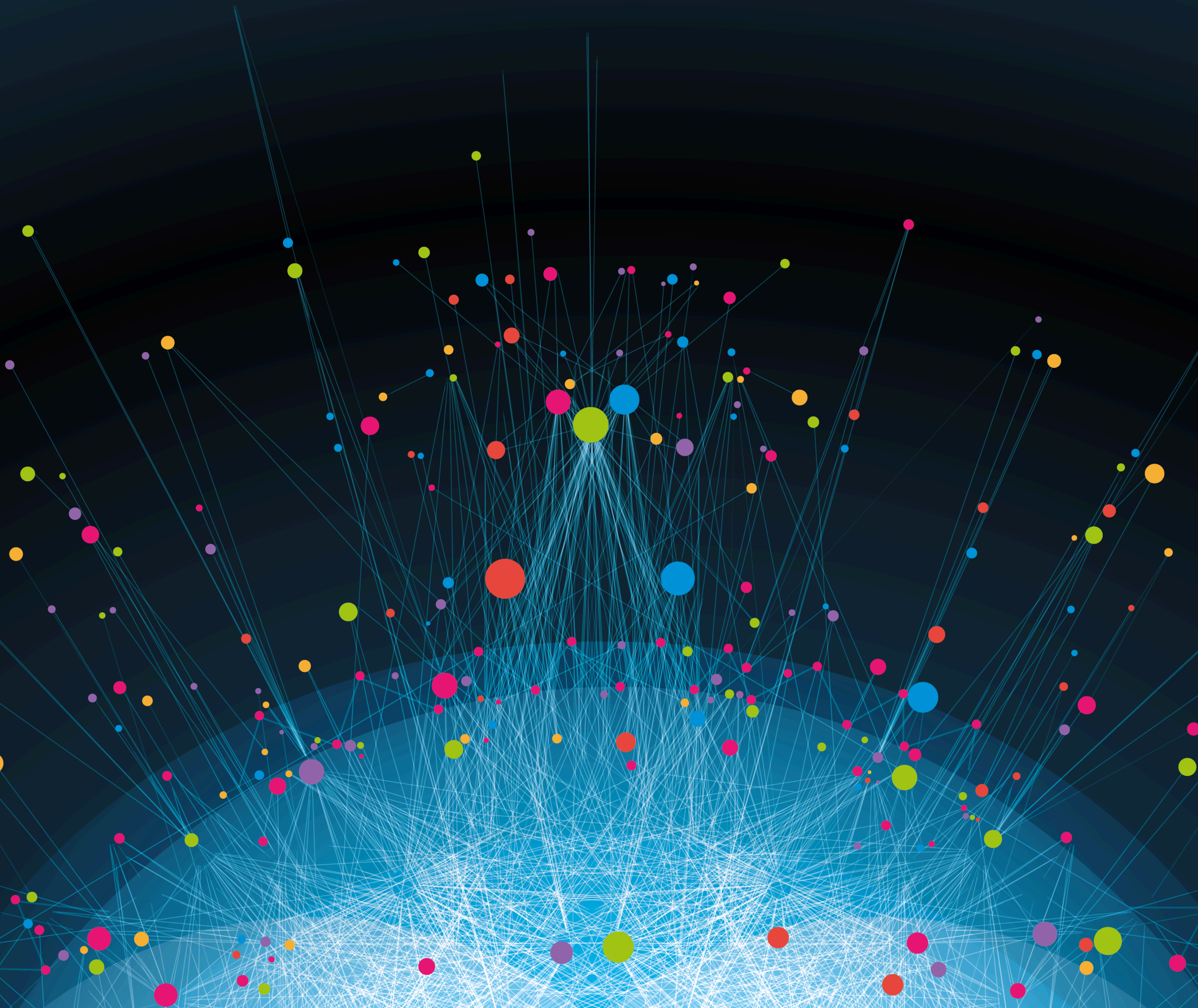
BOOK
OF
ABSTRACTS
Oral Presentations



Nanomaterials for energy

Wednesday March 19th

10:30 A.M. - 12:30 A.M.

ROOM AB

Program of the session :

Chairs: Sophie CASSAIGNON

HOUR	NAME	TITLE
10:30	**Frederic SAUVAGE** **LRCS - CNRS**	**In situ characterization techniques for understanding degradation in hybrid halide perovskites**
11:00	Mehrdad NIKRAVECH Univ. Sorbonne - LSPM	A comparative study on the role of Al versus Zn doping materials in manganese oxide as the cathode material, synthesized by spray plasma CVD, for zinc ion batteries.
11:15	Grégoire MAGAGNIN INL - CNRS	Antiferroelectric fluorite-based capacitors for ultra-high energy storage density applications
11:30	Kazimova NARGIZ LCC CNRS	Nanostructured catalysts for active and sustainable fuel cell cathodes
11:45	Fenzi LUIGI CINaM - CNRS	Towards monocrystalline nanowire transparent electrodes for photovoltaics
12:00	Odilon WAMBA-TCHIO LCPME - CNRS	Vertically oriented mesoporous silica film as host of a new polymeric material based on hybrid polyoxometalate for electrocatalytic application
12:15	Eugenie PARIENTE ICMCB/LOMA - Univ. Bordeaux	Design of metal-semiconductor heteronanostructures by laser photodeposition: Elaboration, growth control and modeling

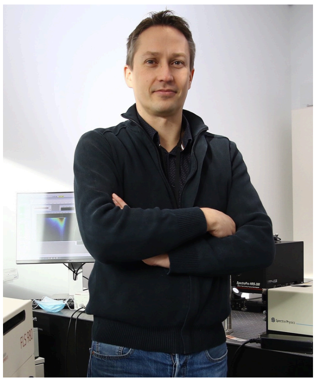
S1

IDENTITY

Frédéric SAUVAGE (CNRS - LRCS, Amiens)

https://www.lrcs.u-picardie.fr/en/

frederic.sauvage@u-picardie.fr



Short Biography

Research Director at CNRS. Joined CNRS in 2010 as a Research Scientist, promoted to Research Director in 2019. Founder and head of the Molecular Photovoltaics and Photocatalysis group at LRCS. Recipient of a 2023 ERC Advanced Grant “GEMINI” Coordinator of H2020 IMPRESSIVE (transparent/colorless PV development), several ANR and industrial projects Co-founder and CTO of G-LYTE since 2019 aiming at development / industrialization of high-performance indoor PV cells for powering consumer electronics. Founder and CTO of CRYSTAL Energy in 2024 aiming at industrializing transparent and colourless PV windows Recipient of Le Point's Innovator Award 2025, REV3 award by ADEME and is currently CNRS Innovation Ambassador. Author/Co-author of 110 publications, 9 patents

Title of Oral Presentation

In situ characterization techniques for understanding degradation in hybrid halide perovskites

Keywords

Lead halide perovskite, stability, photovoltaic, in situ characterization techniques

Abstract of Oral Presentation

Hybrid halide perovskite has established its credibility as high performance thin film photovoltaic technology. In only one-decade, the hybrid organic-inorganic halide perovskite solar cell achieved to compete with all mature crystalline technologies, by reaching a certified 26.7 % power conversion efficiency (PCE) on cells and 20.6 % PCE on small modules. Perovskite's strength stem from their remarkable opto-electronic properties. However, the technology still requires significant attentions regarding stability, in particular rapid structural and electronic degradation can be engendered when exposed to various external stressors (temperature1, humidity2, light3, electrical bias4). To cope with the long-term stability issue, it is a paramount to precisely understand the multiple degradation pathways of the perovskite upon and during the external stressing. To this end, in situ or operando characterization techniques are central tools. In this communication, we will be discussing the degradation of different perovskite composition on the basis of humidity or temperature-controlled in situ x-ray diffraction and corroborated with in situ electron spin resonance spectroscopy and in situ transmission electron microscopy. For example, one key finding which we will discuss is that α-FAPbI3 degradation is substantially accelerated when temperature is combined to illumination and when it is interfaced with the extraction layers, and, second the existence of a temperature gap region which takes place only under illumination involving an intermediate stage between the thermal-induced perovskite degradation and the formation of PbI2 by-product.5

Acknowledgement

Horizon Europe "LAPERITIVO" project under the grant agreement number 101147311, ERC AdG 2023 "GEMINI" under grant agreement 101141284 and ANR MINOTAURE project, Grant # ANR-22-PETA-0015

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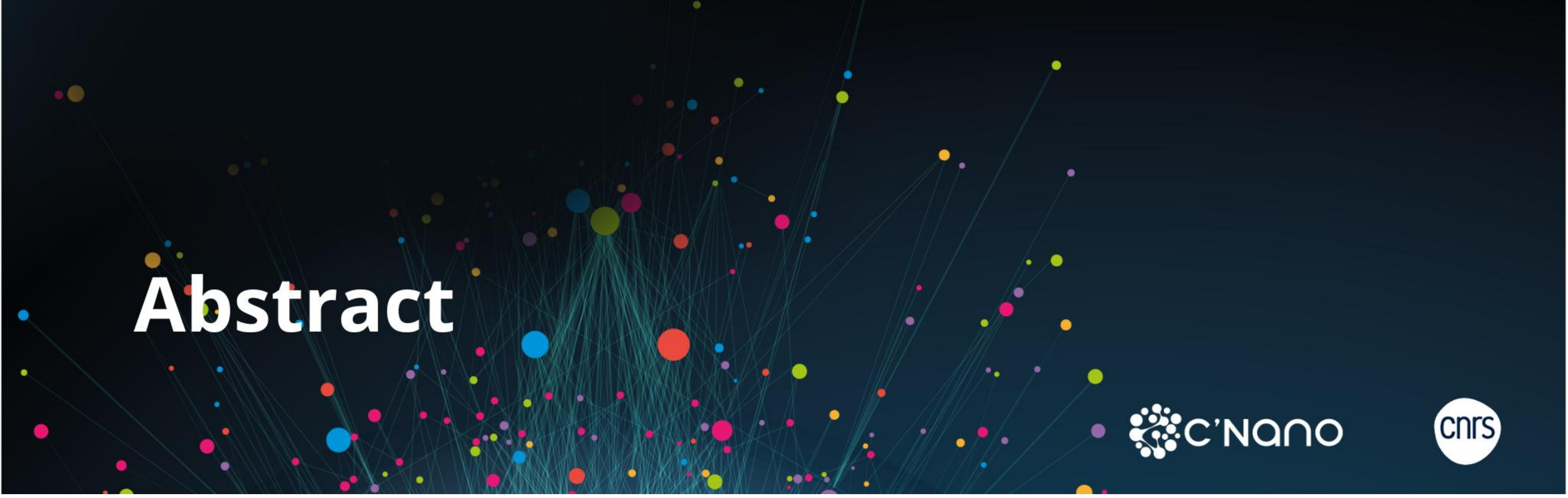

Thematic Session: Couches minces fonctionnelles, Nanostructures & Matériaux 2D, Nanomatériaux pour l'énergie

Disciplinary fields involved (Material science, Plasma CVD, Electrochemistry …)**:**
Keywords (max. 4-5)**:** Zinc-Ion Batteries, Low pressure Plasma, MnO_2 thin film, cathode, Energy

A comparative study on the role of Al versus Zn doping materials in manganese oxide as the cathode material, synthesized by spray plasma CVD, for zinc ion batteries.

Yacouba Seydi[1], Lounis Hakim Bekkar[1], Alex Lemarchand[1], Cyrille Bazin[2], Hubert Perrot[2], Oriana Haddad[1], Mamadou Traore[1] , Mehrdad Nikravech[1]

1. *Université Sorbonne Paris Nord, UPR CNRS 3407, Laboratoire des Sciences des Procédés et des Matériaux LSPM, 93430 Villetaneuse, France*
2. *Sorbonne Université, UMR CNRS 8235, Laboratoire Interfaces et Systèmes Electrochimiques LISE, 4, place Jussieu, F-75005 Paris, France*

Abstract

To mitigate climate changes, the development of renewable intermittent energies implies efficient and ecological energy storage systems.

Aqueous zinc-ion batteries (ZIBs) are considered attractive due to low cost, relative abundance and safety.

Manganese oxide MnO_2 is considered as the promising cathode materials for aqueous ZIBs. However phase transition reactions and dissolution of MnO_2 in the aqueous electrolyte reduces the electrical performance of batteries, in terms of the electrical capacity and the number of charge-discharge cycles, hindering industrial applications.

To meet this challenge, defect engineering by doping with suitable cations and by creation of oxygen vacancies is known to improve the MnO_2 structures and facilitate the intercalation and desintercalation of zinc ions in the structures.

In this work we present a spray Plasma CVD method to elaborate crystallized nano-structures with accurate control of composition at room temperature. This method has demonstrated the role of oxidant and reduction gases on the properties of the cathode materials. SEM, XRD and AFM were used to characterize the structural properties of materials while cyclic voltammetry was used to measure the electrochemical properties of the deposited layers. The electrical capacity of the batteries varies between 140 and 250 mAh/g depending on the elaboration's conditions, while the number of C/D cycles reached more than 3500c without any degradation.

Abstract

Currently Al- intercalated MnO_2 cathodes are investigated to study the influence of aluminum as doping material. The physical characteristic and electrochemical properties of these materials will be presented and compared to $ZnMn_2O_4$ cathode materials.

References (max. 5):

Zhang, H.; Wang, J.; Liu, Q.; He, W.; Lai, Z.; Zhang, X.; Yu, M.; Tong, Y.; Lu, X. Extracting Oxygen Anions from ZnMn2O4: Robust Cathode for Flexible All-Solid-State Zn-Ion Batteries. *Energy Storage Materials* **2019**, *21*, 154–161. https://doi.org/10.1016/j.ensm.2018.12.019.

Zhao, Y.; Zhu, Y.; Zhang, X. Challenges and Perspectives for Manganese-Based Oxides for Advanced Aqueous Zinc-Ion Batteries. *InfoMat* **2020**, *2* (2), 237–260. https://doi.org/10.1002/inf2.12042.

Cong Chen a, Minjie Shi a,, Yue Zhao a, Cheng Yang b, Liping Zhao b, Chao Yan a, Al-Intercalated MnO2 cathode with reversible phase transition for aqueous Zn-Ion batteries. Chemical Engineering Journal 422 (2021)130375, https://doi.org/10.1016/j.cej.2021.130375

Kamal Baba • Claudia Lazzaroni • Mehrdad Nikravech “Growth of ZnO Thin Films by Spray Plasma Technique: Correlation Between Spectroscopic Measurements and Film Properties”, Plasma Chem Plasma Process (2014) DOI 10.1007/s11090-014-9570-0.

Nikravech, M.; Bekkar, L. H. « Procédé De Synthèse De Couches Cristallines D’oxydes
De Manganèse, En Particulier Pour Batteries Rechargeables », May 2, **2024**. Patent n° WO/2024/089193.

Acknowledgement:

The authors acknowledge financial support from the federative research structure NAP Mosaic from Université Sorbonne Paris Nord. They also thank Sarah Din from Laboratoire des Sciences des Procédés et des Matériaux for the technical help.

Abstract

Thematic Session: Nanomaterials for Energy
Disciplinary fields involved: Physics, Electronics, Material Science, Condensed-Matter Science
Keywords: Antiferroelectric, Ferroelectric, Energy Storage Density, Electrostatic capacitors

Antiferroelectric fluorite-based capacitors for ultra-high energy storage density applications

Jordan Bouaziz[1], Grégoire Magagnin[1], Martine Le Berre[1], Sara Gonzalez[1], Ingrid Cañero Infante[1], Damien Deleruyelle[1], Bertrand Vilquin[1]

1. *Ecole Centrale de Lyon, INSA Lyon, CNRS, Universite Claude Bernard Lyon 1, CPE Lyon, INL, UMR5270, 69130 Ecully, France*

For over a decade, ferroelectric and antiferroelectric ultra-thin films of fluorite-structured materials have drawn significant attention for applications requiring high integration density [1]. Among all other dopants, it has been shown that zirconium allows the lowest annealing temperature to crystallize the orthorhombic phase in polycrystalline $Hf_{1-x}Zr_xO_2$ (HZO) thin films, responsible for ferroelectricity [2]. Decreasing the annealing temperature allows the growth of CMOS-compatible thin films. At high doping, HZO layers can become antiferroelectric (AFE) [3].

Antiferroelectric HZO holds significant promise for a large range of applications owing to its potential for high energy storage density (ESD) and high efficiency. The performance and properties of Metal/Insulator/Metal (MIM) capacitors will be presented. The AFE insulator is grown by Plasma-Enhanced Atomic Layer Deposition (PEALD). Several processing conditions are investigated (annealing temperature, thin film thickness, measurement conditions) to reach high energy storage properties.

Our results show one of the highest, if not the highest, ESD ever reported so far of 125 mJ/cm^3 for a ZrO_2 thin film of 10.3 nm. Efficiency and endurance of the MIM stack can also be optimized through material engineering and a wake-up effect is also observed for ZrO_2 thin films, which is rarely observed for ZrO_2 layers. The performances are extremely encouraging for attaining ultra-high energy storage density in multilayer stacks.

References:
[1] T. S. Böscke, J. Müller, D. Bräuhaus, U. Schröder, U. Böttger, Appl Phys Lett. 99, 102903 (2011).
[2] J. Müller et al., Appl Phys Lett. 99, 112901 (2011).
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Acknowledgement:

Abstract

This work was carried out on the NanoLyon technology platform and implemented within the NanOx4EStor project. This NanOx4EStor project has received funding under the Joint Call 2021 of the M-ERA.NET3, an ERANET Cofund supported by the European Union's Horizon 2020 research and innovation program under Grant Agreement No. 958174. This work was supported by the Portuguese Foundation for Science and Technology (FCT) in the framework of M-ERA.NET NanOx4EStor Contract No. M-ERA-NET3/0003/2021; by the Executive Agency for Higher Education, Research, Development, and Innovation Funding (UEFISCDI); and by the Agence Nationale de la Recherche (ANR) under Contract No. ANR-22-MER3-0004-01.

Thematic Session : Nanomaterials for energy

Disciplinary fields involved : Chemistry

Keywords : Nanoparticles, organometallic chemistry, fuel cell, oxygen reduction reaction

Nanostructured catalysts for active and sustainable fuel cell cathodes

Nargiz Kazimova[1*], Nuria Romero[1], Sara Cavaliere[2], Marjorie Cavarroc[3], Karine Philipot[1]

1. *LCC-CNRS, Université de Toulouse, UPS, Toulouse, 31077, France*
2. *ICGM-CNRS, Université de Montpellier, ENSCM, Montpellier, 34095, France*
3. *SAFRAN-Tech, Materials and Processes Department, Magny-Les-Hameux, 78114, France*

**nargiz.kazimova@lcc-toulouse.fr*

Depletion of fossil fuels and environmental pollution raised interest in new technologies for sustainable energy production, conversion, and storage, among which fuel cell technology is greatly studied, in both academia and industry. Proton exchange membrane fuel cells (PEMFCs) are reputed energy devices, due to their high conversion efficiency and low environmental pollution.[1] Nowadays, Pt-based catalysts exhibit the best electrocatalytic activity towards oxygen reduction reaction (ORR), but enhancing their catalytic efficiency and reducing costs are essential for commercializing fuel cell technology.[2]

Our interest relies with the development of Pt-based nanoalloys[2,4] *via* solution organometallic chemistry approach.[3] This approach allows control over the composition, structure, and morphology of metal nanoparticles, and could lead to increased catalytic activity and long-term stability by revealing more active sites of the catalyst. Additionally, the ability to alloy with a range of metals for producing bimetallic compounds is one of the key advantages of this approach.

In this communication, the synthesis of Pt-based nanoparticles and their characterization by state-of-the-art techniques such as ICP, EA, TGA, XRD, IR, TEM and HR-TEM will be described. The influence of the Pt complexes used as precursors and of the reaction conditions on the morphology of the Pt nanoparticles will be shown. The obtained nanostructures offer interesting starting materials to incorporate other metals, such as transition or rare earth metals, in order to have nanoalloys and study their performance in ORR in comparison to pure Pt catalysts.

References:

[1] X. Tang, D. Fang, L. Qu, D. Xu, X. Qin, B. Qin, W. Song, Z. Shao, B. Yi, Chin. J. Catal. 2019, 40, 504–514.
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Acknowledgement:

We would like to thank CNRS, RHyO, Region Occitanie and SAFRAN for funding this project. We would like to thank technical stuff for help in characterization.

Thematic Session: Nanochemistry & Nanoparticles
Disciplinary fields involved: Chemistry, Physics
Keywords: Nanocubes, nanoimprint, transparent electrodes, monocrystalline nanowires

Towards monocrystalline nanowire transparent electrodes for photovoltaics

Luigi Fenzi[1], Beniamino Sciacca[1]

1. *Centre Interdisciplinaire de Nanoscience de Marseille (CINaM), UMR 7325, Nano Matériaux Synthèses et Propriétés, CNRS - Aix Marseille Université, Luminy Campus, Marseille, France*

Transparent electrodes play a crucial role in various optoelectronic devices such as solar cells, photodetectors, LEDs, and touch screens. The efficiency of these devices relies heavily on the transparent electrodes' ability to transport electrons while maintaining excellent photon transparency with minimal absorption and reflection.

High-quality transparent electrodes are typically produced using energy-intensive methods, involving high temperatures and vacuum conditions, often rendering them incompatible with flexible substrates.

Metal nanogrids emerged as a promising alternative to metal oxides such as indium tin oxide[1].

The large conductivity of metals allows efficient conduction of electrons, and the holes in the grid allow transparency[2].

Here I will present an entirely bottom-up approach to making transparent electrodes using colloidal building blocks with nanometric dimensions. This approach aims to minimize environmental impact and cost, and enhance compatibility with flexible substrates.

Colloidal metal nanocubes are transferred by contact printing on a transparent substrate and then arranged in a grid pattern through nanoimprint lithography (NIL)[1,3].

This is achieved by a pre-patterned flexible PDMS mold that pushes the nanocubes from their initial random position to the grid trenches present in the mold.

The present work will (i) show how different parameters in the NIL method (PVP thickness, PDMS composition) impact the quality of the assembly, (ii) explore different approaches to weld adjacent nanocubes and achieve continuous conducting grids, and (iii) characterise the grids' optoelectronic performance.

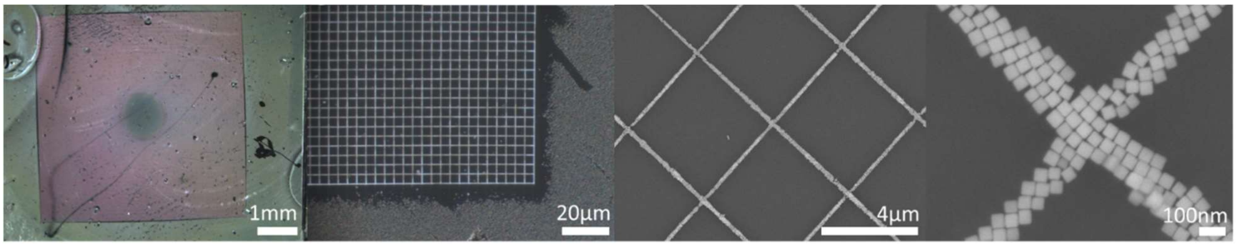


Figure 1: Ag nanocubes assembled in a grid structure (pitch=4µm, width=210nm) on a glass substrate[1,2].

References:

[1] A. Capitaine, B. Sciacca et al., “Nanoparticle Imprint Lithography: From Nanoscale Metrology to Printable Metallic Grids,” ACS Nano 2023 17 (10), 9361-9373.

[2] P. Bellchambers et al., Advanced Materials 2023, 35, DOI 10.1002/adma.202300166.

[3] H. Agrawal, E. Garnett, “Nanocube Imprint Lithography”, ACS Nano 2020, 14, 11009−11016.

Acknowledgements:

The authors thank D.Chaudanson and A. Altié for support with SEM characterization, and F. Bedu for support with e-beam lithography. B.S. acknowledges SOLNIL and the Région Sud - Provence-Alpes-Côte d'Azur for funding.

Thematic Session: Nanomaterials for energy

Disciplinary fields involved: Electrosynthesis, Mesoporous materials, Electrocatalysis

Keywords: Hybrid polyoxometalate, vertically oriented silica films, polymeric material

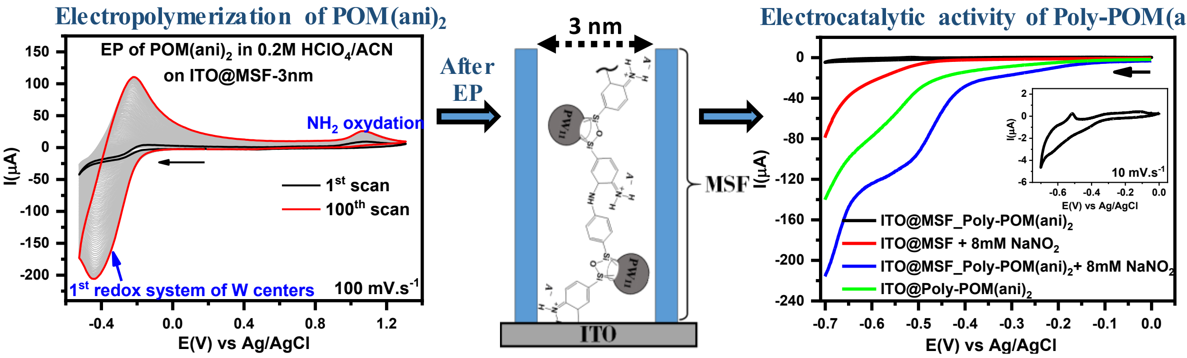
Vertically oriented mesoporous silica film as host of a new polymeric material based on hybrid polyoxometalate for electrocatalytic application

Odilon Wamba-Tchio [1,2], Alain Walcarius [1], Israël Mbomekalle [2] and Neus Vilà [1]

1. *Laboratoire de Chimie Physique et Microbiologie pour les Matériaux et l'Environnement, Université de Lorraine, Villers-lès-Nancy, France*
2. *Institut de Chimie Physique, Université Paris-Saclay, Orsay, France*

Abstract

A hybrid polyoxometalate ($(TBA)_3PW_{11}(SiC_6H_5NH_2)_2O$ named POM(ani)$_2$) has been electropolymerized within the mesochannels of vertically oriented mesoporous silica films (MSFs) prepared on ITO surface (ITO@MSF). The electrochemical characterizations of the ITO@MSF after electropolymerization, coupled with some physicochemical characterizations (TEM/EDX, GISAXS, XPS and IR spectroscopies) have evidenced the formation of a polymeric material (Poly-POM(ani)$_2$)) within the mesochannels, which kept their vertical orientation during the process. This new polymeric material confined in MSFs have been used for the electrocatalytic reduction of nitrite ions knowing the great ability of POMs for such applications.[1,2] The results showed that in comparison with MSFs before polymerization and with Poly-POM(ani)$_2$ synthesized on bare ITO, the electrocatalytic activity with MSFs after polymerization is highly enhanced regarding the increase of the cathodic current related to nitrite reduction and the positive shift of the onset potential (around 340mV). This behavior highlights the fact that the vertical distribution of closely unit of POM along the polymer chain makes them available for the electrocatalytic process.



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(1) Teillout, A. L., de Oliveira, P., Marrot, J., Howell, R. C., Vilà, N., Walcarius, A., & Mbomekallé, I. M. (2019). *Inorganics*, *7*(2), 15

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Acknowledgements:

The authors acknowledge financial support from the ANR through the project (ANR-20- 888CE09-0004).

Thematic Session: Nanochemistry, nanomaterials
Disciplinary fields involved: Chemistry
Keywords: Nanoparticle synthesis; photodeposition; heterodimers; redox reaction.

Design of metal-semiconductor heteronanostructures by laser photodeposition: Elaboration, growth control and modeling

Eugénie Pariente,[1,2] Fenghuan Zhao,[1,2] Kévin Zimny,[1,2] Justine Quinet,[3] Thomas Cottineau,[3] Jean-Pierre Delville,[2] Marie-Hélène Delville[1]

1. Univ. Bordeaux, CNRS, Bordeaux INP, ICMCB, UMR 5026, Pessac 33600, France
2. Univ. Bordeaux, CNRS, LOMA, UMR 5798, Talence 33400, France
3. Univ. Strasbourg, CNRS, ICPEES, UMR 7515, Strasbourg 67200, France

Colloidal metal-semiconductor (M-SC) nanocrystals have recently attracted much attention due to their excellent performance in photocatalysis. The enhanced efficiency of solar-to-fuel conversion is mainly attributed to the highly efficient separation of photo-excited electrons and holes and improved light harvesting. Although metal oxides (TiO_2, ZnO) exhibit excellent stability and photocatalytic activities, their large bandgaps limit their efficiencies to the small UV range of the solar spectrum[1]. Hybrid metal-semiconductor photocatalysts are potential solutions to solve this problem.

To achieve this, we present an innovative approach, that, rather than relying on a conventional UV lamp, uses a laser beam to efficiently photoactivate redox reactions of active ions at the surface of SCs, such as TiO_2 nanoparticles (NPs) in water, leading to the formation of heterodimers[1]. First, we demonstrate that the growth and the size of gold nanodots on TiO_2 can be precisely controlled by varying the reaction parameters[2]. Then we focused on bipyramidal anatase TiO_2 [3] to compare their photoefficiency with that of spheroidal TiO_2 NPs [4]. To check whether defined facets on the TiO_2 NPs increase the photocatalytic activity of the nanoheterodimers, facetted TiO_2 with controlled percentages of {101} and {001} is successfully synthesized and characterized. The photoreduction of different metals and the photooxidation of metal oxides on a specific facet of TiO_2 NPs are investigated. Their growth and their location on the TiO_2 NPs are studied and controlled. Preliminary tests of the photocatalytic activity of these new nanomaterials are performed using water-splitting experiments and show promising results.

References

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(3) Mino, L. *et al. ACS Applied Nano Materials* **2018**, *1* (9), 5355-5365. DOI: 10.1021/acsanm.8b01477.
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François Weill and Sonia Buffière (HR-TEM characterizations), Thierry Toupance (ISM), Miquel Torras
Interdisciplinary scholarship, université de Bordeaux, MESRI

Nanomaterials for energy

Wednesday March 19th

4:30 P.M. - 6:30 P.M.

ROOM AB

Program of the session :

Chairs: Valérie KELLER

HOUR	NAME	TITLE
16:30	**Gabriel LOGET** **ISM - CNRS**	**Matter and materials made from metallic nanoparticles**
17:00	Ali DABBOUS CINaM - CNRS	Bipolar Membranes Electrolyzers with Controlled Nanoparticles Assembly for a Well Compact and Thickness-Controlled Catalytic Layer.
17:15	Olivier DURUPHTY LCMCP - Sorbonne Univ.	Design and comparison of different oxide based photoanodes for water oxidation using various sol-gel approaches
17:30	Leila HAMMOUD LPCNO - Univ. Toulouse	Size-controlled Au and Pt nanoparticles for enhanced CO2, photoreduction with water under visible light
17:45	Soline BEITONE LMGP - UGA	Self-Supported Cu2O Nanowire Heterojunction Membranes for Photocatalysis and CO2, Reduction
18:00	Liudmila TRATSIUK UTT - Univ Troyes	Effects of heat and hot electron generations in ultrafast regime in plasmon-driven chemical reaction
18:15		

S2

IDENTITY

Gabriel LOGET (CNRS - ISM, Bordeaux)

gabriel.loget@cnrs.fr

Short Biography

Gabriel Loget is a CNRS researcher. He received his PhD in Physical Chemistry from the University of Bordeaux (Prof. A. Kuhn - 2012). After that, he performed a postdoctoral stay at the University of California, Irvine in the group of Prof. Robert M. Corn. In 2014, he was awarded an Alexander-von-Humboldt postdoctoral fellowship for doing his research at the Friedrich-Alexander Universität of Erlangen-Nürnberg in the group of Prof. Patrik Schmuki. In 2015, he joined the CNRS as a researcher at the Institut des Sciences Chimiques de Rennes (2015-2023) and, then, at the Institut des Sciences Moléculaires (NSysA group, from 2024). He has received several awards including the DCP “Innovation Prize” of the SCF. His research interests are electrochemistry and material sciences for energy conversion.

Title of Oral Presentation

Nanostructured photoelectrodes for solar H2 production

Keywords

Photoelectrocatalysis, Hydrogen, Urea, Photochemistry, Sun

Abstract of Oral Presentation

Although the integration of solar and wind energies in electrical grids is considerably growing worldwide, a major concern in employing these energy sources to a much larger extent is their intermittency and their diffuse geographic distribution. A solution to solve these two issues is the conversion of renewables into a carbon-free energy carrier that would allow the storage of energy and its distribution on-site and on-demand. Hydrogen (H2) has long been considered a highly promising energy carrier to fulfill this challenge. In this view, solar and wind energies can be converted into H2, which would ensure: energy storage as well as distribution and conversion in fuel cells, devices that readily convert H2 into electricity with water being the only by-product.[1] To this goal, H2 needs to be generated by the conversion of renewable energies through a zero-emission process. This is possible by coupling water electrolysis to a renewable source of energy to yield a completely clean and scalable process that generates highly pure H2 only from water.

In this contribution, I will describe the recent progress of our group[2] in the preparation and study of photoanodes for the oxygen evolution reaction (OER) and the urea oxidation reaction (UOR), which are two counter reactions that can be used to obtain electrons for H2 production. This will include approaches based on nanoelectrodeposition[3], electrodissolution[4] and hydrothermal synthesis.[5] I will also discuss the coupling of efficient nanostructured oxidation catalysts with tandem solar cells.

Acknowledgement

ANR, GPR PPM (Univ. Bordeaux), Fondation Grand Ouest, GDR Solar Fuels

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Thematic Session (Nanomaterials for energy)
Disciplinary fields involved (Nanomaterials, Thin films, Electrochemistry, Catalysis, Energy)
Keywords (Nanoparticles' assembly, Langmuir–Blodgett, Bipolar Membrane, water dissociation)

Bipolar Membranes Electrolyzers with Controlled Nanoparticles assembly for a well compact and thickness-controlled catalytic layer.

Ali Dabbous[1], Carlos G. Rodellar[2], Muhammad L Fajri[1], Sebastian Z. Oener[2], Beniamino Sciacca[1]

1. *Aix Marseille Univ, CNRS, CINaM UMR 7325, 13288 Marseille, France*
2. *Department of Interface Science, Fritz-Haber Institute of the Max Planck Society, Berlin, Germany*

Bipolar membrane electrolyzers (BPMEs) are an emerging technique used to drive water dissociation (WD) reaction[1,2](Fig 1A). The efficiency of WD relies on the activity of the catalytic layers coating the membranes[3,4]. However, up to date, no detailed studies have been reported on the optimization of these catalytic layers and their influence on the WD process. Commonly, spray coating (SC) is used for applying this layer, but it leads to substantial roughness and not well-defined thickness. In this work, we investigate the role of the structural properties of the WD catalytic layer, such as the catalyst coverage and the layer thickness, by preparing a well-compact layer with controlled thickness. For our targeted catalytic process, we will be using small (~3 nm SnO_2 NPs as the best model catalyst) metal oxide catalytic nanoparticles. Compact layers with controlled structure could be achieved using certain NPs' assembly strategies. However, the assembly of small-sized NPs in compact layers in experimental conditions compatible with polymeric membranes (low temperature, friendly solvents…) is challenging. In our approach, we use the Langmuir–Blodgett (LB)[4] method to prepare thin films of highly organized catalytic NPs. The LB process enables the NPs to be packed tightly and uniformly at the air-water interface in experimental conditions compatible with ion-exchange membranes. This allows us to fabricate smooth WD layers (Fig 1B) with precise thickness control. These LB coated membranes are tested in water dissociation conditions, exhibiting superior performance reaching almost 3 times higher performance relative to spray coated membranes with the same catalysts (Fig 1C). Moreover, the investigation of the catalytic layer thickness shows better activity in the case of thinner layers over the thicker ones by achieving a current density of ~1000 mA cm^{-2} in specific cases at relatively low overpotentials (300 mV).

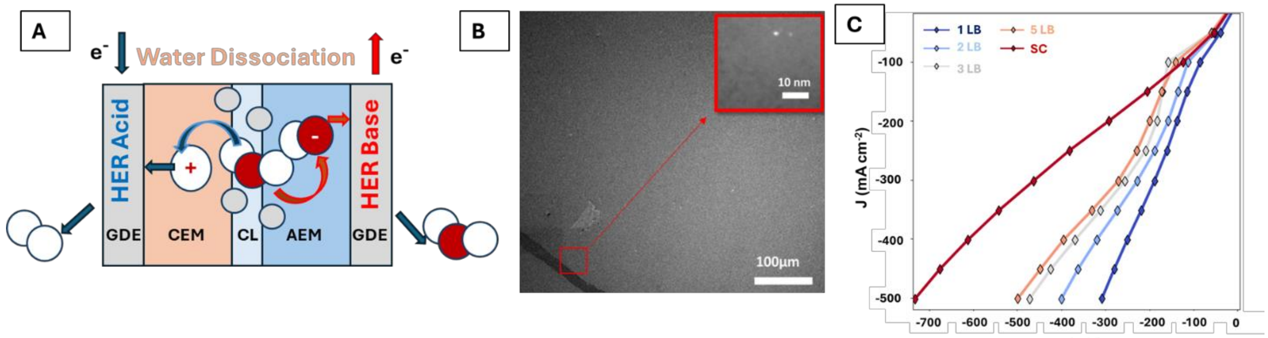

Figure 1: A) Schematic representation of water dissociation in the BPM. B) SEM of the Catalytic layer film prepared by LB. C) Selected electrochemical results of the water dissociation with different catalytic layers.

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Acknowledgement: This work was supported by the French National Research Agency ANR (project Projet-ANR-22-CE92-0023) and the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)–505677835.

Thematic Session: Nanomaterials for energy
Disciplinary fields involved: Chemistry
Keywords (max. 4-5)**: Photoanode, Sol-gel, Oxides, polymorphism**

Design and comparison of different oxide based photoanodes for water oxidation using various sol-gel approaches

Olivier Durupthy[1], Christel Laberty-Robert[1], Adeline Blot[1], Antoine Deswazière[1]

1. *Laboratoire de Chimie de la Matière Condensée de Paris, Sorbonne Université, CNRS, Paris France*

Photoelectrochemical water-splitting is a clean way to produce dihydrogen, by directly convert solar energy into chemical energy using photo-sensitive semi-conductors as electrolysis electrodes. The main bottleneck in the development of performant water-splitting tandem cells is the conception of an efficient and stable photoanode. Indeed, the oxidation of water (OER, oxygen evolution reaction) is the least favourable reaction compare to the reduction. The photoanode material must fulfil several criteria: band alignment allowing the OER reaction, absorption of light radiation in the UV-visible range, fast charge transport and finally durability in aqueous media. [1,2]

Through different materials we have investigated two sol-gel methods to prepare optical grade thin films either from direct deposition of precursors that condense on the charge collector surface or through the deposition of already formed crystalline nanoparticles from a concentrated dispersion. With the first approach we have optimized bismuth vanadate efficiency with Mo doping and surface catalysts or its stability with a thin titania coating. We could obtain photocurrents higher than 2 mA·cm^{-2} at 1.23 V/ESH in a pH = 6 electrolyte medium. In addition we evidenced that the presence of unused photo-generated holes at the electrode electrolyte interface is responsible for the photoanode degradation.

With the nanoparticles approach we compared different polymorphs of TiO$_2$ to demonstrate that the brookite phase efficiency is similar to that of anatase or rutile. Charge carrier dynamics in the three polymorphs were compared using TRMC.

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Acknowledgement:

We would like to acknowledge ED397 and IMAT (Sorbonne Université) for funding and David Montero (FCMAT SU) for SEM experiments and Dennis Friederich (Helmoltz-zentrum Berlin für Materialen und Energie GmbH)) for TRMC experiments.

Thematic Session (Nanochimie, Nanoparticules, Nanocatalyse, Nanomatériaux pour l'énergie)
Disciplinary fields involved (Chemistry)
Keywords (Au, Pt, catalysis, CO_2 reduction)

Size-controlled Au and Pt nanoparticles for enhanced CO_2 photoreduction with water under visible light

Leila Hammoud [1,2], Justine Quinet [3], Katia Fajerweg [2], Clément Roux[4], Guillaume Baffou[5], Thomas Cottineau [3], Valérie Keller [3], Valérie Caps [3], Christian Lorber [2], Pierre Fau [1]

1. LPCNO-INSA, UMR 5215 INSA-UPS-CNRS, 135 avenue de Rangueil, 31077 Toulouse, France, 2.LCC-CNRS, UPR 8241, 205 Route de Narbonne, 31077 Toulouse, France, 3.ICPEES, UMR 7515 CNRS-Université de Strasbourg, 25 Rue Becquerel, 67087 Strasbourg, France, 4.SOFTMAT-CNRS, UMR 5623 Université Paul Sabatier, 118 route de Narbonne Cedex, 31062 Toulouse, France, 5.Institut Fresnel-CNRS, UMR 7249 Aix Marseille Université, 13013 Marseille, France

The photoreduction of CO_2 with water in the gas phase ($CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$) is an attractive route to recycle CO_2 into a highly valuable energy resource, CH_4. This reaction can be catalyzed by titania-supported gold and Platinum nanoparticles, under visible illumination, through plasmonic excitation of the metallic nanoparticles[1]. However, the size of metallic particles significantly affects their catalytic properties[2]. In this study, we introduce a by-products-free synthetic method, the OMCLD (OrganoMetallic Chemical Liquid Deposition) technique[3], which enables the synthesis of size-controlled AuNPs on TiO_2 supports by adjusting the decomposition time of the as-synthesized Au(I)-amidinate precursor. We demonstrate that smaller AuNPs (3.1 nm), synthesized with shorter reaction times (2 minutes), led to 1.5 and 2.5 times increases in methane production compared to the larger AuNPs of 5 nm and 8.6 nm, respectively. These results suggest that photoelectronic effects dominate over photothermal effects which are found to increase with increasing plasmonic NPs size[1]. Additionally, we developed an innovative organometallic approach for synthesizing Pt/TiO_2 catalysts through the decomposition of tris(dibenzylideneacetone) diplatinum(0) ($Pt_2(dba)_3$) using CO or H_2 as a reducing gas in the presence of TiO_2 powder. The actual Pt loadings, determined by ICP-OES, are close to the targeted values, with Pt deposition yields close to 90%. Notably, we demonstrated that the choice of reducing gas significantly affects the size of the Pt nanoparticles. Sub-nanometer Pt clusters were obtained with CO, while 2–3 nm Pt particles were formed when H_2 was used as the reducing gas.

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Acknowledgement:
This project has received financial support from ANR 22-CE50 through the project 0029 ''Together for CO2''. The French GDR OrNano and GDR Plasmonique active networks are gratefully acknowledged to have allowed fruitful and inspiring discussions for these results.

Thematic Session Nanomaterials for Energy
Disciplinary fields involved Photocatalysis
Keywords: Photocatalysis, Z-scheme, heterojunction, metal oxides

Self-Supported Cu_2O Nanowire Heterojunction Membranes for Photocatalysis and CO_2 Reduction

Beitone Soline[1], Ternon Céline[1] and Riassetto David[1]

1. *LMGP laboratory, 61 Rue Félix Esclangon, 38000 Grenoble*

Abstract

Building on the development of ultra-thin and long Cu_2O nanowires and their integration into self-supported membranes, this work investigates their potential in advancing photocatalytic applications. These membranes, fabricated through hydrothermal synthesis and vacuum filtration, serve as a versatile platform for exploring charge transfer processes. In particular, the Z-scheme electronic pathway, inspired by natural photosynthesis, shows great potential for enhancing photocatalytic efficiency by improving charge separation and maintaining a high redox potential [1].

Preliminary studies focus on using these membranes for dye degradation, with additional characterization techniques, such as radical trapping, providing insights into the underlying photocatalytic mechanisms. The flexibility and adaptability of these Cu_2O nanowire membranes present exciting opportunities for broader applications, including CO_2 reduction and the development of heterojunctions with other metal oxides, such as TiO_2 [2] or ZnO [3], to further enhance photocatalytic performance. By contributing to the understanding of nanostructured materials and innovative charge transfer mechanisms, this work establishes a foundation for advancing photocatalytic technologies, supporting global sustainability efforts.

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Acknowledgement:
CDP DefiCO2

Thematic Session: Nanomaterials for energy
Disciplinary fields involved: Chemistry, Physics
Keywords: plasmonic catalysis, hot electrons, heating, ultrafast process

Effects of heat and hot electron generations in ultrafast regime in plasmon-driven chemical reaction

Liudmila Trotsiuk[1], Oscar Ávalos-Ovando[2], Richard Scottie[2], Davy Gerard[1], Sylvie Marguet[3], Anne-Laure Baudrion[1], Yun Luo[4], Claire Mangeney[4], Nordin Felidj[5], Pierre-Michel Adam[1], Alexander Govorov[2], Renaud Bachelot[1]

1. *Laboratory of Light, Nanomaterials, Nanotechnologies (L2n), CNRS UMR 7076, University of Technology of Troyes, 10004 Troyes, France*
2. *Department of Physics and Astronomy and Nanoscale and Quantum Phenomena Institute Ohio University Athens, OH 45701, USA*
3. *CEA, CNRS, NIMBE, Université Paris Saclay, F-91191 Gif sur Yvette, France*
4. *Laboratoire de Chimie et de Biochimie Pharmacologiques et Toxicologiques, Université Paris Cité, CNRS, F-75006 Paris, France*
5. *Université Paris Cité, CNRS, ITODYS, F-75013 Paris, France*

The ability of plasmonic nanoparticles to generate under excitation non-thermalized “hot” carriers and local heat offers great potential for boosting chemical reaction that further can lead to energy-efficient and sustainable industrial processes. In this work, we investigated the interplay of heating and hot-electron effects in plasmon-driven polymerization reactions under continues wave (CW) and femtosecond (fs) pulsed irradiation. We performed polymerization of diazonium molecules on the surface of gold nanocubes that can proceeds via two pathways: radical and cationic ones. In case of radical mechanism, the polymerization reaction is induced by electron transfer, while spontaneous process of polymerization goes via the cationic mechanism and can be boosted by heating. Since the distribution of hot electrons and heat on the surface of gold nanoparticles is different [1], we expected to distinguish both these contributions through the different polymer pattern on the gold nanocube. We showed that at the CW-irradiation of the quadropole mode leads to domination of the hot-electron induced reaction with the polymer located on the nanocube’s corners. While the excitation of dipole mode that has purely scattering character, leads to a chaotic heating-induced growth over the nanoparticle surface. At the same time, the excitation the same dipole mode by the fs-pulses also induced the polymer growth into plasmonic hot spots. Performed theoretical calculations shows that under fs-excitation, temporal heating localized on the nanocube corners occurs during the first ps after irradiation. We believe that this temporally localized heating induces the polymerization reaction into hot spots creating anchoring sites for further polymer growth.

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Authors acknowledge financial support from the French Research Agency (ADVANSPEC and POPCORN projects). Fabrication and characterization were made by the facilities of Nano’mat platform from the French RENATECH + network.

Nanomaterials for energy

Friday March 21th

10:30 A.M. - 12:30 A.M.

ROOM AB

Program of the session :

Chairs: Lionel SANTINACCI

HOUR	NAME	TITLE
10:30	**Ally AUKAULOO** **ICMMO - Univ. Paris Saclay**	**Nanostructured Organic Semiconductors for the Photocatalytic Water Splitting**
11:00	Mathieu DELOM LRS - Sorbonne Univ.	Cyclable and cheap catalysts for hydrogen storage and release by organic liquids
11:15	Heliam KLEIN LCC - CNRS	Solid hydrogen storage: innovative materials for the solvolysis of amine boranes
11:30	Gaëlle KHALIL ITODYS - Paris Cité	Synthesis of Ni-based Heterofunctional Catalysts with Ultra-Low PGM content for the Alkaline Hydrogen Evolution Reaction
11:45	Juliana SOUZA Photoactive Nanomaterials - Universidade Federal do ABC	Enhanced (W)BiVO4/g-C3N4 systems for solar-driven photocatalysis
12:00	Marouane BOUREMAH LPCNO-INSA Toulouse	Homogeneous and Heterogeneous Photocatalysis using InP/ZnS Quantum Dots
12:15	Jean-Charles ARNAULT NIMBE - CEA	Nanodiamonds: an alternative for photocatalysis under solar light?

S3

IDENTITY

Ally AUKAULOO (Univ. Paris Saclay - ICMMO, Orsay)

https://www.icmmo.universite-paris-saclay.fr/en/perso/allyaukauloo/

ally.aukauloo@universite-paris-saclay.fr

Short Biography

Ally Aukauloo obtained his PhD in porphyrin chemistry in 1994. In 1995 he was elected as assistant professor at Université Paris-Sud, where he worked on molecular magnetism. In 2000, after stay in Pr. J. Collman labs at Stanford University to work on Cytochrome c oxidase models, he started his research on Artificial Photosynthesis. He became fullprofessor in 2007 in bioinorganic chemistry. He was elected at the Institut Universitaire de France as a senior member in 2021. He focusses on the chemistry of molecular complexes for water activation, CO2 reduction and organic semiconductors for the water splitting.

Title of Oral Presentation

Nanostructured Organic Semiconductors for the Photocatalytic Water Splitting

Keywords

Artificial Photosynthesis, light capture, charge accumulation, water oxidation , quinone reduction

Abstract of Oral Presentation

The central theme of research in artificial photosynthesis revolves around capturing sunlight to drive the water splitting reaction (WSR), producing O2 and H2. While inorganic oxides have traditionally dominated the materials used for this purpose, organic semiconductors have now emerged as an important contender. Both types of materials allow for the synthetic adjustment of band gaps and energies to enable the WSR. However, optimizing the photophysical properties of these semiconductors often requires complex and labor-intensive synthetic processes. I will discuss on two new findings:

i) A study on a nanostructured semiconducting conjugated polymer, poly(diphenylbutadiyne) (nano-PDPB), and its photocatalytic activity in driving the water oxidation reaction under visible light irradiation when dispersed in water, without the need for sacrificial agents or co-catalysts. Charge recovery, either directly or delayed, was demonstrated through the reduction of quinone, which served as a hydrogen reservoir. In the absence of quinones as electron acceptors, we observed the formation of H2O2, resulting from the partial reduction of O2.
ii) When pyrrole dissolved in distilled water is exposed to high-energy radiation, it forms nanostructured spherical polypyrrole (Nano-PPy) particles, which are characterized as overoxidized polypyrrole. Electrochemical measurements and Tauc's plot analysis reveal that the material exhibits semiconducting properties, with a band gap of approximately 1.8 eV. The conduction band is positioned at around -0.5 V, while the valence band is at about +1.3 V vs NHE. When suspended in water and irradiated with light wavelengths above 420 nm, Nano-PPy induces O2 evolution.

Acknowledgement

IRS Université Paris-Saclay MOMENTOM program for a postdoctoral grant. Université ParisSud (ERM project) is acknowledged for financial support for the Cobalt-60 panoramic gamma source and LABEX CHARMMMAT and NANOSACLAY for technical support. ANRSCOOPE (2022-2026). A.A thanks Institut Universitaire de France for support.

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Thematic Session: Nanomaterials for energy
Disciplinary fields involved: Chemistry
Keywords: Nanoparticles, Nanoalloys, Chemical storage of H_2, Heterogeneous catalysis

Cyclable and cheap catalysts for hydrogen storage and release by organic liquids

Mathieu Delom[1,2,3], Marc Petit[2], Souhir Boujday[1], Christophe Petit[3], Juliette Blanchard[1]

1. *Laboratoire de Réactivité de Surface (LRS), Sorbonne Université, 75005 Paris, France*
2. *Institut Parisien de Chimie Moléculaire (IPCM), Sorbonne Université, 75005 Paris, France*
3. *De la Molécule aux Nano-objets : Réactivité, Interactions et Spectroscopies (MONARIS), Sorbonne Université, 75005 Paris, France*

Hydrogen use is an undeniably attractive solution for developing a low-carbon economy. However, several technical obstacles still stand in the way of its efficient use including those related to H_2 storage and transportation[1]. Liquid Organic Hydrogen Carriers (LOHC) are an appealing solution to lift these two obstacles. LOHC can absorb and release a high weight fraction of hydrogen through chemical reactions[2]. They can be used to store H_2 under ambient conditions, avoiding the problems linked with H_2 storage and transportation under high pressure as well as issues related to its high flammability.

With this work we aim at developing new, affordable, energy-efficient and cyclable catalysts based on metallic nanoparticles immobilised on different supports for the hydrogenation and dehydrogenation of primary (di)amine/(di)nitrile pairs (LOHC). More precisely, we have developed the synthesis of colloidal cobalt NPs[3] and their immobilisation on porous silica particles or carbon nanotubes with the aim of comparing activity and stability of free and immobilised NPs for the acceptor-less dehydrogenation of amine and for the hydrogenation of nitrile.

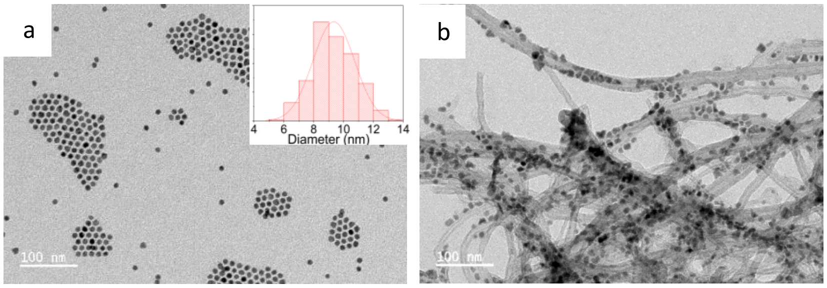

Figure 1 : Cobalt nanocrystals in colloidal solution (a) and immobilized on carbon nanotubes (b)

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Abstract

Thematic Session : Nanomatériaux pour l'énergie
Disciplinary fields involved : Chemistry, Physics
Keywords (max. 4-5)**:** Nanomaterials, Hydrogen, Storage, Plasma, Injection,

Solid hydrogen storage: innovative materials for the solvolysis of amine boranes

Héliam Klein[1,2,3], Jean-Cyrille Hierso[4], Luc Stafford[2], Richard Clergereaux[3], Myrtil L. Kahn[1]

1. *LCC, Team NOS, CNRS UPR 8241, 31077 Toulouse, France*
2. *PHARE, Université de Montréal, Département de Physique, Montréal, Canada*
3. *LAPLACE, SCIPRA, Université Toulouse III Paul Sabatier, CNRS UMR 5213, 31062 Toulouse, France*
4. *ICMUB, Université de Bourgogne, CNRS UMR 6302, 21078, Dijon, France*

Abstract (**<u>no longer than 250 words</u>** or 18 lines max. incl. figure), Calibri 11, single line spacing, black)

The depletion of oil reserves and the increase in greenhouse gas emissions, particularly CO_2, are driving the development of alternative energy sources. In the context of energy transition, efforts focus on three main axes: reducing energy consumption, electrifying uses, and replacing fossil fuels with decarbonized sources.[1] Among these, "green" hydrogen is one of the promising energy vectors for reducing CO_2 emissions and promoting renewable energies.[2]

This thesis focuses on the design of innovative nanocomposite materials,[3] synthesized by environmentally friendly processes,[4] for the storage and chemical release of hydrogen (H_2) through the solvolysis of amine boranes (AB). Inspired by previous works on the catalytic efficiency of nickel nanoparticles for the solvolysis of amine boranes, this project aims to incorporate nanoparticles or isolated atoms of nickel into carbon matrices and to evaluate their catalytic impacts on AB solvolysis for hydrogen storage. Several nickel-based systems supported on carbon have been studied and have shown promising performances, due to the well-known affinity of nickel for hydrogen.[5]

Two distinct plasma processes, at low pressure and at atmospheric pressure, are being explored for the production of nickel containing carbon matrices. An innovative feature of the formation of these materials lies in the use of pulsed injection of liquid solutions into the plasma reactors, allowing for the simultaneous introduction of the metal (Ni) and the carbon precursor.

The parameters influencing the incorporation of nickel, as well as the relationship between processes, and film structure, will be discussed.

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Acknowledgement: This work is funded by the Rhyo program (pôle de recherche et d'innovation sur l'hydrogène en Occitanie) and by the Physic department of Université de Montréal
(*calibri 10)*

Thematic Session Nanomaterials for Energy
Disciplinary fields involved Electrocatalysis, nanomaterials for energy, characterization
Keywords: Hydrogen production, HER, AEM electrolysis

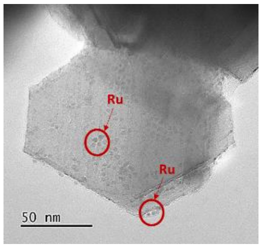
Synthesis of Ni-based Heterofunctional Catalysts with Ultra-Low PGM content for the Alkaline Hydrogen Evolution Reaction

Khalil Gaëlle[1], Dias Fernandes Marie-Sophie[2], Tard Cédric[2], Lassalle Benedikt[1,3], Giraud Marion[1], Peron Jennifer[1]

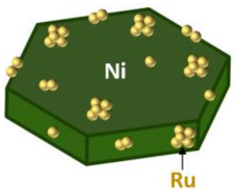
1. *ITODYS, UMR CNRS, Université Paris Cité, 75013 Paris, France*
2. *LCM, UMR CNRS, Ecole Polytechnique, 91128 Palaiseau, France*
3. *Synchrotron SOLEIL, 91190 Saint-Aubin, France*

Hydrogen is a clean energy carrier that serves as an important role in the global energy transition, with green hydrogen offering a near carbon-neutral production from renewable sources. Anion exchange membrane water electrolysis (AEMWE) is a promising technology to generate pure hydrogen, due to its alkaline conditions that allows the use of earth-abundant transition metals as electrocatalysts for both the hydrogen (HER) and the oxygen (OER) evolution reactions. Despite its potential, challenges remain in achieving high and stable AEMWE performance, particularly regarding HER catalysts.[1] To address this, a new concept of heterofunctional catalysts has been proposed to enhance HER kinetics in alkaline medium.[2] In this work, we present the synthesis of Ni-based heterofunctional electrocatalysts with ultra-low noble metal content, that exhibit a significantly low overpotential, highly comparable to the one of the state-of-the-art catalyst Platinum. Using the polyol synthesis method, we achieved highly crystalline materials with controlled particle size, shape, and distribution.[3] Characterization via XRD, XPS, XRF, SEM, and TEM confirmed the presence of ultra-small noble metal nanoparticles decorating Ni platelets, providing heterofunctional properties. Material composition and atomic distribution were further studied using XAS under ex situ and in operando conditions. Performance evaluation in a membrane electrode assembly (MEA) configuration revealed that these electrocatalysts reached 1.85 V at a current density of 1 A.cm^{-2}. These findings demonstrate the potential of heterofunctional catalysts to enhance AEMWE efficiency, offering a sustainable pathway for scalable hydrogen production with reduced reliance on critical noble metals.

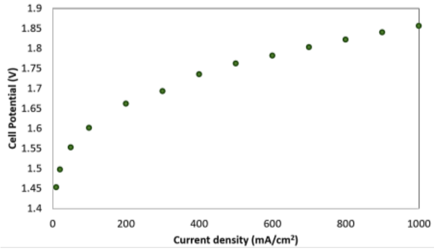
TEM image of Ni_{Ru} Nanoparticles



Ni_{Ru} schematic representation



Polarization curve of Ni_{Ru} catalyst in 1M KOH



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Thematic Session (Nanomaterials for energy)
Disciplinary fields involved (Chemistry)
Keywords: Bismuth vanadate, tungsten oxide, carbon nitride, photocatalysis, nanomaterials.

Enhanced (W)BiVO$_4$/g-C$_3$N$_4$ systems for solar-driven photocatalysis

Juliana S. Souza[1], Caroline Helena Claudino[1]

1. Photoactive Nanomaterials, Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Avenida dos Estados, 5001, zip code 09210-580, Santo André, Brazil

The increasing demand for solar energy in photocatalytic applications has driven significant research into efficient systems. Monoclinic BiVO$_4$ stands out among photocatalysts for its narrow band-gap energy, which is ideal for solar-driven reactions. However, its practical application is limited by challenges like charge recombination, slow electron transfer, and an unsuitable conduction band for hydrogen evolution. Strategies such as doping BiVO$_4$ with tungsten (W) and forming heterojunctions with graphitic carbon nitride (g-C$_3$N$_4$) have shown promise in addressing these issues. Here, we explore two innovative methods to enhance (W)BiVO$_4$/g-C$_3$N$_4$ systems. The first involves synthesizing BiVO$_4$/g-C$_3$N$_4$ heterojunctions via in-situ urea pyrolysis, achieving homogeneous dispersion while preserving the monoclinic BiVO$_4$ structure [1]. The second uses a microwave-assisted pre-treatment of urea before pyrolysis to produce g-C$_3$N$_4$; then, the resultant polymer is combined with (W)BiVO$_4$ during synthesis [2].

Heterojunctions produced through in-situ pyrolysis exhibit a more negative zeta potential, reducing the adsorption of anionic dyes like methyl orange (MO) (Figure 1a) and improving its photocatalytic degradation when compared to the use of pristine BiVO$_4$ as a photocatalyst (Figure 1b). Similarly, heterojunctions combining (W)BiVO$_4$ and microwave-treated g-C$_3$N$_4$ demonstrate significant enhancements, with photocurrents measured during oxygen evolution reaction increasing 5 times in comparison to heterojunctions obtained by using untreated urea for the g-C$_3$N$_4$ synthesis (Figure 1c) These systems also outperform others in tetracycline degradation. These strategies improve the photocatalytic and photoelectrocatalytic performance of (W)BiVO$_4$/g-C$_3$N$_4$ systems, offering valuable insights for future energy and environmental applications.

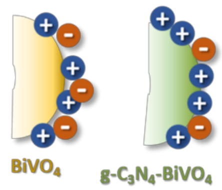

Fig. 1a.Dye adsorption

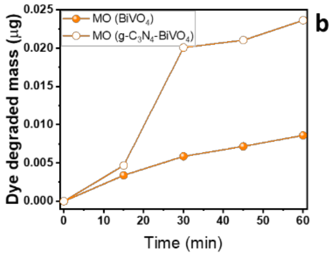

Fig. 1b. Dye photodegradation

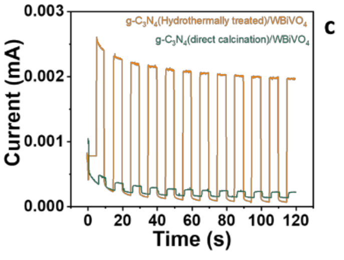

Fig. 1c. Oxygen Evolution Reaction

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Thematic Session: (Nanomaterials for energy)
Disciplinary fields involved: (Chemistry)
Keywords: Semiconductor nanocrystals, Quantum dots, Photocatalysis, Indium Phosphide, Mesoporous silica

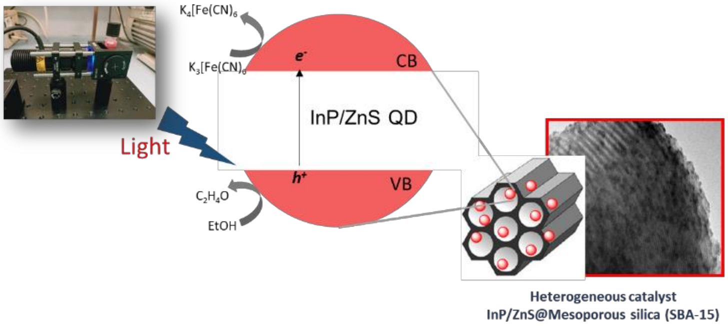
Homogeneous and Heterogeneous Photocatalysis using InP/ZnS Quantum Dots

Marouane Bouremah [1,2], **Kaltoum Bakkouche** [1,2], **Liyan Ouyang** [1], **Nadia Katir** [2], **Abdelkrim El Kadib** [2], **Céline Nayral** [1], **Fabien Delpech** [1]

1. LPCNO, Université de Toulouse, CNRS, INSA, UPS, 135 Avenue de Rangueil, 31077 Toulouse, France
2. Euromed Research Center, Engineering Division, Euro-Med University of Fès (UEMF), 30070 Fès, Maroc

The capabilities of quantum dots (QDs) in photocatalysis is gaining attention because of their distinct light harvesting properties over traditional precious metal- and small molecule-based catalysts. Despite their potential as environmentally friendly alternative to the most developed but toxic cadmium or lead-based QDs, InP-based QDs have been significantly less studied as photocatalysts compared to their cadmium-based counterparts [1].

Herein, we present a study exploring the use of InP/ZnS[2] QDs in aqueous medium as photocatalysts for the ferricyanide reduction[3] as model reaction. Their effectiveness has been explored in both homogenous and heterogeneous conditions. The effects of QD size and stabilizing surface ligands on catalytic performance were examined. The initial ligands of the QDs (Oleylamine) have been exchanged by various mercaptocarboxylic acid ligands: mercaptopropanoic acid, mercaptoundecanoic acid and mercaptobenzoic acid. This latter results in a dramatic enhancement of the activity which was rationalized. Last, the QDs were supported on mesoporous silica (SBA-15), and used as a recyclable supported photocatalysis in the same ferric complex reduction reaction.



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Nanodiamonds: an alternative for photocatalysis under solar light?

J. C. Arnault[1], C. Marchal[2], L. Saoudi[1], H. A. Girard[1], V. Keller[2]

[1] Université Paris-Saclay, CEA, CNRS, NIMBE, 91191 Gif sur Yvette, France
[2] ICPEES, CNRS/University of Strasbourg, UMR 7515, 67000 Strasbourg, France

Among nanoscale semiconductors (SC), nanodiamond (ND) has been rarely considered for photocatalytic reactions. This originates from the confusion with ideal monocrystalline diamond behaving a wide bandgap (5.5 eV) that requires deep UV illumination to initiate photoreactivity. At nanoscale, diamond particles enclose native defects that create energetic states decreasing the light energy needed to initiate charge separation. This is supported by experimental results and DFT calculations that involved our group [1, 2]. The presence of sp^2 carbon in hydrogenated detonation ND allows the emission of solvated electrons in water under visible light (400 nm) according to ultrafast transient absorption spectroscopy [2]. In addition, like bulk diamond, the electronic structure of ND can be strongly modified tuning its surface terminations (oxidized vs hydrogenated) as shown by Miliaieva et al. [3]. With these assets, ND becomes competitive to other SC toward photoreactions.

In the present study, we reveal for the first time that oxidized detonation nanodiamonds (Ox-DND) can produce hydrogen under solar illumination without addition of co-catalyst or formation of heterojunction with another SC [4]. This hydrogen production was investigated using two sacrificial reagents and compared to the one of hydrogenated DND. The effect of the Ox-DND and sacrificial reagent concentrations on the hydrogen production was also studied. At its maximum, a H_2 production yield of 32 $\mu mol.h^{-1}$ was obtained for an Ox-DND concentration of 12.5 µg/mL (using only 1 vol.% of TEOA as a sacrificial reagent). This yield is similar to the one of TiO_2 nanoparticles tested at the same concentration in the same illumination conditions.

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