Journée de la fédération CPPS - Vendredi 12 Décembre 2025

CPPS
Fédération de Chimie Physique de Paris-Saclay

Toutes les communications orales ont lieu dans la salle Magat de ICP, Bât 350.

Les pauses café, le buffet de midi et la séance poster ont lieu dans le Hall du bâtiment.

Programme

8h45-9h15	Accueil des participants		
9h15-9h30	**Introduction**	*Hélène Pasquier (ICP-CPPS)*	
9h30-10h10	**Keynote 1:** Agathe Espagne	**ENS Paris**	*Photoreactions of fluorescent proteins : from time-resolved spectroscopy to biological imaging*
10h10-10h30	O1: Jan Pytel	**ISMO**	*Near-infrared quantum-dot based adaptive optics for in-depth, two-photon neuroimaging*
10h30-11h00	*Pause café*		
11h00-11h40	**Keynote 2**: Cyrille Costentin	**Université Grenoble Alpes**	*Molecular catalysis of electrochemical reactions: principles and applications*
11h40-12h00	O2: Justin Grill	**ICP**	*End-to-end DFT/ML framework for the rational design and computation of nonlinear optical properties of CdTe quantum dots*
12h00-12h20	O3 : Sanket Sen	**SOLEIL/ISMO**	*Photoelectron Circular Dichroism in Chiral [6]helicene*
12h30-15h00	*Buffet* *Séance Posters Hall ICP*		
15h00-15h40	**Keynote 3:** Roberto Flores	**Universidad de Guadalajara (Mexico)**	*Development and application of deMon2k software for the calculation of chemical reactivity descriptors*
15h40-16h00	O4: Rawan Abouhaidar	**LAMBE**	*Solvation Structures and Vibrational Fingerprints of LiPF6 in Mixed Carbonate Electrolytes: A Molecular Dynamics Study*
16h-16h20	O5: Elsa Casette	**LuMIN**	*Ultrafast dynamics of relaxation in well-dispersed & size controlled nanographenes*
16h20-16h40	O6 : Fanny Schnetz	**PPSM**	*Investigation of a photochromic compound for storing and releasing visible solar energy triggered by acid*
16h40	*Fin*		

K1: Photoreactions of fluorescent proteins: from time-resolved spectroscopy to biological imaging

Agathe Espagne

Ecole Normale Supérieure Paris – Département de Chimie

Fluorescent proteins (FPs) are artificial proteins genetically engineered from the Green Fluorescent Protein (GFP) of the jellyfish Aequoria victoria for use as fluorescent probes in biological imaging. They are ubiquitous tools in biology laboratories. However, FPs are not simple molecular beacons: they exhibit a variety of photoreactions whose mechanisms are only partially understood. These photoreactions are harmful when they compete with fluorescence, but they can also inspire the development of innovative imaging methods, as demonstrated for example by the emergence of super-resolution imaging methods. A better understanding of the photochemistry of FPs is essential to improve the performance of biological imaging.

Using the example of our work on Reversibly Switchable Fluorescent Proteins (RSFPs) and on light-induced Reverse Intersystem Crossing (RISC) in EGFP, I will show how detailed studies of the mechanisms and dynamics of FP photoreactions, based in particular on transient absorption spectroscopy (TAS) from the femtosecond to the millisecond scale, can lead to the proposal of new biological imaging methods.

O1: Near-infrared quantum-dot based adaptive optics for in-depth, two-photon neuroimaging

Jan Pytel[1,2], Alice Guillaume-Manca[1,2], Béatrice Jeffries[4], Céline Roux-Byl[4], Thomas Pons[4], Pauline Treimany[3], Fabrice Harms[3], Alexandra Fragola[2], Laurent Bourdieu[1]

[1]*Institut de Biologie de l'Ecole Normale Supérieure, PSL, INSERM, CNRS Paris*
[2] *Institut des Sciences Moléculaires d'Orsay, Université Paris Sud, CNRS UMR 8214, Orsay*
[3] *Imagine Optic SA, 18 Rue Charles de Gaulle, 91400 Orsay, France*
[4] *Laboratoire de Physique et Etude de Matériaux, ESPCI, CNRS UMR 8213, Paris*

Two-photon excited fluorescence microscopy (2PEFM) is widely used in in vivo neuroimaging, because it is resistant to scattering, allowing in-depth imaging with single-cell resolution, in addition to causing minimal photodamage to the observed structures. Nevertheless, image quality deep inside biological tissues remains limited by scattering and optical aberrations due to the refractive index inhomogeneity, which limits both resolution and sensitivity [1]. Adaptive optics can provide a reliable live correction of the aberrations in 2PEFM at the excitation, improving the collected signal and allowing for imaging at greater depths [2,3]. Direct wavefront sensing–based adaptive optics has previously been shown to enhance the resolution of fine structures up to 850 µm deep in murine brains [4,5]. Nevertheless, the accuracy of aberration measurement remains limited in depth due to the scattering properties of the tissue.

In this project we explore the use of NIR-emitting quantum dots for direct wavefront sensing at depth in the mouse cortex. Quantum dots are bright, stable and tunable fluorescent nanoparticles. These properties make them ideal candidates for a guide star, providing a source of ballistic fluorescence signal for the wavefront sensor. We demonstrate the biocompatibility and superior blood circulation time of $CuInSe_2/ZnS$ quantum dots emitting at 700nm compared to a dye-dextran conjugate. These qualities make quantum dots suitable for long-term imaging. By injecting them into the blood vessels, we demonstrate that the optical wavefront can be efficiently and accurately measured deep inside the mouse brain. This allows the signal and resolution in images of fine structures up to 400 µm deep in the visual cortex of genetically labelled, anaesthetised mice to be enhanced.

References

[1] F. Helmchen and W. Denk, *Nat. Methods*, **vol. 2,** pp. 932–940 (2005)
[2] K. M. Hampson et al., *Nat. Rev. Methods Primer*, **vol. 1**, p. 68 (2021)
[3] S. Imperato et al., *Optics Express* **30**(9), pp. 15250-15265 (2022)
[4] R. Liu et al., *Nat. Methods*, **vol. 16**, pp. 615–618 (2019)
[5] K. Wang et al., *Nat. Commun.*, **vol. 6**, p. 7276 (2015)

K2: Molecular catalysis of electrochemical reactions: principles and applications

Cyrille Costentin

Université Grenoble Alpes, Département de Chimie Moléculaire

Molecular catalysis of electrochemical reactions is a rapidly evolving field, with significant emphasis on small molecule activation and the electrification of chemical transformations. Gaining mechanistic insight is crucial for the rational design of more efficient catalysts and processes. In this context, after a brief presentation of the principles of molecular catalysis of electrochemical reactions, we will present some examples of mechanistic analysis. Homogeneous electrochemical catalysis of CO_2 reduction to CO with iron tetraphenylporphyrins as catalysts will be described focusing on the role of proton donors as co-substrates as well as on modification of the catalyst structure. Then we will discuss the catalysis of N_2O to N_2 with a series of organic catalysts and transition metal complexes (rhenium bipyridyl carbonyl complexes) allowing to contrast outer- and inner-sphere mechanisms. In the latter case, the generation of a strong coordinating ligand as co-product of the reaction might be detrimental for an efficient catalysis because it can bind the metal center and block or slow down the catalytic process. This self-modulation phenomenon will be described and further illustrated.

O2: End-to-end DFT/ML framework for the rational design and computation of nonlinear optical properties of CdTe quantum dots.

Justin Grill[1], Christophe Humbert[1], Carine Clavaguéra[1]

[1]*Institut de Chimie Physique, Université Paris-Saclay, CNRS, Bâtiment 349, 91405 Orsay*

Zinc-blende CdTe quantum dots (QDs) exhibit unique electronic structures and optical properties, with applications in photovoltaics (QDSSCs), optoelectronics (QLEDs), and biomedicine (biosensors, biolabeling). High tunability of their optical properties (quantum yield, optical gap) can be achieved by varying their size, structure, and capping ligands. Thus, proper modelling of their surface chemistry is necessary to allow for both stability and quantum confinement of the electron-hole states [1]. Advances in the synthesis of QDs, including growth pathways for the nanocrystalline core and innovative methods to control their surface functionalization [2], have reported magic-sized QDs which exhibit enhanced stability and quantum properties for specific ligands. However, only the optoelectronic properties of small capped-clusters (d < 2 nm), which are below the experimentally relevant range (d = 3–10 nm), can be theoretically studied through the framework of density functional theory (DFT) and its time-dependent counterpart (TD-DFT), due to exponential computational costs. This work aims to bridge this gap by developing an end-to-end machine learning (ML) approach to design and study large QDs with DFT-level accuracy at low computational cost. Deep Neural Network (DNN) algorithms, such as DeepMD, have demonstrated efficiency in constructing machine learning force fields for systems of higher dimensionality down to small PbS/CdSe QDs ($\lesssim$ 1000 atoms) [3, 4]. Nevertheless, they require a comprehensive dataset of reasonable size that accurately encapsulates the relationship between a QD's size, structure, surface passivation, and the corresponding atomic energies and forces. We propose a workflow that enables the generation of an initial DFT-characterized dataset of Cd_nTe_m structures (n = 13–119, m = 16–119) with passivated and geometrically relaxed surfaces. Active learning is considered to gradually scale the range of structures, strengthening model generalization. Once validated, the model will be applied to compute Sum Frequency Generation (SFG) [2, 5] spectra via ML molecular dynamics simulations, aiding the understanding of ligand-QD surface interactions. These nonlinear optical properties depend on the full polarizability tensor and remain largely unexplored in the existing literature.

References
[1] Llusar, J. et al. *ACS Nano* **18**, 1563–1572 (2024)
[2] Humbert, C. et al. *J. Colloid Interface Sci.* **445**, 69–75 (2015)
[3] Zhang, H. et al. *Nano Res.* **17**, 10685–10693 (2024)
[4] Sowa, J.K. et al. *J. Phys. Chem. Lett.* **14**, 7215–7222 (2023)
[5] De La Puente, M. et al. *J. Phys. Chem. Lett.* **15**, 3096–3102 (2024)

K3: Development and application of deMon2k software for the calculation of chemical reactivity descriptors

Roberto Flores-Moreno

Universidad de Guadalajara - Departamento de Quimica, Mexico

The deMon2k linear response module is nowadays quite mature. In this presentation we first give an outline of the development of the linear response module on the context of auxiliary density functional theory. Then the different properties that can be calculated with the current version of the program are presented with numerical and graphical examples. In particular, it is discussed the analytic calculation of chemical reactivity descriptors frequently found in conceptual density functional theory. Overall we provide a description of the potential utility for molecular research, including radiation chemistry.

O4: Solvation Structures and Vibrational Fingerprints of $LiPF_6$ in Mixed Carbonate Electrolytes: A Molecular Dynamics Study

Rawan Abouhaidar[a], Sana Bouguerou[a], Alvaro Cimas[a], Marie-Liesse Doublet[b], Marie-Pierre Gaigeot[a,c]

[a]Université Paris-Saclay, Univ Evry, CY Cergy Paris Université, CNRS, LAMBE UMR 8587, 91025 Evry-Courcouronnes, France
[b]Université de Montpellier, CNRS, ICGM UMR 5253 - Institut Charles Gerhardt Montpellier, 34293 Montpellier, France
[c]Institut Universitaire de France (IUF), 75005 Paris, France

The sustainability of lithium-ion batteries is gaining increased attention, particularly in relation to the carbonate-based solvents commonly used in electrolytes. Understanding the interactions between lithium ions and both the solvent and anions is essential, as these interactions govern key processes such as solvation structure and ion transport. However, experimental techniques often face limitations in probing these interactions at the molecular level. In this work, we employ classical molecular dynamics (MD) simulations to investigate electrolyte solutions of $LiPF_6$ in mixtures of ethylene carbonate (EC), dimethyl carbonate (DMC), and propylene carbonate (PC); solvents that differ in dielectric constant, polarity, and viscosity, and are frequently used in binary or ternary combinations.

Our analyses focus on the structural organization of these electrolytes, including ion-ion, ion-solvent, and solvent-solvent interactions, as well as the diffusion behaviour of ions and solvent molecules, and vibrational spectroscopy (IR and Raman) of these complex and inhomogeneous mixtures.

Solvation environments are characterized with graph theory analysis[1,2]. These insights will guide subsequent ab initio molecular dynamics (AIMD) simulations aimed at calculating the vibrational signatures of distinct solvation structures, thereby supporting the interpretation of experimental spectroscopic data[3,4].

(1) Bougueroua, S.; Spezia, R.; Pezzotti, S.; Vial, S.; Quessette, F.; Barth, D.; Gaigeot, M.-P. *J. Chem. Phys.* **2018**, *149* (18), 184102. https://doi.org/10.1063/1.5045818.

(2) Bougueroua, S.; Aboulfath, Y.; Cimas, A.; Hashemi, A.; A. Pidko, E.; Barth, D.; Gaigeot, M.-P. *Comptes Rendus Chim.* **2024**, *27* (S5), 1–23. https://doi.org/10.5802/crchim.317.

(3) Gervillié-Mouravieff, C.; Boussard-Plédel, C.; Huang, J.; Leau, C.; Blanquer, L. A.; Yahia, M. B.; Doublet, M.-L.; Boles, S. T.; Zhang, X. H.; Adam, J. L.; Tarascon, J.-M. *Nat. Energy* **2022**, *7* (12), 1157–1169. https://doi.org/10.1038/s41560-022-01141-3.

(4) Leau, C.; Wang, Y.; Gervillié-Mouravieff, C.; Boles, S. T.; Zhang, X.-H.; Coudray, S.; Boussard-Plédel, C.; Tarascon, J.-M. *Nat. Commun.* **2025**, *16* (1), 757. https://doi.org/10.1038/s41467-024-55339-y.

O5: *Ultrafast dynamics of relaxation in well-dispersed & size controlled nanographenes*

S. Quistrebert[1], D. Medina-Lopez[2], C. Banga-Kpako[2], T. T. Huynh[1], S. Campidelli[3], J.-S. Lauret[1], E. Cassette[1]

[1]Université Paris-Saclay, ENS Paris-Saclay, CNRS, CentraleSupélec, LuMIn, Orsay, France
[2] Université Paris-Saclay, CEA Saclay, CNRS, NIMBE/LICSEN, Gif-sur-Yvette, France

Recent chemical synthesis development through bottom-up approaches have led to nanographenes with exceptionally well-controlled size, shape and dispersion.**[1]** Among them, rectangular graphene nanoflakes (G-NFs) have provided tunable emission (energy and radiative rate) depending on their lateral sizes, combined with a photoluminescence (PL) quantum yield close to 1.**[2]** Here we use transient absorption (TA) of 40 fs temporal resolution to probe the internal conversion and vibrational relaxation in rectangular G-NFs composed of exactly 96, 114 and 132 conjugated carbons. The strongly limited aggregation allows a clear observation and identification of the discrete ground state bleaching (GSB) and excited state emission (ESE) signals. We selectively excite the different samples at optically active electronic transitions and vibrational replica. Thought the appearance of ESE signal at the energy of the steady-state PL peaks, the dynamics of relaxation were unveiled. The resulting electronic relaxation times range from 130 fs to 180 fs and are limited by the vibrational relaxation step.**[3]**

References

1. Y. Gu, Z. Qiu, K. Müllen, Nanographenes and Graphene Nanoribbons as Multitalents of Present and Future Materials Science, J. Am. Chem. Soc., **2022**, 144, 11499.
2. D. Medina-Lopez, T. Liu, S. Osella, H. Levy-Falk, N. Rolland, C. Elias, G. Huber, P. Ticku, L. Rondin, B. Jousselme, D. Beljonne, J.-S. Lauret, S. Campidelli, Interplay of structure and photophysics of individualized rod-shaped graphene quantum dots with up to 132 sp2 carbon atoms, Nat. Commun., **2023**, 14:4728.
3. S. Quistrebert, D. Medina-Lopez, C. Banga Kpako, T.T. Huynh, S. Campidelli, J.-S. Lauret, E.Cassette, Ultrafast Dynamics of Relaxation in Well-Dispersed Quantum-Confined Nanographenes, *under review*.

Green Hydrogen Objective: Chemical Functionalization of GaN Nanowires for the Development of Innovative Photocatalysts

Hiba El Idrissi Bouyahyaoui[1,2] , *Amel Zorai*[1,2] , *Marie Le Pivert*[1,3] , *Hynd Remita*[1] ,
Noelle Gogneau[2] , *Maria Tchernycheva*[2]

hiba.el-idrissi@universite-paris-saclay.fr

[1]*Institut de Chimie Physique, UMR 8000 CNRS, Université Paris-Saclay, 91405 Orsay*
[2]*Institut de Chimie Moléculaire et des Matériaux d'Orsay, UMR 8182, 91400 Orsay, France*
[3]*Unité Chimie et Procédés (UCP), ENSTA, Institut Polytechnique de Paris, F-91120 Palaiseau*

The transition to sustainable energy sources requires the development of efficient and durable photocatalysts for hydrogen production. Gallium Nitride **(GaN)** nanowires have emerged as promising candidates due to their wide bandgap, high charge carrier mobility, and excellent chemical stability. However, their practical application in photocatalytic water splitting is not fully studied yet and is mainly used in electrocatalysis. Therefore, this study aims to evaluate the photocatalytic performance of **GaN** NWs and to enhance their photocatalytic performance by implementing surface functionalization. Surface functionnalization strategies allow to improve charge separation, optimize reaction kinetics, and increase overall hydrogen evolution efficiency.

GaN nanowires are synthesized via epitaxial growth, a method that enables precise control over their morphology and crystalline structure. They are subsequently functionalized through radiolytic deposition of transition metal nanoparticles **(Pt)** which act as co-catalyst to facilitate interfacial charge transfer and mitigate recombination losses. After characterization by scanning electron microscopy **(SEM)**, the photocatalytic hydrogen evolution reaction **(HER)** performance of functionalized **GaN** nanowires is assessed under simulated solar irradiation in an aqueous medium. The influence of the morphology (density) were studied to investigate the optimum density allowing enough photocatalyst active surface available while avoiding light scattering effect and embarrassed diffusion of water and hydrogen. The functionnalization of GaN NWs with Pt significantly enhances the photocatalytic activity and a production rate of **13.2 mmol/g/h** were reached after 4h in TEOA : H2O (Tri éthanolamine : Water) under Mercury lamp (150W).

These findings contribute to a deeper understanding of GaN-based photocatalysts and highlight the crucial role of surface functionalization in improving photocatalytic efficiency. By offering a rational design strategy for optimizing semiconductor photocatalysts, this work provides valuable insights for the development of scalable and economically viable green hydrogen production technologies.

Refinement of a solution-seeded supercritical fluid pulsed expansion: Optimizing vaporization and molecular cooling

Joulanda Taha, Jean-Xavier Bardaud,[Δ] Eric Gloaguen

CNRS, Institut des Sciences Moléculaires d'Orsay, Université Paris-Saclay, Orsay, France
[Δ] Present address : Université Paris-Saclay, CNRS, Institut de Chimie Physique, UMR8000, 91405 Orsay, France

Introducing molecules into the gas phase as neutrals is a critical challenge in various analytical techniques enabling advanced spectroscopic characterization. Our current molecular-jet source coupled with a supercritical CO_2 fluid chromatography (SFC) setup [1] introduces analytes that are detected after expansion by resonant two-photon ionization (R2PI), yet, its molecular expansion stage only achieves partial vaporization generating by that molecular clusters. To maximize the efficiency of sample vaporization, the source should be improved to achieve complete cluster vaporization and enhanced molecular cooling through multiple modifications including the addition of a heated channel downstream the expansion stage to break down clusters. Therefore, the design variables of the source (Figure 1) influencing the expansion profile are being explored to optimize both vaporization and cooling, in order to produce isolated analytes suitable for conformer-resolved laser spectroscopy experiments. Solution of Caffeine dissolved in Acetonitrile is used as a model sample injected into CO_2 to assess these changes. The poster results presented illustrate the progression of the design process.

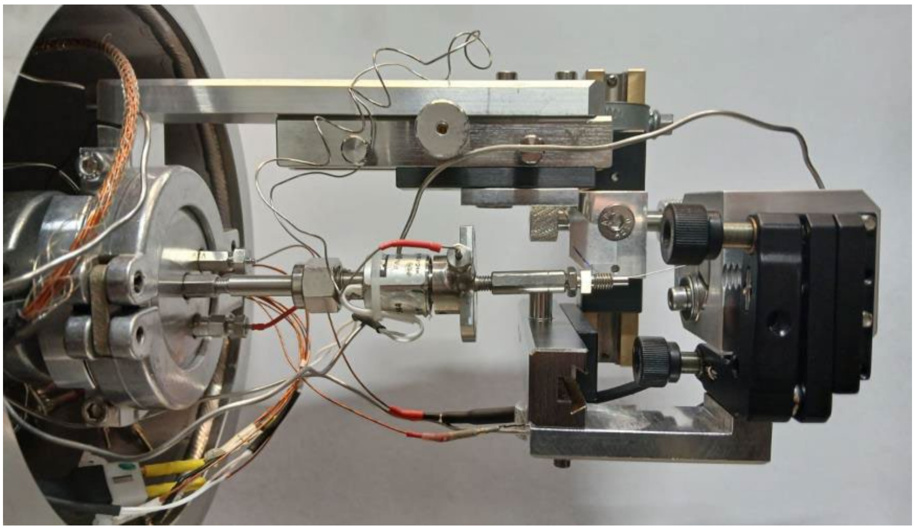


Figure 1: Photograph of the pulsed vaporization source assembly in its current design.

[1] Bardaud, J.-X., Gaveau, M.-A., Mons, M., Gloaguen, E. *Expansion of Solution-Seeded Supercritical CO_2 Characterized by Mass Spectrometry and Laser Spectroscopy*, J. Phys. Chem. A, *2025*, 129 (28), 6532–6537. DOI: 10.1021/acs.jpca.5c02256.

COLLECTIVE EMISSION PROCESSES IN SUPERSTRUCTURES OF METAL HALIDE PEROVSKITE NANOCRYSTALS

T.K.A. Hoang[1], E. Ruby[1], P. Taank[1], C. Mayer[1], E. Deleporte[1], E. Cassette[1]

[1]*Université Paris-Saclay, ENS Paris-Saclay, CNRS, CentraleSupélec, LuMIn, Orsay, France*

Halide perovskite nanostructures are of particular interest for the development of several optoelectronic applications including light emitting devices (LEDs and lasers). However, collective effects between these nano-emitters such as superradiance (SR) or superfluorescence (SF) remain a challenge, despite promising report.1 Here we investigate collective emission process in films of $CsPbBr_3$ perovskite nanocrystals in the weak confinement regime, with time-resolved photoluminescence using a picosecond streak camera, from room- to cryogenic- temperature. The combination of both spectral and temporal resolution allows us to show that the collective emission with a burst of intensity originates from incoherent amplified spontaneous emission while non-radiative Auger recombination dominate at longer time.

References

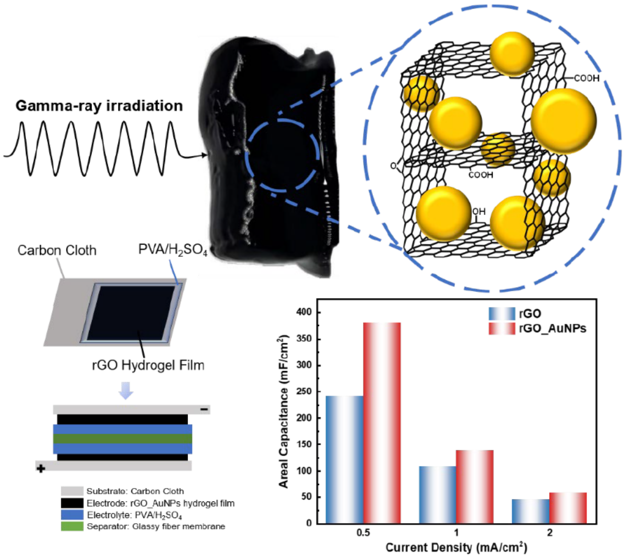
1. G. Raino, M.A. Becker, M.I. Bodnarchuck, R.F. Mahrt, M.V. Kovalenko, T. Stöferle, Superfluorescence from lead halide perovskite quantum dot superlattices, Nature, **2018**, 563, 671-675.

Radiolytically synthesized 3D graphene-based hydrogels for energy storage applications

Liran Hu,[1] Souad Abou-Zeid,[1] Zhenpeng Cui,[1,2] and Samy Remita[1,3]

[1] *Institut de Chimie Physique, ICP, UMR 8000, CNRS, Université Paris-Saclay, 15 avenue Jean Perrin, 91405 Orsay Cedex, France*
[2] *School of Nuclear Science and Technology, Lanzhou University, Lanzhou, 730000, PR China*
[3] *Département Chimie Vivant Santé, EPN 7, CNAM, 292 rue Saint-Martin, 75003 Paris, France*

Three-dimensional graphene-based gels (3D GBGs) have garnered increasingly interest in energy storage due to their exceptional properties, including increased active material per projected area, excellent electrical conductivity, porosity and robust electrochemical and structural stability [1]. However, conventional synthesis methods such as hydrothermal approach, relies heavily on high-temperature processing and external reducing agents, which introduce scalability challenges and post-synthesis contamination. To address these limitations, based on previous research works [2, 3], we developed an alternative approach for synthesizing reduced graphene oxide hydrogels via-gamma ray irradiation, eliminating the need for chemical reductants or energy-intensive thermal treatments. During irradiation, noble metal nanoparticles can be simultaneously synthesized and stably incorporated into hydrogel structure. Electrochemical analysis using the synthesized hydrogels as electrode materials in symmetric supercapacitor demonstrated their excellent performance in energy storage including remarkable specific capacitance, power density and stability, as well as the synergic effects of the incorporated metal nanoparticles. This work establishes a novel, facile and industrially viable pathway for designing 3D GBG composites, bridging the gap between sustainable synthesis and high-performance energy storage technologies.



Graphical abstract for radiolytically synthesized rGO_AuNPs hydrogel and composition and areal capacitance of assembled symmetric supercapacitor

1. H. Wang, X. Yuan, et al., *Adv. Colloid Interface Sci.*, **2015**. 221: p. 41.
2. S. Abou Zeid, S. Bencherif, et al., *New J. Chem.*, **2024**. 48(11): p. 4749.
3. L. Hu, S. Abou Zeid, et al., *Appl. Surf. Sci.*, **2024**. 678: p. 161109.

Effect of confinement within vertically-oriented mesoporous silica films of a new polyoxometalate-based polymer material on the electrocatalytic reduction of nitrites

Odilon Wamba-Tchio [1], Alain Walcarius [2], Israël Mbomekallé [1] and Neus Vilà [2,3]

1. *ICP, Université Paris-Saclay, CNRS, Orsay, France*
2. *LCPME, Université de Lorraine, CNRS, Nancy, France*
3. *Departament de Quimica, Universitat Autonoma de Barcelona*

PolyOxoMetalates (POMs) are anionic metal oxide clusters with nanometric size made from transition metals at high oxidation state. This structural specificity gives them the ability to accept and exchange electrons in a fast and reversible way, triggering keen interest in various fields such as electrocatalysis.[1,2] For their particular use in heterogenous electrocatalysis, POMs are often confined onto electrode surface via chemisorption, electrodeposition and encapsulation in polymers or inorganics matrices.[2] However, such configurations feature an irregular distribution of separate POM units within the template, which does not promote an efficient charge transfer process between the active POM units and, as a result, great electrocatalytic activity.[3]

One way of overcoming this drawback would probably be to covalently combine POM units into a 1D mesoporous nanostructure with uniform diameter deposited orthogonally to the electrode surface to ensure a regular distribution of POM units. With this in mind, a hybrid polyoxometalate ($(TBA)_3PW_{11}O_{39}(SiC_6H_5NH_2)_2O$ named POM(ani)$_2$, with POM = polyoxometalate and ani = aniline) has been synthesized and electropolymerized within mesochannels (3nm and 4.3nm in diameter) of vertically oriented Mesoporous Silica Films (MSFs) prepared on ITO (**Fig. 1a** and **1b**). The aim here is to ultimately have a parallel and uniform distribution of POM units within oriented MSFs. Electrochemical characterizations of MSFs after electropolymerization, coupled with some physicochemical characterizations (TEM/EDX, GISAXS, XPS and IR spectroscopies) have evidenced the formation of a POM-based polymer material (Poly-POM(ani)$_2$@MSF) within the mesochannels, which kept their oriented mesostructure during the process. This new polymeric material confined in MSFs has been used for the electrocatalytic reduction of nitrites, [1] in order to evaluate the effect of the presence of the mesoporous matrix in the electrocatalytic activity toward the reduction of nitrites. The results showed that the electrocatalytic activity of Poly-POM(ani)$_2$@MSF towards the nitrite reduction is enhanced, not only compared to non-polymerized MSFs but also compared to Poly-POM(ani)$_2$ on bare ITO (**Fig. 1c**). This behavior highlights the fact that, despite the low surface concentration of POM(ani)$_2$ (Γ=1.8x10^{-10} mol.cm^{-2}) within MSFs compared to that estimated on bare ITO after polymerization (Γ=3.8x10^{-10} mol.cm^{-2}), the vertical distribution of POM units close together along the polymer chain within MSFs makes them available for the electrocatalytic process.

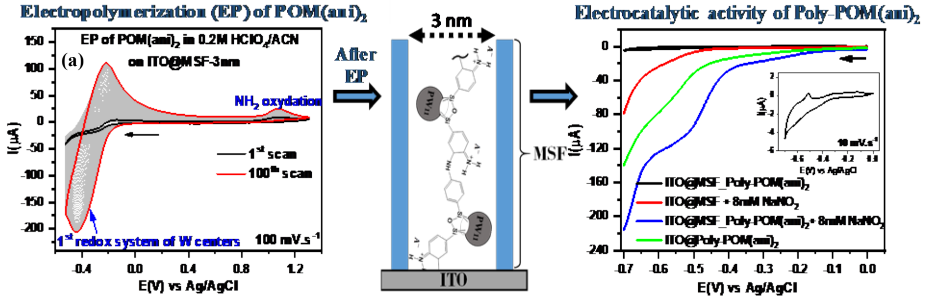


Figure 1. Electrotrosynthesis of Poly-POM(ani)$_2$ within MSF-3nm diameter and electrocatalytic activity

[1] Teillout, A. L., Oliveira, P., Marrot, J., Howell, R. C., Vilà, N., Walcarius, A., & Mbomekallé, I. M. (2019). *Inorganics*, *7*, 15.

[2] Vilà, N., Oliveira, P., Walcarius, A., & Mbomekallé, I. M. (2020). *Electrochimica Acta*, *353*, 136577.

[3] Vilà-Nadal, L., Mitchell, S. G., Markov, S., Busche, C., Georgiev, V., Asenov, A., & Cronin, L. (2013). *Chemistry–A European Journal*, 19, 16502-16511.

Molecular Dynamics study of the HSulf-2 protein: influence of post-translation modifications on dynamics of catalytic pocket

Jianjun Tao,[1] **Nathalie Basdevant**[1]

[1] **Université Paris-Saclay, Université Évry, CY Cergy Paris Université, CNRS, LAMBE, 91025, Évry-Courcouronnes, France.**
underlined: speaker

A sulfatase is an enzyme responsible for modulating the sulfated state of macromolecules, such as heparan sulfate proteoglycan (HSPG), by cleaving the ester-sulfate or sulfamate bond and thus releasing sulfate. It is involved in cellular metabolism and developmental cell signaling [1]. The cysteine or serine in the active site is converted to formylglycine (FGL) in order to perform enzymatic activity. Among the 17 known human sulfatases, endosulfatases 1 (HSulf-1) and 2 (HSulf-2) were discovered in 2002 [2]. These two HSulf isoforms are composed of three domains: the catalytic domain (CAT), the hydrophilic domain (HD), and the C-terminal domain (Cter) (see Figure 1). One of the main differences is that HSulf-1 tends to suppress certain cancer development while HSulf-2 is found to be overexpressed in numerous cancers, particularly breast cancer, making it a promising therapeutic target. Structural exploration of HSulf-2 and especially of ligand binding pocket is essential to design inhibitors as potential anticancer drug candidates.

However, no experimentally resolved structure of HSulf-2 has been yet uploaded in the Protein Data Bank (PDB). One alternative is to use the predicted structure of pro-enzyme proHSulf-2 by AlphaFold2 (AF2) [3], where cysteine at catalytic site is not transformed into FGL. In this context, we firstly identified essential residues involved in ligand binding by amino acid sequence alignment of 17 sulfatases. Then we applied certain numerically possible post-translational modifilcations (PTMs) and performed molecular dynamics simulations to study the dynamic profile of catalytic site and also catalytic pocket, which is related to ligand binding and release.

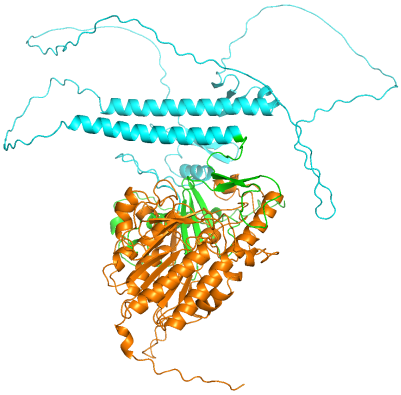


Figure 1: Pro-HSulf-2 structure proposed by AlphaFold2, colored according to domain: CAT in orange, HD in cyan, and Cter in green.

---

[01] Buono, M., Cosma, M.P Sulfatase activities towards the regulation of cell metabolism and signaling in mammals.*Cell. Mol. Life Sci*, **67**: 769–780 (2010).

[02] Morimoto-Tomita M, Uchimura K, Werb Z, Hemmerich S, Rosen SD. Cloning and characterization of two extracellular heparin-degrading endosulfatases in mice and humans.*J. Biol. Chem*, **277**: 49175–49185 (2002).

[03] Jumper, J., Evans, R., Pritzel, A. et al Highly accurate protein structure prediction with AlphaFold. *Nature* , **596** 583–589 (2021).