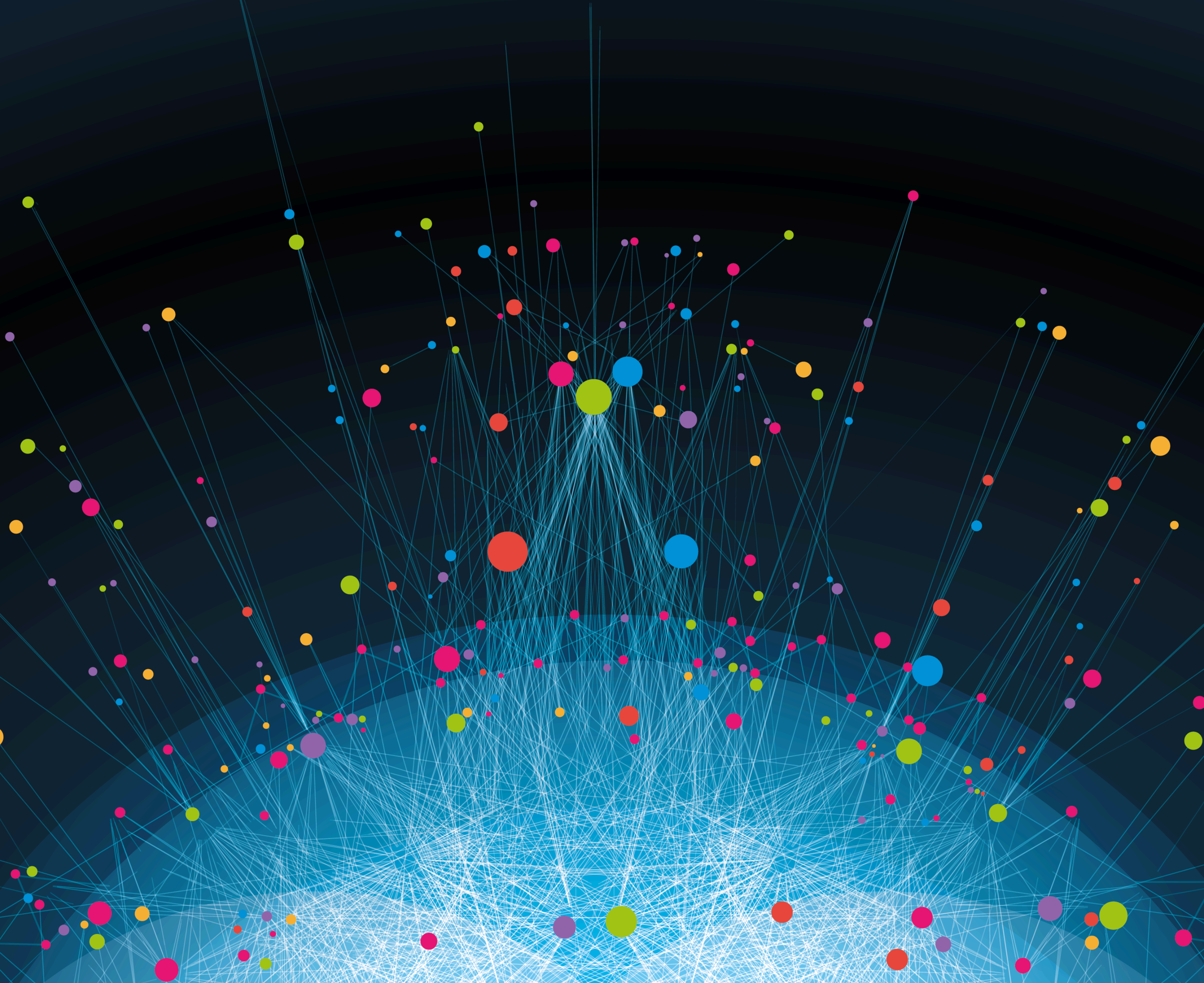
BOOK
OF
ABSTRACTS

Nanochemistry, Nanoparticles, Nanocatalysis



Nanochemistry, Nanoparticles, Nanocatalysis

Tuesday March 18th

3:30 P.M. - 6:45 P.M.

AMPHITHEATRE GASTON BERGER

Program of the session :

HOUR	NAME	TITLE
15:15	**Christophe PETIT** **MONARIS - Sorbonne. Univ**	**Oleylamine and low valency organic precursor : a facile route to metallic and multicomponent N**
15:45	Fadoua SALLEM GET - CNRS	Controlled synthesis of copper-based nanoparticles
16:00	Jean IRLE BELMONT LCC - Univ. Toulouse 3	Towards predictive copper nanoparticles of mastered size and shape
16:15	Guillaume BONIFAS LPCNO - INSA Toulouse	Unraveling the Facet-Dependent Surface Chemistry of Indium Phosphide Nanocrystals
17:00	Marina DESCOUBES LCT - Sorbonne Univ.	Multi-scale modeling of the dissolution/growth dynamics of metallic copper clusters during synthesis or catalysis processes
17:15	Abdennour BENABBAS IC2MP - CNRS	Novel Green Method for the Preparation of Supported Sub-10 nm Non-Noble Metal (Cu, Sn and Ga) Nanoparticles
17:30	David RIASSETTO LMGP - Inst Polytechnique de Grenoble	Growth Mechanism of Ultra-thin, Long and Flexible CuO2 Nanowires for Photocatalytic Membranes Applications
17:45	Lamyae BENHAMOU GEMTEX - ENSAIT	Morphological Control of 3D Hierarchical ZnO Microspheres via Citrate-Assisted Hydrothermal Synthesis
18:00	Michel FERON Institut de Chimie de Toulouse - Univ. Toulouse 3	Following zinc oxide nanoparticles formation
18:15	Brandon AZEREDO LPCNO - INSA Toulouse	Topochemical reactions of P with Co nanorods

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Short Biography

Born in 1962 Christophe Petit is full professor at Sorbonne University and former director of the laboratory MONARIS (2014-2024). He was co-responsible (2011-2017) of the Nanochemistry thematic axe of the Labex MiChem then deputy director of the labex MICHEM (2017-2022). He was deputy director of « Initiative pour les Sciences et Ingénierie Moléculaires » (2020-2024) and co-responsible (2014-2016) of the Nanochemistry axe of the network C'Nano from the "Region IdF" (Former DIM NANO-K). He is actually in the board of the IRN 'nanoalloys' (https://nanoalloys-irn.cnrs.fr/).

Author or co-author of 85 publications in peer-reviewed journals and 8 book chapters, his research is now mainly devoted in the development of new sustainable synthesis to control the shape, size and structure of (bi) metallic nanocrystals and their application in nano-electronic but also in catalysis. Besides the empirical process, the aim is to understand the nucleation and growth mechanism to establish rational synthesis of metallic and multi metallic NCs and to develop their applications

Title of Oral Presentation

Oleylamine and low valency organic precursor : a facile route to metallic and multicomponent N

Keywords (5 words max)

(bi) metallic nanocrystals, nucleation and growth , nanochemistry

Abstract of Oral Presentation

Metallic nanoparticles will initiate important development in nanotechnologies due to their specific chemical and physical properties (i.e. in catalysis, magnetism, optics, etc..) and new development in sustainable energy. It is well known that these properties are mainly controlled by the fine tuning of structural parameters such as the size, shape, crystallinity and composition. However, the understanding of the mechanical steps leading to the shape control of these objects still remains challenging. Recently our group developed a one-pot synthesis of metallic or bimetallic spherical NPs with only two reagents: MCl(PPh3)3 and Oleylamine (M= Co or Ni).1-3 This method showed many advantages like the reproducibility, the low size dispersity and well crystalline NPs.2-3 This synthesis allows also the formation of transition metal phosphorus (TMP) nanorods starting from pure metallic spherical NPs. Herein, we propose a mechanism for the morphological transition from spherical cobalt NPs to Co2P NRs over time in a mixture of [CoCl(PPh3)3] and oleylamine (OAm) heated at 190°C.4 The crucial role of oleylamine in the transition was also confirmed by X-ray photoelectron spectroscopy (XPS) but it discloses also the significant involvement of the organo-phosphorus ligand of the Co(I) precursor during the spheres to rod transition yielding to Co2P nanorods formation. Interestingly this model could be extended to multicomponents NPs as CoNiP. Lastly, the novel synthesis, which produces Co2P nanorods at a relatively low temperature (~190 °C), compared to the standard process (~330 °C), is a notable finding, given the promising applications of this material, particularly in electrocatalytic water splitting.

Acknowledgement

This work was financially supported by Sorbonne Université, CNRS, the ANR in the framework of the program entitled “Nucleation, growth and reactivity of MEtallic and bimetallic Nanocrystals”under reference ANR- 17-CE09-0037 and LabEx MiChem (“Investissements d’Avenir” program) under reference

References (6 lines max)

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Thematic Session: Nanochemistry & Nanoparticles
Disciplinary fields involved: **Chemistry**

Keywords (max. 4-5)**: copper oxide nanoparticles, precipitation, controlled synthesis, growth mechanism**

Controlled synthesis of copper-based nanoparticles

Fadoua SALLEM, Mickael Wagner, Nicolas Rataj, Eloise Annabi, Alain Castillo, Ludovic Menjot, and Astrid Avellan

Laboratoire Géoscience Environnement Toulouse (GET), Observatoire Midi-Pyrénées (OMP), Centre National de Recherche Scientifique (CNRS)

Abstract

Copper-based nanoparticles (CuONPs) presents interesting physical-chemical properties to improve Cu delivery to plant leaves in agriculture. Indeed, CuONPs could be tuned as a copper “nano-reservoir” slowly releasing ionic copper over time, or on trigger. In order to understand the interaction mechanism of CuONPs with leaf surfaces and cells, it is mandatory to understand the keys factors that governs nanoparticles biodistribution. One of these factors is the physico-chemical properties of the applied copper-based nanoparticles.

In the present work, we have designed CuONPs with controlled physico-chemical properties including morphology, size, crystallinity and surface chemistry. An optimized protocol will be presented and the effect of the experimental parameters (reaction temperature, precursor type, concentration) on the shape, the size and the growth mechanism will be discussed. The obtained results have allowed to control the synthesis of CuONPs and propose a hypothesis about their crystal growth mechanism. A panel of copper-based nanohybrids have been synthesized and fully characterized with many characterization techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM), dynamic light scattering (DLS), and fourier-transform infrared spectroscopy (FTIR).

Acknowledgement:

We would like to thank the ERC for the funding throught the ERC StG LEAPHY and the microcharacterization center Raimond Castaing for the TEM analyses.

Thematic Session: Nanochemistry, Nanoparticles and Assemblies
Disciplinary fields involved: Chemistry
Keywords: metal copper nanoparticles, organometallic precursor, morphology, topology, modelling

Towards predictive copper nanoparticles of mastered size and shape

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Well-defined, robust, copper-based metal nanoparticles (Np) are potential candidates as nano-catalysts for releasing H_2 from its secured solid-state chemical storage in amine-borane materials. High-performance delivery solutions from reactive Np have not yet been developed.[1] The main objective of our work is to produce and understand the bottom-up synthesis of copper-based metal Np from the controlled hydrogenolysis of an amidinate family of organometallic precursors in solution.[2] The influence of the amidinate precursor structure on the morphology of the Np is studied by varying the substituent groups introduced ((R^1), Figure 1). The systematic characterization of Np obtained from multiple experimental conditions is achieved using advanced techniques of electron microscopy (TEM), X-ray diffraction (DRX, WAXS), UV-Visible absorption and nuclear magnetic resonance spectroscopy (NMR). This allowed to highlight the most significant parameters for controlling Np size, shape and distribution. Our experimental study is supported by quantum topological analyses of these precursors, which provides important descriptors for correlating these parameters and final Np structures.

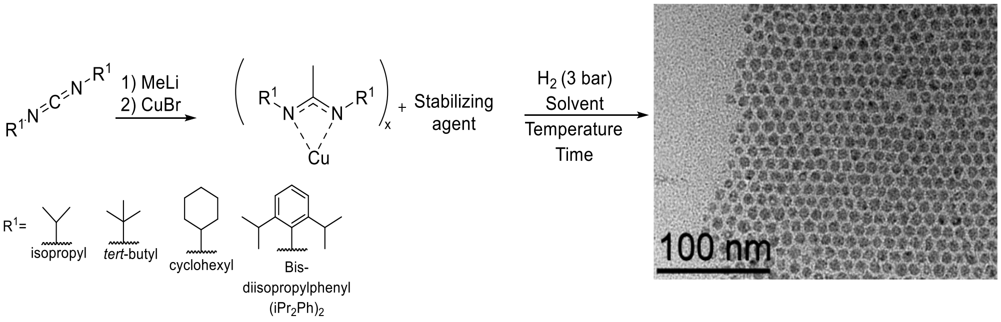

Figure: synthesis of copper Np

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Thematic Session: Nanoscale characterization
Disciplinary fields involved: Chemistry
Keywords: Facet-Dependent Surface Chemistry, Nuclear Magnetic Resonance Spectroscopy, Oxidation, Indium Phosphide, Semiconductor Nanocrystals

Unraveling the Facet-Dependent Surface Chemistry of Indium Phosphide Nanocrystals

G. Bonifas[1], E. Cho[2], M. Kim[2], L. Ouyang[1], H. Kim[2], Y. Coppel[3], S. Jeong[2,4], C. Nayral[1], and F. Delpech[1]

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In less than two decades, semiconductor nanocrystals (NCs) have gone from being laboratory objects to everyday objects in a variety of optical applications (LEDs, electronic, photovoltaic…). However, most of them are made of toxic Cd and Pb elements. InP QDs exhibit lower toxicity and comply with European regulations, making them the preferred choice. However, progress is still needed in terms of size, shape and surface control. Recently, a major breakthrough has been performed with the synthesis of tetrahedrons (TD) and tetrapods (TP). In the former case, the InP NCs possesses only {111} facets while tetrapods (TP) exhibit {110} and {−1−1−1} facets[1], paving the way for studies on facet-selective surface chemistry.

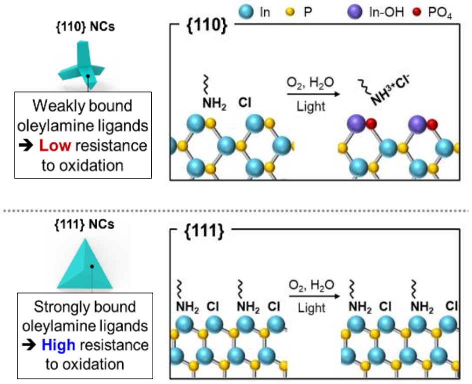

Figure: InP Td & TP NCs oxidation

In this work (Figure), facet-dependent reactivity is explored in the context of oxidation through air exposure. Solid-state/solution NMR, FT-IR, and XPS analyses show that TD and TP possess a dramatic difference in reactivity: TD exhibits strong resistance to photoassisted surface oxidation, whereas TP oxidises significantly[2]. The rationalization of this result will be presented and will highlight the significance of facet-dependent reactivities and, their importance for optoelectronic applications.

References:
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Acknowledgement:

This research was funded by the PHC STAR and ANR, the Université Paul Sabatier, CNRS, the INSA of Toulouse, the french MEAE and MESR and the EUR grant NanoX (ANR-17-EURE-0009). This research was also supported by the NRF of Korea, funded by the MSIT.

Thematic Session : Nanochemistry, Nanocatalysis & Nanoparticles
Disciplinary fields involved : Chemistry
Keywords : Modeling, DFT, nucleation, copper catalysts, reaction path,

Multi-scale modeling of the dissolution/growth dynamics of metallic copper clusters during synthesis or catalysis processes

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Copper nanoparticles (Cu NPs) are valued for their catalytic and plasmonic properties, with size and shape control being critical for optimizing their performance. However, understanding and controlling their synthesis is challenging due to the complexity of high-temperature processes and competing reactions. Understanding the processes involved during the nucleation step is attractive and it could open the way to rational control. Vrancken et al.[1] recently reported a near-ambient temperature synthesis method based on the thermal decomposition of an alkyl copper reagent. This process forms a Cu precursor, which evolves into Cu NPs stabilized by thiolates. The mechanism involves two key steps suggested by Whitesides et al.[2] (Figure 1): a β-hydride elimination forming a Cu-hydride intermediate, followed by reductive elimination yielding $Cu^{(0)}$. The Cu-hydride intermediate is notable for its relevance in energy conversion applications, such as CO_2 reduction. Kinetic studies by Kochi et al.[3] suggest an autocatalytic mechanism involving mixed-valence $Cu^{(I)}$-$Cu^{(0)}$ species, potentially catalytically active. The study also examines how metallic seeds and ligands influence reaction kinetics and species stability, with the role of phosphine additives remaining under investigation.

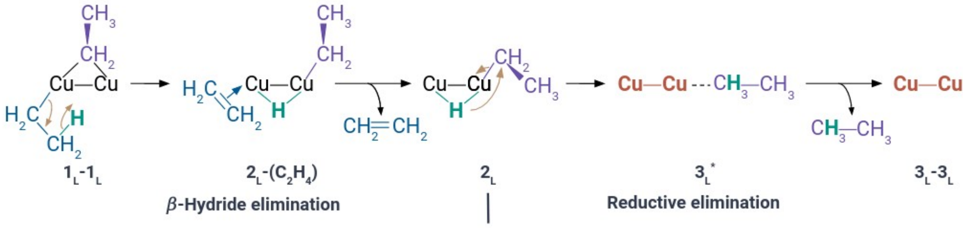

Figure 1 – Example of thermal decomposition mechanism where the green H is a hydride, red copper atoms are metallic copper atoms and L is a Lewis base.

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Thematic Session: Nanochimie & Nanoparticules
Disciplinary fields involved: Chemistry & Catalysis
Keywords: green chemistry, non-noble metal nanomaterials, stable nanocolloids, liquid nanomaterials, oxide-supported nanomaterials

Novel Green Method for the Preparation of Supported Sub-10 nm Non-Noble Metal (Cu, Sn and Ga) Nanoparticles

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Abundant non-noble metal nano-objects are promising alternatives of the excessively used expensive and scarce noble metals in real industrial applications. Unfortunately, their large-scale utilization is limited by the lack of synthetic procedures that combine satisfactory yields and low costs [1].

In this work, we discuss the rational and green colloidal synthesis of monodisperse sub-10 nm metallic nanoparticles (NPs) of copper (Cu), tin (Sn) and gallium (Ga) that exhibit high resistance to surface oxidation. Notably, the fascinating properties arising from nano-confinement in liquid (for Ga) and solid (for Cu and Sn) states at room temperature, little known so far, are studied under identical conditions. Special attention is equally paid to the structural, morphological and chemical modifications in these NPs induced by the presence of a support material, with γ-Al_2O_3 used as a model support [2].

Our oxidation-resistant nanomaterials are ideal candidates for further processing in various applications that do not require inert atmospheres or prior reduction steps. This developed methodology is expected to significantly advance our understanding of the relationship between the physico-chemical characteristics of size-controlled non-noble metals and their subsequent performance.

References:
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Acknowledgement:

The presented work is developed within a fundamental research project funded by French Agence Nationale de la Recherche (ANR) where supported liquid/solid non-noble metals are engineered at the nanoscale for an application in catalysis that enables the production of high-value chemicals.

Thematic Session: Nanochemistry & Nanoparticles
Disciplinary fields involved: Wet Chemistry, Inorganic Chemistry
Keywords: Nanowires growth mechanisms, Nanowires assemblies, Inorganic Membranes

Growth Mechanism of Ultra-thin, Long and Flexible CuO$_2$ Nanowires for Photocatalytic Membranes Applications

Soline Beitone[1], Mouncif Belmohoub[1], Damien Evrard[2], Céline Ternon[1], David Riassetto[1]

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Abstract:

The reduction of CO$_2$ emissions and mitigation of global warming claimed a transition of the economy from fossil to renewable sources in order to achieve carbon neutrality by 2050, particularly in Europe[1].
One promising strategy is based on Carbon Capture and Utilization (CCU)[2] and involves utilizing atmospheric CO$_2$ and solar energy to generate valuable products, referred to as solar fuels. This innovative approach, is based on photocatalytic conversion of CO$_2$ into a variety of species, including methane (CH$_4$), and is inspired by natural photosynthesis.
Since the use of a single photocatalyst alone does not achieve sufficient activity, the association of two different photocatalyst in heterojunction can offer higher performance. Particularly, the Z-scheme electronic transfer is very similar to the electronic transfer obtained in natural photosynthesis[3], allowing for the maintenance of a high redox potential while increasing efficiency by limiting charge recombination.
Our goal is to developed a self-supported inorganic nanowires membranes heterostructures with a Z-scheme electronic transfer. One of two heterostructure materials investigated is CuO$_2$ in the form of nanowires. This presentation will be focus on the optimized hydrothermal synthesis method for producing ultra-thin and long Cu$_2$O nanowires. The growth mechanism is thoroughly investigated, with a focus on the effects of temperature and reaction time on the morphology, crystallinity, and optical properties of the nanowires. Then, ultra-flexible, self-supported membranes composed of Cu$_2$O nanowires were successfully prepared using vacuum filtration method. These membranes exhibit excellent mechanical flexibility and promising optical and electronic properties perfectly compatible with our goal.

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Acknowledgement:

CDP DefiCO2

Thematic Session: nanochimie, nanoparticles
Disciplinary fields involved: Chemistry, Physics
Keywords: Hydrothermal method, ZnO, microstructures, trisodium citrate

Morphological Control of 3D Hierarchical ZnO Microspheres via Citrate-Assisted Hydrothermal Synthesis

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Univ. Lille, ENSAIT, ULR 2461-GEMTEX-Génie et Matériaux Textiles, F-59000 Lille, France

Abstract

ZnO is a versatile material with unique properties, enabling applications in photovoltaics, electronics, optics, and catalysis. Its properties are related to its morphology, as underlined by recent research focusing on the syntheses of ZnO particles with varied shapes and sizes. ZnO particles can be in one-dimensional (1D) and two-dimensional (2D) ZnO micro/nanostructures, such as nanorods [1], nanowires [2], nanofibers [3], and nanosheets [4]. 3D hierarchical ZnO structures are obtained from assembled 0D, 1D, and 2D nanoscale building blocks and have attracted attention for their enhanced properties and potential applications [5]. 3D hierarchical ZnO microspheres were synthesized via a hydrothermal precipitation method using urea as the precipitating base, zinc nitrate hexahydrate as the precursor, and trisodium citrate as a surfactant. The citrate/Zn molar ratio was varied from 0 to 0.67 to investigate its effect on ZnO morphology. Hierarchical zinc hydroxide carbonate (ZHC) precursors were synthesized at 120°C for 6 hours in a hydrothermal autoclave, followed by a calcination at 600°C for 2h. The morphology was characterized using scanning electron microscopy (SEM), which showed that, in the absence of citrate, ZnO grew as nanosheets. At low citrate concentrations, flower-like structures were observed, while higher concentrations led to denser, spherical particles. Excess citrate disrupted the spherical shape, resulting in particle aggregation. These findings demonstrate that trisodium citrate plays a crucial role in controlling the morphology of ZnO hierarchical microstructures. The obtained morphologies enable us to use the ZnO particles as fillers for optical applications.

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Thematic Session: Nanochimie & Nanoparticules
Disciplinary fields involved: Chemistry
Keywords (max. 4-5)**: Formation nanoparticles, growth mechanism, ZnO**

Following zinc oxide nanoparticles formation

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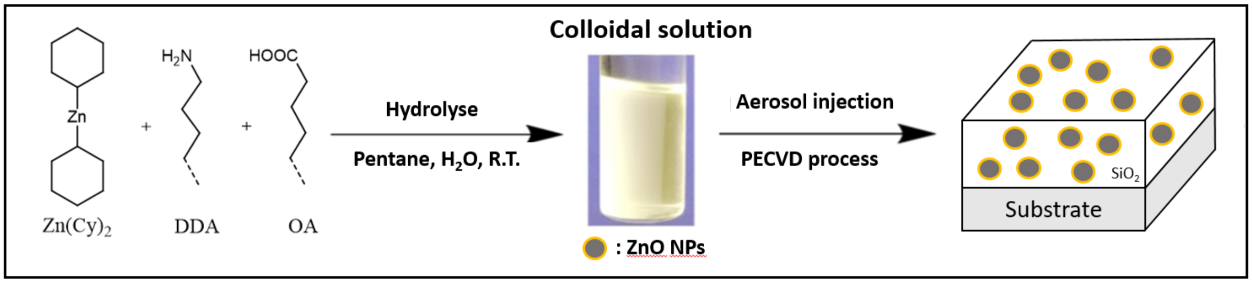
There are different methods of plasma deposition; traditionally, gas injection through vaporization techniques is used. Other methods, such as Plasma-Enhanced Chemical Vapor Deposition (PECVD), allow for the injection of liquids, thereby expanding the range of possibilities. This makes it possible to introduce colloidal solutions where nanoparticles are precisely defined, dispersed, and stable in the solution, enabling the process to produce nanocomposite layers.[1,2]

It is therefore crucial to master the synthesis and stabilization of nanoparticles to prevent their aggregation during injection and plasma treatment. To achieve this, we work with pentane and the hydrolysis of a highly reactive zinc precursor in the presence of ligands.[3] These ligands stabilize the interfaces formed between the solid phase (ZnO nanoparticles) and the liquid phase (pentane).

In our study, we use two ligands: DDA (dodecylamine) and OA (oleic acid).[4] These ligands form a catanionic pair that creates an ionic shell, effectively preventing aggregation. This work aims to achieve photoluminescent properties; therefore, it is essential to control the size of ZnO nanoparticles, as this directly influences the band gap of this semiconductor material.[5]

To precisely control the particle sizes, we studied the phenomena of nucleation and growth using NMR spectroscopy, UV-Vis spectroscopy, and fluorescence analysis, enabling fine-tuned control over crystal formation.



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Thematic Session: Nanochemistry and Nanoparticles
Disciplinary fields involved: Chemistry
Keywords: Cobalt phosphides, nanorods, core@shell

Topochemical reactions of P with Co nanorods

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Cobalt phosphide (Co_xP_y) nanoparticles (NPs) are currently intensively studied as cost-efficient, earth abundant electrocatalysts.[1] Co_xP_y of different sizes, shapes and crystal structures of have been prepared by different methods. The most widely employed strategies for the synthesis of highly monodisperse shape controlled Co_xP_y NPs consist in i) the thermal decomposition in high boiling point solvents of molecular cobalt precursors in the presence of surfactants and a P source[2] or ii) the use of preformed Co NPs as templates that are subsequently submitted to a reaction with a P source.[3] Several approaches have given rise to anisotropic Co_xP_y shapes, among which Co_2P[4] and CoP[5] nanorods, however, no core@shell Co@Co_xP_y nanorods have been reported up to now.
We will present the synthesis of Co@Co_xP_y nanorods through topochemical reactions of bare Co nanorods with P precursors. Two types of Co nanorods obtained through (i) the polyol method and (ii) the organometallic approach, and presenting different sizes and different surface properties, have been employed as templates. The extent of the reaction between the Co and the P source can be controlled through the experimental conditions (type of Co nanorods, type and amount of P precursor, temperature) allowing a control over the thickness and the crystal structure of the phosphide shell, allowing protection of the air-sensitive Co core and modulation of its magnetic properties.

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Acknowledgement:

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Nanochemistry, Nanoparticles, Nanocatalysis

Wednesday March 19th

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

AMPHITHEATRE GASTON BERGER

Program of the session :

Chairs:

HOUR	NAME	TITLE
10:30	**Emilie POUGET** **CBMN - CNRS**	**Design of functional nanostructures via chirality induction**
11:00	Rahul NAG ITODYS - Univ. Paris Cité	Polarization-Sensitive Phototransformation of Chiral Plasmonic Assemblies
11:15	Caroline SALZEMANN MONARIS - Sorbonne Univ.	The intriguing role of L-cysteine on the modulation of chiroplasmonic properties of chiral gold nano-arrows
11:30	Henri LE HOUELLEUR LPEM/ESPCI - PSL	Self-assembly of tartrate ligands on 2D semiconductor nanoplatelets for strong chiro-optical features
11:45	Azadeh EDALAT LCC/CEMES - INSA Toulouse	In situ study of Fe nanoparticles in H2 atmosphere: surface reconstruction and reactivity
12:00	Ritika WADHWA PMC - CNRS	Understanding microstructural evolution in rare earth vanadate nanoparticles upon protected thermal annealing
12:15	Jade RAIMBAULT NIMBE/LIONS - CEA	Dense liquid precursor in mineral crystallization: spinodal morphology and high viscosity evidenced by electron imaging

S2

Emilie POUGET (CNRS – CBMN, Bordeaux)

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Short biography

Emilie Pouget studied the chemistry at the Polytechnic National Institute of Toulouse (INP Toulouse, France) and obtained a Master degree in 2002. In 2006, she obtained a PhD from the University of Rennes for her work on the mineralization of peptidic self-assembled nanotubes. From 2006 to 2008, she went to the Eindhoven University of Technology (Netherlands) to work as a post-doc on biomineralization studies by coupling the cryoTEM tomography and the electron diffraction. She then worked at the Centre de Recherche Paul Pascal in Bordeaux (France) on the mineralization of this biological liquid crystal. Since 2012, she is working as researcher at the CNRS, in the CBMN Institute in Bordeaux, France.

Emilie Pouget's work aims at developing new nanofabrication strategies based on the chirality induction principle in order to control the morphologies from the nanometric scale to the macroscopic level. Such chiral nano-objects are studied for their chiroptical, magnetochiral or catalytic properties.

Design of functional nanostructures via chirality induction.

In the field of functional nano-materials, the chiral structures like helices or twisted ribbons are of great interest because of their specific chemical, optical or mechanical properties. The present work aims at developing new nanofabrication strategies based on the chirality induction principle in order to control the morphologies from the nanometric scale to the macroscopic level. Functional hybrid nano-helices are synthesized by use of organic chiral self-assemblies forming well-defined helix structures as templates.
The mineralization of these self-assemblies allows creating silica nano-helices with controlled morphologies in term of diameter and pitches [1]. A particular focus is given to the length control to create individualized and well-dispersed helices in solution [2], suitable for hierarchical organization from the nano- to the macrometric level.
Such chiral nano-objects are then used as base for the creation of functional nanoobjects. The interaction of such objects with different molecules and nanoparticles induce new chiroptical, magnetochiral or catalytic properties [3, 4, 5].

Keywords

Chirality, Nanohelices, Hierarchical organization, Plasmonic, Magnetism

Acknowledgement

Founding sources: Bordeaux University, CNRS Chimie, ANR (ANR-19-CE09-0018, ANR-23-CE09-0015)

References

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Thematic Session (eg. Nanophotonics & nano-optics, nanomaterials, nanobioscience …)**:** **Nanochemistry & Nanoparticles, Nanomaterials for energy.**

Disciplinary fields involved (eg. Chemistry, Physics, Biology …)**: Chemistry, Physics.**

Keywords (max. 4-5)**:** Photogrowth, Chiral Plasmonic Assemblies, Hot charge carrier, CPL, Photoreduction.

Polarization-Sensitive Phototransformation of Chiral Plasmonic Assemblies

Rahul Nag,[1] Charlène Brissaud,[1] Pamela De La Fuente,[2] Lucas Robin,[2] Jean-Yves Piquemal,[1] Matthias Pauly,[3] Emilie Pouget[2] and Miguel Comesana-Hermo[1]

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3. *Université de Lyon, ENS de Lyon, Laboratoire de Chimie, 69364 Lyon, France*

Solar energy induced asymmetric reactivity is a sustainable means to obtain affordable pharmaceutical chemicals and new agrochemical, food industry items.[1] The outstanding extinction cross-sections and optical tunability of plasmonic photocatalysts make them suitable candidates towards solar driven enantioselective reactivity. The development of plasmonic objects with chiroptical features is novel in the field, in which atomic scale chirality is mandatory to ensure an asymmetric interaction with the molecular substrate. This is possible on a crystalline surface without any mirror-symmetry perpendicular to the surface.[2] A strategy relies in the synthesis of plasmonic nanostructures exposing high-Miller-index facets, composing of asymmetric kink sites rendering the surface intrinsically chiral.

Article from our group discusses the polarization-dependent reactivity of chiral plasmonic systems irradiated with circularly polarized light (CPL) thanks to the chiral generation of hot-charge carriers.[3] In current study, we utilize this process to induce the asymmetric photoreduction of inorganic salts onto chiral plasmonic assemblies, resulting photogrowth of a metallic shell. We hypothesize that the selective photoreduction of the metallic precursor in the inter-particle hot spots under CPL will form highly anisotropic metallic helices where the exposition of crystalline facets with chiral atomic arrangements could be favored. Our results demonstrate that the plasmon-induced photoreduction of noble metal salts onto helicoidal assemblies of spherical Au nanoparticles[4] form thin metallic shells (Figure 1). These new structures present different chiroptical features with a 2-fold increase in the g-factor w.r.t. initial materials. We are currently characterizing the crystallographic features of these objects to implement them in enantioselective organic transformations.

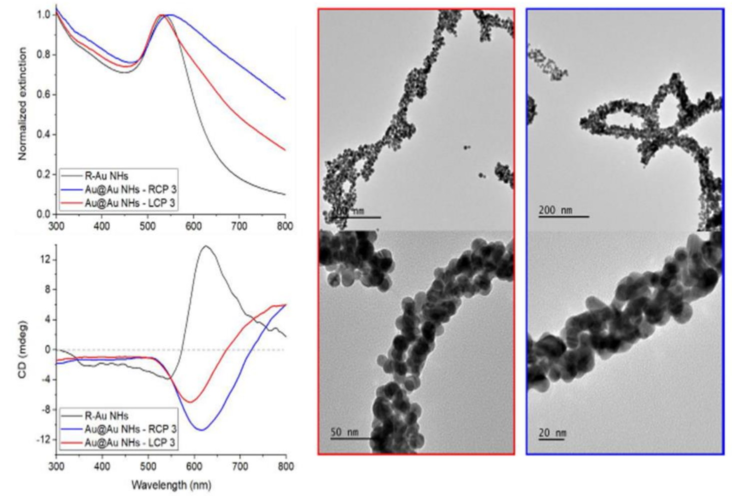

Figure 1. Photgrowth of metallic Au shell on Gold nanohelix.

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Acknowledgement:

RN acknowledges financial support from CAPONE ANR project for his Postdoctoral fellowship.

Thematic Session : **Nanochemistry & nanoparticles**
Disciplinary fields involved : Physical chemistry
Keywords (max. 4-5)**: Gold Nanoparticles, chiroptical properties, seed-mediated growth**

The intriguing role of L-cysteine on the modulation of chiroplasmonic properties of chiral gold nano-arrows

N. Khalfaoui-Hassani[1], M. Tabut[1,2], N. H. Awe[1], C. Desmarets[3], D. Toffoli[4], M. Stener[4], N. Goubet[1], C. Calatayud[1] and C. Salzemann[1]*.

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2. *LCT, CNRS, Sorbonne Université, Paris, France*
3. *IPCM, CNRS, Sorbonne Université, Paris, France*
4. *Department of chemical and pharmaceutical sciences, University of Trieste, Italy*

Abstract:
Developing chiral plasmonic nanostructures represents a significant scientific challenge due to their multidisciplinary potential. Observations have revealed that the dichroic behaviour of metal plasmons changes when chiral molecules are present in the system, offering promising applications in various fields such as nano-optics, asymmetric catalysis, polarization-sensitive photochemistry and molecular detection.[1] In this context, we explored the synthesis of plasmonic gold nanoparticles and the role of cysteine on their chiroplasmonic properties. Specifically, we synthesized chiral gold nano-arrows using seed-mediated-growth synthesis method in presence of L-cysteine into growth solution as a chiral ligand. As expected, the chiral molecule transfers chirality to gold nanocrystals and the morphology is controlled through kinetic growth[2–4]. The main feature consists in chiroplasmonic properties, such as the sign of circular dichroism, that can be modulated using only one enantiomeric form in the growth solution. To understand the origin of such effect, theoretical modelling using density functional theory have been conducted. Our results point to the intermolecular cysteine interactions as a key factor in the dichroic properties of surface-molecule chiral systems.[5]

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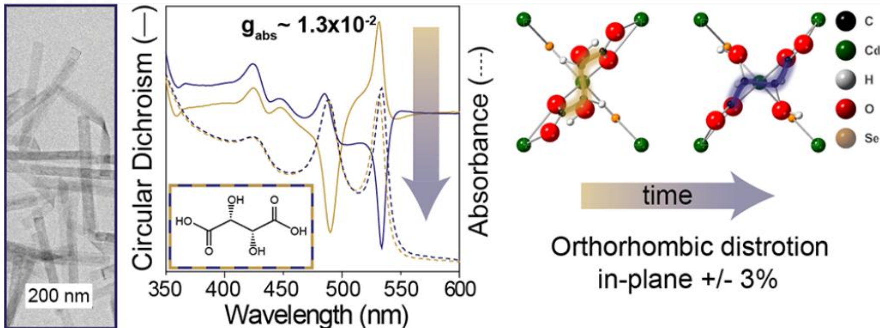
Acknowledgement:

This research was partly funded by the French National Research Agency (ANR) under the project ANR-22-CE09-

0007. Initiative Sciences et Ingenierie Moleculaires-iSiM from Sorbonne Universite is warmly acknowledged for financial support. This work was performed using HPC resources from GENCI- IDRIS (Grant 2023-A0150802131).

Self-assembly of tartrate ligands on 2D semiconductor nanoplatelets for strong chiro-optical features



II-VI semiconductor nanoplatelets (NPLs) present optical features lacking of inhomogeneous broadening thanks to their 2D shape. Their thicknesses only present few atomic planes, such that any modifications of the surface chemistry induces a modification of their optical features. Recent studies have been dedicated to induce chiral light-matter interactions on these particles, to reach strong circular dichroism (CD) and circularly polarized luminescence (CPL) features, for example by grafting cysteine ligands on their surface.

Here, we propose to use chiral tartrate ligands [1]. Surprisingly, the exchange undergoes several stages, with an increase of the CD feature at the position of the heavy hole which red shifts over time followed by an inversion of the CD signal when the absorption saturates. The dissymmetry factor can reach values as high as 1.2 x 10^{-2}. The peak inversion global aspect is influenced by the lateral aspect of the initial particle, the former surface chemistry, and the synthesis conditions.

This inversion is attributed to a mechanical relaxation of the ligand assembly that induces a different coupling between the inorganic core and the chiral ligands. This hypothesis is supported by surface chemistry characterization and XRD analysis.

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Thematic Session: Nanomaterials
Disciplinary fields involved: Chemistry, Physics
Keywords: Nitridation, In situ study, Nanoparticles, ligand

In situ study of Fe nanoparticles in H_2 atmosphere: surface reconstruction and reactivity

Azadeh EDALAT[1], Catherine AMIENS[2], Marc RESPAUD[1], Jaysen NELAYAH[3], Christian RICOLLEAU[3]

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Fe nanoparticles (FeNPs) can serve as valuable starting materials for synthetizing nanostructured Fe nitrides[1] and iron carbides[2], or for acting as catalysts[3]. The optimization of their morphology, and especially of their surface, in terms of exposed facets as well as chemical composition is thus crucial for enhancing their reactivity. Notably, due to their high sensitivity to air, FeNPs are often coated with oxide layers. Reducing these oxide shells is essential in view of the above. In this work, we monitor in situ iron oxide reduction at the surface of ligand-coated spherical FeNPs synthesized via a chemical process[4], presenting a cubic body-centered cubic (bcc) structure, ranging in size from 10 to 15 nm. We focus primarily on the surface activation process under H_2, where ligands detach from the nanoparticle surface (Fig.1), and the oxide shell eventually present is reduced. To capture and analyze these transformations, we employed environmental aberration-corrected scanning transmission electron microscopy (STEM), enabling the in situ observation of the surface, structural, and morphological evolutions of these NPs down to the atomic scale.

Figure 1: (a) is start and (b) is the end of plateau, under H_2 at 1 atm and 300°C.

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Acknowledgements:

We thank the ANR (project FeNMAG), INSA, CNRS, METSA Network and Occitanie region for their financial support of this project.

Thematic Session: Nanochemistry & Nanoparticles
Disciplinary fields involved: Chemistry

Keywords (max. 4-5)**: microstructure, in-situ TEM, colloidal nanoparticles, annealing**

Understanding microstructural evolution in rare earth vanadate nanoparticles upon protected thermal annealing

Ritika Wadhwa[1], Rafael Vieira Perrella[1], Kassiogé Dembélé[2], Thierry Gacoin[1]

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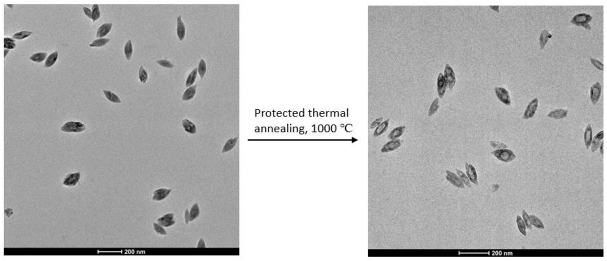
2. *Laboratoire de Physique des Interfaces et Couches Minces, Ecole Polytechnique, Institut Polytechnique de Paris, Route de Saclay, 91128 Palaiseau cedex, France.*

Poor crystallinity and surface quenching lead to low luminescence efficiency of the oxide nanoparticles which limits their optical applications.[1] The size, crystallinity, defect density and morphology of the particles is usually tuned by the synthesis method used and these parameters affects the internal microstructure of the resulting nanoparticles which is poorly characterized.[2,3] Protected thermal annealing treatments helps in achieving the highly crystalline nanoparticles with enhanced physical properties.[4] In the present work, we tried to investigate the evolution of porosity in Eu^{3+} doped yttrium vanadate nanoparticles ($Eu:YVO_4$) during the thermal annealing by using In-situ TEM and tomography. The annealed particles are single crystalline and show enhanced quantum emission yield of ~35 %. Investigation of the effect of initial particle structure and environment conditions on the evolution of pores upon annealing treatment has been done by comparison of ex-situ and in-situ TEM measurements. Careful examination using electron microscopy shows that the smaller pores collapse to form larger pores with the increase in temperature and growth of the pores takes place along the longer axis of the particles. The presence of oxygen affects the evolution of porosity in the nanoparticles with non-orientational growth under vacuum conditions. This work can pave the way for understanding the effect of initial microstructure and thermal annealing on the evolution of porosity in nanoparticles and its impact on their physical and optical properties.



Initial Particles
Annealed Particles

References:
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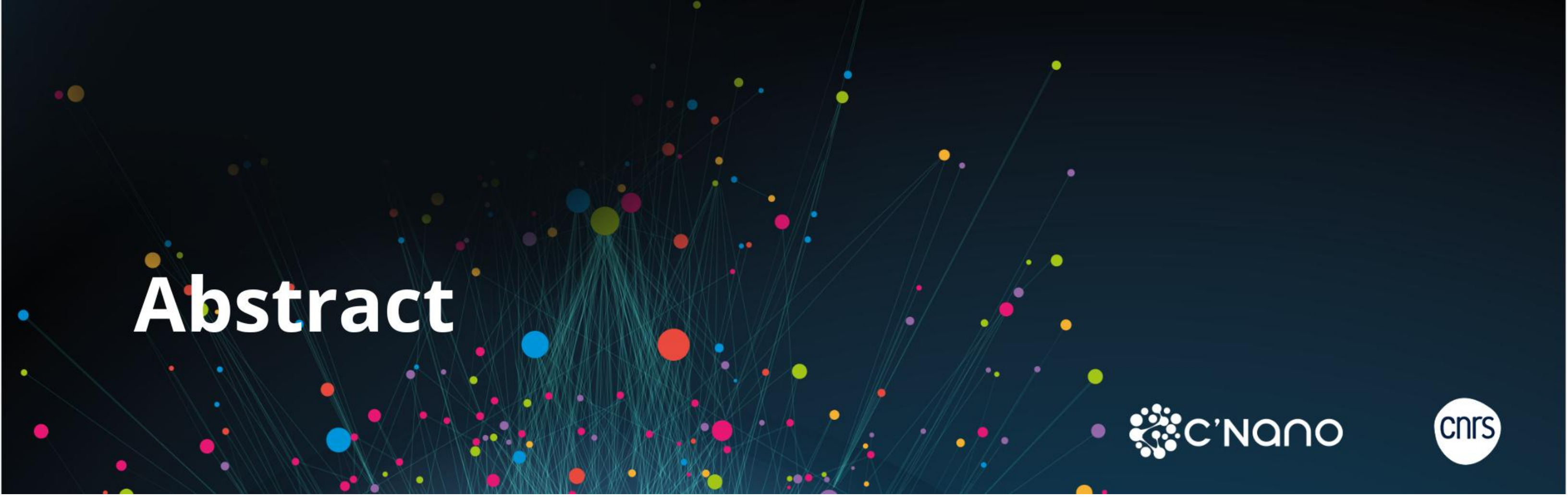
Acknowledgement:

The authors would like to acknowledge the funding by a public grant from ANR (Agence National de la Recherche) project 3D-NanoREV number ANR-22-CE08-0027-01 to carry out the research.



Thematic Session: Nanochemistry & Nanoparticles
Disciplinary fields involved: Physics, Chemistry
Keywords : Crystallization - Liquid-cell TEM – Viscosity – Cryo TEM – Spinodal

Dense liquid precursor in mineral crystallization: spinodal morphology and high viscosity evidenced by electron imaging

Jade RAIMBAULT[1], Corinne CHEVALLARD[1], Dris IHIAWAKRIM[2], Vinavadini RAMNARAIN[3], Ovidiu ERSEN[2], Frédéric GOBEAUX[1] and David CARRIERE[1]

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Crystallization from solution often follows a “non-classical” pathway involving dense liquid or amorphous nanometer-sized precursors before crystal formation. These intermediates can significantly impact how a subsequent crystalline material forms and evolves at the nanometer scale[1], which is a crucial step in the design of nanoparticles. However, they are not accounted for in the “classical” single-step theory (CNT), which is currently the main guideline used to rationalize the synthesis of nanoparticles in solution, underlining the need for new theoretical tools capable of taking them into account.

Among these transient nanostructures, reactant-rich liquid droplets have received considerable attention, as their characteristics can help differentiate between possible crystallization theories[2]. However, theoretical progress is hindered by the difficulty of capturing the physical properties and formation mechanisms of such nanometric species, which can exist for less than a minute[3].

We demonstrated by Cryo-TEM that reactant-rich nanodroplets formed during the crystallization of cerium oxalate exhibit morphologies compatible with spinodal decomposition[4]. By capturing in-situ coalescence events with Liquid-Cell TEM, we provided evidence of their liquid nature and revealed their high viscosity, which is at least five orders of magnitude higher than the water-rich phase. Furthermore, we showed that these structures act as the main nucleation reservoir from which subsequent amorphous nanoparticles directly form. Our results question the single-step nucleation guideline usually used to rationalize the synthesis of nanoparticles in solution, as a viable theory should account for the high-viscosity liquid transient evidenced in our system, which may not result from a nucleation process.

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Acknowledgement:

We acknowledge financial support of the French National Research Agency (ANR-21-CE06-0032), SOLEIL for provision of synchrotron radiation facilities, and Dr. Thomas Bizien for assistance in using the SWING beamline.

Nanochemistry, Nanoparticles, Nanocatalysis

Wednesday March 19th

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

AMPHITHEATRE GASTON BERGER

Program of the session :

Chairs:

HOUR	NAME	TITLE
16:30	**Mona TREGUER-DELAPIERRE** **ICMCB - Univ. Bordeaux**	**Matter and materials made from metallic nanoparticles**
17:00	Aurore LARQUEY ICGM - CNRS	Heater@luminescent nanoplatforms based on Prussian blue core@silica shell nanoparticles for photothermia and thermometry
17:15	Jens KRARUP NIMBE/LIONS - CEA	High-throughput synthesis and characterization of magnetic iron oxides
17:30	Farah ABDEL-SATER ICGM - CNRS	Iron oxide multifunctional nanoplatforms: towards temperature control in photothermia and magnetothermia
17:45	Naoures HMILI LRS - Sorbonne Univ	Mixed manganese and zinc ferrite magnetic nanoparticles for magnetocuring of adhesives
18:00	Thomas NAILLON LCMCP - Sorbonne Univ.	Synthesis of luminescent oxides nanoparticles for nanothermometry measurements in magneto-induced processes
18:15	Amine KHITOUS ICB - CNRS	Ultrafine TiO_2-Coated Gold Nanoparticles: A Robust Platform for Raman Thermometry

S3

Mona TREGUER-DELAPIERRE (Univ. Bordeaux – ICMCB, Bordeaux)

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Short biography

Pr Mona Tréguer-Delapierre, a Professor at the Institute of Chemistry of Condensed Matter (ICMCB) near Bordeaux, focuses on nanoparticles synthesis and assembly into 2D and 3D materials. She obtained her PhD in Physical Chemistry from the University of Orsay and was a post-doctoral fellow at the Radiation Laboratory in USA. She works in several metallic materials of interest in optics and energy. Currently, with her colleagues, she is exploring how metallic nanostructures can be exploited for mastering the fabrication of next-generation materials for optoelectronics and to create innovative visual appearance designs.

Matter and materials made from metallic nanoparticles

Colloidal metallic nanoparticles with well-controlled shapes and surface properties exhibit unusual physico-chemical characteristics. They are of significant interest for advancing applications in a range of exciting research fields : cloacking, imaging, optical communication. Mastering their fabrication enables to make useful novel materials and to gain deeper understanding of the optics of materials at the nanoscale. In this talk, I will show the recent advancements in the colloidal synthesis of metallic nanoparticles for the design of optoelectronic materials and the creation of surfaces with innovative visual appearances.

Keywords

Colloidal synthesis, (bi-)metal, plasmonic, anisotropy

Acknowledgement

French National Research Agency (ANR (ANR-22-PETA-0011), ANR 19CE09-0014) , GPR LIGHT Idex University of Bordeaux, Graduate program ‘EUR Light S&T’)

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Thematic Session (Nanochemistry & Nanoparticles)**:**
Disciplinary fields involved (Chemistry, Physics)**:**
Keywords: nanoparticles; luminescence; thermometry; silica shell; lanthanide complex

Heater@luminescent nanoplatforms based on Prussian blue core@silica shell nanoparticles for photothermia and thermometry

Aurore Larquey[1], Saad Sene[1], Gautier Felix[1], Yannick Guari[1] and Joulia Larionova[1]

1. *ICGM, Univ. Montpellier, CNRS, ENSCM, CNRS Montpellier, France*

Photothermia, which involves the generation of heat by a photothermal agent following exposure to light irradiation, is a phenomenon of great interest in medical and catalytic fields,[1] and for the stimulation of chemical and biological reactions.[2,3] In the realm of photothermal heat generation, a significant challenge lies in accurately regulating temperature not only at the macroscopic level but also in the immediate proximity of the surface of the nano-heater. In this context, considering that conventional temperature measurement instruments are ineffective at the nanoscale due to limitations in sensitivity, accuracy, and spatial resolution, precise tools for temperature measurements are needed.

In this work, we studied the design and investigation of new multifunctional heater/thermometer nano-objects containing (i) Prussian blue (PB) nanoparticles heater core, characterized by the general formula $A_{1-x}Fe^{III}[Fe^{II}(CN)_6]_{1-x}$ (where A denotes an alkaline ion), possessing promising photothermal properties, and (ii) Tb^{3+}/Eu^{3+} based luminescent coordination compound as emissive thermometer for its demonstrated excellent thermometric capacity[4]. The obtained hybrid nano-objects present both, a heating ability under irradiation at 808 nm and a bright luminescence in the visible region characteristic of Tb^{3+} and Eu^{3+} ions, which make them multifunctional. Moreover, the observed emission is temperature-dependent allowing to use these nanoparticles as temperature nanoprobe in the close proximity of the PB core with a satisfactory maximal relative sensitivity of 0.75 $\%\cdot°C^{-1}$ at 20 °C.

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[4] T. Pelluau et al. *Nanoscale*, **2023**, 15, 14409

Acknowledgement:

The authors thank the University of Montpellier and CNRS and the ANR within the frame of the HotSpot project (ANR-23-CE09-0017) for funding. H.B. is grateful to LabUM program, which funded her Master 2 internship (ANR-16-IDEX-0006). Authors are grateful to Platform of Analysis and Characterization of ICGM and platform Electronic and Analysis microscopy at the University of Montpellier for analysis and measurements.

Thematic Session (Nanochemistry, Nanoparticles and assemblies)**:**
Disciplinary fields involved (Chemistry, physics, robotics)**:**
Keywords (max. 4-5)**: wet chemistry, nanoparticles, automation, magnetism**

High-throughput synthesis and characterization of magnetic iron oxides

Jens Krarup[1], David Carriere[1], Damien Faivre[2]

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2. *CEA Cadarache, Zone Cité des Énergies BIAM, Bâtiment 1900, 13108 Saint-Paul-lez-Durance*

The rise of advanced computational chemistry has spurred a rapid increase in material discovery [1], yet experimental methodologies lag behind. A growing trend in addressing this gap is the development of self-driving laboratories that integrate robotics, AI, and automation, significantly enhancing experimental capabilities within chemistry and materials science [2]. Iron oxides, particularly in nanoparticle form, have shown promise for diverse applications, especially in theranostics [3].

In this presentation, we will present our early findings investigating into the gap between traditional laboratory synthesis and small-scale robotics, employed in self-driving laboratories.
Specifically, we aim to prove or disprove if high-throughput synthesis carried out in well plates are representative of traditional lab scale synthesis.

To reach this objective, we have developed a novel synthesis platform that integrates a liquid-handling system with automated small-angle X-ray scattering (SAXS). The platform allows for efficient mapping of synthesis conditions, enabling accelerated rates of optimization of iron oxide nanoparticles in regards to size and crystallography. We will present the parameter space in which the robot syntheses provide good indicators of nanoparticle sizes and phases (magnetite, goethite, amorphous oxohydroxydes) obtained in batch, or in which the robot syntheses should on the contrary be exploited as a separate preparation process, independent of the batch syntheses.

By addressing the knowledge gap, we will contribute to accelerated exploration and rational design of nanomaterials, in particular by utilizing the platform to expand upon the role of bio-derived additives for size control for iron oxide nanoparticles.

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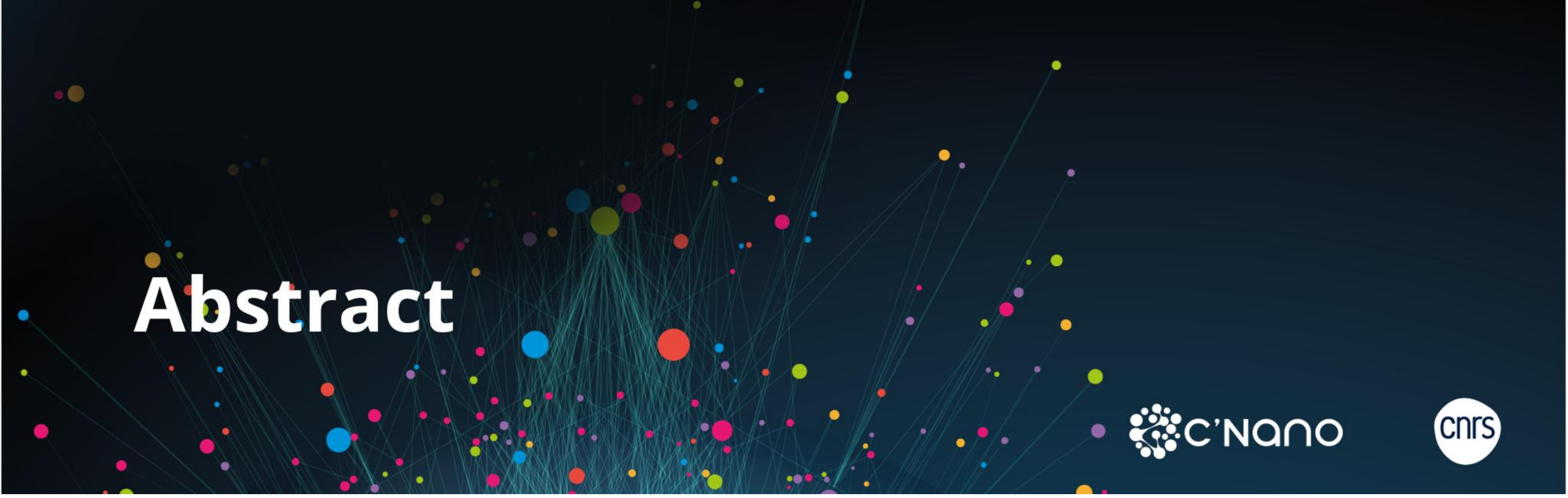

Thematic Session: Nanochemistry, Nanoparticles, Nanocatalysis
Disciplinary fields involved: Chemistry
Keywords: Iron oxide, Nanoparticles, Magnetothermia, Photothermia

Iron oxide multifunctional nanoplatforms: towards temperature control in photothermia and magnetothermia

Farah Abdel Sater[1], Gautier Félix[1], Saad Sene[1], Joulia Larionova[1] and Yannick Guari[1]

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Over the past decades, inorganic nano-objects capable of generating significant heat when remotely activated by external stimuli have garnered considerable attention. For this reason, numerous nano-heaters with diverse compositions, sizes, and morphologies activated either by light irradiation (photothermal agents) or by the application of an alternating current magnetic field (magnetothermal agents), have extensively been reported[1].

Among these, iron oxide nanoparticles received a particular attention due to their capacity of generating heat when it is exposed to external stimuli. This characteristic offers promising applications in hyperthermia treatment, catalysis, and radical release[2]. Yet, a better understanding and control of the temperature rise at the surface of the nanoparticles remains challenging.

The current study aims to expand the investigation into the development of multifunctional nanoplatforms based on iron oxide materials. We will first discuss the use of the generated heat on a magnetite nanoparticle with thermosensitive radical initiators, alkoxyamines R1R2NOR3, anchored to its surface[2]. The magnetic core exhibits a high intrinsic loss power of 4.73 nHm2.kg−1 providing rapid heating of their surface under the action of an alternating magnetic field. This causes the homolysis of the alkoxyamine C–ON bond and triggers the formation of radicals[3,4].

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Acknowledgement:

The authors thank the University of Montpellier, the University of Aix Marseille and CNRS for financial support. The work was developed within the scope of the ANR projects Killer (ANR-22-CE09-0026) , the authors are grateful for funding. Authors are grateful to Platform of Analysis and Characterization (UAR2041) for magnetic, EPR and X-Ray diffraction measurements.

Thematic Session: Nanochemistry & Nanoparticles
Disciplinary fields involved (eg. Chemistry, Physics, Biology …)**:** Chemistry
Keywords (max. 4-5)**:** Magnetic Nanoparticles, synthesis, functionalization, coating, Magnetocuring

MIXED MANGANESE AND ZINC FERRITE MAGNETIC NANOPARTICLES FOR MAGNETOCURING OF ADHESIVES

Naoures Hmili [1], *, Ferdaous Ben Romdhane [1], Tran Quang Dung [2], Raju. V. Ramanujan [2], Terry Steele [2], Souhir Boujday [1], * Juliette Blanchard [1], *

1. *Laboratoire de Réactivité de Surface (LRS) Institut de Chimie du CNRS, Sorbonne Université, Centre National de la Recherche Scientifique. Paris, France*
2. *Division of Materials Science, Nanyang Technological University, Singapore.*

In the last few years, researchers started developing a growing interest in adhesive technology due to its versatility in a variety of applications. Traditionally, conventional adhesives are cured through external stimuli such as moisture, heat and/or light. However, these methods come with significant challenges in terms of feasibility in an industrial context. Thus, developing a remote and cost-efficient strategies for remote curing of adhesives has become such an attractive area for research.

Our project focuses on a technology called *Magnetocuring[1], [2]*, where magnetic nanoparticles (MNPs) are incorporated into the adhesive resins and subjected to an Alternating Magnetic Field (AMF). Under these circumstances, particles generate heat by reaching their curie temperature (Tc*), leading to the curing of the adhesive. (fig.1)

In this project, we elaborated mixed Mn and Zn ferrites ($Mn_xZn_{1-x}Fe_2O_4$) and established a library of particles with varying compositions (x= 0.5 – 0.9) and sizes (8 – 20nm). we have worked on their surface chemistry by different functionalization and coatings to allow for a better and more homogenous dispersion in different media (water based and organic resins) leading to an optimal heat distribution and curing.

(*) Tc: Curie Temperature - the temperature above which MNPs lose their magnetic properties.

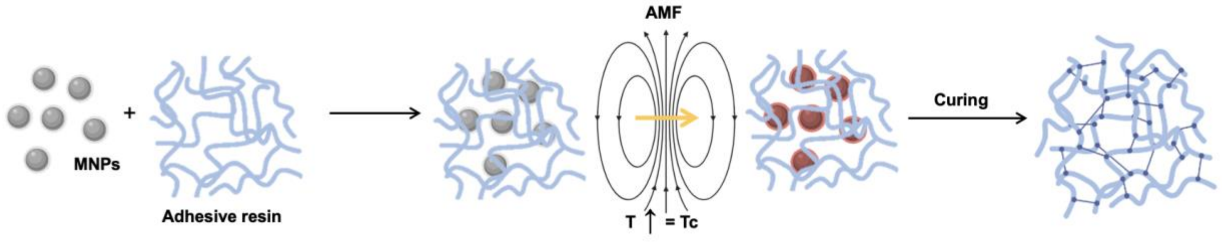

Figure 1 - General scheme of the principal of Magnetocuring

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Thematic Session: Nanochemistry & Nanoparticles
Disciplinary fields involved: Chemistry, Physics
Keywords: Luminescence nanothermometry, Oxides nanoparticles, Soft chemistry synthesis, Microwave route

Synthesis of luminescent oxides nanoparticles for nanothermometry measurements in magneto-induced processes

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Temperature is one of the most common physical quantities that significantly contributes to chemical reactivity and biological processes. Nanothermometry by luminescence is related to temperature measurements at nanoscale with high spatial and temporal resolution using nanoparticles (NPs).[1] The temperature dependence on luminescence can be expressed by the evolution of one or more optical parameters such as: intensity, lifetime,… (see variation with temperature in figure 1.a,b).

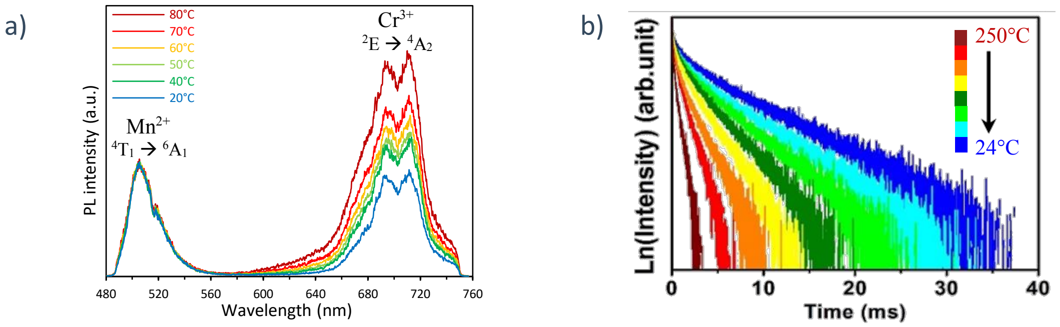

Figure 1: a) Emission spectra as a function of temperature of $Zn_{1.1}Ga_{1.8}Ge_{0.1}O_4$:$Mn^{2+}$,$Cr^{3+}$ ultra small NPs in H_2O (ex. 275 nm); b) Lifetime evolution in function of temperature for $ZnGa_2O_4$:Cr^{3+} NPs (ex. 430 nm).[2]

To address this challenge, we are focusing our interest on oxides matrices doped with transition metal or lanthanides. Such nanomaterials are well known for their chemical robustness and ability to withstand high temperatures (20-300 °C) that are envisioned in applications.[3] To meet the requirement for spatial resolution, we are seeking probes that are uniformly dispersed and as small as possible to optimize this spatial resolution. One of the original approaches in this work is microwave synthesis, which allows us to obtain small crystalline particles (~ 10 nm) while adopting a green synthesis approach (shorter reaction time, less energy consumption).[2]

It is imperative that the probes exhibit a high sensitivity of the temperature on the studied range. In this perspective, recent approaches are converging towards exploring evolution ratios between two parameters.[4] For instance, by studying the ratio between two emission peaks evolving differently with temperature as seen in figure 1.a with the evolution of two luminescent centers ($\mathrm{Mn^{2+}}$ at 500 nm and $\mathrm{Cr^{3+}}$ at 700 nm) under UV excitation for different temperatures.[5]

The temperature range within which nanothermometers could be considered as very effective is the first challenge. The aim of the work is to develop a sensitive nanothermometer either close to room temperature for hyperthermia treatment applications or over a broader range, ideally covering from 20 to 300 °C for catalysis applications. The behaviors of oxide-based nanothermometers within these two temperature ranges will be presented at the conference.

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Acknowledgements:

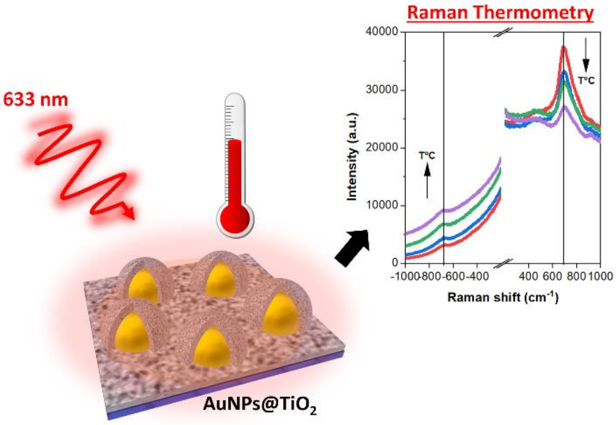
This research was funded by Agence Nationale de la Recherche (ANR-21-CE09-0030 NANOTHERMOMETRY).

Ultrafine TiO_2-Coated Gold Nanoparticles: A Robust Platform for Raman Thermometry

Amine Khitous, Céline Molinaro, Anna Rumyantseva, Serguei Kochtcheev, Pierre Michel Adam, Renaud Bachelot and Olivier Soppera

Abstract

Accurate temperature measurement in metallic nanoparticles is essential for understanding energy dissipation dynamics and enabling temperature-sensitive applications[1]. This study introduces a high-performance approach to Raman anti-Stokes-Stokes thermometry[2] using gold nanoparticles (AuNPs) synthesized through thermal dewetting and functionalized with a 2 nm TiO_2 layer via sol-gel technique[3]. These AuNP@TiO_2 probes demonstrate excellent stability across a wide temperature range from 25 °C to 240 °C under both external thermal and thermoplasmonic heating conditions. By analyzing the anti-Stokes to Stokes signal ratio and accounting for the Raman spectrometer's spectral efficiency and the extinction properties of AuNP@TiO_2, the measured temperatures showed a strong correlation with the applied temperatures throughout the studied range (20 °C–240 °C). Furthermore, comparing applied and measured temperatures using different existing models allowed us to interpret and validate these models. This reliable thermometry technique provides precise measurements over more than 200 degrees, paving the way for advanced thermal optical monitoring in nanomaterial systems.



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Nanochemistry, Nanoparticles, Nanocatalysis

Thursday March 20th

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

AMPHITHEATRE GASTON BERGER

Program of the session :

Chairs:

HOUR	NAME	TITLE
10:30	**Damien VOIRY** **IEM - CNRS**	**Engineering Low-Dimensional Materials for Electrocatalytic Conversion Reactions and Nanofluidics**
11:00	Tatiana STRAISTARI LCC - CNRS	Nanoscale NiCu electrocatalyst for the hydrogen evolution reaction
11:15	Seema SHAFIQ LCC - CNRS	Interfacial ionic liquid based nanocatalysts for low temperature CO2 reduction
11:30	Noa DE CRISTOFARO LCMCP - Stellantis Auto	High Entropy Alloys: from new syntheses to energy conversion
11:45	Felipe QUIROGA SUAVITA LPCNO - INSA Toulouse	Icosahedra like CoPd bimetallic nanoparticles for magnetically induced aromatic ketone hydrodeoxygenation
12:00	Gizem KARACAOGLAN ICMUB _ UBFC	Innovative Organometallic Nanocatalysts for the delivery of H2 from a Safe Solid Storage Source
12:15	Alexis AUSSONNE LCC - CNRS	Colloidal MoS2 nanoparticles by organometallic synthesis as improved catalyst

S4

Damien VOIRY (CNRS – IEM, Montpellier)

https://lowdimensionalmaterials.net/

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Short biography

Damien VOIRY graduated from the National School of Chemistry and Physics of Bordeaux (ENSCPB) and obtained his thesis at the Paul Pascal Research Center (CRPP) of the University of Bordeaux in 2010. From 2011 to 2016, Damien was a postdoctoral associate in the group of Professor Manish Chhowalla from Rutgers University in the United States. Since Feb. 2016, he is a CNRS staff scientist at the Institut Européen des Membranes de Montpellier. His current research aims to explore the use of low dimensional materials for the fabrication multifunctional membranes for separation application as well as energy application. In 2018, he was awarded an ERC starting grant to investigate the electrocatalytic reduction of CO2 from 2D materials. Damien Voiry has received several national and international awards including the CNRS Bronze Medal, the SCF Young Researcher awards and the 2024 Young Scientist Sustainable Development Goals Award. He was nominated at the Young Academy of Europe in 2020.

Engineering Low-Dimensional Materials for Electrocatalytic Conversion Reactions and Nanofluidics

The dual challenges of climate change and population growth have placed immense pressure on global water resources and carbon management systems. To address these issues, innovative materials and technologies are essential. Nanomaterials, particularly two-dimensional (2D) materials, with their atomic-scale thickness, tunable structures, and unique properties, offer transformative solutions for sustainable water purification and CO2 utilization[1]. In water purification, 2D materials such as graphene and MoS_2 nanosheets are redefining the design of advanced membranes. Their exceptional selectivity and permeability provide the potential to significantly reduce the energy footprint of water recovery and desalination processes. In particular, nanolaminated membranes constructed from re-stacked 2D nanosheets exploit interlayer spacing to achieve precise molecular sieving [2]. My research focuses on how nanosheet surface chemistry and stacking defects influence membrane performance, paving the way for scalable, high-efficiency water treatment systems. In parallel, advances in nanostructured catalysts are opening new pathways for controling electrocatalytic reactions to produce value-added chemicals from CO2, water or nitrate[1]. For instance, our work on self-assembled 2D silver nanoprims has demonstrated near-complete exposure of active edge sites, resulting in remarkable selectivity and activity for CO2-to-CO conversion[3]. Similarly, phase-engineered MoS_2 nanosheets have shown high efficiency in catalytic oxidation and selective nitrate reduction to ammonia. These findings underscore the versatility and precision of low-dimensional materials in addressing key energy and environmental challenges. In this keynote, I will provide a comprehensive overview of the current state of 2D materials in water purification and electrocatalysis. I will also discuss how their rational design and engineering can impact nanofluidics, catalysis, and related fields, offering original and practical solutions to meet global sustainability goals.

Keywords

2D materials, Nanofluidics, Electrocatalysis, Energy conversion

Acknowledgement

European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement no. 804320 /ANR, programme PRC-2D-MEMBA (ANR-21-CE09-0034-01)/

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Thematic Session: nanomaterials

Disciplinary fields involved: Chemistry

Keywords: nanoparticle, nickel, copper, electrocatalysis, hydrogen evolution reaction

Nanoscale NiCu electrocatalyst for the hydrogen evolution reaction

T. Straistari[1], N. Romero[1], C. Amiens[1], D. Jones[2], J. Rozière[2], S. Cavaliere[2], K. Philippot[1]

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The investigated NiCu NPs synthesized by an organometallic method [3] as cathode material for anion exchange membrane water electrolysis application. By optimizing the synthesis conditions we obtained alloy-type NiCu nanoparticles with a mean diameter of ca. 4.0–4.3 nm (fig. 1). The composition and structure of the synthesized materials were investigated by ICP, TEM, HRTEM, EDX, XPS and XRD. The nanomaterial was then deposited on a carbon support and evaluated in the electroproduction of hydrogen by a range of electrochemical methods. In alkaline environment, the NiCu electrocatalyst exhibits a good catalytic activity with an overpotential of 273 mV at the current density of -10 mA cm–2, and it shows good stability within 24 h.hydrogen evolution reaction (HER) is one of the most investigated reactions in electrochemistry, electrocatalysis or/and photoelectrocatalysis.[1] The electrode materials in the electrochemical devices containing nickel and copper are the most attractive in the series of transition metals[2], due to their accessibility, electronic and chemical properties.

We have

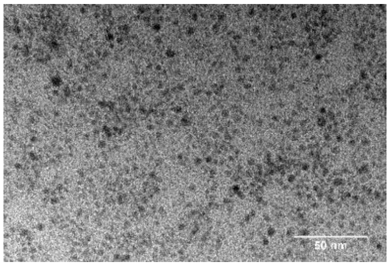

Figure 1. TEM image of synthesized NiCu-NPs

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Acknowledgement:

The authors acknowledge the "Défi Clé Hydrogène Vert – RHyO pôle" for a funding from Region Occitanie and FEDER-ACT (Projet H_2vert ELECTRA)

Thematic Session: Nanochemistry and Nanoparticles
Disciplinary fields involved: Chemistry
Keywords: Nanoparticles, Selective hydrogenation, Ionic Liquids, Supported catalysts

Interfacial ionic liquid based nanocatalysts for low temperature CO$_2$ reduction

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2. *LCC–CNRS, Université de Toulouse, UPR 8241 CNRS, INPT, Toulouse, France*

The catalytic hydrogenation of CO$_2$ to methane (Sabatier reaction) offers a sustainable approach to reduce CO$_2$ emissions, using renewable hydrogen.[1] This exothermic reaction typically occurs between 300-450°C, but developing efficient catalysts for low-temperature operation (below 300°C) remains challenging due to the complex reaction network. Ru/TiO$_2$ catalysts exhibit high activity for this reaction due the inherent activity of Ru, strong metal-support interactions, the presence of oxygen vacancies and hydrogen spillover effect.[2] Key factors like Ru loading, nanoparticle size, and support phase (anatase *vs*. rutile TiO$_2$) critically influence catalytic performance. Smaller Ru NPs enhance CO$_2$ activation, while larger ones improve H$_2$ activation.[3] However, selectivity concerns (CH$_4$ *vs* CO) remain complex, and selectivity shifts have been reported,[4] which have not yet been completely rationalized. This study investigates the complex interplay of electronic and geometric metal-support interactions in ultra-dispersed Ru/TiO$_2$ catalysts to elucidate the factors governing the activity and the selectivity. A large panel of characterization techniques were used to characterize the catalyst before and after catalysis, and insights into working catalyst through operando spectroscopy and microscopy will be discussed.

Additionally, we aim at improving the catalytic performance by coating the Ru/TiO$_2$ catalyst with thin layers of ionic liquids (ILs).[5] This interfacial approach that will be discussed, takes advantage of the unique microenvironment created by the IL. Considering the great structural flexibility of ILs, identification of relevant descriptors for CO$_2$ hydrogenation, by carefully designing through machine learning, task-specific ILs to selectively promote the desired chemical pathways should be feasible.

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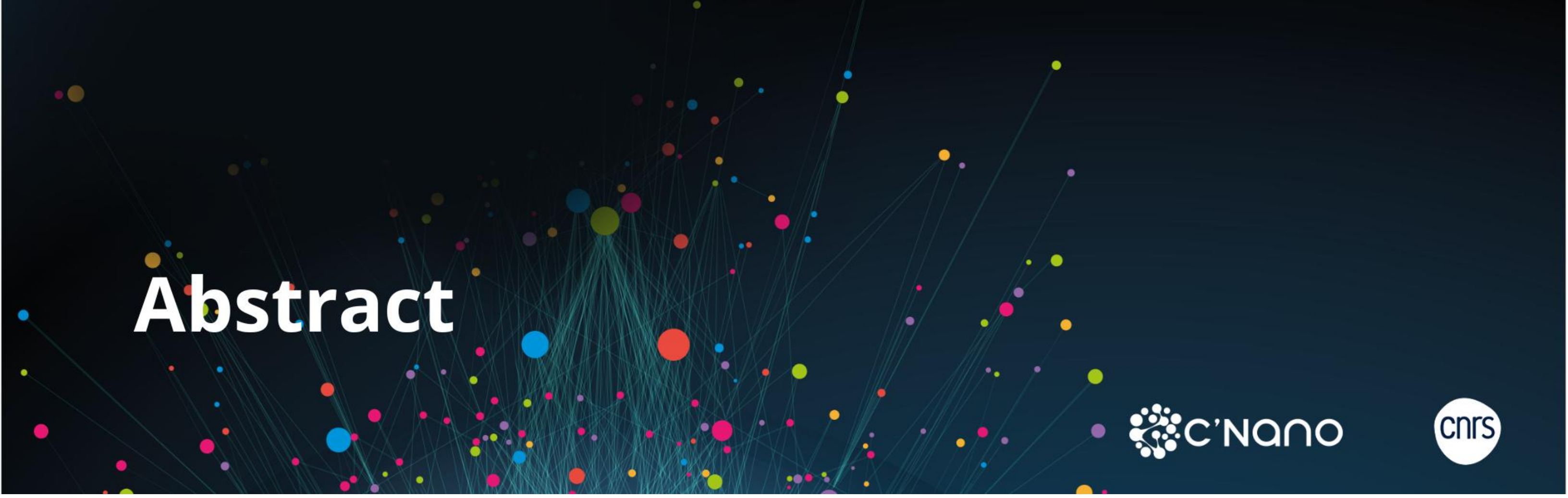
Acknowledgement: *This work has received funding from the French Agence Nationale de la Recherche under grant agreement ANR-22-CE07-0044 (LICORN). We gratefully acknowledge CNRS ANR for funding this research. We also thank Centre of Microcharacterization Raimond Castaing – Toulouse for electron microscopy.*



Abstract

Thematic Session: **Nanochemistry, Nanoparticles, Nanocatalysis**
Disciplinary fields involved: Chemistry, Physics
Keywords: high entropy materials, hydrogen evolution reaction, molten salts, induction heating

High Entropy Alloys: from new syntheses to energy conversion

Noa De Cristofaro[1,2], Ferdaous Ben Romdhane[3], Othmane Darouich[1], Antoine Miche[4], Gildas Bureau[2], Clement Dumand[2], Christel Laberty-Robert[1], David Portehault[1]

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Abstract

High Entropy Alloys (HEAs) are a novel class of materials that have been reported to be high performance electrocatalysts for a variety of processes [1]. In particular, they have demonstrated superior performance in the electrocatalysis of hydrogen production when compared to the current gold standard electrocatalyst composed of pure platinum [2].

Current methods for producing nanoHEAs are based either on wet-chemical approaches or novel synthetic routes involving fast heating and high temperatures. However, the former methods often yield intermetallic alloys rather than HEAs, while the latter class requires specific setups that are difficult to scale up [3].

We have developed a new synthetic method for the synthesis of nanoscale HEAs. By using molten salts as liquid media for colloidal synthesis, flanked by induction heating, we have been able to combine the benefits of the novel process and conventional wet chemistry in a single synthetic method. The advantages of this process are numerous and include in some cases the control over the size and morphology of the nanoparticles, as well as the ability to perform high-temperature reactions at ambient pressure [4].

Our method allows the synthesis of nanoparticles with tunable size below 15 nm of diameter. STEM-EDX analyses have highlighted the high entropic nature of our materials, showing the desired composition at the nanoscale. The synthesized HEAs have shown promising performance for HER electrocatalysis, exhibiting low overpotentials comparable to literature benchmarks with similar composition.

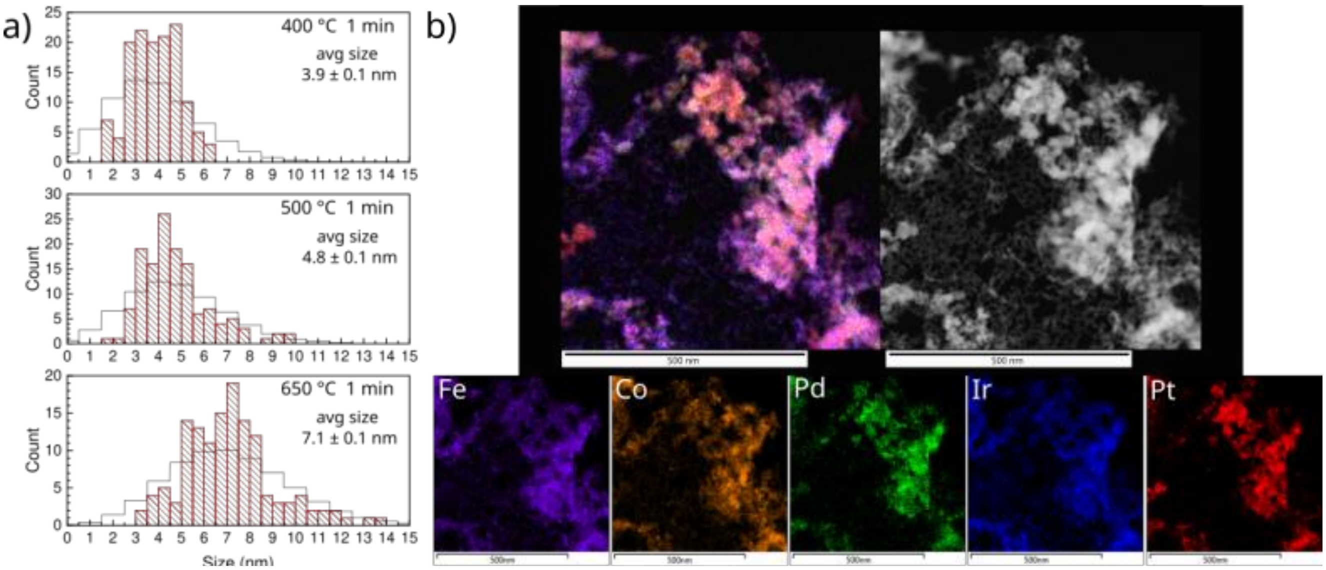

Figure 1: a) Size distribution extracted from TEM images of our HEA synthesized at different temperature. b) TEM-EDS chemical mapping of our HEA alloy synthesized at 400 °C.

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Acknowledgement:

We thank STELLANTIS for funding.

Thematic Session: Nanochemistry & Nanoparticles
Disciplinary fields involved: Chemistry, Catalysis, Electron Microscopy
Keywords: CoPd Icosahedra, Induction Heating, Hydrodeoxygenation

Icosahedra like CoPd bimetallic nanoparticles for magnetically induced aromatic ketone hydrodeoxygenation

Felipe Quiroga-Suavita,[1,2] Víctor Varela-Izquierdo,[1] Teresa Hungría,[3] Damien Alloyeau,[4] Nicolas Ratel-Ramond,[1] Richard D. Tilley,[2,5] Edwin A. Baquero,[6] Bruno Chaudret [1] and Lise-Marie Lacroix [1,7]

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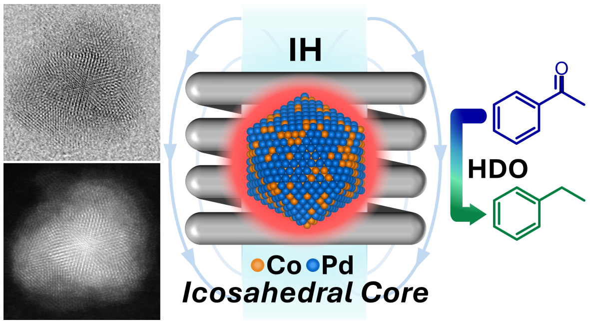

The elaboration of new bimetallic nanomaterials with controlled size, shape and composition capable of effectively catalyzing chemical valorization processes have become crucial for sustainable chemistry.[1] Here CoPd bimetallic nanoparticles (NPs) have been prepared via the organometallic approach using $Co[N(SiMe_3)_2]_2(thf)$ and $Pd(acac)_2$ as molecular sources. Structural characterization by high-resolution transmission electron microscopy (HR-TEM), scanning transmission electron microscopy (STEM), X-ray diffraction (XRD) and wide-angle X-ray scattering (WAXS) revealed an icosahedral Pd rich core with a less crystalline Co rich shell. Magnetic characterization through vibrating sample magnetometer (VSM) and specific absorption rate (SAR) analyses provided relevant insights related to their heating power at a size close to 10 nm, mainly attributed to the enhanced magneto crystalline anisotropy of the bimetallic nanomaterial. This represents a significant advantage in comparison to other magnetic bimetallic combinations such as FeNi or CoNi, which require a larger size to reach their useful hyperthermia properties.[2]

The as-prepared particles were successfully proved as catalyst for acetophenone hydrodeoxygenation (HDO) reaction at low temperature using induction heating (IH), demonstrating the presence of Pd ensembles at the surface. Additionally, multiple *para*-substituents with different electronic properties were scoped. Hence, demonstrating the capability of this non-noble/noble metal combination (CoPd) to carry out difficult reactions at relatively low temperature using magnetically induced catalysis.

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Thematic Session (eg. Nanophotonics & nano-optics, nanomaterials, nanobioscience …)**:**
Nanochemistry & Nanoparticles
Disciplinary fields involved (eg. Chemistry, Physics, Biology …)**: Chemistry, Materials Science**
Keywords (max. 4-5)**: Nanocatalysts, organometallic, ammonia-borane, hydrogen release, heterogeneous catalysis**

Innovative Organometallic Nanocatalysts for the delivery of H_2 from a Safe Solid Storage Source

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Abstract

In the recent years, hydrogen (H_2) has proven to be promising for energy transition issues. However, its storage is still a major challenge, as gas state storage remains bulky and unsafe. To address this question, solid state storage of H_2 in molecules has been investigated, especially with ammonia-borane (NH_3BH_3, AB), which has a high theoretical gravimetric hydrogen density of 19.6 wt%. Its conversion is achieved by mild catalytic process. Here, AB catalytic solvolysis in ambient conditions is studied, in the presence of various types of nanocatalysts, which could also be recycled by filtration,[1] or magnetic separation.[2]

The synthesized organometallic-based nanocatalysts consist in strongly coordinating ligand at the surface of metal (Ru, Ni) nanoparticles. The ligand chosen in this case is either a polyfunctionalized diamondoid (adamantyl derivative), or an organometallic ferrocenyl derivative, both allowing the formation of networks of nanoparticles, which control ultrasmall size of nanoparticles (< 2 nm).[3] For AB hydrolysis expensive metals like Pt or Rh are very effective.[1] Our aim is to use cheaper metals like Ru or Ni. The nanocatalysts are synthesized from an organometallic precursor, which is decomposed at 60-80 °C under hydrogen pressure, in the presence of functionalized ligands. Monometallic and bimetallic nanoparticles were prepared, characterized by XPS, TEM, SAXS and WAXS, then tested in the H_2 productive hydrolysis of NH_3BH_3.

Some Ru-based nanoparticles and Ni/Ru-based bimetallic proved their efficiency in fast H_2 release from NH_3BH_3 hydrolysis at room temperature, and their recyclability over at least 5 cycles with retention of high turnover frequency per min.

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Acknowledgement:

This work was supported by the EUR-EIPHI project PRODHYG (AXE1-OPE-2022-0030-D108). We also thank our collaborators at ICB Dijon and LCC Toulouse for their material and experimental support.

Abstract

Thematic Session: Nanochemistry & nanoparticles
Disciplinary fields involved: Organometallic chemistry, catalysis
Keywords: molybdenum disulfide • nanoparticles • colloidal • catalysis • transamidation reaction

Colloidal MoS_2 nanoparticles by organometallic synthesis as improved catalyst

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Molybdenum disulfide (MoS_2) is currently investigated as an effective heterogeneous catalyst, promoting transamidation reactions,[1] or C–C bond formation such as radical-Friedel–Crafts benzylation of arenes.[2] The use of MoS_2 as "bulk material" limits its reactivity. Thus, using it as nanoparticles (NPs) under a stable colloidal form, might help improving its promising reactivity. MOS_2 nanoparticles are mostly formed by solvothermal methods,[3] which operates at fairly high temperature (> 200 °C) in long-time reactions, or by various exfoliation methods[4] that provide only poor control over the morphology of the NPs. We report a new synthetic procedure forming colloidally stable nanoparticles of MoS_2 in a one-step process at RT. The sulfurization of a zerovalent organometallic precursor in solution in the presence of stabilizing agents provide nicely reproducible MoS_2 NPs of flat morphology (12 x 2nm). X-Ray photoelectron and Raman spectroscopy showed a relevant mixture of 1T and 2H allotropic phases. The catalytic reactivity of this colloidal MoS_2

material was compared to bulk and non-colloidal nanosized systems, allowing to gather the advantages of homogeneous catalysis (high reactivity) and heterogeneous catalysis (recyclability).

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Acknowledgement:

This work was carried with the financial support of Safran.

Nanochemistry, Nanoparticles, Nanocatalysis

Thursday March 20th

2:00 P.M. - 4:30 P.M.

AMPHITHEATRE GASTON BERGER

Program of the session :

Chairs:

HOUR	NAME	TITLE
14:00	**Benjamin ABECASSIS** **Lab. de Chimie ENS - CNRS**	**Synthesis, twisting and self-assembly of semiconducting colloidal nanoplatelets**
14:30	Gregoire HERZOG LCPME - CNRS	Au nanoparticle assemblies at polarized liquid-liquid interfaces for SERS applications
14:45	Florent CARN MSC - Univ. Paris Cité	Towards a new family of ionic colloidal crystals composed of long-chain polyelectrolytes and small spherical nanoparticles.
15:00	Matias FELDMAN INSP - Sorbonne Univ.	Nanoscale control of heat flux in self-assembled ordered nanocrystal solids
15:15	Jisoo OH LPEM - ESPCI	Understanding the Growth Kinetics of Plasmonic CsxWO3-d Nanocrystals for Shape Control and Polarized LSPR
15:30	Miguel COMESANA-HERMO ITODYS - CNRS	Faceted 3D Supercrystals for Plasmonic Photocatalysis: Design, Reactivity and Operando Studies
15:45	Charles VERNIER CINaM - CNRS	Influence of crystalline structure on the acoustic vibrations of elongated nano-objects
16:00	Sajana SEMI ICB - CNRS	Raman Scattering study of Ligand Exchange Effects on the CdS Nanoplatelets
16:15	Safa KHADDAD ICMCB - Aquitaine Science Transfert	Redox reaction between a silicide and coordination complexes for size-tunable silicon particles

S5

Benjamin ABECASSIS (CNRS - Lab. de Chimie ENS, Lyon)

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Short biography

I am a physical chemist working at the Chemistry Lab of the École Normale Supérieure de Lyon. My research lies at the interface between materials science, soft matter and nanotechnology.
My main current interest is ultrathin 2D colloidal nanoparticles: their synthesis, surface chemistry and conformation. I also study the self-assembly of nanocrystals from the perspective of the emergence of collective properties. This implies understanding colloidal forces between particles at the nanoscale. I am also interested in probing the formation mechanism of nanoparticles using in situ synchrotron-based X-ray techniques. I have expertise in Small Angle X-ray Scattering.
I have a PhD (2006) from École Polytechnique and i hold the "habilitation à diriger les recherches" since 2016.

Synthesis, twisting and self-assembly of semiconducting colloidal nanoplatelets

Colloidal nanoplatelets (NPL) are 2D ultrathin (1nm) crystalline nanoparticles coated with a monolayer of surfactants1. Semiconducting NPLs display outstanding optical properties due to their thickness being controlled at the atomic level. I will show that NPLs share many features with soft matter systems. Due to their very small thickness, they can deform under surface stress induced by ligand adsorption to yield shapes ranging from helicoids, helical ribbons, or tubes typically observed in (chiral) surfactant self-assembly. 2 We will argue that NPLs belong to the broad class of geometrically frustrated assemblies and can be very well described in the framework of incompatible elasticity of thin sheets. In some conditions, NPLs assemble face-to-face into micron-long threads which share common features with living polymers3. Long-range FRET exchange occurs between NPLs within these assemblies.4 We also observed twisted chiral threads with defects resembling 1D twist solitons, which have already been observed in various macromolecules.5

Keywords

nanoplatelets, quantum dots, self-assembly, small angle scattering, twisting

Acknowledgement

This project has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement 865995 - SENECA)

References

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Thematic Session: nanomaterials
Disciplinary fields involved: Chemistry
Keywords (max. 4-5)**: surface enhanced Raman spectroscopy, electrochemistry, biphasic systems, gold nanoparticles**

Au nanoparticle assemblies at polarized liquid-liquid interfaces for SERS applications

Grégoire Herzog, Madjid Tarabet, Romiald Yechi-Yavo, Yinxi Zou, Manuel Dossot

Université de Lorraine, CNRS, LCPME, F-54000 Nancy, France.

Gold nanoparticle (AuNP) assemblies formed at both solid-liquid and liquid-liquid interfaces have been widely investigated in spectroscopy because of their plasmonic properties leading to Surface-Enhanced Raman Spectroscopy (SERS). Recently, we have investigated the SERS signal of organic molecules at a liquid-liquid interface modified by a floating AuNP film [1].

We will present here the formation of AuNP films at the interface between two immiscible electrolyte solutions (ITIES) under electrochemical control to explore the possible control of the AuNP assembly through the tuning of the interfacial potential difference. To achieve this, we apply a potential difference between the two immiscible phases, inducing the aggregation of AuNPs at the ITIES, gradually leading to the formation of a film covering the whole interface. We monitor the film formation through two methods: an electrochemical approach involving the monitoring of the capacitance of the electrochemical double layer, and a spectroscopic approach using UV-Visible total internal reflection to follow the evolution of the scattering and absorption properties of the film at the ITIES.
Finally, we will conduct in situ SERS experiments at the ITIES using the electrogenerated films and link electrochemical parameters used during the film formation with the spectroscopic features of the Raman signal obtained for the targeted organic molecules.

References:

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Towards a new family of ionic colloidal crystals based on long-chain polyelectrolytes and small spherical nanoparticles.

The mixing of polyelectrolyte chains and oppositely charged nanoparticles in aqueous solution results in the formation of electrostatic assemblies. The size, shape and compactness of these assemblies can vary greatly with the Debye length, the concentration ratio of the partners and the characteristics of each partner (i.e. charge density, size, shape, persistence length of the chains).[1] It is also known that the nature of the phase separation observed around the charge stoichiometry can vary from one system to another (i.e. liquid/liquid or liquid/solid). However, to our knowledge, this type of 'asymmetric association' between long flexible linear chains and small spherical particles has not been known until now, either theoretically or experimentally, to allow the formation of assemblies with an ordered structure on large spatial scales (i.e. a colloidal crystal). The aim of this talk is to present a recent result showing that, contrary to what is generally observed, it is possible to form colloidal crystals by the electrostatic coupling of a semi-flexible polyanion, hyaluronic acid, and gold nanoparticles coated with a self-assembled layer of cationic ligands.[2] This result is all the more remarkable given that the size distribution of the two partners is not particularly narrow and the polyelectrolyte contour length ($L \approx 230$ nm) is large compared to the particle size ($R \approx 4$ nm).

On the basis of small-angle X-ray scattering (SAXS) measurements, I will show in which region of the state diagram these crystalline structures were formed and highlight the role played by the flexibility of the PEL chains in the formation of these ordered structures.

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Thematic Session: Nanoparticles, Nanomaterials for energy, Nanoscale characterization
Disciplinary fields involved: Physics, Chemistry
Keywords: thermal transport, thermoreflectance, nanocrystals, supercrystal, anisotropy

Nanoscale control of heat flux in self-assembled ordered nanocrystal solids

Matias Feldman[1], Charles Vernier[2], Rahul Nag[3], Juan J. Barrios-Capuchino[4], Sébastien Royer[1], Hervé Cruguel[1], Emmanuelle Lacaze[1], Emmanuel Lhuillier[1], Danièle Fournier[1], Florian Schulz[4], Cyrille Hamon[3], Hervé Portalès[2], and James K. Utterback[1]

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2. *MONARIS, Sorbonne Université, CNRS, Paris, France*
3. *Laboratoire de Physique des Solides (LPS), Université Paris-Saclay, CNRS, Orsay, France*
4. *Institute for Nanostructure and Solid-State Physics, University of Hamburg, Hamburg, Germany*

Nanocrystal based solids are a promising class of materials whose emergent properties are highly tunable as a function of constituent shape, size, material composition and surface-capping ligands. They are of particular interest for the development of plasmonic, optoelectronic and thermoelectric devices. Understanding and controlling heat flow in these materials is fundamental to all such applications as heating due to optical excitation or current leads to performance degradation, instability and unwanted chemical activity. I will present recent results on the thermal properties of supercrystals of gold nanospheres, nanorods and nano-bipyramids. Thanks to correlative SEM and spatio-temporally resolved thermoreflectance we were able to access sub-micron structural and nanosecond dynamical thermal information. In superlattices of gold nanospheres capped with polymeric ligands, we found that thermal transport is faster in monolayers than in multilayers. Quasi-ballistic Monte-Carlo simulations suggest that this effect arises as a consequence of the combination of a long phonon mean free path with ligand interdigitation. In supercrystals of gold nanorods and nano-bipyramids, we demonstrated that heat flow predominantly follows the orientation of the elongated nanoparticles and does so even in curved assemblies. In ordered superlattices, heat transport is anisotropic flowing faster along the particles' long axis. Our measurements together with finite element simulations and effective medium modelling show that this anisotropy can be finely tuned through the nanoparticles' aspect ratio, shape and packing. Leveraging this anisotropy opens the way to enhanced thermal dissipation and thermal routing directly using the device's active material while maintaining control over size-dependent optical and electronic effects.

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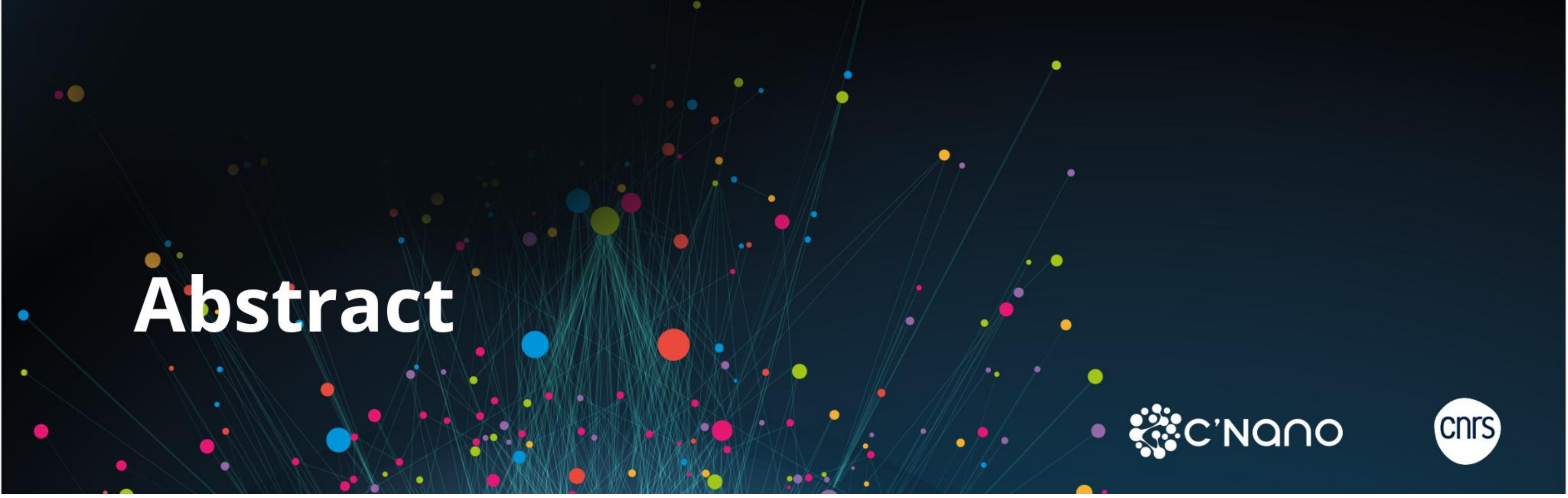

Abstract

Thematic Session : Nanochemistry & nanoparticles
Disciplinary fields involved : Chemistry, Plasmonics
Keywords (max. 4-5)**:** Semiconductor plasmonic nanocrystals, Nanocrystal shape control, polarized LSPR

Understanding the Growth Kinetics of Plasmonic $Cs_xWO_{3-\delta}$ Nanocrystals for Shape Control and Polarized LSPR

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While the synthesis of anisotropic metal nanoparticles is well-established, the shape control of plasmonic semiconductor nanocrystals has remained relatively unexplored.[1] This class of materials shows great promise for hosting LSPR (localized surface plasmon resonance) in the infrared optical region that is inaccessible with metal nanoparticles. Achieving precise shape control, therefore, has been a critical challenge.

We have developed synthesis methods for anisotropically growing plasmonic $CsWO_{3-\delta}$ nanocrystals.[2] By employing seed-mediated continuous growth and selective facet deactivation using halide ions, we precisely control the aspect ratio of nanocrystals in both rod and platelet shapes. We rationalize the observed growth kinetics adapting the fundamental crystal growth theory[3] to the strong crystalline anisotropy of $CsWO_{3-\delta}$[4]: Distinct growth regimes apply to the basal and prismatic planes of $CsWO_{3-\delta}$ resulting in continuous change of relative growth rates as a function of precursor injection rate. This fundamental understanding has enabled exquisite shape control of $CsWO_{3-\delta}$ nanocrystals, even allowing for switching growth directions when necessary, thereby tuning the LSPR spectrum as intended. We also demonstrate that the nanocrystals with strong shape anisotropy can be directionally assembled under electric field. We observe electrically switchable polarization behavior of LSPR, which marks the first demonstration of polarized infrared LSPR in plasmonic semiconductor nanocrystals.

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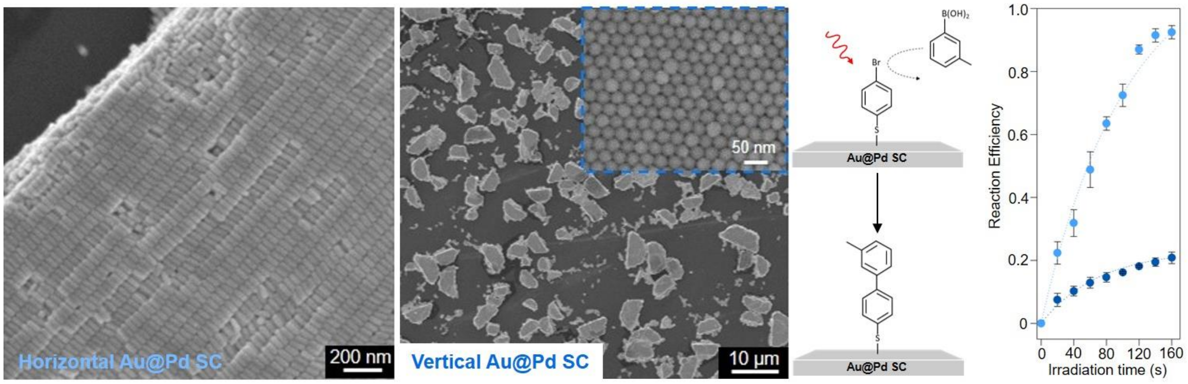
Thematic Session: Nanochimie & Nanoparticules
Disciplinary fields involved: Chemistry
Keywords (max. 4-5)**: plasmonic photocatalysis, 3D supercrystals, self-assembly, organic transformations, operando SERS**

Faceted 3D Supercrystals for Plasmonic Photocatalysis: Design, Reactivity and Operando Studies

Charlène Brissaud, Jean-Yves Piquemal, Miguel Comesaña-Hermo

1. *ITODYS laboratory, CNRS, Université Paris Cité, Paris, France*

Plasmonic photocatalysis has been developed over the last 15 years as a novel means to modulate chemical reactivity, producing improved efficiencies and better control over selectivity in a plethora of organic transformations or the activation of small molecules.[1,2] In most cases, plasmonic nanoparticles are implemented in photocatalysis as colloidal dispersions, with important limitations related to the photo-desorption of stabilizing ligands and overall long-term stability, among other factors. As an alternative, we present the use of 3D plasmonic supercrystals obtained via the depletion-induced self-assembly of plasmonic nanoparticles on a given substrate as heterogeneous photocatalysts for different organic reactions. The anisotropic shape of the objects used leads to the formation of assemblies exposing crystalline facets with very diverse electromagnetic field intensities, thus producing different efficiencies towards a given photochemical process through the generation of hot charge carriers. Moreover, the modulation of the chemical composition of the nanoparticles allows the activation of different organic transformations such as polymerization reactions or C-C cross-couplings. Finally, and in order to study the facet-dependent reactivity of these super-structures, we have monitored their reactivity at the single supercrystal level and in operando conditions by means of Surface-Enhanced Raman Spectroscopy (SERS). The experimental data obtained is complemented by optical and electronic simulations, allowing us to obtain structure-function correlations that help understanding the importance of inter-particle coupling over large areas of these structures and its influence on the final photocatalytic activities (Figure).[3]



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Thematic Session: Nanochemistry and nanoparticles
Disciplinary fields involved: Physical Chemistry
Keywords: spectroscopy – gold nanorods – crystallinity - vibrations

Influence of crystalline structure on the acoustic vibrations of elongated nano-objects

Charles Vernier[1], Hervé Portalès[1]

1. *MONARIS, Sorbonne Université, Paris*

Metals such as gold or silver are polycrystalline at the macroscale. However, colloidal nanoparticles with controlled crystallinity can now be synthesized. It has been shown that different crystal facets may have different catalytic activity,[1] therefore it is necessary to know the crystalline structure of nanoparticles before using them in catalysis. This is possible by using expensive electronic methods, such as high resolution transmission electron microscopy.

In this work, we proceed to uncover the structural features of polycrystalline pentatwinned gold nanorods (AuNRs_PT) and single-crystal gold nanorods (AuNRs_SC) by optical spectroscopies, namely absorption spectroscopy and low frequency Raman scattering.

First, the longitudinal localized surface plasmon resonance wavelength is shown to depend on the tip curvature of the nanorods (AuNRs_PT exhibit more rounded tips than AuNRs_SC, as shown in Figure 1a,b). These findings are supported by calculations carried out using the discrete dipole approximation method.[2]

Second, the acoustic vibrations of AuNRs are demonstrated to depend on crystallinity. We recorded low frequency Raman spectra of both AuNRs_PT and AuNRs_SC samples and found that the former exhibits one major band, attributed to a 5-fold degenerated quadrupolar mode of angular momentum $l = 2$, whereas in the latter, this band is split into two modes, B_{1g} and B_{2g} (see Figure 1c). This result is reminescent of a similar result obtained for gold nanospheres of different crystalline structures,[3] but was never observed in elongated objects such as nanorods.

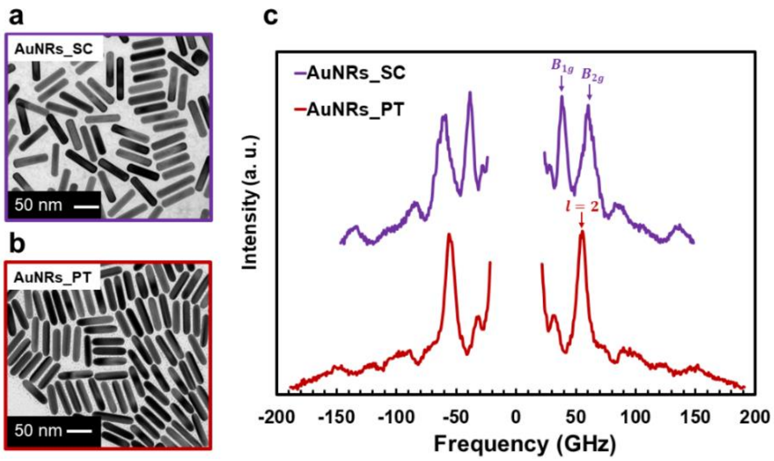

Figure 1 : Transmission electron microscopy images of a) single crystal AuNRs and b) polycristalline AuNRs. c) Low frequency Stokes and anti-Stokes Raman spectra of polycrystalline AuNRs (red) and single crystal AuNRs (purple).

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Acknowledgement: we thank Nicolas Goubet for HRTEM imaging.

Thematic Session Quantum Dots: from synthesis to properties
Disciplinary fields involved Chemistry
Keywords Nanoplatelets, Raman, Interfaces

Raman Scattering study of Ligand Exchange Effects on the CdS Nanoplatelets.

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Thi Thu Dung Lien, Jérémie Margueritat and Benoit Mahler
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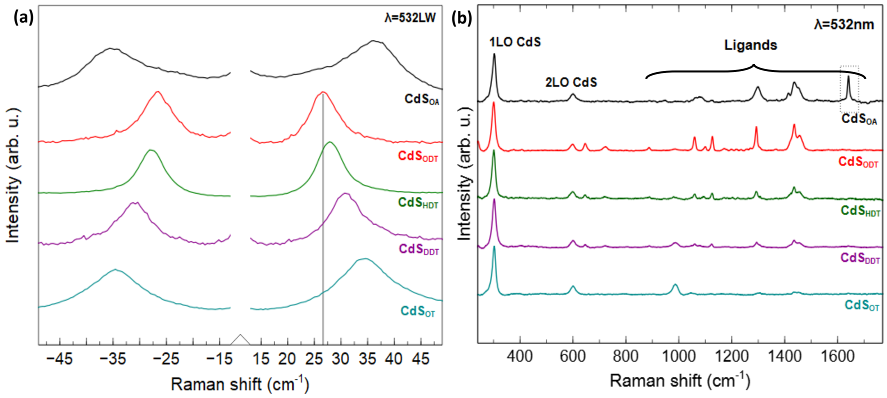
The unique optical and electrical properties of two-dimensional (2D) colloidal cadmium chalcogenide nanoplatelets (NPLs) make them promising materials for the development of various optoelectronic devices. Raman scattering provides key insights about the structure and interfaces in these materials. We report a study of the effects of different ligands on the vibrational dynamics of CdS NPLs of varying thicknesses. In addition to optical absorption and transmission electron microscopy, Raman spectroscopy is used to confirm the substitution of the ligands by monitoring both the LO peak of the NPLs and the various Raman peaks of the ligands. Low-frequency Raman scattering measurements are also performed to monitor the changes in the frequency of the breathing vibration due to the molecular weight of the ligand as observed previously for CdSe NPLs[1,2]. The agreement between the mass–load model and experimental measurements is revisited in the context of carboxylate-to-thiolate ligand exchange.



(a) Acoustic and (b) LO and ligand peaks for CdS NPLs with different ligands (from bottom to top: octanethiol, dodecanethiol, hexadecanethiol, octadecanethiol and oleic acid).

References

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[2]Girard *et al.* (2016) *Nanoscale*, *8*(27), 13251

Acknowledgement

- *DeXCTer (ANR-23-CE29-0003)*

Thematic Session : Nanochimie & Nanoparticules
Disciplinary fields involved : Chemistry
Keywords : Silicon particles, size-control, redox reaction

Redox reaction between a silicide and coordination complexes for size-tunable silicon particles

Safa Khaddad [1], Megan A. Parker [1], D. Portehault[2], A. Ghoridi[2], E. Morvan[3], M. Gonidec[1], P. Rosa [1] and G. L. Drisko[1]

1. University of Bordeaux, CNRS, Bordeaux-INP, ICMCB, UMR 5026, F-33600 Pessac, France
2. Sorbonne Université, CNRS, Laboratoire de Chimie de la Matière Condensée de Paris (LCMCP), F-75005 Paris, France
3. Institut Européen de Chimie et de Biologie (IECB), UAR3033, 33600 Pessac, France

The synthesis of silicon particles in solution presents significant challenges due to silicon's tendency to oxidize spontaneously in the presence of water or air. Discovering new synthetic techniques would allow for greater control over the size and shape of Si particles. Here we demonstrate a novel redox reaction between a hexacoordinated silicon complex, bis(N,N'-diisopropylbutylamidinato)dichlorosilane, and a silicon Zintl phase, sodium silicide (Na_4Si_4).[1] This approach enables the production of silicon particles with tunable sizes, ranging from 45 to 230 nm, depending on the molar ratios of the two precursors. The chemical make-up of the particles produced by this method retain the integrity of polycrystalline Si^0 with a passive oxidation layer. The fabrication of silicon particles in this size range opens new avenues for the production of miniaturized optical components and applications in lithium-ion battery anodes.

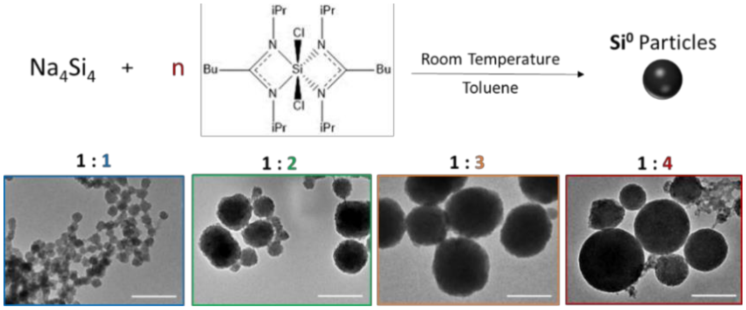

Figure 1. *Top: Reaction scheme toward size-tunable Si particles. Bottom: TEM images of particles produced from varying ratios of Na_4Si_4: silicon bisamidinate. Scale bars represent 200 nm.*

References:

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2. Parker, Megan A., et al. « Unveiling the Potential of Redox Chemistry to Form Size-Tunable, High-Index Silicon Particles ». Chemistry of Materials, août 2024, p. acs.chemmater.4c01439.

Acknowledgement: 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).

Nanochemistry, Nanoparticles, Nanocatalysis

Friday March 21th

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

AMPHITHEATRE GASTON BERGER

Program of the session :

Chairs:

HOUR	NAME	TITLE
10:30	**Damien BOYER** **L2n - UTT**	**Nanosized inorganic and hybrid phosphors for optical applications**
11:00	Leandro SACCO Vs Particle	Automated print technology based on spark ablation for deposition of nanoparticles and nanoporous layers
11:15	Melik MAKSEM LPCNO - INSA TOULOUSE	Integration of soft magnetic materials for RF applications
11:30	Ester BUTERA MAcSE Univ-Rennes	Photochemical synthesis of emissive and photothermal gold-nanoclusters: effect of electron-rich ligand on optical properties.
11:45	Arthur REYMOND L2CM - Univ. Lorraine	Impact of Nanoparticle Shape and Coating Thickness on the Plasmonic Behavior of Au@MnO2.
12:00	Clémence CHINAUD-CHAIX ICMCB - CNRS	Tunable optical properties of silica beads via optimal sequestration of lanthanide ions within it
12:15	Joana VAZ RAMOS ICPEES - CNRS	Magnetic graphene/iron oxide nano-adsorbents for the environmental depollution of polycyclic aromatic hydrocarbons and other relevant pollutants

S6

Damien BOYER (Sigma Clermont – ICCF, Clermont-Ferrand)

Institut de Chimie de Clermont-Ferrand

damien.boyer@sigma-clermont.fr

Short biography

Damien BOYER earned his PhD in "Chemistry of Materials" from Blaise Pascal University, Clermont-Ferrand, in 2000, focusing on the development of sol-gel luminescent materials for optical applications. Following his doctorate, he spent two years as a research associate at the Materials Science Center of the University of Manchester. In 2002, he joined the École Nationale Supérieure de Chimie de Clermont-Ferrand (ENSCCF), now SIGMA Clermont, as an associate professor and obtained his Habilitation in 2009. Over the course of his career, he has supervised or co-supervised 15 PhD theses. His research topics are mainly dedicated to the synthesis of size-controlled inorganic or hybrid phosphors through various materials synthesis processes for optical applications (96 Publications, and 5 patent families). His current research interests include the synthesis of red-emitting phosphors for LED-based lighting, green-emitting phosphors for micoLED displays and infrared-emitting phosphors for biological labelling. he has been leading the Luminescent Materials (LM) group at the Institute of Chemistry of Clermont-Ferrand. The group consists of around 20 members, including 8 permanent researchers

Nanosized inorganic and hybrid phosphors for optical applications

Over the past decade, the demand for nanophosphors has surged, driven by the growing need for advanced materials in a variety of applications. Specifically, nanosized phosphors with superior optical properties have garnered significant attention due to their potential in high-performance displays, fluorescent probes for nanomedicine, and even specialized applications like 3D printing using inkjet technologies. Two main strategies for designing these materials can be considered: bottom-up approaches (constructing them from molecules) and top-down methods (reducing bulk materials to the nanoscale). In this talk, I will explore both strategies for synthesizing various types of nanosized phosphors, including inorganic (oxide and fluoride), organic-inorganic hybrids (organic dyes encapsulated in silica nanoparticles), and semiconductor nanocrystals (Quantum Dots or QDs). I will focus specifically on the preparation of $Y_3Al_5O_{12}:Ce^{3+}$ [1] and $NaYF_4:Yb^{3+},Tm^{3+}$ nanoparticles [2], and discuss their applications: the former as a yellow-emitting phosphor for LED devices based on microLEDs (μLEDs), and the latter as an up-converting phosphor for infrared medical imaging. Additionally, I will present the development of luminescent hybrid nanoparticles, where fluorescein is encapsulated within a silica matrix using the reverse microemulsion method [3]. Lastly, I will discuss a family of cadmium-free quantum dots, consisting of InP cores coated with a ZnS shell. These QDs are particularly promising due to their remarkable size-dependent optical properties, which make them ideal candidates for a variety of applications [4,5].

Keywords

Nanoparticles ; Phosphors ; microLED/LED ; Display ; up-conversion

References

[1] WO2018002556A1, "Method for producing photoluminescent particles", A. Aboulaich (Aledia), G. Chadeyron (ICCF) et R. Mahiou (ICCF) [2] A. Cordonnier et al., Journal of Materials Chemistry B, 9 (2021) 7423-7434. 10.1039/d1tb00777g [3] R. Boonsin et al., Journal of Materials Chemistry C, 4 (2016) 6562-6569.10.1039/C6TC01039C [4] R. Valleix et al., Advanced Materials, (2021) 2103411. 10.1002/adma.202103411 [5] R. Valleix et al., ACS Applied Nano Materials, 4 (2021) 11105-11114.10.1021/acsanm.1c02577

Thematic Session Nanochemistry and Nanoparticles
Disciplinary fields involved Chemistry, Physics, Material Science
Keywords (max. 4-5)**: Dry printing, Nanoparticles, Sensing, Electrocatalysis, Spark Ablation**

Automated print technology based on spark ablation for deposition of nanoparticles and nanoporous layers

Vincent Mazzola[1], Leandro Sacco[1,2]

1. *VSParticle, Oostsingel 209, 2612 HL, Delft, The Netherlands,*
2. *Department of Microelectronics, Faculty of Electrical Engineering, Mathematics & Computer Science, Delft University of Technology, Delft 2628 CT, The Netherlands.*

Abstract

The nanomanufacturing success not only rely on the precise control of the material physical/chemical properties but also on the reproducibility and scalability. In this context, spark ablation is becoming an adopted technology to produce nanoparticles [1]. This fully-dry approach is characterized by the absence of chemical wastes, precursors or binders requirement leading to high pure throughout. Furthermore, it’s considered as a versatile NP generator since any solid (semi)-conductor (pure metals, alloys or doped semiconductors) can be used and mixed, implying that a myriad of material compositions can be produced (Figure 1 schematized a spark ablation process). NPs particles sizes can be also controlled simply adjusting the spark ablation parameters. The produced NPs can be directly deposited onto the desired substrate using inertial impaction through an automated, single-step process. Such a platform tool enable a deterministic nanomanufacturing method capable to produce both complex nanoporous layers and sample arrays high-throughput screening. The tool for this process has been commercialized by VSParticle as a Nanoprinter, and has already been implemented for the fabrication and testing of chemical sensors [2] electrocatalysts for green hydrogen [3] and, among other applications [1]. In this work, it will be discussed the working principles of spark ablation and deposition techniques and the influence of key sparking parameters on the material formation. This manufacturing process aims to accelerate the material discovery and drastically reduce time to market for innovative devices based on nanomaterials.

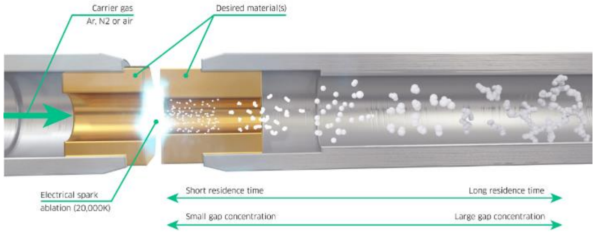

Figure 1: Spark ablation mechanism for synthesis of nanoparticles.

References:

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[2] L. N. Sacco, L. Egger, M. Popov, C. Dösinger, N. Schouten, L. Romaner and A. Köck, "Printing Nanoporous Layers (NPL) Generated by Spark Ablation for Gas Sensing Applications," in *EUROSENSORS XXXVI*, Debrecen, 2024.

[3] V. Mazzola, E. Irtem, S. Asperti, A. Vijayakuma and A. V. Vugt, "Highly Active Nano-Porous Thin-Films for Water Electrolysis Using an Automated Print Technology Based on Spark Ablation," in *Electrochemical Society Meeting Abstracts 245*, San Francisco, 2024.

Thematic Session: Nanochemistry & Nanoparticles
Disciplinary fields involved: Chemistry; Physics
Keywords: Nanomagnetism; Nanoparticles; Magnetophoresis; Radiofrequency applications; Assembly

INTEGRATION OF SOFT MAGNETIC MATERIALS FOR RF APPLICATIONS

Mélik E Maksem[,2], Adrien Bourgine[3], Thierry Leïchlé[2], David Bourrier[2], Alexandre Rumeau[2], Simon Cayez[1], Nicolas Ratel-Ramond[1], Guillaume Viau[1], Thierry Parra[2], Thomas Blon[1], Lise-Marie Lacroix [1]

[1]Laboratoire de Physique et Chimie des Nano-Objets, UMR 5215 INSA, CNRS, UT3, Toulouse Cedex 4, France
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In the context of a digital society with a continuous intensification of wireless communications [1], addressing energy overconsumption is essential. Among different components, the inductors are widespread constituents for integrated circuit. The addition of soft magnetic materials on inductors allows condensing the local magnetic flux and thus reducing losses. Combining high magnetization and insulating electrical properties, nanoparticles are ideal building blocks for fabricating such integrated magnets by a bottom-up approach.

In this work, we studied the effect of the intrinsic properties of the nanoparticles and of the collective assembly on the high frequency characteristics of the inductors. To do so we synthesized Fe, FeNi and FeCo nanoparticles using the co-decomposition of organometallic precursors in the presence of an acid/amine ligand couple under reducing conditions [2,3] and CoNi nanoparticles by a polyol process [4] varying their size from 9 to 90 nm. The nanoparticles were assembled into submillimetre micromagnets by a magnetophoresis process directly onto inductors [5] **(Fig 1-a, b)**. The impact of the experimental parameters on the microstructure has been studied by SAXS **(Fig 1-c)**. Anisotropic assemblies consisting of densely packed NPs were obtained. RF measurements show a 50-60% increase of the inductance value up to 3 GHz in presence of 12 nm FeCo-based magnet but requiring an epoxy protection against oxidation, or with 50 nm CoNi-based magnet.

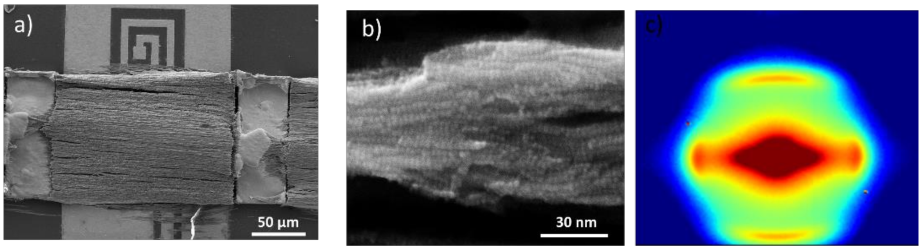

Fig. 1- (a, b) SEM images of the micro-magnets. (c) The corresping 2D SAXS.

References:
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2. Garnero, F; et al, Nano Lett. 2019, 19(2), 1379-1386.
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5. Moritz, P. et al. ACS Nano. 2021, 15(3), 5096-5108.

Acknowledgement:

Funded by INSA Toulouse, TTT, the Occitanie region, MERS, the EUR NanoX, RENATECH network, UPS, CNRS.

Thematic Session: Nanomaterial
Disciplinary fields involved: Chemistry, Physics.
Keywords : photoirradiation, gold nanoclusters, biosensing, phototermal.

Photochemical synthesis of emissive and photothermal gold-nanoclusters: effect of electron-rich ligand on optical properties.

Ester Butera[1,3], Regina Maria Chiechio[3], Valèrie Marchi[4] , Salvatore Petralia[1,2].

1. *Department of Drug science and Health, University of Catania, Catania, Italy.*
2. CNR-ICB, via Paolo Gaifami 18, Catania, Italy.
3. *Dipartimento di Fisica e Astronomia "Ettore Majorana", University of Catania, Catania, Italy.*
4. *Institut des Sciences Chimiques de Rennes, ISCR, UMR CNRS 6226, University of Rennes, 35042 Rennes, France*

Gold nanoclusters (AuNCs) are bright, non-toxic fluorophores with small size, long fluorescence lifetime, and good biocompatibility, making them attractive for biosensing and bioimaging.[1-3] However, their synthesis by efficient, scalable, and environmentally friendly methods has not been deeply explored. In this work, we focused on the development and optimization of a photochemical approach for the synthesis of AuNCs by UV light at 254 nm in the presence of glutathione (GSH), which simultaneously acts as a reducing agent and capping ligand. Using this approach, we achieve rapid formation of monodisperse AuNCs without the need for high temperatures, harsh chemical reductants, or long reaction times. The tuning of their optical properties by varying the Au: GSH molar ratio or in presence of other ligands was also investigated. The obtained AuNCs exhibit, when excited at 390 nm, dual fluorescence emission at 440 nm and 700 nm. This dual emission is attributed to different electronic transitions: the emission at 700nm is related to ligand-metal charge transfer (LMCT) processes, while the emission at 440nm second arises from quantum confinement effects due to the ultrasmall size of the nanoclusters core. These NCs exhibit a good photothermal conversion at different wavelength excitation (405 nm, 470 and 532 nm, $\eta\% \cong 30\%$. Further characterization was performed by UV-Vis absorption spectroscopy. Thus, this method represents a new and versatile method to obtain AuNCs. This approach is thus simple, scalable and environmentally friendly, positioning it as a valuable contribution to the field of nanotechnology.

References :
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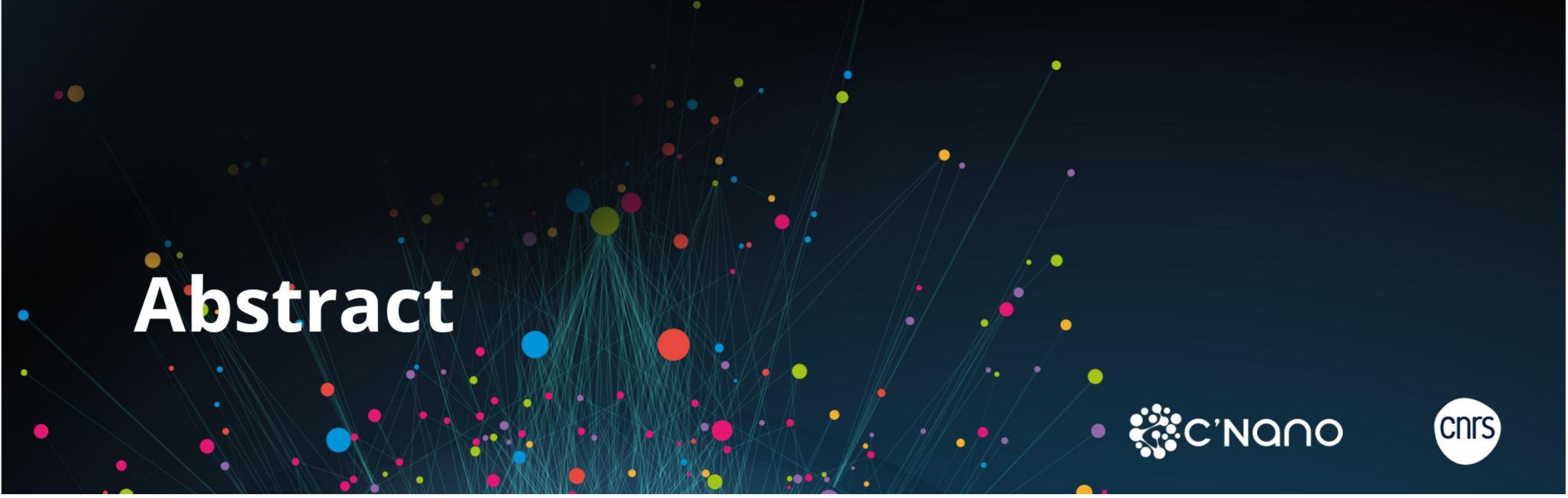
Acknowledgement:



Abstract

This work has been funded by European Union (NextGeneration EU), through the MUR-PNRR project SAMOTHRACE (ECS00000022).

Thematic Session: Nanochemistry, Nanoparticles, Nanocatalysis
Disciplinary fields involved: Chemistry
Keywords: Au@MnO2, core-shell structure, nanostructures, LSPR, photocatalysis.

Impact of Nanoparticle Shape and Coating Thickness on the Plasmonic Behavior of Au@MnO2.

A. Reymond[1,2], I. Abdelsalam[2], P. Camargo[2], A. Marti Morant[1], R. Wojcieszak[1]

1. *L2CM, CNRS, University of Lorraine, UMR 7053, 54600 Vandoeuvre les Nancy*
2. *Department of Chemistry, Universityof Helsinki, FIN-0014 Helsinki, Finland10)*

Abstract

Introduction. Gold nanoparticles have garnered significant interest from the scientific community due to their plasmonic properties when exposed to visible light [1]. Manganese oxide is also noteworthy for its catalytic properties across various fields. It has demonstrated exceptional catalytic performance in oxidation processes, particularly in biomedical therapies [2] and in the biomass conversion of 5-HMF [3], while being low-cost, low-toxicity, and abundantly available [4]. The combination of plasmonic effects with manganese oxide activity offers new perspectives and demonstrates enhanced performance. Thus, this work focuses on the synthesis of plasmonic Au@MnO2 nano catalysts, their characterization and their catalytic results.

Methods. The synthesis of nanoparticles was carried out in a colloidal solution for spherical Au NPs, through a hydrothermal reaction for octahedral Au NPs, and via an α-naphthol-assisted preparation for Au NPs nanowires. Subsequently, these nanoparticles of different shapes were coated with a layer of manganese oxide using a pH-adjusted $KMnO_4$ reduction method.

Results and discussion. LSPR effects were observed for Au NPs and for Au@MnO2 structures. These resonances confer high photocatalytic activity to prepared materials. In addition, the structures were analyzed using TEM, which highlights the core-shell structure, as shown in the image.

The octahedral and nanowire nanoparticles coated with MnO2 represent novel structures not previously reported in the literature. Some of our results highlight the plasmonic and photoactive nature of the Au@MnO2 systems, confirming their effectiveness under specific conditions.

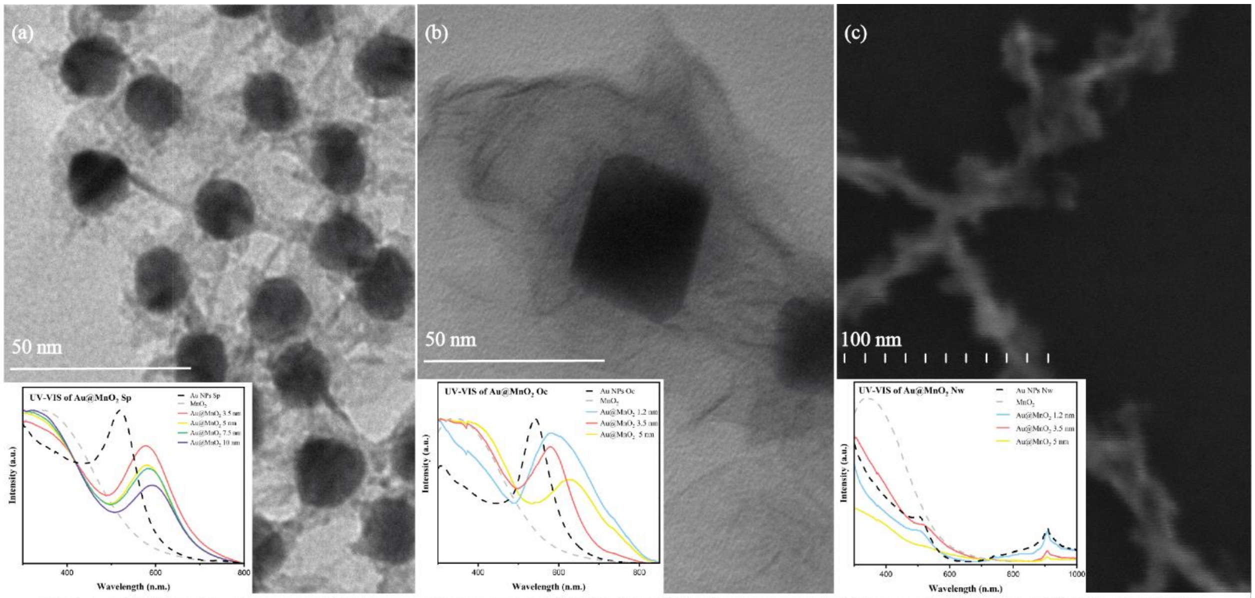


Figure. (a) UV-Vis Spectrum and TEM Image of Spherical Au@MnO$_2$ (b) UV-Vis Spectrum and TEM Image of Octahedral Au@MnO$_2$ (c) UV-Vis Spectrum and SEM Image of Wires Au@MnO$_2$

References:

[1] Camargo, Pedro H. C. and Emiliano Cortés. Plasmonic Catalysis: From Fundamentals to Applications. Wiley VCH, 2021.
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[3] Zhu, Yaoqin, et al. "Au/MnO2 nanostructured catalysts and their catalytic performance for the oxidation of 5-(hydroxymethyl)furfural." Catalysis Communications, 2015, pp. 37-43.
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Thematic Session: Nanochemistry and Nanoparticles
Disciplinary fields involved: Chemistry, Physics
Keywords: Doping, lanthanide, luminescence, zirconia, silica, nanoparticle.

Tunable optical properties of silica beads via optimal sequestration of lanthanide ions within it

Clémence Chinaud-Chaix[1], Pascale Nasr[2], Joshua Davis[3], Clément Sanchez[4], Mathieu Mivelle[2],

Alexandre Baron[3], Sébastien Bidault[5] and Mona Tréguer-Delapierre[1]

1. *Institut de Chimie de la Matière condensée de Bordeaux, CNRS, University of Bordeaux, Bordeaux INP, Pessac, France*
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3. *Centre de Recherche Paul Pascal, CNRS, University of Bordeaux, Pessac, France*
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5. *Institut Langevin, CNRS, ESPCI Paris, Paris, France*

Highly luminescent silica nanoparticles containing lanthanide ions are of interest for isotropic optical materials with applications in imaging and optical communications. For such applications, the dispersion of the lanthanides with the metal oxide matrix and the level of doping must be precisely controlled. To achieve such control, we use a two-step colloidal synthesis approach. Starting from highly monodispersed lanthanide-doped zirconia nanoparticles using a hydrothermal approach, we then coat them with silica by a sol-gel approach. The well-crystallized seeds with a diameter of around 5 nm are homogeneously doped (5 to 10% mole fraction with the emitters). They can be trapped in large quantities in silica beads to give rise to highly luminescent nanoparticles. Using single-cluster spectroscopy, we show that the luminescence properties are reproducible from particle to particle. These findings which allow precise control over size and morphology, open avenues for the manipulation of unusual light-matter interactions.

References:

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Acknowledgement:

This work was supported by ANR agency ANR-22-CE09-0027

Thematic Session (eg. Nanophotonics & nano-optics, nanomaterials, nanobioscience …)**:**
Nanochemistry & Nanoparticles
Disciplinary fields involved (eg. Chemistry, Physics, Biology …)**: Chemistry, Physical Chemistry**
Keywords (max. 4-5)**: graphene; iron oxide; nanomaterials; adsorption; organic pollutants**

Magnetic graphene/iron oxide nano-adsorbents for the environmental depollution of polycyclic aromatic hydrocarbons and other relevant pollutants

Joana Vaz-Ramos[1,2], Théo Lucante[1,2], Anaïs Becker[1], Dominique Bégin[1], Stéphane Le Calvé[1], Sylvie Bégin-Colin[1,2]

1. *Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR-7504 CNRS-Université de Strasbourg, 23 rue du Lœss, 67034 Strasbourg Cedex 2, France*
2. *Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES), UMR-7515 CNRS-Université de Strasbourg, Strasbourg, France*

A lot of different environmental pollutants exist that are harmful to human health and the environment, so removing them and monitoring their presence is essential. Adsorption has gained a lot of attention for pollutant capture and extraction, especially with the development of nanotechnologies. The possibility to design composite nanomaterials of graphene and iron oxide for depollution strategies is particularly attractive because it couples the high adsorption efficiency of graphene with an easy magnetic separation. In this context, we successfully developed graphene/iron oxide nano-adsorbents by a reproducible one-pot polyol method. These nanomaterials proved to be highly efficient in the removal from water of polycyclic aromatic hydrocarbons (PAHs), which are ubiquitous pollutants with associated health risks. We first tested the adsorption of benzo(a)pyrene with our graphene/iron oxide nanocomposites, due to its high carcinogenicity, reaching >99.9% of removal [1]. The simultaneous adsorption of 16 PAHs showed a preferential adsorption of PAHs with higher number of rings, reaching removals >95% for the nanocomposite and surprisingly iron oxide nanostructures alone also showed adsorption potential. Likewise, when studying the simultaneous adsorption of mono- and polyaromatic compounds, there was selectivity for polyaromatics, in agreement with the previous results. The developed adsorbents also showed potential to remove other relevant environmental pollutants. Nevertheless, challenges remain in the adsorbent's development for continuous depollution processes, as they need to be supported in bulk materials to avoid their loss to the environment. We successfully loaded these nano-adsorbents into supports and their depollution performance was tested, showing results in agreement with the previous.

References:
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Acknowledgement:

This research project was co-funded by Institut Carnot MICA through the CAPTALL project, Region Grand Est and ANR through the FIGHTVIRUS project (Resilience Grand Est project), and by ANR through the ON-LINE_PAC_ANALYSIS project.

Poster Session

NANOCHEMISTRY & NANOPARTICLES/NANOBIOSCIENCES & NANOMEDECINE /NANOMATERIALS FOR ENERGY/ SUSTAINABILITY AND ECO DESIGN OF NANOMATERIALS

N° POSTER	TITLE	NOM	Prénom	
31	Plasmon-induced thermo-polymerization of PETA in presence of various thermal initiators	BASTIDE	Mathieu	
32	Green synthesis of curcumin based nanoparticle	BASU	Surita	
33	Synthesis of Polyvinylpyrrolidone nanocomposite with palygorskite for application in water-based drilling fluids	DALMONEKI	Anna Clara	●
34	Carbon supported metal oxides nanoparticles and their applications in biomass valorization	DJELLALI	Ali	
35	Synthesis of Polyacrylamide/Palygorskite Nanocomposites for Application in Water-Based Drilling Fluids	GOMES	Ana Beatriz	
36	Re(CO)-based silica-nanoparticles as multimodal probes for bio-imaging	KAUFFELD	Willem	
37	Chiral CdSe/CdS Nanonails	KUZNETSOVA	Vera	
38	Towards large-scale production of Cobalt nanorods	LISOIR	Emma	●
39	Synthesis and Evaluation of PAMAM G0.5 Dendrimer as a Swelling Inhibitor Additive for Clays in Water-Based Drilling Fluids	LOPES/SPINELLI	Grazielle/Luciana	
40	Plasmonic nanoclusters synthesized by a multi-step colloidal approach	ROMANUS	Martin	●
41	Influence of CuInS2 crystalline structure on the synthesis of CuIn1-xFexS2 quantum dot by cation exchange	ROUX-BYL	Céline	●
42	Chirality in Zinc Oxide nanoparticle synthesis	SARTOR	Valerie	●
43	Application and evaluation of core-shell nanocomposite using silica nanoparticles and AM/AMPS/DMDAAC/AAC tetrapolymer	SPINELLI	Luciana	
44	Design of efficient nanocatalysts for H2 release from boranes and silanes	THIBAULT	Maxime	
45	Influence of crystalline structure on the acoustic vibrations of elongated nano-objects	VERNIER	Charles	
46	Chemistry and biological effects of germanium oxide nanoparticles	VIKRAMAN	Haribaskar	
47	From laser-synthesized nanoparticles to innovative medical devices	AL KATTAN	Ahmed	●
48	Ultra-small Superparamagnetic Iron Oxide Coated Phosphonate-based Ligand for MRI Application	CHE DJI	Lyns Verel	
49	Magnetic hyperthermia tumor ablation and tumor microenvironment modulation monitored by optical imaging	COSTE	Henri	
50	Synthesis of iron oxide nanoparticles and magnetic properties tuning by temperature cycling: towards fine control of crystal phase and size distribution	HUEZ	Cecile	
51	Hybrid plasmon-semiconductor nanoparticles for charge or resonant energy transfer based dynamic phototherapy	JEFFRIES	Beatrice	
52	Re(CO)-based silica-nanoparticles as multimodal probes for bio-imaging	KAUFELD	Willem	
53	Force nanosensor development for measuring mechanical stress exerted by living cells	LACROIX	Noemie	
54	Combination therapy using nanoheaters and CAR-T immunotherapy on 3D tumor models	LEINEBO	Charlotte Amalie	
55	Red-blood-cell-membrane-coated polymer micelles/vesicles as biomimetic nanoassemblies for potential photocatalytic cancer therapy under hypoxia	MA	Yandong	
56	Vivoptic, a preclinical optical imaging platform for the evaluation of diagnostic and therapeutic strategies	MORNET	Stéphane	●
57	On the Roles of Polymer Chemistry, Kinetics, and Mixing in the Assembly of Loaded Polymer Nanoparticles	REISCH	Andreas	●
58	Digital colorimetric biosensing on gold-DNA origami nanostructures	ZHANG	Zixiao	
59	Cu Isotopic Fractionation Following Foliar uptake	CALAS	Aude	
60	New process "Multi-Dip Coating" applied for biological statistical analysis of Antimicrobial Surfaces	CHARLIAC	Jérôme	●
61	One step synthesis using laser pyrolysis of nanostructured carbides molybdenum catalysts for hydrogen production	RIO	Simon	
62	Study of the reactivity of Fe(0) nanoparticles towards ammonia	ZAMBLE	Christian Irie	
63	Chemical Passivation of GaN Nanowires for the Development of Innovative Photocatalysts	ZORAI	Amel	

Thematic Session : Nanomaterials
Disciplinary fields involved: Chemistry
Keywords: Green synthesis, Curcumin, Gold nanoparticles

Green synthesis of Curcumin based nanoparticles

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Abstract

Curcumin, derived from plant species Curcuma longa is a natural polyphenol, has gained significant attention in recent years due to its various biological and medical applications.[1] However, its limited bioavailability and poor solubility have hindered its clinical applications. Gold nanoparticles with its simpler green synthesis has gained great therapeutic applications.[2] In this study, we have explored curcumin coated gold nanoparticles via simple green and facile method for the synthesis .Here, we report a of curcumin-coated AuNPs (Cur-AuNPs) using curcumin itself as both a reducing and capping agent. The synthesized Cur-AuNPs were characterized by various techniques, including UV-Vis spectroscopy, transmission electron microscopy (TEM), and dynamic light scattering (DLS). The results showed that the Cur-AuNPs were spherical in shape with an average size of 30 nm and exhibited excellent stability in aqueous solution.

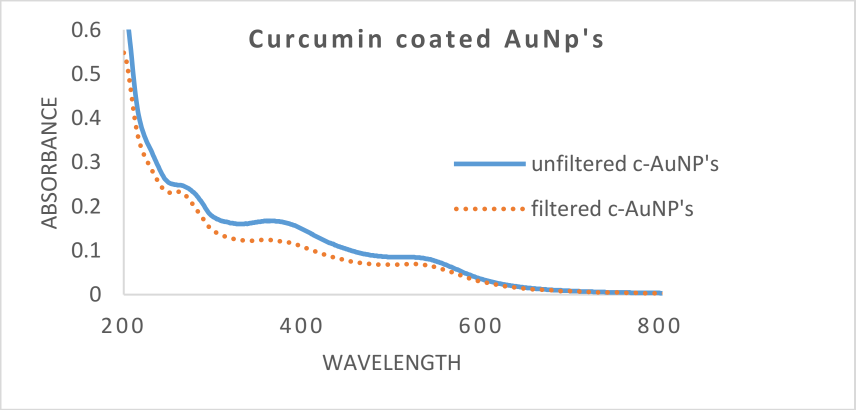

Figure 1: UV-absorption spectrs of curcumin coated gold nanoparticles

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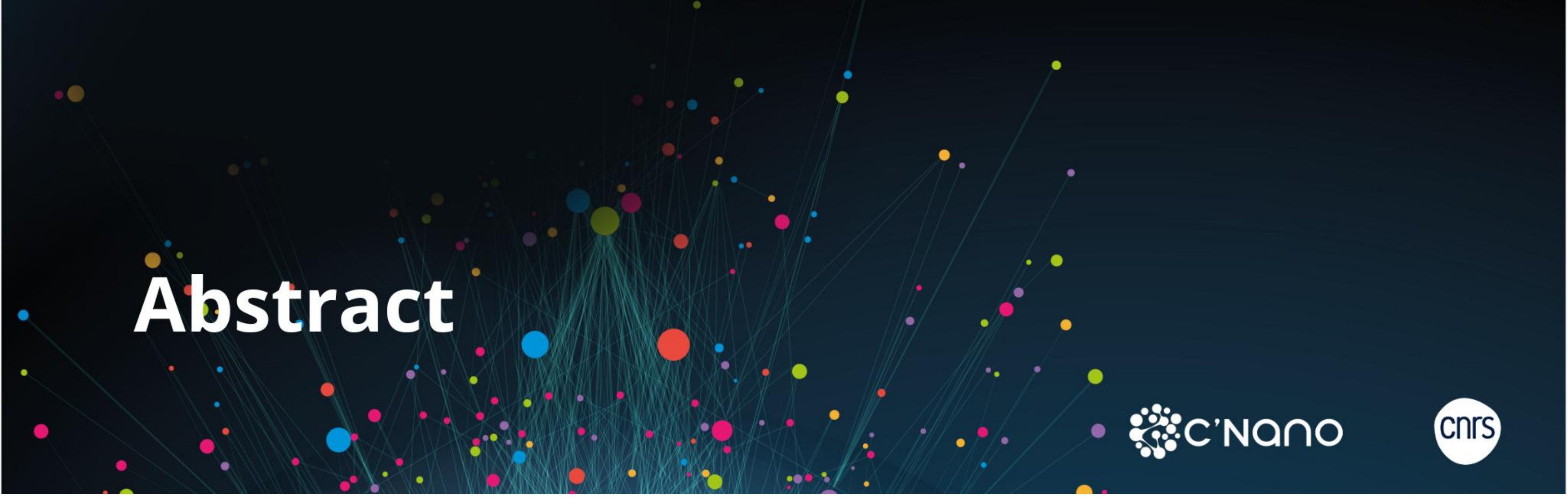

Thematic Session: Nanochemistry and Nanoparticles
Disciplinary fields involved: Chemistry.
Keywords Palygorskite, Polyvinylpyrrolidone, Water-Based drilling fluids and Nanocomposites

Synthesis of Polyvinylpyrrolidone nanocomposite with palygorskite for application in water-based drilling fluids

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Drilling deep and ultra-deep wells faces challenges due to extreme temperature and pressure conditions[1]. Water-based drilling fluids require efficient additives to ensure thermal and rheological stability. Polymer nanocomposites, such as those made from the polymer Polyvinylpyrrolidone (PVP) and the nanometric-sized clay mineral Palygorskite, emerge as promising solutions, combining the properties of polymers and nanoparticles[2]. This work investigates the synthesis and characterization of PVP/Palygorskite nanocomposites and their potential future application in water-based drilling fluid formulations, aiming to maintain the stability of their properties under extreme temperature and pressure conditions. For the synthesis of the (nano)composite, 2.5g of Palygorskite were dispersed in 25mL of water using ultrasonic treatment at 40 kHz for 8 minutes. Meanwhile, 2g of PVP were dissolved in 25mL of water, and the solution was added to the Palygorskite suspension. The reaction mixture was kept in an ultrasonic bath for 30 minutes to ensure efficiency and sustainability. After this period, the formation of three phases (upper, middle, and lower) occurred. The fractions were separated by decantation, centrifuged, and dried in an oven at 70-80°C. The three obtained products were characterized by FTIR and TGA, confirming the success of the synthesis, and SEM was used to determine the morphology of the nanocomposite. Further analyses will be carried out shortly to validate the method and test the application of the nanocomposite in water-based drilling fluids. The development of PVP/Palygorskite nanocomposites represents an innovative approach to operational challenges, contributing to sustainable solutions in the petroleum industry.

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Acknowledgement:

Human Resources Program of the National Agency of Petroleum, Natural Gas and Biofuels - PRH-ANP, supported with resources from the investment of qualified oil companies in the R, D&I Clause of Resolution ANP n° 50/2015. CNPQ n° 312923/2022-8.

Thematic Session: Nanochemistry, Nanoparticles, Nanocatalysis
Disciplinary fields involved: Chemistry
Keywords (max. 4-5)**: Activated carbon, Nanoparticles, Nanocatalysis**

Carbon supported metal oxide nanoparticles and their applications in biomass valorization

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Activated carbon (AC) from olive waste is an eco-friendly material with high surface area and porosity, making it ideal for catalytic applications. When modified with metal oxide (MO) nanoparticles like zirconium dioxide (ZrO_2) and titanium dioxide (TiO_2), its catalytic properties are enhanced, enabling efficient biomass conversion. This modified carbon acts as a catalyst for converting glucose and fructose into 5-hydroxymethylfurfural (HMF), a key chemical for biofuel and bioplastic production. ZrO_2 and TiO_2 deposition improves acidity and stability, facilitating selective dehydration to HMF, promoting sustainable chemical production. Two ACs were synthesized from olive waste using $ZnCl_2$ and H_3PO_4 [01], followed by calcination (AC-Zn and AC-P). MO nanoparticles (5 nm) were deposited onto the carbons and then the nanocomposites were tested as catalysts for converting fructose into HMF in a water/organic solvent system. N2-adsorption analysis of AC shows high surface areas ($1500 m^2/g$) and significant mesopores in AC-P. Increasing %NPs decreased textural properties, suggesting NPs occupy AC pores. XRD patterns confirmed the presence of TiO_2 and ZrO_2 diffraction peaks at higher loadings (above 10 wt%). The AC/NPs catalysts were tested for fructose conversion to HMF using different solvent mixtures (H_2O/THF, H_2O/DMSO, H_2O/MIBK). The HMF yield varied by solvent, with DMSO > THF > MIBK. Adding NPs increased HMF yield, with AC-ZrO_2 outperforming AC-TiO_2 in DMSO, reaching 90% HMF yield at 10 wt% ZrO_2 [02]. ZrO_2 NPs have rarely been used for this reaction, highlighting AC-P-ZrO_2's potential for efficient HMF production. Further characterization of the catalysts' acid-base properties is ongoing, aiming to understand the high selectivity of ZrO_2 NPs. The results will be compared to existing literature and acid-base balance.

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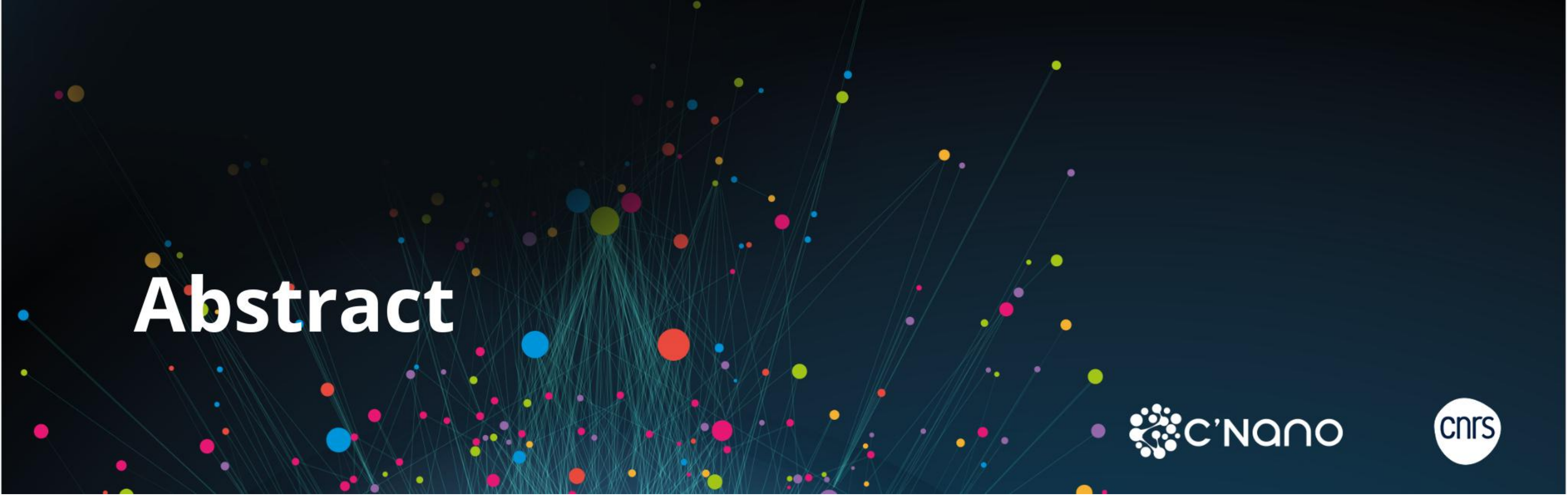
Acknowledgement:

This work presents a sustainable method for producing HMF, a key biofuel precursor, by converting fructose using activated carbon from olive waste. This approach valorizes agricultural by-products, reduces fossil dependence, and achieves high yields with eco-friendly catalysts, highlighting its potential for industrial biorefineries and green chemistry applications.



Thematic Session: Nanochemistry & Nanoparticles

Disciplinary fields involved: Chemistry.

Keywords: Nanocomposites, Palygorskita, Polymer, Water-Based Drilling Fluids.

Synthesis of Polyacrylamide/Palygorskite Nanocomposites for Application in Water-Based Drilling Fluids

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The development of more efficient and sustainable drilling fluids is crucial to meet the growing demands of the oil and gas industry, especially in operations conducted in high-pressure and high-temperature (HPHT) wells. Previous studies have shown that nanocomposites enhance salinity resistance, preserve viscosity, and mitigate the effects of thermal degradation[1]. To combine the polymer's properties with the high surface area of palygorskite, this study explored methodologies for synthesizing polyacrylamide/palygorskite nanocomposites. Three syntheses were conducted using different masses of palygorskite (1.0 g, 3.0 g, and 5.0 g). Palygorskite was dispersed in 120 mL of water for 48 hours. The dispersion was transferred to a three-neck flask and heated to 70°C under an inert atmosphere. A solution containing 0.28 mol of acrylamide in 40 mL of water was added and stirred for an additional 3 hours. Subsequently, 1.85×10^{-5} mol of potassium persulfate dissolved in 5 mL of water was slowly added, and the reaction proceeded for another 2 hours. The product was precipitated with acetone, washed with a methanol-water mixture (75:25), and dried in an oven for 24 hours. The nanocomposites were characterized by FTIR, TGA, XRD, and SEM. These characterizations confirmed the successful synthesis of the nanocomposites and validated the methodology. The three nanocomposites exhibited distinct characteristics, demonstrating the influence of clay mass on the final product. Preliminary results suggest that these nanocomposites have significant potential to enhance the thermal resistance and rheological stability of water-based drilling fluids, contributing to greater efficiency and sustainability in drilling operations.

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Abstract

Acknowledgement: *Human Resources Program of the National Agency of Petroleum, Natural Gas and Biofuels - PRH-ANP, supported with resources from the investment of qualified oil companies in the R, D&I Clause of Resolution ANP n° 50/2015. CNPQ n° 312923/2022-8.*

Thematic Session : Nanobioscience & Nanomedicine
Disciplinary fields involved : Chemistry, Biology
Keywords : Nanoparticles, Re(CO), probes, Cellular studies

Re(CO)-based silica-nanoparticles as multimodal probes for bio-imaging

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Bio-imaging plays a crucial role in elucidating biological processes, offering the capacity to visualize specific biomolecules with high precision. While fluorescence microscopy remains a cornerstone of the field, alternative imaging techniques such as vibrational microspectroscopy and X-ray fluorescence (XRF) microspectroscopy are emerging as powerful modalities. However they suffer from a lack of efficient and specific probes. Metal complexes, such as d^6 low-spin rhenium tricarbonyl compounds, present unique luminescent and vibrational characteristics, positioning them as promising candidates for multimodal imaging applications.[1-2] These complexes demonstrate robust photostability, in contrast of organic fluorophores and exhibit mid-infrared (mid-IR) absorption within the biological transparency window.

This work aims to develop $[ReCl(CO)_3(pyta)]$-based silica nanoparticles (ReSiNPs) to achieve high-density multimodal probes for enhanced sensitivity in mid-IR imaging, fluorescence and synchrotron-based X-fluorescence microscopy. They are also developed as nanothermothers taking advantages of their unique luminescence properties. Utilizing fed-batch co-polymerization methods, the synthesis was optimized to achieve high probe densities within nanoparticles while preserving the desired morphology. Subsequent surface functionalization enhanced nanoparticles dispersion and introduced nano-thermometric properties. ReSiNPs were evaluated for cytotoxicity, mid-IR sensitivity, and imaging efficacy across cellular models, leveraging fluorescence microscopy and synchrotron-based XRF as complementary modalities. Future work of functionalization of ReSiNPs with targeting peptides [3-4] will enable organelle-specific delivery expanding their utility as versatile multimodal probes capable of thermometry as well as IR, XRF, and fluorescence imaging.

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Acknowledgement:

Yi Yuan : M2 intern

Thematic Session: Nanomaterials
Disciplinary fields involved: Chemistry, Biology
Keywords: Chiral nanomaterials, quantum dots, anisotropic nanomaterials, ligand-induced chirality, enantioselective interactions.

Chiral CdSe/CdS Nanonails

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The structural design of quantum-confined nanomaterials plays a critical role in their optical and biological properties. Here, we introduce a novel CdSe/CdS ‘nanonail’ heterostructure, characterized by a nanorod body with a distinct triangular head. This anisotropic morphology enables precise control over rod length, width, and shell thickness, significantly influencing the material’s optical response.

A key feature of these nanonails is their ability to acquire chiroptical activity through ligand exchange.[1, 2] By systematically varying chiral ligand concentration and shell thickness, we demonstrate the emergence of strong circular dichroism signals, highlighting the interplay between structural asymmetry and surface chemistry. These findings suggest a new pathway for engineering chiral nanostructures with tunable optical properties.

Beyond their optical behavior, we explored the biological interactions of chiral nanonails using human lung-derived A549 cancer cells. Cellular uptake studies reveal enantioselective interactions, with one enantiomer exhibiting significantly higher internalization and cytotoxicity than its mirror image.[2] This selective bioactivity underscores the potential for designing chirality-dependent nanomedicine strategies, where controlled interactions at the cellular level could be leveraged for targeted therapies.

Furthermore, monolayer investigations confirm the absence of FRET processes, ensuring stable luminescence in densely packed environments. These results position CdSe/CdS nanonails as promising candidates for bioimaging, biosensing, and chiral photonics, providing new opportunities for integrating nanomaterial design with functional applications in life sciences and optoelectronics.

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Acknowledgement:

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Thematic Session: Nanochemistry, Nanoparticles
Disciplinary fields involved: Chemistry, Physics
Keywords (max. 4-5)**:** Flow synthesis, nanorods, bottom-up approach, automatization, reproducibility.

Towards large-scale production of Cobalt nanorods

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Nowadays, integrated permanent magnets play a major role in daily-life applications, from energy collectors in power-MEMs technologies to energy converters in aircraft engines and wind turbine rotors [1]. Often composed of rare-earths, which pose geopolitical and environmental problems, the bottom-up approach using transition metals is a promising alternative to fabricate nanostructured magnets. We have indeed reported rare-earth free magnets prepared from densely assembled Co nanorods [2], [3].

Our project now aims at up-scalling the polyol synthesis to yield quantitatively cobalt nanorods for the fabrication of hard magnets. For that, we are designing a millifluidic reactor for the continuous synthesis of Co nanoparticles. This flow reactor will not only increase the production, but also improve the reproducibility and homogeneity of the nanorods produced. In the first place, we have carried out a systematic study to illustrate the influence of experimental parameters on the dimensions and anisotropy of the rods obtained, characterizing them by XRD and other physical methods. This preliminary study is essential to adapt the conditions from the batch reaction to the flow synthesis. We showed that by controlling the nature of the cobalt laurate precursor, and dissolving all the reagents at the same time at 80°C before carrying out the classical synthesis, nanorods with a diameter of ~16nm and promising magnetic properties were obtained (**Fig1-a, b**).

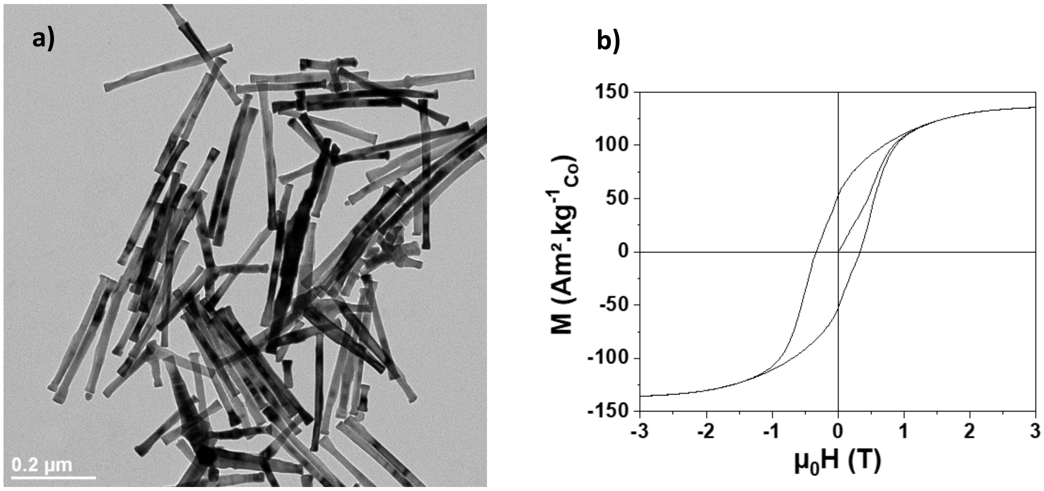

Fig-1(a)*: TEM image of Cobalt nanorods obtained during batch synthesis,* ***(b)****: Hysteresis cycle measured at 300K on a random powder of Co nanorods.*

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Acknowledgement:

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Thematic Session: Nanochemistry & Nanoparticles
Disciplinary fields involved: Chemistry.
Keywords: Dendrimers, clays, nanoparticles, drilling fluids

Synthesis and Evaluation of PAMAM G0.5 Dendrimer as a Swelling Inhibitor Additive for Clays in Water-Based Drilling Fluids

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2. *Laboratory of Macromolecules and Colloids in the Oil Industry, Institute of Macromolecules, Federal University of Rio de Janeiro, Rio de Janeiro, Brazil*

During oil well drilling, approximately 75% of the encountered formations contain hydratable clays, which are responsible for nearly 90% of instability issues, such as collapses, tool entrapment, and wellbore closure[1]. To address these challenges, a growing number of studies have focused on developing additives to enhance the performance of water-based drilling fluids, particularly in reactive formations and under high-pressure and high-temperature conditions[2]. Among the promising solutions are dendrimers, three-dimensional macromolecules at the nanometer scale, which have shown effectiveness in inhibiting reactive clays and reducing formation damage[2]. Thus, this study aims to synthesize and characterize PAMAM G0.5 dendrimers and evaluate their efficiency as swelling inhibitor additives in water-based fluid formulations. The synthesis was performed using a divergent route, starting with a central molecule and forming the first branching layer through Michael addition. In a flask, 50 mL of methanol, 3.3 mL of ethylenediamine (EDA), and 20 mL of methyl acrylate (MA) were added. The system was kept under magnetic stirring for four days at room temperature, and the excess MA and methanol were removed by vacuum distillation. The PAMAM G0.5 dendrimer was obtained and characterized using NMR, FTIR, and GPC techniques, and its clay swelling inhibition capacity was evaluated using the LSM M4600 HPHT equipment. The characterization results confirmed the successful synthesis of the desired product, PAMAM G0.5. Although inhibition tests are still ongoing, preliminary results indicate that the PAMAM G0.5 dendrimer shows great potential for application as a swelling inhibitor additive in water-based drilling fluids.

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Acknowledgement:

Human Resources Program of the National Agency of Petroleum, Natural Gas and Biofuels - PRH-ANP, supported with resources from the investment of qualified oil companies in the R, D&I Clause of Resolution ANP n° 50/2015.

CNPQ n° 312923/2022-8.

Thematic Session: Chemistry and nanoparticles
Disciplinary fields involved: Chemistry
Keywords: gold, silver, surface modification, assembly, discrete clusters, plasmonic.

Plasmonic nanoclusters synthesized by a multi-step colloidal approach

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Metal nanoparticles present peculiar optical responses resulting from their Localized Surface Plasmon Resonances (LSPRs) associated to the resonant excitation of electronic oscillations by light, and whose detailed understanding has been made possible by concomitant progresses in the fields of NP synthesis, optical spectroscopy and modeling. While the LSPR characteristics (spectral features and associated electromagnetic field distribution) of isolated NPs can be tuned to some extent as they depend on NP size, shape and composition, the plasmonic coupling effects occurring when metal NPs are separated by small distances (typically smaller than their size) offer more powerful possibilities for tailoring the optical response of nano-systems. Investigations of plasmonic assemblies began on simple systems, such as dimers of identical NPs. Progresses in NP synthesis now allow to consider more complex assemblies offering larger versatility, such as plasmonic nanoclusters composed by a large number of NPs with different compositions and/or sizes and possibly complex shapes, and NP superlattices, i.e. self-assembled ordered arrays of NPs. In this communication, we will introduce a multiple-step colloidal approach to produce hybrid nanoclusters made of silver nanocubes as core particles and gold satellites. This approach offers a control over the inter-particles gap (few nanometer).

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Thematic Session: **Nanochimie & Nanoparticules**
Disciplinary fields involved (eg. Chemistry, Physics, Biology …)**: Chemistry**
Keywords (max. 4-5)**: nanocrystals, semiconductor, cation exchange**

Influence of $CuInS_2$ crystalline structure on the synthesis of $CuIn_{1-x}Fe_xS_2$ quantum dot by cation exchange

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   ESPCI Paris PSL, CNRS, Sorbonne Université, Paris, France
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Abstract

$CuInS_2$ quantum dots are gaining significant interest due to their ability to efficiently absorb light in the visible and near-infrared ranges, making them particularly suitable for applications in solar cells, display devices, bio-imaging, and detection. Preliminary studies indicate the possibility of synthesizing a solid solution of $CuIn_{1-x}Fe_xS_2$ through direct synthesis, to tune the band gap of $CuInS_2$. In this compound, due to the size of Fe^{3+}, substitution may occur at either the copper or indium sites. In this study, we focus on the synthesis of a solid solution of $CuIn_{1-x}Fe_xS_2$ from $CuInS_2$ by cation exchange. We first optimize the cation exchange synthesis method. Then, by combining EDS analysis, TEM, X-ray diffraction, XPS, and absorption spectrometry, we demonstrate that the initial crystalline structure of $CuInS_2$ influences the final structure, the proportion of exchanged cations, the substitution site, and, consequently, the optical properties.

Thematic Session : Nanochemistry & Nanoparticles
Disciplinary fields involved : Chemistry
Keywords : nanoparticle, zinc oxide, ligand, chirality

Chirality in Zinc Oxide nanoparticle synthesis

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Zinc oxide, an inexpensive metal oxide, is used in various fields like solar harvesting devices, gas sensors, antibacterial and optical devices [1]. Different physical or chemical synthesis methods have been developed to form ZnO nanoparticles (NP), for example, arc plasma, LASER ablation, sol-gel, precipitation and organometallic methods [2] With the organometallic pathway, the size, morphology, solubility, stability, chemical and physical properties of colloidal ZnO NP depends on the synthesis protocol either in solid state or solution and on different parameters such as the zinc organometallic precursor, temperature, solvent and the ligand stabilizer used. In particular, the nature of the ligand stabilizer is crucial to control the size and the morphology of the ZnO NP and the stability and the solubility of the colloidal NP solutions [3]. A large variety of organic molecules and polymers has been used to study the influence of the functional groups, the length, the steric hindrance and the chemical nature of the ligands on the ZnO NP synthesis.

Herein, we have investigated the chirality role of ligand stabilizers on the ZnO NP synthesis by organometallic synthetic pathway. We synthesized chiral ligands based on nucleoside-like motifs able to stabilize colloidal ZnO NP solutions. UV-Visible, EDX and (HR)TEM characterizations of the resulting ZnO nanoparticles will be presented.

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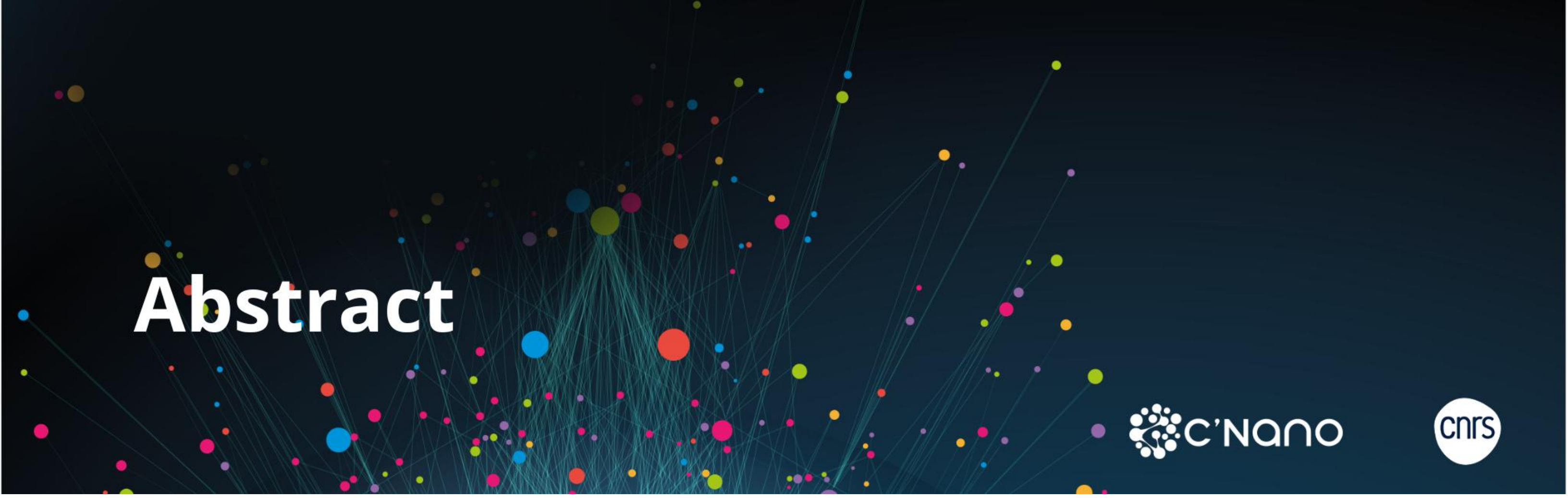

Thematic Session: Nanochemistry & Nanoparticles

Disciplinary fields involved: Chemistry.

Keywords: Silica nanoparticles, Tetrapolymer, Core-shell, Filtrate loss.

Application and evaluation of core-shell nanocomposite using silica nanoparticles and AM/AMPS/DMDAAC/AAC tetrapolymer

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Due to increasing environmental pressures, the number of studies focused on improving water-based drilling fluids has risen significantly. Although these fluids offer various benefits, their performance heavily depends on the use of additives to control functions during drilling, such as reducing filtrate loss. Effective filtrate loss control ensures efficient and safe drilling, preventing excessive fluid invasion into the formation and wellbore instability. This study developed two core-shell nanocomposites and evaluated their use in water-based drilling fluids as filtrate volume-reducing additives. The nanocomposites consisted of silica nanoparticles combined with a tetrapolymer (AADA) composed of acrylamide (AM), 2-acrylamido-2-methylpropanesulfonic acid (AMPS), dimethyldiallylammonium chloride (DMDAAC), and acrylic acid (AAC) monomers. The fluids were formulated with the new additives at concentrations of 0.1%, 0.5%, and 1.0% w/v and assessed using LPLT filtration according to API-13B standards (100 psi/25°C), both before and after aging at 70°C and 90°C for 16 hours. Standard fluids (without additives) and fluids containing the AADA tetrapolymer at the same concentrations were also evaluated. The filter cakes formed were characterized by SEM, contact angle measurements, and thickness to analyze morphology and hydrophobicity, correlating these properties with the obtained filtrate volumes. Fluids containing the core-shell nanocomposites, particularly at a concentration of 0.1% w/v, demonstrated superior performance compared to standard fluids and those with AADA. Thus, the selection and optimization of these additives can enhance the efficiency of water-based drilling fluids, even under high-temperature conditions. This enables more effective use, minimizes waste disposal, and promotes more sustainable operations.

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Thematic Session: Nano-synthesis & Nano-catalysis

Disciplinary fields involved: Chemistry, Materials

Keywords: Organometallic, heterogeneous nano-catalysts, hydrogen release

Design of efficient nano-catalysts for H_2 Release from Boranes and Silanes

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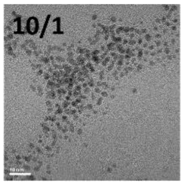
Abstract

The combustion of fuel produces deleterious gas (CO_2) for which the capture and recycling is mostly not achieved. Conversely, the use of chemical hydrogen storage materials, releasing H_2 –for combustion engines or fuel cells– and liquid or solid by-products, gives the important opportunity to easily capture and handle this co-produced waste[1]. On one hand, ammonia-borane NH_3BH_3 (AB, 19.5 wt% H) and $NaBH_4$ (10.8 wt% H) are able to release H_2 by hydrolysis and alcoholysis, in the presence of a metal catalyst in ambient conditions[2]. These reactions have attracted considerable attention, with special focus on the catalysts for fast H_2 delivery[3]. In comparison, critical aspects for the industrial implementation of this approach, like the nature of the solvolysis by-product(s) have been much less investigated, while their identification and recycling will be needed in a righteous circular approach[4]. On the other hand, organosilicons and specially hydrosilanes –as widely manufactured commercial products– may also be attractive as potential sources of H_2. This, following various catalyzed chemical roads, including hydrolysis and alcoholysis of silanes ($R_3Si–H$, R_2SiH_2, *etc.*), or their dehydrogenative oligomerization ($PhSiH_3$ dehydrocoupling)[5]. Here we will present the development of ruthenium, and iridium NPs for AB and hydrosilane (Et_3SiH) solvolytic dehydrogenation (H_2O, MeOH). The synthesis of Ru, and Ir nanocatalysts stabilized by bulky, rigid, σ-donating functionalized adamantane and diamantane ligands will be described and their performances in H_2 production discussed.

$$\begin{array}{l} NH_3BH_3 + \text{solvent} \\ HSiEt_3 \end{array} \xrightarrow[\substack{25\ °C \\ [NH_3BH_3] = 0.1\ M}]{[cat] = 2\ \%} 3\ H_2 + NH_4^+ + \text{borates}$$



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Thematic Session: Nanochemistry and nanoparticles
Disciplinary fields involved: Physical Chemistry
Keywords: spectroscopy – gold nanorods – crystallinity - vibrations

Influence of crystalline structure on the acoustic vibrations of elongated nano-objects

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Metals such as gold or silver are polycrystalline at the macroscale. However, colloidal nanoparticles with controlled crystallinity can now be synthesized. It has been shown that different crystal facets may have different catalytic activity,[1] therefore it is necessary to know the crystalline structure of nanoparticles before using them in catalysis. This is possible by using expensive electronic methods, such as high resolution transmission electron microscopy.

In this work, we proceed to uncover the structural features of polycrystalline pentatwinned gold nanorods (AuNRs_PT) and single-crystal gold nanorods (AuNRs_SC) by optical spectroscopies, namely absorption spectroscopy and low frequency Raman scattering.

First, the longitudinal localized surface plasmon resonance wavelength is shown to depend on the tip curvature of the nanorods (AuNRs_PT exhibit more rounded tips than AuNRs_SC, as shown in Figure 1a,b). These findings are supported by calculations carried out using the discrete dipole approximation method.[2]

Second, the acoustic vibrations of AuNRs are demonstrated to depend on crystallinity. We recorded low frequency Raman spectra of both AuNRs_PT and AuNRs_SC samples and found that the former exhibits one major band, attributed to a 5-fold degenerated quadrupolar mode of angular momentum $l = 2$, whereas in the latter, this band is split into two modes, B_{1g} and B_{2g} (see Figure 1c). This result is reminescent of a similar result obtained for gold nanospheres of different crystalline structures,[3] but was never observed in elongated objects such as nanorods.

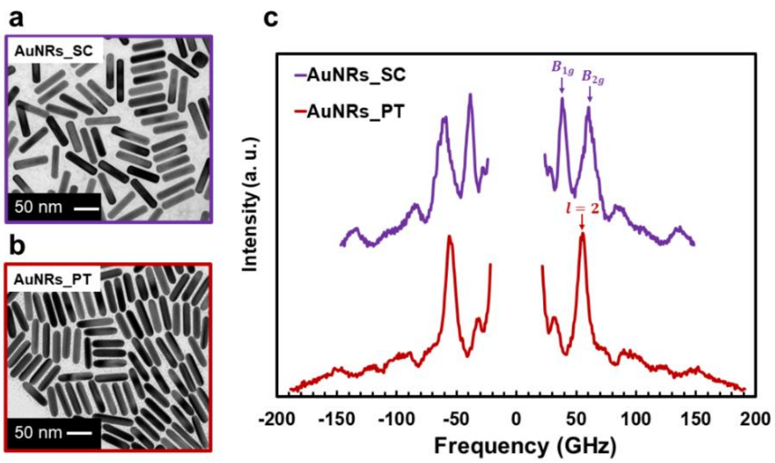

Figure 1 : Transmission electron microscopy images of a) single crystal AuNRs and b) polycristalline AuNRs. c) Low frequency Stokes and anti-Stokes Raman spectra of polycrystalline AuNRs (red) and single crystal AuNRs (purple).

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Thematic Session: Nanomaterials and Nanobioscience
Disciplinary fields involved: Chemistry and Biology
Keywords: Germanium oxide nanoparticles, Sol-gel synthesis, surface modification, cell-material interaction

Chemistry and biological effects of germanium oxide nanoparticles

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Silica-based nanomaterials (SiO_2) have gained significant interest in biomedical applications, particularly in imaging and drug delivery, due to their tunable properties and biocompatibility[1][2][3]. Additionally, the dissolution products of silica have been shown to play beneficial biological roles. As they belong to the same column of the periodic table of elements, germanium and silicon are expected to share some common chemical properties. However, the reactivity of germanium oxide (GeO_2) nanoparticles in biological contexts remain largely unexplored.

This research aims to develop a library of GeO_2 nanoparticles with various size, shape and surface chemistry and investigate their biological effects on human cells involved in tissue regeneration. Cube- and spindle-shaped GeO_2 nanoparticles were synthesized via a surfactant-free sol-gel approach using tetraethoxygermane[4]. Their surface was modified using organosilanes, such as (3-Aminopropyl) triethoxysilane (APTES), to enhance their colloidal stability and tune their reactivity. These nanoparticles were characterized using techniques such as DLS, zeta potential analysis, SEM, TEM, XRD, and XPS. In future, their behaviour in biological media and their effects on cell behaviour, such as viability, migration and metabolic activity will be assessed.

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