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On 26<sup>th</sup> March, 2024, the ISGS will launch a new initiative, the Sol-Gel PhD student eMarathon. The eMarathon will involve a series of lectures by Sol-Gel PhD students, with each lecture being of 30 minutes duration and an additional 10 minutes for questions. Our goal is to showcase the depth and diversity of the sol-gel research being undertaken by our research students and to provide an opportunity for students to present their work to an international audience in a relaxed, online environment.

We look forward to your participation in the inaugural event and to your support of our PhD students, the future leaders of the sol-gel community of practice.

**Date:** Tuesday 26 March 2024

**Time:** 05:00 - USA (East Coast)

**10:00 - UTC**

11:00 - Switzerland, Central Europe, Sweden

13:00 - Russia (Moscow, St Petersburg)

19:00 - Japan, Korea

07:00 - Chile, Argentina and Brazil (São Paulo)

10:00 - UK, Portugal

12:00 - Romania, Israel, Eastern Europe, Ukraine

18:00 - China, Singapore, Malaysia

20:00 - Australia (Queensland)

**ZOOM:** <https://us02web.zoom.us/j/3072916432?pwd=Qk1yN1BobFhYbU1pWkcyU1RXdlVMUT09&omn=82902941443>

Meeting ID: 307 291 6432

Passcode: 8ad9vO9@

# eMarathon Program

Speaker	UTC	Europe Time	Russia Time	Brazil/Argentina Time
<b><u>Paola Amato</u></b> (Department of Chemical, Materials and Production Engineering, University of Naples Federico II, Italy)	10:00 – 10:40	11:00 – 11:40	13:00 – 13:40	07:00 – 07:40
<b><u>Bastian Beitzinger</u></b> (Institute for Inorganic Chemistry II, Ulm University, Germany)	10:40 – 11:20	11:40 – 12:20	13:40 – 14:20	07:40 – 08:20
<b><u>Sofia Moreira Fernandes</u></b> (CERENA, DEQ, Instituto Superior Técnico, Universidade de Lisboa, Portugal)	11:20 – 12:00	12:20 – 13:00	14:20 – 15:00	08:20 – 09:00
<b><u>Paulo Nunes</u></b> (Department of Chemistry and CQVR, University of Trás-os-Montes e Alto Douro, Portugal)	12:00 – 12:40	13:00 – 13:40	15:00 – 15:40	09:00 – 09:40
<b>Coffee Break</b>	12:40 – 13:00	13:40 – 14:00	15:40 – 16:00	09:40 – 10:00
<b><u>Tatiana Lomakina</u></b> (Peter the Great St. Petersburg Polytechnic University, Russia)	13:00 – 13:40	14:00 – 14:40	16:00 – 16:40	10:00 – 10:40
<b><u>Jakub Kusz</u></b> (Laboratoire de Chimie CNRS UMR 5182, Université de Lyon, Ecole Normale Supérieure de Lyon, France)	13:40 – 14:20	14:40 – 15:20	16:40 – 17:20	10:40 – 11:20
<b><u>Andrea Montero-Oleas</u></b> (University of Grenoble-Alpes, France; and the University of Buenos Aires, Argentina)	14:20 – 15:00	15:20 – 16:00	17:20 – 18:00	11:20 – 12:00

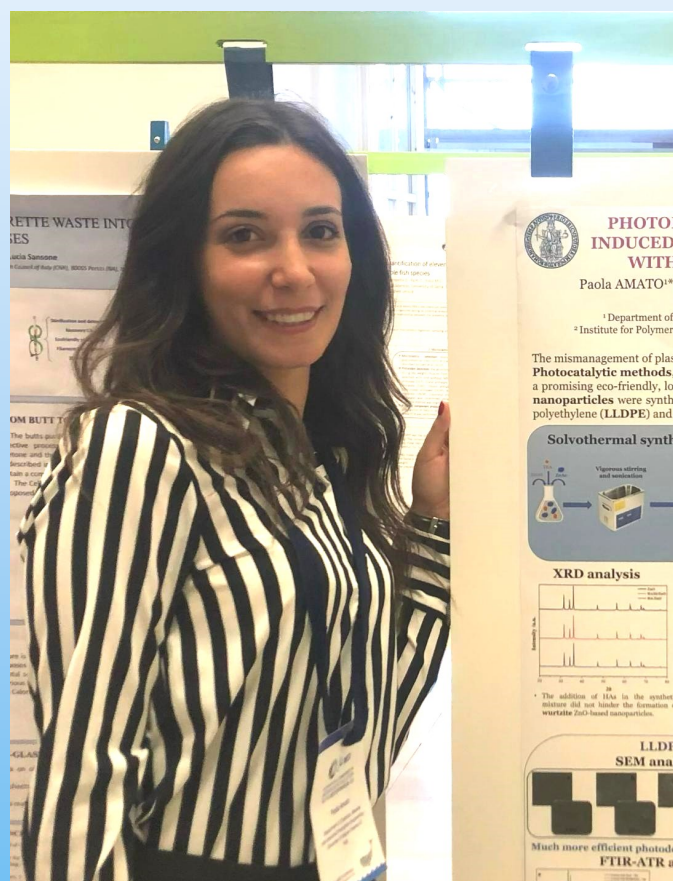
## Sol-Gel synthesis of a bio-waste modified TiO<sub>2</sub> – based material for the oxidative degradation of LLDPE microplastics

Paola Amato

Department of Chemical, Materials and Production Engineering,  
University of Naples Federico II, Naples, Italy

### Abstract

A new hybrid TiO<sub>2</sub>-based material “T-Abi” was synthesized by a trash-to-treasure approach, adopting a sol-gel route that makes use of green solvents, available materials, and energy-efficient protocols. The organic constituent is rosin, a bio-waste material, composed by a mixture of resin acids and natural terpenes derived from the distillation of pine resin, from tall oil (a by-product of the Kraft process) or from aged pine stumps. Rosin often requires costly and time-consuming chemical transformations to be used in the synthesis of new materials. Here its direct conjugation with titanium was obtained by a simple sol-gel procedure. The ligand-to-metal charge transfer complexes formed between rosin and Ti<sup>4+</sup> led to the generation of reactive oxygen species (ROS) without requiring any excitation source. Particularly, it was revealed that radical anions (O<sub>2</sub><sup>•-</sup>) were stabilized on the surface of the bio-waste modified TiO<sub>2</sub> material under ambient conditions, playing a key role in the oxidative degradation of different pollutants. In this work, the obtained T-Abi was able to promote the oxidative degradation at room temperature of linear-density polyethylene (LLDPE) microplastics under indirect daylight conditions. In these mild conditions, a remarkable degradation of LLDPE films was observed within 1 month, as evidenced by the by-products detected by GC-MS analysis and by chemical and structural modifications of the polymer surface. Based on the GC-MS results, an innovative degradation mechanism of LLDPE was also proposed. In a context of waste exploitation, this innovative and sustainable approach represents a promising cost-effective strategy for the oxidative degradation of microplastics, without producing any toxic by-products. The achieved results can also be a preliminary step for a chemical recycling of plastic waste aimed to obtain value-added products by its transformation.



### Unveiling the Potential of Dendritic Mesoporous Silica Nanoparticles: From precise structural characterization to macromolecular drug delivery applications

**Bastian Beitzinger**

Institute for Inorganic Chemistry II, Ulm University, Ulm, Germany

**Introduction:** Recent advances in mesoporous materials have led to increased interest in dendritic mesoporous silica nanoparticles (DMSNs) due to their potential applications in separation processes, catalysis, and biomedical fields. DMSNs are distinguished by their unique, non-ordered pore system, where the pores align radially from the center of the particle and encompass a wide range of mesopore sizes, ranging from 3 to 25 nm in diameter. This wide range of pore sizes makes DMSNs highly versatile for various innovative applications. However, the complex nature of their pore system, which lacks a defined pore geometry, presents challenges in characterization using traditional methods such as nitrogen sorption and transmission electron microscopy (TEM). As a result, a more sophisticated approach is required to fully unlock the potential of DMSNs in various fields.

**Methodology:** To bridge this gap, our research employed electron tomography, a technique superior to conventional TEM by providing three-dimensional spatial information. This method allowed for a detailed examination of the DMSNs' pore structure, overcoming the limitations of 2D projections inherent to TEM. Our investigation focused on a series of DMSNs synthesized via an interface synthesis approach, a method originally developed by Shen et al.<sup>[1]</sup> Varying the surfactant template concentration (CTAC) in the water phase, which also contained triethanolamine (catalyst) and the silica source TEOS in the oil phase yielded a set of three structurally different DMSNs that was subjected to electron tomographic analysis.

**Findings:** Our electron tomography studies provided detailed insights into the pore configurations within DMSNs, showing a strong correlation with the CTAC concentration during synthesis. When the concentration was high, the pores primarily displayed conical shapes, extending from the particle core to the exterior. In contrast, at intermediate concentrations, the pores initially took on conical shapes but then shifted to cylindrical shapes, indicating a propensity to narrow or branch towards the particle rim. At low CTAC concentrations, a distinct dendritic pore system emerged, with pores significantly widening from the center before branching into smaller mesopores.<sup>[2]</sup>

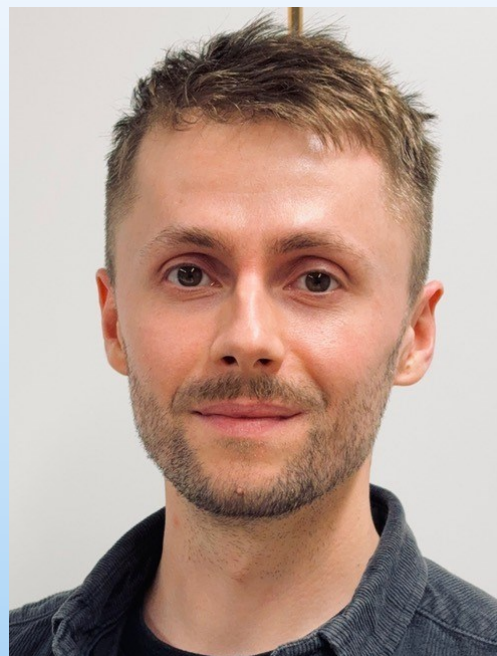
In our research on the use of materials for delivering macromolecular drugs, particularly antimicrobial peptides (AMPs) for combating *Mycobacterium tuberculosis* (*Mtb*) within primary macrophages, we considered it beneficial for the pore openings near the particle rim to be open to facilitate efficient peptide loading and release. Our study of loading peptide-based drugs on DMSN has shown that variations in peptide charge, achieved through adjustments in the adsorption solution's pH, have a significant impact on the loading capacity. Specifically, we found that pore size and hydrophobic interactions play a crucial role in determining the loading capacity. Our study revealed intricate confinement effects on the peptide loading across the range of pore sizes used for the adsorption experiments. Interestingly, our investigation revealed that dendritic mesoporous organosilica nanoparticles (DMON), which contain benzene-bridges within the silica network, exhibit enhanced loading efficiencies in conditions where electrostatic attractions are negligible.<sup>[3]</sup>

**Application and Impact:** The application of AMP-loaded DMSN in treating *Mtb*-infected primary macrophages showcased a notable increase in the intracellular availability of the peptide, thereby amplifying their antimicrobial efficacy. Utilizing fluorescence microscopy-based live-cell imaging and electron tomography, we tracked the intracellular trajectory of the DMSN, monitored the release of AMPs, and observed their impact on *Mtb* viability over several days. Our findings suggest a correlation between DMSN dissolution states and AMP release, with DMSNs predominantly located within endosomal vesicles, proximal to bacterial phagosomes, facilitating the directed delivery and enhanced efficacy of the antimicrobial peptide.<sup>[4]</sup>

**Conclusion:** This aggregated work underscores the significant potential of DMSNs in biomedical applications, particularly in drug delivery and antimicrobial therapy. Through the use of electron tomography, we have provided detailed insights into the structural nuances of DMSN and their practical implications in loading mesoporous particles with peptide-based drugs. We could demonstrate the potential of DMSNs enhancing the delivery and efficacy of therapeutic agents, specifically in the therapy of tuberculosis with antimicrobial peptides, by combining analysis methods that provide information across different length scales.

#### References

- [1] Shen et al. *Nano Lett.* **2014**, *14*, 923–932.
- [2] Beitzinger et al., (in preparation).
- [3] Beitzinger et al., *Langmuir* **2024**, (available online <https://pubs.acs.org/doi/10.1021/acs.langmuir.3c03513>).
- [4] Beitzinger et al., *Adv. Healthcare Mater.* **2021**, 2100453.



## MICROSCAFS®: Microspheres with tailored porosity for diverse applications

**Sofia Moreira Fernandes**<sup>1</sup>, Mário Vale<sup>1</sup>, Mónica Loureiro<sup>1</sup>, Beatriz Trindade Barrocas<sup>1</sup>, Jéssica Verger Nardeli<sup>2</sup>, M. Fátima Montemor<sup>2</sup>, Ermelinda Maços<sup>2</sup>, M. Conceição Oliveira<sup>2</sup>, Carla C. C. R. de Carvalho<sup>3</sup>, Alessandro Lauria<sup>4</sup>, Markus Niederberger<sup>4</sup>, Francesca Langiano<sup>5</sup>, Matteo Gigli<sup>5</sup>, Massimo Sgarzi<sup>5</sup> and Ana C. Marques<sup>1</sup>

<sup>1</sup> CERENA, DEQ, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal;

<sup>2</sup> CQE, DEQ, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal;

<sup>3</sup> iBB - Institute for Bioengineering and Biosciences and Associate Laboratory i4HB—Institute for Health and Bioeconomy, Department of Bioengineering, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisbon, Portugal;

<sup>4</sup> Laboratory for Multifunctional Materials, Department of Materials, ETH Zürich, Vladimir-Prelog-Weg 5, Zürich 8093, Switzerland;

<sup>5</sup> Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice, Via Torino 155, I-30172 Venezia Mestre, Italy.

### Abstract

Multicomponent oxide meso- and macroporous microspheres, called MICROSCAFS®, are synthesized via a modified sol-gel process combined with phase separation by spinodal decomposition. We report on tailoring their sizes and porosities via optimization of the synthesis parameters. Moreover, utilization of alternative waste materials, such as rice husk silica, for their synthesis has been achieved, contributing to circular economy principles and sustainability.

Advanced characterization techniques, including X-ray computed tomography, revealed their coral-like macroporosity, with cryo-SEM allowing direct visualization of 'wet' alkoxide-derived microstructures at different stages of the synthesis, which, together with energy dispersive X-ray spectroscopy (EDS), provided a mechanistic study of the complex process of MICROSCAFS® generation.

MICROSCAFS® find diverse applications, serving as scaffolding and micro-reactors for *in-situ* generation of nanoparticles. Additionally, we report on MICROSCAFS® utilization for chemical grafting of biocides for antifouling, and as catalyst supports for wastewater purification via solar-driven photocatalysis. Silica-titania MICROSCAFS® by themselves are enough to degrade minocycline in aqueous solution by solar-driven photocatalysis. The same MICROSCAFS® with immobilized titanium dioxide (TiO<sub>2</sub>) and gold nanoparticles exhibit enhanced photocatalytic performance, with Au NPs at a concentration as low as 0.04 wt.% improving methyl orange degradation by up to 20%. MICROSCAFS® ensure facile recyclability of the photocatalyst, maintaining its performance across several cycles. High-resolution mass spectrometry experiments (HPLC/MS) revealed the transformation by-products of the pollutants' degradation, while electrochemical impedance and photoluminescence spectroscopies provided insights into mechanisms behind the enhancement of the photocatalysis by gold nanoparticles.

In summary, MICROSCAFS® exhibit significant potential across various domains, promising innovative solutions for various applications.



### Advancements in Sol-Gel Derived Electrolytes for Electrochromic Devices: A Comprehensive Study

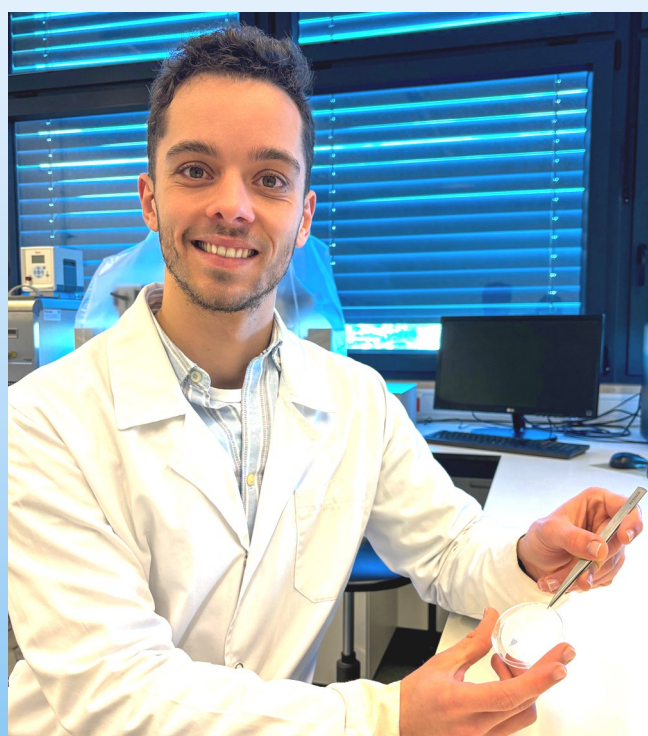
**P.J.Nunes**, V. de Zea Bermudez, and M. Fernandes

Department of Chemistry and CQ-VR University of Trás-os-Montes e Alto Douro (UTAD), 5000-801 Vila Real, Portugal .

#### Abstract

The application of the sol-gel process [1] in the field of electrochromic devices (ECDs) has been known for many years [2]. This chemical route is particularly suitable for the synthesis, under mild conditions of organic-inorganic hybrid networks with a range of attractive features.

The current research delves into the synthesis and characterization of various di-urea cross-linked poly(oxyethylene) (POE)/siloxane and poly(oxypropylene) (POP)/siloxane networks [3], [4], [5] prepared by the sol-gel process. These materials have been doped with ionic liquids (ILs), lithium salts or a mixture of both types of compounds to enhance the conductivity and improve their functionality as electrolytes in ECDs [6]. A range of techniques, including Fourier-transform infrared spectroscopy, X-ray diffraction, confocal Raman microscopy, thermogravimetric analysis, polarized optical microscopy, scanning electron microscopy, atomic force microscopy, and contact angle measurements, have been employed to characterize the xerogel films produced from the standpoint of structure, morphology, thermal stability and wettability behavior. The electrolytes with optimized formulations were ECDs whose electro-optical performance was evaluated using chronoamperometry, cyclic voltammetry, UV-VIS spectroscopy, and the CIE  $L^*a^*b^*$  color space. My research findings offer valuable insights into the potential of sol-gel derived electrolytes and their integration into ECDs, paving the way for future advancements in this field of energy materials and devices.



#### **Acknowledgements**

This work was funded by "SOLPOWINS – Solar-Powered Smart Windows for Sustainable Buildings" (PTDC/CTM-REF/4304/2020) project, financed by the Foundation for Science and Technology (FCT) and FEDER, NORTE2020, and by CQ-VR (CQVR-UIDB/0616/2020). P.J.Nunes acknowledges CQ-VR/FCT for a grant (UI/BD/151084/2021). M. F. acknowledge FCT-UTAD for the contracts in the scope of Decreto-Lei 57/2016 – Lei 57/2017 (<https://doi.org/10.54499/DL57/2016/CP1378/CT0001>). The work was developed under the project A-MoVeR – "Mobilizing Agenda for the Development of Products & Systems towards an Intelligent and Green Mobility", operation n.º 02/C05-i01.01/2022.PC646908627-00000069, approved under the terms of the call n.º 02/C05-i01/2022 – Mobilizing Agendas for Business Innovation, financed by European funds provided to Portugal by the Recovery and Resilience Plan (RRP), in the scope of the European Recovery and Resilience Facility (RRF), framed in the Next Generation UE, for the period from 2021-2026.

#### **References**

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- [2] S. Heusing and M. A. Aegerter, "Sol-Gel Coatings For Electrochromic Devices," in *Sol-Gel Processing for Conventional and Alternative Energy*, Boston, MA: Springer US, 2012, pp. 239–274. doi: 10.1007/978-1-4614-1957-0\_12.
- [3] V. de Zea Bermudez, L. D. Carlos, and L. Alcácer, "Sol-Gel Derived Urea Cross-Linked Organically Modified Silicates. 1. Room Temperature Mid-Infrared Spectra," *Chemistry of Materials*, vol. 11, no. 3, pp. 569–580, Mar. 1999, doi: 10.1021/cm980372v.
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### Sol-gel synthesis and characterization of 10Gd<sub>2</sub>O<sub>3</sub>-90CeO<sub>2</sub> (mol.%) precursors and ceramics

T.E. Lomakina and O.V. Tolochko

Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia

#### Abstract

Ceria-based ceramics are widely used as solid electrolytes in various electrochemical devices for renewable energy such, as solid oxide fuel cells. Such bottom-up manufacturing methods as sol-gel synthesis appear to be effective for the fabrication of ceramics with the fine structure. Thus, the goal of the research was to investigate of the effect of synthesis conditions on the phase compositions and structures of precursors and ceramics based on the gadolinia-doped ceria. For the object of the research 10Gd<sub>2</sub>O<sub>3</sub>-90CeO<sub>2</sub> (mol.%) composition was chosen.

For this work, sol-gel synthesis in variation of the reverse co-precipitation has been chosen. 0.1 M isopropyl alcohol solutions of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O were added dropwise in 0.25 – 3 M isopropyl alcohol solutions of diethylamine (DEA) with the subsequent treatment (washing and drying at 298 or 393 K under pressure). During the synthesis, alkalic media and T = 274–275 K were kept. The received amorphous powders have been subjected to annealing at 573, 673, 773, 873, 973 and 1073 K for two hours. Precursors after synthesis and calcination investigated using the simultaneous thermal analysis (STA, 409 of C/4/G Jupiter, NETZSCH), the X-Ray Diffraction analysis (XRD, Bruker «D8-Advance», Cu-Kα the radiation, λ=1.54 Å), the particle size distribution analysis (PSD, Horiba partica LA-950).



The content of cubic phase in the stabilized CeO<sub>2</sub> powders increased relative to amorphous phase with growth of calcination temperature. It was found that phase formation in 10Gd<sub>2</sub>O<sub>3</sub>-90CeO<sub>2</sub> (mol.%) (10GDC) powders takes place according to Gd<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> diagram. The increase of the DEA concentration from 0.5 up to 1 M barely cause effect on crystallization temperature, but leads to decrease of the average size of the agglomerates from 0.78 up to 0.13 μm. It has been established that a subsequent increase in the concentration of the precipitator up to 3 M increases the average size of the agglomerates. The use of isopropyl alcohol as a rinse for fresh precipitate of hydroxides and drying in air under pressure provides a significant decrease of crystallization temperature ~100 K and decrease of the average size of the agglomerates from 0.13 up to 0.10 μm. The increase of the temperature up to 573 K leads to one-order decrease of the average size of the agglomerates. At the last, CeO<sub>2</sub> powders obtained in optimized synthesis conditions were sintered into the ceramics with a fine structure, grain size ~ 0.2 μm and high relative density.

## Role of the molecular interactions in the self-assembly of organosilanes during the sol-gel synthesis of hybrid mesoporous films

**Jakub Kusz**<sup>1</sup>, Cédric Boissiere<sup>2</sup>, Michel Wong Chi Man<sup>3</sup>, Ovidiu Ersen<sup>4</sup>, Dris Ihiawakrim<sup>4</sup>, Yann Brettoniere<sup>1</sup>, Delphine Pitrat<sup>1</sup>, Jean-Christophe Mulatier<sup>1</sup>, Clément Sanchez<sup>3</sup>, and Stéphane Parola<sup>1</sup>

<sup>1</sup> Laboratoire de Chimie CNRS UMR 5182, Université de Lyon, Ecole Normale Supérieure de Lyon, 46 allée d'Italie, 69364 Lyon Cedex 07, France;

<sup>2</sup> Laboratoire de Chimie de la Matière Condensée CNRS UMR 7574, Université Pierre et Marie Curie, 4 Place Jussieu, 72252 Paris Cedex 05, France;

<sup>3</sup> Institut Charles Gerhardt Montpellier, UMR 5253 CNRS-UM-ENSCM, 34296 Montpellier, France

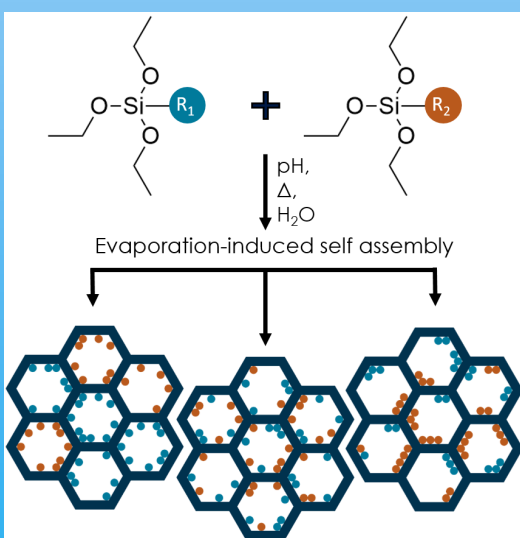
<sup>4</sup> Institut de Physique et Chimie des Matériaux de Strasbourg CNRS UMR 7504, Université de Strasbourg, 23 rue de Loess, 67037 Strasbourg Cedex 08, France

### Abstract

By combining several sections of soft chemistry, Periodic Mesoporous Organosilica Films possess unique properties that make them particularly interesting for catalytic, medical, or functional applications. The introduction of two different functionalities further increases the scope of applications and opens new opportunities. However, predicting the final distributions of moieties is not straightforward as the self-assembly process occurs in seconds and can be influenced by multiple factors. Understanding the nature of these processes would allow us to control the organic-inorganic interface of hybrid mesoporous materials and the arrangement of groups, which is of great value from the applicational point of view. In the following study, we show how the intermolecular forces can affect the self-assembly process, porosity, and domain formation in mesostructured films.

Ordered mesoporous silica thin films were prepared by the co-condensation sol-gel process between hybrid and non-hybrid precursors and the self-assembly of mesophase was achieved by the templating method using an ionic surfactant. We conducted an innovative study of thin films prepared using different organosilanes bearing alkyl, ureido, or aromatic functional groups.

Each of these groups brings different types of weak interactions (van der Waals forces, hydrogen bonding, or  $\pi$ - $\pi$  stacking) which can affect the distribution of moieties within the mesoporous film. We analyzed thin mesostructured films by spectroscopy (infrared, fluorescence, ellipsometry) and microscopy techniques and established the models of the moiety organization inside the pores. Ternary systems of several precursors as well as precursors bearing two distinct functions were evaluated as well, proving the simultaneous existence of different meso-environments.



**Figure 1.** Possible distributions of two organosilanes moieties in the mesoporous film



## Large-pore Au@mSiO<sub>2</sub> nanoparticles: A Promising Platform for Protein Transport

Andrea Montero-Oleas<sup>1,2</sup>, Xavier Cattoën<sup>1</sup>, Yoann Roupioz<sup>1</sup> and Sara A. Bilmes<sup>2</sup>

<sup>1</sup>University of Grenoble-Alpes, France; <sup>2</sup>University of Buenos Aires, Argentina

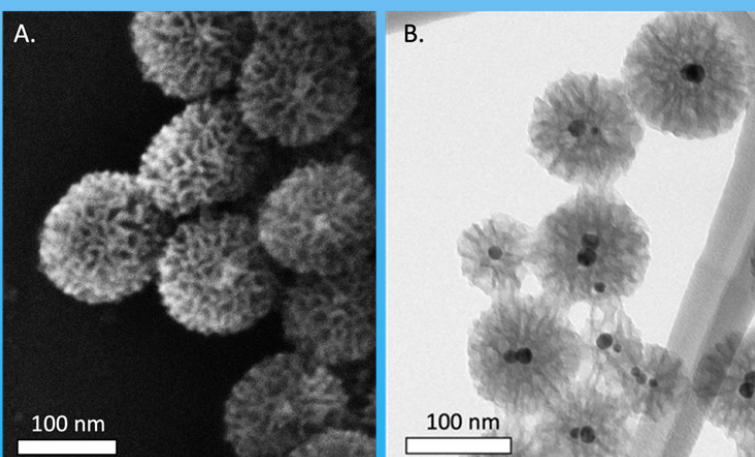
### Abstract

Protein transport within nanoparticles (NPs) offers a promising approach for localized medical treatments. The reliability of these nanocarriers depends on their capacity to protect proteins from degradation during transport and enable controlled release within target cells. In this study, we focus on the sol-gel design of core-shell MPS nanoparticles with a gold core (Au@mSiO<sub>2</sub>) that meets essential criteria for successful protein transport.

NPs synthesis proceed by the formation of a core-shell seed (50 nm) by gold reduction in an alkaline medium, with simultaneous sol-gel growth of a mesoporous silica layer. In a subsequent step, these seeds are coated by a silica layer with calibrated pores in an oil-water biphasic medium. The resulting Au@mSiO<sub>2</sub> particles exhibit 100 ± 15 nm final diameter, with a 10 ± 5 nm gold core and customized mesopore sizes between 3 to 10 nm by controlling the synthesis parameters (Fig 1). These particles remain colloidal and hydrolytically stable under near-physiological conditions (150 mM NaCl, pH 7) for up to five days.

Optimized Au@mSiO<sub>2</sub> particles exhibit high protein retention capacity (0.6 mg BSA/mg NP). In the case of enzymes, horseradish peroxidase enzymatic activity remains close to that of free enzyme. Furthermore, the thermal stability of retained proteins is higher than that of free proteins, as determined by circular dichroism spectrometry.

In summary, large-pore Au@mSiO<sub>2</sub> particles encapsulate proteins and provide protection against external media, allowing them to maintain their structure and functionality. These NPs exhibit promising characteristics for use in medical applications, particularly in the context of targeted enzyme delivery.



**Figure 1.** Micrograph of (A). SEM of large pores Au@mSiO<sub>2</sub> (B) TEM of large pores Au@mSiO<sub>2</sub> loaded with BSA