Functional Materials through Colloidal Engineering

(Integrative Chemistry, Emulsions, Responsive interfaces, Random lasing, optical and acoustic Metamaterials, Colloidal molecules, Photonics)

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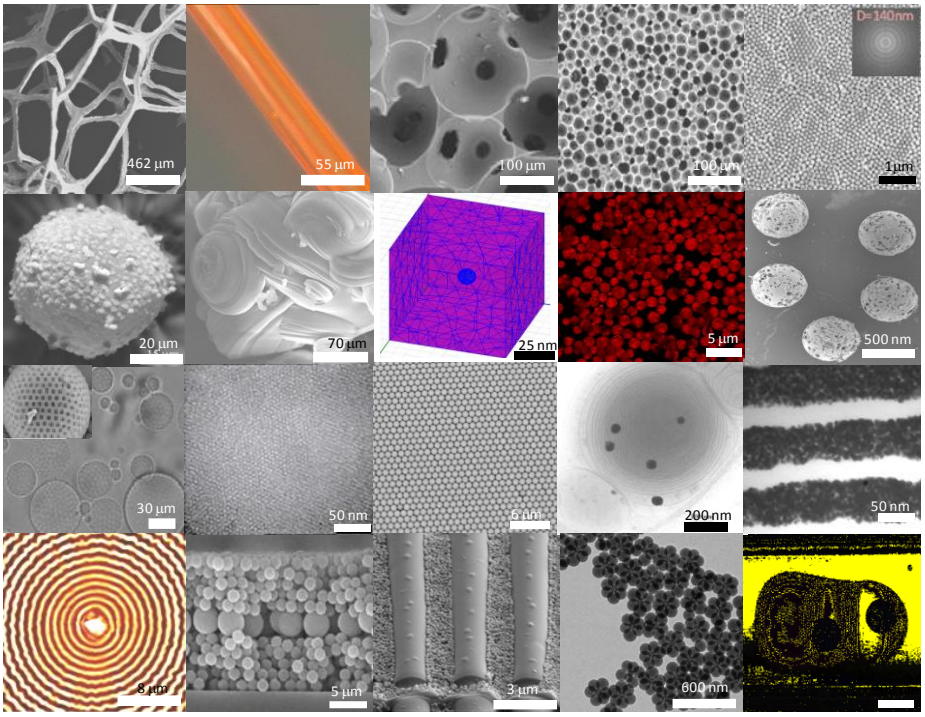
The goal of our **team** is to design, synthesize, and study the properties and functionalities of advanced functional materials. The path chosen is the integration between chemistry - offering almost endless array of functions and materials - and colloidal physical chemistry with its controlled self-assembly methods over large-scale surfaces or volume. The complementary combination of these two disciplines provides access to a huge variety of compounds (organic, inorganic or hybrid), structures and functionalities at scales ranging from nanometer to macroscopic sizes. The created materials can be solid or fluid, amorphous or organized, functional at surface or in the bulk. Potential areas of applications are numerous, with innovations in heterogeneous catalysis (enzymatic or metallic), in photo-catalysis, in photonics and plasmonics, in drug delivery, in the field of optical and acoustic metamaterials, in systems for energy conversion, in stimulable interfaces, hydrogen storage..

The areas of expertise of the team are built around the physics of complex fluids, chemical and colloidal engineering, modeling and numerical simulations of electromagnetic response as well as advanced optical experiments. Our interdisciplinary approach covers a continuous range of activities, from chemical synthesis of functional elements to the assembly of materials, the study and modeling of their properties.

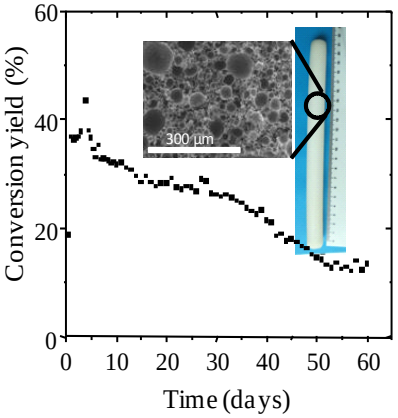
Fundamental and applied aspects are addressed with equal attention. Academic research benefits from many fruitful collaborations on the site of the University of Bordeaux, in France and abroad. The team is partner or coordinator of many regional networks (Labex AMADEUS, cluster Idex APHIA) national (ANR Nanodiellipso, Metakoustic (CO), ...) and international (FP7 - METACHEM (CO), etc.). Strong partnerships with industry are evidenced by a large number of contracts. Also, we pay special care in valorizing our research with an average of 2 to 4 patents deposited per year.



Integrative chemistry Emulsions Smart interfaces Optical metamaterials
Acoustic metamaterials Photonics Plasmonics Colloidal syntons

Heterogeneous Enzyme-based Biocatalysis

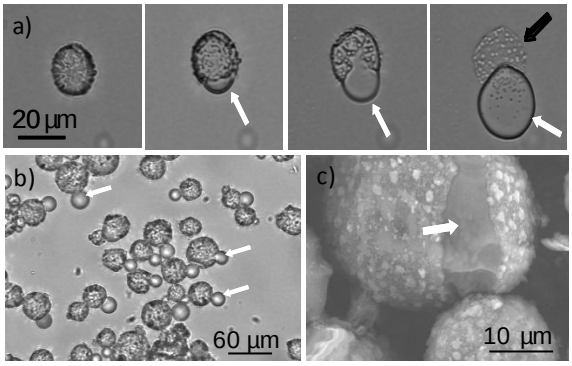
Covalent immobilization of enzymes, through epoxy groups pre-grafting within siliceous macroporous supports, allows the synthesis of promising biocatalysts. Indeed, the versatility of the system, considering the protein nature (*two different source of lipases were used*), the solvent in use (*pure heptane or saturated with water*), but also the final chosen reaction *(esterification, hydrolysis and transesterification*), has been clearly evidenced. Furthermore, structural aspects of the hybrid support addressed with open macroporosity and a monolithic character, are offering optimized mass transport where both and easy recycling and a continuous flux operating mode. In a broader context, beyond conventional mesoporous materials, we demonstrate that macroporous media are outstanding candidates toward heterogeneous catalysis, where a dispersive mass transport is occurring at the fluid/macroporous walls interface while the biocatalyst being accessible at ease, the overall mass transport being enhanced through convection. This scenario is offering a very good reactivity while circumventing the traditional low kinetic process occurring within conventional mesopororous media where accessing the active sites is not such an easy task to reach.



Uni-axial flux catalytic properties of the Col[C-TL-lipase@gGlymo-Si(HIPE)] column for the transesterification of the glyceryl trinoleate with ethanol (40°C in heptane). The curve represents the conversion yield evolution versus time under a debit of 0.1 mL min^{-1}.

Morpho-Syntheses of Thermally-Responsive Capsules

we are currently developing an original synthetic path that combines Pickering emulsions (emulsions stabilized with modified colloidal particles) and sol-gel chemistry dedicated to the generation core-shell capsules wax@SiO_2 enable to break and deliver the wax core through increasing the temperature. The process is versatile and can be extended toward divers wax , alcanes, paraffin, triglycerides..These capsules can be stocked either as a dispersed phase in water or as a powder. The use of such thermo-responsive capsules is opening wide applications in pharmacology, cosmetic, and food industry as triglycerides are the basement of biocompatible and food oils. the ease of the process allows a facile extension toward the industry as no specific equipment is required. As a direct extension of this work, playing with Pickering -based double emulsions, we have recently prepared the first thermo-sensitive capsules bearing a double core (hydrophilic and hydrophobic) that we have labeled water@wax@SiO_2 and wax@water@SiO_2. Beyond, while increasing the concentration of the directed Pickering-based emulsions we have prepared the first macroporous siliceous ceramic, labeled Si-PHIPE (Pickering-based High Internal Phase Emulsion) where the macroscopic voids morphology can be addressed on demand. This work performed exclusively at the CRPP takes the benefit of our colleague V. Schmitt playing a major role within the physical-chemistry of Pickering-based emulsions.

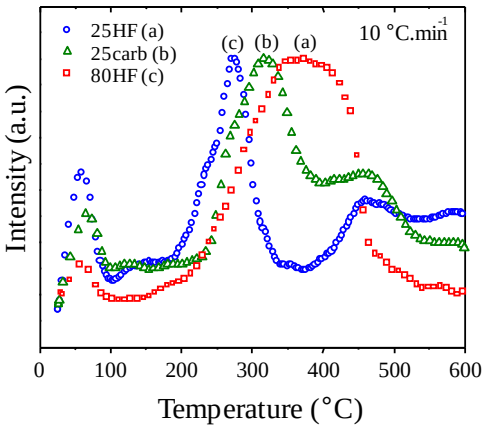


a) Sequence images performed with optical microscopy that depicts the opening of a single shell and the subsequent delivery of the oil when $T>T_{melting}$. b) optical microscopy of several capsules while the oil is out. c) SEM visualization of a capsule in the process of breaking its surrounding shell, induced by the heat of the electron beam. White arrows indicate the liquefied wax, while the black ones indicate the resulting hollow silica shell.

Hydrogen Storage

$Li(BH_4)$ confinement within macro-microcellular carbonaceous foams has shown strong efficiency toward the hydrogen desorption mechanism. Indeed, beyond a soft impregnation method that operates at ambient temperature (25°C), it has been demonstrated for the first time that the microporosity can tune the $LiBH_4$ nucleation and growth mechanisms. For instance, when increasing the microporous surface area and thereby the micropores concentration at the surface of the macroporous walls, the $LiBH_4$ amorphous character has been optimized. Also, beyond increasing the nucleation rate while minimizing the growth, a thermodynamic modification of the hydrogen desorption has been obtained. Thereby, a switch toward the low temperature of desydruration has been noticed when increasing the amorphous character of the LiBH4 heterogeneous nucleated species.

We are actually working on optimizing the "deshydrogenation/hydrogeneation" cycles of such confined borohydrides though a collaboration with R; Janot (LRCS, Amiens) and C. Gervais (LCMC-P, Paris).

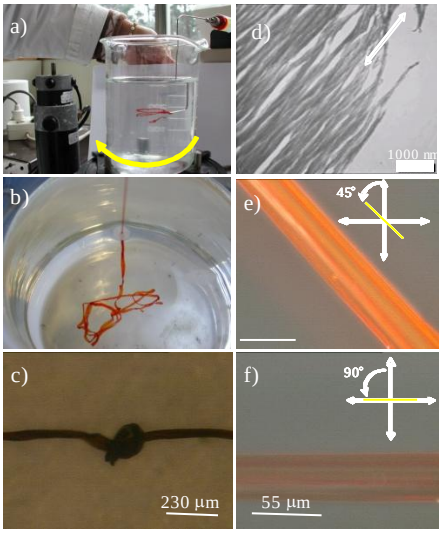


Hydrogen desorption curves obtained through programmed desorption with temperature (primary vacuum heat rate of 10°C min-1) and coupled with a mass spectrometer (m/z = 2). $Li(BH_4)$@80HF (a), $Li(BH_4)$@25Carb (b), $Li(BH_4)$@25HF (c).

Macroscopic inorganic fibers obtained through extrusion

Under certain synthetic conditions, it possible to obtain V_2O_5 gel made of nano-ribbons. Due to their high anisotropy of shape it is possible to align these nano-ribbons at higher length scale through the use of extrusion, as it is the case for carbon nanotubes. In this process, a V_2O_5 gel is extruded through a syringe into a rotating beaker containing a 1 %w PVA (polyvinyl-alcohol) solution. These fibers are outstanding sensors able to detect 1 ppm of alcohol within 4 seconds at 40°C., this high sensitivity being addressed with a strong selectivity. This property in detecting alcohol vapors is relating to a surface Redox reaction that enhances the fiber conducting properties. We have also increased the alignment of the nano-ribbon subunits through varying the extrusion shear rates.

We have extended this shaping mode toward other oxides as TiO_2. In that case the fibers depict good photocatalytic properties when dedicated to unidirectional flux air purification. Also, we are developing fibers made of ZnO nanoparticles bearing collective and anisotropic photoluminescence properties. TiO2 macroscopi fibers have been generated through a continuous industrial process dedicated toward air photopurification.



a) V_2O_5 gel under extrusion, b) V2O5/PVA composite fiber under extraction from the rotating beaker, c) fiber forming a not, d) fiber mesostructure observed through SEM, d) fiber mesostructure observed with SEM, e-f) fiver observed under cross-polarized microscopy.