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CV/ biography (10 lines max.)

Stéphane Cordier is specialist in crystal chemistry and in the chemistry of transition metal cluster-based compounds. He obtained his PhD in 1996; his work devoted to the crystal chemistry of niobium and tantalum cluster halides was supervised by Marcel Sergent and Christiane Perrin. He was recruited at CNRS in 1999 after post-doctoral researches on niobium-based cluster fluorides at the Max Planck Institute for Solid State Chemistry (Stuttgart) in the group of Pr. Arndt Simon. In Rennes, he has developed methodologies that aim at using transition metal clusters as nanosized building blocks for the design of hybrid nanomaterials and functional surfaces. His research covers a continuum from fundamental research -in order to correlate physical properties to crystal and electronic structures of solid state compounds- to the integration of inorganic clusters onto functional surfaces or in composites. He is in charge of the Group Solid State Chemistry and Materials from the Institut des Sciences Chimiques de Rennes (ISCR). He is co-author of 170 publications and 4 patents.

Metal atom cluster building blocks from the solid state to the design of functional surfaces and hybrids

Abstract

Metal atom clusters are aggregates of metal atoms held together by metal-metal bonds. Mo$_6$ octahedral clusters are stabilized by inner ligands (L^i) in face-capping positions or edge-bridging positions and apical ligands (L^a) in terminal positions to form $[M_6L^i_8L^a_6]^{n-}$ and $[M_6L^i_{12}L^a_6]^{n-}$ units respectively. On one hand, the concept of cluster unit constitutes a useful virtual object to describe the crystal and electronic structures of cluster-based solid state compounds. On the other hand, the dissolution of solids affords discrete cluster units in solution that constitute real and handleable molecular nanoobjects with unique physico-structural properties usable as building blocks in the design and structuration of nanomaterials. The delocalization of electrons on all the metal centers leads to specific physical properties as for instance luminescence, magnetic and photocatalytic properties. The judicious choice of apical ligands enables to tune the properties of the cluster units and to control their self-assembly and/or their immobilization onto surfaces.

Optical properties of face-capped $[Mo_6L^i_8L^a_6]^{2-}$ octahedral cluster units are characterized by a large absorption window from UV to visible and a large emission window from 550 nm to the NIR region. Thus, such clusters can be used as red phosphorescent dyes for many potential applications including nanoparticles for biolabelling, liquid crystals and luminescent nanocomposites for lighting and displays. Optical properties of edge-bridged $[M_6L^i_{12}L^a_6]^{4-}$ cluster units are characterized by a large absorption band in the UV region along with absorption bands in the red and NIR regions making them relevant building blocks as absorbers for energy saving applications. $Cs_2Mo_6X^i_8X^a_6$ (X = Cl, Br and I) and $K_4M_6Br^i_8Br^a_6$ ternary compounds are prepared by solid state chemistry route at high temperature. Interestingly, these ceramics are soluble in many common solvent affording functional $[Mo_6X^i_8X^a_6]^{2-}$ cluster and $[M_6L^i_{12}L^a_6]^{4-}$ units that can be further used as building blocks for the design of hybrid nanomaterials. For instance, cluster based hybrid co-polymers associate the mechanical and shaping properties of the organic matrices along with the optical properties of inorganic metallic clusters.

After the presentation of the solid state chemistry of metal atom clusters evidencing the correlation between crystal structures and properties, we will present several examples of the incorporation of $[Mo_6X^i_8L^a_6]^{2-}$ and $[M_6L^i_{12}L^a_6]^{4-}$ cluster units in nanomaterials and immobilization on surfaces.

Keywords: transition metals, clusters, luminescence, building block, functional surfaces, integration

Nanochemsitry, synthesis and assembly

Keywords: synthesis, patchy, clusters, plasmonics

Engineering novel plasmonic nanostructures

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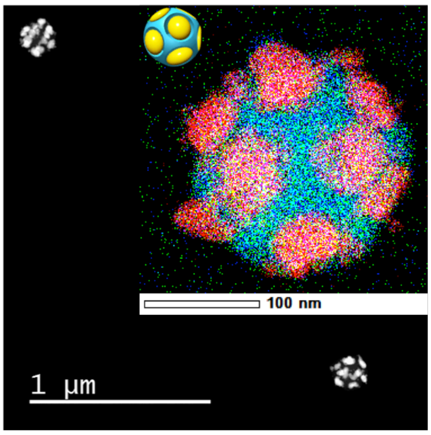
A fundamental goal of material science is the design and synthesis of materials with tailored shape and size. There has been tremendous progress over the past decade in the synthesis of plasmonic nanoparticles of various sizes and shapes and with good yield and monodispersity. In this talk I will overview plasmonic nanostructures that can be elaborated by using the concept of patchy nanoparticles, i.e. spherical nanoparticles with a controlled number of patches. The selective functionalization of the patch areas or the inter-patch areas offers the possibility to create complex supracolloids with extraordinaory optical signatures suitable for applications such as (bio-) sensing, metamaterials and photonics.



Example of an isotropic plasmonic cluster consisting of a controlled number of Au satellites fabricated from patchy particles

V.Ponsinet, P.Barois, M.Gali, P.Richetti, A.Vallechi, M.Albani, A.Le Beulze, S.Gomez-Grana, S.Mornet, E.Duguet, M.Tréguer-Delapierre, Phys.Rev.B, 92, 220414 (2015)

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C.Chomette, M.Tréguer-Delapierre, N. Schade, V.Manoharan, O.Lambert, JC Taveau, S.Ravaine, E.Duguet, Chem.Nano.Mat., 3, 160 (2017)

Session : Nanochemistry, synthesis & assembly
Keywords: nanoparticles, Iron, anisotropic morphology, synthesis, carboxylic acid

Synthesis of zero valent FeNPs with anisotropic morphology

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Iron nanoparticles (FeNPs), given their specific properties, are investigated as multipurpose species for innovative applications like hyperthermia, catalysis, nano-electronics, etc… Physical and chemical properties of FeNPs highly depend on their shape and size monodispersity. Hence, there is a need to pursue a synthesis of zero valent FeNPs with controlled morphology, and especially anisotropy. Indeed, FeNPs with anisotropic shape are seldom reported.[1] Our research group developed a synthetic pathway to obtain controlled FeNPs by using carboxylic acids as stabilizing agent. [2] The results suggest that the carboxylic acid has a direct influence on the FeNPs shape. Thus, in this work we optimized the synthesis pathway by testing different carboxylic acids in order to direct the synthesis towards cube-like or rod-like FeNPs. (fig.1). We now report full characterization of these FeNPs by Wide Angle X-Ray spectroscopy, Vibrating Sample Magnetometer and Transmission Electron Microscopy showing for the first time assemblies of parallelepiped-shaped zerovalent FeNPs.

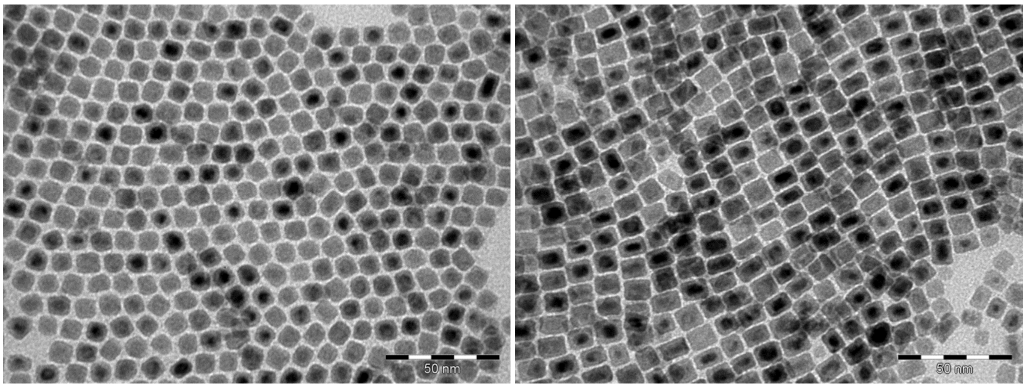

Fig 1: Transmission Electron Microscopy photography of Iron nanoparticles synthesized with two different carboxylic acids

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Congrès 2018, Toulon
11, 12 & 13 septembre
Session Nanomatériaux, Nanochimie, synthèse & assemblage
Keywords: Mesoporous silica nanoparticles, size control, innovative synthesis

Mesoporous silica nanoparticles: an innovative method for controlling pore structure and particle size

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Mesoporous silica nanoparticles (MSNs) combine textural properties of ordered mesoporous materials with an increased diffusion rate of molecules within the short pores. These attractive features set them as excellent candidates for catalysis or sensor technology. However, obtaining monodisperse nanoparticles with controllable texture and high yield is still challenging, thus limiting large-scale production. Our research work proposes a solution by means of a sustainable synthesis method of functional MSNs with uniform particle size and tunable porosity.

The method relies on polyion complex micelles (PIC) in charge of both structuration and functionalization of silica. PIC micelles are formed by electrostatic complexation between a polyamine and a double-hydrophilic block copolymer. The copolymer has a neutral PEO block and a functional polyacid block. The PEO chains are anchored in silica walls during the sol-gel process. PIC micelles are then dissociated in acidic medium. Porosity is thus generated by the polyamine release and the acid functions are revealed in the mesopores.

Control of particle growth and steric stabilization are achieved by adding a second copolymer with a neutral block having no affinity for silica. It allows preparing highly dispersed nanoparticles with uniform sizes and with high silica yields. The mesopore structure was long-range ordered, and it was tunable by simple pH variations. Moreover, the pores were size adjustable and exhibited a very high density of functions.

Therefore, the present process allows synthesizing monodisperse polymer-functionalized mesoporous nanoparticles with adjustable structure and texture. These features are a promising step towards large-scale production of mesoporous nanoparticles.

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11, 12 & 13 septembre

Session Nanomaterials

Keywords: Diamondoids, Nanoparticles network, Organohybrid, Heterogeneous Catalysis

Diamondoid Scaffolds for Gold-Based Organohybrid Networks: Design and Catalytic Application

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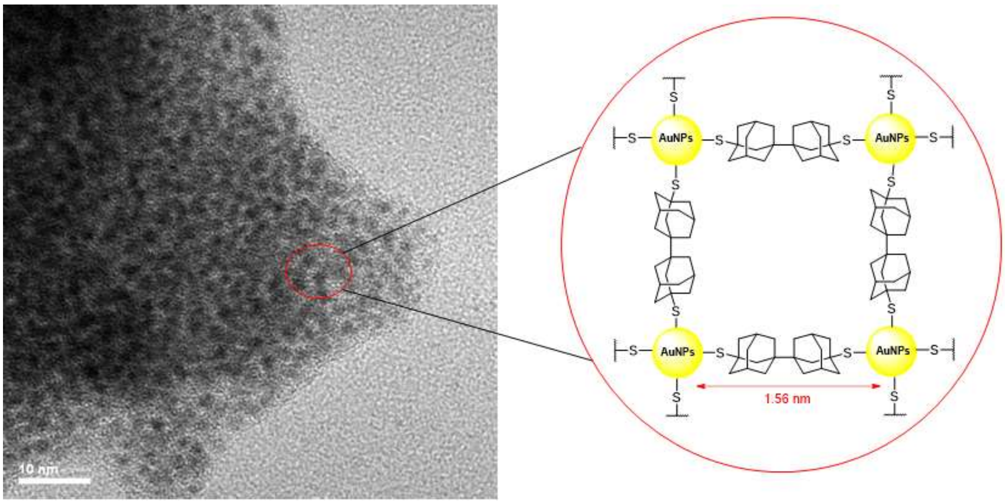
We present an innovative_approach in catalytic material synthesis that aims at overcoming some current limitations of conventional nanocatalystssuch as: (*i*) catalystsstructural inhomogeneity, (*ii*) difficult accessibility of active sites, and (*iii*) rapid degradation under operating conditions. The synthesis of well-organized networks of nanoparticles (NPs) *via* metal/organic nanohybrid construction is both an attractive and challenging issue.[1]Nevertheless, using organic scaffolds as stabilizing/interconnecting ligands between metal complexes or NPs opens the road to nanometric heterogeneous catalytic materials with potentially more accessible active centers and much better controlled environment for active metal centers/surfaces. We already build successfully in gas phase, from functionalized adamantanes and diamantanes,new organic-metal nanohybrids.[2]Herein, we present several thiolated diamondoids that we employed as robust covalent linkers between gold nanoparticles assembly(Figure 1). Strong Au–S bond formation insures a remarkable nanoparticle networking regularity. The resulting ordered networksof gold NPs were fully characterized,and size of the gold NPs formed, as well as the distance of interconnectionNPs–linker–NPs were determined by WAXS and SAXS analyses, respectively. Powerful catalytic applications of these nanohybrid materials concern selective C–C bond formation reactions catalyzed by gold under heterogeneous conditions.



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Session (Nanochemistry, synthesis & assembly)
Keywords: metal phosphide nanoparticles; phosphorus; phase segregation; nanoscale restructuring.

Iron, Nickel and Copper Phosphidation: Crystallization of Metal Phosphides and Phase Speciation at the Nanoscale

Florian D'Accriscio[1], Anh-Minh Nguyen[1], Erik Schrader[2], Hansjörg Grützmacher[2], Sébastien Dreyfuss[3], Nicolas Mézailles[3], Clément Sanchez[1], Sophie Carenco[1]

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Metal phosphide nanoparticles raise a huge interest in materials chemistry due to their unique optical, magnetic, electronic, mechanical and catalytic properties.[1] Within the last 5 years, mono- and bi-metallic metal phosphides were shown to be competitive with Pt in electrochemical hydrogen evolution reaction.[2] However, preparing nanoparticles of controlled composition and crystallinity is a challenge. Most reported works employ tri-*n*-octylphosphine (TOP) as a phosphorus source, but even at elevated temperature (eg 350 °C) it decomposes poorly and it may induce carbon contamination in the nanoparticles.

We work with phosphorus precursors that behave as stoichiometric "P" donors from r.t. to ca 250 °C, thus providing unique structures and an unprecedented knowledge on phase speciation at the nanoscale.[3] Here, we show that these "P" donors allow the formation to two types of well-defined metal phosphide nanoparticles. Iron phosphides with tunable phase (FeP, Fe_2P) and composition were prepared using a cyclotetra-phosphane (Figure 1-left).[4] A more complex reaction pathway was identified for copper-nickel core-shell nanoparticles reacted with white phosphorus (P_4, Figure 1-right).[5] From these two case studies, we distilled three essential rules: (i) migration rate of metal *vs.* phosphorus determines the morphology of the nanoparticle, (ii) preference for certain metals drives the phase speciation at the nanoscale and (iii) both crystallinity and metal-phosphorus ratio influence the air sensitivity of the metal phosphides.

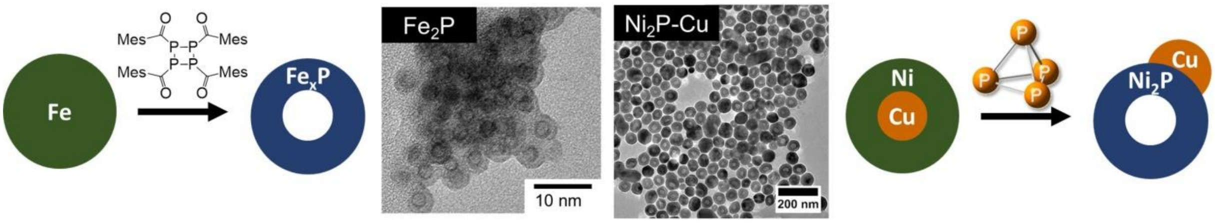

Fig. 1 (Left) Phosphidation of iron nanoparticles by a tetracyclo-phosphane. (Right) Phosphidation of Cu-Ni core-shell nanoparticles by white phosphorus (P_4). The reactions are performed in organic solvents.

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Session (Nanochemistry, synthesis & assembly)
Keywords: Nanowires, hybrid material, molecular beam epitaxy, semiconductors

Hybrid core - shell nanowires grown by molecular beam epitaxy

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Semiconductor nanowires (NWs) have been intensively studied in recent years because of their original physical properties. Unlike other systems, NWs offer the possibility of creating hybrid structures in two geometries: radial (combining materials around the NW growth axis) and axial (combining materials along the NW growth axis). In both cases, precise control of the quality of the interfaces is necessary. In this communication, these two types of heterostructures will be presented, starting from GaAs NWs grown by molecular beam epitaxy using the vapor-liquid-solid method.
The growth mechanism of such hybrid NWs will be discussed, starting from their nucleation [1, 2] until the growth of highly heterogeneous shell such as metals [3] or functional oxides [4]. In this context an oxidation-proof method has been developed and studied in details [5]. A combination of *in situ* diffraction techniques, electron spectroscopy and microscopy have been used in order to growth these heterogeneous NWs. Finally, the potentiality of NW-based photoelectrode for water splitting will be discussed.

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11, 12 & 13 septembre

Nanomaterials Session, Nanochemistry, synthesis and assembly

Keywords: nanoparticles, assembly, surface state,

Influence of CuO nanoparticles and their chemical environment into assembly of Al/CuO nanothermites

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Among energetic materials, nanothermites are known for their high reactivity and thus used for pyrotechnic applications. One of the promising materials for integration into micro devices is Al/CuO nanocomposite because of its high enthalpy of oxidation-reduction reaction [1]. Increasing the contact surface between both components of the thermite composite should lead to improved properties. The control of the particles size, the morphology and the distribution of the nanoparticles inside the composite is therefore of paramount importance.

Recently, we developed an original approach for the preparation of such Al/CuO composites. This approach consists in the formation of the CuO nanoparticles by the controlled hydrolysis and/or oxidation of an organometallic precursor (*i.e.* copper amidinate), in the presence of capping ligands, (*i.e.* octylamine) [2]. Small CuO nanoparticles (ca. 5 nm) are obtained. These latter are associated with metallic Al particle, leading to the formation of CuO/Al aggregates in solution.

The surface state of the CuO nanoparticles turns to be of paramount importance for the nanothermite preparation. Structural information is obtained through wide angle x-ray scattering (WAXS) and x-ray diffraction (XRD). In addition, analyses of TEM images and FTIR spectroscopies highlight formation route and chemical environment differences. The formation of the resulting aggregates is followed by measuring the heat capacity released by the system, by differential scanning calorimetry (DSC) experiments.

Session Nanomaterials: Nanochemistry, Synthesis and Assembly
Gold Nanoparticles, Hybrid nanostructures, DNA, Regioselective functionalization, Self-assembly

Chemical Functionalization and Self-Assembly to Form Hybrid Structures of Nanoparticles

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Hybrid nanostructures by self-assembly of plasmonic building blocks attract significant attention since they display innovative optical properties with promising applications in a variety of domains [1-3]. However, self-assembly of nanoparticles with great precision (orientation, distance, etc.) is still very challenging [4,5]. For this, DNA is an ideal linker and spacer material since it allows controlling inter-particle gap at atomic level [6]. In this work, we design and construct hybrid nanospheres/nanorods structures through DNA hybridization. The regioselective functionalization of nanorods has allowed obtaining well-defined linear dimer and trimer structures. These upstream works give us an insight on designing novel hybrid nanostructures made of noble metals and fluorophores to acquire enhanced optical properties.

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11, 12 & 13 septembre

Session: Nanomaterials

Keywords: Conducting polymer, photocatalysis, hydrogen generation

Conducting polymer nanostructures for photocatalytic degradation of phenol and hydrogen generation

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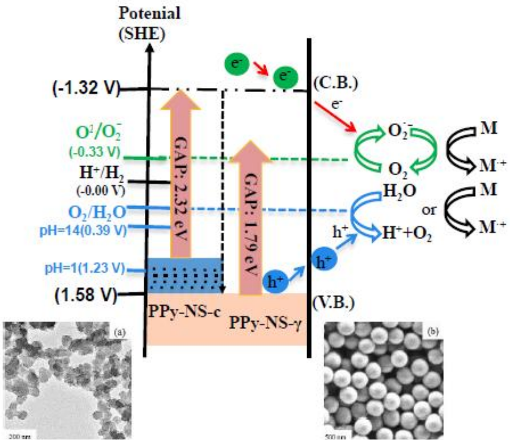
Conjugated polymer nanostructures (CPNs) emerge as a new class of photocatalysts for organic pollutant degradation under UV and visible light[1,2,3,4]. Polyprrole (PPy), as a conjugated polymer, exhibits a wide range of applications. We present here the first illustration of employing pure PPy nanostructures as a very efficient photocatalyst for water depollution[5]. PPy was synthesized in soft template by chemical polymerization (PPy-c), obtained by radiolysis (PPy-γ), and synthesized without template via chemical method (PPy-b) as bulk. These samples were characterized by different techniques such as SEM, TEM, NanoIR, FTIR, UV-Vis spectroscopy. PPy nanostructures exhibit higher photocatalytic performance under UV and visible light compared with PPy-bulk.

We modified PPy nanostructures with co-catalysts based on Pt, Ni nanoparticles for H_2 production. The modified PPy nanostructures give also promising results for hydrogen generation under ultraviolet light. The effect of the nature of the metal precursors and their concentrations were studied.



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Congrès 2018, Toulon

11, 12 & 13 décembre

Nanochemistry, synthesis & assembly

Keywords: silver nanowires; synthesis; random networks; percolation; functional devices

Silver Nanowire Networks for Transparent Film Heaters: Synthesis, Nanoscale Characterization and Integration in Functional Devices

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There is a market need to develop new materials for the fabrication of transparent film heaters, which are currently made of indium tin oxide (ITO). The indium scarcity associated to the lack of flexibility of ITO as well as a relatively high cost of fabrication has prompted the search for alternative materials.

Among them, the use of silver nanowires appear as a potential breakthrough in this field. When used in the form of random networks, these one-dimensional nanomaterials have demonstrated remarkable ability for the fabrication of high performance transparent, electrically conductive flexible materials. They exhibit excellent performances, with sheet resistance of only few Ω/sq and optical transparency above 90%. Moreover, the fabrication of these electrodes is carried out at ambient conditions which renders this technology promising for the straightforward fabrication of various devices.

We will present how it is possible to control the dimensions of the silver nanowires during the polyol synthesis and the importance of the purification process. A focus will then be performed on their assembly on various surfaces and the associated optoelectronic characterizations. We will show how the optimization of the junctions at the nanoscale directly governs macroscopic properties. Integration into various functional devices, in particular transparent film heaters will be presented and discussed.

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