

Tuesday, December 10th

Session: NANOMATERIALS 1

14h15 – 16h00

Keynote speaker: Thierry Gacoin

Microstructure issues in the design of colloidal oxide nanoparticles

Morey-St Denis room

Abstracts

Thematic Session: Nanomaterials

Keywords: nanoparticles synthesis, nanocomposites, magnetic properties, core-shells, raspberry-like particles

Composite magnetic nanoparticles of $\text{Fe}_3\text{O}_4/\text{CoO}$ with different shapes exhibiting exchange bias

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The design of composite nanoparticles (NPs) with well-defined interfaces gives rise to interesting emergent properties. In particular, the association of a ferro(ferri)magnetic phase with an antiferromagnetic one can lead to exchange bias (EB). This exciting phenomenon results in a shift of the hysteresis loop along the field axis and, in some cases an increase in coercivity [1,2]. Use of EB in nanosystems is promising in order to gain magnetic stability at room temperature [3,4], opening the way to applications in magnetic recording, therapeutic mediators, or shielding properties for example.

For the last decades, NPs exhibiting EB have been mainly studied on core-shell systems [4]. In this work, we propose to tailor the shape of the composite NP as raspberry-like, dumbbell-like and core-shells and to use them to study EB (Fig. 1). The two associated materials are magnetite (ferrimagnetic) and cobalt oxide (antiferromagnetic). These composite nanoparticles were prepared via thermal decomposition with sizes between 12 and 15 nm.

By precisely controlling the synthesis parameters, the relationship between shape and resultant magnetic properties (exchange bias) was studied. With this work, we hope to get a better understanding of the EB phenomenon along with a possibility of finely tailoring the NPs, allowing a precise adaptability for the different applications.

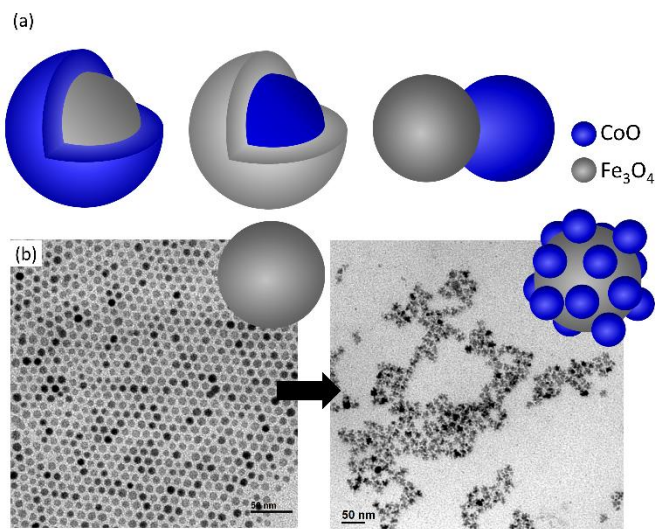


Figure 1. (a) schemes of the different synthesized NP: core-shells and Janus-type. (b) TEM images of pristine magnetite NP with 8 nm average size and raspberry-like with CoO satellites (scale bars : 50 nm).

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Thematic Session: Nanomaterials

Keywords: InGaAs quantum well, scanning tunneling microscopy, Dirac physics, band structure engineering.

Dirac antidot superlattices for electrons in III-V semiconductors

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Recently, artificial honeycomb structures have attracted wide attention for fundamental research due to the tunable interplay between topology and quasiparticle interactions. In fact they offer a fascinating platform for studying Dirac physics especially thanks to the possibility to vary the physical parameters in regimes which are not accessible in graphene or in other 2D materials.

A natural way to fabricate such materials is by modulating the potential seen by a two-dimensional electron gas found in conventional III-V semiconductor heterostructures. The idea is to create a periodic array of cylindrical holes in the active layer in order to form potential barriers for the electrons. Guided by previous works and predictive atomistic tight-binding calculations, we are working on the nanoporation of InGaAs quantum wells (QWs) epitaxially grown on InP substrates using high-resolution e-beam lithography and highly plasma based dry etching. The goal is to push the patterning to its limit in order to reveal Dirac fermions and non-trivial band structures predicted in these artificial 2D materials.

Here, we present the work done to obtain triangular antidot lattices with periodicities of the pores down to 40 nm giving an effective honeycomb lattice constant of 23 nm. Based on initial tunneling spectroscopic measurements, we show that InGaAs/InP heterostructures are appropriate materials to engineer band structure from the nanoporation of the InGaAs QW to be able to observe Dirac cones in the conduction band of the QW. Furthermore, we report the calculations that show the possibility to measure Dirac physics in these type of samples.



Thematic Session: Nanomaterials

Keywords: iron stearates, decomposition mechanisms, controlled doping, shape and size mastering

Mastering size, shape and composition of iron oxide nanoparticles by precursors design

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Due the broad range of application of iron oxide nanoparticles from nanoelectronics to nanomedicine, the control of their size and composition on demand remains a great challenge as these structural parameters are of utmost importance to provide nanoparticles with magnetic properties tailored to the targeted application. Among nanoparticles synthesis methods, the thermal decomposition one was demonstrated very suitable to tune nanoparticle size, composition and shape. However some synthesis problems still occur: i) core-shell $\text{FeO@Fe}_{3-x}\text{O}_4$ instead of homogeneous spinel nanoparticles are often obtained when sizes higher than 15nm are targeted; ii) a heterogeneous doping due to use of precursors with different thermal stabilities, iii) a not well-mastered shape control. To face these challenges, we synthesized ironII and ironIII stearates and different zinc precursors, determined their structure and investigated their thermal decomposition mechanisms by IR and Mössbauer spectroscopies in temperature, MALDI-TOF, cryoTEM, liquid AFM and SAXS and by following the germination and growth steps by *in-situ* TEM in a liquid cell. We evidenced thus that the nanoparticle formation goes through the formation of original structures in solution in which the nucleation takes place. Investigations of iron and zinc precursors decomposition mechanisms combined with modeling showed that the precursor's nature and the nature of ligands and solvents strongly affect the thermal decomposition kinetics which, in turn, influences the final NPs characteristics. We understood thus why ironII stearates favor small-sized nanoparticles and nanoplate formation when ironIII stearates promote high-sized nanoparticles and nanocube formation. Finally, the zinc-precursor design conducts to ferrites with different zinc content.

Thematic Session: Nanochemistry: synthesis & functionalization of nanosystems for bioapplications

Keywords: “LEGO-like” assemblage, functional polyamphiphiles, block/branched architecture, supramolecular structures

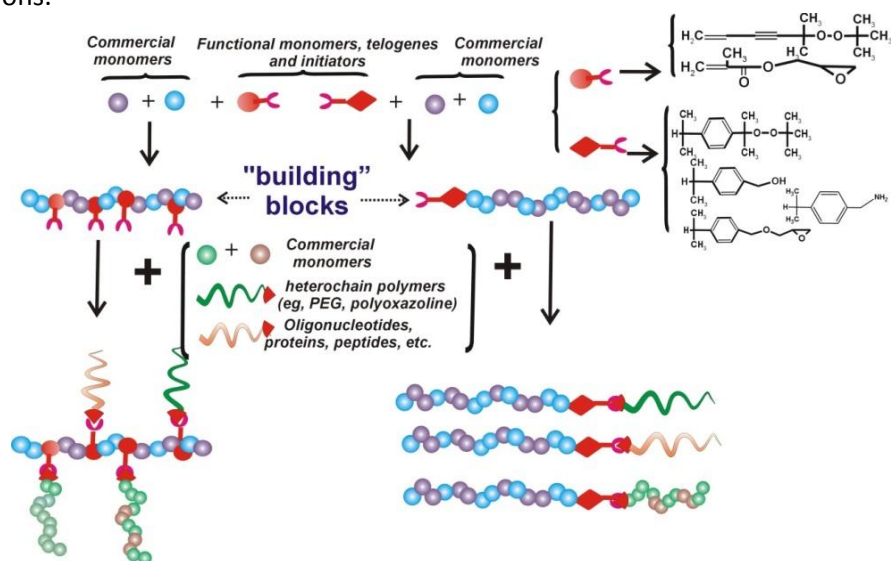
Molecular “LEGO-like” assemblage, characterization and application of functional block/branched polyamphiphiles

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The synthesis and properties of functional polyamphiphiles (PA) and self-assemblies (SA), micelles, interpolyelectrolyte complexes, nanoparticles (NPs), of desired functionality, size, and morphology are discussed. Combined radical and non-radical methods of the synthesis of primary oligomer-precursors containing terminal or side reactive groups and their using for LEGO-like assemblage of PA of block and/or comb-like structures were studied. Proposed approaches are based on polymerization of functional monomers in the presence of functional chain transfer agents. That provides controlling oligomer-precursor chain length and entering reactive side and terminal groups.

The oligomer-precursors were used for construction of PA via: 1) Polymerization using oligomer-precursors with side or terminal peroxide groups as macroinitiators, respectively for preparing comb-like or block-copolymers; 2) Polymerization using oligomer-precursors with terminal hydroxyls (PEGs, polyoxazolines, fluorine alkyl alcohols, saccharides, rhamnolipids) as RedOx macroinitiators forming free radicals in reactions with Ce⁴⁺ salt providing preparing block-copolymers; 3) Using oligomer-precursors with epoxide, amino, hydroxyl terminal groups for attachment of the blocks of various functionality via addition reactions.



Scheme of the synthesis of functional polyamphiphiles



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Novel oligomer-precursors and PA of variable architectures, controlled lengths of the blocks and side chains were studied using GPC, spectroscopy, and colloidal-chemical techniques. PA form SA of different degree of self-organization, size and morphology in liquids of various polarities as well as functional brushes on surfaces. These self-assemblies are specific containers for solubilization of water-insoluble substances and nanoreactors for nucleation of magnetic, luminescent and scintillation NPs. TEM, DLS, SAXS, RAMAN, impedance and luminescent spectroscopy were used for study of SA and NPs.



Thematic Session: (Nanomaterials)

Keywords: (Organometallic chemistry, Nanoparticles, Metal oxide, Hybrid materials, Gels)

Mixing time between organometallic precursor and ligand: a key parameter controlling ZnO nanoparticle size and shape and processable hybrid materials

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Since the advent of nanoscience, chemists' grail is to perfectly and reproducibly elaborate nanoparticles of fully defined size, shape, polydispersity, and surface state. It implies a total control of the experimental parameters impacting the synthesis. In the preparation of metal oxide nanoparticles using an organometallic approach, we evidenced that the mixing time between the precursor and the ligand is surprisingly a parameter of tremendous importance. For example, the formation of Zn-amido oligomers through an acid-base reaction between the organometallic zinc precursor and the amine ligand is demonstrated. Over time, this polymerization process plays a major role on the control of the size and shape of the ZnO nanoparticles formed through hydrolysis reaction. Hence, nanorods are obtained for short mixing time before hydrolysis while isotropic NPs are obtained for longer ones. Furthermore, it induces the formation of a gel with adjustable rheological properties thus opening new opportunities for the design of processable hybrid materials.

In this presentation, we will present how the control of the mixing time between organometallic precursors and alkylamine ligands is determining for mastering the chemistry leading to nanocrystals formation. Not only this parameter impacts the size and shape of the resulting NPs but also it paves the way for processable hybrid materials that can be easily shaped (and reshaped) into complex 3D structures (wires, thin films, 3D moulding, stamping...). These shapes are retained after calcination where the pure metal oxide material is obtained. This opens unprecedented opportunities to shape in a controlled fashion inorganic and hybrid materials.

Thematic Session: Nanomaterials

Keywords: gadolinium, polyion complexes, GdPO₄ nanoparticles, MRI

Gadolinium-based contrast agents: from gadolinium complexes to colloidal systems

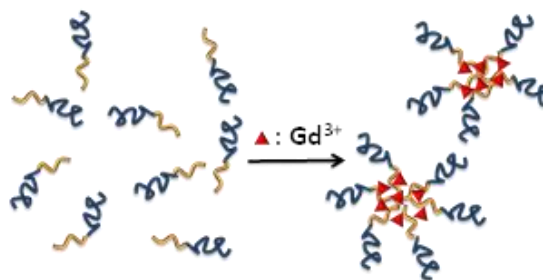
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Mixing double-hydrophilic block copolymers containing an ionizable complexing block and a neutral block with polyvalent metal ions (e.g., Cu²⁺, Zn²⁺...) leads to the spontaneous formation of polymeric colloids.¹ Very recently, we demonstrated that copolymers made of poly(acrylic acid) and poly(ethylene oxide) blocks interact efficiently with gadolinium ions and forms nano-objects with a diameter of 20 nm.²



In vivo, these nano-objects are well tolerated by rats and show surprisingly good stability, fast urinary elimination, low RES uptake, and superior magnetic relaxivity properties even at high magnetic field. With long blood remanence this new type of Gd probe could be used for MRI at lower concentrations than currently used contrast agents. The easiness to elaborate such hybrid systems enables their use in various medical multimodal imaging techniques by combining different ions with specific properties.² Additionally, these assemblies can be used as template leading to the formation of inorganic nanoparticles (GdPO₄,...) with high colloidal stability, controlled morphology and tunable properties.^{3,4}

References.

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² a) C. Frangville, Y. Li, C. Billotey, D.R. Talham, J. Taleb, P. Roux, J.-D. Marty, C. Mingotaud *Nano Lett.* **2016**, 16, 4069-4073. b) C. Mingotaud, J.-D. Marty, C. Frangville, D.R. Talham FR patent (FR3043330 - 2017-05-12 BOPI 2017-19), world extension in progress.

³ N. M. Pinkerton, L. Behar, K. Hadri, B. Amouroux, C. Mingotaud, D.R. Talham, S. Chassaing, J.-D. Marty. *Nanoscale* **2017**, 9, 1403-1408.

⁴ N.M. Pinkerton, K. Hadri, B. Amouroux, L. Behar, C. Mingotaud, M. Destarac, I. Kulai, S. Mazières, S. Chassaing* and J.-D. Marty* *Chem. Commun.*, **2018**, 54, 9438-9441

Thematic Session: Nanomaterials

Keywords: functionalized nanoparticles, Copper Complexes, SERS, plasmon assisted catalysis

Copper complexes functionalized Au nanoparticles for plasmon assisted catalysis

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Gold nanoparticles (GNPs) efficiently absorb visible light due to the resonant excitation of localized surface plasmon (LSP). The non-radiative decay of the excited LSP modes may facilitate chemical transformations taking place at the NP surface by plasmonic heating and/or by involving hot electron transfer to adsorbed molecules. Our work focusses on the interactions between the organometallic complexes grafted onto GNPs and LSP excitation, in order to produce some hybrid nanocatalysts in view of their application as more efficient substrates for copper catalyzed chemical reactions.

Bipyridine based copper heteroleptic complexes bearing a dithiolane anchoring group to allow strong covalent bonding to GNPs were synthesized. The molecular complex and the corresponding functionalized GNP were studied by NMR, UV-visible absorption, Raman spectroscopy and Surface Enhanced Raman Spectroscopy (SERS). Comparison of the Raman response of the complex in powder form and of the SERS spectra of the chemisorbed molecules on the GNP gives clear evidence of the surface functionalization and also of the complex formation and stability. This is supported by further comparing the normal Raman and SERS spectra of the dithiolated ligand before copper coordination. Finally, the functionalized GNP were imaged by STEM – HAADF combined with Energy Dispersive X-ray for elemental analysis, specifically targeting copper atoms from the complex molecules chemically attached at the NP surface.

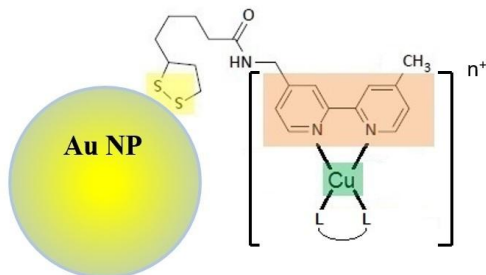


Figure: Generic structure of the used heteroleptic copper complex.

The work is supported by the X-TREM project (Paris scientifique) of the conseil régional Pays de la Loire.

Thematic Session: Cnano Nanomaterials

Keywords: Nanoparticles, SPR, Biosensor, click chemistry

Innovative Surface Plasmon Resonance (SPR) biosensor based on high refractive index nanoparticles assembled on a gold thin film

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We present an innovative method to create an original nanostructured SPR biosensor in order to enhance sensitivity and limit of detection. Our strategy consists in taking advantages of high refractive dielectric materials which increase the sensitivity factor of a gold thin film. The approach consists in using iron oxide nanoparticles assembled onto a gold thin film to improve the sensitivity factor of the gold thin film as well as the specific surface of the sensor. The nanoparticles were easily grafted on the substrate by catalyzed alkyne azide cycloaddition (CuAAC) "click". The biomolecular receptor was grafted at the surface of assembled nanoparticles by performing again the CuAAC "click" chemistry. Furthermore, polyethylene glycol (PEG) derivatives were grafted onto free areas of the gold thin film in between nanoparticles in order to avoid nonspecific adsorption of analytes. The biotin-streptavidin couple was used as an example to prove the efficiency of the sensor. Bovine serum albumin (BSA) was also used to demonstrate that nonspecific absorption is avoided. Finally, we successfully demonstrate that PEG molecules associated with nanoparticles enhance the accessibility of streptavidin to the biotin group, thus contributing to decrease the limit of detection.



Thematic Session: Nanomaterials

Keywords: Nanohybrids, magnetism, photoswitching, plasmonic.

Synergy between Surface Plasmon Resonance and Switching Properties in Gold@Spin Crossover Nano-Composite.

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Spin crossover (SCO) materials are based on coordination complexes of switchable electronic configuration upon external stimuli (temperature, light, pressure...), associated with memory effects (hysteresis loops). Photoswitching of such materials at room temperature remains a challenge, especially when ultrafast and weakly energetic switching is targeted. Based on the pulsed irradiation inside thermal hysteresis loops, photothermal effects can be achieved¹: this intense laser pulse induces a short and huge local heating allowing the materials to experience the spin crossover. Strategies to reduce the energy and time needed for this switching focus on hybrid nanoparticles². These hybrid architectures are based on a strong interplay between surface plasmon resonance of metallic nanoparticles that act as local nanoheaters³ and optical thermos-induced switching of spin state.

We present here the original synthetic approach we followed, based on a direct grafting⁴ of SCO on Au NPs, to elaborate in a controlled way, such core-shell architectures, with gold nanorods embedded in a SCO nanoparticle, Au@SCO. The use of such morphologies targets an efficient diffusion of the heat produced by the gold nanoparticles to the whole SCO component. We will show the strong synergy between the surface plasmon resonance of metallic particle and the spin crossover behavior through a strong modulation of the SPR and an efficient photoswitching of spin state.

Acknowledgements: The ANR program is acknowledged for funding the HEROES project as well as the University of Bordeaux.

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Thematic Session: C'Nano specific sessions: Nanophotonics & nano-optics; Nanomaterials

Keywords: ultrafast nano-optoacoustics, elasticity, thin films, nanomaterials

Probing elasticity of an assembly of nanoparticles with ultrafast nano-optoacoustics methods

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Elaborating nanomaterials based on assemblies of nanoparticles is a versatile and promising route for targeting and tuning a wide variety of properties (optical, magnetic, and electrical). This route usually employs the so-called soft chemistry which has the advantage of being quite cheap and transferable to an industrial level [1, 2]. However, getting quantitative information on the quality of the mechanical consolidation of the nanoparticle assembly (ordered or disordered) in a nondestructive manner is not often achieved, although it is crucial for applications and integration of materials in devices. In this communication we present ultrafast optical pump-probe measurements based on the generation and detection, by femtosecond lasers, of ultrashort acoustic pulses having typically tens of nanometers of wavelength and which propagate in the studied materials [3]. We show how this technique is relevant to probe the elasticity at the nanoscale [4-9]. In particular, with this technique we are able to measure the sound velocity at nanoscale which depends on the elastic stiffness constants of the materials and we can also detect some of its defects that can be generated during the fabrication. We illustrate our communication by providing different examples of characterization of assemblies of nanoparticles ranging from plasmonic gold nanoparticles superlattices [5] to silica nanoparticles thin films [6-7]. Among interesting information, we can distinguish the nature of nanocontacts (van der Waals versus covalent). We also show that such technique permits to image in-depth inhomogeneities of transparent thin films such as low-k materials [8-9].

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Thursday, December 12th

Session: NANOMATERIALS 2

9h30 – 12h30

Keynote speaker: Corine GERARDIN

Polymer-functionalized mesoporous materials: design and properties

Morey-St Denis room

Abstracts

Thematic Session: nanomaterials

Keywords: polymerization, metal surface, oxidative coupling, covalent network, conjugated polymer

Molecular adaptation in supramolecular self-assembly: brickwall-type phases of indacene-tetrone on silver surfaces

Corentin Pigot,^{1,*} Frédéric Dumur,¹ Nataliya Kalashnyk,² Eric Salomon,³ Didier Gigmes,¹ Sylvain Clair,²

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In the blooming field of on-surface synthesis, molecular building blocks are designed to self-assemble and covalently couple directly on a well-defined surface, thus allowing the exploration of unusual reaction pathways and the production of specific compounds in mild conditions. Up to now, most of the single-layered surface covalent organic frameworks (SCOFs) have been prepared by Ullmann dehalogenation reactions of brominated aromatic compounds or trimerization of diboronic acids. Here we present our results concerning the creation of functionalized organic nanoribbons on the Ag(110) surface by mean of an oxidative coupling **which is** unprecedented in the literature¹. Interestingly, length of the resulting nanoribbons could be efficiently controlled by mean of the temperature deposition whereas the anisotropic substrate could act as an efficient template fostering the alignment of the nanoribbons, up to the full monolayer regime. The careful inspection of the phase obtained upon deposition of s-indacene-1,3,5,7(**2H,6H**)-tetrone INDO4 on a Ag(110) surface evidenced the formation of a polymeric conjugated phase resulting from an homocoupling reaction taking place through the release of hydrogen and the creation of C=C double bonds (see Figure 2).

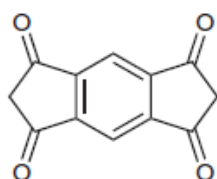


Figure 1 Structure of INDO4.

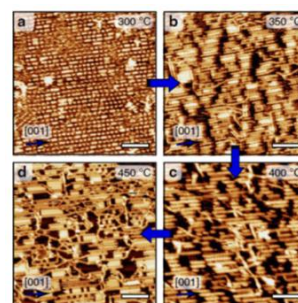


Figure 2. Nanoribbon formation and their evolution upon further annealing

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Thematic Session: (Nanomaterials)

Keywords: (Poly sodium styrene sulfonate, bioactive polymer-gold-nanoparticles, colloid synthesis)

Core-shell flower Nanoparticles: From chemical design to one step synthesis of hybrid gold nanoparticles and their interaction with human proteins.

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This study highlights recent advances in the synthesis of nano conjugates, based on gold (Au) (III) and bioactive polymer bearing sulfonate groups called thiol poly sodium styrene sulfonate (polyNaSS-SH) with various molecular weights (5 kDa, 10 kDa and 35 kDa).

The three nanomaterials obtained, differ substantially by the chelation process of the Au (III) ions during the NPs synthesis process. In particular, we obtained for polyNaSS-SH of 35 kDa a characteristic core-shell flower shape after gold reduction to form PolyNaSS-SH@AuNPs. The mechanism of formation of hybrid nanoparticles (PolyNaSS-SH@AuNPs) was deeply studied from the chemical and physical point of view, using several analytical techniques such as Raman, UV-Visible spectroscopy, transmission electron microscopy (TEM), ¹H-NMR and X-ray photoelectron spectroscopy (XPS). This approach is promising to develop bio-active polymer- gold nanoparticles as carriers and further successful application in the field of nanomedicine.

Thematic Session: Nanomaterials

Keywords: Assembly; Colloidal polymers; Patchy nanoparticles

Programmed Assembly of Colloidal Polymers from Patchy Nanoparticles

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Motivated by the burgeoning need to fabricate next-generation functional materials without human intervention, intensive research focused on the self-assembly of nano-sized building units has been conducted for two decades. Although small clusters, periodic superlattices and linear chains have been successfully produced in the last few years, it remains a great challenge to realize the self-assembly of nanoparticles into arbitrary structures of targeted size and composition with the versatility of 3D printing [1]. Indeed, the formation of complex assemblies, which span length scales orders of magnitude greater than the feature sizes of their constituting building blocks, requires that each subunit carries the information about its precise final location in the structure through the design of its interaction rules. In this context, we have recently developed an efficient strategy to synthesize site-specifically functionalized two-patch silica nanoparticles at the gram scale [2]. We will show that these patchy nanoparticles (“monomer A”) develop specific and directional interactions with complementary functionalized silica nanospheres (“monomer B”), which allowed us to build dimer-like structures (A-B-A) and colloidal polymers with a well-controlled sequence (A-B-A-B-...) (see figure). The extension of the concept to other monomers will pave the route to the synthesis of nanostructures that mimic biopolymers (*e.g.* polynucleotides) with exciting properties.

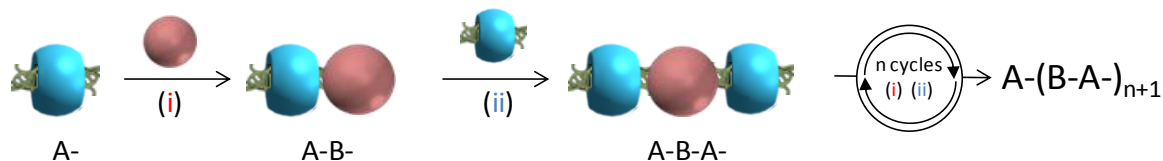


Fig. Synthesis of colloidal polymers from two-patch nanoparticles

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Thematic Session: Nanomaterials, or Nanochemistry: synthesis and functionalization of nanosystems for bioapplications

Keywords: N-Heterocyclic Carbene, Gold Nanoparticles, Size control

Synthesis of N-Heterocyclic Carbene-stabilized gold nanoparticles

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Gold nanoparticles stabilized with thiols on their surface are well known since the 1960's. Unfortunately, thiol-capped gold nanoparticles are unstable and thiol desorption often occurs, limiting their use for various applications, especially in nanomedicine. Therefore, other strategies are sought to improve stability, including the use of new complexing molecules. For the past 10 years, a new family of stabilizing ligands, N-heterocyclic carbenes (NHC), have drawn considerable interest in the field of nanomaterials. NHC are highly reactive,¹ able to give strong and covalent C-metal bonds and allow to prepare gold nanoparticles highly stable in a wide range of pH and temperature.² Three direct syntheses of gold nanoparticles capped with NHC have been developed so far.³ However, no studies have been made to unravel the mechanisms and kinetics of these reactions. Moreover, the precursors of NHC used in these syntheses are introduced in excess compared to the amount really required to stabilize the nanoparticles.

Herein we describe a synthesis of a fast NHC donor. When reacted with a gold(I) complex and a reducer, this NHC-boronium moieties yield gold nanoparticles capped with NHC. By changing the NHC-boronium/Au(I) ratio from 0.3 to 0.6, we are able to tailor the nanoparticles size from 4.3 ± 0.9 to 2.8 ± 0.8 nm. Our approach to design new precursors aims towards a better understanding of the formation of nanoparticles. Therefore, we are using in situ fast-UV spectrometer, and ex situ NMR, HRMS and XPS to characterize the crude and by products in order to propose a mechanism.

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Thematic Session: nanomaterials

Keywords: nanoparticles, ligands, colloids, surface decoration

Unusual ligands for Cu and Ag nanoparticles stabilization

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Silver and copper elements offer a vast panel of fascinating properties thanks to their remarkable electrical, optical, chemical, catalytic and biological features. Their nanoparticles (NPs) present optical properties due to their localized surface-plasmon resonance (LSPR) that can expand from the visible to the near-infrared range.^[1, 2, 3] The synthesis of small size Cu and Ag NPs is therefore desirable, since they offer unprecedented properties for many applications. Colloidal solutions of Cu NPs and Ag NPs (diameter *ca* 8 nm) prepared by the thermal decomposition of Cu (I) and Ag (I) amidinate precursors assisted by a H₂ moderate pressure, are stabilized with few molar equivalent of hexadecylamine (HDA) ligands. However, we demonstrate that not only homogeneously solvated ligands in solution can stabilize Ag and Cu NPs but also various supports in the reaction medium can do so. A substrate or a suspension of particles in solution may play the same role than the molecular ligands and stabilize Ag and Cu nanoparticles on their surface. We present few examples of Cu and Ag NPs stabilization with different media and their applications (carbon nanotubes, silicon substrates, suspension of nanoparticles in organic medium). Golden or carbon coated silicon substrates decorated with Ag NPs are used as high sensitivity electrodes for the electrochemical detection of pollutants in water.^[4] The decoration of nano-sized metal oxide semiconductors with Ag NPs is used to prepare high efficiency catalysts for solar water splitting. Carbon nanotubes have been suspended in organic solvents to stabilize *ca* 6 nm Cu NPs homogeneously distributed on their surface.

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Thematic Session: Nanomaterials

Keywords: Quantum dots, Core/Shell Synthesis, DNA Functionalization, Surface Plasmon Resonance, Non-Toxic Nanoparticles

DNA-Functionalized Core/Shell AgInS₂/ZnS Quantum dots

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The base pairing and the length adjustment of DNA strands are the most powerful specificities that are highly exploited to direct nanoparticles (NPs) self-assembly into structurally well-controlled functional nanomaterials^[1,2]. These functional nanomaterials are usually designed with the objective of optimizing the physical properties of NPs or introducing additional ones. Semiconductor NPs, also known as quantum dots (QDs), are promising materials thanks to their unique optical and electronic properties. Combining non-toxic QDs (as AgInS₂/ZnS) will make them particularly attractive candidates for applications in biomedical, nanophotonic and nano-electronics^[3]. However, the functionalization with DNA of non-toxic QDs emitting to NIR remains challenging while maintaining their stability and their photophysical properties in aqueous medium^[3-5].

In this context, we are investigating an approach that facilitate the synthesis of ternary AgInS₂/ZnS core/shell quantum dots in aqueous medium and the functionalization of QDs with DNA. This has led to stable 3-4 nm QDs with quantum yield of up to 40%. The DNA-QD conjugates were characterized by surface plasmon resonance (SPR) spectroscopy that can detect small change in refractive index. In the near future, these DNA-QD conjugates can be coupled with other buildings blocks through hybridization to give plasmonic nano-antennas^[6], photonic wires^[7], or fluorescent probes^[8].

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Thematic Session: Nanomaterials

Keywords: micelle, hydrogel, thermoresponsive, degradable, drug delivery

Injectable and degradable hydrogel for stroke recovery

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Stroke is one of the three most lethal diseases worldwide for which no efficient clinical treatment has been developed yet. In experimental research on animals, pharmacological treatments and cell transplantation are promising but limited by low drug diffusion and poor cell survival, respectively [1]. Injectable hydrogels are a promising strategy to treat such pathology as they are suitable for tissue engineering and local drug delivery. Additionally, they can be implanted through a minimally invasive surgery by using a thin needle [2].

In this context, we have developed an injectable and biodegradable hydrogel based on an amphiphilic thermoresponsive PNIPAAm-b-PLA-b-PEG-b-PLA-b-PNIPAAm pentablock copolymer [3]. The hydrogel formation at around 30°C was demonstrated to be mediated by inter-micelle bridging through the PEG central block. The hydrogels degraded through hydrolysis of PLA esters, until complete mass loss due to the migration of the recovered PEG and PNIPAAm based-residues in the solution. The mechanical properties of the designed biomaterial were found to be similar to those of soft tissue such as the brain. Interestingly, hydrophobic molecules such as riluzole (neuroprotective drug) or cyanine 5.5 (imaging probe) could be loaded in the micelle cores by simply mixing them with the copolymer solution at room temperature. Drug release was correlated to polymer mass loss. The hydrogels were shown to be cytocompatible (*in vitro*, neuronal cells) and injectable through small-gauge needle (*in vivo* in rat brain).

Thus, these results highlight the relevance and potential of this micelle-based hydrogel platform for stroke recovery, soft tissue engineering and drug delivery.

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