

Posters

HiFunMat conference

26 04 2023

© Thomas Cottineau

Hierarchical & Functional Materials for health, environment & energy

| HiFunMat The **interdisciplinary thematic** institutes

of the **University of Strasbourg**

& **cnrs** & **Inserm**

## Reversible photoisomerization within a 2D self-assembled layer of diarylethene molecules on HOPG

M. Cranney<sup>1,\*</sup>, F. Calard<sup>2</sup>, J.-P. Malval<sup>1</sup>, T. Jarrosson<sup>2</sup>, J.-L. Bubendorff<sup>1</sup>, F. Vonau<sup>1</sup>,  
J.-P. Lère-Porte<sup>2</sup>, F. Serein-Spirau<sup>2</sup>, L. Simon<sup>1,\*</sup>

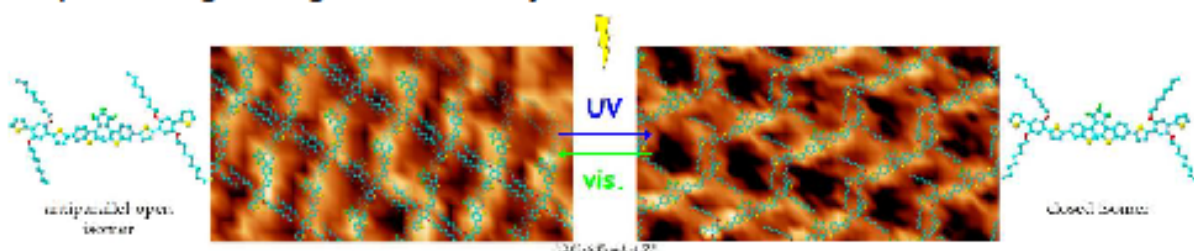
<sup>1</sup> Université de Haute-Alsace, CNRS, IS2M UMR 7361, Mulhouse, France

<sup>2</sup> ENSCM Montpellier, ICGM UMR 5253, Montpellier, France

Email: marion.cranney@uha.fr ; laurent.simon@uha.fr

This study comes within the framework of design and study of smart surfaces. They are based on the self-assembly of functionalized molecules on a substrate, that will respond in a defined way to an external stimulus. As the use of light to control smart surfaces seems to hold promising prospects [1], diarylethenes [2] are one of the most appropriate functionalized molecules for the achievement and study of smart surfaces.

In this study, we report an in situ reversible photoisomerization within a self-assembled layer of diarylethene molecules on a graphite surface at the solid-liquid interface. To achieve this aim, a new diarylperfluorocyclopentene derivative has been designed and synthesized. Its photophysical properties have been investigated by a UV-visible study in solution, confirming its interesting properties. A submolecularly resolved scanning tunneling microscopy study shows that both open and closed isomers form a self-assembled layer on HOPG at the solid-liquid interface, with markedly different organizations, as seen in the figure below. In situ UV and visible light irradiations lead to reversible isomerizations of the molecular self-assembled layer, without degradation and with a conversion ratio of 100%. Using linearly polarized light, we prove that this reversible photoisomerization occurs within the 2D self-assembled layer and not in solvent coupled to a molecular desorption-readsorption process, which should have hindered dramatically the use of these diarylethenes for potential applications. Indeed, we observe a selective isomerization of the domains of closed molecules according to the direction of polarization of the light. This had already been shown in the case of 3D crystals of diarylethenes, where there was isomerization when the direction of polarization was aligned with the moment of molecular electronic transition [3]. Furthermore, the self-assembly of the closed molecules is improvable by light irradiation, leading to expanding closed domains without thermal treatment of the sample which might damage the molecular layer.



**Figure :** Results on the self-assembly of diarylethene BT-(TBT)<sub>1</sub> on HOPG dissolved in 1-phenyloctane.

The molecules are able to isomerize reversibly within the self-assembled layer upon exposure to light.

### References

1. X. Zhang, L. Hou, P. Samorì, Nature Commun., 2016, 7, 11118 ; J. Zhang, H. Tian, Adv. Optical Mater., 2018, 6, 1701278.
2. M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, Chem. Rev., 2014, 114, 12174-12277 ; H.-B. Cheng, S. Zhang, E. Bai, X. Cao, J. Wang, J. Qi, J. Liu, J. Zhao, L. Zhang, J. Yoon, Adv. Mater., 2022, 34, 2108289.
3. T. Higashiguchi, D. Kitagawa, S. Kobatake, CrystEngComm, 2021, 23, 5795-5800 ; S. Kobatake, S. Kuma, M. Irie, Bull. Chem. Soc. Jpn., 2004, 77, 945-210.

## **3D printing of micro-actuators made of liquid crystal.**

Sébastien Dominici<sup>1</sup>, Xingyu Wu<sup>1</sup>, Quentin Bauerlin<sup>1</sup>, Laurent Ranno<sup>2</sup>, Nora Dempsey<sup>2</sup>, Karine Mougín<sup>1</sup>, Arnaud Spangenberg<sup>1\*</sup>.

<sup>1</sup> Institut de Science des Matériaux de Mulhouse, UMR7361, CNRS/UHA, 6805, Mulhouse.

<sup>2</sup> Institut Néel UPR 2940, CNRS/UGA, 25 rue des Martyrs, 38042 Grenoble.

Email: arnaud.spangenberg@uha.fr

Humankind always sought to create tools which allow the accomplishment of tasks that would be difficult or couldn't be done otherwise. Reproduction of simple movements observable in nature often require the design of complex tools but that are limited in terms of degree of motion in particular at the micrometric scale[1]. Among many microfabrication methods, two photons polymerization (TPP), dedicated in the realization of 3D-microstructures, appears as a prime position technique to create new tools. Thus, microrobots fabricated by TPP have been conceived for applications in nanomedicine, allowing to consider new strategies for the targeted release of drugs in the system[2] or even in vitro fecondation[3]. This work aims to fabricate micro-devices made of liquid crystals with different molecular alignments. We used a new technique to programme at the microscale the molecular conformation in 3D and thus the deformation of our material. Upon heating the sample go from a single design to several possible deformation (closure, twist...).

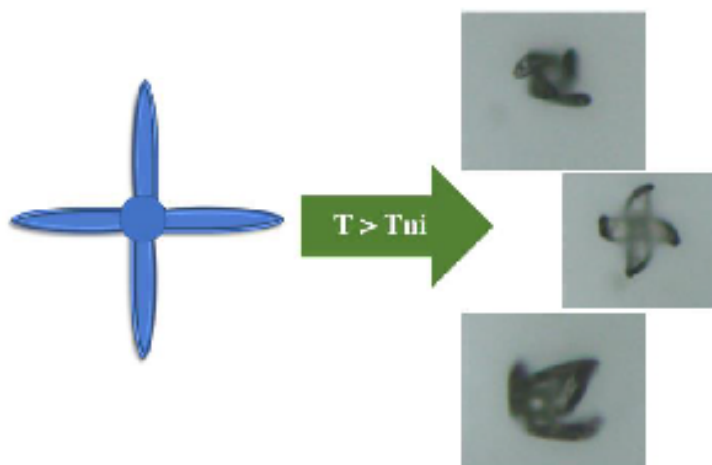


Figure 1 : Micro-clamps with different deformations upon heat.

### Acknowledgements

I would first like to thank the organizing committee for this opportunity to present my work. Also thank you to Dr Arnaud Spangenberg and Dr Karine Mougín for the quality of their mentoring and advising.

### References

1. Michał Zmysłony, Piotr Wasylczyk and Al, *Advanced Materials*, 2020, Volume 32, Page 2002779.
2. Hakan Ceylan, Metin Sitti and Al, *ACS Nano* 2019, Volume 13, Page 3353.
3. Haifeng Xu, Oliver G. Schmidt and Al, *Angewandte Chemie* 2020, Volume 132, Page 15029.



## Adaptive glazing based on photovoltaic spatial light modulators to improve the energy efficiency of buildings.

T. Ducatel<sup>2</sup>, Y. Lin<sup>1,2</sup>, S. Fall<sup>1</sup>, T. Heiser<sup>1,2</sup>.

<sup>1</sup>MaCEPV Team, D-ESSP Department, ICUBE, CNRS Cronenbourg Campus, France

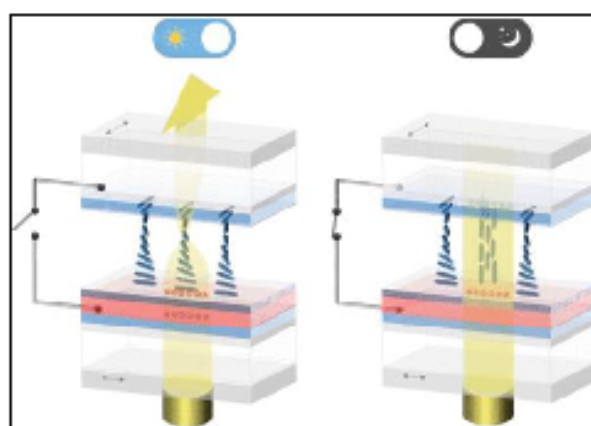
<sup>2</sup>Université de Strasbourg, France

Email: [thomas.ducatel@etu.unistra.fr](mailto:thomas.ducatel@etu.unistra.fr)

Building efficiency is one of the most important challenges we face in limiting global warming. The high heat transfer of our current glazing causes an enormous energy demand which represent 40 % of the total energy consumption in USA, exceeding the consumption of industry (32%) and transport (28%)<sup>1</sup>. In this context, new generations of smart glazing technologies (Thermochromic, Electrochromic, Liquid crystals windows...) are designed to reduce energy consumption by modulating transmission of UV and IR radiation depending on the outdoor climate<sup>2</sup>.

With this aim, the idea of an optical device called PSLM (Photovoltaic Spatial Light Modulator) has emerged in the MaCEPV team. In this apparatus, the orientation of a liquid crystal solution in an initial twisted nematic configuration can be controlled thanks to a photovoltaic unit, which gives rise to an OFF state and a ON state (Figure 1), i.e. allows the transmission or not of light depending on the generated photovoltage. This unusual association shows the possibility of an autonomous device with fast, controllable, and stable (short-range of time) response under light<sup>3</sup>.

PSLMs operate under DC voltage without a significant loss of performance. Therefore, the build-up of residual ions in the liquid crystal near the interfaces, which would screen the photo-induced electric field, appears to be negligible. The origin of the robustness of a PSLM against ion accumulation is still poorly understood. In this work, we probe the physical mechanism(s) that ensure the stable response of a PSLM under illumination by exploring the opto-electric properties of PSLM devices based on different non-conventional liquid-crystal alignment layers. The expected results will provide knowledge to improve the stability of PSLMs but will also be of interest to other opto-electronic devices based on liquid crystals, in which ionic conductivity hinders the utilization of a DC bias.



**Figure 1:** Scheme of the PSLM in OFF state (left side) and ON state (right side)<sup>3</sup>

### References

1. Charles F. Kutscher, *The Conversation*, 2020.
2. Ramakrishna and al, *Solar Energy Materials and Solar Cells*, 2017, Volume 159.
3. *ACS Appl. Mater. Interfaces*, 2023, 15, 3, 4267–4274

## PHOTOLITHOGRAPHIE DE RÉSEAUX MAGNÉTO-OPTIQUE À PROPRIÉTÉS MODULABLES PAR PIÉZO-ÉLECTRICITÉ

**Marwan Fakhry<sup>1,2</sup>, O. Soppera<sup>1,2</sup>, D. Berling<sup>1,2\*</sup>**

1. Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

2. Université de Strasbourg, France

(Marwan.fakhry@uha.fr)

### ABSTRACT:

The integration of magneto-optical (MO) components on conventional platforms (glass, polymer, SOI or semiconductor) is a technological challenge that has persisted since the first demonstration [1].

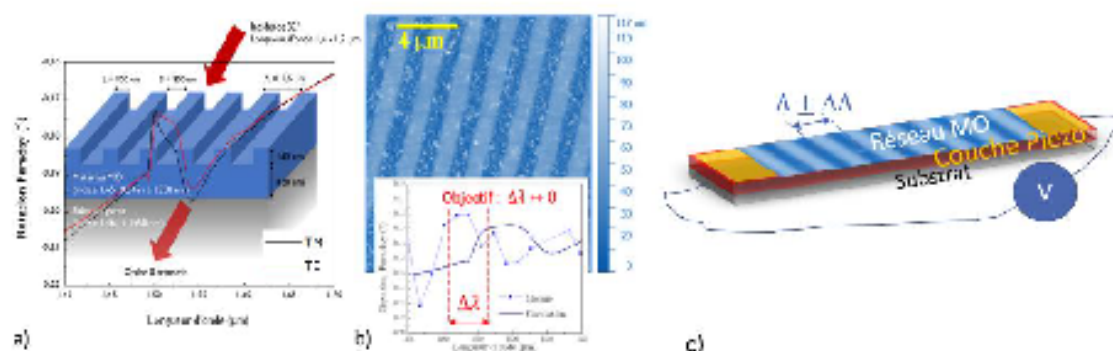
Indeed, MO materials need heat treatments at more than 700°C, incompatible with their integration within optical chips having other functions. It has also been demonstrated that the use of a 1D structuring acting as a distributed Bragg resonator enhances MO properties [2]. Our recent works show the possibility of realizing micro/nano structured MO networks by deep-UV photolithography at RT of a nanocomposite with high MO properties based on a sol-gel doped with magnetic nanoparticles (NPM) and their integrations for applications in guided optics and in free space [3].

Modulation and parameter tunability of MO gratings allow not only a means to adjust for manufacturing errors but also a mechanism to increase device functionality.

The goal is to study and control the modulation of photolithographed magneto-optical networks deposited on a thin layer of piezoelectric material (by applying a voltage). It is more suitable to use ferroelectric polymer materials such as poly (vinylidene fluoride) as they don't require HT treatment [4]. Ultimately, the objective is the complete realization at LT of modular non-reciprocal optical components, hybrid piezo-network MO structures, with a complete study of their properties (piezo, MO, ME coupling).

Currently, at the early stages of this work, we are focusing on the piezo-electric layer. The main goal is the optimization of its PE properties, mainly by maximizing the beta phase of the PVDF. Multiple formulations and coating methods had been used, and interesting results had been obtained using characterization techniques (FTIR, XRD, AFM, SEM, Profilometer, and Michelson interferometry), while the topography and roughness, must also be controlled.

Many other challenges await us, like combining the 2 layers, accurately controlling the mechanical variation of the PE layer, and maximizing the faraday rotation of the MO layer.



**Figure 1: Simulation of a nanocomposite MO network (a), AFM image of a photolithographed network and measurement - simulation of its MO response (b), the device envisaged to modulate the MO properties using a piezoelectric layer (c).**

### References

- 1- J. Caslera, G. Hepner, IEEE Trans. Magn. 13 (1977) 1583-1585
- 2- S. Kahl, A.M. Grishin, Applied Physics Letters, 84 (2004) 1438
- 3- C. Bidaud, Thèse de doctorat UHA-Mulhouse (2018) ; C. Bidaud et al. (2020), Deep-UV Lithography of Nanocomposite Thin Films into Magneto-optical Gratings with Submicron Periodicity. ChemPhotoChem. doi:10.1002/cptc.202000048



# In and Out-of-Equilibrium Interaction of Bare and Lipid-coated Colloidal Particles with Lipid Membranes

**Florent Fessler<sup>1</sup> and Dr. Antonio Stocco<sup>1</sup>**

<sup>1</sup>*Institut Charles Sadron, Physics of Membranes and Soft Matter (MCube)  
E-mail: florent.fessler@ics-cnrs.unistra.fr*

Interactions between micro- or nano-sized objects and lipid membranes are crucial in many processes such as entry of viruses in host cells, drug delivery or biomedical imaging. From another perspective, the use of microscopic colloidal probes to extract rheological properties of a medium close to soft interfaces or membranes already proved to be of relevant accuracy [1]. In this work, we propose to explore this broad range of interactions between a single colloidal particle and a lipid membrane by means of optical tweezers, going from a non-contact microrheological approach to non-specifically driven adhesion leading to large scale deformations of the membrane by the particle [2][3] and eventual topological changes. The experiments are conducted in several lipid membrane geometries, namely solid supported lipid bilayers and Giant Unilamellar Vesicles (GUVs), using optical bright field and fluorescence microscopy to image the system. The use of both isotropic (bare or lipid bilayer-coated) silica spheres as well as anisotropic rod-like silica particles with sizes of the order of a micron allows to track not only the translational motion of the particles but also the rotational motion upon interaction with lipid membranes. Experiments allowed to probe the dynamical effects and energy dissipation in the system associated to the relative motion of the particle with the lipid membrane such as bilayer interleaflet friction or membrane thermal fluctuations, and investigate on the predicted importance of parameters such as membrane spontaneous curvature or tension at this scale. The seeking of such results is motivated by a need to understand and control the interaction of the particles with GUVs in order to trigger active transportation of the particle-GUV system in a modular swimming approach.

## References

- [1] Thomas Boatwright, Michael Dennin, Roie Shlomovitz, Arthur A. Evans, and Alex J. Levine, "Probing interfacial dynamics and mechanics using submerged particle microrheology. II. Experiment", *Physics of Fluids* (2014)
- [2] Florent Fessler, Antonio Stocco, "Entry of Microparticles into Giant Lipid Vesicles by Optical Tweezers", *In preparation* (2022)
- [3] Hendrik T. Spanke, Robert W. Style, Claire François-Martin, Maria Feofilova, Manuel Eisentraut, Holger Kress, Jaime Agudo-Canalejo and Eric R. Dufresne, "Wrapping of Microparticles by Floppy Lipid Vesicles", *Physical Review Letters* (2020)

## Hierarchical nanocomposites materials with anisotropic properties

L. Garnier<sup>1,2</sup>, M. Tschopp<sup>2</sup>, J-L. Putaux<sup>3</sup>, B. Jean<sup>3\*</sup>, O. Félix<sup>2\*</sup>

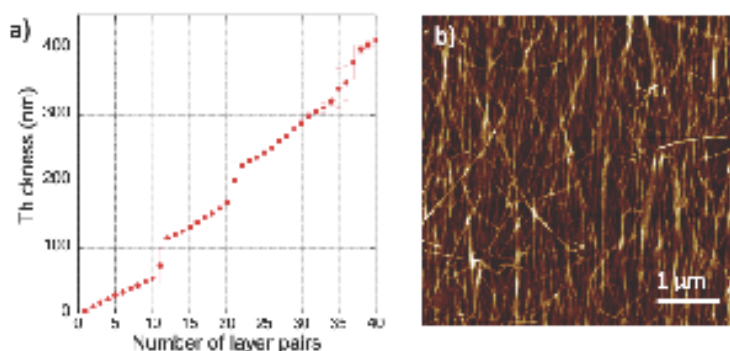
<sup>1</sup>Université de Strasbourg, Strasbourg, France

<sup>2</sup>Institut Charles Sadron (ICS), CNRS, Strasbourg, France

<sup>3</sup>Centre de recherche sur les macromolécules végétales (CERMAV), CNRS, Grenoble, France

Email: [olivier.felix@ics-cnrs.unistra.fr](mailto:olivier.felix@ics-cnrs.unistra.fr) ; [jean@cermav.cnrs.fr](mailto:jean@cermav.cnrs.fr)

The remarkable properties of natural composite materials<sup>1</sup> (e.g. plant cell wall, animal exoskeleton) have attracted a wealth of research to understand their structure-properties relations at all length scales and to design novel materials with superior performance. However, while nature masters the organization of anisotropic nano-objects like nanocelluloses into complex superstructures, the development of synthetic nanocomposite materials with complex and precisely controlled architectures (e.g. helical) has proven to be difficult due to the lack of suitable approaches for their preparation. With respect to the preparation of multimaterial thin films with a high level of control over the spatial positioning of their constituents, layer-by-layer (LbL) assembly<sup>2</sup> has gained its merits as a simple and highly versatile nanofabrication method. Its combination with the grazing incidence spraying (GIS)<sup>3</sup> method permits to design complex (e.g. helical) multilayer films in which the composition and orientation can be controlled independently in each layer. In this context my PhD thesis will focus on (i) the LbL/GIS fabrication and physico-chemical characterization of complex anisotropic nano-hybrid thin films combining nanocelluloses with soft polymer building blocks and (ii) the investigation of their mechanical properties as a function of their architecture and preparation conditions.



**Figure :** a) (t-CNC/PVAm)<sub>n</sub> film assembled by dipping. b) One oriented t-CNC layer deposited by GIS.

### Acknowledgements

The authors acknowledge the ministère de l'Enseignement Supérieur, de la Recherche et de l'Innovation and the Centre National de la Recherche Scientifique for their support. This work of the Interdisciplinary Institute HiFunMat, as part of the ITI 2021-2028 program of the University of Strasbourg, CNRS and Inserm, was supported by IdEx Unistra (ANR-10-IDEX-0002) and SFRI (STRAT'US project, ANR-20-SFRI-0012) under the framework of the French Investments for the Future Program.

### References

1. UGK. Wegst, H. Bai, E. Saiz, AP. Tomsia, RO. Ritchie, Bioinspired structural materials, *Nature Materials*, **2014**
2. G. Decher, Science, Fuzzy Nanoassemblies: Toward Layered Polymeric Multicomposites, **1997**, *277*, 1232.
3. R. Blell, X. Lin, T. Lindström, M. Ankerfors, M. Pauly, O. Felix, G. Decher, Generating in-Plane Orientational Order in Multilayer Films Prepared by Spray-Assisted Layer-by-Layer Assembly, *ACS Nano*, **2017**, *11*, 84.



## PLASMONIC INKS WITH CHAMELEON EFFECT

F. Ghellal<sup>1,2</sup>, K. Mougin<sup>1</sup>, G. Caffier<sup>2</sup> and A. Spangenberg<sup>1</sup>

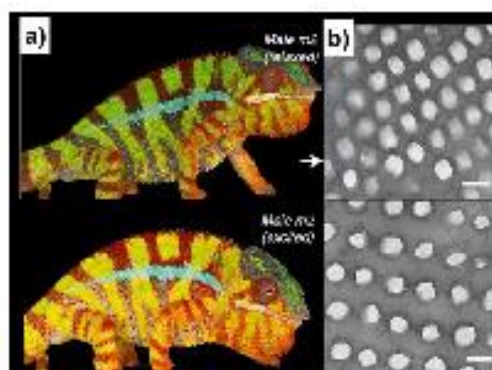
<sup>1</sup> Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

<sup>2</sup> Bic Ecriture 2000, F-77144 Montévrain, France

Email: [feriel.ghellal@bicworld.com](mailto:feriel.ghellal@bicworld.com)

Due to the vibrant colors produced by their interaction with visible light, metallic nanoparticles have been used for centuries by artists. Nowadays, colloidal nanoparticles have shown interest mainly due to their strong size and shape-dependent properties. Indeed, metallic nanoparticles, synthesized by oxidation-reduction reaction, can appear colored by a phenomenon of surface plasmon resonance.

Moreover, the chameleon can produce and modulate its color thanks to the guanine crystals present in its epidermis. By analogy, the plasmonic effect, induced by nanoparticles, is influenced by the interparticle distance. Based on that principle, mechanical or chemical stress can induce, in the material, a color change by reproducing or increasing the particles spacing.



**Figure:** The chameleon capable of changing its skin color explain by guanine crystal distance: (a) macroscopic color change and (b) microscopic correspondence.

Current formulated BIC inks are colored using dyes and pigments. This project focuses on providing a new generation of more sustainable and environmentally friendly coloring agents by exploiting the plasmonic effect which characterizes metallic nanoparticles.

Different nanoparticles synthesis methods using chemical batch and continuous flow processes, have been developed and discussed in this study. Finally, these results open new routes to create inks allowing to generate fixed colors and color changing, inspired by nature.

**Acknowledgements:** BIC Ecriture 2000, CNRS, IS2M, Université de Haute Alsace.

### References

1. A Teyssier, J.; Saenko, S.V.; van der Marel, D.; Milinkovitch, M.C., Photonic crystals cause active colour change in chameleons, *Nature Communications*. 2015, 6, 6368.



## **Degradation of Organic Pollutants under Sun Light Irradiation**

R. Haounati<sup>1</sup>, H. Ighnih<sup>1</sup>, H. Ouachtak<sup>1,2</sup>, R. E. Malekshah<sup>3</sup>, N. Hafid<sup>4</sup>,  
A. Jada<sup>5,6,\*</sup>, A. Ait Addi<sup>1</sup>

<sup>1</sup>Physical Chemistry & Environment Team, Faculty of Sciences, Ibn Zohr University, Agadir, Morocco.

<sup>2</sup>Department of Applied Chemistry, Faculty of Applied Sciences, Ibn Zohr University, Ait Melloul, Morocco.

<sup>3</sup>Medical Biomaterial Research Centre (MBRC), Tehran University of Medical Sciences, Tehran, Iran.

<sup>4</sup>Center For Education & Training Profession Souss Massa, Morocco.

<sup>5</sup>Institute of Materials Science of Mulhouse (IS2M), Haute Alsace University, Mulhouse 68100, France.

<sup>6</sup>Strasbourg University, Strasbourg 67081, France

Email: [amane.jada@uha.fr](mailto:amane.jada@uha.fr)

The effluents resulting from textile, leather, cosmetics and pigment industries, contain organic dyes, and their release into various aquatic systems is responsible for environmental degradation. Such pollution leads in turn to several humans and animals health issues, impacting the economy and affecting the climate change. Several methods such as physical adsorption, biological process, and chemical oxidation, are applied at large scales, for the wastewater treatment and the dye removal from the contaminated aqueous medium. However, the Advanced Oxidation Processes (AOP), such as: photocatalytic degradation using heterogeneous photocatalytic process, has been found to be a superior method, due to its operational simplicity, its high efficiency toward the organic dyes, its economic benefits and its facile mineralization of organic dyes into H<sub>2</sub>O and CO<sub>2</sub>. In the present work, we have designed Z-scheme nanocomposite such as g-C<sub>3</sub>N<sub>4</sub>/Fe<sub>3</sub>O<sub>4</sub>/Ag<sub>3</sub>PO<sub>4</sub>@Sepiolite which we have found to degrade efficiently the organic molecules such as malachite green (MG) dye, under solar light irradiation. The photocatalytic enhancement of the magnetic nanocomposite g-C<sub>3</sub>N<sub>4</sub>/Fe<sub>3</sub>O<sub>4</sub>/Ag<sub>3</sub>PO<sub>4</sub>@Sepiolite, in comparison to others catalysts, such as pure g-C<sub>3</sub>N<sub>4</sub>, g-C<sub>3</sub>N<sub>4</sub>@Sepiolite, and g-C<sub>3</sub>N<sub>4</sub>/Ag<sub>3</sub>PO<sub>4</sub>@Sepiolite, towards organic dye degradation, under solar light irradiation, was attributed to the synergy effects occurring between Ag<sub>3</sub>PO<sub>4</sub> supported by sepiolite clay and g-C<sub>3</sub>N<sub>4</sub> combined with the Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

**Keywords:** Sun Light Irradiation, Z-Scheme, Nanocomposite, Malachite Green, Monte Carlo calculations.

### References

1. R. Haounati, A. El Guerdaoui, H. Ouachtak, R. El Haouti, A. Bouddouch, N. Hafid, B. Bakiz, D.M.F. Santos, M. Labd Taha, A. Jada, A. Ait Addi, **Design of direct Z-scheme superb magnetic nanocomposite photocatalyst Fe<sub>3</sub>O<sub>4</sub>/Ag<sub>3</sub>PO<sub>4</sub>@Sep for hazardous dye degradation**, Separation and Purification Technology, 2021, 277, 119399.
2. R. Haounati, H. Ouachtak, R. El Haouti, S. Akhouairi, F. Largo, F. Akbal, A. Benlhachemi, A. Jada, A. Ait Addi, **Elaboration and properties of a new SDS/CTAB@Montmorillonite organoclay composite as a superb adsorbent for the removal of malachite green from aqueous solutions**, Separation and Purification Technology, 2021, 255, 117335.

## **Photocatalytic Degradation of Rhodamine B Dye using Hybrid Nanocomposite BiOCl@Kaolinite under Sunlight Irradiation**

H. Ighnih<sup>1</sup>, R. Haounati<sup>1</sup>, H. Ouachtak<sup>1,2</sup>, N. Hafid<sup>3</sup>, A. Jada<sup>4,5,\*</sup>, A. Ait Addi<sup>1</sup>

<sup>1</sup>Physical Chemistry & Environment Team, Faculty of Sciences, Ibn Zohr University, Agadir, Morocco.

<sup>2</sup>Department of Applied Chemistry, Faculty of Applied Sciences, Ibn Zohr University, Ait Melloul, Morocco.

<sup>3</sup>Center For Education & Training Profession Souss Massa, Morocco.

<sup>4</sup>Institute of Materials Science of Mulhouse (IS2M), Haute Alsace University, Mulhouse 68100, France.

<sup>5</sup>Strasbourg University, Strasbourg 67081, France

Email: [amane.jada@uha.fr](mailto:amane.jada@uha.fr)

Nowadays, synthetic dyes are considered among the most hazardous organic pollutants, owing to their complex structures, their stability in aqueous medium, and their highly toxicity. In addition, the environmental pollution due to these organic substances is growing continuously leading to various negative impacts. In the present work, nanocomposite BiOCl@Kaolinite, made of kaolinite supported Bismuth Oxy Chloride "BiOCl" photocatalyst, was designed for Rhodamine B dye photodegradation in water under sun light irradiation. The BiOCl@Kaolinite nanocomposite was found to have high photocatalytic activity for the removal of Rhodamine B dye (RhB) from water, with a degradation efficiency reaching 100% within 35 minutes, indicating that photocatalyst has good potential for industrial applications, mainly in the environmental and energy sectors. Further, the degradation efficiency of RhB by using BiOCl@Kaolinite nanocomposite was stable after 5 cycles and the scavenger's tests have shown that the superoxide radical, superoxide radicals ( $O_2^{\bullet-}$ ), is the main species responsible of the dye degradation in water. The photodegradation mechanisms involving various interactions occurring between BiOCl and kaolinite particles, and between RhB molecules and BiOCl@Kaol nanocomposites, were also elucidated by using Monte Carlo calculations.

**Keywords:** BiOCl, Kaolinite, Co-precipitation, Photocatalysis, Rhodamine B, Sunlight Irradiation.

### References

1. R. Haounati, A. El Guerdaoui, H. Ouachtak, R. El Haouti, A. Bouddouch, N. Hafid, B. Bakiz, D.M.F. Santos, M. Labd Taha, A. Jada, A. Ait Addi, **Design of direct Z-scheme superb magnetic nanocomposite photocatalyst  $Fe_3O_4/Ag_3PO_4@Sep$  for hazardous dye degradation**, Separation and Purification Technology, 2021, 277, 119399.
2. R. Haounati, H. Ouachtak, R. El Haouti, S. Akhouairi, F. Largo, F. Akbal, A. Benlhachemi, A. Jada, A. Ait Addi, **Elaboration and properties of a new SDS/CTAB@Montmorillonite organoclay composite as a superb adsorbent for the removal of malachite green from aqueous solutions**, Separation and Purification Technology, 2021, 255, 117335.

## **Design of Organically Modified Sepiolite and its use as Adsorbent for Hazardous Malachite Green Dye Removal from Water**

F. Largo<sup>1</sup>, R. Haounati<sup>1</sup>, H. Ouachtak<sup>2,3</sup>, N. Hafid<sup>4</sup>, A. Jada<sup>5,6,\*</sup>, A. Ait Addi<sup>1</sup>

<sup>1</sup>Physical Chemistry & Environment Team, Faculty of Sciences, Ibn Zohr University, Agadir, Morocco.

<sup>2</sup>Department of Applied Chemistry, Faculty of Applied Sciences, Ibn Zohr University, Ait Melloul, Morocco.

<sup>3</sup>Applied Chemistry & Environment Laboratory, Applied Bio-Organic Chemistry Team, Faculty of Sciences, Ibn Zohr University, Agadir, Morocco

<sup>4</sup>Center For Education & Training Profession ; Souss Massa, Morocco.

<sup>5</sup>Institute of Materials Science of Mulhouse (IS2M), Haute Alsace University, Mulhouse 68100, France.

<sup>6</sup>Strasbourg University, Strasbourg 67081, France

A novel adsorbent design method, based on organic surface modification and carbonization at 350-500°C, of sepiolite, was used to prepare carbon@sepiolite composites which were used for hazardous malachite green dye removal from water. Prior to their use as adsorbent, the structure and the morphology of the carbon@sepiolite composites were assessed by various methods, such as, Fourier Transform Infra-Red (FTIR) spectroscopy, Scanning (SEM) and Transmission (TEM) Electron Microscopy, Energy Dispersive Analysis of X-rays (EDAX), and N<sub>2</sub> adsorption/desorption isotherms (BET method). The designed adsorbents showed good adsorption properties for MG molecules, reaching a maximum dye adsorbed amount of 1198.67 mg/g at 25°C for the carbon@sepiolite composites calcinated at 500°C. Further, the kinetics and the equilibrium adsorption isotherms of the MG molecules from water onto the sepiolite-based composites, were well fitted by, respectively, the pseudo-second-order model ( $R^2 = 0.98$ ) and the Langmuir isotherm ( $R^2 = 0.94$ ) models, indicating that the MG molecules were homogenously adsorbed and formed a monolayer on the organically modified sepiolite surface. Moreover, the values of the thermodynamic parameters, such as  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  related to the adsorption process, indicated that the adsorption reaction was spontaneous, feasible and endothermic. In the overall, the present work offers facile ways for the design of organically modified sepiolite which can be used at large scale as adsorbents for waste recycling.

**Keywords:** Clay; Malachite Green dye; Sepiolite; Adsorption; Waste.

### References

1. F. Largo, R. Haounati, S. Akhouairi, H. Ouachtak, R. El Haouti, A. El Guerdaoui, N. Hafid, D.M.F. Santos, F. Akbal, A. Kuleyin, A. Jada, A. Ait Addi, **Adsorptive removal of both cationic and anionic dyes by using sepiolite clay mineral as adsorbent: Experimental and molecular dynamic simulation studies**, Journal of Molecular Liquids, 2020, 318, 114247.
2. R. Haounati, H. Ouachtak, R. El Haouti, S. Akhouairi, F. Largo, F. Akbal, A. Benlhachemi, A. Jada, A. Ait Addi, **Elaboration and properties of a new SDS/CTAB@Montmorillonite organoclay composite as a superb adsorbent for the removal of malachite green from aqueous solutions**, Separation and Purification Technology, 2021, 255, 117335.



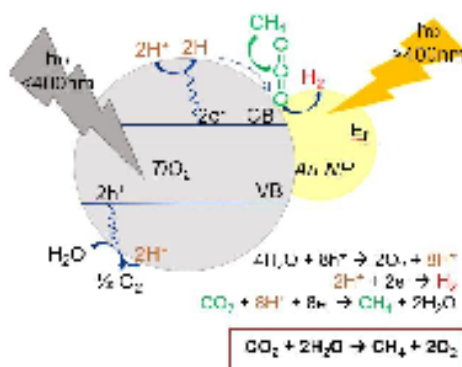
**BIMETALLIC PHOTOCATALYSTS FOR ARTIFICIAL PHOTOSYNTHESIS**

C. Jonis, L. Hammoud, C. Strebler, V. Keller, V. Caps\*

ICPEES (CNRS UMR 7515, Université de Strasbourg), 25 Rue Becquerel, 67087 Strasbourg, France

Email: caps@unistra.fr

Carbon dioxide, one of the main greenhouse gas and a key element in global warming, is rejected by the use of most major fuels. One solution to its over-production is to recycle CO<sub>2</sub> into a useful chemical such as methane, then used as a fuel. Recycling goes through the photo-reduction of CO<sub>2</sub> in the gas phase with water, also known as artificial photosynthesis. The properties of the reagent (highest oxidation state and strong bond, the dissociation energy is around 750 kJ/mol<sup>-1</sup>) and the competition with the Hydrogen Evolution Reaction make it necessary to use a catalyst<sup>1</sup>. Metallic nanoparticles are known for their particular interaction with light called Localized Surface Plasmon Resonance (LSPR), which allows them to be great photocatalysts<sup>2</sup>. We have recently shown that alloy nanoparticles of gold and platinum dispersed over titanium dioxide were active and selective for the photo-reduction of CO<sub>2</sub> with water<sup>3</sup>. We here show that the methane production rate can be optimized by designing smaller Au-Pt nanoparticles. By studying the effect of the composition of the nanoalloy on the photocatalytic performances, we also show that a synergy between gold and platinum can be found in Pt-rich compositions, which yield higher activity and selectivity than the monometallic nanoparticles.

Scheme of the CO<sub>2</sub> photo-reduction process**Acknowledgements**

This project has received financial support from the CNRS through the MITI interdisciplinary programs (SelCO2PlasmonRed project). This work of the Interdisciplinary Thematic Institute HiFunMat, as part of the ITI 2021–2028 program of the University of Strasbourg, CNRS and INSERM UMR 1121, was supported by IdEx Unistra (ANR-10-IDEX-0002) and SFRI (STRATUS project, ANR-20-SFRI-0012) under the framework of the French Investments for the Future Program. Dr T. Dintzer (UMR CNRS 7515) is thanked for acquiring SEM images and Dr V. Papaefthimiou (UMR CNRS 7515) is thanked for acquiring XPS data.

**References**

1. X. Chang, T. Wang, J. Gong, CO<sub>2</sub> photo-reduction: insights into CO<sub>2</sub> activation and reaction on surfaces of photocatalysts, *Energy Environ. Sci.*, 2016, 9, 2177-2196.
2. M. Wang, M. Ye, J. Iocozzia, C. Lin, Z. Lin, Plasmon-mediated solar energy conversion via photocatalysis in noble metal/semiconductor composites. *Adv. Sci.*, 2016, 3, 1600024.
3. L. Hammoud, C. Strebler, J. Toufaily, T. Hamieh, V. Keller, V. Caps, The role of the gold-platinum interface in AuPt/TiO<sub>2</sub>-catalyzed plasmon-induced reduction of CO<sub>2</sub> with water, *Faraday Discuss.*, 2023, 242, 443-463.

## VERY HIGH-ASPECT-RATIO POLYMERIC MICROPILLARS MADE BY TWO-PHOTON-POLYMERIZATION

K. Kamranikia<sup>1,2</sup>, N. Kube<sup>1,2</sup>, S. Dominici<sup>1,2</sup>, M. Keller<sup>1,2</sup>, K. Mougin<sup>1,2</sup>, A. Spangenberg<sup>1,2</sup> \*

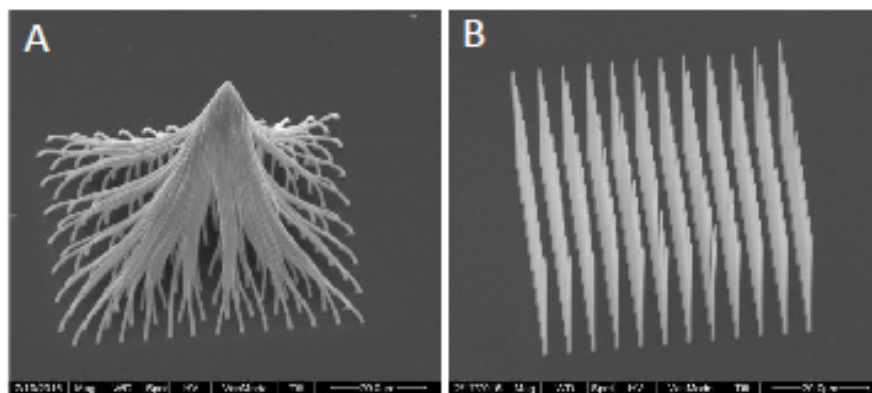
<sup>1</sup>Institut de Science des Matériaux de Mulhouse (IS2M), CNRS – UMR 7361, Université de Haute-Alsace, Mulhouse, France

<sup>2</sup>Université de Strasbourg, France

Email : [arnaud.spangenberg.uha.fr](mailto:arnaud.spangenberg.uha.fr)

Micropillars, polymeric microstructures with a high-aspect-ratio (HAR), are of interest to a wide range of applications, including drug delivery, dry adhesives that simulate the fibrillar structure of gecko feet, immunoassay chips for sensing cell response, and micro-electro-mechanical systems (MEMS) actuators [1,2]. The most common fabrication method for HAR (ratio of height to lateral feature size) microstructures is molding [3]. This method remains challenging due to its difficulty in demolding the final structure. On the other hand, solvent evaporation maximizes the adhesion force of HAR micropillars during the development step due to capillary force. It is therefore difficult to fabricate very HAR polymeric micropillars without collapsing [4] (Figure 1-A).

In this work, we present very HAR micropillars by using two-photon polymerization (TPP) which is an established technique for creating complex 3D microstructures. Different parameters have been optimized to overcome the capillary force (Figure 1-B). These include surface modification, fabrication parameters such as using different laser power, exposure time, distance between the pillars, length of the pillars. As a result of adapting these techniques, we were able to fabricate micropillars with very HAR of 80.



**Figure 1:** SEM images of micropillars obtained by TPP. (A) Capillary force self-assembled HAR micropillars. (B) Very HAR micropillars obtained by using a supercritical CO<sub>2</sub> dryer.

### References

1. P. Kim, W E. Adomo-Martinez, M. Khan, J. Aizenberg, Enriching libraries of high-aspect-ratio micro- or nanostructures by rapid, low-cost, benchtop nanofabrication, *Nature protocols*, **2012**, 7, 311-327.
2. S G. Higgins, M. Bece, A. Belessiotis-Richards, H. Seong, J E. Sero, M M. Steven, High-Aspect-Ratio Nanostructured Surfaces as Biological Metamaterials, *Advance materials*, **2020**, 1903862, 1-44.
3. Y. Zhang, C W. Lo, J A. Taylor, S. Yang, Replica Molding of High-Aspect-Ratio Polymeric Nanopillar Arrays with High Fidelity, *Langmuir*, **2006**, 22, 8595-8601.
4. A D. Campo, E. Arzt, *Fabrication Approaches for Generating Complex Micro- and Nanopatterns on Polymeric Surfaces*, American Chemical Society, **2008**, 108, 911- 945.

## **Integration of nanostructured sensor for the electrochemical detection of biomarkers: towards search for life in space**

**Marc KELLER<sup>1</sup>, Karine MOUGIN<sup>1</sup>, Jérôme LAUNAY<sup>2</sup>, Delphine FAYE<sup>3</sup>, Vincent VIVIER<sup>4</sup>,  
Amaud BUCH<sup>5</sup>, Pierre BAUER<sup>6</sup>, Pierre PONTIAUX<sup>7</sup>**

<sup>1</sup> Institut de Sciences des Matériaux de Mulhouse, F-68057 Mulhouse Cedex, France,

<sup>2</sup> Laboratoire d'Analyse et d'Architecture des Systèmes, F-31400 Toulouse, France

<sup>3</sup> Centre National d'Etudes Spatiales, F-31400 Toulouse, France

<sup>4</sup> Laboratoire de Réactivité de Surface, F-75252 Paris Cedex 05, France

<sup>5</sup> CentraleSupélec, F-91192 Gif-sur-Yvette Cedex, France

<sup>6</sup> Institut NEEL, F-38042 Grenoble Cedex 9, France

<sup>7</sup> Laboratoire Génie des Procédés et Matériaux, CentraleSupélec, F-91190 Gif-Sur-Yvette, France

Email: [marc.keller@uha.fr](mailto:marc.keller@uha.fr)

Nowadays, metallic nanoparticles with various shape have been largely used for the fabrication of new sensors due to their fascinating properties. One particular shape has attracted much attention because of its large surface-to-volume ratio and high sensitivity: the dendritic nanostructures. These anisotropic nanoparticles are often made of noble metals, such as gold that owns a good biocompatibility and high plasmonic effect<sup>1</sup>.

The present work describes a controlled growth pattern-directed organisation of gold flower-like crystals deposited onto gold quartz QCM resonator to achieve large-scale nanostructured surfaces of detection. This technique consists first, in the deposition of a nanoporous polymer template, on which gold crystals are electrochemically grown. Then, the adsorption of amino acids on those structures can be realized by different ways. The detection of the adsorbed molecules onto these nanostructured surfaces, has been carried out optically and electrochemically.

The last step of this work focuses on the regeneration of the substrate that allows the recovery of the sensor to its initial state to continue another cycle of detection of molecules. This device is a first step before its integration in a lab-on-chip system.

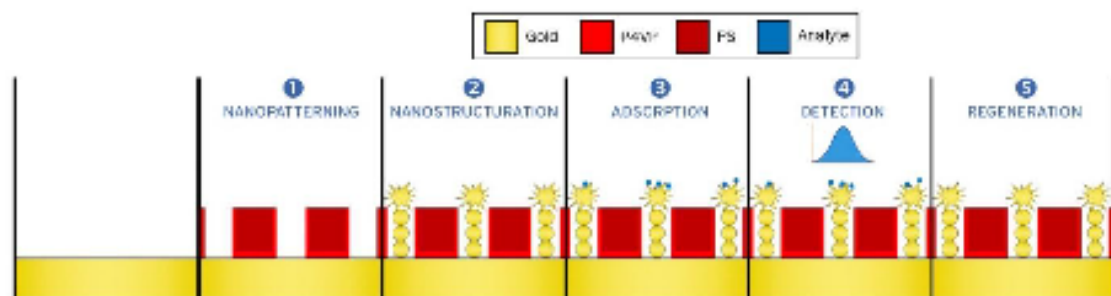


Figure 1: The different steps of the sensor development based on gold nanoparticles and gold QCM resonator.

### Acknowledgements

CNES and CNRS

### References

1. E. Le Ru and P. Etchegoin, Elsevier, 2009.



## Improvement of heterogeneous plasmonic photocatalysis performance by coupling gold nanoparticles by TiO<sub>2</sub>

A. Khitous <sup>1,2</sup>, L. Noel <sup>1,2</sup>, C. Molinaro <sup>1,2</sup>, L. Vidal <sup>1,2</sup>, O. Soppera <sup>1,2</sup>

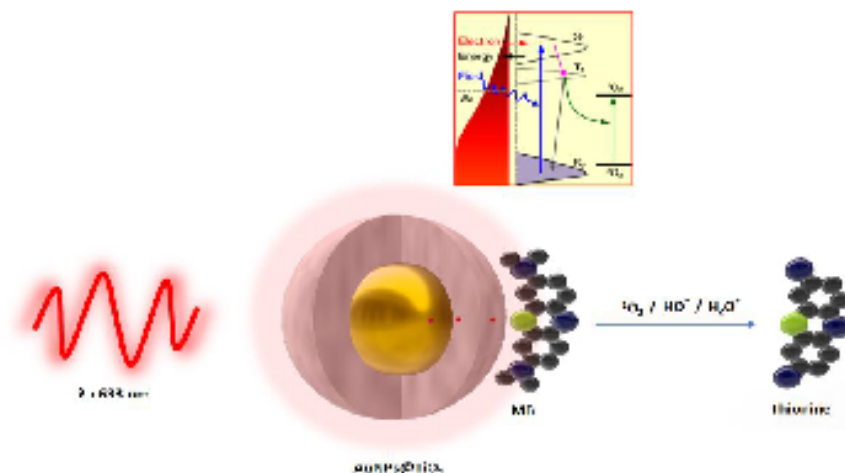
<sup>1</sup> Université de Haute-Alsace, Mulhouse, France

<sup>2</sup> Université de Strasbourg, Strasbourg, France

Email: olivier.soppera@uha.fr

Thanks to the localized surface plasmon resonance (LSPR) of metal nanoparticles (MNPs), plasmonic photocatalysis and photovoltaics have become emerging disciplines in the field of clean energy [01]. The use of MNPs can induce the light-to-energy conversion due to the three admitted photoinduced effects of LSPR: near-field light enhancement, hot electron transfer and thermoplasmonic effect. There is much debate about the effect responsible for LSPR photocatalysis [02], previous work has highlighted the efficiency of hot electrons in the generation of H<sub>2</sub> and other photocatalytic reactions, however the hot electrons of LSPR have a very short lifetime (1-100 fs) which limits their involvement in catalysis which requires longer times (ms-s) [03]. In this perspective, gold nanoparticles (AuNPs) were functionalized with TiO<sub>2</sub> nanolayers by sol-gel, controlled by spin-coating. This approach is easy to implement.

N-demethylation (ND) reaction of methylene blue (MB) was used as a reference reaction to investigate the efficiency of the photocatalytic process according to parameters such as the thickness and nature of the inorganic layer on the MNPs. The reaction was followed using surface enhanced Raman spectrometry (SERS). Comparing the efficiency of the photoreaction with these parameters, we can propose insights into the mechanism responsible for MB ND (near-field light exaltation and/or hot electron transfer and/or thermoplasmonic effect).



**Figure:** N-demethylation of methylene bleu (MB) on the optical near-field of AuNPs@TiO<sub>2</sub>  
References

1. Wei, Yunjia, et al. "Investigation of the Plasmon-Activated C-C Coupling Reactions by Liquid-State SERS Measurement." *ACS Applied Materials & Interfaces* 14.48 (2022): 54320-54327.
2. Mukherjee, Shaunak, et al. "Hot electrons do the impossible: plasmon-induced dissociation of H<sub>2</sub> on Au." *Nano letters* 13.1 (2013): 240-247.

## CAPILLARY FORCE DRIVEN SELF-ASSEMBLY OF 3D PRINTED HIERARCHICAL STRUCTURES PREPARED BY TWO-PHOTON POLYMERIZATION

K. Kamranikia<sup>1,2</sup>, N. Kube<sup>1,2</sup>, S. Dominici<sup>1,2</sup>, M. Keller<sup>1,2</sup>, K. Mougín<sup>1,2</sup>, A. Spangenberg<sup>1,2,\*</sup>

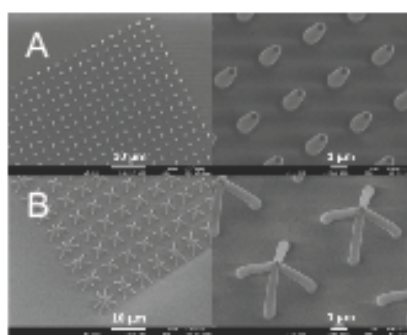
<sup>1</sup>*Institut de Science des Matériaux de Mulhouse (IS2M), CNRS – UMR 7361, Université de Haute-Alsace, Mulhouse, France*

<sup>2</sup>*Université de Strasbourg, Strasbourg, France*

*Email: arnaud.spangenberg@uha.fr*

Hierarchical structures in nature have inspired numerous applications in chemistry, biology, optics, and mechanics, as well as in scientific research and technical implementations [1]. Among many microfabrication techniques, two-photon polymerization (TPP) is a well-established method for creating complex 3D micro-objects with stimuli-responsive and reconfigurable surface properties [2,3]. TPP-based laser printing capillary-assisted self-assembly (LPCS) strategy appears as a convenient technique for fabricating periodic structures at the microscale [4]. A highly controllable hierarchical microstructure can be assembled by utilizing capillary force as shown in Figure 1.

This work aims to fabricate periodic hierarchical architectures through two-photon laser polymerization and controlled capillary force assembly by solvent evaporation. Various assemblies of micropillars with different configurations can be achieved by adjusting the height, arrangement, laser power and printing speed of micropillars to guide capillary force. This mechanical tunable self-assembly of microstructures can be used for surface modification applications, micro-optics, and microfluidics.



**Figure 1:** Controlled capillary force assembly of micropillars. (A) Top and tilted SEM view of 3D-printed micropillars obtained by using a supercritical CO<sub>2</sub> dryer. (B) Top and tilted SEM view of capillary-assisted self-assembly of micropillars.

### References

1. L. J. Gibson, The hierarchical structure and mechanics of plant materials, *J. R. Soc. Interface*, **2012**, 9 (76), 2749-2766.
2. M. Belquart, X. Wu, J. Morris, K. Mougín, T. Petithory, L. Pieuchot, Y. Guillaneuf, D. Gignes, J. Clément, A. Spangenberg, Customizable and Reconfigurable Surface Properties of Printed Micro-objects by 3D Direct Laser Writing via Nitroxide Mediated Photopolymerization, *Adv. Funct. Mater.*, **2023**, 2211971.
3. Q. Ji, J. Moughames, X. Chen, G. Fang, J. J. Huaroto, V. Laude, J. Martínez, G. Ulliac, C. Clévy, P. Lutz, K. Rabenoroosa, V. Guelpe, A. Spangenberg, J. Liang, A. Mosset, M. Kadic, 4D Thermomechanical metamaterials for soft microrobotics, *Commun. Mater.*, **2021**, 2, 93-98.
4. Y. Hu, Z. Lao, B. P. Cumming, D. Wu, J. Li, H. Liang, J. Chu, W. Huang, M. Gu, Laser printing hierarchical structures with the aid of controlled capillary-driven self-assembly, *PNAS*, **2015**, 112 (22), 6876-6881.

## **Porous materials with functionalized surface for the adsorption of indoor formaldehyde and acetaldehyde**

**C. Kustner<sup>1,2</sup>, T. Tran-thi<sup>1,2</sup>, A. Grandjean<sup>1,3</sup>, R. Migneret<sup>1</sup>, R. Severac<sup>2</sup>, A. Becker<sup>1</sup>, A. Hebraud<sup>1</sup>, G. Schlatter<sup>1</sup>, S. Le Calvé<sup>1</sup>**

<sup>1</sup> Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé, Université de Strasbourg, CNRS, ICPEES UMR 7515, F-67087 Strasbourg, France

<sup>2</sup> ANGUS Chemical company, 6 avenue du Marais 95100 Argenteuil, Paris, France

<sup>3</sup> Airmotec/Chromatotec, 15 rue D'Artiguelongue 33240 Saint-Antoine, Bordeaux, France

Email: [coralie.kustner@etu.unistra.fr](mailto:coralie.kustner@etu.unistra.fr)

Formaldehyde and acetaldehyde are two Volatile Organic Compounds (VOCs) ubiquitously found in indoor environment<sup>1,2</sup>. Their indoor presence is raising more and more concerns due to their harmful impact on the human health. Indeed, the International Agency for Research on Cancer (IRAC) classifies formaldehyde as a carcinogenic to humans (group 1), and acetaldehyde as a possible carcinogenic to humans (group 2B). Therefore, many efforts are being made to remove these two aldehydes from the indoor air. Adsorption is one of the most promising methods to decrease indoor concentration of VOCs because of its efficiency and low-cost. Nonetheless, due to the high volatility, high polarity, and small size of formaldehyde and acetaldehyde, their adsorption requires very specific adsorbents with the appropriate physical properties (large specific surface area and pore volume) and surface chemistry (polar surface with functional groups)<sup>3</sup>. For this reason, the studies are directed to highly microporous materials like activated carbons, zeolites, or metal organic framework, with surface modification. In this context, our research is directed in the development of formaldehyde and acetaldehyde adsorbents made by impregnation of activated carbons or by electrospinning of polyurethane-based membranes. The materials developed are functionalized with a crystalline organic molecule which is expected to greatly increase the adsorption capacity. For industrial protection reasons, this molecule will not be specified. The developed materials are characterized by a large variety of methods (SEM, XRD, TGA, and BET). In addition, the adsorption capacities of the materials are determined by dynamic adsorption experiments under controlled temperature, relative humidity, and gaseous aldehyde concentration. The first results demonstrate that under its crystalline form the organic molecule shows no significant adsorption. However, by impregnation it is possible to cover the surface of activated carbon with amorphous organic molecule which improve greatly the adsorption capacity. For acetaldehyde, the adsorption capacity of the impregnated activated carbons is up to 15 times higher than those of the non-impregnated. Concerning the polymeric membrane, the direct electrospinning of a blend solution containing the organic molecule, the template polymer and the polyurethane induce a partial recrystallization of the organic molecule. Even with the partial recrystallization, the functionalized membrane has an adsorption capacity of 0.35 mg g<sup>-1</sup> while the non-functionalized one show no adsorption. In the future, the polyurethane-based membrane will be functionalized by impregnation to prevent recrystallization of the organic molecule during the process.

### **Acknowledgements**

I would like to thank the staffs the university of Strasbourg, CNRS, ANGUS, and ICPEES.

### **References**

1. Marchand, C.; Bulliot, B.; Le Calvé, S.; Mirabel, Ph. Aldehyde Measurements in Indoor Environments in Strasbourg (France). *Atmospheric Environment* **2006**, *40* (7), 1336–1345. <https://doi.org/10.1016/j.atmosenv.2005.10.027>.
2. Lovreglio, P.; Carus, A.; Iavicoli, S.; Drago, I.; Persechino, B.; Soleo, L. Indoor Formaldehyde and Acetaldehyde Levels in the Province of Bari, South Italy, and Estimated Health Risk. *J. Environ. Monit.* **2009**, *11* (5), 955. <https://doi.org/10.1039/b819843h>.
3. Zhu, L.; Shen, D.; Luo, K. H. A Critical Review on VOCs Adsorption by Different Porous Materials: Species, Mechanisms and Modification Methods. *Journal of Hazardous Materials* **2020**, *389*, 122102. <https://doi.org/10.1016/j.jhazmat.2020.122102>.



## **Photo-induced formation of biobased-vitrimer**

**Cuong-Minh-Quoc LE<sup>1</sup>, Rayane TOUTAOU<sup>1</sup>, Gautier SCHRODJ<sup>1</sup>, Hatice MUTLU<sup>1,\*</sup>**

<sup>1</sup> Institut de Science des Matériaux de Mulhouse (UMR 7361 - CNRS / UHA)  
68057 Mulhouse, France

Email: [hatice.mutlu@uha.fr](mailto:hatice.mutlu@uha.fr)

Vitrimer represents a very promising class of materials with self-healing, recyclable, reprocessable properties. Accordingly, they have been intensively investigated in the past decade. In this regard, the incorporation of dynamic covalent bonds in the polymer networks plays a critical role in manipulating the molecular transport and viscoelasticity of the materials. However, the path toward more sustainable polymer materials is not only focusing on recyclability but also finding alternatives to replace petroleum-derived monomer feedstock by renewable resources. Therefore, it is highly desirable nowadays to develop cost-effective reaction conditions like photoactivation that allows to integrate both the dynamic covalent bonds and bio-based monomers into polymer networks of vitrimers. In order to realize this aim, we herein have developed photopolymerization processes which applied to broad monomer substrates, metal-free and photocatalyst-free, and ambient conditions.

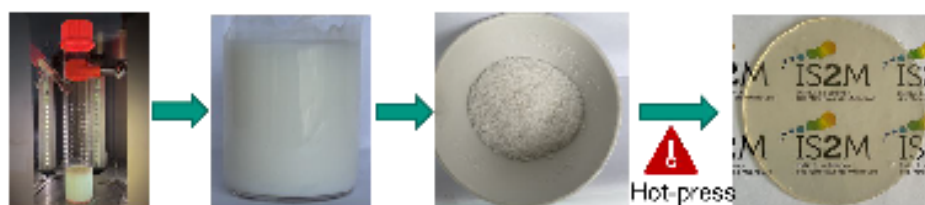


Figure 1 : Photochemical formation of biobased monomer, and the product after hot-pressing at 100 °C for 20 min.

### References

1. Marvel, C. S.; Shen, E. H. H.; Chambers, R. R. Polymercaptals and polymercaptoles. *J. Am. Chem. Soc.* **1950**, *72*, 2106
2. Zeng, H.; Tang, Z.; Duan, Y.; Wu, S.; Guo, B. Recyclable crosslinked elastomer based on dynamic dithioacetals. *Polymer* **2021**, *229*, 12407.
3. Orrillo, A. G.; Escalante, A. M.; Furlan, R. L. Dithioacetal Exchange: A New Reversible Reaction for Dynamic Combinatorial Chemistry. *Chemistry* **2016**, *22*, 6746.
4. Ge, M.; Miao, J.-T.; Zhang, K.; Wu, Y.; Zheng, L.; Wu, L. Building biobased, degradable, flexible polymer networks from vanillin via thiol-ene "click" photopolymerization. *Polymer Chemistry* **2021**, *12*, 564.

### Acknowledgements

This project was funded by IS2M/CNRS

## Virus-Like Particle as a nano-signaling platform to control cell behavior

Hasna Maayouf<sup>1</sup>, Thomas Dos-Santos<sup>2</sup>, Isabelle Brigaud<sup>3</sup>, Tatiana Petithory<sup>4</sup>, Karine Anselme<sup>5</sup>, Carole Arnold<sup>6</sup> and Laurent Pieuchot<sup>7</sup>

Université de Haute-Alsace, IS2M-CNRS 7361, F-68100 Mulhouse, France

[hasna.maayouf@uha.fr](mailto:hasna.maayouf@uha.fr)<sup>1</sup>, [thomas.dos-santos@uha.fr](mailto:thomas.dos-santos@uha.fr)<sup>2</sup>, [isabelle.brigaud@uha.fr](mailto:isabelle.brigaud@uha.fr)<sup>3</sup>,  
[tatiana.petithory@uha.fr](mailto:tatiana.petithory@uha.fr)<sup>4</sup>, [karine.anselme@uha.fr](mailto:karine.anselme@uha.fr)<sup>5</sup>, [carole.arnold@uha.fr](mailto:carole.arnold@uha.fr)<sup>6</sup>,  
[Laurent.pieuchot@uha.fr](mailto:Laurent.pieuchot@uha.fr)<sup>7</sup>

Virus-Like Particles (VLPs) are self-assembled protein-based nanoparticles that provide versatile delivery platforms for a variety of biomedical applications thanks to their biocompatibility and their ability to encapsulate therapeutic molecules<sup>1,2</sup>. However, they have not yet been employed in the field of biomaterials. Here we show that VLPs can be used to develop cell-signaling nanoscaffolds for the control cell behavior. Using cloning techniques, we fused short bioactive peptides to the C-terminus of the AP205 coat protein. We produced recombinant particles expressing adhesion (RGD, YIGSR) and osteogenic (BMP2) peptides at their surface and purified them by affinity and size exclusion chromatography techniques. We show that VLP-RGD particles stimulate adhesion and spreading of C2C12 myoblast cells with the same efficacy as native fibronectin whereas VLP-BMP2 particles do not. With similar methods, we were able to produce heteromeric particles co-expressing RGD and BMP2 peptides. We showed that the presence of RGDs on our multifunctional particles can promote cell adhesion similarly to VLP RGD-BMP2. These results demonstrate that it is possible to combine bioactive peptides on the AP205 particle surface in order to create multifunctional signaling nanoscaffolds that control different facets of cell biology.

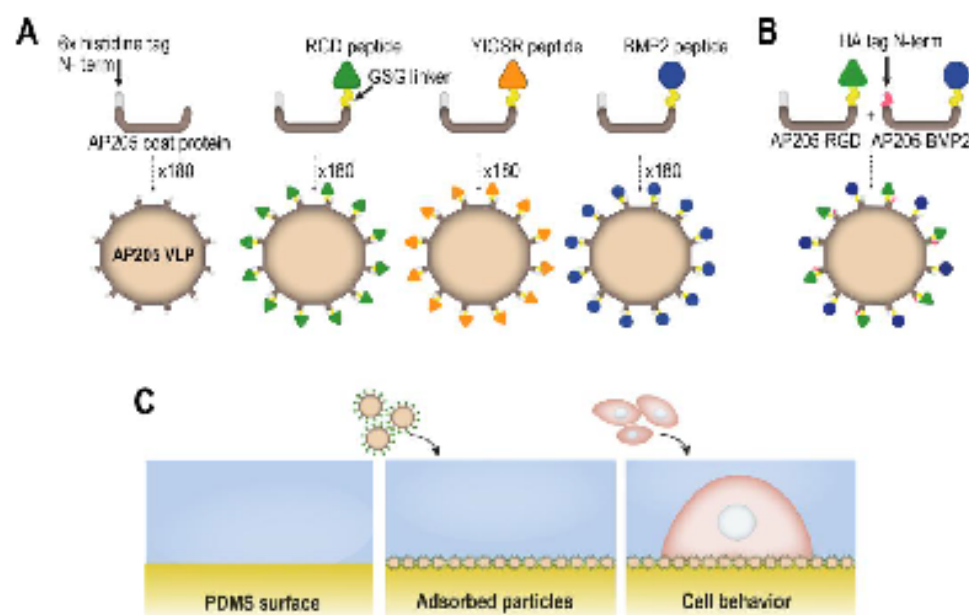


Fig. 1: Virus-Like Particle as a signaling platform to concentrate nanoscale ligands for the control of cell behavior

### References

1. Shirbaghaee, Z. and Bolhassani, A. (2016), *Biopolymers*, 105(3), pp. 113–132.
2. Pushko, P., Pumpens, P. and Grens, E. (2013), *Intervirology*, 56(3), pp. 141–165.

## Polymerization induced through the heat generation of gold nanoparticles under laser illumination

C. Molinaro<sup>1,2,\*</sup>, A. Khitous<sup>1,2</sup>, O. Soppera<sup>1,2</sup>

<sup>1</sup>Université de Haute Alsace, CNRS, IS2M 7361, Mulhouse, France

<sup>2</sup>Université de Strasbourg, Strasbourg, France

Email: [celine.molinaro@uha.fr](mailto:celine.molinaro@uha.fr)

Localized surface plasmon-induced polymerization of free-radical acrylate monomers is an efficient, smart, and versatile method for preparing metal/polymer hybrid nanoparticles (NPs) with accurate control of the thickness and spatial distribution of the polymer on the NP surface. Despite a growing number of practical demonstrations, the mechanism leading to polymerization of the acrylate monomer by localized surface plasmon resonance is still controversial. Indeed, through decay processes, the plasmon emitted light, hot charge carriers and heat, in less than tens of ns (Figure 1). If these processes are well-known, the main difficulty is to discriminate between them.

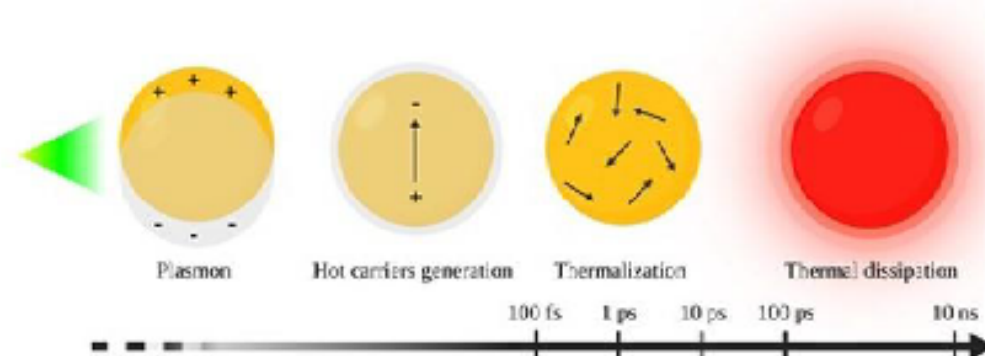


Figure 1: Plasmonic heat generation time-scale<sup>1</sup>.

Previous experiments performed in the laboratory, highlighted the photochemical pathway as the main mechanism under mild irradiation<sup>2</sup>. The thermoplasmonic pathway was already used to cure InZnO thin films<sup>3</sup>.

Here, we investigated thermoplasmonic to graft thermopolymer onto gold NPs. Different parameters were considered to address specifically thermopolymerization through the plasmonic excitation of NPs such as the NPs resonances, laser power and regime. Overall, to generate thermopolymerization through thermoplasmonic effect, high irradiation condition is required. Moreover, we observed thermopolymerization in ns-pulsed and continuous laser regime with different grafting features.

### References

1. C. Molinaro, A. Khitous, L. Noel, O.Soppera, Nanochemistry by Thermoplasmonic Effects, *Progress in Nanophotonics* 7, 2022, 71-91.
2. F. Kameche, W. Heni, S. Telitel, L. Vidal, S. Marguet, L. Douillard, C. Fiorini-Debuisschert, R. Bachelot, O. Soppera, Probing Plasmon-Induced Chemical Mechanisms by Free-Radical Nanophotopolymerization, *The Journal of Physical Chemistry C*, 2021, 128, 8719-8731.
3. C-F. Lin, A. Khitous, H-W. Zan, O. Soppera, Exploiting Thermoplasmonic Effects for Laser-Assisted Preparation of Au Nanoparticles/InZn Thin Film with Visible Range Photodetection Properties, *Advanced Optical Materials*, 2021, 9 (21), 2100045



## SURFACE COLOR ON DEMAND: Chameleon Effect

K. Mougin<sup>1</sup>, H. Hoelscher<sup>2</sup>, A. Spangenberg<sup>1</sup>

<sup>1</sup> Institut de Science des Matériaux de Mulhouse, UMR 7361 CNRS-Université de Haute Alsace, 15 Rue Jean Starcky, 68057 Mulhouse, France.

<sup>2</sup> Institut für Mikrostrukturtechnik (IMT), Karlsruher Institut für Technologie (KIT), Hermann-von-Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

Email: karine.mougin@uha.fr

Colors affect our everyday life as they provide critical functions in both recognition and communication. Nearly all artifacts of our everyday are manufactured from polymers colored by dyes. This approach allows an endless variety of colors and the colors of housewares, cloth, cars, and interior decoration offered by industry. And yet, each individual item is produced in one color, which cannot be changed after its production. This is a serious problem for manufacturers, as some goods cannot be sold anymore when their color is outdated. This issue can also cause tremendous costs and waste if products cannot be recycled and have to be deposited. So, it is of high interest to add color-changing surfaces to the portfolio of manufacturing. In nature, changing colors are frequently observed in the animal's world for camouflage by misleading natural enemies or for courting by standing out from the environment. The most prominent examples are chameleons that are able to exhibit complex and rapid color changes during social interactions due to dispersion/aggregation of pigment within dermal chromatophores. A direct copy nature is not typically practical for everyday items but is the inspiration of our approach to create color change in polymeric material.

The idea was to create a novel hybrid material able to color change of surfaces at will. The key element of this novel technology is based on the combination of two phenomena observed in the nature and transferable to material science: plasmonic and structural colors. The developed functional nanomaterial is composed of colloidal metallic nanoparticles (NPs) that are properly synthesized and assembled into latex to ensure a variety of plasmonic colors under mechanical stresses. By changing height and width of a latex film and/or the size of nanostructures through the shape memory effect, the distance between the nanoparticles are modified inducing a color change in the composite material [1].

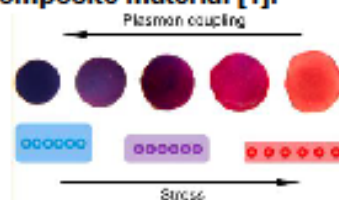


Figure 1: Basic principle of a colorimetric stress memory sensor developed by Han et al. [1]. Gold nanoparticle chains embedded in a polymer matrix. Applying stress to the film increases the distance of the gold nanoparticles resulting in a color change of the sample. (Reproduced from [1])

To enhance the color palette of this stimuli-responsive nanocomposite, its surface will be later structured with diverse diffractive nano&micropatterns.

*As result, combining the color emission of the nanoparticles with the structural colors will allow enhancing specific wavelengths and the palette of reachable colors.* The specificity mechanical properties of the latex ensure the outstanding reversibility of color by properly controlling the reassembly of the nanoparticles inside and on the surface of the material.

### References

1. X. Han, Y. Liu, Y. Yin, *Nano Letters*, **2014**, *14*, 2468-2470.
2. K. Mougin, H. Hoelscher, A. Spangenberg, *JOM*, **2022**, *74*, 847-852.

## N-rich porous carbon materials using g-C<sub>3</sub>N<sub>4</sub> as a new porogen agent

A. Gashi,<sup>1,2,3</sup> P. Fioux,<sup>1</sup> C. Vaultot,<sup>1</sup> R. Marsalek,<sup>2</sup> J. Parmentier<sup>1,\*</sup>

<sup>1</sup> Institut de Science des Matériaux de Mulhouse (IS2M), Université de Strasbourg, Université de Haute-Alsace 15 rue Jean Starcky, BP 2488, 68057 Mulhouse Cedex, France

<sup>2</sup> Department of Chemistry University of Ostrava 30. Dubna 22, Ostrava, 701 03, Czech Republic  
<sup>3</sup> Universum College, Main Road Prishtine-Ferizaj km 10, 14000, Kosovo

Email: [julien.parmentier@univ-mulhouse.fr](mailto:julien.parmentier@univ-mulhouse.fr)

N-rich porous carbon (> 20 wt % N) materials are difficult to prepare without an activation process owing to their low thermal stability and trend to yield poorly porous materials. Most of the studies related to "N-rich" porous carbon materials focused in fact on low N content (e.g. <10 wt%) since carbon materials with N-heteroatoms have shown metal-free catalytic properties and particular adsorption properties.

On the opposite, the synthesis and properties of N-rich porous carbon are barely explored although of their potentially interesting properties. Here, we report the first synthesis of N-rich porous carbon (30 > wt % N > 20) with BET surface area ranging between 280 to 600 m<sup>2</sup>/g. For that purpose, we have prepared nanocomposites composed of g-C<sub>3</sub>N<sub>4</sub> and C-rich nanodomains.<sup>1</sup> Graphitic carbonitride (g-C<sub>3</sub>N<sub>4</sub>) is a lamellar compound with semiconductor properties largely studied for photocatalysis applications. Owing to its low thermal stability compared to carbon materials and its reactivity with O<sub>2</sub> different than C domains, it was used as a porogen agent during the controlled oxidation of the nanocomposites. It led to N-rich carbon with micro- and mesoporosity without the need for activation agents. These materials were further characterized by physicochemical techniques (N<sub>2</sub> and CO<sub>2</sub> adsorption, XPS, TEM, and FTIR).

### References

1. Gashi, A., Parmentier, J., Fioux, P., Marsalek, R... Tuning the C/N Ratio of C-Rich Graphitic Carbon Nitride (g-C<sub>3</sub>N<sub>4</sub>) Materials by the Melamine/Carboxylic Acid Adduct Route. *Chemistry – A European Journal* n/a, 2022, e202103605. <https://doi.org/10.1002/chem.202103605>

**Lead-free halide perovskites encapsulated in mesoporous silica**

A. Ryzhikov<sup>1,2\*</sup>, D. Aldakov<sup>3</sup>, P. Reiss<sup>3</sup>, B. Lebeau<sup>1,2</sup>, M. Bonne<sup>1,2</sup>, J.-L. Paillaud<sup>1,2</sup>, T. Ors<sup>1,2</sup>

<sup>1</sup> *Université de Haute-Alsace, CNRS, Institut de Science des Matériaux de Mulhouse (IS2M), UMR 7361, Axe Matériaux à Porosité Contrôlée (MPC), F-68100, Mulhouse*

<sup>2</sup> *Université de Strasbourg, F-67000 Strasbourg, France*

<sup>3</sup> *Université Grenoble Alpes, CEA, CNRS, IRIG-SyMMES UMR-5819, 38000 Grenoble, France*

*Email: andrey.ryzhikov@uha.fr*

Recently, metal halide perovskites based on lead with general formula  $ABX_3$  ( $A = Cs^+$ , methylammonium;  $B = Pb^{2+}$ ;  $X = I, Br$  or  $Cl$ ) have spectacularly emerged as a promising class of materials for optoelectronics due to their high efficiency, low cost and easy fabrication. Owing to strong absorption coefficients, appropriate bandgaps, spontaneous dissociation of excitons, high defect immunity, and strong photoluminescence (PL), very efficient and record-breaking optoelectronic devices were fabricated. By the reduction of the size and dimensionality of the perovskite crystals and the control of surface chemistry, their properties can be tuned and enhanced. Colloidal nanocrystals (NCs) are generally synthesized in solution using surface ligands for stabilization. Meanwhile, they complicate direct integration of the NCs into devices due to hindered charge transfer: additional steps of purification and surface engineering are required affecting their stability, currently being one of the biggest obstacles for their deployment. One of the promising ways to increase the stability of perovskite nanostructures is to use nanoporous matrices with ordered porosity as hosts for their encapsulation. They can allow for a fine control of NCs size and shape, protecting their surface and avoiding the need to use surface ligands. The first examples of such encapsulation of the perovskites began to appear only very recently.

In spite of outstanding properties, lead-based perovskites have a considerable drawback: toxicity. The most promising alternative, less toxic materials are tin- and bismuth-based perovskites. In this work, we present the synthesis of new nanocomposites of lead-free perovskites encapsulated in mesoporous silica matrices.  $MA_3Bi_2Br_3$  NCs, where MA = methylammonium, with a size of 3-7 nm have been obtained inside the pores of SBA-15 mesoporous silica (4-8 nm pore diameter) by simultaneous impregnation of methylammonium and bismuth bromide solutions. UV-Vis and PL spectra of the NCs have been measured. The decrease of pore size leads to the blueshift due to quantum confinement.

**Acknowledgements**

The authors thank CNRS MITI for financial support to Empereur project.



## Synthesis of 2-aminoindenone derivatives through an ynamide carbosilylation / Houben-Hoesch cyclization 2-step sequence

Pierre Hansjacob,<sup>[a]</sup> Célia Schwoerer,<sup>[a]</sup> Frédéric R. Leroux<sup>[a]</sup> and Morgan Donnard\*<sup>[a]</sup>

<sup>[a]</sup>Dr. Pierre Hansjacob, Célia Schwoerer, Dr. Frédéric R. Leroux and Dr. Morgan Donnard  
LIMA – UMR 7042

Université de Strasbourg, CNRS, Université de Haute-Alsace  
ECPM, 25 rue Becquerel, 67000 Strasbourg – France

Email : [donnard@unistra.fr](mailto:donnard@unistra.fr)

While the general synthesis of 1-indenone scaffolds has been extensively studied, the selective access to heteroatom-substituted indenones and more especially 3-substituted 2-amino-indenones remains a challenge<sup>1</sup>. With this in mind our group has previously developed a method to form 2-amino-indenone derivatives through a Larock annulation between ynamides and ortho-iodobenzaldehydes<sup>2</sup>. Given the moderate regioselectivity observed in some cases, we have recently designed a 2-step sequence to access silylated 2-aminoindenones in a highly regioselective manner. The sequence starts with a silylcyanation of the ynamide<sup>3</sup> followed by a cyclization via an intramolecular Houben-Hoesch reaction<sup>4</sup>. The resulting 2-amino-indenones could be valorized through iododesilylation giving access to various cross-coupling reactions. Interestingly some substrates bearing a sulfonamide allowed the obtention of stable 2-amino-indenimines which could be valorized via transformation of the imino group.

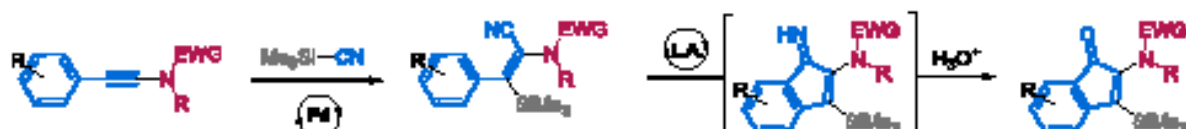


Figure : 2-Step sequence for the selective synthesis of silylated 2-amino-indenones

### Acknowledgements

The authors thank the CNRS and the University of Strasbourg for financial support. P.H. and C.S. are grateful to the French Ministry of Higher Education, Research, and Innovation for PhD fellowships. The authors thank Emeric Wasiliewski and Matthieu Chesse, in charge of the NMR and Analytical platforms of LIMA (UMR7042 CNRS-Unistra-UHA), who contributed, by their precious technical and scientific support, to the realization of this research project.

### References

- (a) H. Shimizu, M. Murakami, *Synlett* **2008** (12), 1817–1820. (b) X. Wang, W. Xiong, Y. Huang, J. Zhu, Q. Hu, W. Wu, H. Jiang, *Org. Lett.* **2017**, *19* (21), 5818–5821. (c) B. D. Mokal, D. B. Huple, R.-S. Liu, *Angew. Chem., Int. Ed.* **2016**, *55*, 11892–11896. (d) J. Sun, G. Zheng, T. Xiong, Q. Zhang, Y. Li, Q. Zhang, *ACS Catal.* **2016**, *6*, 3674–3678.
- S. Golling, P. Hansjacob, N. Bami, F. R. Leroux, M. Donnard, *J. Org. Chem.* **2022**, *87*, 16860–16866.
- P. Hansjacob, F. R. Leroux, V. Gandon, M. Donnard, *Angew. Chem. Int. Ed.* **2022**, *61*, e202200204; *Angew. Chem.* **2022**, *134*, e202200204.
- E. Campagne, D. E. Mais, *J. Heterocycl. Chem.* **1975**, *12*, 267–271.

## **Engineering Polymer Microparticles by Droplet Microfluidics**

**C.A. Serra<sup>1</sup>, Z. Chang<sup>1</sup>, M. Bouquey<sup>1</sup>, M. Schmutz<sup>1</sup>, I. Kraus<sup>2</sup>, I.U. Khan<sup>1,3</sup>, T. Vandamme<sup>3</sup>, N. Anton<sup>3</sup>, C. Ohm<sup>4</sup>, R. Zentel<sup>4</sup>, A. Knauer<sup>5</sup>, M. Köhler<sup>5</sup>**

<sup>1</sup> *Université de Strasbourg, CNRS, ICS UPR 22, F-67000 Strasbourg, France*

<sup>2</sup> *Université de Strasbourg, CNRS, IPCMS UMR 7504, F-67000 Strasbourg, France*

<sup>3</sup> *Université de Strasbourg, CNRS, CAMB UMR 7199, F-67000 Strasbourg, France*

<sup>4</sup> *Institute of Organic Chemistry and Excellence Graduate School MAINZ, University of Mainz, D-55099 Mainz, Germany*

<sup>5</sup> *Department of Physical Chemistry and Microreaction Technology, Institute of Physics, Technical University of Ilmenau, D-98684 Ilmenau, Germany*

*Email: ca.serra@unistra.fr*

Most conventional processes for the production of polymer particles imply heterogeneous polymerization processes (emulsion, suspension) or precipitation processes in a non-solvent. Although these processes lead to polymer particles having a different size domain, the size is very sensible to the operating parameters and cannot readily be adjusted, not to mention the large particle size distribution which is often observed. In the last decade microfluidic processes have been considered because of their unique capacity to generate microdroplets with a very narrow size distribution. Thus, if the microdroplets generated are polymerizable liquids, it is possible to obtain polymer particles with well-defined characteristics like size, shape and morphology [1]. Here we present an overview of our developments on microfluidic processes for the production of sized-controlled polymer microparticles.

Capillary-based flow-focusing and co-flow microsystems were developed to produce polymer microparticles of adjustable sizes in the range of 50 to 600  $\mu\text{m}$  with a narrow size distribution ( $CV < 5\%$ ), different shapes (spheres, rods) and morphologies (core-shell, janus, capsules). Influence of operating conditions (flow rate of the different fluid, microsystem characteristic dimensions and design) as well as material parameters (viscosity of the different fluids, surface tension) was investigated. Empirical relationships were thus derived from experimental data to predict microparticle overall size, shell thickness or rods length.

Besides the morphology, we will also present microparticles with various compositions and will emphasize their potential applications: drug loaded microparticles for new drug delivery strategies, composed inorganic-organic multiscale microparticles for sensorics and liquid crystalline elastomer microparticles showing an anisotropic reversible shape change upon temperature for thermal actuators or artificial muscles.

### **References**

1. V. Hessel, C. Serra, H. Löwe, G. Hadziioannou, *Chem.-Ing.-Tech.*, 2005, 77, 1693-1714.; C.A. Serra, Z. Chang, *Chem. Eng. Technol.*, 2008, 31 (8), 1099-1115.
2. J.L. Steinbacher, D.T. McQuade, *J. Polym. Sci. Part A: Polym. Chem.*, 2006, 44, 8505-8533.

## CHARACTERIZATION OF A GERMANENE/Al(111) MONOLAYER

Ph. Sonnet<sup>1,2\*</sup>, K. Zhang<sup>3</sup>, M.C. Hanf<sup>1,2</sup>, D. Sciacca<sup>4</sup>, R. Bernard<sup>3</sup>, Y. Borensztein<sup>3</sup>, A. Resta<sup>5</sup>, Y. Garreau<sup>5,6</sup>, A. Vlad<sup>5</sup>, A. Coati<sup>5</sup>, I. Lefevre<sup>4</sup>, M. Derivaz<sup>1,2</sup>, C. Piri<sup>1,2</sup>, R. Stephan<sup>1,2</sup>, G. Prévot<sup>3</sup>

<sup>1</sup>Université de Haute Alsace, CNRS, IS2M UMR7361, F-68100 Mulhouse, France

<sup>2</sup>Université de Strasbourg, 67000 Strasbourg, France

<sup>3</sup>Sorbonne Université, Centre National de la Recherche Scientifique, Institut des NanoSciences de Paris, INSP, F-75005 Paris, France

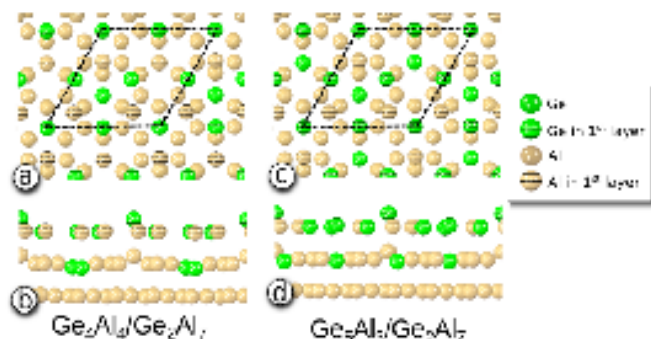
<sup>4</sup>Université de Lille, CNRS, Centrale Lille, Université Polytechnique Hauts-de-France, Junia-ISEN, UMR 8520 - IEMN, F-59000 Lille, France

<sup>5</sup>Synchrotron SOLEIL, L'Orme des Merisiers Saint-Aubin, Boîte Postale 48, 91192 Gif-sur-Yvette Cedex, France

<sup>6</sup>Université Paris Cité, Laboratoire Matériaux et Phénomènes Quantiques, CNRS, F-75013, Paris, France

Email: philippe.sonnet@uha.fr

Synthesizing honeycomb monolayers from group IV elements (Si, Ge, Sn, Pb) is a great challenge, as attested by numerous studies. Indeed, these systems are expected to present remarkable electronic properties, akin to those of graphene<sup>1</sup>. Whereas the existence of silicene, a honeycomb layer of Si atoms, is clearly documented, the description of germanene, resulting from the deposition of germanium on a substrate, is more complex. Here we deposited germanium on a Al(111) single crystal and characterized the system by means of surface X-ray diffraction (SXRD), while various germanene models were explored by means of density functional theory (DFT) calculations. The comparison between the SXRD results and the atomic structure and thermodynamic stability of the different models indicates that the overlayer is not a pure Ge layer, but contains both Ge and Al atoms, that are however arranged in a honeycomb structure<sup>2,3</sup>.



Models of Ge layers on Al(111) relaxed by DFT.

### Acknowledgements

This study was financially supported by the French National Research Agency (Germanene project ANR-17-CE09-0021- 03). K.Z. was supported by the Chinese Scholarship Council (CSC contract 201808070070). The authors would like to acknowledge the High Performance Computing Center of the University of Strasbourg for supporting this work by providing scientific support and access to computing resources., in part funded by the Equipex Equip@Meso project (PIA) and the CPER Alsacalcul/Big Data.

### References

1. F. Zhao, Y. Feng, W. Feibg, Germanium-based monoelemental and binary two-dimensional materials, *Titre, Infomat*, **2022**, 4, e12385(82).
2. K. Zhang *et al*, Structure of germanene/Al(111): a two-layer surface alloy, *J. Phys. Chem. C*, **2021**, 125, 24702-9.
3. K. Zhang *et al*, Combined surface x-ray diffraction and density functional theory study of the germanene/Al(111)-( $\sqrt{7} \times \sqrt{7}$ )R19.1° structure, *Phys. Rev. B*, **2022**, 106, 045412-79.



## INVESTIGATION OF TWO-PHOTON POLYMERIZED MICROSTRUCTURES USING FLUORESCENCE LIFETIME MEASUREMENTS

X. Wu<sup>1,2</sup>, M. Belqat<sup>1,2</sup>, B. Leuschel<sup>1,2</sup>, G. Noirbent<sup>3</sup>, F. Dumur<sup>3</sup>, K. Mougin<sup>1,2</sup>,  
A. Spangenberg<sup>1,2,\*</sup>

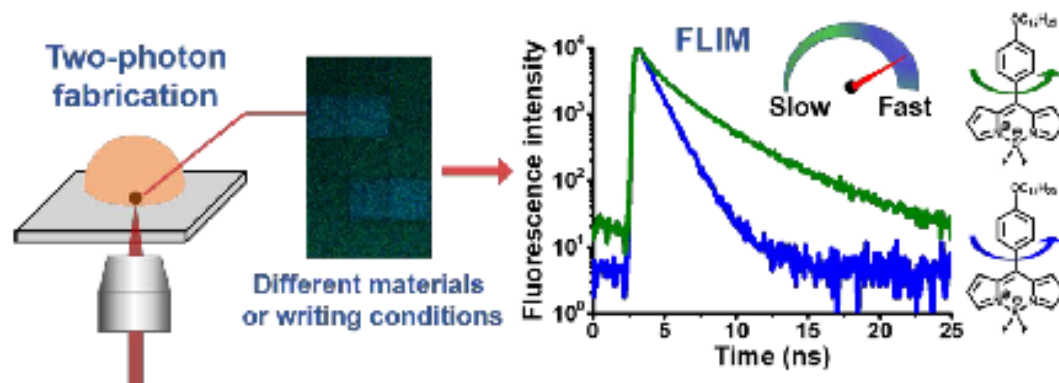
<sup>1</sup>*Institut de Science des Matériaux de Mulhouse (IS2M), CNRS – UMR 7361, Université de Haute-Alsace, Mulhouse, France*

<sup>2</sup>*Université de Strasbourg, Strasbourg, France*

<sup>3</sup>*Aix-Marseille Université, Institut de Chimie Radicalaire (ICR), F-13397, Marseille, France*

*Email: arnaud.spangenberg@uha.fr*

3D Microfabrication by two-photon polymerization (TPP) has become a very popular method to sculpt the matter at the microscale.<sup>1,2</sup> One of the today's challenges is to exert a better control on the processing route and to achieve to build relationship between final properties of the material and the conditions of fabrication process. We report the use of fluorescence lifetime measurements for investigating two-photon polymerization (Figure 1).<sup>3</sup> The dependency of the fluorescence lifetime of Bodipy-C12 with respect to its local environment was exploited to reveal heterogeneity in multi-material microstructures based on PETA and PEGDA-700. Furthermore, a correlation between writing conditions and local viscosity changes within polymerized microstructures made from PEGDA-700 was established by investigating the fluorescence lifetime changes of the molecular rotor. Based on these results, we anticipate that fluorescence lifetime measurement can be successfully applied to explore kinetics of two-photon polymerization or probe the 4D character of active 3D structures made by TPP.



**Figure 1** : Molecular rotor as viscosity probe to reveal heterogeneity in two-photon polymerized microstructures.

### Acknowledgements

The authors thank the Agence Nationale de la Recherche (ANR ANR-16-CE08-347 0020 2PhotonInsight, the Institut Carnot MICA, the M2A and the Région Grand Est (MIPPI4D) for financial support.

### References

1. X. Wu, B. Gross, B. Leuschel, K. Mougin, S. Dominici, S. Gree, M. Belqat, V. Tkachenko, B. Cabannes - Boué, A. Chemtob, J. Poly, A. Spangenberg, *Adv. Funct. Materials*, **2022**, 32, 2109448.
2. M. Belqat, X. Wu, J. Morris, K. Mougin, T. Petithory, L. Pieuchot, Y. Guillaneuf, D. Gignes, J-L. Clément, A. Spangenberg, *Adv. Funct. Mater.*, **2023**, 2211971.
3. X. Wu, M. Belqat, B. Leuschel, G. Noirbent, F. Dumur, K. Mougin and A. Spangenberg, *Polymer Chemistry*, **2022**, 13, 2902-2906.

## GRAFTING ON 3D-PRINTED POLYMER USING NITROXIDE-MEDIATED POLYMERIZATION

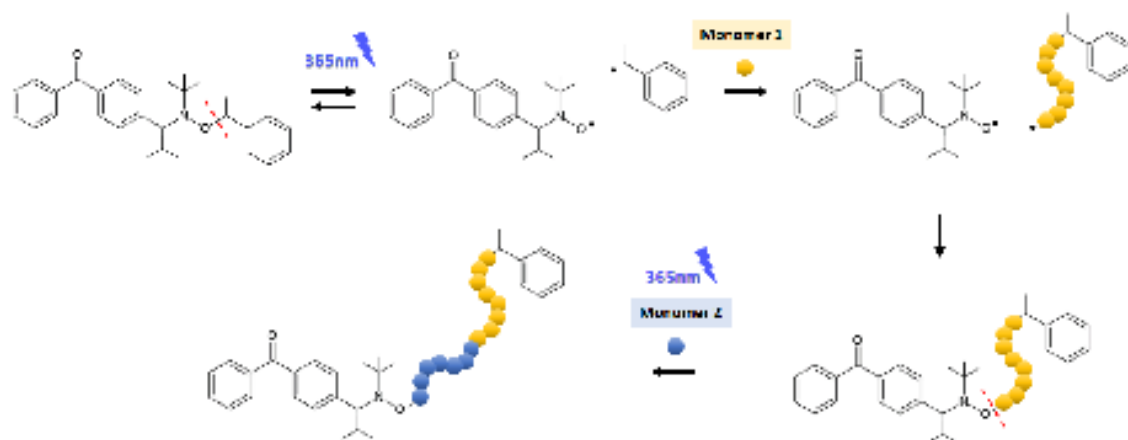
C. Thomas<sup>1</sup>, J.-L. Clément<sup>2</sup>, Y. Guillauneuf<sup>2</sup>, O. Soppera<sup>1,\*</sup>

<sup>1</sup>Université de Haute-Alsace, IS2M-CNRS UMR 7361, Mulhouse, France

<sup>2</sup>Aix-Marseille Université, ICR-CNRS 7273, Marseille, France

Email: [olivier.soppera@uha.fr](mailto:olivier.soppera@uha.fr)

Nitroxide-controlled radical photopolymerization (NMP2) is a well-known and versatile technique for controlled macromolecular synthesis and surface modification [1,2]. The objective of this study is to complete the understanding of the mechanisms involved and to optimize the results to generate a grafted layer of high thickness by UV irradiation. After UV polymerization, the chain ends carry nitroxide functions which allow the dissociation of the molecule under light irradiation generating the growth of the chains without addition of photoinitiator. It is then possible to graft monomer layers up to a hundred micrometers thick. It appears that the irradiation and rinsing conditions have a significant impact on the efficiency of the grafting. A maximum of three grafted layers without addition of photopolymerizable resin allows to validate the successive growth of chains. A double hydrophilic/hydrophobic grafting proves the efficiency and the ease of surface functionalization via nitroxides. This behavior is compared to UV photopolymer containing a classical Norrish I photoinitiator. This allows to highlight the mechanisms involved. It is now easy to imagine systems using this process to answer industrial requests, in microfabrication (optical fiber sensors, microfluidic circuits, etc...).



**Figure:** Mechanism of living polymerization from the dissociation of alkoxyamine.

### Acknowledgements

The authors thank all the person involved in this project and the Agence Nationale de la Recherche (ANR) for funding (DYNABIO- ANR-19-CE19-0012).

### Reference

1. G. Audran, E.G Bagryanskaya, S.R.A Marque, P. Postnikov, New variants of Nitroxide-Mediated Polymerization, *Polymers MDPI*, **2020**, 12(7)-1481. doi: 10.3390/polym12071481.
2. S. Telitel, J. C. Morris, Y. Guillauneuf, J.-L. Clément, F. Morlet-Savary, A. Spangenberg, J.-P Malval, J. Lalevée, D. Gigmes, O. Soppera, Laser Direct Writing of Arbitrary Complex Polymer Microstructures by Nitroxide-Mediated Photopolymerization. *ACS Applied Materials & Interfaces* **2020**, 12 (27), 30779-30786. doi: 10.1021/acsami.0c06339.

## **Volatile Organic Compounds adsorption isotherm on functionalized materials under controlled humidity and temperature conditions**

**Thi Tuyen TRAN<sup>1,2\*</sup>, Coralie KUSTNER<sup>1,2</sup>, Anaïs BECKER<sup>1</sup>, Guy SCHLATTER<sup>1</sup>, Romain SEVERAC<sup>2</sup>, Anne HÉBRAUD<sup>1</sup>, Stéphane LE CALVÉ<sup>1</sup>**

<sup>1</sup>*Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES), Université de Strasbourg, CNRS UMR 7515, F-67087 Strasbourg, France.*

<sup>2</sup>*ANGUS Chemical Company, 6 avenue du Marais 95100 Argenteuil, France*

*Email: thi-tuyen.tran@etu.unistra.fr*

Chronic exposure to indoor air pollution can negatively affect human health. Among indoor air pollutants, Volatile Organic Compounds (VOC), such as formaldehyde, can be harmful and can create long-term health problems [1]. Different materials such as activated carbons, zeolites, MOFs, and hypercrosslinked polymeric resins have been studied to effectively remove airborne VOCs. Most previous studies were carried out with adsorbents having large specific surface areas and pore volumes which promote an efficient physisorption. However, the most common adsorbent may be not effective for removing every VOC in every condition. In our study, hexanal and toluene, i.e., the 2 most widespread VOC after formaldehyde in indoor air [2], were studied and their adsorption capacities were determined on different materials involving physisorption and/or chemisorption. These materials are polymer nanofibers or activated carbon (AC) which are functionalized by depolluting molecules (DM). These DM contain organic functions which may react at the gas/solid interface with certain VOCs. Once the materials are doped with DM, the amount of DM is quantified by UV-VIS spectroscopy or HPLC/UV after extraction and derivatization. Two different polymeric matrices based on polyacrylonitrile (PAN) and polystyrene (PS), were doped respectively with 13.6 wt% and 3.9 wt% DM by blend electrospinning. Similarly, 4.5 wt% DM doped AC and pure AC were studied. These materials were then characterized by SEM and XRD to determine the morphology and the nature of solid phase within the sample.

Once the materials were prepared, adsorption isotherm studies were carried out at 23°C and 50% RH. First, pure crystalline DM adsorbed very negligible hexanal ( $q < 0.1$  mg/g) and did not adsorb any toluene. Concerning the polymeric matrices, pure PAN adsorbed neither hexanal nor toluene, while pure PS adsorbs limited amount of hexanal ( $q = 0.9$  mg/g) and toluene ( $q = 0.5$  mg/g). The hexanal adsorption capacities ( $q$ ) on 13.6 wt% DM doped PAN and 3.9 wt% DM doped PS were slightly higher, with values of  $q = 1.4$  mg/g and  $q = 6.2$  mg/g, respectively. These results suggest that the combination between polymeric matrix and DM enhances hexanal adsorption confirming a potential chemisorption. Nevertheless, VOC adsorptions on polymer-based materials are still low. Concerning the AC matrix, the hexanal and toluene adsorption capacities on pure AC and 4.5 wt% DM doped AC can reach up 127 to 200 mg/g, being considerably higher than those obtained for polymer-based materials. In this context, novel approaches are in progress to develop more efficient adsorbents.

### References

1. V. Soni, P. Singh, V. Shree, et V. Goel, « Effects of VOCs on Human Health », in *Air Pollution and Control*, N. Sharma, A. K. Agarwal, P. Eastwood, T. Gupta, et A. P. Singh, Éd. Singapore: Springer Singapore, 2018, p. 119-142.
2. S. Kirchner, M. Derbez, C. Duboudin, P. Elias, A. Gregoire, *Indoor air quality in French dwellings*, Indoor Air 2008, 2008, Copenhagen, Denmark. Paper ID 574, 8 p. ffhai-00888556.



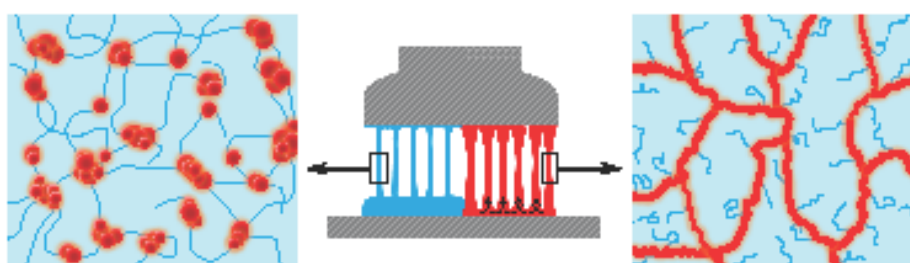
# Topology-specific nonlinear mechanical behavior of nanostructured hydrogels

Mehdi Vahdati<sup>1</sup>

<sup>1</sup>University of Strasbourg, CNRS, Institut Charles Sadron (UPR 22), 67200 Strasbourg, France

Email: mehdi.vahdati@ics-cnrs.unistra.fr

Stimuli-responsive hydrogels based on weak supramolecular interactions are potentially useful for a range of biomedical applications including soft surgical adhesives. We investigated the linear and non-linear rheological properties as well as the adhesive properties of two thermoresponsive graft copolymers with inverse topologies, poly(*N*-isopropyl acrylamide)-*g*-poly(*N,N*-dimethylacrylamide) (PNIPAM-*g*-PDMA) and PDMA-*g*-PNIPAM.[1] Except for their topologies, these copolymers are analogous in terms of chemistry, architecture (graft), and monomer composition (50 – 50 wt %). Over a wide range of concentration, they both form homogenous solutions at room temperature and turn into soft and sticky viscoelastic hydrogels close to body temperature. We find that the linear viscoelastic properties of these two hydrogels are not discernible far above the thermal transition temperature. However, the PNIPAM-*g*-PDMA hydrogel having long thermoresponsive backbones shows a distinctive strain-hardening behavior in large strains both in probe tack tests and in shear. The inverse topology, PDMA-*g*-PNIPAM, shows no hardening and simply softens until failure. This distinction was observed regardless of polymer concentration (in the entangled regime). We attribute the hardening to a continuous, load-bearing nanostructure from strong hydrophobic PNIPAM associations while the softening is due to the easy pullout of short PNIPAM grafts from separate hydrophobic clusters bridged by PDMA backbones. The findings of this work highlight the importance of macromolecular design in determining the nanostructure and thereby the mechanical performance of soft hydrogels for specific applications.



## References:

[1] Vahdati, M, et. al., *Macromolecules*, 2020, 53, 9779.