two-dimensional materials manifest a number of intriguing superconducting phenomena. In crystalline monolayers of Pb on Si(111) the superconducting condensate is an intrinsic Josephson network formed by superconducting terraces coupled by Josephson links at individual atomic steps [1]. The detailed atomic arrangement at each step decides the strength of the Josephson coupling. In a magnetic field, the superconducting vortex phase contains different kinds of vortices, ranging from Abrikosov (Pearl) to Josephson limits. By contrast, amorphous monolayers of Pb are non-superconducting correlated metals. Playing with geometry of in-situ grown samples enables realizing ultimately thin lateral SNS junctions, reveal and study Josephson proximity vortices inside their N-parts [2].

When individual magnetic impurities are added, the Cooper pairs are diffused forming so-called Yu, Shiba and Rusinov (YSR) bound states. While in three-dimensional superconductors these states rapidly decay around impurities on atomic scale, superconductors with two-dimensional electronic structure such as Pb-monolayers on Si(111) or 2H-NbSe<sub>2</sub> host YSR bound states with spatial extents orders of magnitude larger [3]. These long-range magnetic states could be used to produce new topological phases in hybrid systems such as arrays or clusters of magnetic atoms and molecules coupled through the 2D-superconducting medium.

In our lecture we describe a series of recent experiments which mapped superconductivity, vortices and YSR states in Pb/Si(111) and 2H-NbSe<sub>2</sub> by scanning tunneling microscopy and spectroscopy at ultralow temperatures.

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# **POSTER SESSION**

# List of Poster

- PO-01 Transformation from amorphous to helical supramolecular Co-aggregates through molecular recognition  
*K. Aratsu*
- PO-02 Surface-functionalization with iron of gallium nitride GaN nanopowder particles  
*J. F. Janik*
- PO-03 From magnetic cubic pre-kesterite to semiconducting tetragonal kesterite  $\text{Cu}_2\text{ZnSnS}_4$  via mechanochemical synthesis route  
*J. F. Janik*
- PO-04 Ammonolytical nitridation in the binary gallium pnictide systems  $[\text{GaE}+\text{GaE}']/\text{NH}_3$  (E, E' = As, P, Sb) towards polytype specific GaN nanopowders  
*J. F. Janik*
- PO-05 Molecular magnets: From single molecule to 3D self-assembly  
*D. Longo*
- PO-06 Magnetic dichroism in soft X-rays at ultra-low temperature on DEIMOS beamline (Synchrotron SOLEIL)  
*E. Otero*
- PO-07 Helical organization of hydrogen-bonded oligothiophenes: Impact on photovoltaic properties  
*H. Ouchi*
- PO-08 Low temperature synthesis of NiCoMn-mixed hydroxide and ternary NiCo-MnO<sub>2</sub> nanocomposites and their application as a novel high energy supercapattery device  
*K.O. Oyedotun*
- PO-09 Hierarchical engineering of 2D self-assembled porous organic-based nanoarchitectures on metal surfaces  
*F. Silly*
- PO-10 Characterization and optimization of hematite nanorods photoanodes elaborated by aqueous chemical growth  
*D. Stanescu*
- PO-11 Blue organic luminophores with azaheterocyclic skeleton: Synthesis and properties  
*V. Vasilache*
- PO-12 Investigation by X-ray natural linear dichroism (XNLD) and X-ray magnetic circular dichroism (XMCD) towards magnetic properties of 6nm  $\text{CsNiCr}(\text{CN})_6$  nanoparticles single layer assembled on graphite  
*L. Zhang*

# Transformation from Amorphous to Helical Supramolecular Co-aggregates through Molecular Recognition

K. Aratsu<sup>1</sup> and S. Yagai<sup>2</sup>

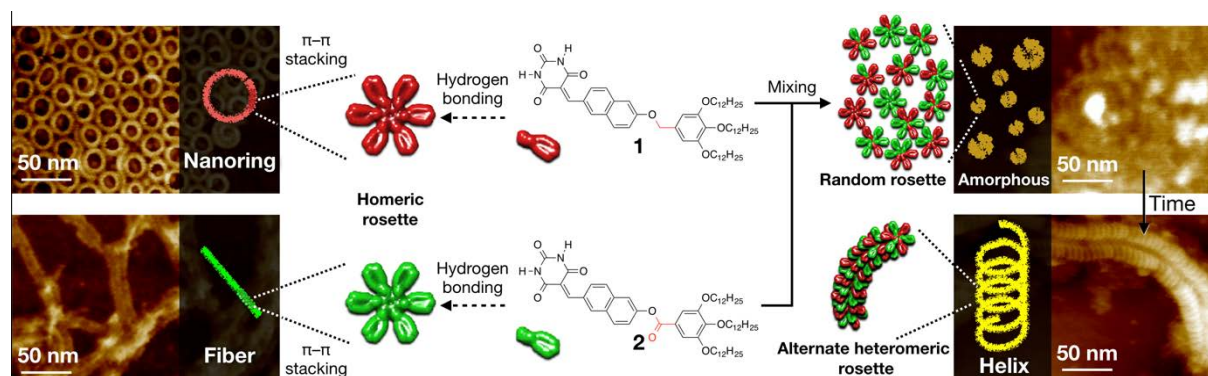
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## ABSTRACT

In nature, complex functions and higher-order structures of molecular ensembles have been accomplished by high fidelity recognition properties. For example, a heterodimer composed of  $\alpha$ - and  $\beta$ -tubulins which have almost identical structures but different polarities, self-assembles into microtubules. In contrast, multicomponent assemblies in artificial systems have been achieved generally by using complementary binding molecules. Without using complementary interactions, usually different molecules are mixed randomly, or in some cases, they are narcissistically self-sorted.<sup>1</sup> Hence, the construction of well-defined polymeric architectures through “integrative” self-sorting with well-defined alternative sequence of non-complementary components is a challenging topic.

Previously, we reported self-assembly of naphthalene molecule **1** possessing barbituric acid hydrogen bonding unit and aliphatic tails. Molecule **1** self-assembles into cyclic hexamers (rosette) through complementary hydrogen bonding, which further form toroidal supramolecular polymers (nanoring) in nonpolar solvent.<sup>2,3</sup> In this study, we synthesized new molecule **2** wherein the ether linkage of **1** is changed to the ester linkage. Molecule **2** self-assembled into fibrous one-dimensional supramolecular polymers. Upon mixing **1** and **2**, UV-vis and AFM analyses showed that they kinetically formed amorphous co-aggregates, which transformed into thermodynamically stable helical supramolecular copolymers over time. Small angle X-ray scattering analyses showed that the transformation occurs in solution.



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# Surface-functionalization with Iron of Gallium Nitride GaN Nanopowder Particles

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## ABSTRACT

We have recently reported on GaN nanopowders modified with magnetic manganese centers to yield, potentially, a new class of diluted magnetic semiconductors (DMS), *i.e.*, Mn-surface-functionalized GaN particles [1]. In this regard, suitable DMS materials are envisioned for many exciting applications in modern spintronics [2]. Herein, outlined is a study on another magnetic center, namely, iron Fe in the system with the GaN nanopowders.

Two GaN nanopowders with increased specific surface areas  $S_{\text{BET}}$  were prepared *via* the known anaerobic route [3] at 800 °C ( $S_{\text{BET}}$ , 58 m<sup>2</sup>/g) and 975 °C ( $S_{\text{BET}}$ , 17 m<sup>2</sup>/g) nitridation temperatures. The former material was phase-inhomogeneous/cubic GaN whereas the latter one was prevalingly hexagonal GaN. The powders were soaked in a hexane solution of iron precursor  $\text{Fe}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}_2$  and later vacuum-dried. Such GaN/Fe-precursor raw powders were pyrolyzed under flowing ammonia initially at 200 °C, 4 h and finally at 800 °C, 4 h to afford the target nitride nanopowders labeled, respectively, GaFeN\_800 and GaFeN\_975. The pyrolysis steps (i) enabled transamination with  $\text{NH}_3$  of amine groups and the formation of easily removable volatile  $\text{H}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}_2$  and (ii) favored the deamination of transient Fe-NH<sub>2</sub> groups towards metal nitrido species chemically bound on the GaN particles surface.

Magnetization of the nanopowders was measured as a function of magnetic field (up to 7 Tesla) and of temperature (2-300 K) using a superconducting quantum interference device magnetometer. Sample GaFeN\_800 was prevalingly paramagnetic obeying Curie's law. This was consistent with diluted iron centers thought to be built in the surface layer of GaN particles as previously observed in the system with manganese [1]. Sample GaFeN\_975 showed magnetization composed of the paramagnetic and ferromagnetic contributions. The latter component was likely due to thermal decomposition of some excess of the iron precursor to an extraneous ferromagnetic phase. The adjusted amounts of the paramagnetic magnetization correlated well with the specific surface area of the parent nanopowders.

The study demonstrates the feasibility of surface-functionalization of semiconducting GaN nanopowders with magnetic Fe-centers. The optimization of the specific surface area of GaN nanopowders and the amount of the Fe-precursor can afford purely paramagnetic materials.

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# From Magnetic Cubic Pre-kesterite to Semiconducting Tetragonal Kesterite $\text{Cu}_2\text{ZnSnS}_4$ via Mechanochemical Synthesis Route

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## ABSTRACT

The semiconducting tertiary metal sulfide  $\text{Cu(I)}_2\text{Zn(II)Sn(IV)S}_4$  (kesterite) has become in recent years a subject of a number of studies on affordable and environmental-friendly photovoltaics [1]. In this regard, development of an efficient synthesis method as well as clarification of important issues of kesterite's complex structural and optical properties are still open challenges to many concerned researchers in the materials science community.

Herein, presented is a report on a refinement of the known mechanochemical synthesis of kesterite from the elements upon high energy ball milling conditions [2, 3], which in our hands is tuned to make at ambient a pure cubic phase with the nominal  $\text{Cu}_2\text{ZnSnS}_4$  composition. The phase is tentatively called a pre-kesterite and it is shown by EPR to be magnetic. This is further corroborated by no detected copper and/or tin nuclear magnetic resonances during the attempted <sup>65</sup>Cu and/or <sup>119</sup>Sn MAS NMR determinations. Also, this material shows no well-defined absorption in the UV-vis range expected either for the plausible metal sulfides or the target semiconducting kesterite. The formation of magnetic Cu(II) centers and random site occupation of all the metal centers taking place in the mechanochemical synthesis step are proposed to account for the observed properties of pre-kesterite. Upon subsequent thermal treatment under argon at temperatures above 300 °C, preferably at 500 °C, the cubic phase is converted/rearranged to the tetragonal phase of kesterite. This is apparently accompanied by redox chemistry and resulting diamagnetic Cu(I) moieties. Such materials show now the expected <sup>65</sup>Cu and/or <sup>119</sup>Sn MAS NMR characteristics whereas their UV-vis spectra provide with the bandgap in the range of 1.4-1.5 eV typical for kesterite.

The interplay between the conditions of the mechanochemical milling step linked to the structural/magnetic properties of the pre-kesterite as well as the characteristics of the thermally treated kesterite, including the role of excess elemental sulfur along essential process stages, are the subjects of our on-going investigation of the system.

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# Ammonolytical Nitridation in the Binary Gallium Pnictide Systems [GaE+GaE']/ $\text{NH}_3$ (E, E' = As, P, Sb) Towards Polytype Specific GaN Nanopowders

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## ABSTRACT

We have quite recently reported on the convenient and efficient synthesis methods for making semiconducting gallium nitride GaN nanopowders by a single-step ammonolysis of any of the individual microcrystalline/monocrystalline gallium pnictides GaE (E = As [1], P [2], Sb [3]). In each case, a specific interplay of the thermodynamic and topochemical factors was crucial in deciding on the reaction outcome. Thermodynamic circumstances favored the formation of the stable h-GaN (hexagonal) whereas conditions supporting topochemistry yielded a certain proportion of the metastable c-GaN (cubic), especially, in the GaAs/ $\text{NH}_3$  system.

Herein, presented are results of the study on ammonolytical nitridation of the related binary pnictide systems (GaAs+GaP)/ $\text{NH}_3$ , (GaAs+GaSb)/ $\text{NH}_3$ , and (GaP+GaSb)/ $\text{NH}_3$ , GaE:GaE' = 1:1, mainly, as a function of the substrates grain size. In all these cases, complete nitridation under the selected conditions is achieved. Also, the substrate high energy ball milling results in lower conversion temperatures by ca. 200 °C compared to the manually ground option.

Specifically, in the system (GaAs+GaP)/ $\text{NH}_3$  the limiting component is GaP both in terms of the required conversion temperatures/times and the GaN product polytype make-up. The temperatures needed for the GaP-component nitridation higher than 900 °C result in the prevailing h-GaN. In the system (GaAs+GaSb)/ $\text{NH}_3$ , a rather unexpected persistence of GaAs up to 1000 °C (manually ground substrate) is observed whereas equally unexpected is the complete nitridation of GaSb already at 700 °C (ball milled substrate). Similarly as in the previous system, the predominant polytype in the product is h-GaN. In the system (GaP+GaSb)/ $\text{NH}_3$ , again, the limiting component is GaP persisting in the manually ground option up to 1000 °C. Here, the products are found to contain exclusively the stable h-GaN.

There are some synergistic effects in the nitridation of the binary systems compared with the related individual pnictide systems, which on overall favor the thermodynamically-supported reaction outcome.

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# Molecular Magnets: From Single Molecule to 3D Self-assembly

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## ABSTRACT

Recent investigation of ultrathin metal films with atomically well-defined thickness and high crystallinity has shown the existence of 2D superconductivity in a single atomic layer of Pb epitaxially grown on a Si(111) substrate [1].

As this system consists of a surface composed of heavy atoms, there also exists a strong Rashba spin-orbit coupling modifying the electronic properties. Combining this Pb monolayer with local magnetism makes it an ideal template to engineer and realize topological superconductivity [2]. Indeed, the introduction of magnetic impurities can induce the appearance of localized bound states in the 2D superconducting gap, known as Shiba states. Under some specific conditions, the magnetic interaction between several Shiba states in a either one-dimensional or two-dimensional array of magnetic impurities on the surface of a superconductor may realize new topological phases [3].

The atomic layer of Pb has different structural phases depending on the coverage around the monolayer range and the temperature. In particular, a reversible structural phase transition from a (1x1) phase to a ( $\sqrt{7}\times\sqrt{3}$ ) one occurs at about 250 K for a coverage of 1.20 ML. The low temperature ( $\sqrt{7}\times\sqrt{3}$ ) phase presents a superconducting transition at 1.5 K [1].

Magnetic phthalocyanines (Pc) are very promising metallo-organic molecules which can be used to introduce the above-mentioned local magnetism []. Moreover, Pcs' are known to form 2D self-assemblies on various metallic surfaces [5] and they can make it possible to tailor two-dimensional ordered magnetic structures, as we have already seen by STM.

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# Magnetic Dichroism in Soft X-rays at Ultra-low Temperature on DEIMOS Beamline (Synchrotron SOLEIL)

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## ABSTRACT

X-ray magnetic circular dichroism (XMCD) is a spectroscopy technique available in nearly all synchrotron radiation centres and is an extremely valuable tool in the study of magnetic properties of advanced materials. It is an element selective technique with orbital sensitivity capable to probe for magnetic properties of a specific element in a multi-elements sample. In the soft x-rays range XMCD is most sensitive to first atomic layers and is thus well adapted to study self-assembled, evaporated or isolated molecules on surface. Magnetically bistable molecules, known as Single Molecule Magnets (SMM) are attracting broad interest thanks to their potential technological applications in molecular spintronics and quantum computation. Self-assembled monolayer (SAM)-based protocols are among the most used techniques to achieve a bidimensional organization of these molecules adsorbed on surface and can also stabilize or even enhance SMM behaviour. Yet, until now their most original quantum properties have only been observed under 1 Kelvin. At Synchrotron SOLEIL, DEIMOS is a soft-ray beamline dedicated to natural and magnetic dichroism spectroscopies with a sample preparation environment optimized for surface physic and chemistry. Starting in January 2018, a new device will allow to measure down to 50 millikelvins.

# Helical Organization of Hydrogen-bonded Oligothiophenes: Impact on Photovoltaic Properties

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## ABSTRACT

Control over self-organization of  $\pi$ -conjugated molecules is essentially important in bulk-heterojunction organic photovoltaic (BHJ-OPV) devices, because their power conversion efficiency (PCE) depends on nanostructures of semiconducting donor and acceptor molecules. To control the nanostructures, use of supramolecular interaction such as hydrogen-bond is a promising strategy. We previously reported self-assembly of regioisomeric barbiturated oligo(hexylthiophene)s **3H** and **4H** (Fig. 1a). Compound **3H** formed nanorods via the formation of hydrogen-bonded cyclic hexamer, showing PCE = 3.0% in BHJ-OPV devices with PCBM.<sup>1,2</sup> In contrast, **4H** formed lamellae via the tapelike hydrogen-bonded supramolecular chains, showing lower performance (PCE = 0.4%) in comparison with **3H** because of microscopic phase separation with PCBM.<sup>3</sup>

Herein, we found that self-assembly of similar regioisomers **3B** and **4B** equipped with butyl chains (Fig. 1a) results in more prominent structure-dependence on device performance. STM study revealed that both compounds form tapelike hydrogen-bonded supramolecular chains at liquid–solid interface (Fig. 1b,c). AFM observation of self-organized **3B** and **4B** in nonpolar media revealed the formation of distinct nanostructures, i.e., helical fibers from **3B** and heavily bundled tapes from **4B**, respectively (Fig. 1d,e). Remarkably, BHJ-OPV devices fabricated using **3B** with PCBM showed much higher performance (PCE > 4%) in comparison with **4B** (PCE < 1.5%).<sup>4</sup>

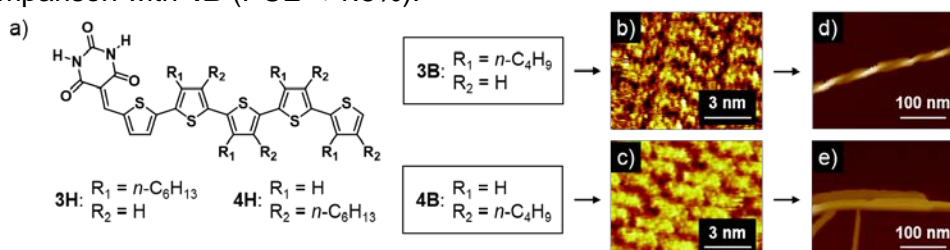


Fig. 1 a) Molecular structure of compounds **3H**, **4H**, **3B** and **4B**. b,c) STM images of b) **3B** and c) **4B** at 1-phenyloctane–HOPG interface. d,e) AFM images of d) **3B** and e) **4B** aggregates formed from toluene solution.

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# Low Temperature Synthesis of NiCoMn-mixed Hydroxide and Ternary NiCo-MnO<sub>2</sub> Nanocomposites and their Application as a Novel High Energy Supercapattery Device

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## ABSTRACT

Supercapacitors (SCs) are classified as emerging high power-delivery storage devices which are known to be able to hold much more electrical charge than standard parallel-plate capacitors. They are also easily able to discharge at a very fast rate in delivering the necessary high power as compared to batteries and thus can complement batteries in many domestic, commercial and industrial applications. [1-2].

In this study, NiCoMn-mixed hydroxide and ternary NiCo-MnO<sub>2</sub> electrode materials were successfully synthesised by a force-driven hydrolysis of hydrated nickel, cobalt and manganese nitrate salts at 40 °C for 2 h with an additional annealing step adopted in producing the NiCo-MnO<sub>2</sub> sample. The morphological, structural and compositional and textural characterization of the samples were obtained using scanning electron microscope (SEM), high-resolution transmission electron microscopy (HRTEM), X-ray powder diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and N<sub>2</sub> physisorption. The materials electrochemical performance in a three-electrode cell set-up using KOH electrolyte revealed an improved specific capacity ( $Q_s$ ) of 132.1mAh g<sup>-1</sup> for the annealed ternary metal oxide compared to the NiCoMn(OH)<sub>2</sub> with a  $Q_s$  of 118.05 mAh g<sup>-1</sup> at 0.5 A g<sup>-1</sup>. In addition, the ternary NiCo-MnO<sub>2</sub> electrode exhibited a better cycling stability compared to NiCoMn(OH)<sub>2</sub> electrode. Notably, an assembled NiCo-MnO<sub>2</sub>//Fe<sub>3</sub>C hybrid asymmetric supercapattery, displayed a specific capacitance of 130.67 F g<sup>-1</sup>, high energy and power densities of 48.83 Wh kg<sup>-1</sup> and 896.88 W kg<sup>-1</sup> at 1 A g<sup>-1</sup> respectively. An excellent cycling stability with a coulombic efficiency of 99.98% and capacitance retention of 96.78 % was recorded for up to 10,000 cycles within an operating voltage of 1.5 V, at a current density of 3 Ag<sup>-1</sup>

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# Hierarchical Engineering of 2D Self-assembled Porous Organic-based Nanoarchitectures on Metal Surfaces

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## ABSTRACT

Engineering novel atomic and molecular nanostructures on surfaces is a challenge in nanosciences. We develop new process to engineer novel two-dimensional porous nanoarchitectures based on molecular self-assembly. We show that novel porous hybrid nanoarchitectures can be engineered by mixing PTCDI molecule with ionic compounds. We fabricated three two-dimensional self-assembled hybrid PTCDI–NaCl nanoarchitectures (Fig.1). Scanning tunneling microscopy (STM) reveals that NaCl-dimers selectively interact with molecular N–H groups. [1,2]

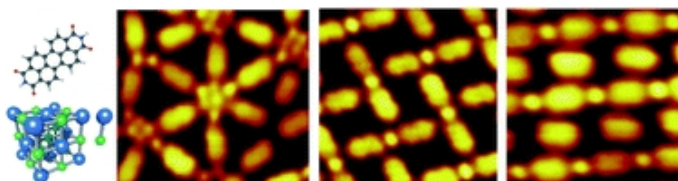


Fig. 1. Hierarchical engineering of self-assembled of PTCDI-NaCl porous nanoarchitectures. [1]

We also use on-surface synthesis to create patterned graphene nanoarchitectures via Ullmann coupling. We show that Star-shaped 1,3,5-Tris(4-iodophenyl)benzene molecules (Fig.2) form covalent polygonal nanoarchitectures at the gold surface step edges at low coverage. With coverage increasing two-dimensional halogen-bonded structures appear and grow on the surface terraces. At high coverage the competitive growth between the covalent and halogen-bonded nanoarchitectures leads to formation of a two-layer film above one monolayer deposition[3].

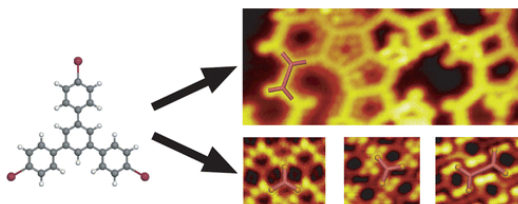


Fig. 2. On surface-synthesis of covalent structures versus engineering halogen-bonded nanoarchitectures. [3]

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# Characterization and Optimization of Hematite Nanorods Photoanodes Elaborated by Aqueous Chemical Growth

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## ABSTRACT

Solar water splitting offers long-term potential for sustainable hydrogen production with low environmental impact, *i.e.* low or no greenhouse gas emissions. During the photoelectrolysis process, electron – hole pairs are generated in insolated semiconductors, which will then participate to the water oxido-reduction reactions where O<sub>2</sub> is produced at the photoanode and H<sub>2</sub> at the photocathode [1]. Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), commonly known as rust, is a semiconductor material with a band gap of 2.15 eV allowing to absorb 40% of the solar spectrum which is quasi optimal for direct solar water splitting applications. The maximum expected photocurrent when hematite is used as photoanode is around 12.6 mA/cm<sup>2</sup> [2]. Photoanodes nanopatterning was shown to have multiple benefits: diminishes photo-charges recombination by adjusting the lateral sizes of nanostructures to the holes mean free path, increases the active surface at the photoanode/electrolyte interface, can change surface chemistry and in consequence surface photo-activity and kinetics [3].

Hematite continuous films of perpendicularly grown and perfectly defined iron oxide nanorods were deposited on FTO (Fluorine doped Tin Oxide) substrates by aqueous chemical growth (ACG) [4], a very affordable and technological viable method, needed for a rapid and easy transfer to industrial process. The samples were characterized using SEM (Scanning Electron Microscopy), XRD (X-Ray Diffraction), PEC (Photo-Electro-Chemical) measurements and STXM (Scanning Transmission X-Ray Microscopy). We report on correlations between the photocurrent values and films morphology, electronic structure and chemical composition as a function of deposition parameters like pH, time and air-annealing temperature. A significant increase of PEC activity was observed on photoanodes decorated with Au nanoparticles due to both electric conductivity increase and plasmonic effects [5].

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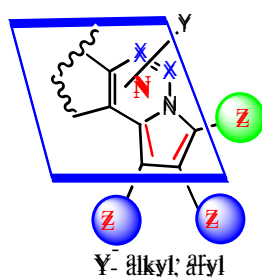
# Blue Organic Luminophores with Azaheterocyclic Skeleton: Synthesis and Properties

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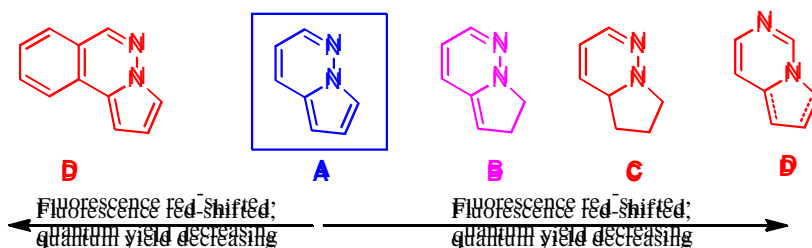
## ABSTRACT

Over the past decades, five and six member ring azaheterocyclic compounds have received considerable attention due to their important applications from pharmacological, industrial, and synthetic points of view. On the other, synthesis of highly fluorescent derivatives with extended  $\pi$ -conjugation continues to arouse strong interest because of their applications as sensors and biosensors, electroluminescent materials, lasers, and other optoelectronic devices



As part of our ongoing research in the field of azaheterocycles derivatives and in the field of blue luminous materials for practical applications, we present herein some core results obtained by our group concerning design and synthesis and of highly fluorescent derivatives with pyrrolo(di-) azine skeleton.

The synthesis was performed both under conventional thermal heating (TH) and nonconventional methods, using microwave (MW) and ultrasounds (US) irradiation. Remarkably, under MW and US irradiation the yields are higher, sometimes substantially, the reaction time decrease considerably and, the amount of used solvent is smaller. The structures have been elucidated by elemental and spectral analysis: IR, NMR (1H-, 13C- and 2D-experiments), X-ray analysis on monocrystal including. The fluorescence studies reveal that some fully aromatised pyrrolo- azine, dazines, bipyridyl and phenanthroline, have very interesting fluorescent properties, e.g.: pyrrolopyridazine derivatives are very intense blue emitters and have



high quantum yields (up to 90%), pyrrolophthalazine compounds are still intense blue emitters but the quantum yield is negligible. A certain influence of the substituents the pyrrolo ring concerning fluorescence was found. The number of the

substituents from the pyrrolo ring doesn't seem to play an important role regarding fluorescence but, with the increase of the number of substituents a certain hypsochromic shift in the absorption spectra was found. A feasible explication for all these behavior is presented.

**Acknowledgements.** Authors are thankful to CERNESIM for NMR experiments..

# Investigation by X-ray Natural Linear Dichroism (XNLD) and X-ray Magnetic Circular Dichroism (XMCD) towards Magnetic Properties of 6nm CsNiCr(CN)<sub>6</sub> Nanoparticles Single Layer Assembled on Graphite

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## ABSTRACT

From previous work by Mallah *et al.*<sup>[1-4]</sup>, we have synthesized bimetallic cyanide-bridged networks of Prussian Blue Analogues (**PBAs**) under the form of nanoparticles (**NPs**) of general formula Cs[Ni<sup>II</sup>Cr<sup>III</sup>(CN)<sub>6</sub>]. The present work investigates the magnetic properties of these **NPs** with 6 nm diameters assembled as single layer on Highly Oriented Pyrolytic Graphite (**HOPG**) substrate. Comparing to Prado's work<sup>[4]</sup>, a combination of angular dependent X-ray absorption spectroscopy (**XAS**) and advanced theoretical analysis using Ligand Field Multiplet (**LFM**) calculations<sup>[5-6]</sup> has been carried out, which allows us to determine the local structural distortion around Ni<sup>II</sup> and the corresponding magnetic anisotropy.

In this work, all spectra have been recorded on **DEIMOS** beamline at Synchrotron **SOLEIL**. These data elucidate the relations among X-ray Natural Linear Dichroism (**XNLD**) and X-ray Magnetic Circular Dichroism (**XMCD**) spectra recorded at the Cr<sup>3+</sup> and Ni<sup>2+</sup> L<sub>2,3</sub> edges concerning structural and magnetic information. **XNLD** experimental data and the associated theoretical analysis show that the Ni local environment is not cubic but an elongation along the C<sub>4</sub> axis of the octahedral coordination sphere of nickel ions. The analysis of the **XMCD** data coupled to the atomic magnetization curves allow the determination of the magnetic anisotropy that is fully consistent with the geometric environment determined by **XNLD**. We conclude that the **NPs** possess an easy plane of magnetization parallel to the plane of the monolayer.

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