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Oral presentations

Plants are fighting back against metals: An example of “green” (bio)(geo) inorganic chemistry

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Since the industrial revolution, industrial activity, and more especially metallurgy of non-ferrous metals, induced the contamination of large agricultural areas with trace metal elements. The use of amendments coming from the processing and re-use of sludges from wastewater treatment plants or of dredged sediments is another way for these metals to enter the soil and the associated ecosystems. Although they are necessary for plant growth when present at low concentrations, metal elements can be toxic if the concentration “available” to the plant becomes too high in the soil. These concentrations remain too low to be economically interesting, however, and the surface areas of impacted terrains makes it unrealistic to extract these non-degradable contaminants.

When confronted to such soil pollution, some plants have developed a strategy to reduce their exposure to trace metal elements by turning them into solid and insoluble precipitates. The modification of the metal chemical form (their speciation) reduces in turn their toxicity. Such a protection mechanism has been reported in some grasses grown on soil amended with sediments highly contaminated with zinc and other metals. The formation of metal precipitates at the surface of grass roots was observed after a few months of cultivation, reducing plant exposure to the contamination and allowing their “normal” growth.

This presentation will present a set of experimental results aiming at the determination of the composition and structure of these precipitates, their location in relation to the plant roots, but will also explore hypotheses about the mechanisms used by the plant for self-protecion.

Recycling better metals to be found in everyday technological objects : Why and how ?

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This presentation will first give a brief overview of the meaning of ‘urban mines’ (volumes, contents etc.). Then the chemistry principles of aqueous biphasic systems (ABS)[1], will be detailled. These systems are innovative ways to recover metallic elements from urban mines. Examples will deal with recent results of our group, in particular about NiMH batteries.

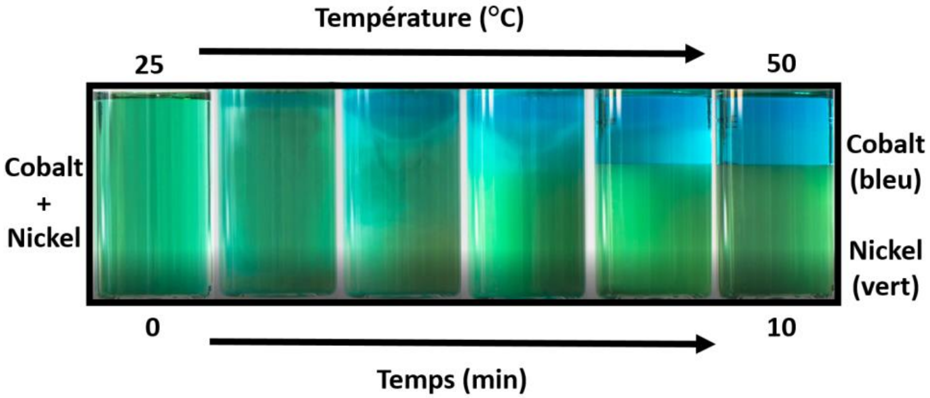

Figure 1 : passage d’un état monophasique à biphasique en fonction de la température et séparation subséquente du couple cobalt/nickel.

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Developing new antibacterial molecules: a needle in a haystack ?

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In the last two decades, the prevalence of infections related to multidrug resistant bacterial strains has raised dramatically. Nowadays, 65% of the bacterial infections in hospital centres are due to six pathogens classified as 'ESKAPE' because they escape to the action of most of the antibacterial drugs available on the market by the mean of multiple resistance mechanisms. Developing new classes of antibacterial agents is therefore becoming one of the biggest challenges in human health for the next decade.

The involvement of chemists in this process is of crucial importance, not only for the design of original structures, but also when it turns to the elucidation of their mechanisms of action or for the improvement of their physicochemical/pharmaceutical properties.

We are currently developing two classes of synthetic compounds possessing some original structures and mechanisms of actions.[1,2] In the course of these studies, our academic chemist points of views are confronted to problems with multiple variables on a regular basis. Some examples of this confrontation will be provided here.

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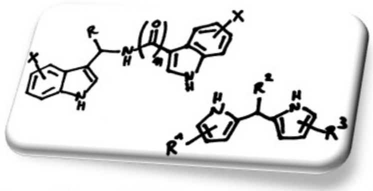
Composés antibiotiques originaux



https://www.linksium.fr/projet/act-on-bact/

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technology transfer & startup building
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Molecular approaches to artificial photosynthesis and solar fuel production

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Photosynthesis is a fascinating source of inspiration to design innovative molecular devices, typically dye-sensitized photoelectrochemical cells, for the conversion and storage of solar energy under a chemical form, a "solar fuel" such as hydrogen H_2.[1]

Our research efforts regarding the construction of dye-sensitized photocathodes for H_2 production from water and sunlight will be presented,[2] together with the molecular strategy behind the development of an artificial photosynthetic system for charge photoaccumulation.[3]

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Tracing nitrate in a subalpine watershed, or the unexpected journey of an isotope from the stratosphere to the prairies

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Mountain hay meadows are a heritage habitat with high conservation stakes. Nitrogen, as a limiting nutrient, has strong control over plant growth and community composition, on which many ecosystem services (carbon storage, water quality maintenance, forage quality, etc.) depend. Nitrogen inputs to these high-altitude ecosystems have recently increased[1] and are expected to increase further in the coming decades, as a result of both anthropogenic atmospheric deposition and changes in agro-pastoral practices. This combines with changes in snow cover and summer precipitation, with important uncertainties concerning the relative importance of those drivers.

Isotopes have long been used to trace sources of or processes affecting various chemical compounds in the environment. Nitrate, which represents an important fraction of atmospheric nitrogen deposition, has long been traced in ecosystems by a dual isotopes approach ($\delta^{15}N$ and $\delta^{18}O$). Recently, a novel isotope indicator has been developed. Photolysis in the stratosphere induces a mass independent fractionation that results in a strong ^{17}O anomaly, noted $\Delta^{17}O$ in stratospheric ozone. This anomaly gets transferred to tropospheric nitrate through mixing and O_3 - NO_x reactions, giving atmospheric nitrate a unique signature, which can be used to directly measure the processing of atmospheric nitrate in ecosystems[2].

Applying this strategy at the col du Lautaret, we could show that a fraction of atmospheric nitrate is not processed by the ecosystem. This fraction depends on topography and water transfer velocities, and more interestingly on plant types[3], which in turn is heavily influenced by former extra nitrogen inputs due to agro-pastoral practices. This evidences the possibility of landscape bifurcations due to inadvertent atmospheric nitrogen inputs[4].

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Biomimetic Optoelectronic Tongues/Noses for Imaging Taste and Smell

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Nowadays, there is an increasing demand for novel tools for reliable, inexpensive and rapid analysis in diverse domains. On the one hand, traditional techniques such as gas chromatography and mass spectroscopy, though accurate and reliable, are often time-consuming and laborious to perform. They can provide a complete component-by-component analysis for a mixture sample; however, they are not able to give any sensory information. On the other hand, food & fragrance industries employ human sensory panels to evaluate the quality of a taste and/or an odor. However, sensory methods are also time-consuming. Panelists are expensive to train and employ and they can give biases on results. All these approaches are thus impractical for their use in a larger scale.

To bridge the gap, an interesting alternative could be miniaturized multi-sensor systems such as electronic tongues (eTs) and electronic noses (eNs). They are engineered to mimic the mammalian olfactory system, consisting of an array of low-selective sensors with cross-sensitivity to different species in complex mixtures and using advanced mathematical procedures for signal processing based on pattern recognition and/or multivariate analysis. The last three decades have witnessed great progress in their development. Nevertheless, most existing commercial devices are based on few non-specific sensors having different physical adsorptions and they suffer from a general lack of selectivity. Thus, they are limited for the fine discrimination of samples with similar structures and properties.

In this context, we have developed innovative biomimetic optoelectronic tongues[1-4] and noses[5,6] based on an optical detection system, surface plasmon resonance imaging. The obtained eTs and eNs are capable of generating temporal responses with vivid 3D images or barcodes as "fingerprints" for the differentiation and identification of the samples in liquid and in gas. Based on our eN approach, the start-up company Aryballe Technologies was created in 2014 for the miniaturization of the eN.[7] In 2017, the first portable and universal odor detection and identification device, NeOse, was developed. It has promising applications for food and beverage industries, fragrance and cosmetic industries, and air quality control, *etc*.

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Cellulose nanofibrils chemical pretreatment for producing functional materials by twin screw extrusion

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Cellulose Nanofibrils (CNF) are considered as one key priority in European bioeconomy since 2016. They are highly performant and biobased materials already used in composite, paints or medical application.

Chemical modification of cellulose fibers is considered as an efficient solution of pretreatment for CNF production. Such strategy represents today around 25% of the studies concerning nanocellulose. Many pretreatments are now available to improve the nanofibrillation of cellulose fibers. They lead to CNFs with low energy processes and different qualities to address particular applications.

Meanwhile a new mechanical process, i.e. the twin screw extrusion, has been developed for producing high solid content CNF. This process is not possible without any pretreatment and this study is an overview of the interest of various pretreatment especially for this extrusion process. Several pretreatments like oxidation with tempo or with ozone have been performed. The CNF obtained have been analyzed with a quality index procedure. Good quality CNF suspensions have been obtained in spite of non deteriorated micrometric fibres. A special focus onto fibre phosphorylation will be proposed. The adsorption and the effect of phosphorylation on cellulose fibers was studied using elemental analysis, solid 13C and 36P NMR or conductimetric titration method. Different phosphoric salts with different constants of solubility were used to optimize the pretreatment adsorption kinetic and efficiency. Then, phosphorylated CNFs of different quality were produced using a twin screw extruder process recently developed for other pretreatments. In some case, CNF nanopaper with high Young's modulus and high transparency were successfully obtained. Moreover, the method offers fire retardancy properties to CNF which may be very interesting in many applications, such as composites, buildings or coatings

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Electrocatalysis of oxygen reduction reaction for proton exchange membrane fuel cell application

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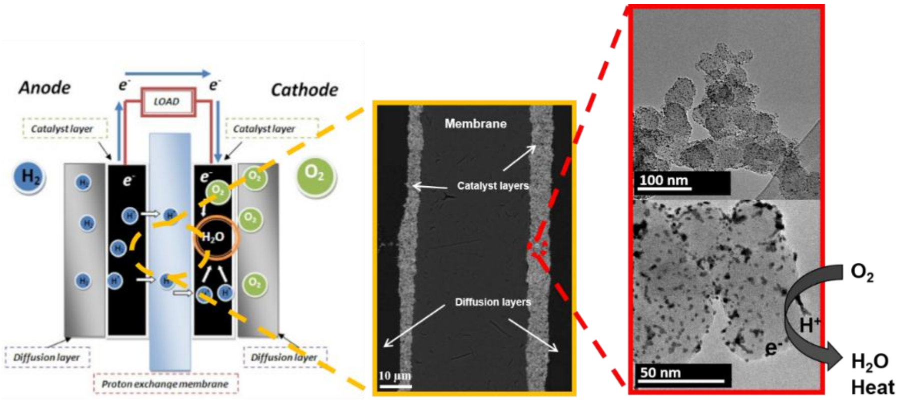
The ever-growing energy demand worldwide and the announced end of the so-called “fossil fuel era” are currently boosting the development of electrochemical energy technologies, such as fuel cells, batteries and supercapacitors. In proton-exchange membrane fuel cells (PEMFC), special effort has been paid to improve the catalytic activity for the oxygen reduction reaction (ORR) of the cathodic material, its stability and to decrease its precious metal content. Pt/C or bimetallic Pt_3M/C electrocatalysts (with M = Cr, Fe, Co, Ni, Cu) are now classically used at the cathode because of their enhanced oxygen reduction reaction (ORR) activity (Figure 1). However, an increased ORR activity is meaningless if it cannot be maintained over time.

This presentation will describe the stability issues encountered by Pt_3M/C cathode materials in model and real operating conditions [1]. From this results, mitigation strategies in terms of design of architectured nanoparticles will be addressed [2,3].



Electrochemical reactions occurring in a PEMFC.

SEM image of a MEA cross-section.

TEM images of a Pt/C catalyst.

Figure 1. Components of a single PEM fuel cell: schematic (left); scanning electron microscopy (SEM) image of the MEA (middle) and transmission electron microscopy (TEM) images of a commercial Pt/C catalyst

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Organic Nanocrystals for Bioimaging

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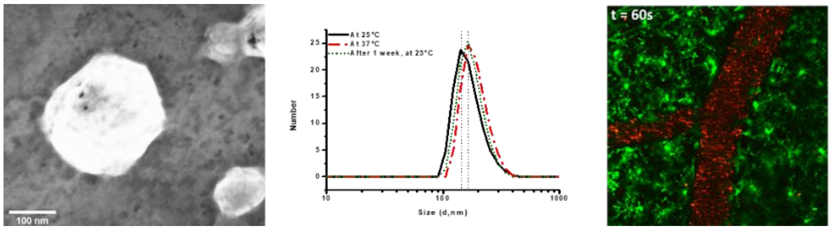
Fluorescence imaging may constitute a valuable tool for bio-imaging, provided highly fluorescent and safe biotracers are developed. In particular, three-dimensional, deep-tissue imaging may be improved following the development of two-photon emitting probes excited and emitting in the biological transparency window. Silica-based nanoparticles are widely used for bioimaging, as the silica matrix is biocompatible and can be easily surface-modified to target cancer tissues or induce stealth in biological fluids. However, the dye loading in such cases is usually very low, which limits the overall brightness. Following the groups' experience in organic nanocrystals, we were interested in developing nanoparticles of organic fluorophores displaying high two-photon absorption cross sections and bright emission in the red-NIR region in the crystal state following a dye engineering at ENS Lyon. This strategy allows a very high loading in organic fluorophores while keeping a strong brightness.[1] In this talk, we will show that nanoparticles featuring a crystalline organic core and a silicate shell can be produced in one step thanks to the spray-drying technique,[2] and functionalized in water with PEG chains using click reactions to provide colloidal stability in biologically-relevant media. *In vivo* imaging of mice vasculature revealed the very strong brightness of such nanoparticles.[3] Furthermore, colloids of crystal-state emitters can be produced using an original sono-crystallization technique. The application of such colloids for imaging of cancer cells under two-photon excitation will be presented. In particular, the crystallinity of the organic fragments will be discussed on the basis of electron diffraction studies. Furthermore, such organic nanocrystals are ideal candidates to develop a new crystallography methodology based on DNP-enhanced solid-state NMR experiments. ^{13}C-^{13}C and ^{13}C-^{14}N 2D sequences indeed allow to extract the matrix of distances between atoms, from which the 3D structure can be deduced.



SEM image of an organic nanocristal constituting the core of an organic@silicate NP ; DLS of a colloid of such NPs and imaging of the brain vasculature of a mice using such colloids.

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Posters

A peculiar nickel binding site: *Rr*CooT single cysteine motif.

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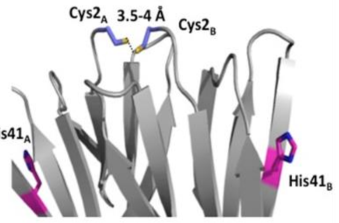
CODH reversibly oxidized CO into CO$_2$ and plays a central role in carbon metabolism of anaerobic microorganisms, determining their ability to use CO as carbon and energy source. The crystal structures of CODH from C. hydrogenoformans and R. rubrum[1] revealed a unique active site: a [NiFe$_3$S$_4$] cubane coordinated to a mononuclear iron site, known as C-cluster. While the reaction mechanism of CODH is well established[2], very little is known about the activation of the C-cluster. Nickel insertion is essential for the enzyme activation and requires the intervention of the accessory proteins CooC, CooJ and CooT, able to supply the nickel into the CODH.



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RrCooT
12
MCMAKVVLTKADGGRVEIGDVLEVRAEGGAVRV
        41
TTLFDEEHAFPGLAIGRVDLRSGVISLIEEQNR
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Fig. 1 Sequence and structure of dimeric apo-CooT. The Cys2 and His41 are highlighted as main possible players in the metal binding coordination.

The CooT study, recently published by our group[3], reported the ability of this protein to bind one nickel per dimer with high affinity (Kd=9 nM). In addition, the crystal structure of the apo-protein shown that the possible amino acids involved in the metal coordination, Cys2 and His41, are too far apart from each other to be both contributing to the final nickel coordination. (**Fig.1**) Here we present our recent biochemical characterization of holo-CooT, reporting its peculiar nickel coordination motif. The only cysteine, present in second position in sequence, has been recognized as the main protagonist in the nickel binding coordination, highlighting the importance of the N-terminal amino acids. The proposed binding model, characterized via CD, EXAFS, NMR and mutants and computational studies, is going to be shown. This work proves for the first time, based on our current knowledges, a nickel binding coordination supported just by a single cysteine in the N-terminal solvent exposed sequence.

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At the interface of the material world:
DNP enhanced ssNMR of ZnO nanocrystals

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Zinc oxide nanoparticles (ZnO NPs) are versatile materials with applications in numerous fields such as solar cells, optics, sensing, and catalysis. Hence, it has become important to optimize synthetic methods to produce these NPs with tunable properties. The shape, size, and composition determine their suitability for a particular application. Producing a particular shape can involve selective adsorption of ligands to specific facets, ligand adsorption energy and coverage, surface energy of unpassivated surfaces, temperature, and polarity of facets. Thus, to understand how the NP acquires a particular morphology, it is important to study the interactions at the NP-ligand interface of these materials. Solid-state NMR is a well-known spectroscopic technique for obtaining rich site-specific information. In this work, we study diphenyl phosphate stabilized ZnO NPs using ^{1}H, ^{13}C and ^{31}P solid-state NMR enhanced by dynamic nuclear polarization (DNP) to analyze the interactions at this organic-inorganic interface. We show that the different coordination modes of the ligand on the surface can be characterized and that we can determine the inter-ligand distances. This work combined with other studies in our lab, on differently ligated ZnO NPs, will help us build an understanding of the role of the ligand-surface interactions in the morphology of NPs.

Synthesis and characterisation of bioinspired binuclear copper species and their reactivity.

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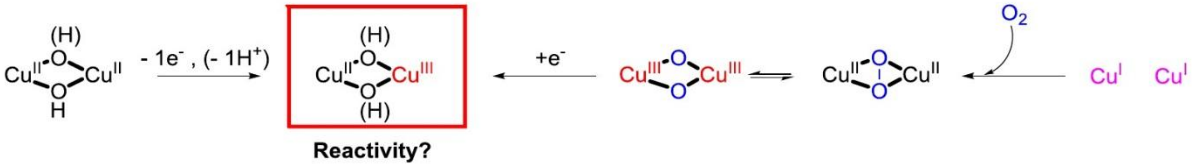
Cu_2:O_2 species are key intermediates invoked as the active motif for the mechanistic performance of several kinds of enzymes such as tyrosinase (Ty) and particulate Methane Monooxygenase (pMMO). Among these species, a mixed valent $Cu^{II}(O_2^{2-})Cu^{III}$ (possibly protonated) species has been proposed for the activity of pMMO,[1] an enzyme capable of oxidising methane to methanol.[2,3] There have been very few synthetic examples of such a species and hence very little spectroscopic data compared to the wealth of spectroscopic data available for similar species. There is also only one limited example in the literature of the reactivity of a $Cu^{II}Cu^{III}$ species.[4]

Herein we present the study of $Cu^{II}Cu^{II}$ complexes synthesised using ligands based on a 1,8-naphthyridine. Spectroscopic, electrochemical techniques and theoretical calculations were used to identify and characterise the corresponding mono-oxidised species.[5] An evaluation of the reactivity of such a species will also be given.



Scheme 1: outline of the formation of a $Cu^{II}Cu^{III}$ species.

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Development of Microstructured Electrochemical Biosensors

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Use of micro and nano-structured transducers for electrochemical biosensors has garnered considerable attention over recent years[1,2]. Precise control of structural surface dimensions is a key factor to enhance the biosensor performances (e.g., limit of detection (LOD), sensitivity, etc.), as well as to improve feasibility towards scalable manufacture. By using the electrochemical technique amperometry, this study explores the controlled structural features of platinum electrode surfaces modified with microdot arrays (Figure 1). With electron-beam lithography, not only is it possible to develop and control such structures, but it is also possible to adapt their size to tailor them to multiple purposes.

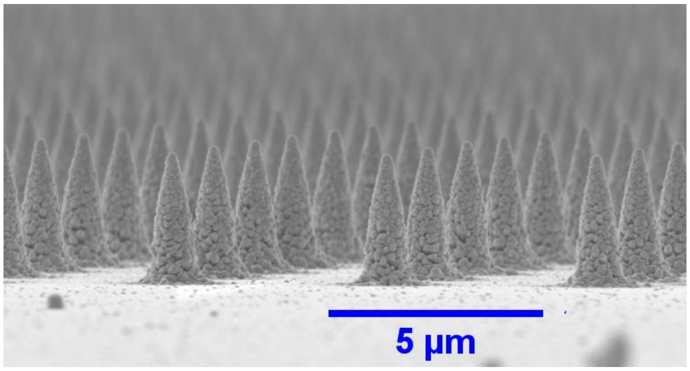

Figure1. SEM image of a platinum electrode modified with microdots.

Glucose biosensors[3] were fabricated as a model to study the sensitivity and the LOD of electrodes modified with microdot arrays. The glucose biosensors were constructed by immobilization of glucose oxidase via covalent interactions with electrogenerated polypyrrole-N-hydroxysuccinimide as already demonstrated in a recent immunosensor[4]. Performing electrochemical measurements with these microstructured electrodes showed significant improvement in the sensitivity (by a factor 12), considering just a relatively small increase in surface area (by a factor 2) when compared to a planar electrode surface. This demonstrates enhanced electrochemical detection of the generated H_2O_2 and the motivation for using microstructured surfaces.

This work benefited from the support of the project ImmuNanoCaps (ANR - 2016 CES09) of the French National Research Agency.

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Nano-garnets synthesis biological imaging and for white-LED lighting

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Rare-earth doped nano-garnets have promising properties for various applications. They can be used as nanoprobes in biology: as luminescent tracers (Ce^{3+}-doped $Y_3Al_5O_{12}$ (YAG)) or nanothermometers (Nd^{3+}- or Dy^{3+} doped YAG or $Gd_3Sc_2Al_3O_{12}$ (GSAG)). They are also used as nanophosphors for LED white lighting (Ce^{3+}- or Tb^{3+}-doped YAG).

All these applications require a strong control of the YAG crystal quality to ensure efficient optical properties, as well as a good size control with a targeted size in the 50–100 nm range. Indeed, this size range is often considered as a good size compromise for lanthanide-doped luminescent nanoparticles, allowing minimizing surface effects and optimizing light absorption while preserving a sub-micrometer size, essential for biophotonics and for light-scattering control in solid-state lighting devices.

Solvothermal synthesis route is a wet chemical route under mild temperature and high-pressure conditions. We develop an original solvothermal method to obtain well-crystallized nanocrystals thanks to the control of various synthesis conditions: high pressure (up to 200 bars), temperature (up to 400 °C), concentration, solvent, etc. This route enables the control of the nanoparticle size from 40 nm to 300 nm. The obtained nano-garnets are then optically characterized via photoluminescence spectroscopy, internal quantum yield measurements and X-ray absorption near edge structure, as well as structurally characterized via X-ray diffraction, transmission and scanning electron microscopy.

This work allows us to synthesize Nd^{3+}-doped GSAG nanocrystals with good colloidal stability and high thermal sensitivity, opening the door to temperature measurements at the nanoscale in biological media. In parallel, we produce Ce^{3+}-doped YAG nanoparticles with high luminescence quantum yield (up to 60 %) and now work on their shaping (ceramics or films) for testing their performances as phosphors for LEDs in operating conditions.

Silicon nanowires as a powder material for Li-batteries

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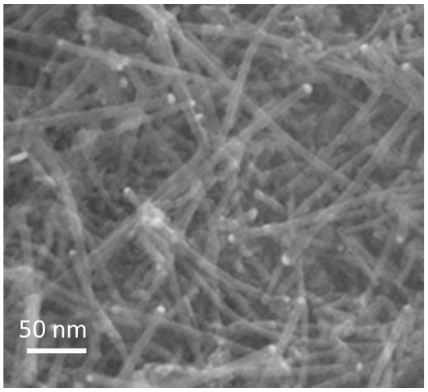
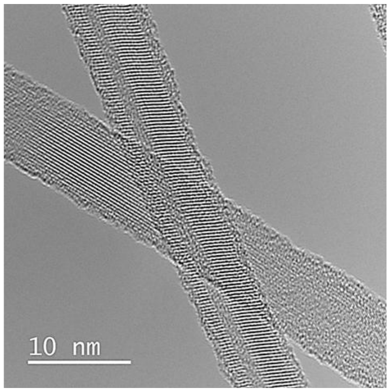
Silicon has emerged as highly promising material in lithium-ion battery anodes because of its absorbing 10 times more lithium than the standard carbon anodes, allowing up a 30% gain in the overall weight of the battery. However, as Si swells to 4 times its initial volume during lithiation, only Si crystals below 80nm can stand the mechanical constrains in battery charge/discharge cycling. Silicon nanowires are particularly efficient as they can withstand such constraints and maintain battery cycling over several hundreds of cycles. However, classical silicon nanowire growth methods produce thin films of low mass (µg/cm^2 by CVD), a too small amount for making batteries.

We recently developed a new synthesis of silicon nanowires[1] designed for mass production as a powder. The nanowires are grown in a glass or steel reactor at medium temperature (430°C) and medium pressure (<20 atm.) from Au or Sn nanoparticles deposited on an inert support, and from an air-stable organosilane as the silicon source along the reaction:

$$2\ \mathrm{Ph_2SiH_2} \rightarrow \mathrm{Si_{NW}} + 2\ \mathrm{H_2} + \mathrm{Ph_4Si}$$





Finely grinded table salt (NaCl) used as a support can be conveniently removed by washing with water after growth. Growth on salt also avoids handling silicon nanowires as a dry powder, preventing risk of inhaling nanoparticles. The synthesis yields silicon nanowires in gram scale, with a yield of 40% (max theoretical yield 50%).

Tests of the pure silicon nanowires in lithium-metal batteries show a good capacity retention over >500 cycles. Composites with graphite offer a specific capacity of >800mAh/g$_{\mathrm{anode}}$ with <10% loss in 200 cycles at a cycling rate of 2C (full discharge in 2h). We now try to reduce the 25% capacity loss in SEI (passivation layer) formation during the first cycle by tuning the silicon nanowire surface area.

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Dual Light-Emitting Iodate Nanoparticles: Up-conversion emission and Second Harmonic Generation

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The search for efficient luminescent nanoprobes has spread out with the development of life science and nanomedicine. Among the different types of optical contrast agents, nanomaterials that can be excited by a two-photon process in the near infrared (NIR) region are particularly interesting as they allow for a better spatial resolution due to the quadratic nature of the excitation process and prevent the biological tissues from degradation.[1] Such excitation can produce either Second Harmonic Generation (SHG - if the compound is non-centrosymmetric) or fluorescence excited by two photons (such as up-conversion (UC)). SHG and fluorescence mechanisms are very different in terms of emission dynamics, polarization sensitivity, nanoparticle size dependency and are generally used independently in bioimaging techniques.

We here report the possibility to simultaneously exploit both mechanisms (SHG and UC) in Er^{3+}-doped lanthanum iodate (α-$La(IO_3)_3$) nanoparticles (NPs), paving the way to new multiphoton microscopy approaches. α-$La(IO_3)_3$ NPs were synthesized using a microwave-assisted hydrothermal process. A tight control of the synthesis conditions (temperature, pressure, stoichiometry) is necessary to avoid the formation of multiple iodate polymorphs.[2] Various techniques (Electron Microscopy, Dynamic Light scattering) consistently indicate an average NP size of 50 ± 10 nm. SHG signal of NPs dispersed in solution was measured by the Hyper Raleigh Scattering technique,[3] allowing for quantitative measurement of the average nonlinear optical coefficient: $\langle d \rangle \sim 8$ pm V^{-1}, a value comparable to the one obtained for bulk α-$La(IO_3)_3$.[4]

When doped with Er^{3+}, up-conversion emission, mainly centered at 550 nm, is also detected under a single excitation at either 800 nm or 980 nm.[5] Both SHG and UC emission signals are thus observed from Er^{3+}-doped α-$La(IO_3)_3$ NPs with an excitation in the first NIR biological transparency window.

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Nouveaux matériaux multiferroïques : synthèses sous hautes pressions et hautes températures.

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Récemment des concepts théoriques ont prédit la possibilité de générer de la ferroélectricité par la rotation des octaèdres d'oxygènes dans des structures dérivées de la structure pérovskite : c'est la « Ferroélectricité Hybride Impropre » [1-3]. Parmi les structures prédites nous nous sommes intéressés à la classe des doubles pérovskites ordonnées $AA'BB'O_6$.

Nous avons synthétisé la série des composés $NaLnCoWO_6$ avec Ln = (La, Pr, Nd)^{A}, (Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb and Y)^{B}. Les trois premiers membres de la série ont été obtenus par une méthode A type céramique à 900°C sous air. Les membres de la série correspondant aux terres rares plus petites ont été obtenus pour la première fois par stabilisation sous Hautes Pressions – Hautes Températures (HP-HT) : méthode B [4]. Ces méthodes spécifiques ainsi que les caractérisations structurales obtenues par diffraction des rayons X haute résolution et diffraction des neutrons seront présentées avec les premières mesures magnétiques et électriques. La série a été étendue à l'étude des composés au Fer ($NaLnFeWO_6$) et au Nickel ($NaLnNiWO_6$) conduisant à l'obtention de nouvelles phases.

Fig. 1: Equipements HP-HT à l'Institut Néel Belt (gauche) and Conac (droite)

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Forgeage de composés à base de magnésium pour le stockage de l'hydrogène

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L'hydrure de magnésium est particulièrement attractif en tant que matériaux pour le stockage réversible de l'hydrogène : sa densité gravimétrique est élevée (7.6 % massique) et le magnésium abondant et bon marché. Le procédé de co-broyage de MgH2 avec un métal de transition (Ball-Milling) est particulièrement efficace pour produire des poudres nanostructurées et atteindre des cinétiques d'absorption / désorption rapides. Il pose néanmoins des problèmes en termes de coût (énergie consommée, manutention) et de sécurité (poudres hautement pyrophoriques). Pour répondre à des enjeux tels que le stockage des énergies renouvelables intermittentes, la mise en œuvre de nouveaux procédés facilement extrapolables à une production de masse, peu couteux en énergie, et plus sûrs s'avère indispensable.

Différents procédés de Déformation Plastique Sévères (SPD) tels que le laminage à froid [1] ou le forgeage à froid [2] ont été testés en tant qu'alternative au broyage mécanique. Ces procédés SPD ont effectivement permis d'améliorer les propriétés de sorption de l'hydrogène grâce à un affinement de la microstructure. Néanmoins, appliqués sous air, les auteurs se sont limités à des traitements à température ambiante et se sont systématiquement trouvés confrontés à un compromis entre activation efficace du matériaux et perte de performances liée à leur oxydation.

Nous avons conçu au laboratoire un dispositif original de forgeage en température et sous atmosphère contrôlée grâce auquel un grand nombre de paramètres ont pu être testés: microstructure de la poudre de magnésium utilisée comme précurseur, impact de la température de forgeage (transition fragile ductile de Mg), introduction d'une faible proportion de MgH2, introduction de nickel conduisant à la formation d'un phase intergranulaire Mg2Ni favorisant la diffusion de l'hydrogène dans le matériau massif, etc.... Après optimisation, le procédé de forgeage sous atmosphère contrôlée permet d'atteindre - en une seule étape - des cinétiques d'absorption/désorption rapides et stables au fur et à mesure des cycles.

[1] A new approach to the processing of metal hydrides J. Lang, J. Huot, Journal of Alloys and Compounds 509 (2011) L18-L22.
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Biomimetic photonic cellulose films

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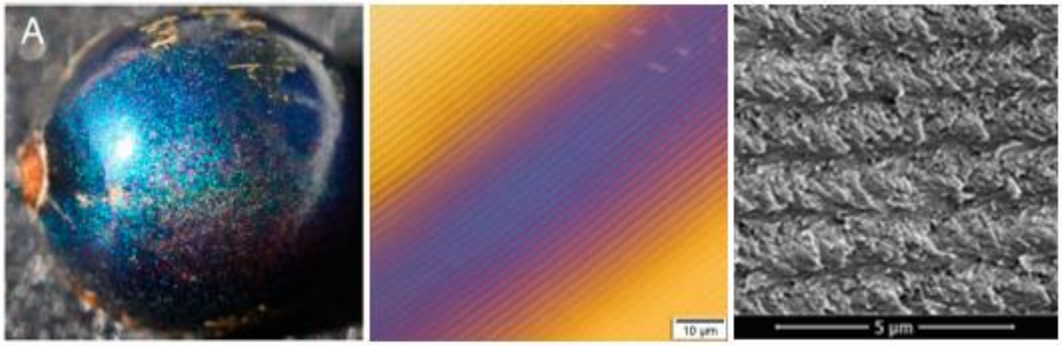
Cellulose nanocrystals (CNCs) are an excellent example of biosourced nanomaterials with a unique combination of mechanical and optical properties, and as recently shown, with unique polarization properties. These nanorods form a stable suspension in aqueous media and arrange into a cholesteric liquid crystalline phase above a critical concentration. Such behavior can be preserved in dry films, leading to the strong reflection of specific wavelength in the visible with a left circular polarization. Nevertheless, the films produced so far usually display a polydomain structure, whereby the orientation of the helix **h** is not controlled and leads to a pixelated and polychromatic aspect[1].



Although chemical and physical methods have both been used to control cellulose nanocrystals' optical response, the use of external fields, e.g., electric and magnetic, has been limited to only a few examples. Recently, our two groups (Vignolini and Heux) have demonstrated the possibility of using magnetic and electric fields to control the optical response of photonic cellulose-based structures.

On this poster, we will discuss how electric and magnetic fields can be engineered to generate various degrees of orientation of the cholesteric domains and how it can be used to shape a dynamic optical response of CNC suspensions/films[2].

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(2) B. Frka-Petesic et al, Adv. Mater. **2017**, 29, 1606208

Aptamer Engineering in DLD microfluidic cell sorting for early detection of extracellular vesicles

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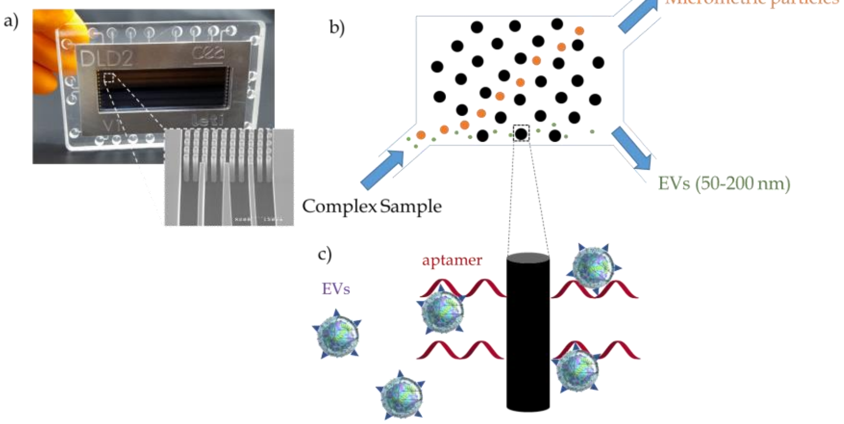
Extracellular Vesicles (EVs) have been identified to be key modulators of the tumor microenvironment that facilitate communication between cells and potentially induce the formation of metastases. This could make them powerful cancer biomarkers as they are also found in biological fluids such as blood or urine. However, even if these EVs are abundant in biological fluids, they are difficult to extract. The most frequently used isolation technique, ultracentrifugation, has several drawbacks. In addition, this method is not fully adapted to heterogeneous populations such as EVs, resulting in high contamination and low recovery rates. Microfluidic devices offer the possibility of designing systems for EV isolation in a more compact format and with low sample consumption.

CEA Leti – DTBS team has developed a microfluidic sorting technique based on the DLD (Deterministic Lateral Displacement, Figure 1a, b) principle that separates particles in size: particles larger than the cut-off diameter of the device are gradually deviated by a network of micrometric silicon pillars, while smallest particles progress without deviation to the output.[1]

Figure 1:



While implementing DLD devices for isolation of EVs may be a challenging route to pursue, combining this strategy with aptamer probes could be a promising way to achieve label free isolation. Using bio-targeted chemistry, ligation of DNA strands will be performed in the sorting device and will allow a controlled binding and release of these vesicles of interest. Selected aptamers directed towards proteins presented on EV surfaces will be coated on DLD micrometric silicon pillars. Different aptamers have already been applied to exosome detection[2] and will be used to capture EVs. Our current work is focused on the silicon surface functionalization chemistry with aptamers and validation of DNA probes. This poster will present our first results about covalent grafting of aptamers on silicon surfaces.

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Analytical method for NAcGal ligand quantification on the surface of lipid nanoparticles

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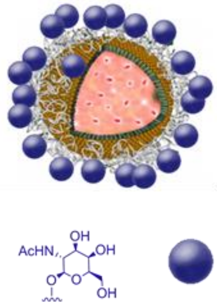
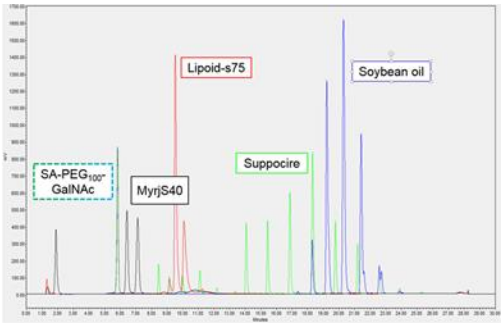
In recent years, nanoparticles have been extensively studied for drug delivery applications. Drug-loaded nano-carriers can overcome one of today challenge: efficient targeted delivery in specific organs. To achieve this goal, the functionalization of nanoparticle surface by targeting ligands such as antibodies, peptides, saccharides has been investigated to ensure specific recognition with the biological target and thus decrease undesired effects. A limitation in the development of these targeted nanocarriers is the access to precise design of multivalent ligand systems and required precise quantification of the amount of targeting ligands on the nanoparticle surface.

In this project, Nanostructured Lipid Carriers (NLC) were decorated with N-acetyl-D-galactosamine (GalNAc) units to target the specific liver ASGPr (Asialoglycoprotein receptor). Different molar percentages of the synthesized SA-PEG$_{5000}$-GalNAc (0%, 2%, 5% and 10%) were incorporated in the formulation of NLC. An analytical method based on ultra-high performance liquid chromatography separation and evaporative light-scattering detection (UPLC/ELSD) was developed to allow the quantification of GalNAc units introduced on the surface of NLC.





The method allowed the accurate quantification of SA-PEG$_{5000}$-GalNAc in the colloidal solution and the determination of key parameters of these multivalent ligand systems. As a direct measurement was performed, this method could be extended to PEG-modified surfactants for the accurate quantification of various PEGylated nanoparticle coverage.

This work has been supported by ARC1 Santé - Région Rhone-Alpes Auvergne, Labex ARCANE, CBH-EUR-GS (ANR-17-EURE-0003)" and "Investissement d'avenir" program Glyco@Alps (ANR-15-IDEX-02).

Luminescent materials for lighting and nanomedicine

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In this poster we will present the principal research works realized in the chemistry field of the Optics and Materials (OPTIMA) Team in Néel Institut.

Our chemistry activities gather a complete chain of competences that goes from the design of new materials (at different scales, from macroscopic to nanoscopic) to their shaping : chemical engineering of non-centrosymmetric compounds with laser and nonlinear optical properties ; confined nucleation and growth of molecular luminescent nanocrystals in sol-gel matrices or emulsions ; solvothermal synthesis of inorganic nanocrystals ; elaboration of amorphous luminescent thin films and powders; crystal growth in solution at low (close to room temperature) and high temperatures (flux method) ; crystal quality characterization by X-ray topography

This very broad range of competences enables us to conceive new materials in the highly competitive field of bio-imaging, lighting and laser optics.

The main results are presented in the following papers :

Toward a new generation of white phosphors for solid-state lighting using glassy yttrium aluminoborates.
Guimaraes, V. ; Maia, L. ; Gautier Luneau, I. ;Bouchard, C. ; Hernandez-Rodriguez A., Thomas F., Ferrier A., Viana B., Ibanez A. ; *J. Mater. Chem. C*, **2015** ,3, 5795-5802.

Evidence of organic luminescent centers in sol-gel synthesized yttrium aluminum borate matrix leading to bright visible emission Burner, P.; Sontakke, A. D. ; Salaün, M.; Bardet, M.; Mouesca, J.-M., Gambarelli, S.; Barra, A.-L. Ferrier, A. ; Viana, B.; Ibanez, A.; Maurel, V. and Gautier-Luneau, I. ; *Angew. Chem. Int. Ed*., **2017**, 56 , 13995 –13998.

Microwave synthesis and up-conversion properties of SHG-active α-(La,Er)(IO_3)$_3$ nanocrystals. S. Regny, J. Riporto, Y. Mugnier, R. Le Dantec, S. Kodjikian, S. Pairis, I. Gautier-Luneau, G. Dantelle, *Inorg. Chem.,* **2019**, 58,1647-1656.

A new solvothermal method for the synthesis of size-controlled YAG:Ce single-nanocrystals, Dantelle, G.; Testemale, D.; Homeyer, E.; Cantarano, A.; Kodjikian, S.; Dujardin, C.; Hazemann, J.L.; Ibanez, A.; *RSC Advances*, **2018**, 8, 26857-26870.

Luminescent coatings prepared from optimized YAG:Ce nanoparticles. Dantelle, G. ; Salaün, M. ; Bruyère, R. ; Kodjikian, S. ; Ibanez, A. ;*Thin Solid Films*, **2017**, 643, 36-42.

Red-emitting fluorescent organic@silicate core–shell nanoparticles for bio-imaging
Shenoi-Perdoor, S. ; Cattoën, X. ; Bretonnière, Y. ; Eucat, G. ; Andraud, C. ; Gennaro, B. ; Kodjikian, S. ; Dubois, F. ; Ibanez A. ; *New Journal of Chemistry*, **2018**, 42, 15353 - 15360.

Optimization of the fabrication of an abiotic bioelectrode for implantable biofuel cell.

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For more than fifty years lithium-based batteries were used to supply power Implantable medical devices (IMD) [1]. However, in order to respond to the DMI's conditions, the required lithium based battery's size and lifetime fail to reach more than few tens of microwatts. In this context, implantable enzymatic glucose/oxygen biofuel cells (BFCs) are increasingly seen as a potential future technology for replacing lithium batteries [2]. One of the major limitations of enzymatic BFCs is the short lifetime of enzymes especially in the biocathode case. Thus, the use of abiotic catalysts is preferable over enzymes for long-term application of implantable glucose BFC's.Here, we present for the first time a nitrogen/iron doped graphene-based biocathodes able to operate for several months under physiological conditions. These biocathodes were fabricated using two different printing technics: i) a flexible cathode where the catalyst is spread over a larger area fabricated using a doctor blade printing technic ii) a 3D printed cathode with a high surface area fabricated with 3D bioprinter. Electrochemical characterizations under physiological conditions for both cathode types show maximum current densities of 70µA/cm^2. Moreover, long-term stability of 6 months is obtained in physiological conditions. Biocompatibility tests reveal also the biocathodes biocompatibility and the ability to operate inside the animal body without any inflammation reactions.

Figure 1: *a) 3D printed cylindrical electrode 3D b) Flexible electrode.*

Keywords: *Abiotic BFC, Abiotic, Doctor Blading coating, 3D printing.*

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Understanding interface-type resistance changes in Ti/$La_2NiO_{4+\delta}$ devices

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The simple Metal-Insulator-Metal (MIM) capacitor-like structure has gained increasing interest with the recent development of research around ReRAMs (*Resistive Random-Access Memories*) as well as for neuromorphic (brain-inspired) computing. ReRAM is an emerging type of non-volatile memory which has already shown impressive performances in most memory benchmarks (operation speed, memory density, retention time, ON/OFF ratio and endurance). Nevertheless, they still present a major shortcoming: their device to device memory characteristics reproducibility, especially in the case of multilevel memory cells (where more than one bit of information can be stored). The strive to increase control over the switching phenomenon as well as to increase their reliability and reproducibility has led to a multitude of creative ideas to engineer the materials composing the MIM memristive stacks (composition, structure, additional layers or metallic nanoparticles, doping, etc.).

The present work focuses on the study and understanding of the memristive response of Ti/$La_2NiO_{4+\delta}$/Pt heterostructures. The $La_2NiO_{4+\delta}$ structure is formed by the alternation of $LaNiO_3$ blocks and LaO rock-salt blocks along the c-axis direction, and allows for the accommodation of over-stoichiometric oxygen within the rock-salt layer. Contrary to perovskite materials in which the oxygen migration occurs due to the movement of oxygen vacancies, for $La_2NiO_{4+\delta}$ the oxygen diffusion takes place through an interstitialcy mechanism. Therefore the resistive switching response in these devices could be very different to other more common devices based on perovskite materials.

Highly-oriented and dense $La_2NiO_{4\pm\delta}$ thin films were grown on $SrTiO_3$ single crystal substrates by pulsed-injection metal-organic chemical vapor deposition (PI-MOCVD). The structural and microstructural characterization confirms the high crystal-quality of the epitaxial films, which presented a columnar microstructure. The oxygen content in the films was varied ex-situ by annealing the samples both in oxidizing (O_2) and reducing (Ar and 6%H_2:Ar mixture) atmospheres. The electrical characteristics of the samples were measured both by current-voltage and pulsed measurements, and showed a continuous change in resistance, giving rise to multilevel programming capabilities in these nickelate-based devices. Near the Ti/$La_2NiO_{4+\delta}$ interface, the heterostructures have been characterized by a wide range of structural, chemical and spectroscopic techniques, which has allowed us to have a first insight into the electrochemical processes giving rise to the resistance change response. The creation of a metal-oxide layer at the interface, which also influences the electrical characteristics of the device, was observed. Finally, the key role played by the oxygen content of the films on the initial resistance and on the operation window of the Ti/$La_2NiO_{4+\delta}$/Pt heterostructure will be discussed.

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Structure determination of supramolecular nano-assemblies using dynamic nuclear polarization (DNP) enhanced solid state NMR.

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MAS-DNP is a hyperpolarization technique that allows enhancing the sensitivity of solid-state NMR experiments of samples at natural isotopic abundance to such a level that they can provide atomic-scale structural information such as surface functionalization or inter-nuclear distances. In MAS-DNP, hyperpolarization is achieved by transferring the large electron spin polarization from stable organic biradicals to the desired nuclear spins via the proton network of the sample. This leads to experimental time-savings of several orders of magnitude allowing the study of very challenging systems (such as porous materials, self-assembled nanostructures, silicon nanoparticles/nanowires) at natural abundance. Recently, our group has developed a new structure determination procedure, called DNP crystallography[1], to solve the crystal structure of those organic materials whose dimensions are not well suited for X-ray crystallographic studies. In DNP crystallography, crystal structure information is extracted using the inter-molecular distance information provided by dipolar buildup curves. The supramolecular structure of cyclo-diphenylaniline (cyclo-FF) has been solved and verified with the known X-ray crystal structure of cyclo-FF, using DNP crystallography.[1]

This project aims to demonstrate the generalization of the DNP crystallography procedure to other challenging nano-sized organic systems, for example, nanostructured Cyano-MethOxy-Nitro-Stilbene (CMONS) dye.[2] CMONS dye has been shown to possess multiple polymorphic forms which possess different efficiency in quadratic non-linear optics. It is highly fluorescent in the crystalline state and is a potential candidate as a biomarker. We have started to investigate CMONS nanocrystals at natural abundance using the large sensitivity gain obtained from DNP, with the goal to provide detailed structural information.

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Role of CNC dispersion on functionalization with fatty acids as solvent

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In current economic and ecological context, cellulose, one of the most abundant and available natural polymers, appears to be a material of choice for a wide range applications. More specifically, since the last decades, production and use of nanomaterials prepared from cellulose has gained the interest of lot of researchers. These nanomaterials can be mechanically extracted from cellulose (cellulose micro/nanofibrils (CNF)) or chemically produced (cellulose nanocrystals (CNC)) by applying an acid hydrolysis to cellulose.

Through their biodegradability, renewability, mechanical and barrier properties, both of CNF and CNC are relevant for the development of new biomaterials, especially in nanocomposites field, where they can be used as nano-reinforcement.

However, their hydrophilicity -due to the presence of numerous hydroxyl groups at their surface- limits their incorporation in non-polar polymer matrices classically used in nanocomposites.

In this work, CNC are functionalized in a way of compatibilization with a hydrophobic polymer matrix. This functionalization aims to limit the use of toxic solvent by using the reagent as solvent which could be recycled (SolReact method).

Firstly, study of the dispersion of commercial spray-dried CNC in different solvents is investigated, in order to ensure a large surface available for further functionalization in suspension.

In a second time, CNC suspensions are grafted with a large excess of lauric (C12) or stearic (C18) acid which play the role of solvent, in order to make them hydrophobic. Grafting occurs at a higher temperature than those of acid melting point, and after total evaporation of acetone, acid becomes the solvent. The grafting is characterized by direct methods (FTIR, Elemental analysis, NMR) and indirect methods (contact angle, dispersion in water). Efficiency of the functionalization has been highlighted and final nanomaterials have been successfully designed for further incorporation in polymer matrices.

Stable *N*-centered radical complexes: synthesis, characterization and catalytic applications

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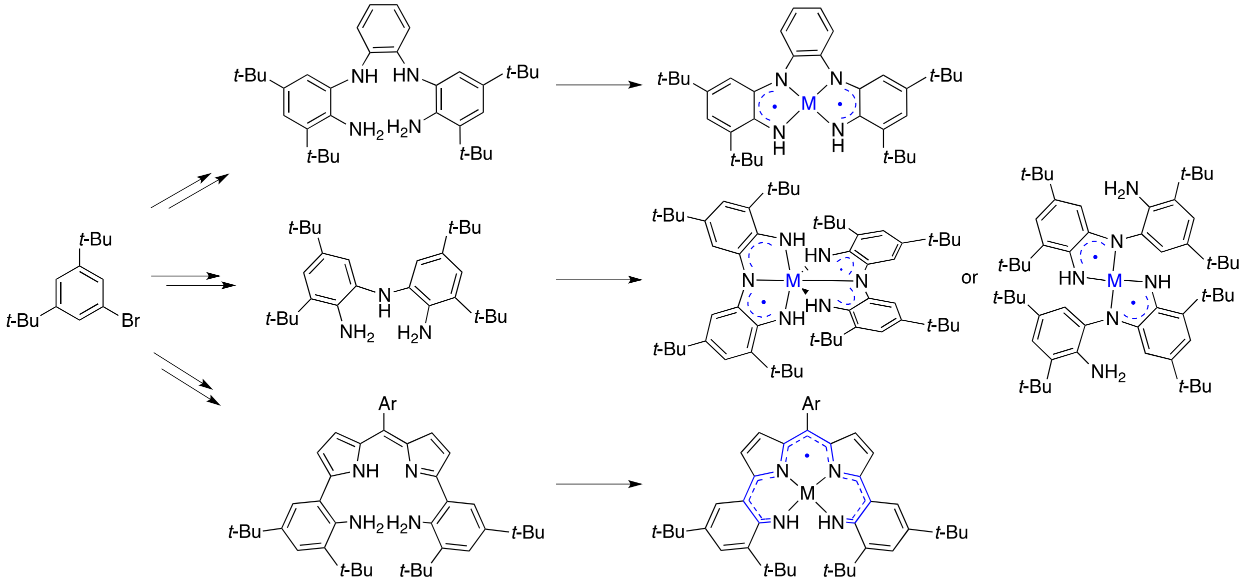
Metal-radical species were long considered as naturally occurring curiosities in biological systems such as metalloenzymes. Their in-depth study shed light on the decisive role of redox-active, i.e. non-innocent, ligands in various chemical transformations, and motivated the chemists to develop a large array of structural and functional models. Thanks to modern analytical techniques, the precise understanding of radical metal complexes arouses interest in applications far beyond biology. Hereafter, further major achievements will be obtained with the design of brand new radical entities.

Our research is devoted to the design of unprecedented pro-radical ligands and to their coordination chemistry. The newly prepared materials are extensively characterized to elucidate unique electronic structures. Among various valuable applications, one of our research priorities is the implementation of radical complexes as efficient homogeneous catalysts in synthetic methodologies.

The poster presentation will give a short overview of our recent results, emphasizing on polydentate ligands derived from *o*-phenylenediamines or anilines (Scheme 1).



Scheme 1

When Additive Molecular Dynamics Fails: Quantum Effects in Calcium-dependent Lectin/Carbohydrate Complex

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The developments of additive carbohydrate force fields[1] increased the reliability of molecular dynamics simulations (MD) of protein-carbohydrate complexes. The presence of bridging Ca^{2+} ions can, however, pose problems for structural and energetic description due to quantum effects, such as charge transfer.[2,3,4] To overcome this limitation, we have developed Ca^{2+} parameters with effective electronic polarisation for use with additive force fields[4] and applied them to a calcium-dependent lectin/carbohydrate complex. Such a treatment improved the structural description of the binding site (Ca^{2+}…Ca^{2+} distance matching that of the crystal structure) but failed to reproduce the pattern of protein/carbohydrate interactions and the location of specific bridging water molecules. This system thus necessitated the use of polarizable force fields.[5] Coupled with quantum mechanical/molecular mechanical (QM/MM) calculations, we were able to describe the polarization phenomena of the Ca^{2+} ions, protein carboxylate side chains, carbohydrate hydroxyls and specific water molecules in the active site which together define the structure and energetics of the complex. In summary, we utilized new Ca^{2+} parameters and advanced computational techniques (polarizable MD, QM/MM calculations) on the crystallographic structure to gain atomistic and energetic understanding of the Ca^{2+}-dependent lectin/carbohydrate complex.

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Versatile biosensor deciphering glycoenzymatic activities

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To date, glycosyltransferases (GTs) are an essential family of enzymes poorly characterize both structurally and mechanistically which is being a major bottleneck in Glycoscience. They play a crucial role in living organisms catalysing the stereo- and regiospecific transfer of an activate donor sugar to an acceptor moiety to build up complex oligosaccharides onto the cell surface (1). It requires the development of new methodologies able to elucidate and characterize the interactions between the glycosyl moiety and the enzyme. Surface plasmon resonance imaging (SPRi) has spread as a powerful analytical tool for deciphering many biomolecular processes exploring the kinetics and monitoring multiple interactions of biological and chemical substrates at real time and without any labels (2). We aim at the development of a biosensor enable to rationalize the characterization of glycosyltransferases activities involved in the plant cell wall biosynthesis. To this aim, a fucosyltransferase from the plant Arabidosis thaliana (AtFUT1) (CAZY family GT37), was selected as model glycosyltransferase. This enzyme participates in the last step in the biosynthesis of xyloglucan (XG) transferring L-Fucose molecule from GDP-Fucose (donor) to a galactose sugar (acceptor) (3). To that end, multiple chemical strategies to functionalize large moieties of xyloglucan to graft it on the gold surface have been developed (4) (5). Depicting and monitoring the interactions between the AtFUT1 and the xyloglucan in terms of both specificity and activity represent a strong challenge. Complementary techniques such as isothermal titration calorimetry (iTC) may guide to streamline the comprehension and support the rationalization of the glycosylation process (6).

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Deposition of calcium phosphate coatings using the electrostatic spray deposition technique

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Replacement of missing or diseased hard tissues has become a common procedure in medicine and dentistry. In this field, coatings are frequently applied onto the surface of metallic implants, such as titanium and titanium alloys in order to improve their biological performance -i.e to enhance bone contact or bone anchorage, defined as osseointegration-. Because of its similarity to the inorganic component of bones and teeth, calcium phosphate (CaP) ceramics were considered as a suitable material for use as a surface coating.[1]

Currently, the most frequently applied method to coat titanium implants with CaP films is the plasma spraying technique, which has considerable drawbacks, for instance, unpredictable phase changes because of high-temperature differences, the large thickness in order to completely cover the implant and possible particle release and delamination.[2,3] Because of the disadvantages of the plasma-spray technique in depositing calcium phosphate coatings, several alternative methods of depositing CaP coatings have been pursued. Regarding this, Electrostatic Spray Deposition technique (ESD) was investigated.

ESD is a method based on electrohydrodynamics laws, cheap and that allows a larger variety of phases (including possibly out-of-equilibrium ones) to be formed on the surfaces. In this study, different hydro-alcoholic precursor solutions containing calcium and orthophosphate ions and several ESD deposition parameters were varied in order to investigate the microstructural and structural properties of the CaP coatings deposited on Ti alloy. Spraying distance, substrate temperature, electrical field, spraying flow rate and spraying time were considered as the ESD process variables as well as the solutions of precursors characterized by different physical-chemical properties. The microstructure and composition of the obtained coatings were characterized by scanning electron microscopy (SEM) associated with energy dispersive X-ray spectroscopy (EDX). Their structural properties were determined using X-ray diffraction (XRD) and Fourier-transformed infrared spectroscopy (FTIR).

Electrostatic Spray Deposition proved to be a viable and potentially interesting technique to coat metals (Ti alloy) with calcium phosphate layers, thus rendering them adherent and osteoconductive. Its potential has yet to be developed to take full advantage of its characteristics: cheap process, a low temperature that enables the retention of out-of-equilibrium phases and versatility of the obtained coatings.

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Spatial Atomic Layer Deposition (SALD): surface and interface nanoengineering made easy

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Atomic Layer Deposition (ALD) is a chemical deposition method based on self-terminated, surface limited reactions. As a result, ALD offers unique assets: i) a very precise control over film thickness down to the nanometer, ii) high uniformity and dense, crack-free coatings, even on high-aspect-ratio and porous substrates, and iii) lower deposition temperatures as compared to chemical vapor deposition. That allows conformal coatings, even in nanometric geometries, with dense films of a wide variety of materials[1]. ALD has become very popular in the materials science community when tackling surface and interface nanoengineering, which is a key aspect of device performance. Despite the benefits of ALD, the facts that it is usually processed in vacuum, and that deposition rates are rather slow have limited its industrial application since mass production of devices requires low-cost, high-throughput and scalability. To this end, an alternative approach to ALD, namely Spatial ALD, offering a fast deposition (even in the open air) of materials by ALD has been developed in the last years[2,3]. The approach is based on a spatial separation of reactants, rather than a temporal one (as in conventional ALD). This is achieved by controlling the geometry of the system and by the physical movement of its components. The inherent characteristics of SALD provide a potential for scalability when thinking of industrialization and opens the door to widespread industrial application of ALD for the deposition of functional materials. At LMGP, a SALD deposition system has been designed and developed to enable deposition of a wide range of functional materials. Here, we present the principle of SALD and of the system at LMGP. An overview of the activity of the SALD team at LMGP, which include transparent conductive oxides (TCO), semiconductor materials, hybrid materials, and applications such as passivation for silicon solar cells or transparent electronics, will also be presented.

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Design of biomimetic constructs

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Using elementary building blocks to mimic and reconstruct biological structures is intriguing both from fundamental aspects, providing a simple model to study a complex environment, as well as from the applicative point of view, opening the possibility of utilizing such constructs for the creation of new bio-inspired materials. Understanding the key parameters governing the interaction between the building blocks of such systems is highly important.

In this frame work of bio-inspired materials, the plant cell wall provides an interesting model since its basic building blocks are abundant, eco-friendly and possess outstanding properties. In the plant kingdom, one of the first steps of cell wall constitution is the deposition of cellulose microfibrils on top of the plant plasma membrane.

In this work we have investigated the interaction between cellulose nano-crystals (CNCs) and lipid membranes using 2D and 3D architectures. Quartz Crystal Microbalance with Dissipation (QCM-D) and Total Internal Reflection Fluorescence microscope (TIRF) were used for the investigation of the 2D system, in which CNCs were deposited on top of supported lipid membranes (SLBs). The interaction between lipid vesicles and CNCs was studied in suspension using Isothermal Titration Calorimetry (ITC), light scattering and Transmission Electron Microscopy (TEM). Key parameters governing the interaction were elucidated and the results are discussed in the context of plant cell wall inspired materials.

Détection de pathogènes à l'aide de peptides antimicrobiens immobilisés sur biopuces analysées par imagerie à résonance de plasmons de surface

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L'analyse microbiologique pour assurer l'absence de bactéries dans des échantillons biologiques normalement sains (sang, urine…) est une routine dans de nombreux laboratoires. L'efficacité de ces analyses repose sur le fait d'identifier précisément et rapidement le pathogène incriminé. La méthode standard pour la détection bactérienne repose jusqu'ici sur la culture directe des échantillons prélevés sur les patients, afin d'obtenir une population suffisante pour analyse. La contamination initiale est alors de l'ordre de seulement quelques bactéries par millilitre. Ce délai retarde les essais d'identification jusqu'à parfois plus de 24 heures. Cette étape initiale d'enrichissement ralentit donc le diagnostic, en plus de nécessiter des opérateurs qualifiés.

Il existe ainsi un besoin important pour des tests de détection rapide de bactéries pathogènes dans des échantillons biologiques complexes tels que le sang. Des biocapteurs à large spectre de reconnaissance pourraient répondre à ce besoin. Néanmoins, il reste encore la nécessité de développer les sondes permettant d'atteindre cet objectif. En effet à l'heure actuelle, la plupart des approches utilisent des sondes spécifiques, telles que les anticorps ou les aptamères, nécessitant donc de développer quasi autant de sondes que de souches visées.

Nous proposons donc l'introduction d'un nouveau type de sondes, les peptides antimicrobiens (AMP). Ces courts peptides cationiques et amphiphiles, présentent l'avantage d'un large spectre d'interaction couplé à une haute stabilité (chimique, thermique et séchage) comparativement aux anticorps et aptamères. Leur immobilisation sur des prismes SPRI permet d'évaluer simultanément l'affinité de plusieurs AMP à la même souche bactérienne. Cette phase s'effectuant lors de la croissance des bactéries, permettant ainsi de parvenir à une détection des pathogènes le plus précocement possible. Des pathogènes tels qu'*E. coli, S. aureus, L. monocytogenes* ou *Salmonella* ont ainsi pu être détectés en quelques heures, avec des concentrations initiales de l'ordre de quelques bactéries par millilitre. Une analyse statistique multidimensionnelle de ces données a montré qu'il y avait effectivement une signature distincte d'une souche à une autre, ouvrant la voie à l'utilisation de notre système non seulement comme un outil de détection mais potentiellement également de reconnaissance.

Resistive switching response of $LaMnO_{3+\delta}$-based devices with different oxygen content

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This work presents the design of memristive heterostructures using $LaMnO_{3+\delta}$ (LMO) as "sandwiched" switching material between Au top and Pt bottom electrodes. A number of different strategies were explored to integrate these manganite films on silicon-based devices, overcoming the challenge of the high temperatures required for their deposition. Dense LMO thin films were grown electrode by injection metal-organic chemical vapour deposition (PI-MOCVD) on top of a silicon-heterostructure including a 100 nm-thick film of Pt as bottom electrode. LMO-based devices were fully characterized using a combination of microscopic, spectroscopic and physical techniques. A rhombohedral phase is obtained for films treated under O_2, pointing out to higher oxygen concentration (3+δ); whereas films treated under Ar showed an orthorhombic phase, linked to a lower oxygen content (higher $V_O^{\cdot\cdot}$ concentration). The electronic properties have been related to the structural and compositional properties of both type of LMO films. Valence change-type resistive switching (RS) was optimized as a function of the nature of the LMO films, i.e. orthorhombic vs rhombohedral, by cyclic voltammetry. Both types of LMO-based devices showed an asymmetric bipolar counter-eightwise-type switching response, requiring different electroforming steps. The memory windows attained by tuning the voltage and the current compliance were about 10^3 in both cases. Abrupt SET and RESET processes occurred for negative and positive polarity, respectively, indicating a filamentary-type switching mechanism. A qualitative RS model is proposed based on multiple pre-existing filaments in the LMO films. The results obtained go one step further towards the elucidation of the mechanisms involved in the RS response in LMO heterostructures.

Nitrones as synthetic tools for the discovery of novel classes of iminosugars

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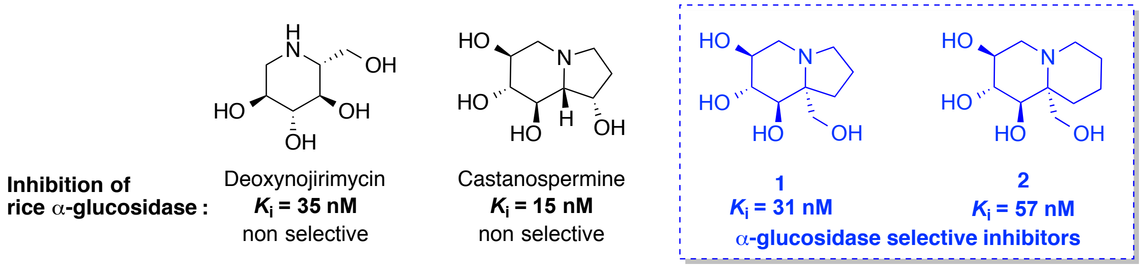
Due to their stability *in vivo* and their activity as glycosidase inhibitors or activators, iminosugars are among the most promising drug candidates for the treatment of diseases such as diabetes, viral infections and lysosomal storage disorders.[1] Recently, our group has identified a series of iminosugars (i.e. compounds **1** and **2**), exhibiting a quaternary center in α-position of their nitrogen atom, which proved to be excellent inhibitors (nanomolar K_i) of α-glucosidases with unprecedented selectivity.[2]



Inhibition of rice α-glucosidase :

Deoxynojirimycin
K_i = 35 nM
non selective

Castanospermine
K_i = 15 nM
non selective

1
K_i = 31 nM

2
K_i = 57 nM

α-glucosidase selective inhibitors

In this communication, the synthesis of novel iminosugars from carbohydrate-derived nitrones will be presented. The variety of synthetic methods that can be applied to nitrones to prepare bioactive molecules will be emphasized by successful syntheses of original iminosugar scaffolds.[3] Investigation of the biological activities of these new molecules will also be presented.

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Hybrid System for Solar Energy Conversion into Hydrogen

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The generation of H_2 from water and sunlight offers a promising approach for producing a sustainable carbon free economy. One of the challenges of solar-to-hydrogen technology is the design of efficient, long-lasting scalable and low-cost photocathodes, which are responsible for absorbing sunlight and driving catalytic hydrogen evolution reaction (HER), mimicking photosynthesis.[1,2]

In this work, we combine a light-harvesting semiconductor ($CuFeO_2$)[3] with efficient noble metal-free Co-based cobaloxime catalysts (CoHEC)[4] to prepare hybrid photoelectrodes for H_2 evolution from sunlight (**Figure1**). $CuFeO_2$ delafossite precursors have been deposited by spin coating on FTO substrates and annealed at 600°C. The obtained thin layers were characterized by SEM, EIS and UV-vis spectrometry, to ascertain the structure and electronic properties (energies of the conduction and valence band) of the material. The grafting of CoHEC catalyst allowed the hybrid system to reduce protons into hydrogen in aqueous solution under 1 sun irradiation as demonstrated by cyclic voltammetry, LSV and chronoamperometry techniques.

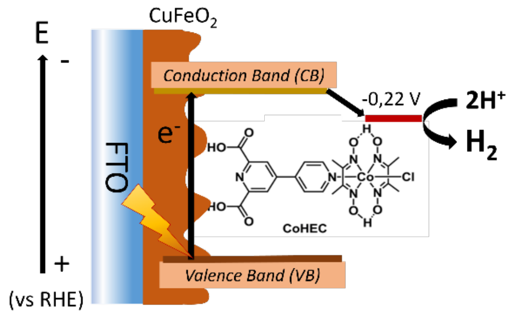

Figure1. Scheme of the photocathode design.

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Polymetallic sulfides for bioinspired-electrocatalysis

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Ammonia is an important precursor for many necessary commodity products, especially fertilizers. Currently the prevailing industrial method for nitrogen fixation (conversion of nitrogen into ammonia), the so-called Haber-Bosch process is not sustainable. It consumes 2% of world energy and is responsible for 1% world carbon dioxide emissions.[1] Thus researchers are encouraged to develop alternative ways for ammonia production. One appealing approach is to develop electrocatalytic processes involving protons and electrons by mimicking nitrogenase, the only enzyme that is able to reduce N_2 into ammonia. The catalytic center in nitrogenase is an iron molybdenum sulfide cluster [$MoFe_6S_9C$] called FeMo-cofactor.[2] Inspired by this enzyme, we choose to use the well-known $[Mo_3S_7]^{4+}$ cluster for the nitrogen fixation. In nitrogenase, the complex environment provided by the protein matrix around the cofactor plays an essential role in its catalytic function. In this study, we try to use a tunable cavity-liked porphyrin ligand to stabilize and to modulate the $[Mo_3S_7]^{4+}$ catalytic center. In this poster, I will present my efforts towards the synthesis of the porphyrin ligand the $[Mo_3S_7]^{4+}$ cluster, as well as the prelaminar complexation study between them.

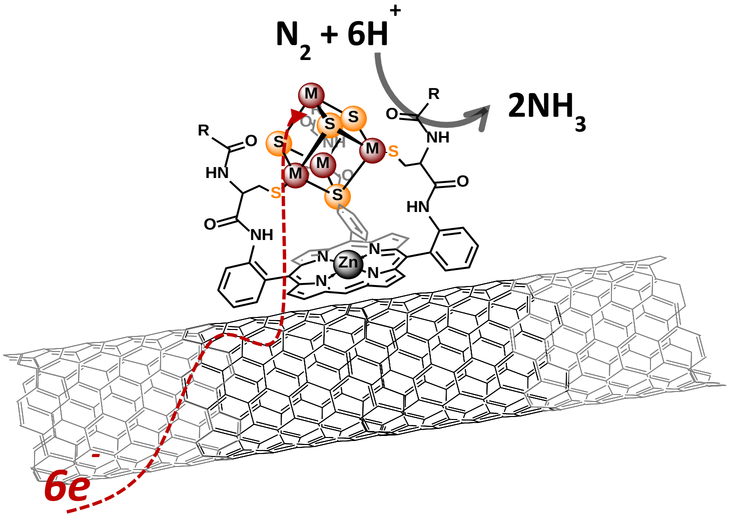

Figure: Proposed catalyst assemblaged on carbon nanotube.

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