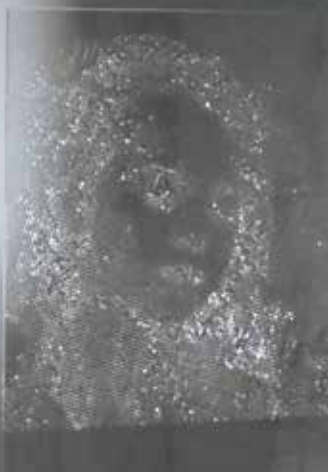
IS2M annual meetings

2D Materials: from synthesis to applications

Faculté des Sciences et Techniques
Université de Haute-Alsace, Mulhouse – France

June 2-3, 2022



Registration and information
https///www.is2m.uha.fr/event/is2m-annual-meetings/

"God invented the volume and the devil the surface" This quote from W. Pauli, one of the founding fathers of quantum physics, about crystals is well known to all scientists who are interested in the mechanisms / properties revealed on the surface of a material. What would he have told us about a material which is only a surface and has the thickness of an atom? This is the case of graphene and many other 2D materials, in contrast to 3D bulk systems, and which can be combined on top of each other by stacking. In this IS2M annual meeting on 2D Materials, we aim to have a broad multidisciplinary approach in physics, chemistry and material science to explore the state of art 18 years after the discovery of graphene. We wish to investigate 2D layers made of graphene – and other materials –, combined with systems exhibiting another dimensionality (0D, 1D, ...) in so called Van der Waals heterostructures, but also functionalized by different methods, and present their potential applications. As IS2M is a wide multidisciplinary laboratory devoted to materials, we also aim to explore the change of properties related to the decrease of dimensionnality from 3D to 2D for a wider class of materials such as, for example, the characteristics of water/ice confined in clays, or of 2D-Metal-Organic Frameworks (MOFs), to name but a few."

Keynote speakers

Vincent Bouchiat, Institut Néel, Grenoble (to be confirmed)
Jean-François Dayen, IPCMS, Strasbourg
André Gourdon, CEMES, Toulouse
Klaus Leifer, Ångström Laboratory, Uppsala University, Sweden
Laurent Michot, Laboratoire PHENIX, Sorbonne Université, Paris
Geoffroy Prévot, Institut des NanoSciences, Paris
Paolo Samorì, ISIS, Strasbourg

Scientific and organizing committee

(University of Haute-Alsace – Institute of Materials Science of Mulhouse, CNRS)

Jean-Luc Bubendorff, **Gérald Chaplais**, **Marion Cranney**, **Liva Dzene**, **Marie-Christine Hanf**, **Laurent Simon**, **Olivier Soppera** and **Laurent Vonna**

For more information and registration

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Front cover photography and artwork by Dominique Peysson

"Dominique Peysson is a visual artist and art researcher. She has two doctorates, in arts at Paris 1 and in physics at Paris 7, and an ESPCI engineering degree. She conducted her research and taught at ESPCI, then at the École Nationale Supérieure des Arts Décoratifs Paris (Ensad), and at the University of Paris-Est Marne-la-Vallée. Promoting the fertile encounter between contemporary arts and sciences, she regularly exhibits her work in France and abroad." https://dominiquepeysson.net/

The artwork proposed by Dominique Peysson during these two days is part of her project "Dancing in the rain" for the video and "Portée comme Ophélie dans les eaux endormies" for the photography.

Portée comme Ophélie dans les eaux endormies – 2022 – Gouttes sur verre, lumière – Artiste : Dominique Peysson

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Summary

Monolayers of graphene produced by CVD, from fundamentals to “real-world” industrial applications

Vincent Bouchiat

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After a more than a decade and tens of thousands of publications, graphene produced by chemical vapour deposition on copper foils still remain at the sweet spot regarding cost , speed and quality for large scale production of monolayers on insulators. I will briefly recall the principle of these technique and then present the use of this technology for biological (1) and medical applications from both the academic and industrial point of view. In particular I will be insisting on the possibility to combine therapeutics (biostimulation, healing) and diagnostics (biosensing) features in the same device.

To explore more that possibility, I will show results of in-vitro cellular growth (neurons and skin fibroblasts) on graphene-covered glass which shows the stimulation of growth (1) and migration of cells promoted by the graphene substrate together with the possibility of probing their activity down to the sub-cellular scale (2). I will present the preclinical results on animal studies and the perspectives of their commercial (3) use for wound-care, in particular the treatment and diagnostics of chronic wounds that affect the diabetics and elderly.

I will also present more recent works on the realization of in vitro diagnostics based on the same material. we are developing a concept of an electronic strip based on a new material for medicine, graphene, whose maturity finally allows its introduction on an industrial scale. The implementation of synthesis techniques of this material from microelectronics allows to produce it in mass at low cost. These sensors powered by a simple smartphone will be coupled with a digital monitoring solution via the smartphone that will improve the diagnosis in the field and the monitoring of chronic diseases. I will detail the functioning of the testNpass, for the detection of the SARS-CoV-2 virus, in particular the process of conversion of the biochemical signal into an electrical signal. Finally, I will show that a myriad of other use cases of this technology exists beyond the Covid crisis.

(1) F. Veliev et al. Biomaterials. 86, 33-41, (2016)
(2) F. Veliev et al. 2D Materials (2018) 10.1088/2053-1583/aad78f
(3) www.grapheal.com

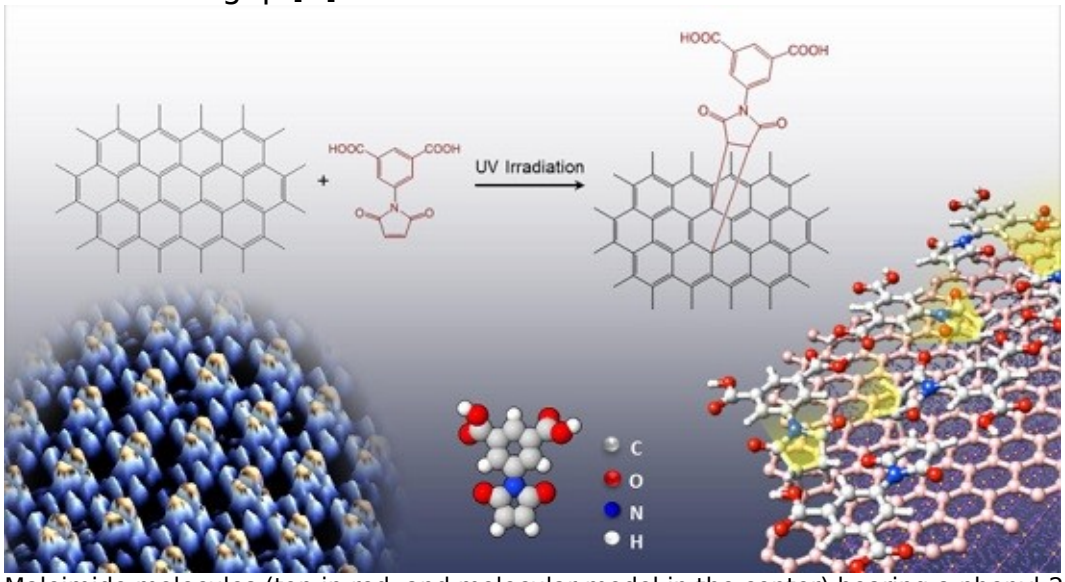
Chemical functionalization of graphene

André Gourdon

CEMES Toulouse

Chemical functionalization of single layer graphene (SLG) is an attractive challenge, not only to modify its electronic properties but also to extend its applications as a 2D material, as for instance in chemical sensors.

Room temperature reaction of maleimide dienophiles substituted by CF3 groups with pristine defect-free defect free SLG on SiC(0001) leads to cycloadditions that have been characterized by XPS, ARPES and STM showing standing wave patterns [1]. Alternatively, SLG on Cu (111) or on mica can be functionalized in a controlled manner by photo-cycloaddition reactions with a monolayer of a maleimide dienophile substituted by phenyldicarboxylic groups. The formation of covalent bonds between the molecules and the graphene substrate by cycloadditions [2 + 2] or [2 + 4] is activated by irradiation in ultra-violet. This grafting modifies the properties of graphene with the formation of an electronic gap [2].



Maleimide molecules (top in red, and molecular model in the center) bearing a phenyl-2,5-dicarboxylic group can be grafted to the surface of graphene (in black) by photochemical cycloaddition reactions involving one or two double bonds of graphene, which disrupts the delocalization of graphene electrons. Bottom left, scanning tunneling microscopy image of the graphene surface after grafting.

1 Lakshya Daukiya, et al. ACS Nano ACS Nano 2017, 11, 1, 627–634. https://pubs.acs.org/doi/10.1021/acsnano.6b06913#

2 Miao Yu, et al. Nature Chemistry (2020), 12, 1035–1041 https://www.nature.com/articles/s41557-020-0540-2

Graphene with flat bands obtained by intercalation

A. Zaarour, M. Cranney, F. Vonau, E. Denys,

A. Florentin D. Aubel, and L. Simon

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Since the discovery of graphene, many studies on its functionalization are made in order to modify its band structure (for ex: to get a gap opening at Dirac points) or simply control the level of doping in order to explore novel physical properties. On the team we study the intercalation process, which consists of starting with a pristine epitaxial graphene layer on SiC, then under ultra-high vacuum, with the evaporation of atoms followed by an annealing, it is possible to intercalate the elements between the substrate and the top graphene layer. This was first done with noble metal such as gold (mainly to make an electrical contact with the graphene) and, inspired by the community of graphite intercalation compounds (GiCs) with the application in battery (charging a Li-ion battery consists in the intercalation of Li ion) or the observation of superconductivity for some Gics (for ex: Ca-GiCs), Alkaline atoms were widely studied in the case of graphene. Most of the elements in the periodical table are able to intercalate, among them the lanthanide atoms providing the highest level of doping. We demonstrate here the possibility of obtaining a highly ordered n-doped graphene monolayer with a charge carrier density reaching 10^{15} cm^{-2} with linear dispersion band around K and a shift of Dirac point energy by about 1.63 eV below the Fermi level. The measured Fermi surface by ARPES shows that the Lifshitz transition is reached.

2D materials beyond graphene : silicene, germanene, stanene and plumbene

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As graphene analogues, honeycomb monolayers of other group 14 elements (Si, Ge, Sn, Pb) have attracted a great interest for electronic applications. Intensive efforts to synthesized silicene, germanene, stanene and plumbene have been made after the prediction of a metastable state for free standing silicene and germanene. As graphene, the electronic structure of the group 14-Xenes display Dirac cones at the Fermi Level. However, due the presence of a larger spin orbit coupling gap, they appear as promising topological insulators for valley- and spin-dependent quantum Hall conductivity.

As they cannot be obtained by exfoliation from a bulk material, they have to be synthesized on a substrate. Up to now, several works have reported the formation of silicene, germanene, stanene and plumbene on metal surfaces, but also on insulating or semi-conducting substrates. However, a lot of works remain controversial.

In this presentation, I will review the research of the last ten years on these group 14-Xenes. I will show how they can be grown on selected substrates, and which techniques can be used to determine their structure and electronic properties. Finally, I will present the perspectives offered by this class of 2D materials.

(a) (b)

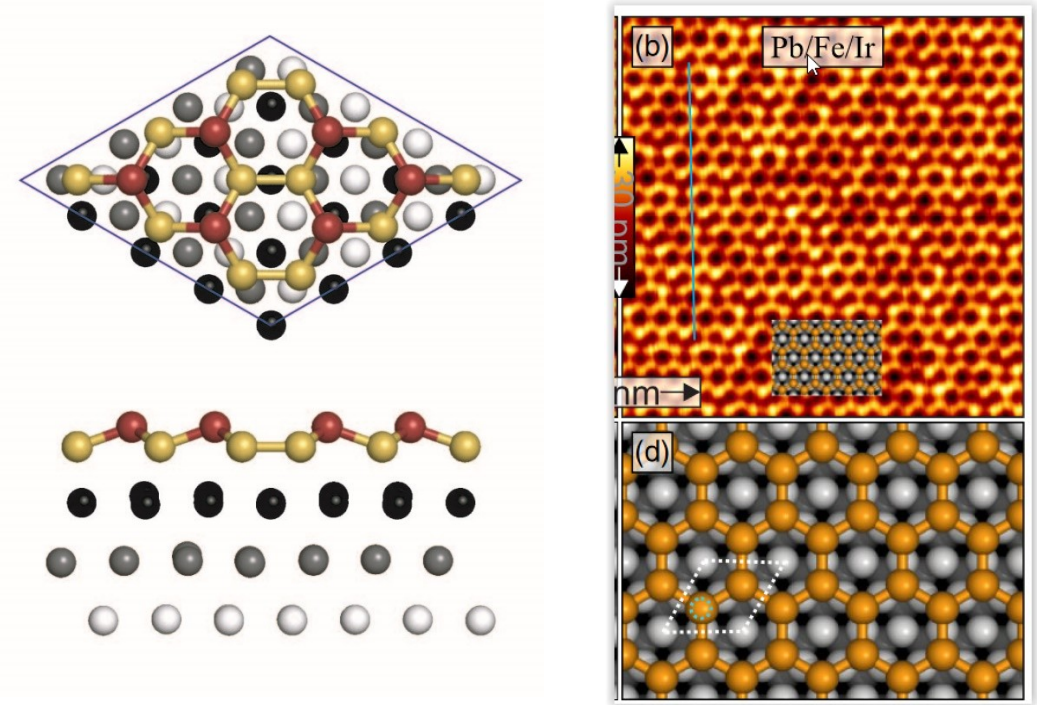

Fig. (a) Structure of silicene on Ag(111) [A. Curcella et al. Phys. Rev. B 99, 205411 (2019]. (b) Plumbene on a Fe/Ir(111) film: Scanning Tunneling Microscopy image and atomic model [G. Bihlmayer et al., Phys. Rev. Lett. 124, 126401 (2020)].

Boosting 2D materials with (supra)molecules

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Two-dimensional materials exhibit exceptional physical and chemical properties which can be further enhanced and enriched via their controlled interfacing with molecules and (supra)molecular assemblies. In my lecture I will introduce the importance of functionalization of 2D materials to engineer hybrid systems with ad hoc characteristics. I will show how non-covalent and covalent approaches can offer viable solutions to impart new functions to 2D semiconductors rendering them multiresponsive, to leverage the dimensionality for enhanced electronic transport in 2D semiconductors and to develop highly-sensitive pressure sensors for health monitoring. The presented modular strategies offer a simple route to generate multifunctional coatings, foams and nanocomposites with pre-programmed properties to address key global challenges in electronics, sensing and energy applications.

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

Marion Cranney,[a] François Calard,[b] Jean-Pierre Malval,[a] Thibaut Jarrosson,[b] Jean-Luc Bubendorff,[a] Arnaud Spangenberg,[a] François Vonau,[a] Olivier Soppera,[a] Jean-Pierre Lère-Porte,[b] Françoise Serein-Spirau,[b] Laurent Simon[a]

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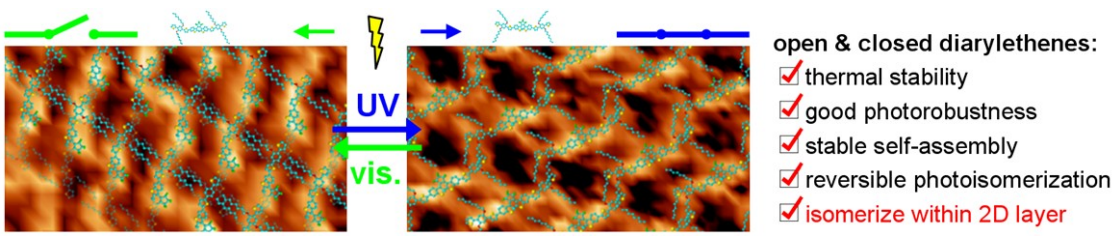
This study comes within the framework of design and study of smart surfaces. They are based on the self-assembly of functionalized molecules on a substrate, that will respond in a defined way to an external stimulus. As the use of light to control smart surfaces seems to hold promising prospects [1], diarylethenes [2] are one of the most appropriate functionalized molecules for the achievement and study of smart surfaces. We will show in this presentation that we obtain 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. 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%. This photoisomerization is proven to occur within the 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. Using these newly synthetized molecules, we should then be able to obtain photoresponsive supramolecular 2D self-assemblies on large scale that isomerize within the molecular layer with thermal stability and good photorobustness, and where STM might be used as a non-destructive readout tool.

[1] X. Zhang et al., Nature Commun. 7:11118 (2016) ; J. Zhang, H. Tian, Adv. Optical Mater. 6, 1701278 (2018).[2] M. Irie et al., Chem. Rev. 114, 12174 (2014).



Animate matter, How to create interactive artworks of another kind, bypassing digitally ?

Dominique Peysson

The emerging matter designed nowadays in our laboratories is cleverly effective: scientists reproduce smart arrangements that the living matter has optimized over generations, or they structure the infinitely small to attain previously unimaginable properties. It can be activable and animated, a performer substance to create singular artworks. Its intense presence and ability make reality foreign to us and arouse very rich aesthetic feelings. They embody interactive works of another kind with which we enter into relation directly through the language of matter, bypassing digitality.

Van der Waals heterostructures and hybrids : a versatile platform from optoelectronics to molecular electronics.

Jean–François Dayen

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Because of their atomically-thin structure, high surface to volume ratio, and reduced electric screening, new properties and functionalities are expected to emerge when exploiting the interactions of two dimensional (‘2D’) materials placed in contact with other nanomaterials such as zero dimensional (‘0D’) systems including clusters, nanocrystals and molecules. These so-called Mixed-dimensional van der Waals Heterostructures are now at the forefront of basic nanoscience and applied nanotechnology, providing new sets of possibilities to tailor device functions and novel physical properties.[1]

Today, I will present some of our recent achievements and on-going works illustrating the possibilities offered by such heterostructures in various fields of nanoelectronics including single-electron electronics [2], molecular electronics [3,4] and optoelectronics[5]. These 0D-2D devices take advantage of the functionalities of the 0D systems (electronic, magnetic, optic…) and of the specific properties of 2D materials such as : i) van der Waals interface, ii) high diffusion of metals enabling self-ordered growth of nanoclusters, iii) dual electric behavior combining in-plane charge transport with out-of-plane electric field transparency (they are thinner than the Debye screening length), iv) exacerbated surface/interface sensitivity. The works selected for this talk will allow me to introduce some of these concepts.

References :

[1] D. Jariwala et al., **Nat. Mater.** 2017, 16, 170
[2] Mouafo et al, **Adv. Mater**. 2018, 30, 1802478; Mouafo et al., **Adv.Func.Mat.** 2021, 31, 2008255 Godel et al., **Adv. Mater**. 2017, 29, 1604837
[3] Konstantinov, **J. Mat. Chem. C.** 2021, 9, 2712
[4] J.F. Dayen et al. **Mater. Horiz.**, 2021, 8, 2310-2315 ; [5] Noumbe et al., **ACS Nano** 2020, 14, 4567.

Fluorinated graphene synthesised by particle beam assisted methods

Klaus Leifer

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Graphene is an extraordinary material which has fascinated science with its properties such as its high charge carrier mobility, fractional quantum Hall effect and its high Young's modulus. Graphene remains though a challenging material since it is an inert material. This makes chemical functionalisation and the synthesis of new, graphene-based materials difficult. Here, we have overcome this obstacle by focussed ion and electron beam induced functionalisation. In this process, a precursor gas containing fluorene streams over graphene and, when in contact with the particle beam, some of the precursor gases will decompose. This leads to fluorene radicals getting in contact with the graphene surface, where they form C-F bonds. When ions induce this highly efficient fluorination process, the fluorene attaches to a large extent to the defects and vacancies created by the ions. Using electron beam induced fluorination, the graphene surface is fluorinated without introducing defects. Using XPS, a bandgap could be achieved enabling the fabrication of isolated and semiconducting C_xF. Due to the nanoscopic nature of the electron beam, fluorinated nanowires with a width of less than 20 nm can be written by this technique. Thus, this technique is a maskless technique enabling to fabricate high quality nanomaterials ranging from conductors to isolators on a substrate surface. Recently, we could show that fluorinated, semiconducting graphene emits visible light.

When fluorination is carried out on a graphene double layer, the upper lattice plane becomes fluorinated and thus has a different lattice parameter. This leads a to the formation of a Moiré lattice. In contrast to well analysed twisted Moiré lattices, the fluorinated graphene double layer is a novel material with a two-fold Moiré lattice and a periodicity in the 10 nm range. Fluorinated graphene is thus a novel material showing a very good materials quality and promising electronic, optical and sensor properties.

Development of a graphene based gas sensor: fabrication and characterization of graphene, fluorographene and graphene/boron nitride devices

Vincent Malesys[1], Amandine Andrieux-Ledier[1], Pierre Lavenus[1], Laurent Simon[2], Klaus Leifer[3], Tianbo Duan[3]

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Nowadays the reinforcement of health and environmental standards implies a compact and ppb sensitive air quality monitoring. This can be achieve through graphene ultrasensitive [1] gas sensor as a third way between optical and metal oxides sensors. We have been developing a chemo-sensitive graphene sensor. Our sensor has proven to be ppb sensitive to NO_2 (fig. 1). Nevertheless, we are experiencing low selectivity, high response time and instabilities due to the substrate.
In order to enhance our sensor selectivity and sensitivity to NH_3, we are willing to fluorinate the graphene with an electron beam in order to mute graphene into fluorographene with a high spatial resolution [2]. Indeed, there is a strong binding energy between fluorine and ammonia, which leads to the enhanced sensitivity of the gas sensor. Before performing electrical and gas sensing characterizations with such sensor, we are working to determine the performance over time and temperature of the fluorographene through an X-ray photoelectron spectroscopy (fig. 2.). This technique will support us to investigate the electron affinity between the gases and the graphene or the fluorographene by studying adsorption and desorption mechanisms.
The second step of this work involves the use of a Boron Nitride substrate as it will enhance electron mobility and sensor response time meanwhile reducing substrate effect [3]. We are exploring two leads. Firstly, the processing of an “all-CVD” (Chemical Vapour Deposition) device build with consecutives liquids transfers of commercial CVD BN and CVD graphene (Graphene Supermarket and Graphenea). Secondly, the use of a BN substrate synthesized by CVD in our laboratory, at the ONERA [4]. This BN shows continuous, single crystalline and sp2-hybridized multilayer film on the nickel (111) substrate. (fig 3). A new approach would be to build the sensor directly on the BN growing substrate of nickel, avoiding the damage induced by the liquid transfer of the BN film.
Lastly, our aim is to combine the use of fluorinated graphene with a BN substrate as an innovative solution for the development of an ultrasensitive NO_2 and NH_3 gas sensor.

[1]F. Schedin et al., Nat. Mater., 6 (2008) 652 [2]H. Li et al., Appl. Phys. Rev., 7 (2020) 011403 [3]E. Mania et al., Sensors Actuators B Chem., 266 (2018) 438 [4]H. Prevost et al., 2D Mater., 7 (2020) 045018

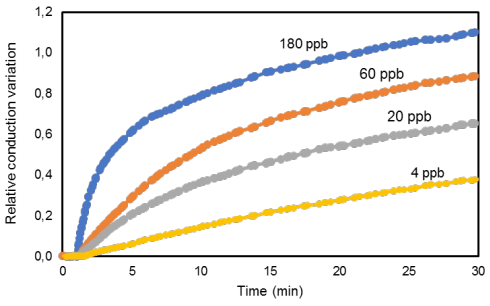

Figure 1: ONERA graphene based gas sensor response to several NO2 concentration exposure

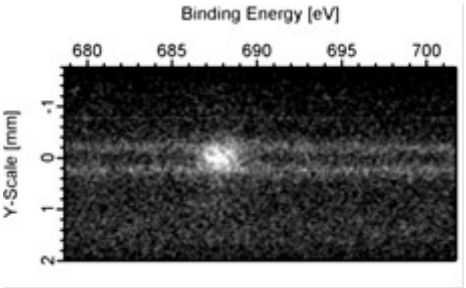

Figure 2: XPS cartography of the fluorinated graphene area after annealing at 450°C

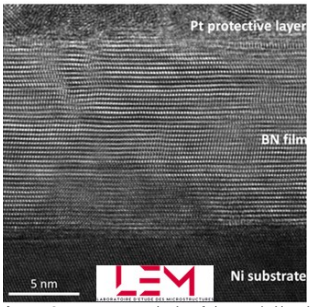

Figure 3: HRTEM analysis of the BN/Ni(111) interface:

Structure and dynamics of water confined in the interlayer space of swelling clay minerals.

Laurent Michot

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Confinement of water in pore spaces smaller than a few molecular diameters leads to various effects that are currently the object of intense study in view of the possible applications of these anomalous behaviors in various situations. In any case, the effect of extreme confinement is linked to the fact that the structure and dynamics of water and ionic solutions are strongly affected in those conditions. In that regard, in addition to their strong environmental and industrial relevance, swelling clay minerals are ideal objects for studying how various structural and physico-chemical parameters modify the behavior of 2D confined ions and water molecules. We will review some of the work we have been performing on this issue by combining various experimental techniques (Water adsorption gravimetry, X-ray diffraction, Neutron diffraction, Quasi-Elastic Neutron Scattering, Inelastic Neutron scattering) with computer simulations (Grand Canonical Monte Carlo, Classical and Ab-initio Molecular Dynamics). We will show that the combination of experiments and simulation is crucial for better understanding the phenomena at play in confined solution and will try to identify various points deserving further research efforts.

Functional nanomaterials by plasmon assisted photopolymerization

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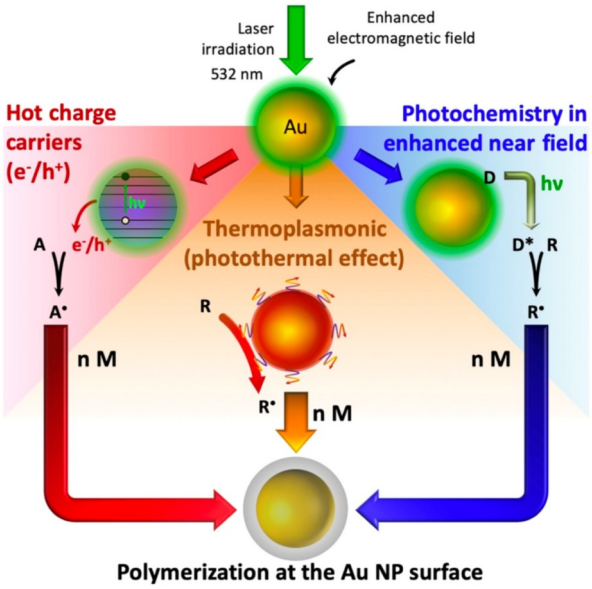
Over the past years, localized surface plasmons have been exploited for triggering photochemical and photophysical reactions, opening the door towards the fabrication of functionalized nanoparticles. Achieving such hybrid nanosystems with strong coupling between metal nanostructures and organic or semiconducting material is a major challenge for applications in nanophotonics, sensors or spectroscopy.
In our case, surface plasmon resonance of metal nanoparticles was used as an optical near-field source to locally trigger different polymerization reactions.
Free radical photopolymerization was first developed, [1] investigated [2,3] and used for obtaining hybrid nanoparticles functionalized by plastic antibodies or Quantum Dots [4]. The concept was recently extended to living polymerization to obtain complex surface chemistry. [5]
To further extend the possibilities of functionalization, we exploited also thermoplasmonic effects, which makes it possible to couple the metal nanoparticles to thin semiconducting films. [6]



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4. D. Ge et al, Nature Communications **2020**, 11 (1), 3414.
5. F. Kameche et al, Materials Today **2020**, 40, 38.
6. C.-F. Lin et al, Advanced Optical Materials **2021**, 2100045.