Journées de l’École Doctorale 397 Physique et Chimie des Matériaux

ED397 Doctoral School Days

7 & 8 Décembre 2017
December 7\textsuperscript{th} & 8\textsuperscript{th} 2017
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Session 1
Physico-Chemistry

Joining of the Ti$_2$AlC ceramics

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Keywords: Ti$_2$AlC; brazing; nickel; DFT

The MAX phases, which refer to a group of nanolaminate ternary carbide or nitride ceramics, have attracted increasing interest from researchers in recent years. After their discovery in the 1960s, they were systematically studied and introduced by Barsoum et al. [1] in 2000. These compounds possess excellent combination of metal and ceramic properties, including the low density, high elastic modulus, superior thermal and electrical conductivity, low coefficient of thermal expansion and excellent machinability [2]. Among them, Ti$_2$AlC, a typical member of MAX phases with 211 structure [3], has been widely investigated since the compound has the lowest density and the best oxidation resistance [4, 5], which is considered to be applicable in many structural and functional applications, especially in the high temperature fields.

Although numbers of studies have been carried out on the synthesis of Ti$_2$AlC, still it is difficult to fabricate bulk Ti$_2$AlC with big dimensions and complex shapes in practice due to the narrow phase range in the Ti-Al-C ternary phase diagram [6], which severely hampers its widespread application. Joining technology is a convenient and effective approach to overcome this problem [7], being essential to the widespread application of the Ti$_2$AlC ceramics in many fields. Moreover, the joining of MAX phases to metals has attracted much attention in recent years since the technology extends both the applications of ceramics and metals.

The major purpose of this work is to achieve proper brazing parameters for the joining of Ti$_2$AlC ceramics and Ni metal substrate, thereby broaden the application of both substrate materials in high temperature field. Firstly, the brazing experiments are carried out in a high vacuum heating furnace using nickel based filler alloy, the mechanical properties of the Ti$_2$AlC/Ni joints are evaluated, thereby the optimal brazing parameters are achieved. Afterwards, the phases in the joints are determined, and the microstructure evolution during the brazing process is revealed. Finally, DFT calculation is performed to illustrate the interaction mechanisms between Ti$_2$AlC structure and brazing filler elements. Using the combination of experiments and simulations, we are trying to reveal the brazing mechanisms of the Ti$_2$AlC/Ni joints from the nature of physics, also for better understanding the intrinsic structural features of MAX phases.

A full description of the conformational landscape of cyclized peptides using a robotics approach

Maud JUSOT1,2,*, Juan CORTES2, Jacques CHOMILIER1 and Dirk STRATMANN1

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Keywords: cyclic peptides, energy landscape, robotics, molecular dynamics.

The use of peptides for pharmaceutical purposes is constantly increasing, in particular thanks to improved methods to enhance bioavailability by introducing various kinds of chemical modifications. An interesting application of peptides is the inhibition of protein-protein interactions, aiming to modulate the activity of the complex. Peptides extracted from one chain at the interface of a protein-protein complex can bind to their partner and hence compete with the dimerization process. For this, the extracted fragments (in solution) must be able to mimic their embedded conformation in the initial complex. Their cyclization and chemical modifications are promising pathways to stabilize these highly flexible molecules in the desired conformation. For those reasons, the study of conformational and chemical properties of peptides, alone and with their targets, is crucial for drug design.

The first step of the present study is the exploration of the peptide’s energy landscape in order to find the local minima (most stable conformations) and the transition paths between them. We are currently developing a faster exploration approach than classical simulation methods. To do so, we use a mechanistic representation of the cyclic peptide which allows us to use algorithms originating from robotics for conformational sampling [1]. Our method can also treat D-form and N-methylated amino acids. In order to validate our approach, we sampled the conformational landscape of a set of 19 cyclic RGD designed pentapeptides [2][3]. An exhaustive description of these peptides has been made by complete enumeration of the backbone dihedral angles, phi and psi. The results have been compared to those obtained with Replica Exchange Molecular Dynamics simulations, showing the good performance of the robotics approach.

CHEMISTRY

Growth and spectroscopic characterization of novel laser crystals

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Keywords: Single crystal growth; Optical spectroscopy; Visible laser

Lanthanide ions have been widely employed for laser applications taking advantage of their fluorescence transitions. Over the past few decades, high-quality laser outputs in the visible were mainly realized by frequency conversion from the infrared emission of Nd3+ and Yb3+. This method, however, bears intrinsic disadvantages such as the requirement of non-linear crystal and energy loss during the frequency conversion. The advent of commercially available semiconductor laser pump sources at shorter wavelengths makes it possible and efficient to pump the active ions to higher energy levels and thus visible lasers can be realized by direct emission1. Trivalent lanthanide ions such as Tb3+ and Dy3+ that display characteristic fluorescence in the visible spectral range are considered as suitable candidates. We aim to grow and characterize single crystalline materials doped with Tb3+ and Dy3+ ions and use them as gain media to realize visible laser oscillation. Crystals of Ba3Tb(PO4)3, Sr3Tb(BO3)3, Li6Tb(BO3)3, Ca4TbO(BO3)3, Dy:CaYAlO4, Dy:Ca4YO(BO3)3 were grown by the Czochralski technique. The growth conditions were optimized to obtain high-quality crystals (Fig. 1). The spectroscopic properties of the as-grown crystals were characterized by absorption and emission spectra, fluorescence decay measurements, and electron paramagnetic resonance. Radiative lifetime and branching ratios were calculated in the framework of Judd-Ofelt theory. The results indicate that the Tb3+ and Dy3+-doped crystals are promising gain media to achieve green and yellow laser outputs. Laser operations of these materials are in progress using blue laser diodes as pump sources.

Fig.1 Single crystals grown by the Czochralski technique

Phase diagram of ammonia monohydrate at high pressure and temperature

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Keywords: phase diagram, pressure, temperature

Abstract:
Water and ammonia are considered major components of the interiors of the giant icy planets and their satellites. The phases formed by their mixtures under temperature and pressure conditions of these giant planets are significant for understanding observable properties like magnetic field, gravitational moments and atmospheric composition. The present study focuses on the 1:1 compound, ammonia monohydrate (AMH). Our previous work [1] has shown that AMH transforms at room temperature and above 8 GPa to a mixture of a partially ionized bcc phase, previously reported as the DMA phase [2], and a fully ionic P4/nmm phase [3]. Here we investigate the phase diagram of ammonia monohydrate at high P-T by using Raman spectroscopy, synchrotron radiation and infrared (IR) absorbance spectroscopy up to 40 GPa at temperatures from 296 K to 700 K. A phase transition to a simple bcc structure is observed upon heating, and the phase line is drawn from our data set. Another phase is recovered upon cooling, with complex structure. We also report melting line measurements up to 10 GPa, 690 K.

Role of asphaltenes on the foaming of oil mixtures

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Keywords: Foamability, Interface, Marangoni effect, Asphaltenes

After extraction of crude oil, undesirable foaming can occur during the liquid/gas separation process leading to unwanted production shutdowns. Since the formation of these oily foams lowers the rate of production a better knowledge of the properties of oil/gas interfaces is needed. Here, we focused on the role played by asphaltenes (Figure 1), the most polar components of crude oil, on the foamability and the stability of oily foams. To this end, several experiments were conducted.

These experiments include classical foaming tests by gas injection through a fritted glass filter and single bubble lifetime measurements. It was demonstrated that concentration of asphaltenes and their state of solubility contribute significantly to foamability of oil mixtures. Effects of bulk viscosity, presence of anti-foaming components, evaporation phenomena and crust formation were also investigated.

Moreover, since the main mechanism controlling the bursting of bubbles is the Marangoni effect, a set up has been designed (Figure 2) in order to evaluate quantitatively the phenomena occurring at the liquid/gas interface. This experiment allows us to reproduce Marangoni flows visible in bubble cap films by applying stresses induced by extremely low concentrations of volatile solutes (Figure 3). Theoretical laws were developed and showed good agreement with the experimental data. In contrast with usual surface active components, the presence of asphaltenes does not modify the Marangoni flows, showing that they do not adsorb at the interface over short time scales. The entrapment of asphaltenes nano-aggregates within the films is currently investigated as a possible explanation of the increased stability of foams in presence of asphaltenes.

CHEMISTRY

Plasmonic Biosensor based on Gold Nanoparticles

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Keywords: Biosensor, Gold Nanoparticles, Localized Surface Plasmon Resonance

A biosensor is a device consisting of two parts, a biological receptor element and a physical transducer. The receptor binds specific molecules and the transducer translates the biochemical interaction into a measurable signal. [1] The unique optical properties of noble nanoparticles, especially silver or gold nanoparticles (AuNPs), due to their localized surface plasmon resonance (LSPR) [2] and the possibility of surface functionalization with a wide variety of different biomolecules (antibody, peptide etc) [3] make them very attractive as optical biosensing platform.

The LSPR spectral position of nanoparticles is highly dependent on their composition, size or shape as well as the refractive index of the dielectric medium around them. [4,5] Size and shape dependence provides us with a wide spectral tunability along the whole visible spectrum, which is extremely useful to optimize the biosensing response of the nanoparticles. Depending on the origin of LSPR changes, there are two types of sensors: refractive index sensors and aggregation sensors. The first group is based on the red-shift of the LSPR which is induced by a refractive index increase around nanoparticles. The second group is based on the drastic color change which is induced in nanoparticle aggregates.

A colorimetric biosensor based on AuNPs conjugated with antibody for the detection of staphylococcal enterotoxin A (SEA) in milk has been well established. [6] With a weak SEA concentration, the red-shift of the LSPR could be detected with simple optical equipment. As long as the SEA concentration increased more, the aggregation of AuNPs led to the color change of the solution which could even be seen by naked eyes. This biosensor has a high sensitivity, with a limit of detection 5ng/mL, which is lower than that obtained by quartz crystal microbalance.

Fig. Sensitive LSPR Biosensing of SEA in milk using stable AuNP-Ab bioconjugates (adapted from [6])

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Session 2
Fully quantum dynamics of protonated water clusters: combining Quantum Monte Carlo and Path Integral Langevin Dynamics

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Keywords: Quantum Monte Carlo, Molecular Dynamics, Nuclear Quantum Effects

We introduce a novel approach for a fully quantum description of coupled electron–ion systems from first principles. It combines the variational quantum Monte Carlo (QMC) solution of the electronic part with the path integral formalism for the quantum nuclear dynamics. Nuclear quantum fluctuations are included via a set of fictitious classical particles (beads), linked by harmonic interactions, whose dynamics is driven by accurate ionic forces computed at the QMC level [1]. The stochastic noise affecting the QMC forces contributes to thermalize the particles in a path integral Langevin dynamics framework. Our general algorithm relies on a Trotter breakup between the dynamics driven by ionic forces and the one set by the harmonic interbead couplings. The latter is exactly integrated, even in the presence of the Langevin thermostat, thanks to the mapping onto an Ornstein–Uhlenbeck process. This framework turns out to be also very efficient in the case of noiseless (deterministic) ionic forces. The new implementation is first validated on the Zundel ion (H5O2+) by direct comparison with standard path integral Langevin dynamics calculations made with a coupled cluster potential energy surface. We then applied our method to the protonated water hexamer, where we computed thermal distribution functions, provided for the first time by a method which explicitly includes electron correlation, together with thermal and quantum nuclear effects [2].
Semiconducting Materials Based on Donor/Acceptor Units for Optoelectronic Applications

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Keywords: Semiconducting Materials, Liquid Crystals, Optoelectronic

In this project, we will design and study 3 families of semiconducting materials based on donor/acceptor units.

The first set of molecules is two liquid crystalline fluorescent compounds based on a calamitic architecture (Figure 1). For this series, the conjugated part is based on a benzothiadiazole core, which is a good electron acceptor. It is one of the most widely used moieties in photoluminescent compounds and in organic electronics applications. In addition, they can form well-ordered crystal structures because they are strongly polarized, and therefore they can induce strong intramolecular interactions. These molecules are high fluorescent properties and high charge transport properties. We design these molecules in order to get emissive devices.

![Figure 1 Chemical structures of the calamitic liquid crystalline compounds based on benzothiadiazole core.](image1)

The second family is a more complex system incorporating different mesogenic units such as [1]Benzothieno[3,2-b][1]benzothiophene (BTBT) or terthiophene for high charge transport properties and previous luminescent calamitic derivative as emissive units (Figure 2). The objective is to obtain multi-lamellar organization with high charge carrier mobility and high fluorescent properties for Light Emitting Transistor application.

![Figure 2 Chemical structures of the liquid crystalline fluorescent dyad and triad architecture.](image2)

The third set of molecules is narrow bandgap derivatives (Figure 3). These molecules will be designed based on central naphthalene diimide core, benzothiadiazole, cyano group and donor unit thiophene. These donor/acceptor derivatives are promising candidate for n-type and/or ambipolar behavior and to be use as semiconducting layers in Organic Field Effect Transistor devices.

![Figure 3 Chemical structures of narrow-bandgap molecules based on naphthalene diimide central core.](image3)
Elaboration of lignin-based materials via graft copolymerization

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Keywords: biomass, lignin, thermoplastics, polyesters, graft copolymerization, characterization

The abundance and the renewable character of lignins make them potential oil substituting raw material for the synthesis of chemicals and new materials.

Currently, the valorization of lignins in the polymer field relies essentially on their incorporation within blends, or in the synthesis of thermosetting resins1,2.

Lignins have an aromatic structure along with several interesting reactive functions (primary and secondary aliphatic alcohols, phenols, carboxylic acids). Therefore, it is possible to use them as comonomers in the synthesis of value added biobased and potentially biodegradable technical thermoplastic copolymers.

Issues are related to the complexity and the variability of the structure, the thermal instability, and the low solubility of lignins. One of the challenges of this work is to develop new thermoplastic materials by identifying and controlling their structures in order to manage the properties that result from them.

The study was carried out on an organosolv wheat straw lignin provided from the CIMV company. In order to improve its solubility and to homogenize the nature of the reactive chemical functions, purification and various chemical modifications were completed. Then, the synthesis of copolymers using lignin as a macromonomer was studied according to two strategies:

- Ring-opening polymerization (ROP) of lactones using lignin as a macroinitiator (grafting from);
- Controlled graft copolymerization of monofunctional polymers terminated with carboxylic acid end groups (grafting onto).

The obtained copolymers were characterized in detail by appropriate analytical techniques (1H NMR, 2D NMR 1H-13C HSQC, 31P NMR, SEC, TGA, DSC).

References

Blending liquid into a flowing dry granular materials

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Keywords: wet granular materials, accretion, capillarity, imbibition

Wet granular materials are common precursors of construction materials, food, and health care products as well as relevant in many geophysical processes [1]. Indeed, the addition of liquid drastically modifies the behavior of a granular medium, and its rheological properties strongly depend on the proportion of the liquid [2]. For large liquid volume fractions, a dense suspension is produced exhibiting fluidlike properties [3]. By contrast, the presence of small amounts of liquid induces the formation of liquid bridges between grains, providing a strong cohesion to the material and a solidlike behaviour [Fig. 1(a)] [4]. These effects are commonly used in civil engineering processes that require mixing dry grains with a liquid to obtain new physical or chemical properties. Although the final product is homogeneous at the large scale, strong spatial heterogeneities in the liquid content are present during the blending, with rheological properties ranging from a dry state to a suspension in the mixture.

Figure 1 (a) Capillary bridges observed by fluorescence microscopy [2]. (b) Artistic view of the accretion of impacting dry beads on a wet granular packing [6].

Most of investigations on the wet granular materials focus on the liquid distribution in static granular packings to describe the morphology of the liquid connections between the grains. In this work, we propose to study a dynamical situation corresponding to the interaction of a dry granular flow with a wet granular substrate. Depending on the liquid saturation rate in the wet phase, different phenomena can occur at the interface such as the erosion of the substrate by the granular flow [5], the accretion of dry grains by the wet substrate [Fig. 1(b)] [6] or the impregnation of the interstitial fluid into the flowing dry grains. We carry out model experiments with glass beads and simple fluids to highlight the physical mechanisms which govern each phenomenon and to characterize their dynamics.

CHEMISTRY

Elaboration of carminic acid – smectites hybrids pigments: Focus on chemical interactions

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Keywords: Pigment, Photodegradation, Clay, Carminic Acid

Fading of dyes is a common phenomenon observed on painting. Many cases were reported as famous painting “L’Église d’Auvers sur Oise” from Vincent van Gogh (pink fading of Eosin [1]). Other painters, as Auguste Renoir with “Bal du Moulin de la Galette” 20 years later, were so surprised by the degradation of their painting that they did not recognized their own work.

Reasons of fading are various: exposition to light, wet atmosphere, temperature changes, pollution from human activities or urban area, and also the activity of pests and microorganisms as fungi and bacteria.

Meanwhile, a well-known example of organic-inorganic pigment called Maya blue crossed ages with its astonishing resistance [2]. Most of the painted walls from the 9th century was degraded but the Maya blue remained unspoiled.

This study aims to synthetize new hybrid materials with enhanced photo-chemical resistance, by using an inorganic matrix to prevent the decomposition of unstable organic dyes. Carminic acid was used as natural red dye, and several smectite (mainly Montmorillonite) were employed as supporting mineral.

The clay mineral surface charge was inversed by a cationic polymer. Adsorption of the later and the carminic acid molecules was done by wet impregnation in presence of an excess of water. The free organic molecules were removed by washing with water. The cationic polymer is intercalated in the interlayer space as attested by XRD. The dye molecules are probably adsorbed on the edges. 13C NMR spectroscopy stress on the presence of hydrogen bonds between the edges of the clay mineral and the carminic acid. The interactions involved between the inorganic and organic parts influence directly the release properties of the organic molecules in different solvent. The photo-stability of the new pigments was investigated under focused light. Color changes were followed using CIE L*a*b* parameters. The inversion of surface charge seems to increase the photo-stability of the new pigments compared to the one prepared without any cationic polymer.

In tissue engineering, biomaterials create a scaffold and give the cells an environment similar to the extracellular matrix (ECM), providing suitable mechanical properties and precise chemical signals to trigger cell adhesion, migration, proliferation and differentiation.\[1\] Fibrillar proteins like collagen or fibronectin, as well as synthetic peptide polymers (e.g. Peptide Amphiphile (PA)) are widely used as structuring scaffolds.\[2\] In ECM, the heterogeneities in biomolecule distribution is a key signal to trigger a given cell behavior. To understand and mimic this clustering, it is necessary to engineer biomaterials with well-defined structuration at the nanoscale.

In the composite approach, the incorporation of silica nanoparticles (SiNPs) grafted with functional peptides into PA scaffolds aimed at providing a unique way of tuning the scaffold bioactivity with improved modularity. In this work we were able to highlight the impact of spatial presentation of the fibronectin-derived peptide on cell response. Fibroblasts cultured on RGDS-clustered at the SiNP surface and embedded in a PA matrix showed increased cell spreading and more mature focal adhesions than on RGDS homogeneously introduced into PA nanofibers. Moreover the required amount of signal to have a nice fibroblast spreading is more than four times lower when SiNPs are used to display the peptide epitope thanks to the condensation of the signal.

In order to create a more precise nanostructuration and clusterization we describe a new method to create bi-functional patchy SiNPs. Several alkoxysilane precursors were designed and synthesized. Their self-assembling properties were analyzed in solvent of different polarity and then immobilized at the surface of the SiNP by sol-gel chemistry. This method enabled us to create size-controlled patches at the surface of the particle that can be functionalized with bioactive epitopes. Another molecule of interest can be grafted between the patches simultaneously to create bi-functional particles. Those nanostructured SiNPs would be embedded in an extruded or electrospun collagen matrix to create a new generation of biomaterials with an improved modularity for tissue regeneration.

Figure 1. Multifunctional Particles – Biopolymers Hybrids Scheme

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Session 3
Rare-earth-doped Single Crystal for Quantum Information Processing

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Keywords: Rare earth, high resolution spectroscopy, quantum information processing, cryogenics

Crystals doped with paramagnetic rare earth (RE) ions are promising materials for quantum information processing because they can be coupled to microwave photons\textsuperscript{1} or provide large bandwidth memories\textsuperscript{2}. Furthermore, it was recently demonstrated that coherence transfer with high fidelity was possible between electron and nuclear spins in these materials, opening the way to long storage time capability\textsuperscript{3}.

Yb\textsuperscript{3+} has very good optical properties in Y\textsubscript{2}SiO\textsubscript{5}, especially in terms of oscillator strength and narrow inhomogeneous linewidths at low concentrations\textsuperscript{4}. Here we report on the hyperfine structure of $^{171}$Yb\textsuperscript{3+}, which is the only paramagnetic rare earth ion with a nuclear spin I=1/2, leading to a simple energy level structure. Thanks to the narrow inhomogeneous linewidths (<1 GHz), the nuclear spin transitions are optically resolved, which is convenient for an efficient optical pumping into the spin levels and can facilitate a state preparation for quantum processing applications.

$^{171}$Yb\textsuperscript{3+}:Y\textsubscript{2}SiO\textsubscript{5} shows the ability to shape the level structure by applying a magnetic field which could allow the coupling between $^{171}$Yb\textsuperscript{3+} ions and superconducting quantum processors as those currently developed by IBM or Google.

Cold compression of ceramics granules : role of the organic binder

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Keywords: compression, zirconia, spray-drying, binder

One of the most common ways to obtain dense ceramics is to compress granules (size~100µm) obtained by spray-drying a suspension of ceramics nanoparticles (size~100nm) in water. Before spray-drying, a polymeric component, called a binder, is added to improve the final granule’s properties at compression. The compressed material is called the “green body” and it is then sintered at high temperature, around 1500°C, to obtain final dense products with defined shapes. The “green body”’s properties affect the sintered body’s ones. In particular, its density is an essential parameter that determines the post-sintering porosity and thus the strength of the material; homogeneity of the green body is also crucial since density gradients lead to the formation of cavities that are responsible for fractures during the sintering step; finally large values of the green body’s tensile strength is also essential to ensure a successful demolding step.

The objective of this PhD is to understand how the organic binder will affect the green body properties. Indeed, by using different types of binder, strong differences can be observed on the compressed green samples:

![SEM observations of 100MPa compressed ceramics granules with two different binders (PEG = Poly(EthyleneGlycol) ; PVA = Poly(VinylAlcohol))](image)

During this PhD we have shown that during the spray-drying process, a large amount of binder is driven away to granules’ surface and finally form a polymeric shell around spray-dried granules. This polymeric shell can affect friction between granules but we have also shown, by calculating deformation energies, that finally the binder spatial distribution in spray-dried granule doesn’t play any role. On the contrary, binder’s mechanical properties are a key parameter during granules compression since they determine the needed energy for compression and can also be at the origin of an elastic rebound. Using a hard binder (thus with a glass transition temperature above the room temperature) will harden the compression of our samples. On the contrary, using a soft polymer (whose glass transition temperature is close or below the room temperature) will lead to less porosity between granules after compression.

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Chemistry

Nanostructured Silica Nanoparticles: Degradation Pathways and Application in Biomedical Engineering

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Keywords: Silica nanoparticles, Degradation, Drug delivery, MR imaging

Abstract

Recent years, silica nanomaterials attract wide attention in cell imaging, drug delivery and tissue engineering. Silica nanoparticles not only own variety of unique features, such as versatile synthesis, controllable size and architecture, easy surface modification, etc. Moreover, “all in one” multifunctional strategy makes it possible to construct multifunctional silica nanomaterials which can gather a variety of functions in single nanoparticle at the same time. Up to now, a number of silica-based nanomaterials with engineered shape, structure and surface modification have been prepared and evaluated for applications in biomedical area. In order to use them for intracellular multifunctional application, the control of intracellular behavior of the nanoparticles remains highly challenging, especially because the question whether mammalian cells exhibit specific biological mechanisms to degrade silica remains open. In this communication, we firstly prepare three types of PEGylated fluorescent silica nanoparticles with various internal structures (core-shell bio-composite, multilayered and hollow mesoporous) and studied their degradation in contact with human dermal fibroblasts. All particles were uptaken by cells with limited cytotoxic effect. Their intracellular degradation occurred faster than in solution but following almost similar dissolution mechanisms. These results strongly suggest that silica nanoparticles must be considered as bioresorbable but not biodegradable, a point of importance for their future application in drug delivery. After, we designed a novel GSH-triggered drug delivery system by wrapping MnO₂ nanosheets around doxorubicin-loaded hollow mesoporous silica nanoparticles and then decorating with aptamers to form a multifunctional nanoplatform for the first time. The obtained nanoplatforms had a high loading capacity for an anti-cancer drug and controlled release properties. More importantly, it exhibits MRI contrast-enhanced imaging in 3D tumor models. Such new multifunctional nanomaterial systems combining diagnostic and therapeutic functions are of great significance for potential cancer diagnosis and treatment.

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Toward tendon reconstruction: collagen self-assembly in microridged freeze-casted scaffolds

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Keywords: tendon, collagen, freeze-casting, tissue-engineering

Tendon injury is a clinical, societal and economical issue. Because of poor vascularization and low cellularity of the tissue there is limited spontaneous regeneration. Tendon repair thus represents an important clinical challenge, partly due to the mechanical constraints that occur at the junctions between muscle and bone. Biomaterials bring new hope for tendon reconstruction, with the need of scaffolds that achieve both the common requirements for tissue regeneration, such as bioactivity, biodegradation and high porosity, and the specific requirements for tendons, such as anisotropy, high mechanical modulus and strength1. Collagen foams made by freezing collagen solutions are good candidates and raise high hopes as they demonstrated encouraging results for ACL reconstruction2. The use of collagen solutions ensures the bioactive and biodegradable aspect while freeze-casting provides anisotropy and porosity. However, the self-assembly of collagen is not triggered, resulting in weak and soluble foam3. Chemical cross-linkers are used instead, representing a risk of toxicity.

We present the protocol we established to freeze-cast pure collagen I solutions into porous scaffolds and achieve the self-assembly of the constituting collagen, as evidenced by transmission electron microscopy observations. Self-assembled fibrillar collagen gives the macroporous foams suitable mechanical properties without the need for chemical cross-linking usually used to prevent dissolution and improve the stiffness of collagen sponges. The obtained samples, 1.2 cm long and approximately 5 mm in diameter, present pores oriented along the longitudinal axis. The size of these canals and their wall thickness vary all along the tube, the major axis of the pores observed in the transverse planes ranging from 39 ± 23 µm to 106 ± 88 µm. The scaffold also displays a lower order of structure inside the pores with parallel ridges running along the main direction. The distance between ridges is about 8±1 µm in the thinner pores and 17±2 µm in the larger ones. The scaffold demonstrates high bioactivity and its anisotropy and micro-ridges fosters cellular alignment along the main axis.

**Physics**

**Velocity and Density of Fe-Si alloys at High Pressures: Constraints on the Composition of Earth’s Core**

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**Keywords:** Iron Alloys, High Pressure, Earth’s Inner Core

While Iron is known to be the main constituent of the Earth’s core, its density at inner core pressure (330-360 GPa) and temperature (5000-6500K) is too high¹ with respect to seismological models. This argues for the presence of light elements such as silicon in large quantities alloyed to iron to account for the density deficit. We use a combination of Picosecond Acoustics and synchrotron X-ray Diffraction to measure the sound velocity and density of Fe-Si alloys as a function of pressure, temperature and composition. By comparing experimental results to seismological observations, constraints are placed on the Si abundance in the Earth’s inner core.

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Fundamental interplay between cationic–anionic redox that governs lithium-rich cathodes for batteries

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Keywords: energy storage, lithium-ion batteries, anionic redox, X-ray spectroscopies

A sustainable transition towards renewable energy and electrified transportation is being facilitated by energy storage technologies, mainly rechargeable lithium-ion batteries, with an important thrust area being the energy density of their cathode materials. Today’s cathodes such as LiCoO2, which operate via a lithium de-insertion/re-insertion electrochemical reaction during charge/discharge (LiCoO2 ↔ Li1–xCo3+2O2 + xLi+ + xe–), have limited charge-storage capacity that is restricted to the cationic redox of their transition metal ions (Co3+ ↔ Co3.5+). However, the recent demonstration of reversible anionic redox (O2– ↔ O2–, n < 2) in lithium-rich layered oxides, e.g., Li2RuO3 that are also expressed as Li[Li1/3Ru2/3]O2, has revitalized the search for higher energy battery cathodes. To facilitate the success of such materials, the fundamentals of the promising anionic redox mechanism need to be further advanced.

In this presentation, we will focus on the cationic–anionic redox processes in Li3Ru0.75Sn0.25O3 – a “model” lithium-rich layered cathode in which Ru (cationic) and O (anionic) are the only redox-active sites, whereas Sn is redox-inactive but provides structural stability. We will lay out its charge compensation mechanism and local structural evolutions, as revealed via operando (and complementary ex situ) X-ray absorption spectroscopy (XAS). We will also present several interesting local effects discovered by extended X-ray absorption fine structure (EXAFS) modelling, e.g., the anionic-oxidation-driven distortion of oxygen network around Ru atoms. We will complement these findings by presenting a direct proof of lattice oxygen’s reversible redox reactivity, as revealed via hard-X-ray photoelectron spectroscopy (HAXPES).

Lastly, we will demonstrate a spectroscopy-driven visualization of electrochemical reaction paths, which was achieved through a chemometric approach, based on principal component analysis (PCA), for interpreting the operando XAS data. This enabled us to neatly decouple the individual cationic–anionic contributions on the dQ/dV electrochemical curve (see Figure). The results were consequently leveraged to explain the electrochemical kinetics and thermodynamics of these electrodes, providing fundamental insights that will be crucial for improving the existing anionic-redox-based cathodes and for evaluating the ones being discovered rapidly.

Cationic–Anionic redox deconvolution via PCA and MCR-ALS analyses

Session 4
PHYSICAL-CHEMISTRY

Towards Photo-Rechargeable Li-Ion Batteries

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Keywords: Photo-electrochemistry, Li-ion batteries, Mesoporous thin film electrodes

Li-ion batteries need to be charged by being plugged into the grid, limiting their autonomy. Charging a battery consists of applying an external current to reverse the spontaneous electrochemical reactions occurring during discharge. A strategy to improve their autonomy is to design nanostructured electrodes whose composition and architecture allow for these recharging reactions to be driven by light.

Classical electrochemical experiments (in the dark and under light) demonstrate that light promotes the de-insertion reaction of 3D Li,TiO₂ mesoporous thin films due to the participation of photogenerated holes. These holes allow the oxidation of Ti³⁺ into Ti⁴⁺, simultaneously giving rise to Li-ion extraction. Galvanostatic experiments performed on Li-rich TiO₂ mesoporous films show that competition between ion insertion and de-insertion occurs, leading to electrodes with potentially infinite capacity. This work constitutes a proof of concept that low potential Li-ion batteries (TiO₂ // Cgraphite) can solely be recharged by exposure to light.

Illustration of the potential for “infinite” capacity of the mesoporous TiO₂-based battery. The galvanostatic experiment was realized in a water-cooled cell: glass/FTO/TiO₂//LiPF₆ 1 M in EC : DMC (1 : 1 in vol) // Li²⁺, ref. Li²⁺. Two successive discharge-charge curves (1–2, 3–4) at C/7-rate if the theoretical capacity is set to 335 mAh.g⁻¹ under dark (black) or light (red) conditions. The light had to be turned off overnight after 8 hours.

Comprehensive phase diagram of two-dimensional space charge doped Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$)

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Keywords: Superconductivity, High-$T_c$ superconductors, Phase Diagram, 2D materials.

The phase diagram of hole-doped high critical temperature superconductors as a function of doping and temperature has been intensively studied with chemical variation of doping. Chemical doping can provoke structural changes and disorder, masking intrinsic effects. Alternatively a field-effect transistor geometry with an electrostatically doped, ultra-thin sample can be used. However to probe the phase diagram, carrier density modulation beyond $10^{14}$cm$^{-2}$ and transport measurements performed over a large temperature range are needed. Here we use the space charge doping method$^{1,2}$ to measure transport characteristics from 330–K to low temperature. We extract parameters and characteristic temperatures over a large doping range and establish a comprehensive phase diagram for one unit cell thick Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ as a function of doping, temperature and disorder$^3$.

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Probing *in situ* the wetting at metal/oxide interface via plasmonics combined with photoemission

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Keywords: Plasmonics, Photoemission, adhesion, wetting

The *in situ* and real time characterization of the wetting of a surface by growing films is a crucial issue in surface science [1]. We address herein the case by combining plasmonics sensitivity to morphology (UV-vis Surface Differential Reflectivity Spectroscopy, SDRS [2]) and X-ray Photoelectron Spectroscopy (XPS) sensitivity to chemistry to study the effect of a metallic buffer (Cr) on a metal/oxide interface (Zn/\(\text{Al}_2\text{O}_3\)(0001)). The system is inspired by the new Advanced High Strength Steel grades used in automotive industry of which drawback is to exhibit segregated oxide adlayers (here alumina) that prevent the adhesion of Zn in the galvanization process.

Our fundamental study performed at 300 K involves (i) Cr/\(\text{Al}_2\text{O}_3\) film growth as function of thickness and (ii) deposition of Zn (16Å) overlayer on top. Cr allows Zn sticking on \(\text{Al}_2\text{O}_3\) at 300 K while much lower temperature (100K) is required to reach a sizeable condensation of Zn on bare alumina [2,3]. At early stages of growth, SDRS shows that Cr forms initially 3D clusters that cover partially the surface of alumina until an early percolation for kinetic reasons. Photoemission points at Cr in metallic state and the lack of reduction of alumina. Only a reaction limited to surface OH is detected. Concerning Zn sticking, the thickness of deposited Zn determined through XPS correlates with the Cr thickness (Fig. a). Both the shape of the Zn LMM Auger transition and the Auger parameter \(\alpha=2013.9\text{eV}\) highlight metallic zinc (Inset of Fig. a). Consistently, dielectric simulation of experimental SDRS of a Zn film grown over a thick Cr deposit that completely covers alumina (Fig. b) reveals a 2D morphology (that contrasts with the 3D growth on alumina at 100 K, Fig. b) in agreement with *ab initio* predictions on Zn/Cr/\(\text{Al}_2\text{O}_3\) [4]. Finally, Zn is shown to poorly wet oxidized Cr. The contrasted behavior of Zn wetting over metallic and oxidized Cr highlights the interest of optics and photoemission combination in the case of the *in situ* study of the wetting/adhesion during the growth of thin films.

CHEMISTRY

NEW SYNTHESIS OF GOLD NANOPARTICLES USING N-HETEROCYCLIC CARBENE BORANES

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Keywords: Gold nanoparticles, Synthesis, N-Heterocyclic Carbene Borane

Gold nanoparticles have potential applications in many fields such as medicine, optics, electronics or catalysis. Their most common syntheses generally require three components: a gold precursor, a reducing agent and a stabilizing ligand.

N-Heterocyclic Carbenes (NHCs) are highly tunable molecules which exhibit a better binding affinity for gold than thiols1, and a few studies have shown the possibility to use NHCs to stabilize gold nanoparticles2-4. NHCs, which are Lewis bases, can also form with borane (Lewis acid) stable adducts5, which exhibit reducing properties. NHC-boranes might thus be used as reducing agent and precursor of stabilizing ligands in the synthesis of gold nanoparticles.

A synthesis of NHC stabilized gold nanoparticles is reported for the first time from NHC-borane, as a "2-in-1" reagent, and AuClSMe2 as gold precursor6. XPS analysis confirms the presence of NHC as surface ligand. Varying the reaction conditions allows tuning of the nanoparticle size in the range 5-10 nm.

6. L. Hippolyte, N. Bridonneau, F. Ribot, et al., manuscript in preparation
PHYSICS

TIME AND SPACE-RESOLVED MAGNETO-ACOUSTICS

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The constantly increasing demand for enhanced performance of data storage and transfer has resulted in a continuous search for new solutions. One of the approaches is to minimize power consumption in data processing [1]. That quest brought the attention of researchers to magnonics. Spin waves (SW) can carry information that can be modified without applying an external current, however only over a few micrometers, due to a strong intrinsic damping. In order to bypass this issue, the use of acoustic waves and magnetoelastic interactions was proposed. Spin waves can be generated by acoustic waves several millimeters away from the excitation source. In other words SWs can be excited remotely in the required point of the magnetic medium, by the acoustic waves.

Different types of acoustic waves can be used to excite SWs. In this work we focus on surface Rayleigh acoustic waves (RAWs), specific for the coexistence of longitudinal and transverse component of the strain. The generation of RAWs can be done electrically (via piezoelectricity) and optically (via thermoelasticity). This propagating distortion of the material, can act on the magnetization by modifying the magnetoelastic part of the energy in magnetostrictive materials. Under specific conditions it may trigger the magnetization precession. The studies we present here were carried out on two classes of magnetostrictive materials, dilute ferromagnetic semiconductors (DFS) and ferromagnetic metals. They possess different advantages that were used depending on the RAW excitation source.

HYDROGEN BONDED SILICONE RUBBER: CORRELATION BETWEEN CHEMICAL STRUCTURE AND MECHANICAL PROPERTIES

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Keywords: Silicone, hydrogen bonds

Silicones are mainly used in the industry for their good mechanical and insulation properties at elevated temperature. The aim of this study is to bring a self healing ability to such elastomers.

To meet the requirements of the rubber industry we focused our work on the system of supramolecular modified silicone compounds previously investigated by Yilgor et al¹,². These systems (shown in Figure 1) contain hard segment (HS) which can interact by hydrogen bonding alternated by silicone soft segment (SS). The enormous difference of solubility parameters³ of both segments creates a microphase separation. Wacker has moreover commercialized the GENIOMER© based on this technology. These compounds exhibit good thermal and mechanical properties⁴ which are consistent with the specifications expected.

Our strategy is to establish a correlation between the chemical structure and the physical properties of the materials. In this context we have synthesized different systems with variable HS and analyzed the mechanical response.

Figure 1 – Schematic representation of intermolecular interaction in silicone-urea copolymers²

References.
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Gold nanoparticles on surfaces: work-function and optical signature

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Keywords: functionalized gold nanoparticles, Kelvin Probe Force Microscopy, surface differential spectroscopy

Gold nanoparticles are well-known for their particular optical properties due to the plasmon absorption in the visible, and they also could be used in electronic devices like transistors. For this last type of application, and essential property must be studied, the work-function, defined as the energy needed to extract an electron from the Fermi level to the vacuum. The work-function of the nanoparticle provides the access to its charge state, which is influential in the plasmon response. In this work, we want to measure the work-function modification of the gold nanoparticles, induced by a molecular functionalization, and how it can modify the plasmon response.

We have first studied by differential spectroscopy the plasmon response of the nanoparticles grafted on many surfaces (glass, silicon) in transmission or in reflection and determined the appropriate model. This is particularly helpful for the reflection on silicon where the measured signal is unusual and do not appeared like a positive absorption plasmon band but like a small derivative shape¹.

Then we have measured the work-function modification of gold nanoparticles induced by a molecular functionalization (see the figure below). The employed technique is a conductive atomic force microscope (AFM), a Kelvin Probe (KPFM). When the particles are functionalized, our results show an evolution of the work-function modification as a function of the particle diameter. They also show two different behaviors from two different functionalizing molecules. These two behaviors have also been seen in optic where two plasmon band shifts have been measured.

KPFM measurements of gold nanoparticles grafted on gold and functionalized with 16-mercaptohexadecanoic acid: a) topography and b) relative work-function.

Session 5
Mechanophores for the detection of stress and strain in soft materials

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Keywords: Mechanophore; Multiple Networks

Macroscopic toughness is strongly related to the ability of materials to transfer forces away from a broken bond to a large number of neighboring bonds. The key to progress on these questions is the technique to probe molecular forces. In mechanochemistry, the detection of bond forces and bond breakage can be done with mechanophores, which are polymers responsive (color change) to mechanical stimulus \cite{1,2}. Spiropyran (SP) as a mechanophore is incorporated into multiple network elastomers acting as cross-linker. SP can be activated into a merocyanine (MC) isomer under various loading conditions and generate changes in optical signals (absorbance and fluorescence) (Figure 1). Analyzing the optical signals of MC allows to reconstruct the spatial distribution of molecular forces in soft materials.

![Figure 1](image)

Figure 1. (a) The conversion between colourless SP and coloured MC. (b) Mechanical responsiveness of SP in ploy (ethyl acrylate).

\textsuperscript{2}E. Ducrot; Y.L. Chen; M.Bulters; R. P. Sijbesma; C. Creton, Science, 2014, 344, 186-189.
Phonon lifetime of MgO by inelastic x-scattering and ab initio calculations: Implications for thermal conductivity

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Keywords: Phonon, Thermal conductivity, Periclase, IXS

Thermal conductivity is a fundamental physical parameter that largely controls the heat transfer in Earth’s interior. Despite its importance, the thermal conductivity of mantle minerals is one of the least constrained properties at high pressure (P) and high temperature (T) as direct laboratory measurement at pertinent P-T conditions remains a technical challenge [1]. So far geophysical models rely on extrapolations of lower P data and, more and more, on results from ab initio calculations [2-4]. However, the validity and versatility of the various theoretical approaches used in literature remain to be tested by experiments. The direct measurements of vibrational and anharmonic properties such as phonon energy and linewidth as a function of P and T provide the most straightforward benchmark for the theoretical calculations as these are the key parameters entering the Boltzmann transport equation.

**Étude structural de glaçures plombifères**

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**Keywords:** Raman, NMR, lead silicate, glasses

Au premier siècle avant notre ère, les potiers romains découvrent que l’emploi de plomb comme fondant permet de confectionner simplement des glaçures de bien meilleure qualité que les glaçures alcalines traditionnelles jusqu’alors employées¹. C’est à partir de cette époque que l’emploi de glaçures plombifères se généralise peu à peu à travers tout le monde occidental. Cette innovation technologique apparaît également à la même époque en Chine¹. En Amérique, au 14ème siècle, des glaçures très similaires à celles employées en Europe à la même époque ont également été retrouvées sur des céramiques Pueblos². Il semble donc que les céramistes de différentes civilisations aient indépendamment découvert des recettes de glaçure plombifères principalement basée sur un système ternaire PbO-SiO₂-Al₂O₃. Le très large emploi, au cours de l’Histoire, de ce type de système nous a poussé à nous intéresser à la structure de ces matériaux vitreux.

S’il existe de nombreuses études sur le système binaire PbO-SiO₂, l’influence de l’addition d’alumine n’a que très peu été étudiée à notre connaissance. Dans ce travail, nous avons élaboré des verres renfermant des teneurs en Al₂O₃ de 0 à 15 mol% dans un domaine restreint de compositions du système ternaire autour de 40 mol% PbO (Fig. 1), que nous avons étudiés par spectroscopie Raman (Fig. 1) et RMN (²⁷Al,²⁹Si).

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CHEMISTRY

Study of the sol-gel transition in geopolymers

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Keywords: geopolymers, gelation, silicates, activating solution

Geopolymers are a class of alumino-silicates binders envisaged for diverse applications as civil engineering or toxic and nuclear wastes conditioning. They are obtained by reacting an alumino-silicate source (powdered clay) with an “activating solution” containing soluble alkali silicates. It is now accepted that the powdered source is dissolved by the activating solution. This provides chemical entities which will act as building blocks to form the alumino-silicate gel phase constituting the geopolymer 1. Nevertheless, the whole process of geopolymerization is still not well understood. The gelation step is particularly subject to interrogations. Despite the rheological behavior shows it is similar to a solution-gel transition 2, uncertainties remain concerning the chemical origin of this phenomenon. To answer, the effects of different chemical composition parameters of solutions on the reactivity of fresh geopolymer pastes are investigated by microcalorimetry and Nuclear Magnetic Resonance. In addition, a UV-Visible spectroscopic method was developed to quantify the basicity of initial activating solutions. The alkali and hydroxide contents, and the presence or absence of initial soluble silicate, have already been screened. It enabled to highlight the combined roles of hydroxide and silicates ions during the geopolymerization. Research on the effects of aluminate and silicate concentrations in solution are now under progress 3 to elucidate some thermodynamical issues relative to the geopolymerization reaction.

Molecular Magnets: From single molecule to 3D self-assembly

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Recent investigation of ultrathin metal films with atomically well-defined thickness and high crystallinity has shown the existence of 2D superconductivity in a single atomic layer of Pb epitaxially grown on a Si(111) substrate [1].

As this system consists of a surface composed of heavy atoms, there also exists a strong Rashba spin-orbit coupling modifying the electronic properties. Combining this Pb monolayer with local magnetism makes it an ideal template to engineer and realize topological superconductivity [2]. Indeed, the introduction of magnetic impurities can induce the appearance of localized bound states in the 2D superconducting gap, known as Shiba states. Under some specific conditions, the magnetic interaction between several Shiba states in an either one-dimensional or two-dimensional array of magnetic impurities on the surface of a superconductor may realize new topological phases [3].

The atomic layer of Pb has different structural phases depending on the coverage around the monolayer range and the temperature. In particular, a reversible structural phase transition from a (1x1) phase to a (\sqrt{7}x\sqrt{3}) one occurs at about 250 K for a coverage of 1.20 ML. The low temperature (\sqrt{7}x\sqrt{3}) phase presents a superconducting transition at 1.5 K [1].

Magnetic phthalocyanines (Pc) are very promising metallo-organic molecules which can be used to introduce the above-mentioned local magnetism [4]. Moreover, Pcs’ are known to form 2D self-assemblies on various metallic surfaces [5] and they can make it possible to tailor two-dimensional ordered magnetic structures, as we have already seen by STM.

Ultra-sensitive graphene-based gas sensors for the detection of toxic gases

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Keywords: Graphene, gas sensors,

Graphene is a one atom-thick crystal of carbon and it was the first bi-dimensional material to be discovered [1]. Because it is 2D, it is very sensitive its environment. Graphene is therefore a very promising material for gas sensing applications. Gas molecules adsorbed onto a graphene sheet strongly modify its conductance, as shown in Figure 1. As a result, the detection of individual molecules of nitrogen dioxide has been achieved by measuring the conductance [1].

Figure 1: (a) Evolution of the graphene-based devices during a typical experiment. When exposed to a target gas, molecules adsorb onto the graphene sheet (b) causing a strong rise in the conductance. When the device is heated, all the molecules are desorbed (c) and the sensor reach the initial value of the conductance again after cooling.

The relative change in conductance \((G_{\text{end}} - G_{\text{start}})/G_{\text{start}}\) is often used in the literature as the definition of the response function of graphene-based gas sensors. However, it has been shown that such devices do not reach equilibrium when they are exposed to a target gas, even after a long time [2]. The end value of the conductance is therefore chosen arbitrarily, which makes this definition of the response function unsuitable for graphene-based gas sensors. As a result, several authors modelled the transient behavior of the device in order to derive a relevant definition of the device response function [2]. Yet, their models are based on unchecked hypotheses regarding the sensor working principle.

My work aims at investigating experimentally the mechanisms responsible for the change in conductance of graphene-based devices.

The first step was to develop a fabrication process for the graphene-based devices in ONERA’s clean room. Then I devised an experimental set-up to measure the electrical properties of the devices when they are exposed to very low concentrations of nitrogen dioxide at different temperatures. Building on these measures, I derived a new definition for the sensor response function that is directly linear with respect to the concentration of target gas.

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Session 6
Determination of heat induced by plasmonic effect using a ZnGa$_2$O$_4$:Cr$^{3+}$ luminescent nanothermometer

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Keywords: nanosensor, thermometry, nanoheater, chromium luminescence,

The study of the variation of luminescent properties with temperature is one promising way to measure temperature. Recent studies showed that luminescent nanomaterials allow a local and contactless temperature determination [1]. This could be very useful in many applications like medicine, aeronautic, and marine or in the understanding of catalytic mechanism. ZnGa$_2$O$_4$:Cr$^{3+}$ is a potential nanothermometer because of its high sensitivity on a large temperature range. Indeed, the luminescence lifetime of the $^2E$ emitted state is drastically dependent on temperature since the $^4T_2$ and $^2E$ levels are in thermal equilibrium [2]. In this study, we firstly optimized the luminescence properties of 10 nm in diameter nanoparticles with the aim of improving their capability as thermal nanosensor. In order to generate a local temperature increase, gold nanorods are then synthetized [3]. Under an appropriate excitation such gold nanoparticles may induce a heat due to their plasmonic properties. This anisotropic shape is chosen because of the suitable wavelength excitation in the longitudinal band, which is not absorbed by the nanothermometer (at 960 nm). Once the calibration of the nanosensor is effective and the heat generation is highlighted by thermal camera pictures, both nanoheater and nanothermometer were introduced in the same medium. The variation of the optical nanosensor response is promising and should envisioned to consider this coupled system as a potential candidate for hyperthermia treatment with a precise and controlled temperature.

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Physics

Silicene: a bidimensional silicon layer

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Keywords: silicene, 2D, silicon

In the last decade, the research of new bidimensional materials has exponentially increased, triggered by the advent of graphene, an atomically-thin carbon sheet. Its interesting and promising properties, due to the 2D confinement, have stimulated the curiosity and imagination of many researchers, beginning the quest of the bidimensional allotropes of other 14th group atomic species.

Obviously, the first candidate was silicon, as it is widely used in microelectronics and it lays just below carbon in the periodic table of elements. Theoretical studies predicted a metastable 2D structure, consisting in a low-buckled honeycomb arrangement of Si atoms. The calculations show that this new material, baptised as silicene, should have several features in common with graphene, such as high electronic conductivity and Dirac cones, along with new exotic properties, namely quantum spin Hall effect and giant magneto-resistance. Eventually, gap-engineering could lead to the realisation of silicene-based transistors.

Experimentally, it is not possible to isolate one silicene layer with the same exfoliation technique used for graphene. It is necessary to perform in-situ Si evaporation in ultra-high vacuum (UHV) conditions. Bidimensional silicon arrangements have been reported on several substrates, for example Ag(111), Ir(111), ZrB2(0001), MoS2, graphite. The most thoroughly studied is Ag(111), as in 2012 the realisation of a silicene layer with Dirac cones was reported on such a substrate1. Further investigations showed that the strong interaction between the silicon sheet and the substrate prevent Dirac cones an the other predicted properties from showing up. Afterwards, the synthesis of the so-called multi-layer silicene, a stacking of silicene monolayers, was proposed to overcome these limits, but this subject is still a matter of debate.

During my PhD I have studied monolayer and multi-layer Si deposition on Ag(111) by combined experimental and theoretical means. I mainly focused on the structure and growth process using real-time in-situ measurements and simulations based on density functional theory. In particular, this approach allowed to determine the exact atomic structure of the (4x4) phase of silicene on Ag(111) putting in evidence also the deformation of the substrate2, the growth mode of thicker (> 1 layer) Si deposits, which result in the formation of bulklike diamond Si terminated by a reconstruction of Ag atoms expelled from the substrate3,4.

Synthesis of colloidal alloyed CdSe$_{1-x}$S$_x$ nanoplatelets with continuously-tunable electroluminescence and heterostructure shell growth

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Keywords: Colloidal nanoplatelets, CdSe$_{1-x}$S$_x$, electroluminescence, alloying, shell growth

Abstract: The synthesis of colloidal nanocrystals (NCs) has constantly evolved and improved since the first organometallic synthesis of highly monodisperse semiconductor NCs$^1$. New core/shell or core/crown structures, new materials and the discovery of new mechanisms extended our knowledge of these objects. A better understanding of these nanomaterials recently helped to control their morphology. Initial protocols allowed the synthesis of spherical NCs but different shapes were obtained later i.e. nanorods, nanowires, and nanoparticles with two-dimensional (2D) morphologies such as nanoribbons or nanoplatelets$^2$ (NPLs).

These 2D objects arouse interest because of their exceptional electrical, optical and mechanical properties. NPLs, in particular, show a 1D confinement along one axis, their thickness, and can exhibit extremely narrow emission line widths around 10 nm$^2$. Existing protocols have been optimized in order to control the atomic-layer thickness and elaborate atomically flat NPLs$^2$. This leads to narrow emission resulting from minimal inhomogeneous broadening. Contrary to spherical NCs, which exhibit a bandgap that can be finely tuned by adjusting nanoparticle size thanks to 3D confinement, NPLs have not demonstrated continuously tunable emission. For instance, varying the number of monolayers (MLs) in CdSe NPLs produces discrete emission wavelength peaking at 460, 510, or 550 nm$^3$. Recent works$^4$ on 4 MLs alloyed CdSe$_{1-x}$S$_x$ NPLs have shown that the emission wavelength can be modulated by adjusting the composition in selenium and sulfur of these NPLs. Herein, we report the synthesis of 3 and 5 MLs alloyed CdSe$_{1-x}$S$_x$ NPLs. It allowed us to retain NPLs emission sharpness and precise atomic-layer thickness control, while adjusting emission wavelength over a wide spectral range from 430 to 550 nm.

Growing a shell on these objects can greatly improve their quantum yields, by passivating the surface of the cores. Thus, we also present different shell structures deposited on the alloyed CdSe$_{1-x}$S$_x$.

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**Rheology of hydrophobically modified soft colloids in water**

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**Keywords:** soft colloids, jamming, associations, shear banding

Soft colloids have attracted a lot of interest among the scientific community due to the appealing perspective of studying and modelling colloidal interaction on one hand, and the promising outlook of designing smart materials on the other. In both cases, the research efforts have focused on the development of colloidal materials that easy to synthesize, stimuli responsive and versatile in terms of applications. Here we present recent results on a new class of pH responsive soft colloidal particles - i.e. microgels, that can assemble through hydrophobic moieties covalently crosslinked at their surfaces, which are able interact through short range attractive forces in water. This system is thus a valuable candidate to explore the importance of interactions on the physics of jamming, when they are varied from soft repulsive to soft associative by tuning the architectural parameters of the particles (i.e. the crosslink density and the composition and architecture of the associative groups). Using linear viscoelasticity, non linear rheology, static and dynamic light scattering we establish the dynamical state diagram of these associative microgels. The comparison with purely repulsive microgels with exactly the same composition, crosslink density, and particle size highlights the specificities of associative microgels. In the jammed glass regime, attractive interactions are responsible for flow heterogeneities – a competition between wall slip and/or shear-banding- controlled by the strength of the attractive interactions. We propose a two-state model involving two characteristic time scales, which are associated to the relaxation of in-cage associations and cage opening, respectively. Shear banding occurs when the shear rate exceeds the relaxation frequency of in-cage associations which is measured by linear rheology and is directly related to the characteristics of the hydrophobic groups. These results establish a link between the strength of short-range attractions and macroscopic flow instabilities.

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CHEMISTRY

(Gd,Ce)₂O₂S Oxysulfide Nanoparticles:

Tuning the band-gap through the Ce/Gd ratio

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Keywords: oxysulfide, bimetallic nanoparticles, tunable band-gap.

With the development of nanotechnologies in the past 20 years, a large variety of inorganic nanoparticles such as oxides M₂O₃ or sulfides M₂S₃ were synthesized using soft chemistry (typically in water or organic solvents, and below 400 °C). Oxysulfide materials M₂O₃S₃, in which the sulfur atoms are reduced (S²⁻), are harder to reach in these conditions because of preferential affinity of the metal for one anion compared to the other. Nevertheless, Ln₂O₂S nanoparticles (Ln = lanthanide, structure on Figure A) were found to form by reacting Ln₃(acac)₃ and elemental sulfur at 310 °C. For example, the versatile colloidal synthesis of Ding et al led to several Ln₂O₂S nanoparticles (Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Tb).1 Yet, Ce₂O₂S nanoparticles were never reported. The interest of cerium lies in its unique electronic properties in the lanthanide series (Ce₂O₂S is the only one with a low band-gap). Using in situ spectroscopy at synchrotron SOLEIL, we showed that failure of previous syntheses was due to the swift oxidation of Ce⁴⁺ to Ce⁵⁺ in air and water. By isolating the nanoparticles under air-free conditions, we obtained Ce₂O₂S as a pure phase.² Moreover, we prepared new bimetallic nanoparticles of Gd₂(1-x)CeₓO₂S, stable in air up to y = 80 % (Figure B), because Gd stays at oxidation III and helps to prevent the nanoparticle’s oxidation. Lastly, varying the Ce⁴⁺/Gd⁴⁺ enabled us to tune the nanoparticles’ band-gap over a wide range (Figure C) while keeping a similar crystalline structure.

(A) Gd₂O₂S structure. (B) Hexagonal nanoparticles of Gd₁₋₂Ce₂₅⁷S₃O₂S as seen from the top and the side. (C) Evolution of the light absorption along the Gd₂(1-x)CeₓO₂S nanoparticles series.

PHYSICS

Micro-structural Multi-scale Characterization of the Calcination and Rehydration of Gypsum

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Keywords: Microstructural analysis, gypsum plasters, cultural heritage,

Gypsum (CaSO₄·2H₂O) can be heated at 80-200°C to lose part of its water content and turn into bassanite (CaSO₄·0.5H₂O), which in turns readily dissolves in water and precipitates Gypsum : this cycle forms the basis of plasters manufacture and is simple in its ideal form.

Practical manufacture of plaster however is severely complicated by of phases that appear when gypsum is overheated in the calcination stage, as well as by the microstructures that depend on the conditions of elaboration and affect reactivity of the bassanite powder as well as the properties of set plaster.

The goal of this PhD is to try to understand better the relationship between elaboration conditions and microstructures on scales ranging from the atomic defects in crystals up to micrometric porosity through the use of powder X-ray diffraction, electronic microscopy and X-ray microtomography.

In addition to this fundamental part, applications are sought in two fields : the optimisation of industrial processes (with partner Saint-Gobain Recherche) and the study of cultural heritage, with a focus on XVth century Florentine Stucco works kept in museum collections.
Session 7
**Fossilisation of biogenic apatites: crystal-chemical approach and geochemical applications**

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**Keywords:** fossilisation, vibrational spectroscopy, NMR spectroscopy, Ab initio

Vertebrate skeletons, i.e. bones and teeth, consist of composite materials containing a mineral component and a fraction of organic and water molecules. The inorganic component is usually described as nanocrystalline carbonate-bearing hydroxylapatite (Ca\(_5\)(PO\(_4\))\(_3\)OH). The stable isotope composition of fossil remains of vertebrates, particularly the composition (\(\delta^{13}C, \delta^{18}O\)) of structural carbonate groups in apatite, is an important geochemical marker used to infer past climates, biomineralization processes, dietary preferences and habitat of vertebrates. However an important limit for successful palaeoenvironmental and palaeoclimatic studies based on stable isotope analysis of fossils is the preservation of the isotopic composition in biogenic apatites. Fossil apatites generally exhibit an overall decrease in carbonate content, enrichment in fluorine, incorporation of trace elements and an increase in crystallinity. Detailed understanding of these transformations induced by fossilisation is thus required to improve the interpretation of isotopic records in apatites.

In this contribution, we use vibrational (ATR-FTIR, RAMAN) and solid-state NMR spectroscopies to investigate the crystal-chemical transformations, and more specifically the environment of carbonate groups and fluoridation mechanisms, in both fossil bones from the Bolt’s Farm fossiliferous area (Cradle of Humankind, South Africa) and modern bio-apatites altered under controlled conditions. Experimental observations are interpreted in terms of structural changes at the atomic and mesoscopic scale of materials, through modelling of ATR-FTIR spectra based on an effective medium approach\(^1,2\) and DFT calculations of the theoretical equilibrium isotopic fractionation properties of apatite\(^3\). Based on the combined experimental and theoretical results, we discuss the fluoride incorporation mechanisms and their implications for reconstructions based on the isotopic composition of apatite carbonates.

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Simulation of interactions between screw dislocations and radiation-induced defects in α-Iron using Dislocation Dynamics

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Keywords: Mechanical properties; Iron; Simulation; Dislocation Dynamics.

Low-alloy ferritic steel is widely used for pressure vessels fabrication in European nuclear reactors. It is mandatory to ensure its integrity during the reactor operational lifetime, including normal and up normal conditions. Due to continuous neutronic irradiation, radiation-induced defects are nucleated in steel. Such defects have a major influence on the mechanical properties, for example, a significant increase in hardening and embrittlement.

This work is part of a quadrennial European project (SOTERIA). It aims to provide an assessment of ageing phenomena through a multiscale modeling approach. At the mesoscopic scale, dislocation dynamics (DD) is an important tool to provide the link between atomistic and macroscopic scales. This study is done using a three-dimensional nodal DD code NUMODIS, an in-house code developed in CEA (Atomic Energy Commission). This simulation technique is based on solving set of finite elements equations describing dislocations motion in the crystal.

At the microscopic scale, mechanical deformation of materials is related to the movement of dislocations. Notably, there are two types of dislocations; edge and screw. Interactions of edge dislocations with radiation-induced defects have been extensively studied compared to those of screw dislocations. The later are nevertheless of great interest, because their specific mobility has a significant impact on the mechanical properties of steels at low and moderate temperatures. Furthermore, prior molecular dynamics (MD) studies [1, 2] have shown that their interactions with irradiation loops lead to significant hardening.

The ultimate objective of this PhD work is modelling the collective behavior of dislocations to quantify the different contributions of radiation-induced defects. Consequently, we aim to identify and incorporate the relevant parameters in a crystal plasticity simulation to validate our multiscale strategy. In order to achieve this goal, the individual dislocation-defect interactions are studied, and they are successfully reproduced compared to MD.

Figure 1: Dislocations interacting with irradiation defects (simulation using NUMODIS).

**PHYSICAL-CHEMISTRY**

**Atomic mobility of Zr in SiO$_2$-Na$_2$O-CaO-Al$_2$O$_3$ glass**

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Keywords: Zirconium, Glass, Refractory, Diffusion

Zirconium is widely used in glass ceramic as a nucleating agent. It can also enter a few specific glass compositions like nuclear waste insulation tank. We know that in MgO-Al$_2$O$_3$-SiO$_2$-ZnO classical parent glass used in glass ceramic, it can generate some nanoscale phase separations before crystallization $^{[1]}$. In that case, one phase is highly concentrated in Zr while the main phase is Zr-poor. This phase separated state is a precursor of the crystallization. During classical SiO$_2$-Na$_2$O-CaO-Al$_2$O$_3$ industrial forming glass, some Zr can leave the Zr-containing wall of the furnace to enter the glass structure. This Zr may generate a macroscopic glassy phase looking like a droplet and inducing defects on the final glass. These droplets can sometime crystallize to create another kind of defect. A structure study of NCAS glassy phases with variable amount of Zr led to understand how Zr environment impacts its crystallization. Various analyses have been realized (XANES,EXAFS,RMN…) to describe Zr environment from its first neighbors to the polymerized glass lattices in order to determine if phase separation also affects crystallization in this system.

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PHYSICAL-CHEMISTRY

Drop deformation in microfluidics for viscosity measurements

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Keywords: Microfluidics, droplet deformation, viscosity, high-throughput

Measurement of solution’s viscosity is important for a variety of areas including industrial, chemical and biological applications. Numerous single-phase microfluidic viscometers have been reported in the literature. However droplet-based microfluidics allow the use of much smaller volumes and especially the possibility to handle and analyze multiple samples at the same time and in a high throughput manner. The aim of our work is thus to develop a microfluidic device using droplets that can perform high-throughput measurements of viscosity.

To achieve this objective, we chose to study the phenomenon of deformation and relaxation of a droplet at the exit of a microfluidic constriction. As the droplet exits the constriction, it experiences a deformation in the direction perpendicular to the flow. This deformation reaches a maximum before the droplet relaxes to a rest spherical shape. The viscosity of the droplet phase can theoretically be extracted from two parameters, the droplet relaxation time and the droplet maximum deformation. The latter is experimentally easier to measure and is thus the one we chose to study.

Assuming the dimensionless numbers controlling the maximum deformation of the droplet are the capillary number, a geometrical number and the viscosity ratio, no overall scaling relationship was found when the droplet is confined. However, when the droplet is unconfined, all data collapse on a master curve. A measurement of the droplet viscosity can thus be achieved. The calibration of the power law was achieved on silicone oil droplets in water-glycerol mixtures without surfactant varying the viscosity of the two phases for viscosity ratios between 1 and 10 and droplet phase viscosities between 20 and 100 mPa.s. The scaling was found to be also valid for systems with Newtonian polymers and surfactants.

New multifunctional hybrid organic-inorganic materials. Impact of hybridation on mechanical properties of shape memory polymers.

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Keywords: Polymer – Hybrid material – Shape memory properties

Shape memory materials are a new class of smart materials. These materials have the ability to change their shape and recover their original shape upon application of an external stimulus. Shape memory polymers (SMPs) possess the advantages of high elastic deformation, low cost and have a broad range of application temperature. For these reasons, SMPs could be used in the automobile industry as shape memory actuator, bumper and seat fabric.

Most SMPs are thermo-responsive materials. A typical shape memory cycle for a thermo-responsive shape memory polymer is described in Figure 1. First, stable temporary shape is accomplished by heating up the sample above its transition temperature ($T_{\text{trans}}$). Then, it is deformed under stress and cooled below the $T_{\text{trans}}$ maintaining the stress. Permanent shape recovery is accomplished by heating above $T_{\text{trans}}$ without any stress. SMPs properties are characterized by the rate fixity $R_f$ which quantifies the ability to fix the temporary shape; the rate recovery $R_r$ which determine the ability to recover the permanent shape.

In this study, the goal is to synthesize shape memory hybrids and determine their thermal and mechanical properties. Polymers are cross-linked by inorganic component to tune nanostructuration and nature of the hybrid interface. Hybirdation allow to modify deformation, to increase drastically stiffness and bring new properties such as self-healing. Basically, the use of an organic-inorganic hybrid material enable to obtain a custom-made material. The ultimate purpose is to quantify shape memory properties and compare them with the pure organic material.

![Figure 1. Schematic representation of the thermally induced shape memory effect](image)

**Micro mechanics of binders for insulation glass wool**

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Keywords: micromechanics, polyester, moist ageing

Insulation glass wool consists of an assembly of glass fibers with micrometric diameter (typically 1 µm to 10 µm) arranged into a disordered intertwined structure. This structure is responsible for the acoustic and thermal insulation properties of glass wool. To ensure adequate mechanical stiffness of glass wool panels, a polyester binder (= a highly crosslinked polymer) is also incorporated to create permanent joints between fibers. Currently, the correlation between the binder mechanics and the stiffness of glass wool panels is still unclear and impedes the optimization of the industrial product. One of the main limitations is the binder foamability coupled to its fast polymerization during its processing, preventing the fabrication of macroscopic samples under relevant preparation conditions.

To overcome this limitation, binder samples with micrometric size (typically 10 µm) and controlled geometries have been prepared. The major mechanical properties have been measured through three micro-mechanical tests which have all been developed during the PhD. Elasticity and fracture properties have been characterized by tensile tests on micro fibers. Compression tests on micro pillars have given access to the plastic properties. Internal stresses in binder/glass bilayers have also been characterized by measuring the bending of the bilayer. Finally, the evolution of these mechanical properties has been investigated upon moist ageing and related to the material structure.
Session 8
**PHYSICAL-CHEMISTRY**

**Swelling and friction of hydrogel thin films:** anti-fog coatings

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**Keywords:** Hydrogel films, Swelling, Mechanical confinement, Friction

Hydrogel coatings have raised increasing interest for applications ranging from the functionalization of glass substrates to biomedical field. Their hydrophilic properties and their transparency make them suitable candidates for anti-fog coating.

In this work, we first investigate the swelling kinetics of thin (less than 15 µm) hydrogel films on glass or silicon wafer surfaces which are cooled down and exposed to a controlled humid air flow. It sets the time for mist formation. Then, we focus on the friction properties of the swollen gel in relation with the water drainage out of the gel film under contact loading.

Poly(PEGMA) (poly(ethylene glycol)methyl ether methacrylate) and poly(DMA) (dimethylacrylamide) films were crosslinked and grafted onto glass substrates using a well-controlled thiol–ene click chemistry route.

First, changes in the film thickness under constant humid air flow were monitored over time as a function of the temperature difference between the substrate and the incoming humid air flow using an interferometric method. Regarding the swelling kinetics, we derived a convecto-diffusive model (Figure 1) for water vapor accounting for our observations of the film swelling kinetics. The role of the initial film thickness, physico-chemical polymer properties, humid air flow rate and of the substrate temperature is fully described with in this model. This allows to predict the time delay for mist formation on such coatings, and thus their anti-fogging efficiency.

In a second time, the friction properties under steady-state sliding are studied as a function of the load and sliding velocity. Briefly, a glass sphere was squeezed against the film and slid sideways while contact area and lateral forces were measured (Figure 2). We show that the poroelastic drainage of water out of the squeezed hydrogel film accounts for the load and velocity-dependence of the frictional force.

![Figure 1: Swelling of an hydrogel thin film exposed to a humid air flow](image1)

![Figure 2: Friction of a glass lens on an hydrated hydrogel thin film in confined geometry](image2)

PHYSICS

Study on rough surfaces: link between optical and morphological properties

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Keywords: rough surfaces, morphology, optics

The link between surface morphology and optical properties has been studied for a long time. Nowadays, the optical properties of smooth (or weakly rough) surfaces are mastered [1]. Yet, dealing with rough and highly rough surfaces remains a not so easy task. Two kinds of approaches allow for theoretical description of the light scattering from rough surface: geometrical optics and physical optics. In all, there are several different groups of models, varying in the ranges of applicability, amount of computational time and the facility of comparison with macroscopic optical experimental data. In order to test the limitations of those models, their predictions must be confronted to experimental data on rough surfaces with large set of statistical parameters (roughness and correlation length etc.).

In order to perform this confrontation, we realized a complete morphological and optical study of rough surfaces. The surface topography can thereby be characterized at the nanometric scale with an Atomic Force Microscope, and at the micrometric scale with contact profilometer or an optical profilometer (based on confocal microscopy), as presented on Fig.1. Then, the optical characterization can be realized with simple setups as glossmeter or hazemeter for quick evaluation of integral optical properties (gloss and haze), and also with more complex facilities like goniospectrophotometer, see Fig.2 (distribution of scattered light in 3D) and spectrophotometer (spectral properties of diffused light).

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Toward CIGS solar cells synthesized by Atomic Layer Deposition.

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Keywords: ALD – Solar cells – CIGS

Solar photovoltaic (PV) has the largest growth among all the renewable energy with 303 GW installed worldwide at the end of 2016.\textsuperscript{1} The solar PV panels harvest the solar light and convert it directly into electricity using the photoelectric effect discovered by Edmond Becquerel. Aside from the crystalline silicon technologies, thin film technologies solar cells attract interests from researchers and industries for reducing both the amount of materials needed and the manufacturing cost. Cu(In,Ga)(S,Se)$_2$ (CIGS)-based thin film solar cells is considered as one of the most promising PV technology, with the champion cell having a record efficiency of 22.6%.\textsuperscript{2} Yet it is made of scarce and costly raw materials such as In, Ga and Se.

That is why making thinner CIGS solar cells has been the goal for several projects.\textsuperscript{3,4,5} Moreover, the stack of solar cell is composed of several layers (see figure 1) deposited by various techniques, such as sputtering, chemical bath, co-evaporation or atomic layer deposition (ALD) making it difficult and costly to be manufactured. ALD is a thin-film deposition technique based on self-saturated surface chemical reactions produced by a sequential gas injection in a heated reactor under vacuum (see figure 2).\textsuperscript{6} It leads to the control of the thickness with a precision as low as the nanometer scale. Besides it produces uniform and conformal films. The abilities of ALD to be used for depositing all the layers of the CIGS solar cell stack\textsuperscript{7,8,9,10}, and its industrial potential have been evidenced\textsuperscript{11}. Our project aims to synthesize the three top layers: absorber, buffer layer and window layer by ALD and to combine them in order to create a working solar cell. Depositing the quaternary material CIGS by ALD is very challenging and has never been demonstrated. One step to reach this goal is to work on the synthesis of the ternary material CuInS$_2$. We provide an insight into the first result of a CIGS-type working cell with 4 layers over five: CuInS$_2$/In$_2$S$_3$/ZnO/ZnO:Al deposited by ALD.

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**Chemistry**

**Low temperature molten salt syntheses of low valence titanium oxide nanocrystals**

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**Keywords:** Molten salts, Nanoparticles

Low valence oxides of transition metals such as titanium or vanadium are intensively studied since these materials show high electronic conductivity, interesting metal-to-insulator transitions, optical, catalytic as well as thermoelectric energy conversion properties.\(^{(1)}\) Among them are Magnéli phases: a family of mixed valence titanium oxides (Ti\(^{4+}/\)Ti\(^{3+}\)) discovered in 1956 which structure derives from TiO\(_2\) rutile.\(^{(2)}\) These oxides are conductive due to electron hopping between Ti\(^{4+}\) and Ti\(^{3+}\) sites, and stable towards highly acidic or alkaline media. These properties make them very interesting candidates for electrocatalytic processes. This is the case of Ti\(_4\)O\(_7\) that is studied for oxygen reduction reaction.\(^{(3)}\) Other potential applications are pollutant oxidation for water remediation and electrodes for Li-S batteries.\(^{(1,4)}\) These applications of Magnéli phases should strongly benefit from nanostructuring, especially the synthesis of nanoparticles with high surface-to-volume ratio. However usual methods to obtain such oxides such as carbo-reduction or reduction by hydrogen rely on high temperatures, which leads to sintering and crystal growth.\(^{(1)}\) As a consequence nanostructures are very difficult to reach and the literature on this type of oxides at nanoscale is scarce.\(^{(5,6)}\)

In this presentation we will show a simple one pot pathway at 600 °C using molten salts as a solvent to enable selective reduction of TiO\(_2\) by hydrides to form Magnéli phases. This pathway leads to low valence titanium oxide nanoparticles such as the Magnéli phase Ti\(_4\)O\(_7\) (Figure 1). It also offers a relative control over the titanium oxidation state. Some insights into the reaction mechanism will be presented.

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**Figure 1** TEM picture of Ti\(_4\)O\(_7\) nanoparticles synthesized in a eutectic molten salts

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Hydrogels with thermo-responsive toughness

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Keywords: hydrogels, thermoresponsive polymers, mechanical reinforcement

Aim: To reinforce hydrogels mechanical properties by introducing purely organic nanocomposites as thermoreversible physical crosslinks into covalent 3D network.

By covalently crosslinking water-soluble polymers, soft elastic materials with defined shape can be designed displaying very interesting swelling and sieving properties. They are actually involved in many applications such as superabsorbents or scaffolds for tissue engineering. However, an important issue with hydrogels is that these elastic materials are generally brittle. An interesting way investigated to reinforce the mechanical properties of hydrogels is to introduce physical interactions into a hydrophilic covalent 3D-network [13]. To this extent, thermoresponsive polymers, leading to both hydrophobic interactions and H-bonds, have been used to design original networks where the physical interactions can easily be switched “on/off” by temperature [4-6]. Such innovative hydrogels, designed with a 3D hydrophilic network grafted with macromolecular side-chains exhibiting a Lower Critical Solution Temperature (LCST) in aqueous media (or reverse topology), have shown a dramatic and reversible enhancement of their mechanical properties upon heating. The reinforcement mechanism is attributed to the phase separation process of the thermoresponsive polymer leading to the formation of purely organic nanocomposites while the water-soluble macromolecular counterpart allows the hydrogel to keep its volume integrity at macroscopic scale above the LCST [5, 6] (see Fig. 1).

Figure 1: Thermoresponsive polymer network exhibiting Lower Critical Solution Temperature [4]

Based on this strategy, new hydrogels made from two polymers exhibiting opposite thermoresponsive behaviors, LCST and UCST (Upper Critical Solution Temperature), were designed. With this approach, the elaborated hydrogels demonstrate a reversible double thermo-responsive phase transition both at low and high temperature thereby modifying their swelling, rheological and mechanical properties. These novel hydrogels pave the way for the use of thermoresponsive hydrogels in a broad range of temperature. Modifications of the hydrogel topology, performed by changing the average molar mass of the thermoresponsive polymer grafts and the grafting or crosslinking density while keeping the same hydrophilic covalent network, were also investigated. Those different parameters are varied in order to better understand the structure/properties relationships of these new hydrogels with temperature. They especially influence the size of the thermoresponsive purely organic nanocomposites induced by phase separation of the thermoresponsive part which enhances their mechanical properties.

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Development of Electron Paramagnetic Resonance (EPR) spectroscopy on human fingernails for bio-dosimetry of radiological accidents

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Keywords: EPR bio-dosimetry, dose assessment, fingernails

In case of acute irradiations localized to hands, it is usually difficult to estimate the received dose. Up to now, only EPR analysis of amputated bone phalanx could provide this information, but with a limited field of application. As this typology of accidents is the most frequent, new alternative method of dose evaluation are investigated to permit an initial and rapid dose estimation based of none or minimally-invasive method. Fingernails, because they are easily collect and can provide cartography of the dose on hands, are studied as a new bio-dosimeter.

While this approach has many advantages, e.g ease of sampling, signal stability and the ability to map the absorbed dose at the extremities, the analysis of EPR spectra is very complex and many parameters affect both the production and the stability of the measured radicals. Indeed, the EPR spectra of irradiated nails sample have two identical features but of different origin: an endogenous signal (named as BKS) which is affected by humidity and highly variable from one individual to another, and a radio-induced signal (RIS) which is stable but with low signal intensity. Therefore, the challenge lies in the characterization of the chemical entities associated with the two signals in order to develop methods for segregating the different components of the spectrum and extract dosimetric information.

Up to now, the radical nature of the BKS and the RIS was not confirmed. Several chemical experiments coupled with numerical simulations have been realized and now support the hypothesis that they both come from the same paramagnetic species: an o-semi-quinone anion radical formed from tyrosine, a common amino acid found in human nails.

Moreover, a study on the variability of the BKS between individuals and with external parameters such as moisture content, UV exposure or temperature has also been realized in order to discriminate it from the RIS. Because of the large variability of the BKS in intensity between individuals up to 60%, it wouldn’t be reliable to subtract an averaged BKS intensity to the total intensity in order to extract the radio induced signal of interest. Investigations are still performed with the aim of discriminating BKS from the RIS.

Finally, in order to diminish uncertainties associated to variables of interest (such as intensities, peak to peak amplitudes...) and then, the estimated doses, we are developing with researchers from Chimie Paris Tech a new way of treating EPR spectra combining both Fourier Transforms with Chebyshev polynomial sampling. Very promising results have already been obtained. After a fully noise characterization of the EPR spectrometer, we are able now to reduce properly noise on EPR experimental data and then to get more precise variables of interest.
Session 9
**PHYSICAL-CHEMISTRY**

Electrostatic interactions vs. second order Jahn Teller distortion as the source of the structural diversity in Li$_3$MO$_4$ compounds (M = Ru, Nb, Sb and Ta)

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**Keywords:** Li – ion batteries, rocksalt oxide, solid state chemistry

With the advent of layered rock salt oxides cathode materials showing anionic redox activity towards Li$^+$ there has been an increased focus on designing new rocksalt structures and more particularly compounds pertaining to the Li$_3$MO$_4$ family$^2$. Indeed, according to theoretical predictions, such compounds show enhanced anionic redox activity compared to the so-called Li-rich Li$_2$MO$_3$$^3$. Li$_3$MO$_4$ family presents a structural diversity nested in its ability to host many different cations leading to the formation of superstructure patterns whose predictibility is still limited$^4$. Thus the need to understand the synergetics of such superstructures as cationic arrangement has a crucial effect on their physical properties. Herein we proposed a combined experimental and theoretical approach to understand the interactions governing cation ordering in binary systems Li$_3$M$_{1-x}$M$'_x$O$_4$ (M = Ru, Nb, Sb and Ta). Through complementary X-ray diffraction and absorption technics, we revealed a solid solution behavior for Li$_3$Ru$_{1-y}$Sb$_y$O$_4$ system as opposed to Li$_3$Sb$_{1-y}$Nb$_y$O$_4$ which counts four rock salt structures with different cation orderings. We have used DFT calculations to rationalize such a structural diversity and found that it is controlled by a delicate balance between electrostatic interactions and charge transfer due to the second order Jahn-Teller distortion. This insight provides a new way to look at cationic arrangement in rocksalt structures, and by the same token guidance to design novel phases for applications such electrode materials or ionic conductors.

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**Thin Ge epitaxial template for GaAs solar cell on glass**

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**Keywords:** Metal Induced Crystallization; Germanium; Molecular Beam Epitaxy

GaAs-based solar cells are currently the most efficient single junction solar cell in (28.8\%)\(^1\). However, the limiting factor for the spreading of this technology is the high cost of the III-V substrate. Out of the volume of a III-V wafer only the final micron is useful for the actual device fabrication or epitaxy. The rest plays no other role than mechanical support while it has the same purity and cost. We investigate the potential of a low-temperature technique to obtain thin (~20 nm) mono-crystalline patches of germanium on glass (thermal silica/fused silica), based on the peculiar crystallization properties of Al/Ge bilayers. The presence of Al next to amorphous Ge material substantially lower the Ge crystallization temperature from ~500°C down to ~250°C\(^2\). Several parameters impact the final Ge crystal texture and crystallinity quality including annealing temperature, layer thicknesses and the GeOx/AlOx diffusion barrier between the two layers. By using in-situ optical and TEM characterization we identify the desired Aluminium-induced crystallization process\(^3\) (111-oriented) and some competing parasitic crystallization (poor crystal texture), see Figure 1.

![Figure 1. TEM cross-section and top view optical image of the Al/Ge bilayer after crystallization showing the standard MIC (blue) and parasitic MIC (red) structures, from.](image)

In parallel, we also study the epitaxy of GaAs layer on conventional 111-oriented Ge wafers by molecular beam epitaxy. Here the 111-orientation should help to avoid the formation of anti-phase domain. However rotational twins are still possible\(^4\), but preliminary result shows that large defect-free area can be obtained by using the appropriate growth conditions.

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How to colour stained-glass in the Middle Age

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Keywords: colourimetry, oxido-reduction, stained-glass

Stained glasses are amongst the most impressive artworks from Middle Age in Western Europe and are a crucial component of the magic of the great gothic cathedrals, thanks to the variety of colours they display. The process of colouration of medieval glasses has still not be completely unveiled, especially for colours like yellow and purple. [1] Moreover, most of the stained-glass windows exposed in today’s cathedrals have been more-or-less heavily restored and thus contains pieces of glass which may be much younger. The study of the medieval glasses is not facilitated by the ban of any destructive analysis. We developed a special device which allows quick optical spectroscopy and colour measures on stained-glass windows without any handling of the artwork [2]. We used this device on the Grande Rose of the Reims Cathedral, which allowed us to compare the colouring process and the resulting colour of medieval glass with those of modern restoration glass. This can prove useful for later determination of authenticity on other corpus. Together with PIXE and XANES, we studied also a set of medieval characters’ faces which had been stolen from various French cathedrals in the 19th century. Through the determination of oxido-reduction state of manganese and iron in the glass, we are able to explore the medieval techniques for obtaining the purple colour in glasses.

Figure 1: Studied panels in the Grande Rose of Reims
Figure 2: Example of a medieval stained-glass face

Elaboration of hybrid dynamic polyurethane networks

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Keywords: Polymer ; Hybrid material ; Healing ; Thermoforming

Over their lifetime, polymers suffer from damages, such as cracking or scratching, which lead to a change of appearance and a loss of functionality and mechanical properties. Many strategies have been developed to increase the materials service life. One of them is a class of smart materials, the self-healing materials. It is well known now that covalent or supramolecular bonds reversibility allows materials to show some unusual properties like the ability to self-heal or to heal upon application of an external stimulus.

Hybrid materials are composites with an organic and an inorganic components in which at least one of them has at least one dimension of the order of nanometers. The important parameters are the amount and the chemical nature of organic/inorganic interface which brings about enhanced and tuned mechanical properties and unusual properties. For example, hybrid materials can reach some attractive applications, like impact detection, anti-fogging, anti-adhesion… Moreover, coordinative chemistry, dealing with polymers and metallic cations, offers both advantages: versatility of complexing function in polymers and wealth of properties thanks to metallic cations (photochromism, oxydoreduction…).

This study aims to synthesize healing hybrid materials, based on polyurethane macromolecular chains crosslinked by an inorganic component. The reversibility of the bonds at the hybrid interface brings dynamics in the material and, consequently, ability to heal itself upon an increase of temperature. Moreover, the ability of the network to rearrange by bonds redistribution without any loss of its integrity leads to thermoforming materials. The thesis purposes are not only to observe healing and thermoforming abilities, but also to quantify them and to explain how dynamics works in these materials.

Figure 1: Scratch before thermal treatment (a) and after thermal treatment (b)

PHYSICAL-CHEMISTRY

Radiolysis of gold-ion trapped in an organic mold

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Keywords: Radiolysis, copolymer, colloid, surface

We developed an innovative method combining the self-assembled properties of organic amphiphilic molecules and the metal reduction induced by water radiolysis to form nano-objects with adjustable shapes and functionalities [1, 2, 3, 4]. The different shapes are obtained by using the organic structures as molds, which are covered by a metallic layer of nanometric thickness. In order to obtain more complex shape and elaborate mixed nanostructures we enlarged the mold to neutral-charged diblock copolymers. PS-b-PDMAEMA positively charged PDMAEMA block combined with a polystyrene hydrophobic block provided a good study system combined with negatively charged AuCl4− ions allowing us to produce gold nanoparticles embedded in the organic mold as a hybrid system of interest.

We studied this copolymer/gold ions system in 2 geometries. First a copolymer monolayer at the air-water interface enabling the formation of adsorbed monodisperse nanoparticle. We also used this system as frozen micelle which allowed the formation of hybrid micelle with gold nanoparticle in the corona or gold nanoshell around the copolymer frozen micelle. We will present some of the structure formed.

Widmanstätten microstructures in metallic alloys: phase-field coupling between diffusion, elasticity and plasticity

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Keywords: Phase-field, elastic anisotropy, plasticity, phase transformation

Metallic alloys developed for structural applications are multiphase materials. The spatial arrangement of the phase domains, called microstructure, strongly impacts the mechanical properties of these alloys. A proper understanding of how microstructures evolve is helpful in order to control them through thermal and thermo-mechanical treatments. The present work is devoted to Widmanstätten microstructures because of their known negative impact on resistance to fatigue. These microstructures, consisting in acicular precipitates growing in colonies (Fig. 1a), are observed in many metallic alloys (Ti alloys, brass, steels ...). Their formation, and in particular the precipitate growth at constant velocity (in isothermal conditions), is singular for a diffusion controlled phase transformation.

Despite several analysis, the mechanisms responsible for this growth mode are not fully understood. By analogy with the dendritic growth during solidification, it has often been stated that the anisotropy of the interface energy is of prime importance, in spite of unrealistic amplitudes needed to simulate any platelike growth. Recently, using a phase field approach and 2D simulations (Fig 1b), Cottura et al. [1] have shown that the anisotropy of the elastic energy caused by the change of crystalline structure during the phase transformation is a key ingredient to explain the acicular shape of plates and their growth kinetics.

Along this line, the present work brings new insights on the Widmanstätten growth process. First, a phase-field model coupling both chemical and elastic effects is developed to analyse the growth of needles and plates in three dimensions. In agreement with observations performed in several alloys, our calculations predict a lengthening at constant velocity (Fig. 1c – green arrows) and a thickening proportional to √t (Fig. 1c – red arrows). We have then examined the tip sizes and shapes. For model cases, we have derived a criterion based on elasticity to predict both the tip radius and velocity, a prediction that the classical growth description does not enable. The phase-field model is extended to include the plastic relaxation that is expected to occur when high transformation-induced stresses are generated in the microstructure. We show on specific examples that plasticity can significantly impact the growth kinetics and the size of the tip.

Fig.1 - a) SEM image of a Widmanstätten structure in a steel alloy [Cheng et al. Mater. Charact. 2009] – b) Snapshot of a simulated growing plate at 3 different times (in white) – c) Snapshot of a simulated growing needle at 3 different times (in purple)

Session 10
Materials with variable permittivity for vibrational energy harvesting

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Keywords: 1: energy harvesting; 2: vibrational energy; 3: composite; 4: emulsion; 5: giant permittivity

The Internet of Things (IoT) aims at connecting everyday physical objects into the Internet without any human interaction. Eliminate the batteries and the wires for providing electrical power to these objects is a key to success for IoT. To overcome this problem, a promising route is harvesting mechanical energy from ambient vibrations. One way to convert mechanical energy into electrical power is to use variable capacitors. A recent approach is the use of polymers loaded with conductive particles as a variable dielectric layer. It is necessary to finely control the morphology of the inner network formed by the particles within an elastic polymer. The aim of the present work is the development of near percolated reduced graphene oxide (r-GO) or carbon black (BC) network within an elastic polymer matrix. Two novel emulsions formulations routes are employed to achieve a fine control over the structure of the materials. First, r-GO solution is dispersed in the continuous phase of an O/W PDMS emulsion. The r-GO platelets are segregated after water removal between the PDMS droplets and can form near percolated networks controlled by the emulsion droplets. In the second route, droplets of a BC solution are dispersed in a PDMS matrix. After water removal, BC is confined in the interior surface of pores. We have studied the dielectric properties of these two types of nanocomposites at rest and under deformation. In the high filler concentration situation, the values of the permittivity are giant. The power harvestable with the composites has been measured but remains still low (nW) because of high value of conductivity (higher than 10⁻⁷ S/m). But, the high values of piezoresistivity measured in the high filler concentration situation, open the road to use these materials for stress or strain sensor applications considering their giant responses to mechanical deformations.
Role of phosphorous in the nucleation of aluminosilicate glasses

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Keywords: Glass-ceramics, Lithium aluminium silicate, nucleating agent, glass structure

The lithium aluminium silicate (LAS) ternary is one of the most studied and commercialized glass-ceramics systems. To promote bulk crystallization, nucleating agents are used, such as TiO2, and ZrO21. P2O5 has also been shown to be effective for bulk crystallization of some aluminium silicate glasses2,3, but the mechanism remains unclear.

The aim of this study is to understand the structure of aluminosilicate glasses doped with P2O5 and determine structural changes occurring in these glasses during the first steps of crystallization.

LAS glasses with 74%mol SiO2, having different Al2O3/Li2O ratios and different P2O5 contents (0, 1 and 3%mol) were prepared by melt quenching. DSC thermal analysis and XRD were performed to determine the crystallization profile of the glasses31P, 27Al, 29Si MAS-NMR and NMR correlation techniques were employed for structural characterization of parent glasses and glass-ceramics. Electron microscopies (SEM and TEM) were employed to determine microstructure of the glass-ceramics.

We focus mainly on two compositions with low and high alumina content, and with 1%mol P2O5. 27Al{31P} D-HMQC (Dipolar Hetero-nuclear Multiple-Quantum Coherence) NMR technique was performed to determine spatial proximities between the two nuclei on parent glasses. While they reveal presence of Al(IV)-PO4 complexes in both glasses, structural model of the entities seems different.31P MAS-NMR of the glass and glass-ceramics shows differences with the thermal treatment. In particular, modifications around phosphorus environment prior to crystallization have been observed, with apparition of a “disordered Li3PO4” species. This suggests reorganization that cannot only be due to glass relaxation. We observe the formation of Li3PO4 crystals concomitant with crystallization of the first appearing phases (lithium disilicate and metasilicate). At high alumina content, the phosphorus environment is not significantly modified prior crystallization of a lithium aluminium silicate β-quartz type phase.

These results show that phosphor acts differently on the nucleation process depending on the Al2O3 content, due to phosphorus-aluminium interactions.

1. Höland W., Beall G.H. “Glass-ceramic technology” (2012)
Self-assembly of gold nanoparticles induced by trapping into topological defects of a smectic liquid crystal

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Keywords: Liquid crystal, self-assembly, gold nanoparticles, plasmon

Gold nanoparticles are very interesting materials because of their plasmonic properties. It is also well known that when gold nanoparticles are close enough, the electromagnetic coupling happening modifies the plasmonic properties. This is the reason why more and more research focuses on controlling the self-assembly of nanoparticles. Liquid crystals are very good candidates for this purpose since they usually contain disordered areas called topological defects which can be used for nanoparticle trapping. In this work we combined gold nanoparticles (diameter ~ 6 nm) to a smectic liquid crystal structure called “oily streaks” (Figure 1) made of arrays of parallel dislocation lines (linear defects).

Figure 1. a) Optical microscope image of the oily streaks (scale bar : 7,5 µm). b) Full model of the structure of oily streaks, presented in side-view in the plane perpendicular to the hemicylinders axis. Blue line : curvature wall, red dotted lines : rotating grain boundaries, green area : central defect, red and blue dots : dislocations lines parallel to the hemicylinders axis

Measurements of the plasmon resonance of the gold nanospheres indicate that they form chains parallel to the direction of the dislocation lines, in agreement with a trapping phenomenon of the nanoparticles by the dislocations. We also show that it is possible to modify this organization by increasing the concentration of nanoparticles or by heating treatment.

PHYSICAL-CHEMISTRY

Strongly confined HgTe 2D nanoplatelets as narrow near-infrared emitters

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Keywords: Nanocrystals, Near-infrared, Cation exchange

Currently, some colloidal nanocrystals such as PbS or CIS (copper indium sulfur) are promising candidates for IR imaging because of ease of size control. However, these materials have extremely broad luminescence features (>100 nm). Two-dimensional semiconductors nanoplatelets (NPLs) recently developed provide a great control of the optical features for cadmium chalcogenide nanocrystals in UV-visible. Consequently, 2D mercury chalcogenides nanoplatelets are considered as colloidal nanocrystals absorbing in near infrared. However these materials cannot directly be obtained from a single step synthesis, thus cation exchange appears as an alternative solution to make these materials. CdTe NPLs are used as initial nanocrystals and the cation exchange is performed with bulky mercury amine complex. HgTe NPLs present exceptionally narrow near IR optical feature (57 meV for an emission around 890 nm) and an emission quantum yield in the order of 10%. We demonstrated by EDX analysis that the exchange is completed and by XRD that zinc blende structure is preserved after cation exchange. Owing to the strong quantum confinement in HgTe NPLs, the band edge energy can be tuned thanks to the surface chemistry because of the partial delocalization of the wavefunction into the ligand shell.

Optical density and photoluminescence of CdTe and HgTe after cation exchange

Physics / Chemistry / Physical-chemistry

Li-CO$_2$ battery: dual advantages of carbon footprint reduction and energy storage?

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Keywords: Energy storage, Carbon footprint, Li-CO$_2$ batteries, electrochemical CO$_2$ reduction

Increases in energy demands, together with the rise in atmospheric CO$_2$ concentration, have stimulated the on-going search for renewable energy technologies. So far several electrochemical storage systems like batteries have been developed aiming to reduce the global reliance on fossil fuels so as to decrease CO$_2$ emission. Nevertheless, not only our production of CO$_2$ must be decreased, but the atmospheric CO$_2$ concentration must be mitigated back to pre-industrial level. For that purpose, CO$_2$ capture and sequestration process are rather critical. Within this context, a novel concept of battery system, Li-CO$_2$ battery, was proposed with the potential not just to sequester CO$_2$, but also to transform this detrimental greenhouse gas to value-added energy product.$^{1,2}$ However, to activate CO$_2$ in such system is a very challenging task, since CO$_2$ is thermodynamically stable. The direct electrochemical reduction of CO$_2$ requires highly negative potential, which limits the energy efficiency of Li-CO$_2$ battery as well as induces copious parasitic reactions with electrolyte. This talk will describe two strategies envisaged to achieve CO$_2$ activation in Li-CO$_2$ battery with minor electrolyte degradation. Besides, the potentiality of Li-CO$_2$ battery will be rationalized.$^{3}$

Use of Reflectance Anisotropy Spectroscopy for enhanced sensitivity of localised surface plasmon resonance sensor

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Keywords: LSPR, plasmon, Gold, sensor

Localised Surface Plasmon Resonance (LSPR) is a collective oscillation of conduction electrons at the surface of metal nanoparticles. In the case of noble metals, this resonance is located from near infrared to near ultraviolet. It is dependent on the metal used, the nanoparticles’ shapes and their environment. The LSPR in a nanoparticle exhibits an enhanced electric field in its surroundings, making the LSPR very sensitive to possible molecular or ionic adsorption. This modification of the nanoparticle’s surface leads to a shift in the resonance, and is the basis for LSPR sensing.

In a number of experimental or theoretical investigations, strong efforts are made to increase the sensitivity of these systems. All these techniques rely on the spectral measurement of the LSPR’s position and therefore its shift in wavelength being accurately measured. Hence, these methods require the use of a monochromator, limiting the sensitivity due to the intrinsic resolution limitations of these apparatus (between 1 nm to 0.01 nm for the more accurate systems), as well as the integration of such sensors and increase in cost.

In order to greatly increase the sensitivity of such measurements as well as reducing the bulkiness of the equipment, an alternative method was used which improves on the stability, sensitivity and reproducibility. This was achieved not by measuring the shift of the LSPR but instead by focusing solely on the change in signal intensity at a given wavelength. Indeed, anisotropic samples formed either with anisotropic nanoparticles or anisotropically organised nanoparticles exhibit a LSPR for each symmetry. Reflectance Anisotropy Spectroscopy (RAS) was used for measuring the anisotropy of the two plasmon resonances. This differential technique has proven to be very sensitive and has been used mainly for investigating optical surface anisotropies and anisotropic metallic nanoparticles deposited on surfaces.

The detection of dihydrogen in argon was studied on anisotropic gold samples. Firstly, gold samples were exposed to cycles of these two gases in order to investigate the interaction of dihydrogen with gold. In spite of the inertness of the bulk metal, our results show that a small amount of dihydrogen does adsorb on the nanoparticles. This leads to a slight red shift of the LSPR due to the charge transfers between the metal and the adsorbed gas, that we tentatively estimate. Secondly, palladium nanoparticles were added on top of the gold. The use of this chemical probe, specific to dihydrogen, greatly increases the optical response of the gold nanoparticles which act as the plasmonic transducer. Thanks to the use of the anisotropic properties of the sample and the method of measurement, much smaller quantities of gas could be detected compared to conventional techniques.[1]