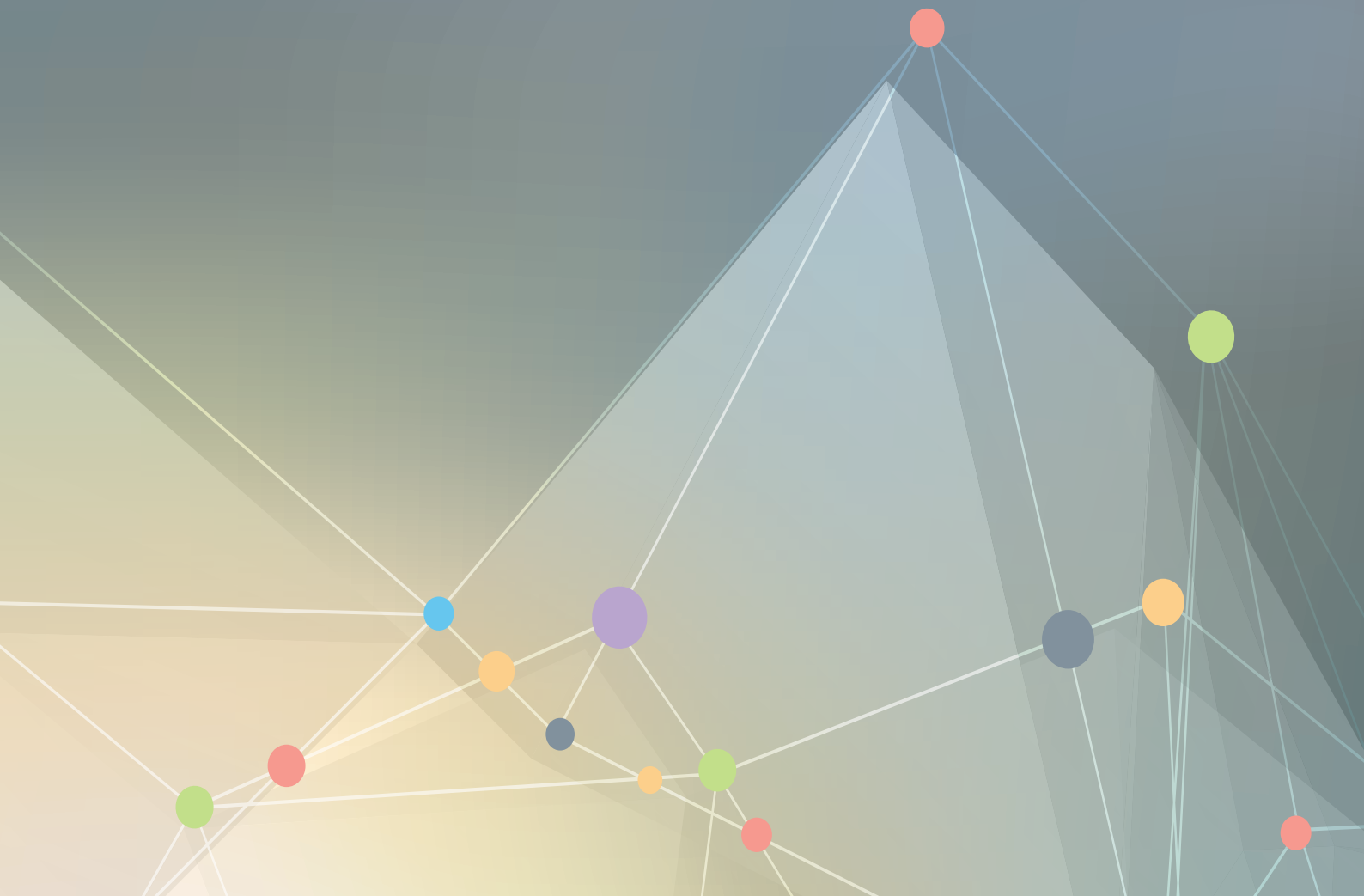


BOOK OF ABSTRACTS

Oral Presentations



2023



Nanochemistry, Nanoparticles, Nanocatalysis

(Last update: August 23th, 2022)

Description

Nanochemistry enables the synthesis of nanostructures with controlled properties (size, shape, crystallinity, chemical composition, surface composition...) for applications in numerous fields such as optics, nanomedicine or nanocatalysis. Mono- or multi-metallic nanoparticles can be either used directly (i.e. as unsupported nanocatalysts) or stabilized using a support (oxides or carbon) for thermal-activated-, photo- and electro-catalysis. Optimizing their performance requires a better understanding of their structure at the atomic level in relation to their properties, especially under real conditions of use. In this context, this session will be devoted to the understanding of the nucleation and growth mechanisms of chemically synthesized nanostructures, and of their integration in macroscopic systems. It will also address the determination of the relationships between the main features (composition, shape, structure, surface state) and performances of these materials in various applications. A particular focus will be on the understanding of the evolution of nanostructures and active sites under reaction conditions and its impact on the catalytic performance. Experimental and theoretical results will be discussed. This session is organized in partnership with the GDR NINO, CNRS research network (study group on inorganic nanostructures elaborated in solution) and the GECAT (Study Group on Catalysis).

Keywords

Wet chemistry, inorganic nanoparticles, nucleation and growth mechanisms, in situ and operando studies, catalysis, modelling

Scientific committee

Fabien CAN* (Univ. Poitiers – IC2MP)

Florence EPRON* (CNRS – IC2MP, Poitiers)

Manuel GAUDON (Univ. Bordeaux – ICMCB, Bordeaux)

Myrtil KAHN (CNRS – LCC, Toulouse)

Ksenia PARKHOMENKO (CNRS- CPEES, Strasbourg)

Jean-Yves PIQUEMAL (Univ. Paris Cité- ITODYS, Paris)

** session Coordinator*

In partnership with GDR NINO CNRS research network, GECAT group of the French Chemistry Society (SCF)

2023

Wednesday March 15th

11.00 am – 1.00pm

Main Amphitheater

Program of the session

Chairs: Manuel GAUDON & Ksenia PARKOMENKO

NANOCHEMISTRY, NANOPARTICLES, NANOCATALYSIS

11:00	Surface redox reactions for tuning the surface composition of bimetallic nanoparticles and their catalytic properties: the contribution of Poitiers catalysis laboratory	Catherine ESPECEL • Univ. Poitiers – IC2MP, Poitiers – France
11:30	Cerium as a co-catalyst in nanostructured PGMS-based materials for glycerol oxidation in alkaline media: value-added products generation	Fabiano DOS SANTOS CURSI • Univ. Sao Paulo - IC2MP, France
11:45	Understanding the mechanisms involved in the formation of silicon particles from the thermal decomposition of hydrogen silsesquioxane: an in situ study by ETEM	Cynthia CIBAKA NDAYA • CNRS - ICMCB, France
12:00	Synthesis of nickel nanoparticles via an organometallic pathway	Dimitri ROUBERT • Univ. Paul Sabatier Toulouse - LCC, France
12:15	Green Synthesis of Water Splitting Electrocatalysts: IrO ₂ Nanocages via Pearson's Chemistry	Jennifer PERON • Univ Paris Cité - ITODYS, France
12:30	Nanostructured catalysts for the selective electro-conversion of bio-sourced molecules into value-added compound	Thibault RAFAIDEEN • CNRS - IC2MP, France
12:45	Core@Shell Co@CoS Nanorods on the Way to Magneto-Plasmonic Probes	Thi Thiet VU • INSA Toulouse - LPCNO, France

Keynote Speakers

NANOCHEMISTRY, NANOPARTICLES, NANOCATALYSIS



Catherine ESPECEL

University of Poitiers | Professor

Institute of chemistry of environments and materials of Poitiers

<https://ic2mp.labo.univ-poitiers.fr/membres/especel-catherine/>

BIOGRAPHY

Catherine ESPECEL is professor at the Institute of Chemistry Materials and Natural Resources of Poitiers (IC2MP). She obtained her PhD in 1997 at the University of Poitiers in heterogeneous catalysis involving supported metallic systems, and in 1998, she did a postdoc at the French Synchrotron Laboratory (LURE-Orsay). In 2008, she was nominated Associate Professor and since 2014, she is the co-head of the SAMCAT group of IC2MP, which comprises 37 permanent staff and around 30 PhD and postdoc researchers. Her main research topics include the preparation of multimetallic catalysts notably by using surface redox reactions, with applications in fine chemistry, energy and biomass valorisation (selective hydrogenation and hydrogenolysis, catalytic reforming, selective ring opening). She has supervised or co-supervised 19 PhD students, 4 postdoc, published as co-author near 80 peer-reviewed journal articles (hindex 26), 3 patents, 3 book chapters, and given around 45 oral communications.

SURFACE REDOX REACTIONS FOR TUNING THE SURFACE COMPOSITION OF BIMETALLIC NANOPARTICLES AND THEIR CATALYTIC PROPERTIES: THE CONTRIBUTION OF POITIERS CATALYSIS LABORATORY

Bimetallic catalysts have emerged as an important class of heterogeneous catalysts since they have played a significant role in petroleum refineries, especially in enhancing the octane number of gasoline. After this discovery, a number of bimetallic catalysts have been reported for a range of reactions including oxidation, hydrogenation, hydrogenolysis, and reforming reactions. The properties of bimetallic catalysts are significantly different from their monometallic analogues. Indeed, the modification of a monometallic catalyst by the addition of a second metal is an important approach for tailoring the electronic and geometric structures of the nanoparticles to enhance their catalytic activity and selectivity. In many cases, bimetallic nanoparticles have higher catalytic efficiencies than their monometallic counterparts, owing to strong synergy between the metals.

Nowadays, many research activities are devoted to the development of new bimetallic catalysts, because of the tremendous demand for high-performance catalysts for various practical applications. Because of the presence of a second metal component, the complexity in preparing these materials increases, and in many cases it is the method of preparation which determines the final structure, and hence properties, of these materials.

During this presentation, the preparation of various supported bimetallic systems for applications in the transformation of bio-renewable substrates and in energy will be presented, with a focus on the surface redox reactions developed in our research group since the 1990s. The preparation of bimetallic M1-M2 catalysts by surface redox reactions occurs at the surface of the monometallic M1 nanoparticles and an oxidized form of the M2 modifier and is governed by the electrochemical potential of the species implied in the reaction. This process can be direct (direct redox reaction or galvanic replacement) or may involve an intermediate reducing agent activated at the surface of M1, as H₂, for reducing the oxidized form of the M2 modifier (refilling or catalytic reduction).

KEYWORDS:

Bimetallic catalysts; surface redox reactions; galvanic replacement; refilling; catalytic reduction

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- [2] F. Epron, C. Especel, G. Lafaye, P. Marécot, in Nanoparticles and Catalysis (Ed. Didier Astruc), Wiley-VCH, pp 279-302, 2008.
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- [4] D. Messou, L. Vivier, C. Especel, Energ. Convers. Manage., 127 (2016) 55-65.
- [5] X. Di, G. Lafaye, C. Especel, F. Epron, J. Qi, C. Li, C. Liang, ChemSusChem, 12 (2019) 807-823.

Keywords: nanocatalysts (PGMs), alkaline fuel cell, clean energy production, glycerol electro-oxidation

Disciplinary field involved: Chemistry (Electrochemistry)

Sustainable Development Goals* eventually involved in your research: Affordable and clean energy (Goal 7) and Climate action (Goal 13)

Cerium as a co-catalyst in nanostructured PGMs-based materials for glycerol oxidation in alkaline media: value-added products generation

Fabiano S. Cursi^{1,2}, Karine Servat², Cláudia Morais², Teko W. Napporn², Adalgisa R. de Andrade¹ and K. Boniface Kokoh²

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2. *Université de Poitiers, IC2MP UMR 7285 CNRS, Équipe SAMCat, 4, rue Michel Brunet, B27, TSA 51106, 86073 Poitiers Cedex 09, France.*

Currently, most of available glycerol comes from the production of biodiesel, which makes this by-product a residue. It is also known that its oxidation generates high value-added products. With that in mind and focusing on the production of clean energy, the glycerol oxidation on PtCe/C, PdCe/C and AuCe/C nanocatalysts in an alkaline fuel cell was investigated. The Pt, Pd and Au nanomaterials supported on Vulcan carbon and modified with rare earth element such as cerium (Ce) were prepared using two synthesis methods: Bromide Anion Exchange (BAE) and microwave-assisted polyol. The prepared materials were physicochemically characterized by ICP-OES, XRD, TEM and EDX, and electrochemically studied via cyclic voltammetry, chronoamperometry and stability tests via CO-stripping analysis. Their performance toward the oxidative process of glycerol was then compared. In addition to concluding that the modification of nanomaterials with Ce increases the catalytic activity for glycerol oxidation, probably due to its oxygen supplier capacity, it was also possible to show that the polyol method generates supported nanoparticles with higher electrocatalytic activity, certainly because this synthesis approach produces smaller nanoparticles than the BAE one, and consequently greater active surface area for the reaction. Furthermore, the oxidation products were analyzed by HPLC after 4 h of fuel cell operation and by *in situ* FTIR spectroscopy, showing the selectivity for obtaining products such as glycerate, tartronate and oxalate for the Pt- and Pd-based nanocatalysts and glycolate and formate for Au-based catalysts.

References: *Catalysts*, 9 (2019), 980; *ChemPhysChem* 18 (2017), 2573-2605; *Sustainable Energy Fuels*, 2019, 3, 1866; *ChemSusChem* 9 (2016) 252.

Acknowledgment: Caes-Cofecub program (88887.643343/2021-00), Capes (001), Fapesp (2021/01134-7), CNRS and Région Nouvelle-Aquitaine.

Keywords: Silicon particles, in-situ electron microscopy, hydrogen silsesquioxane, dewetting process

Disciplinary fields involved: Chemistry, Physics

Understanding the mechanisms involved in the formation of silicon particles from the thermal decomposition of hydrogen silsesquioxane: an in situ study by ETEM

Cynthia Cibaka-Ndaya¹, Kevin O'Connor², Emmanuel Opeyemi Idowu¹, Jonathan G.-C. Veinot², Lucian Roiban³, Glenna L. Drisko¹

1. ICMCB, UMR 5026, CNRS, Univ. Bordeaux, Bordeaux INP, Pessac F-33600, France
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3. MATEIS, UMR 5510, Univ Lyon, INSA Lyon, Université Claude Bernard Lyon 1, CNRS, 69621 Villeurbanne, France

Hydrogen silsesquioxane (HSQ) compounds, often applied as a resist in lithographic processes, were previously demonstrated to be efficient precursors for the preparation of silicon particles. (1–3) In this approach, spherical silicon particles result from the thermal decomposition of HSQ at high temperatures (> 1000°C), which leads to its disproportionation into crystalline Si particles embedded in a matrix of silica. The particles are then collected after etching the silica matrix with HF. The thermal processing temperature can be adjusted in order to tailor the size of the resulting silicon particles from ~3 to ~200 nm. (2,3) In a previous study, the formation of Si nanostructures through this route has been investigated using spectroscopic and diffraction techniques, which supported the growth and increased crystallinity of the silicon nanodomains above 900°C. (4)

The purpose of the present study is to deepen the understanding of the mechanisms involved in silicon particle formation and growth. To achieve this, in situ observations of HSQ decomposition at high temperatures were performed by environmental transmission electron microscopy. While the nucleation of Si nanodomains was observed from 1000°C, confirming the conclusions of the work in ref (4), particle growth mechanisms were also identified. The coalescence of small particles into larger ones was observed. In addition, above the melting point of silicon, silicon particles evolved in a liquid phase, growing while moving inside the matrix towards the surface. These real time observations were complemented with SEM analysis of the treated HSQ and in situ XRD measurements up to 1200°C.

References:

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C'Nano

THE NANOSCIENCE MEETING

Positiers

March, 15, 16 and 17

2023



Acknowledgments: This project is supported by funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (*Scatter*, Grant agreement No. 948319). The authors acknowledge the French national project METSA for providing them with access to the microscope platform of CLYM in Lyon. David Montero performed FEG-SEM observations at the Institut des Matériaux de Paris Centre (IMPC FR2482), which was co-funded by Sorbonne Université, CNRS and by the C'Nano projects of the Région Ile-de-France.

Keywords: nickel, organometallic chemistry, nanoparticles

Disciplinary field involved: Chemistry

Synthesis of Nickel nanoparticles via an organometallic pathway

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2. *Université de Montréal, 1375 Ave. Thérèse-Lavoie-Roux, QC H2V 0B3, Montréal, Canada*

Nanoparticles possess unique properties linked to their size and shape. Thereby, they are used in a multitude of domains such as the formation of nanocomposite materials. The addition of nanoparticles bestows certain properties to materials such as an improved mechanical resistance or an improved electrical or thermal conductivity.¹ Many methods to produce nanocomposite materials exist,² among them, the organometallic pathway offers a good control on the final size and shape of the nanoparticles.³

The first step of this study lies in the identification and synthesis of organonickel precursors which are the most favourable for the formation of Ni(0) nanoparticles through hydrogenolysis. This study focuses on the influence of various reaction parameters such as temperature, reaction time and nature of the ligands on their final size and shape (Fig.1). The study of these parameters is done through an extensive NMR analysis of the reaction media before reduction, as well as through the use of 2D plots⁴ and their multivariate analysis which allows us to grasp the nucleation and growth phenomena.

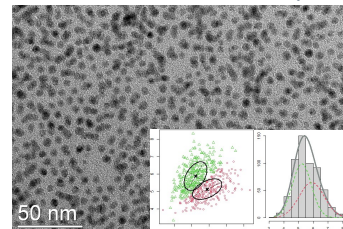


Fig.1: Synthesis of nickel nanoparticles through the hydrogenolysis of organometallic nickel complexes

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¹ G. L. Drisko *et al.* Nano Letters 2018 18(3), 1733-1738

² K. Yoshimura *et al.* Jpn. J. Appl. Phys. 1995, 34, 2440; (b) C. S. Carney *et al.* Mater. Sci. Eng. A 2006, 431, 1; (c) K. C. Liu *et al.* J. Electrochem. Soc. 1996, 143, 124.

³ S. Mourdikoudis *et al.* Langmuir 2013 29(44), 13491-13501

⁴ Z. Zhao *et al.* Nanoscale Advances 2021, 3, 6696 – 6703

Acknowledgement:

This project takes place within the framework of the RI Plasma project involving the LCC (Myrtil Kahn, Katia Fajerweg, Christine Lepetit, Pierre Fau, Yannick Coppel and Vincent Collière), the Laplace (Richard Clergereaux), the ICMUB (Jean-Cyrille Hierso) and the University of Montréal (Davit Zargarian and Luc Stafford) with the participation of the IMRCP (Anne-Françoise Mingotaud).

Keywords: nanocages, hydrogen, noble metal, water-based synthesis

Disciplinary fields involved: chemistry, electrochemistry

Sustainable Development Goals* eventually involved in your research: Affordable and Clean Energy (Goal 7)

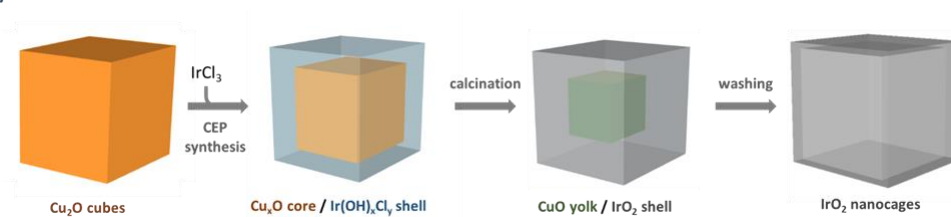
Green Synthesis of Water Splitting Electrocatalysts: IrO₂ Nanocages via Pearson's Chemistry

Jennifer Peron¹, Marine Elmaalouf¹, Marion Giraud¹, Silvia Duran,² Cédric Tard,² Jean-Yves Piquemal¹

1. Laboratoire ITODYS, UMR CNRS 7086, Université Paris Cité, Paris, France

2. Laboratoire Chimie Moléculaire, UMR CNRS 9168, Ecole Polytechnique, Palaiseau, France

Despite its scarcity and high price IrO₂ is still the catalyst used in commercial Proton Exchange Membrane Water Electrolyzers, the only devices today allowing for large scale and sustainable H₂ production. In order to decrease iridium loading while maintaining high performance, we have recently extended an original strategy based on the Pearson's hard and soft acid-base (HSAB) theory, to produce IrO₂ porous nanocages that are highly active toward the electrochemical splitting of water.¹ The formation of iridium oxide nanostructured cages, illustrated in the figure thereafter, is performed via a water-based process at room temperature, using cheap Cu₂O cubes as template. In this synthetic approach, the replacement of the Cu₂O core by an iridium shell is permitted by the difference in hardness/softness of cations and anions of the two reactants Cu₂O and IrCl₃. Calcination followed by acid leaching allow the removal of residual copper oxide cores and leave IrO₂ hierarchical porous structures with outstanding activity toward the oxygen evolution reaction. Fundamental understanding of the reaction steps and identification of the intermediates are permitted by coupling a set of *ex situ* and *in situ* techniques including *operando* time-resolved X-ray absorption spectroscopy during the synthesis.



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Keywords: Nanoparticles, Electro-Catalysis, Biomass, Hydrogen

Disciplinary field involved: Electrochemistry

Nanostructured catalysts for the selective electro-conversion of bio-sourced molecules into value-added compound

Thibault Rafaïdeen¹, Christophe Coutanceau¹

1. IC2MP, CNRS, Université de Poitiers, Poitiers, 4 rue Michel Brunet, TSA 51106, 86073, cedex 9, France

Non-edible ligno-cellulosic-biomass a huge carbon reservoir or a chemistry free from fossil resources. Glucose and xylose are the main sugars in hydrolysates after lignocellulosic biomass pretreatments to separate lignin from carbohydrates, and it has been proposed that the economically feasible production of valuable chemicals from lignocellulosic biomass should lean on the conversion of both xylose and glucose.¹ Electrochemical methods are non-thermal activation processes that can be used for the controlled oxidation reactions of organic molecules into valuable chemicals compounds at the anode of an electrolysis cell together with production of hydrogen at the cathode.

The development of active and selective nano-electrocatalysts is therefore of paramount importance. Here we study the electro-oxidation of different aldoses, glucose and xylose, and of their mixtures on Pd_xAu_{1-x}/C catalysts. The catalysts were synthesized using a micro emulsion method and comprehensively characterized by DRX, TEM, AAS, ATG and electrochemical methods². From in-situ Fourier transform infrared spectroscopy measurements and linear scan voltammetry, it was shown that Pd_{0.3}Au_{0.7}/C led to the best electrochemical behavior for the oxidation of glucose, xylose and glucose/xylose mixtures in terms of activity (higher current densities at lower potentials) and selectivity. Six-hour chronoamperometry measurements were performed at 293 K in a 25 cm² electrolysis cell at different potentials, sugars concentration and glucose/xylose ratio (90/10, 70/30 and 50/50 molar%) in order to accumulate reaction products and to quantify them by high performance liquid chromatography³. The main products were gluconate, xylonate at the anode and whereas hydrogen was produced at the cathode.

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3. T. Rafaïdeen, S. Baranton, C. Coutanceau, *ChemElectroChem* 2022, 9, e202101575, Doi :10.1002/celec.202101575

Acknowledgment:

The authors acknowledge financial support from the European Union (ERDF) through the Econat project, Région Nouvelle Aquitaine and the PHC Tournesol (French-Belgian cooperation Hubert Curien). Part of this work was supported by a grant overseen by the French National Research Agency (ANR) through the GLUCONIC Project (ANR-20-CE43-0005).

Part of this work also pertains to the French government program "Investissements d'Avenir" (EUR INTREE, reference ANR-18-EURE-0010)

Keywords: Magneto-plasmonic nanorods

Disciplinary fields involved: Chemistry, Physics, Biology

Sustainable Development Goals* eventually involved in your research: Industry, Innovation and Infrastructure (Goal 9)

Core@Shell Co@CoS Nanorods on the Way to Magneto-Plasmonic Probes

Thi Thiet VU¹, Brandon AZEREDO¹, Audrey MARTY¹, Guillaume VIAU¹, Katerina SOULANTICA¹

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Cobalt nanorods (NRs) exhibit high magnetic moment and high magnetic anisotropy which are very interesting for various applications such as information storage, permanent magnets, magnetic sensors, magnetic composites, magnetic resonance imaging (MRI), etc. However, Co is readily oxidized upon exposure to air or water, which results in a deterioration of their magnetic properties. Therefore, the poor resistance of Co NRs to oxidation limits their implementation in applications necessitating a stability to ambient conditions or aqueous environment. The protection of Co NRs can be achieved through an efficient coating by an adequate shell which prevents the penetration of air and water into the magnetic Co core. Furthermore, the shell can act as a platform for further coating and surface functionalization to fabricate multifunctional materials^[1].

In this study, we report the design of cobalt sulfide (CoS) coated Co NRs (Co@CoS NRs). The effect of crystallinity of CoS on the protection of magnetic Co core is examined. TEM and VSM are used to confirm the formation of core-shell structure and its stability in water. This protective CoS layer can act as an intermediate layer to open the way for Au coating on the surface of CoS because Au has strong affinity for sulphides^[2]. The targeted Au coated Co@CoS NRs should present magnetic properties as well as shape dependent plasmonic properties. After biofunctionalization, they could be used as probes for the in vivo detection of soluble biomarkers associated to diabetes.

References:

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Acknowledgment: *This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No. 899612*

2023

Thursday March 16th

10.30 am – 12.30 pm

Main Amphitheater

Program of the session

Chairs: Fabien CAN & Florence EPRON

NANOCHEMISTRY, NANOPARTICLES, NANOCATALYSIS

10:30	Predicting realistic shape and structure of nano-catalysts under working conditions: Are we there ?	Hazar GUESMI • CNRS – ICGM, Montpellier – France
11:00	Ab-initio study of the properties of metal-oxide nanoparticles: the case of ZrO ₂	Ravikant KUMAR • Univ. Limoges - IRCER, France
11:15	Towards DNA-coated patchy silica nanoparticles for programmable self-assembly	Auriane BAGUR • Univ. Bordeaux - ICMCB/CRPP, France
11:30	Elaboration of plasmonic enantiomorphs	Nada KHALFAOUI HASSANI • Sorbonne Univ. - MONARIS, France
11:45	Rate-limiting chemical reactions as the origin of non-classical nucleation in some co-precipitated compounds: the case of YbVO ₄	David CARRIERE • CEA - NIMBE, France
12:00	Chemical nanowelding of Cu@Ni bimetallic nanowires for transparent electrodes in room conditions	Andela KRIZAN • Univ. Bordeaux - ICMCB, France
12:15	Copper, Silicon, Phosphorus: new ternary nanocrystals for electrocatalysis	Anissa GHORIDI • CNRS - LCMCP, France

Keynote Speakers

NANOCHEMISTRY, NANOPARTICLES, NANOCATALYSIS



Hazar GUESMI

CNRS I Researcher

Charles Gerhardt Montpellier Institute

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BIOGRAPHY

Hazar GUESMI earned her Ph.D. degree in Materials Science at the University of Aix-Marseille III, France (2005). She performed her doctoral work under the supervision of Prof. Müller and Dr. Tréglia at the "Centre de Recherche de la Matière Condensée et des Nanosciences" in Marseille, where she studied the adsorption mechanisms on Si surfaces. From 2005 to 2006 she worked as assistant professor at the university "Pierre et Marie Curie", Paris VI and she developed her research activity on gold nanodots in the Institut des NanoSciences de Paris. In September 2006 she obtained a Post Doctoral grant via the European Network of Excellence and she worked for two years on the modeling of DeNox reaction in zeolites at the Institut Charles Gerhardt in Montpellier. In October 2008 she was appointed as a permanent CNRS researcher in the "Laboratoire Réactivité de Surface" in Paris (Sorbonne université) and after four years she moved to the ICGM. Currently, she is member of the Theoretical Physical Chemistry and Modeling department at the "Institut Charles Gerhardt" where she develop computational and theoretical studies on surface science and heterogeneous catalysis.

PREDICTING REALISTIC SHAPE AND STRUCTURE OF NANO-CATALYSTS UNDER WORKING CONDITIONS: ARE WE THERE ?

Metallic and bimetallic nano-catalysts typically operate under high-pressure and high-temperature conditions, and this reactive environment may substantially influence the structure and the surface composition and therefore the reactivity of these nano-materials. Theoretical studies of catalytic properties are often investigated on model systems (extended surfaces and/or small nanoparticles) where no account is taken for the possibility that the catalyst surface composition can be modified after the gas exposure [1]. This is a serious drawback that may prevent reliable description of the catalyst reactivity that mainly depends on the configuration of the surface. Nowadays, modeling the equilibrium structure and the shape of nano-catalysts in a "realistic" reactive environment is still a barely studied subject and remains an extremely challenging task.

Recent works in the group were focusing on the prediction and the study of the structural changes of metallic and bimetallic systems under reactive gas and on their related catalytic properties [2-5]. Different theoretical approaches based on Density Functional Theory (DFT) calculations, Monte Carlo (MC) and ab-initio molecular dynamic (AIMD) simulations were developed to predict "realistic" catalytic surfaces under reaction conditions. In this talk, I will present an overview of our main recent results and I will focus on the advantages and limitations of the developed theoretical approaches.

KEYWORDS:

Structural dynamics; heterogeneous catalysis; DFT and molecular dynamics; Surfaces and nanoparticles; Effect of reactive gas

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[1] "Realistic Modeling of Dynamics at Nanostructured Interfaces Relevant to Heterogeneous Catalysis." Kevin Rossi, Tzonka Mineva, Jean-Sebastien Filhol, F. Tielens, H. Guesmi, *Catalysts*, 2022, 12, 52.

[2] "Revealing size-dependent structural transition in supported gold nanoparticles at atmospheric pressure. "

A. Nassereddine, Q. Wang, D. Loffreda, Ch. Ricolleau, D. Alloyeau, C. Louis, L. Delannoy, J. Nelayah and H. Guesmi, *Small* (2021), 2104571.

[3] "Cu segregation in Au-Cu nanoparticles exposed to hydrogen atmospheric pressure: how is fcc symmetry maintained ?" Q. Wang, A. Nassereddine, D. Loffreda, Ch. Ricolleau, D. Alloyeau, C. Louis, L. Delannoy, J. Nelayah and H. Guesmi, *Faraday Discussion*, (2022) <https://doi.org/10.1039/D2FD00130F>.

[4] "Reshaping dynamics of gold nanoparticles under H₂ and O₂ at atmospheric pressure: Environmental gas transmission electron microscopy and theoretical modeling." A. Chmielewski, J. Meng, B. Zhu, Yi Gao, H. Guesmi, J. Nelayah, et. al., *ACS Nano* 13 (2019) 2024-2033.

[5] "Combined DRIFTS and DFT Study of CO Adsorption and Segregation Modes in Pt-Sn Nanoalloys. " Q. Wang, D. Tichit, F. Menier, H. Guesmi, *Journal of Physical Chemistry C* 124, 18 (2020) 9979-9989.

Keywords: ZrO₂, Metal oxide nanoparticles, Modeling, PDF, Quantum confinement, DFT

Disciplinary fields involved: Chemistry, Physics

Sustainable Development Goals* eventually involved in your research: Affordable and clean energy (Goal 7)

Ab-initio study of the properties of metal-oxide nanoparticles: the case of ZrO₂

Ravikant KUMAR, Assil BOUZID, Abid BERGHOUT, Olivier MASSON

CNRS, Université de Limoges, Institut de Recherches sur les Céramiques (IRCER), UMR 7315, Centre Européen de la Céramique, Limoges, France

In order to investigate the structure, stability, and electronic properties of zirconia (ZrO₂) nanoparticles, we have modeled several nanoclusters with diameters ranging from 0.9 nm to 2.04 nm by resort to first principles molecular dynamics (FPMD) and density functional theory (DFT) based calculations. Water molecules were placed on top of Zr atoms at the nanoparticle surface to passivate the dangling bonds and stabilize the nanoparticle's surface. We thermally equilibrated our modeled nanoclusters by using thermal annealing cycles at various temperatures which led to equilibrium structure models that, as shown by the pair distribution function (PDF) analysis, are in good agreement with the experiments.

In order to separate the surface and core of the nanoclusters, we use the smooth overlap of atomic position (SOAP) descriptor to assess the similarity of the Zr environments in the nanoparticles to that found in cubic and monoclinic ZrO₂. As a result, our findings show that the surface has Zr environments closer to the monoclinic phase, while the core region has environments more similar to the cubic phase. These results allowed to separate the structural contributions of nanoparticle surface and core, as well as to explain the evolution of the PDF as a function of nanoparticle size.

By analyzing the electronic properties, we found that the calculated band gap difference between ZrO₂ nanoclusters and bulk follows the quantum confinement law and increases as the particle size decreases.

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Acknowledgment:

This work was granted access to the HPC/AI resources of IDRIS under the allocation 2022-A0120913448 provided by GENCI.

Keywords: Hybrid nanoparticles, Patchy nanoparticles, Self-assembly, Click-chemistry, DNA

Disciplinary field involved: Chemistry

Sustainable Development Goals eventually involved in your research: Not applicable

Towards DNA-coated patchy silica nanoparticles for programmable self-assembly

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2. Centre de Recherche Paul Pascal, UMR5031, Université de Bordeaux, CNRS, Pessac, France

The self-assembly of nanoparticles into well-organized nanostructures has attracted strong interests during the last decade as a strategy to access elusive materials with exciting electronic or photonic properties [1]. In this context, the design of building blocks with controlled geometries and encoded directional interactions is the starting point of such self-assembly. Patchy nanoparticles, i.e. nanoparticles presenting chemical or topological discontinuities promotes self-assembly into clusters, chains or periodic superlattices. We report a synthetic strategy to silica nanoparticles of ~100 nm with a predefined number of polystyrene (PS) nodules as patches. This route includes sol-gel nucleation and growth, and seed-growth emulsion polymerization of styrene, allowing a fine control of the number and location of patches [2]. Typically, a morphology yield of 97 % was reached for bipods, silica particles presenting two PS nodules at their surface [3]. To guide the assembly, we rely on DNA coatings as a programmable glue to encode the interactions between particles. An amphiphilic azide terminated block copolymer is anchored at the surface of PS patch through a selective swelling-deswelling process with THF [4]. DBCO-terminated DNA strands are then coupled to the resulting azidated patches through click-chemistry via a SPAAC reaction. We show that these DNA-coated patchy nanoparticles can reversibly self-assemble upon thermal annealing [5]. We envision the assembly of colloidal chains of precise sequence and morphologies, as well as 2D and 3D lattices, depending on the shape and specific coatings of the building blocks.

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Keywords: Chirality, chiral structure nanomaterials, circular dichroism, Plasmonic enantiomorphs, seed mediated growth

Disciplinary fields involved: Chemistry, inorganic material

Sustainable Development Goals* eventually involved in your research: green synthesis of nanomaterials

Elaboration of plasmonic enantiomorphs

Nada KHALFAOUI-HASSANI¹, Nicolas GOUBET¹, Caroline SALZEMANN¹

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Chirality is defined by an absence of symmetry. It is a geometrical propriety for objects that are non-superposable in their mirror image. It induces, under circular polarized light (left or right), a specific optical response in circular dichroism (CD) [1]. Actually, the development of new chiral structure nanomaterials has attracted many attentions. They have strong potential in many fields such as asymmetric catalysis, molecular detection and nano-optics [2,3]. In this context, our goal is to elaborate chiral gold enantiomorphs by seed mediated growth. To this, we use anisotropic nanoparticles of high index of miller used as seed. The main strategy of our study is to lower the symmetry of gold nanocrystals in order to obtain enantiomorphs with chiral intrinsic morphology. The chirality is induced by using chiral ligands like amino acids.

Recently, we prepared chiral gold nanoarrows from gold nanorods used by seed mediated growth (figure 1). Our results show clearly that in the absence of chiral ligand, no dichroism signal is obtained. While in the presence of L-cysteine, chiral plasmon and morphology are observed. Actually, our study is oriented to understand the mechanism how does cysteine transfer the chirality to gold nanocrystals?

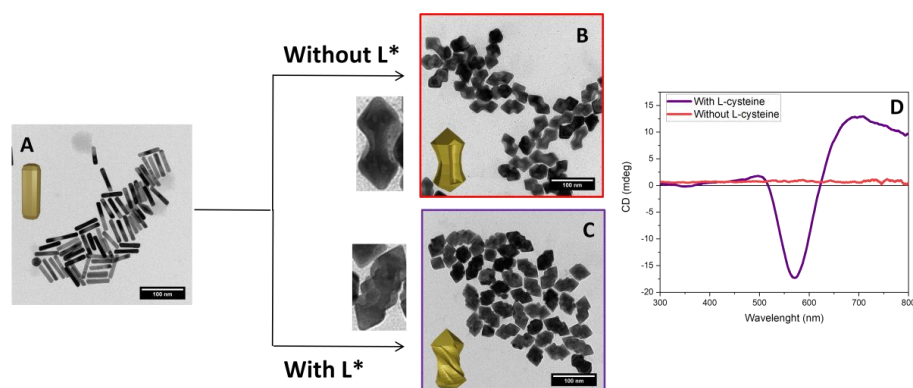


Figure 1 : Synthesis of chiral gold nanoarrows : A) TEM of gold nanorods used as seed B) TEM of gold nanoarrows without L-cysteine C) TEM of chiral gold nanoarrows in the presence of L-cysteine D) Circular dichroism of chiral gold nanoparticles.

C'Nano

THE NANOSCIENCE MEETING

Positiers

March, 15, 16 and 17

2023



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Keywords: co-precipitation, non-classical nucleation, EXAFS, SAXS

Disciplinary fields involved: Chemistry, Physics

Sustainable Development Goals: Affordable and Clean Energy (Goal 7)

Rate-limiting chemical reactions as the origin of non-classical nucleation in some co-precipitated compounds: the case of YbVO₄.

Raj Kumar Ramamoorthy¹, Marie-Alexandra Neouze^{1,2}, Maxime Durelle¹, Pascal E. Reiller³, Eric Larquet², Francois Baudalet⁴, Thierry Gacoin², and David Carriere¹

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The synthesis of nanocrystals by co-precipitation of aqueous salt solutions remains an attractive route due to its flexibility, low environmental impact, and ease of scaling up. In such processes, the formation of amorphous particles prior to crystal nucleation has been commonly observed, which both challenges the proper control over nanocrystal structure, and also may open new ways to synthesize original materials.¹ However, assessing when such "non-classical" crystallization prevails over direct crystallization from ions lacks a clear guideline, and relies on a case-by-case detection using spatial resolutions in the nanometer range.

Here, by combining induction times measured by EXAFS, computed supersaturations, and the multistep classical nucleation theory, we find that during non-classical nucleation of YbVO₄ nanocrystals, cluster growth is limited by the rate of the reaction of chemical transformation of amorphous intermediates into crystals. It suggests that occurrence of rate-limiting chemical reactions is a general cause for non-classical nucleation. In this frame, we provide a map that relates observable induction times, supersaturation and interfacial tension, to the preferred classical vs non-classical crystallization path.²

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Acknowledgment: synchrotron SOLEIL for beamtime provision and ANR-10-LABX-0035, FP7 Marie Curie Enhanced Eurotalents, ANR-14-CE08-0003 for funding.

Keywords: Bimetallic nanowires, Transparent electrodes, post-treatment, Optoelectronics

Disciplinary fields involved: Chemistry, Physics

Sustainable Development Goals* eventually involved in your research: Affordable and Clean Energy (Goal 7), Industry, Innovation & Infrastructure (Goal 9)

Chemical nanowelding of Cu@Ni bimetallic nanowires for transparent electrodes in room conditions

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Transparent electrodes (TE) are essential components for a wide range of devices including solar cells, touch screens, Light Emitting Diodes, transparent heaters¹, etc. Currently, the most prominent materials used for TEs are n-type degenerated semiconductors, for instance, indium doped tin oxide deposited by sputtering. Although the latter exhibits very good physical properties in terms of electrical conductivity and optical transparency, indium is scarce and hence expensive, and is a brittle material. Metallic nanowire (MNW) percolating networks constitute a promising emerging material for TE due to their desirable optical and electrical properties, flexibility, and a more accessible price range.^{2,3} Here, we have explored a bimetallic NW system based on copper and nickel, instead of the most studied silver nanowires. In addition to a novel synthesis, we will report a novel way of optimizing performance of a Cu@Ni TE through enhancing interconnectivity of NWs, based on a reducing treatment at room conditions. We have investigated the extent of protection that the Ni shell provides in regard to chemical and thermal stability, electrical stability and ageing. The proposed nanowelding process is expected to serve as useful tool to fabricate low-cost TE on flexible substrates, as shown by the proof of concept integrating an optimized Cu@Ni TE as a flexible transparent heater.

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Acknowledgment:

This work has received funding from Agence Nationale de la Recherche (ANR, France) via the program ANR_18-CE09-0040.

Copper, Silicon, Phosphorus: new ternary nanocrystals for electrocatalysis

Anissa Ghoridi^a, Ngoc Huan Tran^b, Amandine Séné^a, Marzena Baron^a, Daniel Janisch^a, Edouard De Rolland Dalon^a, Fernando Igoa^a, Emile Defoy^a, Antoine Miche^c, Cristel Gervais^a, Cristina Coelho-Diogo^a, Pierre-Olivier Autran^d, Isabelle Génois^a, Sandra Casale^c, Marc Fontecave^b, David Portehault^a

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In the search for new electrocatalysts having high activity and selectivity, incorporating p-block elements in transition metals is a way to subtly modify their electrocatalytic properties by playing on local structure distortion, charge transfer, and hybridization^[1]. Among foreign elements combined with metal, copper phosphides and silicides are especially studied as efficient catalysts or pre-catalysts for electrochemical water splitting^[2] and as anodes for Li-ion batteries^[3,4]. Nevertheless, the properties of the corresponding ternary phosphosilicides, which exhibit structures differing from binary phases, have not yet been explored. Indeed, only three ternary phases are currently known (CuSi₂P₃, CuSi₄P₃, Cu₄SiP₈)^[5,6] and have remained at the status of scientific oddities. We hypothesize that by combining not only one, but two p-block elements, the properties of copper atoms as catalytic sites would be further tuned and possibly enhance the electrocatalytic selectivity and activity for the CO₂ reduction reaction (CO₂RR) into high-added value products containing C-C bonds. However, to enhance the catalytic activity, it is necessary to design nano-objects with large surface/volume ratio.

We report herein the first successful synthesis of copper silicophosphide (CuSi₂P₃ and CuSi₄P₃) nanocrystals by inserting P and Si into copper in inorganic molten salt^[7]. The crystallization mechanisms have been studied by using *in situ* X-ray diffraction measurements (ESRF ID11 beamline) and reveal the formation of different intermediate phases from the initial metal salts to the ternary phases. After presenting in-depth characterization of the structure, composition and morphology of the nanomaterials (TEM, HRTEM, STEM-EDX, EDS mapping, XPS), we will discuss their promising electrocatalytic properties for CO₂RR.

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2023

Thursday March 16th

3.30 pm – 6.00pm

Main Amphitheater

Program of the session

Chairs: Myrtil KAHN & Jean-Yves PIQUEMAL

NANOCHEMISTRY, NANOPARTICLES, NANOCATALYSIS

15:30	Engineering Nanodiamonds from Gas Phase or Solution: Applications in Ammonia and Dihydrogen Sensing and Catalysis	Jean-Cyrille HIERSO • Univ. Bourgogne – ICMUB, Dijon – France
16:00	Green synthesis of Gd ³⁺ -doped ultrasmall carbon-based nanohybrids from coffee wastes	Kostiantyn PALIENKO • Univ. Kyiv- ILM, France
16:15	Elaboration of new hybrid perovskite@graphite composites and mixed 2D perovskites with enhanced stability for X-ray detection via a solvent-free mechanochemical approach	Yihui CAI • Univ. Strasbourg - ICPEES, France
16:30	Emulsions de Pickering stabilisées par un nanotubes aluminosilicaté Janus : propagation d'un front d'huile dans un réseau gelifié d'imogolites hybrides	Estelle PUEL • CEA - NIMBE, France
16:45	Coffee & tea break	
17:15	Ultra-small colloidal rare-earth aluminium/gallium garnet nanoparticles that are seed-mediate-grown beyond the surface of the YAG seed nanoparticles	Yige YAN • ENS Lyon - LCH, France
17:30	The effect of metallic precursors in the synthesis of metal nanoparticles at the liquid/liquid interface in Ouzo emulsions towards their use in catalytic hydrolysis of amine-boranes	Olivier GAZIL • Polytechnique Montréal - ISCR, France
17:45	Role of water in self-assembly of colloidal CdSe nanoplatelets	Benoit WAGNON • CNRS - Lab. Chemistry, France
18:00	Phosphate ions interactions with TiO ₂ nanoparticles: effect of the shape, crystallinity and oxidative stress	Rémi BÉRARD • CEA - NIMBE, France
18:15	Continuous Anisotropic Growth of NIR-Plasmonic Cs _x WO _{3-y} Nanocrystals	Jisoo OH • Ecole Polytechnique - PMC, France

Keynote Speakers

NANOCHEMISTRY, NANOPARTICLES, NANOCATALYSIS



Jean-Cyrille HIERSO

University of Bourgogne | Professor

Institute of Molecular Chemistry of the University of Bourgogne

<https://sciprofiles.com/profile/1115906>

BIOGRAPHY

Having a PhD from Université Paul Sabatier, Toulouse, Jean-Cyrille HIERSO is now full professor of Chemistry since 2009, at the Institute of Molecular Chemistry at the Université de Bourgogne, Dijon. He has interest in the fields of organometallic chemistry, ligand design, homo- and heterogeneous catalysis, chemical physics and material sciences. In 2011 he was awarded the National Prize for Coordination Chemistry from the French Chemical Society (SCF) and at the end of 2012 he was elected Member of the French Professors Academy "Institut Universitaire de France" (IUF). He has been nominated Junior Distinguished Member of the SCF in 2015. Topics developed in his group concern catalytic C–H bond functionalization, C–C and C–heteroatom bond formation, and sp³-C-based nanochemistry with applications in transition metal reactivity, especially palladium, gold and ruthenium.

ENGINEERING NANODIAMONDS FROM GAS PHASE OR SOLUTION: APPLICATIONS IN AMMONIA AND DIHYDROGEN SENSING AND CATALYSIS

Diamondoids (aka molecular nanodiamonds) are cage hydrocarbon molecules that can be described as fully hydrogen-terminated nanometer-sized diamonds. Adamantane and diamantane are the smallest diamondoids, and their selective functionalization can be achieved with high efficiency at various positions of the hydrocarbon cage [1]. We reported the mild physical vapor deposition of such functionalized nanodiamonds, which provides robust nano- and microstructured self-assembly of organic micro and nanocrystals [2]. Then, a bottom-up construction of hybrid organic–inorganic nanocomposites with a coated metal surface as ultrathin nanolayer on phosphine-functionalized nanodiamonds was stepwisely achieved from the gas phase by the low-temperature chemical vapor deposition (45 °C) of an organometallic complex over the self-assembled diamondoid scaffold [3]. Palladium nanolayered composites can be used to detect toxic NO₂ and NH₃ gases. NO₂ detection down to 50 ppb and NH₃ detection at 25 ppm concentration with fast response and recovery processes at 100 °C was demonstrated [4].

Other functionalization of adamantane and diamantane, including the introduction of sulfur functions [5], opened the way to the synthesis in solution of dense networks of metal nanoparticles. The control of the growth of sub-2-nm gold nanoparticles is achieved by the formation of well-defined networks, assembled in a single step reaction by employing bifunctional bis-adamantanedithiol (BAd-SH) or diamantanedithiol (DAd-SH). These are serving both as bulky surface stabilizers and short-sized rigid linkers. Uniformly small gold NPs (1.3 ± 0.2 nm to 1.6 ± 0.3 nm) embedded in insoluble frameworks are organized alongside short interparticular distances ranging from 1.9 to 2.7 nm. These were used for highly selective heterogeneous gold-catalyzed enyne cyclization to five-membered diene [5], while this reaction suffers from serious selectivity troubles in homogeneous catalysis. The control over the selectivity results from atoms cooperation at the gold surface that we analyzed in joint experimental and theoretical studies combining XPS, NMR and DFT. Further applications of such recoverable nanocatalysts in networks extend to ruthenium-catalyzed selective alkyne hydrogenation [6] and ammonia-borane solvolysis for high rate H₂ production [7,8].

KEYWORDS:

Nanocomposite; Nanodiamonds; Organometallic; Interface; Reactivity

Keynote Speakers

NANOCHEMISTRY, NANOPARTICLES, NANOCATALYSIS



Jean-Cyrille HIERSO

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<https://sciprofiles.com/profile/1115906>

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Keywords: carbon-based nanohybrids, green synthesis, coffee wastes, doping with Gd^{3+}

Disciplinary fields involved: Chemistry, Physics, Biology

Sustainable Development Goals* eventually involved in your research: Good health and well-being (Gal 3)

Green synthesis of Gd^{3+} -doped ultrasmall carbon-based nanohybrids from coffee wastes

K. Paliienko^{1,2}, A. Topchylo³, S. Alekssev⁴, A. G elo en⁵, Y. Milovanov^{2,3}, T. Lysenko^{1,2}, V. Skryshevsky^{2,3}, T. Borisova¹ and V. Lysenko⁶

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5. UMR Ecologie Microbienne Lyon (LEM), CNRS 5557, INRAE 1418, Claude Bernard University of Lyon, Villeurbanne, France
6. Light Matter Institute, UMR CNRS 5306, Claude Bernard University of Lyon, Villeurbanne, France

Carbon-based nanomaterials are a huge subgroup of nanosized materials of the IVth group. Carbon dots (CDs) have sparked a special interest among the all other carbon-based nanomaterials because of their unique properties, multidisciplinary applications, as well as extremely cheap and simple production methods [1]. According to the great principles of green synthesis, bio-wastes treated with microwave energy sources appear to be the best feedstock to produce CDs [2]. Waste-derived CDs are very perspective for a variety of applications: sensorics, catalysis, drug delivery, bioimaging, diagnostics and therapy [1].

The main goal of our work is to synthesize ultra-small nontoxic carbon-based nanomaterials which will be able to ensure perfect contrast in magnetic resonance imaging (MRI). Microwave-assisted green synthesis of Gd^{3+} -free CDs (GFCDs) and Gd^{3+} -doped carbon-based nanohybrids (GDNHs) from coffee wastes will be reported in details. A special attention will be paid to an impact of Gd^{3+} -ions on size distribution, surface chemistry, optical properties and biological toxicity of the GDNHs in comparison with the Gd^{3+} -free CDs obtained from the same coffee waste sources.

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Keywords: mechanosynthesis, hybrid perovskite, X-ray detection

Disciplinary fields involved: Chemistry, Physics

Sustainable Development Goals* eventually involved in your research: industry, innovation and infrastructure (Goal 9)

Elaboration of new hybrid perovskite@graphite composites and mixed 2D perovskites with enhanced stability for X-ray detection via a solvent-free mechanochemical approach

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In the last years, hybrid perovskites (HP) have emerged as a new class of semiconductors with outstanding performance, becoming a key player in optoelectronic, especially as X-ray detectors. Indeed, they exhibit high charge mobility, long carrier recombination lifetime, large light absorption coefficient and tunable bandgap. However, their development is hampered because of their chemical (air) and thermal instabilities and their low yield synthesis. Recently, a new solvent-free method, the mechanosynthesis, has emerged as a powerful alternative to produce HP with a high yield. We have successfully mechanosynthesized (MS) a commonly studied 3D hybrid perovskite: methylammonium lead iodide (MAPbI₃) and optimized the synthesis parameters. We have then combined HP with different amounts of graphite by mechanosynthesis as graphite may protect HP from moisture due to its hydrophobicity and combine its good electronic properties. Both static and time-resolved photoluminescence spectra and resistivity measurements as a function of graphite content evidenced strong optoelectronic interactions between graphite and HP. Their fine characterizations including InSitu high-resolution TEM and XRD in temperature highlighted an orientated aggregation of nanograins in nanopowders. As another strategy to further enhance the HP stability is to combine the outstanding optoelectronic properties of the 3D HPs with the high robustness of the layered 2D phase, we have successfully inserted the 3D phase into the layered 2D structure through a one-pot mechanochemical approach, characterized them, determined the synthesis mechanism and studied the effect of the ammonium chain nature driving the 2D phase on their optoelectronic properties and X-ray detection performance.

Keywords: Hybrid imogolite, Pickering emulsion, gel oil network
disciplinary field involved: Chemistry

Pickering emulsions stabilized by a Janus nanotubes aluminosilicate: oil propagation into a gel-like network

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This work deals with the conditioning of non-incinerable radioactive oil, issued from the nuclear industry, and which is still deprived of an appropriate treatment. A direct incorporation of oil in cement-based matrix could be a way to overcome this issue but compatible technologies must be found. The investigated strategy consists in exploring Pickering emulsions with Janus particles interacting favourably with the cement and oils.

Janus particles are hybrid nano-clays (aluminosilicate imogolites) with tubular shape¹. The nanotubes internal surface being covered by hydrophobic Si-CH₃ groups, it can trap and stabilize hydrophobic compounds². The external surface formed by alumina surface is hydrophilic. It has potential compatibility with Portland cement and mixing water.

Presentation will be dedicated to the study of the interaction between model solvent (hexadecane) and imogolites and to the stabilization mechanism of Pickering emulsions. The stabilization mechanism is a two steps process. The first one, revealed by drop interfacial tension measurements (pendant droplet), consists in a fast stabilization of the water/oil interfaces by adsorption of hybrid imogolites to form a gel layer. The second (interfacial tension and rheology measurements) shows that the gel layer evolves slowly with time. The stability improves by aggregation of the nanotubes generating a stable gel structure between the drops³.

Direct Pickering emulsions incorporate oil up to 60%_{v/v} by only adding a mass fraction of hybrid imogolite materials lower than 1 wt%. These emulsions stabilized by a Janus particle have a typical behavior of both gel and Pickering emulsion, allowing to efficiently encapsulating oils.

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Keywords: Seed mediate growth, ultra-small nanoparticles, garnet, glycothermal, autocatalytic surface reaction.

Disciplinary field involved : Chemistry

Ultra-small colloidal rare-earth aluminium/gallium garnet nanoparticles that are seed-mediate-grown beyond the surface of the YAG seed nanoparticles

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We have successfully used the undoped ultra-small colloidal YAG nanoparticles (NPs) as seeds to grow colloidal particles of cerium doped rare-earth (Tb, Gd, Eu) gallium/aluminium garnet (RE(G/A)G:Ce³⁺) via glycothermal route, that are otherwise difficult to obtain. The resulted seed-mediate grown particles showed several interesting properties: 1) Aggregations and thus the hydrodynamic radius of NPs are greatly reduced compared to the seed free ones (Figure 1). 2) The particles showed characteristic Ce³⁺ photoluminescence (PL) properties as if that in respective pure garnet host. 3) Competitive formation of perovskite phase has been inhibited. 4) Advanced elemental cartographic analysis revealed that most of the seed-mediated grown NPs are constituted only by the to-be-grown garnet exclusive elements, while most of the YAG seed particles stayed individually intact without core-shell structure features (Figure 2). Computational studies suggested that the nucleation of the seed-mediate grown garnet NPs might start beyond the surface ligands of the seeds, to be known as an “autocatalytic surface reaction” mechanism.

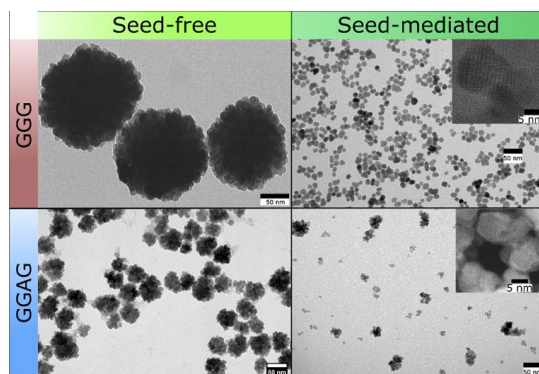


Figure 1: TEM images of the seed-free and seed-mediated-grown cerium doped Gadolinium Gallium Aluminium Garnet (GG2A3G:Ce3%) NPs and the seed-free and seed-mediated-grown Gadolinium Gallium Garnet (GGG:Ce3%) NPs, the insert images are HRTEM image with a scale bar of 5 nm.

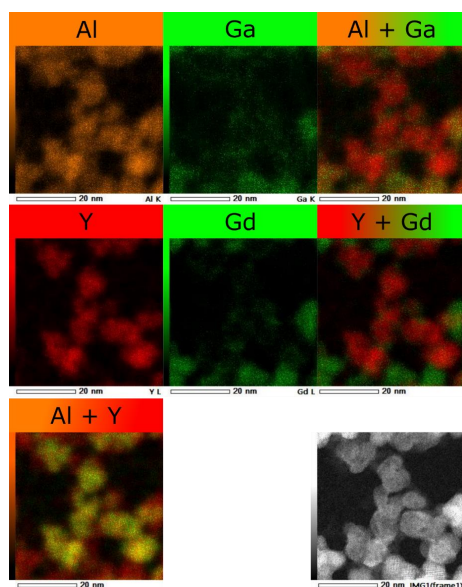


Figure 2 : HR EDX elemental cartography of AL, Y, Ga and Gd, combination of Y and Ga, combination of Y and Gd and combination of Al and Y of the seed-mediated grown cerium doped Gadolinium Gallium Aluminium Garnet (GG2A3G:Ce3%) NPs. Bottom right is the HRTEM image of the analyzed zoom.

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Keywords: Metallic nanoparticles, interfacial chemistry, dehydrogenation, Ouzo emulsion.

Disciplinary fields involved: Inorganic chemistry

Sustainable Development Goals: Affordable and clean energy (Goal 7)

The effect of metallic precursors in the synthesis of metal nanoparticles at the liquid/liquid interface in Ouzo emulsions towards their use in catalytic hydrolysis of amine-boranes

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It was recently demonstrated that Ouzo emulsions can be employed as a soft matter template to synthesize nanomaterials via an interfacial reaction at the liquid/liquid interface, yielding various morphologies such as shells composed of metal nanoparticles (NPs), or continuous shells.¹ Ouzo emulsions are typically composed of a dissolved hydrophobic solute (in an organic solvents) that nano-precipitates with the addition of water, leading to the spontaneous formation of submicronic droplets. In this work, we demonstrate that the metallic precursor itself can act as the hydrophobic solute and is able to form an Ouzo emulsion on its own – increasing the yield of the synthesis. This metallic precursor can be reduced interfacially by the addition of a reducing agent (e.g. NaBH_4) in the continuous phase, and different interfacial syntheses are obtained depending on the type of organometallic precursor. As an example, changing the triphenylphosphine ligand to an acetate yields respectively a Pd continuous shell, or discrete PdNPs. The formation mechanism of these emulsions is addressed first by dynamic light scattering and transmission electron microscopy. Second, the effect of the metallic precursor on the synthesized nano-objects (morphology and composition) is studied by wide-angle X-ray scattering and X-ray photoelectron spectroscopy. Finally, atomic resolution transmission electron microscopy has revealed that using simultaneously two different metallic precursors yields bimetallic NPs, and not two discrete types of pure, distinct metal NPs. Finally, catalytic hydrolysis of amine-boranes to produce hydrogen is performed with these objects to study the catalytic properties of the nanoparticles.

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Keywords: CdSe, Nanoplatelets, Self-assembly, FRET

Disciplinary fields involved: Chemistry, Physics

Role of water in self-assembly of colloidal CdSe nanoplatelets

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CdSe nanoplatelets (NPL) have aroused a growing interest over the past few years thanks to their ultrathin thickness that can be controlled to the atomic layer [1]. Excitons quantum confinement imposed by this thickness leads to an intense fluorescence with a narrow spectral width and a large spectral overlap. Thus, inter-NPL ultrafast FRET can occur when NPLs in stacks and can reach distances of 500 nm [2] when happening in micrometer-long nanoplatelet threads [3]. Such assemblies are promising objects to present novel collective photophysical properties involving hundreds of emitters but are difficult to synthesize because mechanisms to explain their formation remains unclear.

In this work we explored the experimental conditions to obtain long stacks with high yield through the slow evaporation of a dispersion of NPL in presence of oleic acid. We tuned the evaporation rate, the concentration in oleic acid and the relative humidity of the atmosphere during evaporation. We found that water captured from atmosphere by oleic acid during evaporation is essential to obtain long threads. Understanding this effect is a step forward to synthesize new long threads made of NPLs with higher quantum yield or smaller ligands leading to new opto-electronics properties.

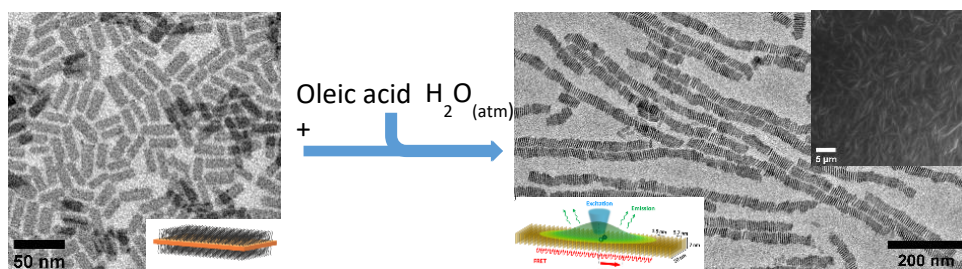


Figure 1 – TEM pictures and scheme of NPLs prior and after hexane drying at a controlled relative humidity in presence of oleic acid. Top right inset show epifluorescence picture of thread solution.

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Keywords (max. 4-5): TiO₂, phosphate, radiolysis, aging, linteraction

Disciplinary fields involved: chemistry, physics

Phosphate ions interactions with TiO₂ nanoparticles: effect of the shape, crystallinity and oxidative stress

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Numbers of applications such as painting, photocatalysis and food additives involve TiO₂ nanoparticles. Due to their probable carcinogenic effect^[1], the French government has banned them from food products until studies acknowledge health effects. This carcinogenic effect is commonly attributed to the formation of radical oxidative species (ROS) that cause damages on cellular functions or to the DNA. The contact with the cell may occur with the phospholipid bilayer^[2]. However, those mechanisms are dependent on the crystallinity and on the morphologies of the TiO₂ nanoparticles.

We present here controlled synthesis of anatase and rutile TiO₂ nanoparticles with different shapes such as needles, rods and bipyramids^[3]. The diversity of morphologies allows investigating the role of crystalline facets on the adsorption of phosphate, chosen here to mimic molecules of biological interest, at three scales. First, we evaluate its efficiency depending on the nanoparticles by isotherm studies. Then HRTEM analysis shows the phosphate adsorption on the different crystalline facets. In addition, infrared spectroscopy allows studying interactions between phosphate and TiO₂ nanoparticles. Finally, we investigate the behavior of the TiO₂/phosphate system under radiolysis, which enables generating ROS and studying the effect of oxidative stress on the medium.

Those results allow a first approach of the behavior of TiO₂ towards a model of molecules of biological interest and the possible damages they can undergo. This is also an opportunity to get an insight into the role played by the facet structure and the adsorption sites of various TiO₂ nanoparticles that could be useful for catalytic studies.

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Keywords: Semiconductor plasmonic NCs, Shape anisotropy

Disciplinary fields involved : Chemistry, Plasmonics

Sustainable Development Goals* eventually involved in your research: Sustainable Cities and Communities (Goal 11)

Continuous Anisotropic Growth of NIR-Plasmonic Cs_xWO_{3-y} Nanocrystals

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Heavily doped semiconductor nanoparticles exhibit Localized Surface Plasmonic Resonance (LSPR) at the near-infrared (NIR) wavelength ranges. This extends the potential application of LSPR in the fields of solar energy, telecommunication, biomedicine, and imaging. Among the recently proposed host materials of NIR-plasmons, cesium doped tungsten oxide (Cs_xWO_{3-y}) nanocrystals are of significant interest due to their dual-mode LSPR tunable across the entire NIR range (700 ~ 3000 nm). The doping level in Cs_xWO_{3-y} can reach an exceptionally high value (near 1 electron per 1 W-atom), which enables intense LSPR in the NIR adjacent to the visible range. Moreover, the doped free electrons can resonate in two directions with respect to different crystalline axes, producing a unique dual-band LSPR property [1].

In this presentation, we demonstrate synthetic methods to finely control the crystal phase and morphology of the Cs_xWO_{3-y} nanocrystals thereby achieving a large tunability of their dual-band LSPR feature. Small nanocrystals with variable aspect ratios (length/width) from 1 to 6 could be synthesized by controlling the nature of precursors and their injection methods such as heat-up or hot-injection [2]. Furthermore, we realize an exquisite control of the anisotropic nanocrystal growth – either *longitudinal* or *lateral* growths – by a continuous dropwise addition of precursors to the seeds that are prepared by a separated one-pot synthesis. This new synthetic strategy enables to precisely select a target shape of nanocrystals within an extended range of aspect ratio from 0.2 to 20, thereby achieving extreme LSPR spectral characteristics even beyond the NIR region. We attribute this anisotropic growth mechanism to the distinct surface energies on different crystal facets being adjusted by the nature of activated precursors.

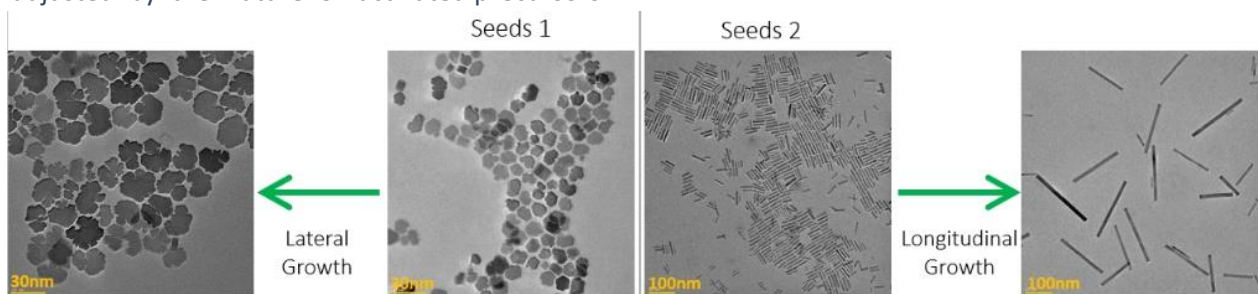


Figure 1 TEM images of seeds and grown particles. Seeds formed by one-pot synthesis can be grown into particles having extremely small or big aspect ratios by using the continuous injection method.

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