The SFNano C'NANO joint meeting 2019

Abstracts

Poster Session

P6 - NANOCHEMISTRY: SYNTHESIS AND FUNCTIONALIZATION OF NANOSYSTEMS FOR BIOAPPLICATIONS

SFNano cnrs C'NANO

The SFNano C'Nano joint meeting 2019

Thematic Session: Nanochemistry: synthesis and functionalization of nanosystems for bioapplications
Keywords: Synthesis, biomaterial, polysaccharide, functionalization, formulation

Characterization of OSA modified pectin solutions at a nanoscale level

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Pectin is a biosourced polymer belonging to the chemical class of polysaccharides and exclusively originating from cell walls plants. Water solution properties of hydrophilic pectin can be tailored by chemical grafting of hydrophobic moieties on hydroxyl functions of the pectin backbone. For this purpose, the grafting of octenylsuccinic anhydride (OSA) at various rates (10%, 19% and 30%) was performed, according to Monfregola process on low-methoxyl pectin (LMP), in order to obtain new artificial materials. When dissolved in water, these new materials can adopt various conformations depending on molar mass, salinity, temperature, pH or polymer-solvent interactions. Intrinsic viscosity measurements using an Ubelhode viscosimeter (C<1g/L) reveal a systematic decrease in the hydrodynamic volumes of the modified pectins (199 mL/g, 171 mL/g, 113 mL/g for respectively 10%, 19% and 30% OSA modified pectins) compared to native LMP pectin (286 mL/g). This behaviour could be discussed towards both the degradation of the backbone during the chemical modification and the emergence of hydrophobic interactions between OSA moieties. These results are confirmed by the decrease in hydrodynamic diameters measured by dynamic light scattering in the same conditions (1647 nm, 835,5 nm, 654,9 nm, 523,4 nm for respectively LMP, 10%, 19% and 30% OSA modified pectins). Consequently, OSA grafting clearly influences the pectin properties in aqueous solution which is a key-point since the goal of this work is to investigate the impact of the chemical modification on the design of drug delivery systems (microspheres or thin films).

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

Keywords: carbon quantum dots, diazonium modification, antibacterial material

Surface modification of carbon quantum dots: fine tuning of antibacterial activity

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Over recent years a biomedical application of nanomaterials based on carbon can be considered as the emerging trend in science and technology[1]. Due to their unique properties, carbon quantum dots are in the center of interest in a huge range of research focused on the sensor application, biomedicine, and electronic materials. One of the most interesting application of such nanomaterials is the therapy of infectious diseases caused by resistive strains [2]. In this study, we proposed the general approach to the tuning of antibacterial properties of carbon quantum dots (CDs-NH2) via surface modification by 4-((triethylammonio)methyl)benzenediazonium tosylate. The desired functional groups have been grafted to the surface using convenient and versatile procedure [3]. The covalent modification of CDs surface with 4-((triethylammonio)methyl)benzene groups sufficiently enhanced the antibacterial activity of CDs under visible light irradiation.

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Thematic Session: Nanochemistry: synthesis and functionalization of nanosystems for bioapplications
Keywords: Polyelectrolyte complexes; Pullulan; miRNA; Drug delivery

Development of pullulan-based cationic nanoparticles for the delivery of miRNA

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Abstract (No longer than 250 words, Calibri 11, single line spacing, black)

Different types of polymers have been used in gene delivery systems, including the use of cationic polymers. They are able to form particulate structures through the creation of polyelectrolyte complexes (PECs): a simple, versatile and inexpensive method to produce nanosystems. Pullulan is a natural polysaccharide of potential interest for biomedical applications due to its non-toxic, non-immunogenic and biodegradable properties. The aim of this work was to synthesize cationic pullulan derivatives in order to form PECs with small regulatory RNAs (miRNAs) driven by electrostatic interaction. The direct mixing of the cationic pullulan and miR-155-5p in aqueous media resulted in spontaneous formation of round-shaped PECs (210.47 ± 4.56 nm) with a monodisperse size distribution (PdI = 0.07 ± 0.04) and negative ζ (-14.62 ± 5.06 mV). The miRNA loaded was detected by agarose gel electrophoresis, which confirms the ability of cationic pullulan to form complexes with anionic miRNA via electrostatic interactions. *In vitro* tests performed onto human umbilical vein endothelial cells (HUVECs) did not evidenced cytotoxicity (100-200 µg/mL) up to 1 day of incubation. Delivery into HUVECs and quantity of miRNA were evaluated using a fluorescent miRNA sequence by confocal microscopy and flow cytometry respectively. PEC formation of cationic derivatives of pullulan with miRNA provided an easy and versatile method to produce polysaccharide nanoparticles for miRNA delivery in which no toxic reagent neither organic solvent was used and could be a promising platform for miRNA therapeutics.

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

Keywords: Functionalization; nano-bio-hybrid materials; Inorganic maghemite nanoparticles; superparamagnetism

Synthesis by polyol and characterization of iron oxide nanoparticles soluble in water

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Superparamagnetic iron oxide nanoparticles (SPION) with suitable surface chemistry have been widely used experimentally for several in-vivo applications such as MRI contrast enhancement, hyperthermia and drug delivery, etc. All these biomedical applications require that these nanoparticles have high magnetization values and size smaller than 100 nm. Moreover, these applications need a special surface coating of the magnetic nanoparticles, which has to be non-toxic and biocompatible.

In our work, we synthesized by polyol method inorganic maghemite nanoparticles (γ-Fe_2O_3) using citric acid as coating molecule to stabilize the maghemite particle suspension in water. The size of these nano-objects were measured by DLS, SEM and TEM, and showed diameters of 5, 10 and 15 nm. The phase purity of the maghemite nanoparticles was confirmed by DRX and XPS. Moreover, FTIR experiments were performed to ensure the success of the coating process. ZFC/FC magnetization and magnetic hysteresis measurement were performed using a SQUID magnetometer to investigate the magnetic properties of nanoparticles. The SQUID measurements revealed superparamagnetism of nanoparticles with the blocking temperature of 44 K, 310 K and 290 K, and high saturation magnetization 60, 74 and 67 emu/g for the 5, 10, and 15 nm respectively.

In the next step, those SPION will be grafted to the surface of plant virus to enhance their magnetic properties, and the new magnetic nano-bio-hybrid material could be used for many biomedical applications.

Thematic Session: Nanochemistry

Keywords: Magnetic silica, Core-shell nanocomposite, Magnetic hyperthermia, Drug loading

Engineering of magnetic silica nanoplatforms for the remote delivery of therapeutics under alternating magnetic field

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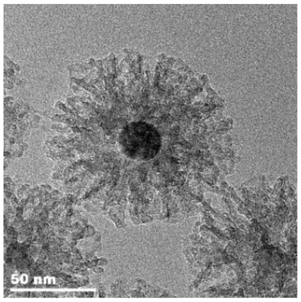
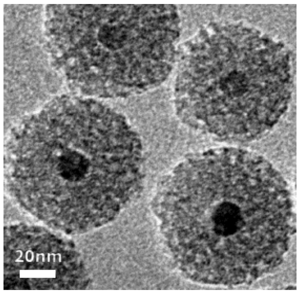
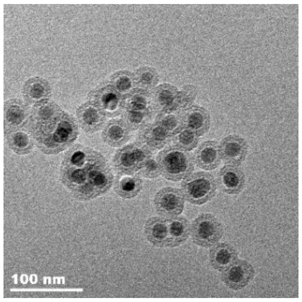
The use of magnetic nanoplatforms for sensing and theranostics has increased significantly in the last decade. There is an important challenge to design smart stimuli-responsive carriers that can respond remotely to magnetic field or near infrared (NIR) light by releasing drugs for anticancer treatments or tissue engineering.[1],[2]

The research project aims at developing magnetic nanocomposites (iron oxide core and silica shell) in order to support and release therapeutics using alternating magnetic field.[3],[4] This alternating magnetic field acts a trigger and the interaction with the iron oxide nanoparticles leads to the heating of the surrounding medium. To insure the support function of therapeutics, the magnetic cores are coated with a mesoporous silica shell. This shell has been tuned in terms of morphology and thickness and its influence on the magnetothermal properties of the nanocomposites is studied. The synthesis of hollow nanocomposites structures can also increase drastically the loading capacity and thus the efficiency of the material. The properties of the different shell structures are evaluated thanks to the temperature profiles and the calculation of the specific absorption rates (SAR) under alternating magnetic field.

Herein, we describe the synthesis and modification of these nanoplatforms and their respective performances. The thickness of the silica shell is a key parameter to control the drug loading but also the distance to the core. The temperature at the surface of the nanocomposites can be displayed by using thermal nanoprobes. This is crucial to deliver the appropriate amount of energy leading to a thermal release of drugs.







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Thematic Session: Nanochemistry, Bio-inspired nanosystems,
Keywords: nanomaterials & biomaterials, Characterization, personalized therapy, Proteins, colloids

Protein-based nanoparticles as protein carrier: Synthesis, characterization, and antibacterial application

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Human serum albumin nanoparticles (HSA-NPs) are of paramount importance as drug carriers due to their biocompatibility, penetrability, and lack of toxicity. HSA-NPs were successfully used before for the delivery of a wide variety of drugs with different properties for cancer therapy and brain targeting. HSA-NPs were prepared before by various methods such as emulsification, coacervation, nab technology, etc [1]. On the other hand, peptides and proteins starts to gain attention as therapeutic agents for a variety of human diseases. For this reason, several research focus on delivering those macromolecules using nano vectors [2]. However, literature lacks any attempt of using protein nanoparticles as protein carriers. In this work, HSA-NPs were prepared via nanoprecipitation process, a fast one-step method. A full systematic study was done to identify the effect of all experimental parameters on the colloidal properties of HSA-NPs. In addition, these particles were separately loaded with two different enzymes, Human neutrophil elastase (NE), and secretory leucocyte protease inhibitor (SLPI) as protein models. The validity of the system was confirmed through DLS, electrophoresis, and western blot tests, and the antibacterial activity of these enzymes was exploited in-vitro against *Pseudomonas aeruginosa* colonies. The results of this work show the ability to fully control the colloidal properties of HSA-NPs using nanoprecipitation method, the proficiency of using protein nanosystems as protein carrier, and the anti-bacterial efficacy of NE and SLPI once loaded within HSA-NPs. Findings that are considered as novelty and can promote HSA-NPs as effective carrier for protein and peptide based therapeutic agents.

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Thematic Session: *Nanochemistry*

Keywords: *Nucleic acid delivery, magnetic cationic liposome, reverse phase evaporation, cosolvent sonication, MRI relaxivity*

Magnetic Cationic Liposomes for Nucleic Acid Delivery

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Magnetic nanoparticles (MNPs) have been well studied and widely applied in many fields of science thanks to their unique properties and low toxicity. In nanomedicine, MNPs play several roles such as contrast agent for magnetic resonance imaging (MRI), targeting agent for drug delivery or heating agent for hyperthermia. In this work, nucleic acid delivery systems based on magnetic cationic liposomes (MCLs) were developed with an objective to fabricate a multifunctional non-viral vector for gene therapy. 10 nm citrated γ-Fe_2O_3 particles was used, and two different techniques, reverse phase evaporation and cosolvent sonication, were employed for liposome preparation. Characterization of the MCLs were carried out by dynamic light scattering, transmission electron cryomicroscopy image and relaxivity measurement at 7T. The cationic liposomes then were tested their ability to make complex (lipoplex) with plasmid encoding luciferase. Lipoplex formation was monitored by gel retardation and Picogreen® assay. Results show that both strategies produced magnetic cationic liposomes of less than 200 nm with highly positive charge of more than + 60 mV. Moreover, agarose gel electrophoresis and Picogreen® assay pointed out a high ability to make complex with pDNA of both formulations. Enhancement of r2 and r2/r1 was obtained with these two kinds of magnetic liposomes compared to free MNPs. However, the movement of MCLs upon exposure to an external magnetic field was faster in case of cosolvent sonication method compared to the other one. These results suggest an opportunity for using these MCLs to integrate MRI and magnetically targeted gene delivery for theranostic strategy.

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

Keywords: Gold, synthesis, inorganic nanoparticles, PEGylation and functionalization

Influence of PEGylation on the in vivo behavior of radiosensitizing gold nanoparticles

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Gadolinium coated gold nanoparticles have a promising potential for magnetic resonance imaging (MRI) guided radiotherapy. However this potential is not exploited plentifully because of a too fast renal elimination. In order to postpone the renal clearance, which is essential for non-biodegradable nanoparticles, gold nanoparticles coated with PEGylated chelators were synthesized and characterized. The PEGylated chelators are composed of an anchoring site, a thioctic acid moiety used for the immobilization onto the gold cores and a macrocyclic chelator, DOTA or DOTAGA, well known for their ability to form stable complexes with gadolinium ions (T_1-weighted MRI) or radioisotopes (nuclear imaging). In between, a polyethylene glycol (PEG) chain with various length (0, 4, 11 ethylene glycol units) was inserted to study their influence on biodistribution. The reduction of gold salts in presence of PEGylated chelators provides ultra-small nanoparticles Au@TAPEG$_n$DOTA and Au@TAPEG$_n$DOTAGA ($Ø_{core}$ < 3 nm). This strategy which rests on the use of PEGylated macrocycles appears attractive because it does not require, in contrast to the classical route of PEGylation, the post-functionalization of the nanoparticles by PEG chains. Preliminary results showed the potential of Au@TAPEG$_4$DOTA to improve the treatment of 9L Gliosarcoma bearing mice by radiotherapy in comparison to non-PEGylated nanoparticles.

Thematic Session: (Nanochemistry, Nanoparticles & targeting, Nanoscience for Cancer)
Keywords: (Azacitidine, Prodrug, Self-assembly, cathepsin B, myelodysplastic syndromes)

Self-assemblies of azacitidine prodrug: an innovative therapy against myelodysplastic syndromes

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5-Azacitidine, a cytidine analogue and a hypomethylating agent, is one of the main drugs being used for the treatment of myelodysplastic syndromes [1]. However after administration, it exhibits several limitations including restricted diffusion and cellular internalization due to its hydrophilicity, and rapid enzymatic degradation by adenosine deaminase. The aim of this study, was to improve the drug diffusion and protect it from metabolic degradation via the formulation of an amphiphilic prodrug and its self-assembly into a nanoparticle. The alcohol groups of azacitidine were first protected using TBDMS to inhibit secondary conjugations, followed by the coupling of an unsaturated fatty acid [2] to the amine group, and subsequently deprotection was accomplished using TBAF thus yielding an amphiphilic prodrug. Next, the obtained prodrug was solubilized in acetone and mixed with water at different ratios to obtain self-assemblies by nanoprecipitation, thus protecting the active molecule from enzymatic degradation. This prodrug should be cleaved by cathepsin B [3], overexpressed in cancerous cells [4], therefore increasing the specificity of the drug. Furthermore, its amphiphilic nature will should diffusion. This strategy would allow protection while increasing azacitidine's specificity and bioavailability.

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Thematic Session: Nanomaterials, Nanochemistry: synthesis & functionalization of nanosystems for bioapplications
Keywords: Curcumin derivated, Organic nanoparticles, Iron oxide nanoparticles, Hyperthermia

Superferrimagnetic curcumin derivated nanodispersion for magnetic fluid hyperthermia

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Magnetic fluid hyperthermia consist of the application of an external high-frequency alternating magnetic field on magnetic nanoparticles (MNPs), commonly iron oxide nanoparticles (γ-Fe_2O_3), to generate local heat. Nevertheless, to obtain an efficient heating, a high concentration of MNPs is necessary, which can lead to toxicity issue. To drastically increase heating properties, ordering several MNPs in nanoassembly is a promising route. These assemblies are known as superferrimagnetic nanodispersion. In order to preserve this magnetic order, the control of nanoassembly size is crucial. In this approach, we propose to use an organic matrix composed of curcumin derivative to encapsulate MNPs and to obtain monodisperse nanodispersion.

Curcumin is the active compound of turmeric (*Curcuma longa*). Researches over last few decades have shown that curcumin presents anti-inflammatory and anti-cancer activities[1]. However, curcumin is not stable under basic condition or light irradiation[2]. Hydrophobic compounds, with clogP > 9 are known to form nanoassemblies with good stability[3]. Curcumin, with a clogP around 2.3-2.6, is too water-soluble to nanoprecipitate. So, in this study, we propose a simple and efficient synthesis route to modify curcumin skeleton and increase hydrophobicity. Moreover, these structural modifications avoid natural degradation of curcumin.

For this purpose, we used several alkyl chains with different length to obtain curcumin derivatives with controlled clogP value. Nanoprecipitation of these compounds in presence of iron oxide nanoparticles will lead to nanoassemblies with variable size and variable amount of encapsulated MNPs. Heating efficacity of nanoassemblies will be tested to highlight correlation between nanodispersion size and amount of MNPs in the organic matrix.

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Thematic Session: Nanochemistry: synthesis & functionalization of nanosystems for bioapplications
Keywords: polymers, nanoparticles, thermoresponsive, ornithine, synthesis

Thermoresponsive, biodegradable polymer nanoparticles for hyperthermia-triggered drug delivery

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One of the main problems encountered in the field of nanomedicine is the poor targeting efficiency of the developed systems. Stimuli-responsive nanoparticles loaded with drugs are thus gaining interest since they could allow for a local drug release to a specific diseased area in response to physical changes, while reducing their diffusion into other organs. Among these systems, thermoresponsive nanoparticles exhibiting an upper critical solution temperature (UCST) are promising. The polymers constituting these nanoparticles become soluble in aqueous solution above a defined temperature, leading to the release of the encapsulated drug. Thermoresponsive polymer nanoparticles made of poly(acrylamide-co-acrylonitrile)-*b*-poly[(oligoethylene glycol) methacrylate] (P(AAm-*co*-AN)-*b*-POEGMA) were previously developed in our team and exhibited an UCST around 40°C[a]. However, they are not biodegradable given their carbon-carbon backbone. Thus, we aim to develop new biodegradable copolymer nanoparticles based on PEGylated synthetic poly(amino acid)s exhibiting a UCST behavior.

Herein, we report on the synthesis of a small library of PEG-*b*-poly(L-citrulline-*co*-L-ornithine) with different polymer chain lengths by ring-opening polymerization of L-ornithine-*N*-carboxyanhydride. The idea is then to finely-tune the UCST by varying the citrulline/ornithine molar ratio and to select the copolymers with UCST values in the 40–45°C range to be further formulated into nanoparticles. Eventually, encapsulation experiments with corticosteroids will be performed to assess the applicability of this new system.

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Thematic Session: (Nano for imaging, diagnosis and theranostics ; Nanochemistry: synthesis & functionalization of nanosystems for bioapplications)

Keywords: (magnetic resonance imaging ; T_1-weighted MRI ; nanoparticle synthesis ; continuous flow synthesis ; parametric study)

Continuous flow synthesis of iron oxide nanoparticles : experimental parameters influencing the size and magnetocrystalline properties of small-sized nanoparticles designed for T_1-weighted magnetic resonance imaging

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For the last decades, multiple research has been carried out in the field of iron oxide nanoparticle synthesis owing to their wide range of applications. Especially in the medical imaging field, the efficacy of these nanoparticles as contrast agents is highly dependent on the particle size and the particle magnetic and crystalline state. In recent years, continuous flow processes have emerged as reliable and robust alternatives for the preparation of inorganic nanoparticles. In this context, a continuous flow process was adapted for the preparation of small-sized iron oxide nanoparticles obtained through a thermal decomposition method. Of the experimental parameters studied (i.e. temperature, pressure, capillary inner diameter and flow rate), none of them were found to have a noticeable influence on the particle size determined by transmission electron microscopy (TEM). However, it was observed that the nanoparticle relaxometric properties, obtained by the study of their nuclear magnetic resonance dispersion (NMRD) profiles, are to a certain extent proportional to the reaction time (i.e. the residence time in the capillary reactor). These differences in the relaxometric properties of the iron oxide nanoparticles were attributed to changes in the crystalline state of the nano-objects. This hypothesis was corroborated by characterizing the synthesized nanoparticles with two techniques : vibrating sample magnetometry (VSM) and X-ray diffraction (XRD). The results open the way to new versatile processes enabling the production of iron oxide nanoparticles with suitable properties for applications as MRI T_1 contrast agents.

Thematic Session: Nanochemistry: synthesis & functionalization of nanosystems for bioapplications
Keywords: Lipid/polymer nanoparticles, fluorescent labeling, electrophoresis, nanoprecipitation

Assembly of Lipid-Core/Polymer Shell Hybrid Nanoparticles Assessed by Fluorescence Labeling

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Among the lipid nanoparticles, Lipid Polymer Hybrid Nanoparticles (HNPs), composed of an oily core and a polymeric shell, display interesting features as efficient drug carriers. Herein we formulated lipid-core/polymer-shell hybrid nanoparticles (HNPs) by a simple nanoprecipitation method involving Vitamin E Acetate (VEA) as the oily core and a tailor-made amphiphilic polymer as a wrapping shell. The fluorescence labeling of the oil, using a newly developed green fluorogenic BODIPY tracker, and of the polymer using a covalent attachment of a red emitting rhodamine allowed to assessing the formation, the composition and the stability of these new hybrid nanoparticles using dual color electrophoresis gel analysis. This technique, combined to conventional DLS and electronic microscopy analysis, allowed us to quickly determining that 20 wt % polymer was an optimal ratio for obtaining HNPs by nanoprecipiation. Finally, we showed that using different polymeric shells, various HNPs can be obtained and finely discriminated by this approach.

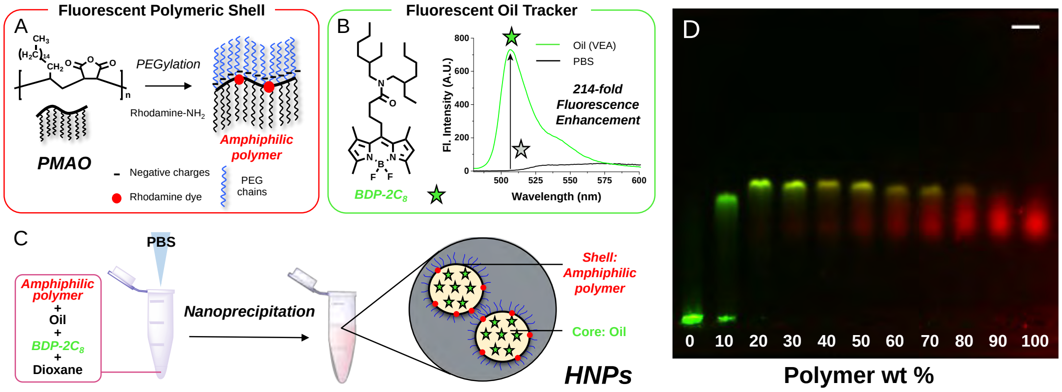

Figure 1: (A) Synthesis of fluorescently labeled amphiphilic polymer. (B) Development of fluorescent oil tracker based on BODIPY BDP-2C$_8$. (C) Formulation of HNPs by nanoprecipitation and their schematic representation. (D) Assessment the HNPs' formation by fluorescently revealed electrophoresis.

Thematic Session: Nanochemistry: synthesis and functionalization of nanosystems for bioapplications
Keywords: Bioapplications, Synthesis, Nanoparticles, Silica, Functionalization, Iron, Sodium.

Functionalized silica stellate nanoparticles for iron capture as an option of diseases treatment

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These last years, there was several studies reporting the capacity of organic and inorganic nanomaterials to ensure a function of depollution of molecules or ions[1,2] the importance of removing these elements in body is to ensure the equilibrium in the biological process, contrary, an excess could be fatal[3,4].

Among all the potential nanomaterials for depollution (Metallic Nanoparticles-iron oxide[5], gold[6]…-, graphene sheets[7] and many others), we chose the stellate mesoporous silica nanoparticles (STMS) due to their big specific surface area (*ca.* 500 m^2/g), their cost-effective synthesis, the easy function ability and because of the previous successful applications for medical treatments as drug transport/delivery vehicles since 2001[8].

In our case, we treated iron excess diseases: the hemochromatosis, a genetic illness (and other iron excess problems concerning treatments for β-thalassamia or iron poisoning). For that, a high and specific chelating agents which target iron was grafted by covalent links on the STMS surface. In order to capture iron, the chosen complex was deferoxamine B $(\beta=10^{30})$[9] which is also already accepted for medical treatments since 1980[10]. For these system, we studied the best conditions for the simulation of iron capture under physiological conditions, the high selectivity and the recyclability of the nanocomposites.

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Thematic Session: Nano for imaging, diagnosis & theranostics, Nanochemistry: synthesis and fonctionalization of nanosystems for bioapplications
Keywords: Silica nanoparticles, Contrast agents, MRI, Optical imaging, Diagnosis

Silica Nanoplatforms as Bimodal Contrast Agents for ^{1}H MRI and Optical Imaging

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Among the numerous imaging techniques, magnetic resonance imaging (MRI) has become the most powerful tool for diagnosis owing to its high spatial resolution, unlimited tissue penetration, and nonionizing nature. Nevertheless, one can mention its lack of sensitivity, which constitutes a major drawback especially in the field of molecular imaging. The combination of MRI and optical imaging (OI), detecting the luminescence emitted by a tracer, offers the high spatial resolution of the former and the high sensitivity of the latter. In this context, this study focused on the improvement of the relaxation properties of a commercial gadolinium chelate, Gd-HP-DO3A, by a non-covalent confinement of the complex in a semi-permeable nanosystem. To induce the bimodality, a fluorescent compound, i.e. ZW800-1, has been co-encapsulated inside the nanoparticle in a one-pot process. Thanks to their exceptional properties (i.e. biocompatibility, chemical stability, low toxicity) silica nanoparticles (SiO_2 NPs) have been chosen as a matrix. Narrow size distribution SiO_2 NPs were obtained by a reverse microemulsion process (D_H: 80 nm). Relaxometric measurements of the synthesized nanoplatforms have proven its efficiency to decrease $T_{1,2}$ of water proton molecules. The fluorescent properties were kept after the encapsulation of the fluorophore. The final system was characterized by Dynamic Light Scattering (DLS), Nuclear Magnetic Resonance (NMR) spectroscopy, relaxometry measurements, UV-Vis and IR spectroscopies and Transmission electron microscopy (TEM).

Thematic Session: Nanochemistry

Keywords: Surface functionalization, Biological interaction, biomarker, protein, aptamer

Influence of the Aptamer Grafting on its Conformation and its Interaction with Targeted Protein

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Abstract

Aptamers are functional small single-strand oligonucleotides (ssDNA) that show high affinity to their target molecules such as proteins or small analytes through the formation of specific secondary structures. In the present work, we study the interaction of one aptamer with its target protein, the manganese superoxide dismutase (MnSOD), under specific conditions of surface chemical grafting. For this purpose, we exploit two different chemical strategies to graft the aptamers onto pegylated gold nanoparticles: the carbodiimide chemistry (EDC/NHS method) and the thiol covalent bond (S-Au bond). We also study the influence of the presence of a spacer of 15 thymine bases at the aptamer extremity. The aptamer interactions with the MnSOD were characterized by UV-Vis absorption on a large range of MnSOD concentrations (from 10^{-12} up to 10^{-5} M). We observe that the interaction is strongly dependent on the MnSOD concentration and also on the aptamer structure at the surface of the gold nanoparticles. We demonstrate that the highest affinity is obtained for the aptamer with the 15 thymine bases spacer and grafted with the carbodiimide method. We assume that the grafting method has a strong influence on the accessibility and the conformation of the aptamer at the nanoparticle surface and thus on its possibility to interact with the MnSOD.

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C. Arib, Q.Q. Liu, N. Djaker, W. Fu, M. Lamy de la Chapelle, J. Spadavecchia, Plasmonics, 14, 1029, 2019

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

Keywords: hybrid poly ion complexes, self-assembly, bioimaging, nanoassembly characterization

Physico-chemical characterisation of Hybrid Poly Ion complexes: towards a versatile platform for imaging applications

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Hybrid polyion complexes (HPICs) result from the mixing of double hydrophilic block copolymers and oppositely charged polyvalent metal ions. [1,2] We recently proposed HPICS containing Gd^{3+} ions as new probes for Magnetic Resonance Imaging as they showed high stability over a large range of pH and ionic strengths and relaxivity values higher than standard molecular complexes.[1]
This approach of mixing of ions and polymers within micellar architectures opens many opportunities to develop new families of HPICs for future biological applications. In this context, we are interested on HPICS based on ZrO^{2+}, Cu^{2+} or Ga^{3+} ions for positron emission tomography or Eu^{3+} for fluorescence guided imaging.
We will describe the physico-chemical characterization of HPICs formed by poly(ethylene oxide)-b-poly(acrylic acid) and Ga^{3+} ions. The structural evolution as a function of the composition together with the ion distribution inside the self-assemblies is analysed by Small Angle X-ray Scattering and Anomalous Small Angle X-ray Scattering (Figure 1). Besides, the kinetics of formation of HPICs is studied thanks to stopped flow light scattering experiments.

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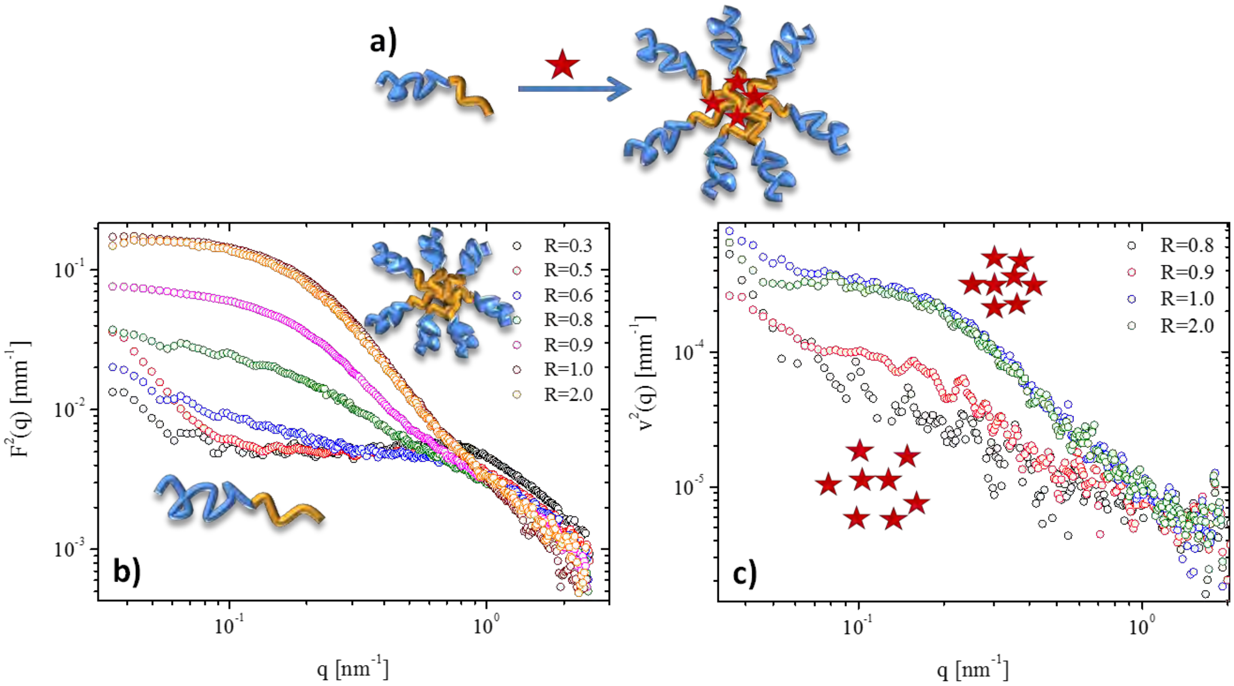

Figure 1. **a)** Schematic formation of HPICs; scattering intensity distribution as a function of the scattering vector relative to **b)** the block-copolymer and **c)** the Ga^{3+} ions.

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

Keywords: core-shell, gold nanoparticles, dextran, theranostic

Multifunctional gold nanoparticles for cancer imaging and therapy

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Cancer is one of the most important causes of death in the world with a number of diagnosed cancers which is rising rapidly. Currently, the main therapeutic approaches used to treat cancer are surgery, chemotherapy and radiotherapy. In this context, it is desirable to develop highly efficient systems that first selectively target cancerous tissues and then, once localized in the tumor, can be remotely activated to induce a local cytotoxic effect.

Over the past few years, gold nanoparticles (AuNPs) have emerged as interesting candidates in the biomedical field because of their unique optical and physical properties[1]. Besides their biocompatibility and stability at physiologic pH, AuNPs can be functionalized by numerous agents (polymers, ligands, drugs, DNA, proteins, peptides, …) which can provide them suitable applications for imaging, targeting and treatment of cancer cells[2,3,4].

Our goal project is to develop a core-shell nanoparticles which will allow the combination of imaging and treatment via chemo, photo and radio-therapy by targeting cancer cells. A gold core was selected for its well-established strong absorbance (X-rays and IR) suitable for radiotherapy or for induced local hyperthermia.

For the shell, we have selected a modified polysaccharide carboxymethyl-dextran (CM-dextran) interesting for its biocompatibility, its furtivity and its easy degradation in the body. The key point is the presence of reactive carboxylic acids in this derivative which opens an easy functionalization by a wide range of molecules of interest (targeting peptides, drugs, fluorophores…).

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

Keywords: Docetaxel, gold nanoparticles, nanoflowers

Docetaxel Gold Complex Nanoflowers: Chemo-Biological Evaluation for better Therapeutic Efficiency

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This study is based onto a previous original methodology to obtain novel chemo-therapeutic metallo-drugs complex in the form of hybrid nanoparticles with application in chemobiology. Docetaxel (DTX) is one of the most efficient anticancer drugs, and is currently used for the treatment of Non-Small-Cell Lung Cancer (NSCLC). However, its poor water solubility and systemic toxicity have greatly limited its clinical application. In order to improve DTX solubility and efficacity, in the present study gold salts ($HAuCl_4$) were complexed with the antitumor drug in the presence of dicarboxylic acid-terminated polyethylene-glycol (PEG) to form the nanometric complex named DTX-Au-PEG. Following reduction with sodium borohydride ($NaBH_4$), the DTX-Au-PEG complex formed hybrid-metal nanoparticles (DTX IN PEG-AuNPs), where DTX was protected in the gold core embedded within the polymer chains. Further, for therapeutic targeting, DTX-Au-PEG complexand DTX IN PEG-AuNPs were functionalized with the human anti-EGFR polyclonal antibody, which specifically recognizes the hERG1 channel aberrantly expressed on the membrane of human lung cancer cells. The active targeting was evaluated by analytical techniques (Raman and UV-Vis spectroscopies). In vitro experiments in complex 3D tumoroids grown at the Air-Liquid Interface (ALI) demonstrated that DTX encapsulation within a gold core strongly influenced the therapeutic efficacy of the drug in lung cancer treatment, with a significant increase of the DTX therapeutic index when AuNPs were specifically targeted against EGFR. Collectively, our study demonstrated that a drug delivery system based on Au (III)-DTX complexes as building blocks of PEGylated AuNPs constitutes a promising chemical approach to transform promising Au (III) complexes into real chemotherapeutic drugs for the treatment of cancer.

The SFNano C'Nano joint meeting 2019

Thematic Session: Nanochemistry, nanoparticles & therapeutic targeting

Keywords: Carbon nanotubes, mesoporous silica, photoresponsive platforms, drug delivery

Combined Phototherapy and NIR Light Induced Drug Delivery to Cancer Cells Achieved by Protein Capped Carbon Nanotubes-Mesoporous Silica Nanocomposites

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One of the most promising developments in the nanomedecine field is the design of smart activable nanosystems remotely releasing drugs upon externally applied stimuli (e.g., light, magnetic or electric fields). Among the various activable nanomaterials, carbon-based nanocomposites are still few investigated for remotely controlled drug delivery. In this work, we address the design of original carbon nanotube base composite nanoplatforms endowed with phototherapy combined with a drug release mediated by NIR laser excitation. These responsive carbon nanotubes are surrounded with a mesoporous silica shell having small pores which are chemically modified with isobutyramide (IBAM) grafts. These IBAM binders allow first the loading of an antitumor drug doxorubicin with a very high drug loading capacity (⩾to 80%) followed by the adsorption of an additional tight human serum albumin (HSA) shell ensuring a biocompatible interface and drug gate keeping. Such smart photoresponsive platforms are shown to deliver the drugs upon several pulsatile NIR excitations with controlled T profiles according to the conditions used (concentrations, power laser etc…) These nanosystems are in fine integrated within a hydrogel mimicking/resembling the extracellular matrix and the biological response with cells on this resulting smart nanocomposite hydrogel scaffold is assessed upon NIR light irradiation. Such nanocomposites are hence highly promising as new components of implantable scaffolds that respond in time and location to external stimuli for a better disease management.

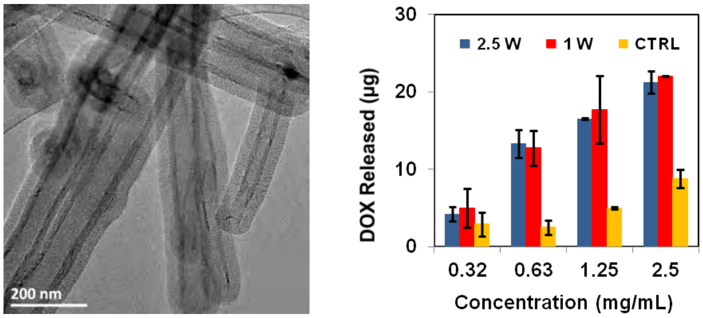

Fig.1 TEM image of CNT@MS and DOX release under different conditions

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Thematic Session: (Nanochemistry)

Keywords: (Plasmon, nanoparticles, C-C coupling, photocatalysis)

Plasmonic catalysis for Suzuki-Miyaura cross coupling reaction using palladium nanoflowers

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Plasmonic catalysis enables to achieve reactions using solar light with less energy and time consumption. Pd nanoflowers synthesized by radiolytic reduction of $Pd^{II}(acac)_2$ in ethanol under CO atmosphere exhibit a broad plasmon band in the visible-near infrared domain (Fig.1) [1, 2]. These plasmonic nanostructures present a remarkably enhanced photocatalytic activity for Suzuki--Miyaura reactions under visible light irradiation [3]. The reaction carried out using iodobenzene **1a**, phenylboronic acid **1b** and Cs_2CO_3 as base, have showed the highest conversion under light irradiation 96% versus 53% in the dark (Fig. 2).

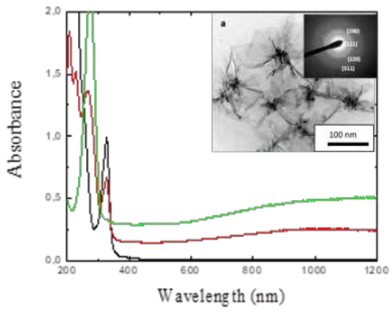

Fig 1: Absorption spectra of Pd nanoflowers

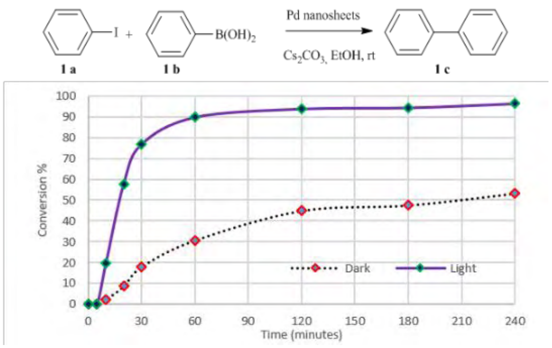

Fig.2: Catalytic activity of the Pd nanoflowers for the Suzuki-Miyaura reaction under visible light and in the dark

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Thematic Session: Nano for imaging, diagnosis and theranostics
Keywords: Upconverting nanoparticles, prostate cancer, bio-orthogonal chemistry, fluorescence imaging, scintigraphy

Preliminary evaluations of PSMA-targeted NIR upconverting nanoparticles for dual scintigraphic/fluorescence-guided surgery in prostate cancer

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Over the last few years, upconversion nanoparticles (UCNPs) have been widely investigated in nanomedicine due to their high potential as imaging agents in the near infra-red optical window of biological samples and tissues. In this project, active targeted UCNPs for dual fluorescence and scintigraphy-guided surgery of PSMA-expressing prostate cancers were developed and evaluated.

The β-NaYF$_4$-based UCNPs co-doped with Yb^{3+} and Tm^{3+} ions were designed to provide an 800 nm emission upon excitation at 980 nm. A one-pot thermolysis synthesis was performed to obtain core-shell UCNPs with a mean diameter of 32±2 nm, confirmed by both DLS and TEM measurements.

Several phosphate, bis and tetraphosphonate-based polyethylene glycol (PEG) ligands were synthesized and used to hydrophilize UCNPs and their stability was assessed by DLS in different media (water, NaCl 0.9%, PBS, biological culture media). An azide analogue of the most efficient PEG was then synthesized in order to conjugate both PSMA targeting ligands (i.e. KuE) and radiolabeled prosthetic groups to UCNPs by bio-orthogonal chemistry.

In competition binding assays performed on LNCaP cell line, KuEs and fully functionalized KuE-UCNPs showed a good affinity towards their target. These results were also confirmed by flow cytometry using PSMA-negative and PSMA positive human prostate cancer cells. Intravenous injections of KuE-UCNPs in healthy mice were well tolerated and allowed the detection of injected UCNPs *in vivo* using fluorescence optical imaging. These results encourage us to radiolabel and evaluate the biodistribution and optical/scintigraphic imaging potential of KuE-UCNPs in PSMA-expressing prostate cancer xenograft models.

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

Keywords: Gold nanoparticles, Green synthesis, plasmonic properties, electron microscopy, absorption spectroscopy

Functionalized anisotropic gold nanoparticles for *Surface Enhanced Raman Spectroscopy* and bio-applications

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During last decade, gold nanoparticles (Au-NPs) have been emerging materials for bio-imaging applications or as drug carriers in therapy due to their remarkable optical and electronic properties[1]. Our anisotropic nanoparticles synthesis method consists in using *Aloe Vera* leaf extract as the reducing agent[2]. By varying the ratio between the reducing agent and gold precursors, size and shape of Au-NPs are controlled, as demonstrated by transmission and scanning electron microscopy, as well as atomic force microscopy measurements. In a second step, the anisotropic particles were functionalized using 16-mercaptohexadecanoic acid. UV-vis and infrared absorption spectroscopy measurements as well as Raman studies were performed highlighting both the plasmonic properties[3] of the anisotropic Au-NPs and the chemical changes induced by the functionalization. Thus, interactions of Au-NPs with biological systems could be investigated.

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Thematic Session: Nanochemistry: synthesis & functionalization of nanosystems for bioapplications
Keywords: dendrimers, MRI, Gd-chelates, targeting

Polynuclear Gd-chelates for targeted MRI-imaging: influence of internal structure on relaxivity performance

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Thanks to its excellent spatial resolution, MRI imaging is one of the most popular medical imaging techniques. However, it lacks from sensitivity and this drawback can be counterbalanced by the use of paramagnetic contrast agents (CA), such as gadolinium polyaminocarboxylate chelates. However, in order to obtain good contrast between tissues, injected gadolinium doses are actually very high (e.g. for DOTAREM® 0.2 mL per kg of a 0.5 M solution for adults). One way to resolve this problem consist in developing multimeric contrast agents of nanometric sizes.
For this, we have developed the synthesis of polymetallic objects with dendron-like structure. Due to their macromolecular nature, those compounds can be functionalized with additional chemical units, able to bring other imaging functionalities (for example, fluorophores for optical microscopy) and/or peptides for targeted delivery. In this presentation, we will detail two synthetic approaches for preparation of such dendronic compounds, based on pre- and post-metallation strategies. We will also show how the chemical nature of the linker between Gd-chelates and the dendron scaffold influences the relaxometric performance of the agents.[1] Finally, the possibilities of multimeric contrast agents targeting will be discussed.

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Thematic Session: (Nanochemistry, nanomaterials)
Keywords: (Upconversion, nanoparticles, energy transfer, sensing, DNA)

Energy transfer-based DNA sensing using upconversion nanoparticles

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Optical biosensors based on Förster resonance energy transfer (FRET) are the most used in biosensing because of the rapid signal generation, non-destructive operation, and low detection limits. The detection sensitivity in FRET-based biosensors is determined by the energy donors (fluorophores).[1] Among all, upconversion nanoparticles (UCNPs) display improved properties such as narrow emission bands, high signal-to-noise ratio, no photobleaching, and no photoblinking. In addition, UCNPs can emit UV/Vis light upon near-infrared (NIR) irradiation, which allows a remarkably deep penetration into tissues. Therefore, UCNP-based probes are promising for highly sensitive biosensors. [2]

Interestingly, the high surface to volume ratio of UCNPs makes it possible to attach many biosensing elements to their surfaces, leading to enhanced performance with increased sensitivity and detection limits of several orders of magnitudes lower.[4] Surface modification of UCNPs with DNA will endow the nanoparticles with water dispersability, biorecognition properties, biocompatibility, and biostability. The synergistic effect between UCNPs and DNA can allow the design of FRET biosensors with improved characteristics and nanoscale spatial resolution, opening new ways for gene delivery, gene therapy, and diagnosis and monitoring of diseases.

We have developed a novel nanobiosensor based on DNA-capped UCNPs (UCNPs@DNA) able to carry out a homogeneous hybridization assay for the detection of DNA. The resultant nanohybrid displayed high stability in different buffers, even several months later. The sensitivity, selectivity, and detection limit of UCNP@DNA nanohybrid to detect the complementary DNA strand by FRET upon NIR excitation will be discussed.

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Thematic Session: (Nanochemistry: synthesis & functionalization of nanosystems for bioapplications, nanomaterials)

Keywords: (Nanoparticles, zinc oxide, photocatalysis, synthesis)

Synthesis and Characterization of Cu doped ZnO Nanoparticles

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Enhancing the chemical and physical properties of metal oxide nanoparticles (NPs) by doping with transition metals have been received great attention due to their variety of applications such as environmental pollutant issues. In this work, we synthesized the Cu doped ZnO NPs ($Zn_{1-x}Cu_xO$) through surfactant free method to improve its photocatalytic activity. Structural and morphological characterizations of the as-prepared NPs performed on XRD, TEM, STEM, EDX and SEM have been showed that the obtained nanoparticles were crystalline particles with all reflections matching to wurtzite. Rhodamine 6G was involved in order to compare photocatalytic activity of the doped and non-doped ZnO NPs. Experimental results showed that photocatalytic activity of ZnO NPs was enhanced as increasing the doping concentration.

Thematic Session: Nanochemistry: synthesis and functionalization of nanosystems for bioapplications
Keywords: Supramolecular dendrimer, DNA delivery, siRNA delivery, gene therapy

Bola-amphiphilic dendrimers as modular nanovectors for nucleic acid delivery

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Our increasing understanding of the genetic roots of diseases in the current post-genome era offers us bright opportunities to develop nucleic acid therapeutics for treating diseases via specific modulation of gene expression.[1] However, nucleic acid is not stable and can be easily degraded. In addition, nucleic acid cannot readily cross cell membranes because of the abundant negative charges. Therefore, safe and effective delivery is essential for implementing nucleic acid therapeutics.[2] Dendrimer, by virtue of its well-defined structure and unique multivalent cooperativity, constitutes a promising non-viral vector for nucleic acid delivery[3] . We have recently developed a series of amphiphilic dendrimer as nanovectors for effective delivery of small interfering RNA (siRNA).[4] Here we report our design and synthesis of bola-amphiphilic dendrimers for nucleic acid delivery. These bola-dendrimers bear a long hydrophobic alkyl chain as the core and positively charged poly(amidoamine) dendrons at the terminals. They are capable of interacting and compacting the negatively charged nucleic acid into nanoparticles, hence masking the negative charges of nucleic acid, protecting nucleic acid from degradation and promoting cellular uptake. Most interestingly, by modulating generation, these dendrimers can specifically deliver large DNA and small interfering RNA (siRNA) respectively. Consequently, they constitute smart modular nanovectors for the delivery of various nucleic acid therapeutics.

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Thematic Session: SFNano & C'Nano common sessions

Keywords: Surface colloid functionalization Biological interaction, biomarker, PEG-AuNPs, Raman Spectroscopy, aptamer.

Spectroscopic Characterization of Grafting and Aptamer Interactions on a Target Protein (SOD)

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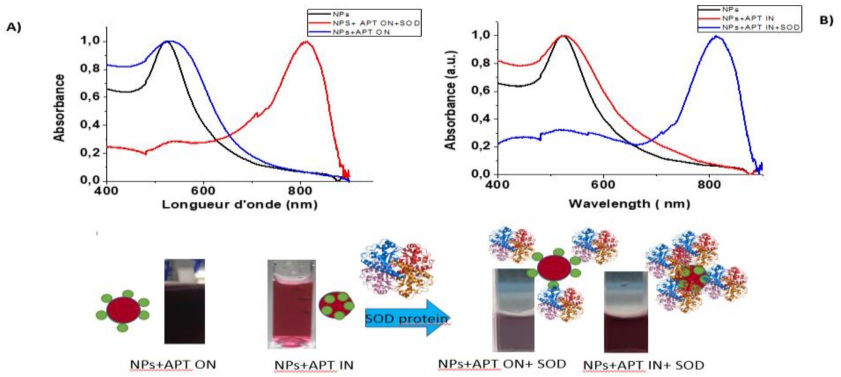
ABSTRACT

Aptamers are short synthetic sequences of single-stranded DNA or RNA nucleic acids with great binding affinity to the diverse targets. Proteins, enzymes, growth factors, drugs, bacteria, virus, spores, toxins, small molecules, and also, metal ions are some of the targets for aptamers. In the present paper we study the interaction of a specific aptamer with its target protein, the superoxide dismutase (SOD), under specific conditions of surface chemical functionalization. And we exploit two different chemical strategies to graft the aptamers. The aptamer's interactions with the SOD were characterized by UV-Vis absorption and Raman Spectroscopy on a large range of SOD concentration (from 50nM to 10µ M). We observe that the interaction is strongly dependent on the SOD concentration and also on the aptamer structure at the surface of the gold nanoparticles.



Thematic Session: Nanomaterials, Nanomedicines

Keywords: Colloidal gold nanoparticles, Nanostructured surfaces, Biocompatibility, Protein adsorption, Weak energy binding

Predictive tools for designing biocompatible nanoparticles and nanostructured materials.

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Colloidal gold nanoparticles (AuNP) have been extensively studied as theranostic tools or even to enhance medical devices efficiency[1]. Proteins tend to bound on NP influencing the pharmacokinetic of functionalized particles or causing inflammation. Therefore, biocompatibility prediction of colloidal nanoparticles or nanostructured materials remains a key point for designing new nanomedicines. The interaction between albumin with AuNP capped by several agents either under a colloidal form or after their immobilization was investigated. Albumin fluorescence quenching at several temperatures and AuNP concentrations was tested. Thermodynamic parameters of proteins bound to anionic (citrate ions, dihydrolipoic acid[2]), cationic (cysteamine) or neutral (polyethylene glycol) AuNP were determined. Stern-Volmer constant indicated a static quenching of albumin complexed to AuNP citrate and cysteamine. Surprisingly, the electrostatic association between albumin (negative) and AuNP cysteamine (positive) was the least favorable. Suggesting that surrounding ions in NP solvation layer should also be considered. As a model of nanostructured material, surfaces coated by polyelectrolyte multilayer thin films embedding AuNP citrate were used. This architecture was modified according to its outer layer. Preliminary results showed a lower protein adsorption on polyanion (PAA) compared to a polycationic (PAH) or AuNP outer layers. Protein antifouling enhancement by graft or block PAA-PEG copolymers as the last layer will be investigated. Protein adsorption will be quantified indirectly with bicinchoninic acid assay and directly with Quartz Cristal Microbalance. Protein adsorption will also be monitor by Capillary Zone Electrophoresis through film surface charge modification[3]. Pulled together all these results will provide predictive models to design biocompatible colloidal nanoparticles or nanostructured materials.

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The SFNano C'Nano joint meeting 2019

Nanochemistry : synthesis & functionalization of nanosystems for bioapplications
Keywords : metallic nanoparticles, green chemistry synthesis, bismuth, sonication

Metallic Bismuth Nanoparticles Synthesis *via* a Greener Process

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Few studies have reported bismuth nanoparticles use in different applications : in imaging (computed tomography or photoacoustic), in therapy (photothermal therapy or radiotherapy) and sometimes both for theranostic.[1] However the bismuth has several advantages : a highly biocompatible and inexpensive metal with a high atomic number which confers an important X-rays opacity.[2] Metallic bismuth nanoparticles, which contain a high density of metallic atoms, are therefore highly attractive for X-rays imaging. So the development of these nanoparticles is really interesting but few synthesis are described in literature by following a top-down approach or a bottom-up approach *via* a thermal decomposition of bismuth salts or a reduction in organic solvents or in polyol.[3] A new robust, efficient and green process is reported here to obtain metallic bismuth nanoparticles.[4] The procedure, which has been optimized to get a reproducible synthesis, will also tend to minimize chemical hazards to health and environment. By applying the green chemistry principles,[5] several experimental parameters were studied such as reaction time, reactants choice and stoichiometry, temperature and purification steps number.

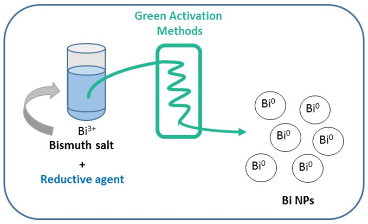

Figure 1: A green process to get metallic bismuth nanoparticles.

Several activation techniques were compared (heating,[6] microwaves, sonication) but also intensification processes (batch, continuous flow). Two purification methods (centrifugation and ultrafiltration) were tested to isolate metallic bismuth nanoparticles. Several analytical techniques were used to characterize products (structures, sizes and morphology) such as Infrared analysis, Dynamic Light Scattering (DLS) and Transmission Electron Microscopy (TEM).

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Thematic Session: Nanomaterials
Keywords: Microspheres; cancer; Imatinib; Ethylcellulose; Protein kinase inhibitor

Preparation and Characterization of Imanitib loaded Ethylcellulose Microspheres

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Abstract:

The present investigation emphasizes on preparation and characterization of imatinib loaded ethylcellulose microspheres for sustained release of anticancer drug, through the polymer. Microspheres were prepared by the solvent evaporation method. The surface charactererization of microspheres was performed by various analytical techniques such as SEM, AFM. The entrapment efficiency of the drug was found to be 76%. Polymer and the drug compatibility study are done by FTIR. Furthermore, the dissolution study for sustained release of the drug was performed and achieved as well. So that we can conclude that the formulation can show its efficacy for a longer period of time since imatib is having greater bioavailability.

Abstracts

Poster Session

P7 - NANOMATERIALS

Thematic Session: POSTER Nanomaterials
Keywords: Nanoparticles, Probe-sonicator, Spin Coating, Scanning electron microscopy, Zeta potential, Metrology

Sample preparation steps to measure the size of constituent particles by SEM

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Additives potentially under the nano form widely used in commercial products in food and cosmetics sectors. The physico-chemical feature of nano-objects is described in the ISO/TR 13014:2012. The dimensional parameters play an important role for identifying nanoparticles. Various direct and indirect techniques are available for measuring the particles size and shape. Electron microscopy-based techniques are often considered as the preferred methods for characterizing their dimensional properties. But, in all cases the sample preparation step remains a key step indispensable prior condition. The characterization of NPs is performed using different technics, but we need reference tests and protocols. Scanning electron microscopy (SEM) observations measurements require well-dispersed particles with a distribution representative of sample population corresponding to a statistically representative sample, calling for complex validated preparation methods. This work presents a new approach, to prepare samples by combining several factors such as pH, zeta potential, duration and power of sonication, concentration and spin coater parameters, that can influence electrostatic interactions and agglomeration of nanoparticles.

Thematic Session: POSTER Nanomaterials
Keywords: Size, TiO_2, SAXS, SEM, Nanomaterials

Dimensional measurement of TiO_2 particles in powder form by SAXS and SEM

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Developments of nanomaterials had an important known evolution during the last thirty years for different industrial sectors[1]. Titanium dioxide is one of the most produced and exploited nanomaterials in the industry[2]. Indeed, TiO_2 has various applications; it can be used as a white pigment for paint and food products and is also used as a UV filter in sunscreen lotions. The characterization of TiO_2 nanoparticles, contained in consumer products remains a challenge because of their structure (polydispersity, polymorphism) and their environment which remains generally complex and requires several characterizations techniques. Electron microscopies are the first recommended techniques for the dimensional characterization of nanomaterials. In comparison with the results obtained by the scanning electron microscope (SEM), another technique, SAXS (Small Angle X-Ray Scattering), can be used for the indirect characterization of nanomaterials (simple or introduced into a complex matrix).

The first step of this study is to compare the dimensional measurements of TiO_2 nanoparticles in powder form with two different techniques: SEM (direct method) and SAXS (indirect method) and with two different measurands, an equivalent area diameter for SEM and specific surface area for SAXS. The second part should be to avoid the sampling preparation steps with *in situ* dimensional measurement.

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Thematic Session: Nanomaterials, colloidal synthesis, Self-assembly
Keywords: Nanocube, nanocrystal, superlattice, assembly

Synthesis, self-assembly and thermal stability of monodisperse silver nanocubes for microelectronic applications

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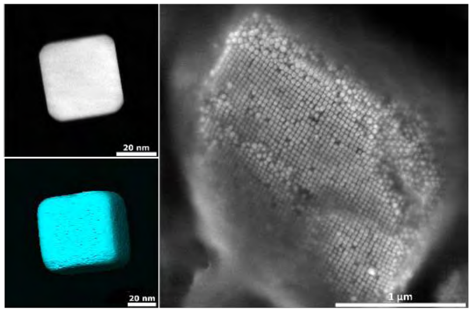
Abstract:

The use and exploitation of silver nanostructures is of high interest in the fields of conductive inks particularly for the fabrication of plastic and flexible electronic devices such as solar cells or organic electronics. One of the challenges for the development of such material is to obtain printing conductive patterns based on nanoparticles, with uniform sizes and shapes, that can aggregate/sinter at low temperature.

In this presentation, we will focus on synthetic strategies of metal nanocrystals by soft chemistry approaches, their assembly into supercrystals and their coalescence at low temperature. Cubic Ag nanocrystals were chosen for this investigation in order to get high packing density. Traditionally prepared by polyol approach, we additionally adapted an alternative route in aqueous medium allowing to synthesize sub-20 nm with narrow size distribution, high crystallinity and high reproducibility. Their morphology, their structure and their thermal properties were analyzed by TEM, SEM and advanced transmission electron tomography using a heated sample holder*. The superlattices were formed by different self-assembly strategies. The impact of the size and the surface chemistry on the assembly and coalescence of the nanobuilding units was investigated and will be described.



(*) Albrecht, W.; Bladt, E.; Vanrompay, H.; Smith, J.; Skrabalak, S.; Bals, S. Thermal Stability Of Gold/Palladium Octopods Studied In Situ In 3D: Understanding Design Rules For Thermally Stable Metal Nanoparticles. ACS Nano 2019, 13, 6522-6530.

Thematic Session: Nanomaterials

Keywords: Nanomaterials, Synthesis, Catalysis, Functionalization, API, SEM, TEM, XPS, XRD

Magnetic Nanohybrids for Active Pharmaceutical Ingredients Manufacturing

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New magnetic nanohybrids were designed to target the scavenging of trace amount of free metals and the recyclability of expensive catalysts. In industry, 90% of chemical reactions use catalysts whose major drawbacks are cost and recycling and the removal of metal traces from the active pharmaceutical ingredients (API). Thus, in accordance with the need for ecological and sustainable development, an optimized manufacturing of API targeted magnetically recyclable solid catalysts and scavengers.

These magnetic nanohybrids were prepared from an iron oxide (Fe_3O_4) based inorganic core and the subsequent grafting of either a ligand or a metal onto their surface. These nano-composites were extensively characterized by XRD, SEM, TEM and XPS. These characterizations showed the presence of the magnetic phase, the grafting of the metal and/or the ligand onto the magnetic support and indicate that the samples were thoroughly purified.

The magnetic nanohybrids were used for C-C coupling reactions (Suzuki, Heck, Sonogashira) and efficient sample decontamination from various metals, respectively. The nanocatalysts provided an excellent performance and a reuse over a large number of catalytic cycles while maintaining a high conversion. The nanoscavengers could remove up to trace amount of free metals within a sample.

The first tests at pilot scale showed that the catalyst was efficient, recoverable magnetically and reusable over several cycles, paving the way for an ecological and economical production of API. Other applications may be envisioned for such a technology.

Thematic Session: nanomaterials
Keywords: metal oxide nanoparticle, micromachined silicon substrate, gas sensor

MOX gas sensors obtained by mixing p-type and n-type nanostructured metal oxides for air quality sensors.

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Indoor air quality is major health concern in our societies and European recommendations (2008/50/EC) will be fulfilled with the help of efficient air quality monitoring systems. MOX gas sensors have proven their interest for the air quality monitoring in open air or indoor areas.[1] The main drawbacks of these sensors concern their stability over time and their lack of selectivity among mixtures of gases as well as in variable humidity environment. If attention has been focused on n-type semiconducting oxides, few studies have been devoted to the p-type gas sensors. Among p-type oxide semiconductors, CuO have demonstrated considerable potential for detection of gases such C_2H_5OH, NO_2, H_2S, H_2, CO and NH_3.[2] The mixture of n-type and p-type metal oxides have been used to modify the response of gas sensors,[3] but there is still a lack of knowledge about the role of n-p heterojunction to overcome the effect of the hygrometry changes. In order to increase the sensitivity and the selectivity of semi-conducting gas sensors, SnO_2, WO_3, CuO and ZnO nanopowders have been synthesized by a metalorganic approach. Efficient sensitive layers were prepared using mixed binary or ternary blends that were further integrated on silicon substrates. The optimum blending of different metal oxides (n-type and p-type) was achieved by mixing the nanopowders in an organic solvent. The mixed metal oxides have been prepared as a screen-printing paste and deposited on silicon micro hotplates. The gas sensing performances will be presented and discussed.

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The SFNano C'NANO joint meeting 2019

Thematic Session: Nanomaterials
Keywords: Nanopores – Protein sequencing – Molybdenum disulfide MoS_2– Time series – MD simulations

Identifying Patterns in Time Series Data: Application to Biological Peptide Translocation through single-layer MoS_2 Nanopores

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Solid-state nanopores (SSN) have emerged as one of the most versatile tools for biomolecule detection and manipulation. One of the most promising features of SSN is DNA and protein sequencing at the single monomer resolution, at a low cost and faster than the current standards. SSN sequencing experiments are based on the measurements of ionic current variations when a biomolecule in ionic solution translocates through a nanopore. As the biomolecule passes through the nanopore, it occupies the pore volume, blocking the passage of the ions. Therefore, ultrafast monitoring of ionic flow during the passage of the biomolecule yields information about its structure and chemical properties. Transition metal dichalcogenides such as molybdenum disulfide (MoS_2) are potentially advantageous SSN due to a well-controlled fabrication process at the nanoscale and also due to their rich optoelectronic and mechanical properties.

The objective of this work is to extract relevant information such as the sequence of the biomolecule that translocates through MoS_2 nanopores from ionic current time series. Time series of biomolecule translocation were simulated by using all-atom molecular dynamics (MD) simulations. First, we investigated the translocation of KTKEGV peptides through MoS_2 nanopores. From the computed ionic current signal extracted from MD, we provided a general method to detect relevant translocation events and to characterize them using different time series analysis techniques such as the construction of effective free-energy landscape from single-molecule time series, permutation entropy or detrended fluctuation analysis. Second, mutant peptides, i.e. KTKKGV and KTKEGR were investigated and comparison between wild-type and mutants showed that single amino acid mutations can be detected from the analysis tools presented here. The use of time series analysis techniques allows us to go one step further towards the application of MoS_2 nanopores for protein sequencing at the single monomer resolution.

Thematic Session: C'Nano specific session, Nanomaterials
Keywords: nanotubes, functionalization, imogolite, emulsion,phosphonic acid

Imogolite nanotubes partially transformed by decylphosphonic acid to form an interface active composite material

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Abstract:
The natural Imogolite clay ((HO)3Al2O3SiOH) with nano-tubular structure of 2-3 nm diameter is a promising candidate for polymer reinforcement, water treatment and other applications.[1] However, its hydrophilic external gibbsite like surface limits its use in hydrophobic environment. Among the different possible grafting functions for the outer surface, the phosphonic acid moiety is the most used. It shows strong reactivity with imogolite [1]. If the resulting product can be dispersed in a hydrophobic environment, the impact of the reaction on the tubular structure was never demonstrated and experimental evidence of grafted dispersed imogolite tubes with a brush-like layer on their exterior is still missing [2].

By combining different experimental techniques (SAXS, IR, MAS NMR, SEM and TEM) we systematically characterized the reaction product of imogolite and (decyl)phosphonic acid [3]. The product shows properties which were previously ascribed to grafted tubes [2], but no evidence for grafting is found. Instead, we observed the formation of a lamellar phase at the expense of the tubular structure, which forms a composite material with the remaining imogolite tubes. This newly formed material has unusual interfacial properties able to stabilize water droplets in toluene. The exhibited reactivity can be explained by the surface chemistry of the imogolite. Beyond the particular case of imogolite reactivity, the approach described here opens an interesting synthetic strategy to form hierarchical materials from nanoparticles dispersion.

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Thematic Session: Nanomaterials
Keywords: Corrosion, Additive Manufacturing, Microstructure, nano-inclusions, nano-cells

Microstructure impact on high temperature corrosion behavior of AISI 316L stainless steel additively manufactured by Selective Laser Melting (AM-SLM)

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AM-SLM is a near-net shaped method producing dense and geometrically complex materials from micrometric powder. This process involves complete melting and very high cooling rates whose induces a refinement of the grain size microstructure, improving the mechanical properties of the material [1,2]. However, the impact of these new microstructures on high temperature durability needs to be studied. In this purpose, AISI 316L, elaborated by AM-SLM and by conventional metallurgy, was oxidized under laboratory air at 900°C for periods up to 3000h.

The results highlight better behaviour for AM samples, which present a very good corrosion resistance throughout the 3000 hours. The conventional samples show a good resistance only during the first 1000 hours. These differences come from the nature of the oxide layer growing on the surface of the samples during the high temperature ageing: protective chromia for AM-SLM and non-protective iron oxides for conventional samples.

To explain these differences of reactivity, several hypotheses have been studied by XRD, SEM-EBSD and TEM, such as the composition, grain size and the crystallographic texture of the initial materials. The most promising hypothesis seems to be related of the microstructure (probably at nanometric level) of the samples. For AM-SLM coupons, a typical cellular structure was identified by TEM, with a size between 0.2 and 1 µm, corresponding to a very dense network of dislocations, which accumulate forming cell walls. Still at the nanoscale, non-metallic nano-inclusions were found in extremely large quantities and are known to influence corrosion behaviour.

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Synthesis of a fluorinated nanoporous SAPO-34 application to the adsorption of CO_2

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Abstract:

In this study, we examined the effect of the fluorinated medium on the synthesis of chabazite aluminophosphate SAPO-34, in addition, other parameters were examined such as the effect of the silica source and the concentration of silica in the synthesis medium, the synthesized samples were characterized by the different analysis techniques: thermo gravimetric analysis (TGA), X-ray diffraction (XRD), Fourier-Transfer infrared spectroscopy (FT-IR), nitrogen adsorption and scanning electron microscopy (SEM), the fluorinated SAPO-34 represents a better crystallinity that confirms the mineralizing effect of fluorine, selected solids were chosen for application of CO_2 adsorption, the results show that the fluorinated sample has the best amount of adsorbed CO_2 due to high surface area which improve the CO_2 adsorption

Keywords: Chabazite, SAPO-34, fluor, Characterization, CO_2 adsorption.

Thematic Session: (Nanomaterials)
Keywords: Heterojunction, Thin films, Bismuth vanadate -Titanium dioxide, Visible light driven photocatalysis, Characterization

DESIGN AND CHARACTERIZATION OF TiO_2-$BiVO_4$ HETEROSTRUCTURES FOR VISIBLE LIGHT DRIVEN PHOTOCATALYSIS

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Titanium dioxide (TiO_2) and Bismuth vanadate ($BiVO_4$) are well established compounds in the realm of visible light driven photocatalysis. As part of their extension into the real-life application, the fabrication of heterojunction thin films by sputtering technique has been achieved and further thermal treatment allowed the growth of the desired phases on selected substrates. The realized heterojunctions with an internal layer of Bismuth vanadate and a peripheral layer of titanium dioxide aim at enhancing the photogenerated charge carriers and their recombination life-times. These features are required to improve the photocatalysis efficiency for water purification from contaminants such as organic dyes, heavy metals etc. The characterizations have been performed on the synthesized films and the presence of suitable polymorphs as anatase (TiO_2) and monoclinic scheelite ($BiVO_4$) were identified by X-Ray diffraction analysis and transmission electron microscopy. Comparative photocatalytic efficiencies were evaluated as function of the interfaces area involved in the heterostructures.

Thematic Session: (eg. Nanophotonics & nano-optics, nanomaterials, …)
Keywords: (4-5 keywords are required)

GRAPHENE OXIDE QUANTUM DOTS SYNTHESIZED FROM BIOMASS WASTES: WHITE LIGHT EMITTING MATERIAL IN THE SOLID STATE

(Calibri 14, Bold, mauve color)

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Abstract (No longer than 250 words, Calibri 11, single line spacing, black)

Graphene oxide quantum dots (GOQDs) are part of a fascinating class of recently discovered nanocarbons that display both graphene oxide and quantum dots properties. Besides, GOQDs are extremely valuable materials owing to their electronic and luminescent properties (*e.g.* wavelength-tunable emission, excellent photostability and a high quantum yield) combined with their chemical stability, water solubility and biocompatibility.

In that context, microwave heating is becoming a fast, efficient and reliable synthetic method to prepare GOQDs, following a usual 2 steps procedure (*i.e.* carbonization and passivation). Current research is focusing on more sustainable and economical syntheses, greener chemistry and more diversified starting materials. This is why much effort has been devoted to developing new means of synthesizing nanocarbons from raw materials such as citrus fruit peels, ground coffee, orange juice, overcooked meat.

In this context, we report herein the synthesis of GOQDs from various biomass waste materials with the use of a monomode microwave reactor. After purification and separation, the prepared GOQDs were then systematically characterized in terms of chemical structure, size and photophysical properties. Very small GOQDs (≈ 1-2 nm) with identical morphological and photophysical features were elaborated regardless of their biomass waste source. The water-soluble particles show excitation-dependent photoluminescence ranging from blue to orange emission wavelength in solution. Interestingly, thin films display white light emission under UV excitation, while aggregation-induced quenching is usually observed in the solid state. This latter observation opens the way to applications in OLED devices that are currently under investigation.

Thematic Session: Nanomaterials
Keywords: Layered oxides, perovskite, functionalization, microwave

Microwave-assisted functionalization and post-synthesis modification of an Aurivillius phase : an easy approach to new functional layered perovskites

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Ion-exchangeable layered perovskites exhibit especially interesting physical properties such as ferroelectricity or optical properties for instance. One key-interest of these materials is that they can be functionalized by various mono or divalent cations, including alkyl-ammonium. This feature allows to finely tune the interlayer spacing size and content, and hopefully the properties of the final hybrid compounds.

We are particularly interested in the functionalization of an Aurivillius phase of formula $Bi_2SrTa_2O_9$ (BST), known for its ferroelectric properties. The conversion from BST to $H_{1,8}Bi_{0,2}Sr_{0,8}Ta_2O_7$ (HST) has been reported and this protonated form can be further functionalized by n-alkylamines or α,ω-diaminoalkanes. Yet, the published synthetic methods have the important drawback of being extremely long.[1,2] Due to these very long reaction times, only a limited number of amines have been tested for insertion into protonated Aurivillius phases. Moreover, this reaction timescale intrinsically limits the type of molecules which can be inserted to very stable and very simple ones. In order to overcome this problem, we have explored the microwave-assisted protonation of $Bi_2SrTa_2O_9$ Aurivillius phase and its subsequent functionalization by various amines and alcohols (including "interesting" molecules, chiral or aromatic ones for instance). We will show that this method enables to functionalize the starting BST in a few hours instead of more than a weak *via* classical conditions.[3–5]

In addition, we will present our latest results, beyond "simple" insertion, concerning the microwave assisted post-synthetic modification of an Aurivillius phase, either for the *in situ* synthesis of an organic molecule or for the controlled insertion of transition metal ions.[6]

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Thematic Session: nanomaterials
Keywords: core-shell nanoparticles, CO_2 methanation,

Core@shell nanoparticles: synthesis, properties and catalytic performances

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Conventional heterogeneous catalysts containing metallic nanoparticles (NP) supported onto an oxide carrier are usually prepared via synthesis involving interactions between a molecular precursor and the oxide surface sites. However, this approach suffers drawbacks which limit the development of new catalysts and still improvements are expected in order to solve barriers such as deactivation by thermal sintering, coke deposition or surface and bulk poisoning. In that context, the preparation of metal NP coated with mesoporous oxide shell, represents a potential breakthrough in the area of heterogeneous catalysis [1-2]. Indeed, the metal core@oxide shell systems exhibit exciting properties due to the protection effect of the shell which could reduce or inhibit the previous phenomenon. This work highlights the strong oxidation and sintering resistance of two mesoporous core@shell systems: Co@m-SiO_2 and Pd@m-SiO_2 (m for mesoporous) prepared via a modified Stöber or a precipitation method ("trapped" NP). Oxidation resistance of the metallic core has been followed under severe thermal treatments flowing air until 700°C with an in situ XRD analysis. The different core@shell systems or equivalents ("trapped" NP by precipitation) oxidize much more slowly than reference solids obtained by incipient wetness impregnation technique (same NP just deposited onto an oxide carrier, Figure 1a). Shape controlled Pd nanoparticles (cube and octahedron morphologies presenting mostly (100) and (111) facets, respectively) embedded in mesoporous silica (Pd_{cub}@SiO_2 and Pdoct@SiO_2, respectively) were used as catalysts for the CO_2 methanation and compared to a Pd impregnated reference (Pd_{imp}/SiO_2). Comparing the first order rate constants (k, moles of CO_2 converted per mole of exposed Pd atoms) (Figure 1b), Pd_{cub}@SiO_2 and Pd_{imp}/SiO_2 have similar activities and Pd_{oct}@SiO_2 is less active. Interestingly, in terms of stability, the activity of both Pd@SiO_2 catalysts increases, whereas Pd_{imp}/SiO_2 shows a significant deactivation (-35%). This fact might be due to the particle size increase (observed by TEM) and modification of the morphology of impregnated particles: decrease of corners/edges and increase of (111) facets, which seem to have lower intrinsic reactivity considering the Pd_{oct}@SiO_2 result.

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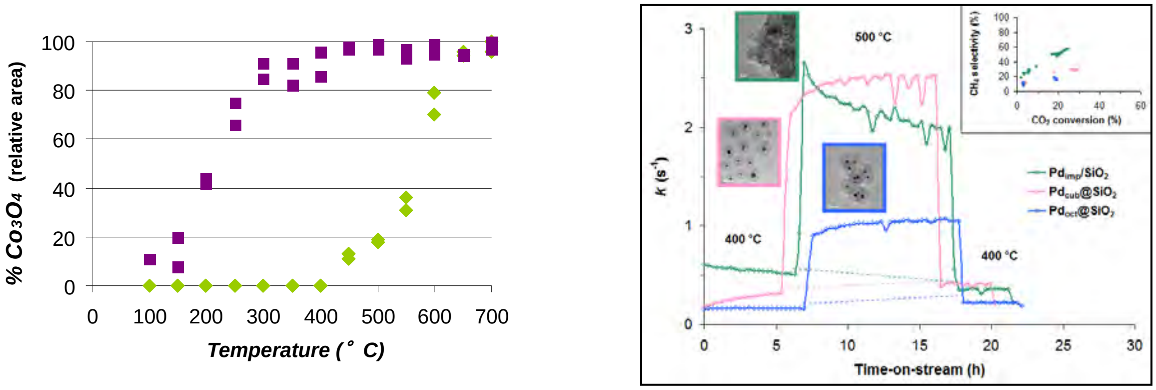

Figure 1: a Co_3O_4 relative particle size versus T for impregnated Co° (green diamond) and embedded Co°@m-SiO_2 (dark square), b: pseudo order 1 rate constant for CO_2 hydrogenation of Pd_{cub}@SiO_2 , Pd_{oct}@SiO_2 and Pd_{imp}/SiO_2

Thematic Session: (Nanomaterials)
Keywords: silicon nanocrystals; boron doping; multilayers; photoluminescence; transmission electron microscopy

Elaboration, structural and optical properties of SiO:B/SiO_2 multilayers

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Silicon nanocrystals (Si NCs) are the subject of an intense research activity, due to their original optical and electronic properties. Actually, as in the case of bulk semiconductors, the fine tuning of their optical and electronic properties is related to the effective capability to control doping, i.e. incorporation of atoms such as phosphorous or boron within these nanostructures.

We present in this study the preparation method, the structural and the optical properties of SiO:B/SiO_2 multilayers.

The multilayers were prepared by successive evaporations of SiO and SiO_2. Boron was introduced in the SiO layers during the evaporation. The films were annealed at different temperatures until 1100°C in order to obtain the dismutation of SiO which results in Si nanocrystals embedded in a SiO_2 matrix. Transmission electron microscopy (TEM) observations and secondary ion mass spectrometry (SIMS) experiments show that boron remains in the SiO layers, even for annealing at 1100°C. Electron energy-loss spectrometry (EELS) shows that boron is located either inside or at the surface of the nanocrystals.

Infrared absorption spectrometry allows us to observe an absorption band at 1380 cm^{-1} attributed to O-B bonds only for boron contents greater than 12%.

For boron contents lower than 4 % and for annealing temperatures equal to 1100°C, a band attributed to Si nanocrystals is visible near 800 cm^{-1}. For low boron contents, a PL band can also be observed in the infrared range at low temperatures. This band could be related to an electronic level of boron atoms.

Thematic Session: (Nanomaterials)
Keywords: (Lipid nanoparticles, drug delivery, miRNA, intervertebral disc)

Lipid nanocapsules for the sustained release of therapeutic miRNA: new perspective in regenerative medicine of intervertebral disc

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INTRODUCTION: Dysregulation of miRNAs, notably miR-155, has been associated with disc degenerative disease (DDD). miRNAs therapeutic applications suffers from their fast *in vivo* degradation. Thus, nanocarriers is needed. Lipid nanocapsules (LNCs) offer a suitable strategy thanks to their ability to encapsulate nucleic acids. The purpose of this work was to formulate and characterize innovative miR-155-LNCs for a potential use in DDD treatment.

METHODS: miR-155-LNCs were formulated by phase inversion process. After purification, miR-155-LNCs were fully characterized (size, polydispersity index (PDI), zeta potential). Encapsulation efficiency (EE) and drug loading (DL) were assessed by Quant-IT-dye® quantification. miR-155 release and enzymatic protection were investigated by dialysis and gel electrophoresis. The miR-155-LNCs cell internalization and the biocompatibility in human adipose stromal cells (hASC) were assessed by confocal/FACS analysis and MTT assay, respectively. Then, the bioactivity was confirmed by RT-qPCR and Western blot.

RESULTS: miR-155-LNCs exhibit a diameter of 75.0 ± 1.3 nm, a PDI of 0.06 ± 0.03 and a positive zeta potential. EE and DL were estimated to 75.2 ± 1.2% and 590 ± 9.3µg/g of LNC respectively. miR-155 sustained release from LNCs was observed. miRNA endonuclease protection by LNC was confirmed by electrophoresis. After 24 h of incubation of miR-155-LNCs, hASC viability was of 71.66% ± 4.23% for 59 ng/mL of miRNA. Internalization and bioactivity of miR-155-LNCs in hASC cells was also demonstrated.

CONCLUSIONS: LNCs could be promising approach to protect and deliver therapeutic miRNA. Further *in vivo* experiments will be needed to confirm the interest of this nanoplatform in order to counteract DDD.

Thematic Session: Nanomaterials
Keywords: Aerogel; Silver Nanowires; Freeze-drying; Ice-templating

Extra Low Density and High Porosity Conductive Silver Nanowires Aerogels

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S. S. Kistler discovered aerogels in 1931 and since the seventies this class of materials has attracted high attention, mainly for sound and heat insulation, due to their very low density, and high porosity.[1,2]

Herein are studied new aerogels made from silver nanowires (AgNWs). High electrical conductivity, high porosity and very light-weight are expected for these nanostructures.

This study is in continuation to previous developments carried out in our laboratory for the fabrication and the integration of metallic nanowires[3–5].

First, we will present the fabrication process which is based on the assembly of nanowires into a 3D network from suspensions in water by a simple freeze-drying process. Cryoprotectants were used to control the ice crystal formation, ice-templating the spatial organization of the 3D network. Aerogels made from AgNWs with various dimensions and different embedding agents such as PEDOT and cellulose are compared.

The structures are characterized by their very high porosity and very low densities (few mg.cm^{-3}) coupled with high specific surface areas (hundreds of m^2.g^{-1}) and high electrical conductivities (hundreds of S.cm^{-1}). The link between structure and properties will be studied to bring a better understanding of the effect of network density, nanowires' aspect ratios and post-treatments. Low-temperature electrical measurements (3K-350K) with electrical conduction mode modelling are also ongoing to determine the electrical conduction mechanism in the aerogels.

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Thematic Session: Nanomaterials
Keywords: nanoclusters, gold, synthesis, n-heterocyclic carbenes, functionalization,

Gold nanoclusters synthesis and functionalization aiming at properties enhancement.

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Gold nanoclusters (Au NCs) have been an attractive frontier of nanoparticle research due to their small size (1-2 nm). Indeed, these smaller particles lose their metallic character and behave like molecular entities: they exhibit unique properties such as an enhanced catalytic activity and luminescence. At this size, the plasmon band is no longer clearly identifiable by UV spectroscopy but their fluorescence properties make it possible to use them in the biological field for example. [1] They are also widely used in oxidation catalysis of CO because of the gold surface reactivity. [2] The past few years have witnessed the development of many successful strategies for the preparation of stable Au NCs capped by organic molecules. The influence of the nature of the ligand on the Au NCs has been widely studied: results proved that depending on the ligand, Au NCs properties can be modulated. [3]

Recent works showed the stabilization of gold nanoclusters by N-heterocyclic carbenes (NHCs). NHCs feature a strong metal-carbon single bond which was proven to be stronger than the one with thiols.[4] They are also compatible with post functionalization reaction steps which could improve the stability of Au NCs.[5] Different synthesis methods have been explored such as ligands exchange [6] and direct synthesis. [7] [8]

Our group interest is to develop a new synthesis method of N-heterocyclic carbenes (NHC) capped Au NCs based on our previous experience with NHC gold nanoparticles functionalization [9]. This synthesis is based on the use of imidazolium salts as NHC precursors, gold salt $AuClPPh_3$ and $NaBH_4$ as a reducer.

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Thematic Session: Nanomaterials
Keywords: Nanoparticles synthesis – Continuous hydrothermal process – $Ba(Ce,Zr)_{1-x}Y_xO_{3-\delta}$ – Protonic Ceramic Fuel Cell

Continuous hydrothermal synthesis of doped barium zirconate powder for PCFC application

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Perovskite materials (ABO_3) have been widely studied in the past decades due to their attractive properties in term of conductivity, optoelectronic, magnetic or ferroelectric behavior. In this study, $Ba(Ce,Zr)_{1-x}Y_xO_{3-\delta}$ materials are focused due to their remarkable property of protonic conduction at intermediate temperature (400-600°C). For example, Fabbri et al. have reported a protonic conductivity of 2.10^{-2} $S.cm^{-1}$ at 600°C for $BaCe_{0,7}Zr_{0,1}Y_{0,2}O_{3-\delta}$ [1]. This property allows them to be applied in many areas such as electrolyte materials for Protonic Ceramic Fuel Cells (PCFC).

However, the most common way to synthesize these materials is the solid-state reaction requiring high temperatures (1700°C) and giving rise to particles of micrometric dimensions [1] making their sintering ability really difficult. In order to decrease the very high sintering temperature of such compounds (1900°C), this work focused on a synthesis method for obtaining nanoscale particles. Then, a continuous hydrothermal process in supercritical conditions was used to synthesize $Ba(Ce,Zr)_{1-x}Y_xO_{3-\delta}$ ceramic oxides. This process allows the formation of several nanometric powders [2]. In addition, supercritical hydrothermal synthesis has many advantages such as it's a "soft-chemistry" route at a low cost and with high purity. Finally, the continuous hydrothermal process developed in our group since 2001 allows a large scale production (about ten grams per hour).

In this presentation, the synthesis process will be described and the final obtained products characterization by SEM and XRD will be presented. Finally, the possible application of these materials as electrolyte for PCFC will be discussed.

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Thematic Session: Nanomaterials
Keywords: peptides, oral, solid lipid nanoparticles, nanostructured lipid carriers, Hydrophobic Ion Pair

Evaluation of solid lipid nanocarriers to increase peptide oral bioavailability

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Therapeutic peptides can treat a wide variety of diseases with specific and potent action. However, their oral bioavailability is strongly limited by enzymatic degradation in the intestinal lumen and poor permeability across the intestinal epithelium[1].

The objective of this study was to evaluate and compare the ability of Solid Lipid Nanocarriers (SLN) and Nanostructured Lipid Carriers (NLC) to encapsulate, protect and increase the intestinal permeability of Leuprolide (LEU), a model hydrophilic nonapeptide.

To increase peptide lipophilicity a Hydrophobic Ion pair (HIP) was formed by complexation between LEU and sodium docusate[2]. The HIP was loaded in SLN and NLC obtained by High Pressure Homogenization using Precirol®ATO5 (glyceryl distearate), Kolliphor®RH40 (PEG-40 Hydrogenated Castor Oil) and eventually Capryol™90 (propylene glycol monocaprylate) for NLC. The systems were characterized regarding their size, polydispersity index, morphology, encapsulation efficiency and drug loading. Evaluation of the protective effect of the nanoparticles was done in presence of trypsin. Interactions with the intestinal barrier were studied with an enterocyte-based (Caco-2 cells) and a mucin-secreting (Caco-2/HT29-MTX) intestinal models[3].

A precipitation efficiency of 99.9% indicated a successful formation of the HIP. Its encapsulation in SLN and NLC significantly improved LEU loading[4]. The nanoparticles were platelet-shaped and measured 120 nm. NLC demonstrated a significant protective effect towards trypsin-induced degradation. Both nanocarriers were highly internalized by Caco-2 cells and were able to cross the mucus barrier. However, stability of LEU HIP needs to be improved to withstand biorelevant conditions.

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Thematic Session: Nanomaterials

Keywords: Patchy, nanoparticles, self-assembly.

Synthesis of patchy nanoparticles for self-assembled diamond-like structure

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For years the scientific community has been investigating the synthesis of particles having the ability to self-assemble into superstructures. By making these particles anisotropic, the notion of valence can be replicated at the colloidal scale to manage the particle-particle interactions and lead to directional assemblies. This concept is known as patchy particles [1] which can be seen as colloidal atoms endowed with a specific valence, limiting the number of nearest neighbors and imposing a predefined geometry to the assembly. Theoretical studies have in particular shown that the self-assembly of spherical particle with four patches on their surface can lead to the self-assembly of diamond-like structures which exhibit interesting photonic properties [2].
We describe here the synthesis of silica nanoparticles with four patches organized in a tetrahedral configuration by the selective growth of the silica core of binary colloidal molecules obtained by seeded-growth emulsion polymerization of styrene. The kinetics of the silica growth has been carefully studied, which allowed us to develop a multistep approach to avoid unwanted formation of silica nanoparticles.

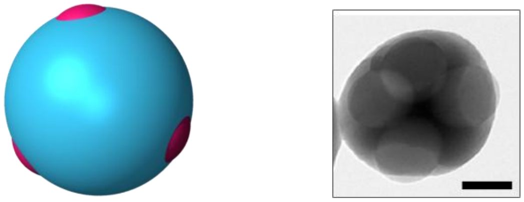

Figure: Scheme and TEM image of a 4 patch-silica particle. Scale bar: 100 nm

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Thematic Session: Nanomaterials,
Keywords: 2D materials, Exfoliation, Functionalization, Layered Transition Metal Oxide

Mechanical-assisted liquid exfoliation of functionalized transition metal oxide

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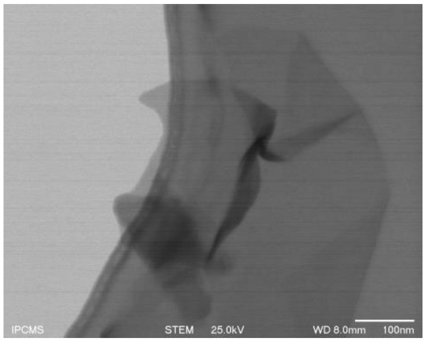
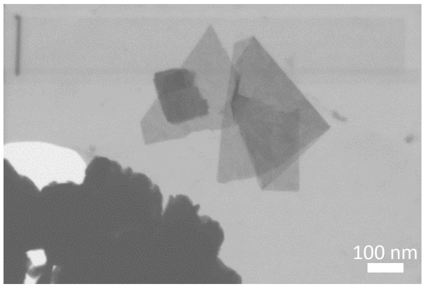
As 2D materials display very exciting properties, plenty of synthetic approaches have emerged and are still being explored. The bottom-up ones result in highly crystalline flakes with a controlled lateral size[1]. On the other hand, top-down method might appear less performant especially in crystallographic aspects. However, liquid phase exfoliation of layered materials is a promising way to reach the quality of bottom-up-synthesized materials[1, 2].





Indeed, inorganic nanosheets are commonly produced by the use of a delaminating agent (*e.g.* the bulky tetrabutylammonium cation) whose insertion into the interlayer space leads to the decrease of the slabs' interactions and their exfoliation[3]. However, regarding the long time process of this chemical approach, mechanical exfoliation in liquid media might appear as a suitable alternative[1-4]. Indeed, Coleman *et al*. have developed an exfoliation process based on an applied shear-force gradient on Van der Waals layered materials[5]. This procedure may be applied to charged transition metal oxide slabs if beforehand the strong interactions between them are decreased. This promising strategy thus relies on the prior functionalization of the inorganic layered materials before exfoliation step. The resulting 2D materials are then obtained as colloidal decorated nanosheets in suspension, whose the properties might be tune by the grafted molecule.

Herein, we report a short way to get colloidal functionalized nanosheets with a large lateral size. The starting inorganic material is a lamellar transition metal oxide ($H_2Bi_{0.1}Sr_{0.85}Ta_2O_9$, $HLaNb_2O_7.xH_2O$ or $H_xTi_{2-x/4}\square_{x/4}.H_2O$). It is functionalized with alcohols by microwave assistance according to our published procedure[7-9]. We focused on two simple grafted molecules: dodecan-1-ol and benzyl alcohol. The subsequent exfoliation procedure is based on shear-force in liquid media thanks to a high-speed disperser. We will present here the Influence of the exfoliation conditions (nature of the inserted molecule and of the solvent, disperser speed and exfoliation time) on the obtained nanosheets.

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Thematic Session: nanomaterials

Keywords: (flexoelectricity, nanomanipulation, carbon nanotubes, energy harvesting)

Flexoelectric coefficient of single carbon nanotubes

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Flexoelectricity is the proportionality between stress gradient and electric polarization of a material and was rarely considered for electromechanical transduction because of its small relative importance for macrosystems. However, flexoelectricity can be obtained from any material, unlike piezoelectricity which requires that the material unit cell be non centro-symmetric. Furthermore, the flexoelectric effect increases as the scale of the system goes down, hence the idea to use this effect in a nanosystem that would harvest energy for a micro-device .

Since multi-wall carbon nanotubes (MWCNTs) are quite flexible, very stable and possess interesting electric properties, we would like to study their potential for the generation of flexoelectricity from mechanical deformations. A first study of this kind, presents experimental results on a thin film filled with MWCNTs bearing PZT microparticles.

We have started exploring the flexoelectric capabilities of single MWCNTs through their manipulation with a SEM-FIB based microrobotic system along with computer vision tools. We managed to grip and bend single MWCNTs of about 30 nm diameter, while tracking the region of bending over successive images and computing its brightness. Preliminary experiments showed an increase of brightness with respect to an increase of bending , possibly related to the excess charges due to the polarization of the MWCNT as a result of the imposed strain gradient (flexoelectric effect). Our ultimate goal is to transform these measurements of brightness into measurements of local charges so as to be able to compute the effective flexoelectric coefficient of the bent MWCNT.

Thematic Session: Nanomaterials
Keywords: ink-jet printing, laser sintering, optical sensor, AZO nanostructures

Effect of laser sintering on Al-doped ZnO thin films prepared by ink-jet printing

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In this study, laser sintering of aluminum doped ZnO (AZO) nanoparticle films printed on silicon substrate was conducted in order to improve their homogeneity and flatness. Our studies were focused on the printing of AZO-based formulations by the inkjet printing (IJP). This technology behaves some advantages like a single-step deposition of the functional material on flexible or rigid substrates. Besides, it is a low-cost and contactless method. Piezoelectric drop-on-demand printer was used to deposit AZO nanoparticles on a silicon and glass substrate. Two nanoparticle shapes were studied and the printing parameters were optimized. For the ink preparation, isotropic spherical nanoparticles and nanoplatelets of AZO were firstly synthesized by aqueous coprecipitation. AZO solvent-based formulations properties were characterized such as viscosity, ink stability and nanoparticles dispersion. Once the AZO thin layer was deposited by IJP, sintering was carried out thanks to a nanosecond-pulsed Nd:YAG and KrF excimer lasers. Then, thin film morphological properties were investigated by scanning electron microscopy (SEM) and structural properties by X-ray diffraction (XRD).

The SFNano C'NANO joint meeting 2019

Thematic Session: Solar Energy

Keywords: Conducting polymer, polypyrrole, H_2 generation, photocatalysis

Conducting polymer nanostructures for photocatalytic applications

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ABSTRACT

Conducting 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 depollution of water. PPy nanostructures were synthesized by 2 different methods: (i) by chemical polymerization in confined oil domain of the hexagonal mesophase used as a soft template (PPy-c), (ii) by radiolysis (PPy-γ), and bulk PPy was synthesized by chemical oxidation without any template (PPy-b). Among these three samples, PPy-c shows the best photocatalytic activity for water treatment under UV light, while PPy-γ exhibits the highest activity under visible light5. These samples were characterized by different techniques: SEM, TEM, NanoIR, FTIR, UV-Vis spectroscopy, cyclic voltammetry. We modified PPy nanostructures with co-catalysts based on mono- and bimetallic nanoparticles (Pt, Ni, and PtNi) for H2 production. The modified PPy nanostructures give also promising results for hydrogen generation under UV-vis light. The effect of the nature of the metal precursors and their loading were studied.

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Thematic Session: (**C'Nano specific sessions** Solar energy)

Keywords: Ni-Al_2O_3 nanocomposites thin films, electrophoretic deposition, solar thermal energy

Ni-Al_2O_3 nano-composites thin films obtained by EPD for solar energy application

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2. *CNRC, Canada.*

Abstract:

Ni-Al_2O_3 nano composites coatings of various compositions (Ni 25%, 50%,75%) on aluminum substrate are obtained by elecrphorectic deposition EPD..

Phase composition, ceramic and metal crystallite size of obtained nanocomposite coatings were examined by XRD technique (using a Bruker D8 Discover diffractometer equipped with a position-sensitive linear detector and multi-capillary primary optics) in dependence on nickel particle content.

The nanocomposites coatings surface morphology microstructure were examined by SEM, whereas the chemical composition (ceramic phase content) was determined by energy dispersive spectroscopy (EDS) analysis. Reflectance is measured by uv-visible spectrophotometer with integrated sphere (UV2600).

It was found that the Ni Al_2O_3 nano composites coatings with Ni 75% composition exhibited better optical properties of absorptance /thermal emittance .

The SFNano C'Nano joint meeting 2019

Thematic Session: Nanoplastics & Nanocomposites

Keywords: Plastic scintillators, nanostructures, composites, radiation detection

Nanostructured plastic scintillators for enhanced radiation detection

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Many molecular nuclei emit naturally (or man-made) radiations through unstable isotopic forms in order to gain more stability. The energy supplied during this phenomenon is used in various domains, for instance medicine, power supply, etc. Despite the numerous benefits, radiations need to be handled with caution and identified precisely, due to high hazardous potential while emitted particles interact with biological media. The precise identification in a reduced time of exposure is paramount for workers and persons exposed. Current hand-held radiation detectors are limited in performances, namely to discriminate beta radiation in high and fluctuating gamma environments, and in terms of sensitivity.

Our Research project uses unique properties offered by nanoscale technologies to improve sensitivity and overall performances of plastic scintillator based radiation detectors. The proposed solution relies on the incorporation of optically active nanostructures on the material surface in order to control the scintillation photon directivity and to enhance the spontaneous emission rates. In order to obtain such effects it is however necessary to increase the refractive index of these materials. This is achieved by incorporating nano-objects of higher refractive index, i.e. diamond nanoparticles (NDs). Those modifications will lead to improve sensitivity, better discrimination capabilities between beta and gamma radiation and better reliability regarding to handheld detectors. Through the session, we will show the methods used to obtain our polymer matrix, the different steps to nano-pattern and the integration of nanomaterials into the matrix. The novel properties of these nanocomposites will be discussed as well.

Thematic Session: Nanochemistry : synthesis & functionalization of nanosystems for bioapplications, Nanomaterials
Keywords: Core-shell nanoparticles, nanoplatform, synthesis, functionalization, biosensing.

Elaboration of silica coated gold nanorods (AuNR@SiO$_2$) towards versatile nanoplatforms for biomedical applications

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Core-shell AuNR@SiO$_2$ nanorods are hybrid nanocomposites of great interest for their use in bioimaging, targeted drug delivery, photothermal therapy and biosensing. Silica as an outer shell coating material is known to improve the colloidal and thermal stability while preserving the optical properties of the core. It can then be used as a nanoplatform for further functionalization or bioconjugation[1]. A fine control of the coating procedure yielding reproducibly a thin silica shell in the absence of self-nucleated homogeneous silica particles is crucial in order to get efficient nano objects for such applications. It proves to be a real challenge yet poorly discussed in the literature. We report here such formations of silica coating with various shell thicknesses and pore topographies through the classic Stober method using silanes such as tetraethylorthosilicate (TEOS) or using MPTMS (3-(mercaptopropyl)-trimethoxysilane) and sodium silicate for water based techniques[2].

In this work, we explore the influence of the pH as a key parameter for the hydrolysis/ condensation of TEOS and pore organization within the silica shell and the use of MPTMS as a linker prior to TEOS condensation. Therefore, three strategies were compared to synthesize core-shell AuNR@SiO$_2$ leading either to a thick and porous silica shell where pores are found to be perpendicular to the surface (*Figure A);* a thin and non porous silica shell around the surface (*Figure B);* and to a thick silica shell were pores are parallel to the surface (*Figure C*). We will then show how, due to their high sensitivity of refractive index change in the surrounding medium compared to other particles, AuNR@SiO$_2$ were finally functionalized and conjugated with antibodies to develop a localized surface plasmon resonance (LSPR) based sensor of high stability and sensitivity. For these properties, AuNR@SiO$_2$ are first choice candidates for biomedical applications.

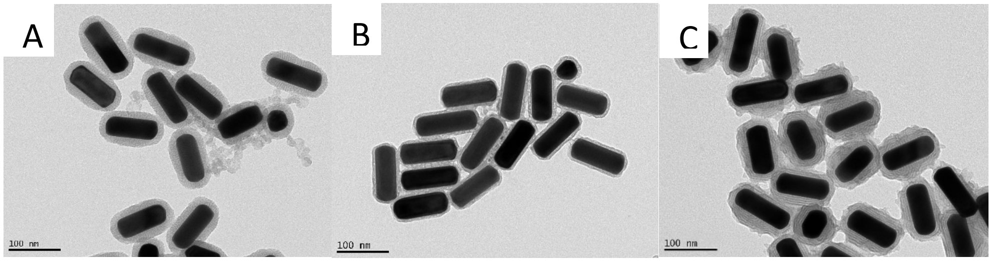

Figure: TEM images of (A) AuNR@SiO$_2$ from strategy 1 (B) AuNR@SiO$_2$ from strategy 2; (C) AuNR@SiO$_2$ from strategy 3

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Thematic Session: Nanomaterials
Keywords: Lanthanides, Nanoparticles, UpConversion, Luminescence

Supramolecular Nanohybrid architectures for Optimized UpConversion through controlled enERgy migration

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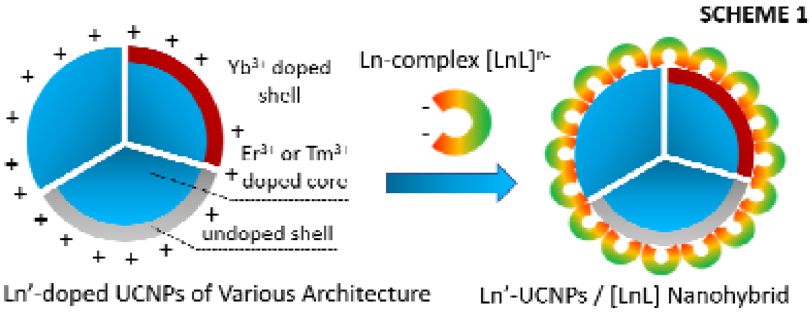
The development of UpConverting nanoparticles (UNCPs) has greatly impacted the field of biomedicine [1]. This interest is due to the low background signals from biological tissues and deeper penetration depths into it when the excitation with NIR light matches the biological transparency window [2]. Such materials can be designed with lanthanides-containing nanomaterials and molecules [3] to organic/inorganic nanohybrids in order to enhance UpConversion (UC) efficiency. The project aims at designing a material fitting this description and is presented in scheme 1. We will present the main techniques used to obtain such material.



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The SFNano C'NANO joint meeting 2019

Thematic Session: Nanomaterials
Keywords: Nanocolloids, Charge, Patches

Synthesis of Inverse Patchy Nanoparticles

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Colloidal structures prepared by self-assembly find applications in photonic devices, nanoscale electronics and miniature diagnostic systems. This colloidal self-assembly enables easier and cost-effective fabrication compared to standard fabrication methods based on top-down approaches such as optical lithography. However, this bottom-up approach is limited by the available building blocks that are mostly spherical and by the interactions between them, which are mostly isotropic. To expand the range of building units, one emerging approach is to engineer the surface of the colloidal particles with "patches" to confer particles predetermined "instructions" for assembly [1].
In this work, we focus on the synthesis of inverse patchy nanoparticles (IPNs) [2], that consist of charged patches that repeal each other and that are attracted by the rest of the nanoparticle (Figure 1). We will first show that binary bipods, which consist in a silica nanoparticle surrounded by two polystyrene nodules, can be produced with a yield higher than 95% by seeded emulsion polymerization. The regioselective functionalization of the silica surface followed by the dissolution of the PS nodules allowed us to produce IPNs in large quantities.

Figure 1: Scheme of electrostatic interactions between inverse patchy nanoparticles

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