



Tuesday, November 23th

Session Multifunctional Nanocomposites

15:00 - 15:30 Keynote

Normand MOUSSEAU • Univ. Montréal - Dpt of
Physics, Canada

15:45 - 16:15 Keynote

Françoise MASSINES • CNRS - PROMES, France

Abstracts

Keynote Speakers



Normand MOUSSEAU

Professor at Université of Montréal

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Biography

Normand Mousseau is professor of physics at Université de Montréal and academic director of the Trottier Energy Institute. He holds a Ph.D. in physics from Michigan State University and he pursued post-doctoral studies at the University of Oxford and Université de Montréal. He was professor at Ohio University before moving to his current position in 2001. His work focuses on the atomistic kinetics of complex materials and biomolecules, with more than 180 scientific articles. Over the years, he has developed numerous simulation methods, such as the activation-relaxation technique (ARTn) and kinetic ART, for exploring the energy landscape of these materials and accessing experimental time scales. His codes are used by tens of groups from around the world.

He intervenes regularly on energy, climate and questions regarding science and society and has authored numerous books on these topics. In 2013, he co-chaired Québec's Commission on energy issues. His latest book « Pandémie. Quand la raison tombe malade » was published by Éditions du Boréal in Novembre 2020.

UNDERSTANDING THE KINETICS OF FORMATION OF NANOSTRUCTURES THROUGH ENERGY SURFACES

Atoms move and assemble following local rules that can be understood, in a collective sense, as a walk of a system on an energy surface that describes its physics. While this concept is a useful way to approach often complex atomistic kinetics, this high-dimensional construction remains challenging to fully picture and characterize quantitatively. In recent years, many tools have been developed to explore, describe and classify the energy landscape of complex materials. For example, using various exploration methods, such as the activation and relaxation technique (ART nouveau) — a very efficient open-ended transition-point search method— and kinetic ART — an off-lattice kinetic Monte Carlo algorithm with on-the-fly catalog building, we have attempted to conduct exhaustive sampling in various systems, ranging from crystalline metals with amorphous semiconductors. The results of these studies allow us to better understand the diversity of diffusion mechanisms. In this presentation, I will rapidly provide an overview of these and other numerical and theoretical approaches developed to characterize the energy landscape of complex systems and nanostructures.

Building on our recent work that explains the correlations between the diffusion barrier and the prefactor, a correlation called “compensation law” or “Meyer-Neldel law”, I will also discuss why it is necessary to go beyond the energy mapping to include entropic effects to provide a more accurate description of the atomistic kinetics of nanostructured materials.

Keywords: atomistic kinetics; energy surface; activation-relaxation technique; kinetic ART; kinetic Monte Carlo; Meyer Neldel Law; formation of nanostructures; disordered materials.

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Thematic Session: Multifunctional Nanocomposites

Keywords: nanoparticle, coordination polymer, self-assembly, spin crossover, charge transport

Spin crossover in Fe(triazole)–Pt nanoparticle self-assembly structured at the sub-5 nm scale

Suhail Usmani,¹ Mirko Mikolasek,^{2,3} Angélique Gillet,¹ José Sanchez Costa,^{2,4} Mathilde Rigoulet,¹ Bruno Chaudret,¹ Azzedine Bousseksou,² Benedikt Lassalle-Kaiser,⁵ Phillipe Demont,⁶ Gábor Molnár,² Lionel Salmon,² Julian Carrey¹ and Simon Tricard¹

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A main goal of molecular electronics is to relate the performance of devices to the structure and electronic state of molecules. Among the variety of possibilities that organic, organometallic and coordination chemistries offer to tune the energy levels of molecular components, spin crossover phenomenon is a perfect candidate for elaboration of molecular switches. The reorganization of the electronic state population of the molecules associated to the spin crossover can indeed lead to a significant change in conductivity. However, molecular spin crossover is very sensitive to the environment and can disappear once the molecules are integrated into devices. Here, we show that the association of ultra-small 1.2 nm platinum nanoparticles with FeII triazole-based spin crossover coordination polymers leads to self-assemblies, extremely well organized at the sub-5 nm scale. The quasi-perfect alignment of nanoparticles observed by transmission electron microscopy, in addition to specific signature in infrared spectroscopy, demonstrates the coordination of the long-chain molecules with the nanoparticles. Spin crossover is confirmed in such assemblies by X-ray absorption spectroscopic measurements and shows unambiguous characteristics in both magnetic and charge transport measurements. Coordinating polymers are therefore ideal candidates for the elaboration of robust, well-organized, hybrid self-assemblies with metallic nanoparticles, while maintaining sensitive functional properties, such as spin crossover.

Reference: Usmani, S.; Mikolasek, M.; Gillet, A.; Sanchez Costa, J.; Rigoulet, M.; Chaudret, B.; Bousseksou, A.; Lassalle-Kaiser, B.; Demont, P.; Molnár, G.; et al. *Nanoscale* **2020**, *12*, 8180.

Acknowledgment: SOLEIL synchrotron, Agence Nationale de la Recherche, Marie-Curie research program, Indo-French Centre for the Promotion of Advanced Research – CEFIPRA, EUR grant NanoX, Spanish MINECO



Keynote Speakers



Françoise MASSINES

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Biography

Françoise Massines is a senior scientist at the CNRS Processes, Materials and Solar Energy (PROMES) laboratory located in Perpignan, France. She received a doctorate in Physics from the University of Toulouse (1987). After five years of studying polymer physics at the Canadian National Research Council (CNRC) Industrial Materials Institute (IMI), she joined CNRS in 1989. Since that time her research activities have been devoted to atmospheric pressure plasma surface treatment. Her team at the Toulouse Electrical Engineering Laboratory (LGET- LAPLACE) was initially involved in polymer surface activation studies and later focused on the development of polymer thin film coatings. In 2007, she joined the PROMES laboratory and oriented her activities to atmospheric pressure plasma enhanced chemical vapor deposition (AP-PECVD) for photovoltaic applications focusing on nanocomposite thin film AP-PECVD. She was instrumental in the development of novel large area plasma sources. She is a coordinator of the IRN-NMC [1].

PLASMA BASED SOLUTIONS TO PRODUCE NANOCOMPOSITE THIN FILM COATINGS

As part of the Franco-Canadian network on controlled nanomaterials (IRN NMC)¹, different plasma-solutions to produce nanocomposite thin films are investigated. The aim is to embed nanoparticles (NPs) in a plasma polymerized thin film. Different composites are considered: TiO₂/polymer, TiO₂/SiO₂, ZnO/DLC, Porous SiO₂/polymer, Au/polymer... The challenge is to form or inject the NPs avoiding their aggregations and to control their quantity and organization in the thin film. The key point is the control of the NPs size, quantity and dispersion in the thin film. Different plasma sources are studied; however, the presentation will be focused on DBD (dielectric barrier discharges) which are atmospheric pressure plasma useful for in-line coating of large surfaces.

Three different configurations are considered: the injection into the plasma of an aerosol of a dispersion of NPs in a polymerisable solvent, in-line formation of NPs upstream of the plasma and NPs formation in the plasma. The aggregation of the NPs contained in an aerosol droplet when the solvent evaporates limits the interest of the first solution even if the functionalization of the NPs avoid this drawback. However, this study allowed to develop simple solutions to control the proportion of NPs in the nanocomposite based on DBD frequency alternation [2-3]. Upstream formation of the NPs is a more promising solution first used in low pressure plasma. It allows the production and the spraying of isolated nanoparticles in a pulsed regime [4]. This concept of reactor-injector is under investigation at atmospheric pressure. Finally, the production of NPs directly in the plasma, during the thin film polymerization appears like a useful and easy to set up solution. Metal/polymer nanocomposite with non-aggregated NPs are made from a spray of metallic salt dissolved in a polymerisable solvent.

To conclude promising safe by design processes to produce controlled nanocomposite on large surfaces are under development and applied to various materials and properties.

References

[1] <https://www.gdri-nanomateriaux.org/>

[2] Brunet P. *et al.*, *Langmuir*, 2018, 34 (5), pp 1865–1872

[3] Profili J. *et al* *Journal of Applied Physics* **120**, 053302 (2016); <https://doi.org/10.1063/1.4959994>

Keywords: safe by design hybrid process; in line plasma process; nanocomposite; thin film; atmospheric pressure.

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Thematic Session: Multifunctional Nanocomposites

Keywords: nanocomposite (NC) thin films, low pressure plasma.

Hybrid PECVD / direct liquid injection of a Colloidal Solution for SiO₂:TiO₂ nanocomposite thin film deposition

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** : Auteur correspondant*

One of the most significant challenges in the development of nanocomposite (NC) thin films is the control of the growth mechanisms and the incorporation of the nanoparticles (NPs). Here, we propose a hybrid process consisting in injecting a colloidal solution in a low pressure plasma. Such a process is attractive since it is versatile, as both the nature of the NPs and the matrix can be varied, and it is safe since there is no manipulation of the NPs. This work focusses on the deposition of homogeneous SiO₂:TiO₂ NC films with a tunable content of TiO₂ NPs. They were obtained by injecting a 3 nm anatase TiO₂ NPs colloidal solution [1] in an O₂/ HMDSO at low-pressure inductively coupled plasma [2]. The deposition and the optical properties of the NC film were monitored in situ by ellipsometry. The film structure was investigated by high resolution TEM, Raman spectroscopy and XPS. First, the strategy used to optimize the process (direct liquid injection and O₂/HMDSO plasma parameters) to obtain films with a homogeneous distribution of NPs will be described. Second, the interaction between the injected droplets and the plasma will be discussed. Finally, the structure and optical properties of the NC will be detailed. As a conclusion, the main results of this study is the fact that both the anatase structure and the 3 nm size of the TiO₂ NPs are retained in the NC film and that the anatase NP content in the SiO₂ matrix can be tuned from 1 to 50% by varying the frequency of the pulsed liquid injection system.

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[2] D. Li, S. Elisabeth, A. Granier, M. Carette, A. Goulet, and J.-P. Landesman, Plasma Process. Polym. 13, 918 (2016)

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Thematic Session: nanocomposites or nanoparticles

Keywords: nanocomposites, diamond-like carbon, plasma, aggregation, Dynamic Light Scattering

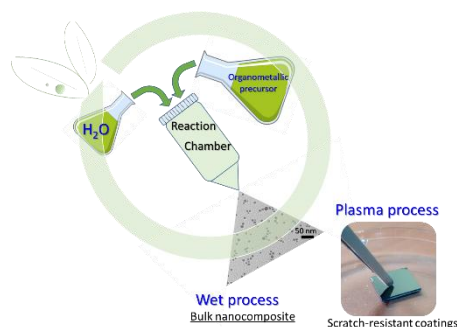
How to avoid nanoparticle aggregation in single step formation of nanocomposites

Guillaume Carnide^{1,2}, Yohan Champouret^{1,2}, Zacharoula Zavvou^{1,2}, Louise Dumas¹, Constantin Vahlas³, Anne-Françoise Mingotaud⁴, Richard Clergereaux¹, Myrtil L. Kahn²

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The strong development of nanocomposites is linked to their interesting properties and wide applications, going from optics, energy, medicine, automotive... However, they suffer from two drawbacks. First, their properties strongly depend on the actual dispersion of the nanoparticles (NP) inside the matrix. Presence of NP aggregates will yield a material behaving like one with particles of micron size, therefore losing partial properties associated to the nanometric size, such as electronic or optical ones. Control of the NP dispersion is therefore critical. Secondly, from a hazard standpoint, processing NP is associated to possible danger for the manufacturer. Technologies enabling the production of nanocomposites without ever exposing the worker to this risk is thus critical. This presentation will describe how we developed a process enabling the *in situ* formation of NPs followed by on-line encapsulation into diamond-like carbon matrix performed by plasma deposition.

This will be the occasion to have a critical overview of the phenomenon of NP aggregation which is remarkably avoided during this process. A comparison between reaction in organic solvents and this new process will be presented.



References : M. L. Kahn, R. C., A.-F. Mingotaud, C. Vahlas, Y. Champouret, G. Carnide. Process for the preparation of nanoparticles. N° EP16305977.7, PCT/EP2017/068831 (2016)

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Acknowledgment: The authors wish to thank L. Vendier, V. Collière and E. Chalhoub for help in characterizations. This work was financially supported by the CNRS and the STAE-RTRA foundation (STAE/2014/P/VIMA/12 project grant).



Wednesday, November 24th

Session Multifunctional Nanocomposites

16:00 – 16:30 Keynote

Milo SHAFFER • Imperial College London – Dpt of
Chemistry, UK

Abstracts

Keynote Speakers



Milo SHAFFER

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Biography

Professor Milo Shaffer is Professor of Materials Chemistry at Imperial College and was co-Director of the London Centre for Nanotechnology (2010-2020). He is a leader in nanomaterials synthesis, modification, and hierarchical assembly, for applications including composites and electrochemical devices. He has pioneered the development of redox methods for nanocarbon processing, and at a larger scale, he developed new hierarchical combinations of nanocarbons as structural electrochemical energy storage electrodes (www.sorcerer.eu). He was an investigator on a major UK Programme Grant developing high performance ductile composites (www.hiperduct.ac.uk), and now leads the UK NextCOMP program on next generation composites in compression (www.nextcomp.ac.uk). He was awarded the [RSC Meldola Medal](#) (2005) and the [RSC Corday-Morgan Prize](#) (2014). He has published around 240 peer reviewed journal papers and 30 patents, with 26700 citations, and an h-index (GS) of 72.

VERSATILE AND SCALABLE APPROACHES TO CHEMICAL PROCESSING OF NANOCARBONS

Individual perfect nanocarbon structures have exceptional properties; the challenge is often how to exploit their potential in real macroscopic systems. Chemical functionalisation is critical to a wide range of nanocarbon technologies, but needs to be versatile and applicable at scale. Existing approaches tend to rely on liquid phase reactions, often requiring damaging sonication or lengthy work up through filtration or centrifugation. The formation of individualized functionalised single wall nanotubes (SWNTs) and graphenes is a particular challenge.

One particularly promising approach, relies on reductive charging to form pure charged nanocarbon anions which can be redissolved, purified, or optionally functionalised, whilst avoiding the damage typically associated with sonication and oxidation based processing. This simple system is effective for a host of nanocarbon materials including MWCNTs, ultralong SWCNTs, carbon blacks, graphenes, and related materials. The resulting nanocarbon ions can be readily chemically grafted for a variety of applications. The chemistry of these discrete nanions raises interesting fundamental questions, but is also practically useful. Dispersed nanocarbon related materials can be assembled, by electrophoresis, cryogel formation, or direct cross-linking to form Joule heatable networks, protein nucleants, supercapacitor electrodes, and catalyst supports, particularly suited to combination with other 2d materials, such as layered double hydroxides. Comparative studies allow the response of nanocarbons with different dimensionalities to be assessed to identify fundamental trends and the most appropriate form for specific situations. The use of nanostructured materials often provides opportunities to simultaneously address otherwise conflicting materials property requirements, such as high ionic conductivity with high stiffness, or self-healing with high absolute strength.

References

Clancy, Shaffer, et al, Charged Carbon Nanomaterials: Redox Chemistries of Fullerenes, Carbon Nanotubes, and Graphenes, Chem.Rev., 118, 7363–7408, 2018

Keywords: nanocarbon; nanotubes; graphene.

Magnetic Stimulation of Phase-changing Nanocomposites

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Rubber-based materials have recently suffered from a bad reputation for being one of the prominent materials in waste generation. A third of the micro-plastics found in the oceans are actually believed to come from tires and other similar consumer goods.[1] However, because of their unique physical properties, their production remains of the utmost importance for applications in several industrial sectors. In this project, we directed our focus towards their repairation by designing strong and phase-changing rubbers. Unlike supramolecular materials, such elastomers possess high strength and toughness in service, and rely on abundant ingredients: a thermoplastic polyurethane (segmented copolymer), and a responsive nanofiller. We voluntarily abandon the *self-healing* paradigm, to move to the *stimulus induced healing*, being more realistic for the production of truly healable materials endowed with high mechanical properties.

In this framework, rubber healing consists in the dissociation of semi-crystalline “hard” segments encompassed within the soft matrix, enabling chain diffusion and the subsequent cicatrisation of the material (Figure 1). While this phenomenon is most often controlled through the external temperature, we propose here to use induction heating as an alternative offering well-controlled, contactless and localized heating.[2] Induction heating, also referred as *Magnetic Hyperthermia*, originates from different spin relaxation mechanisms that depend on the particles’ nature, size and their environment viscosity[3]. Through this study, we seek to understand and optimize the healing capabilities of the samples processed in this work. We first follow the heat production as a function of the material’s formulation and structure through thermal imaging (Figure 2). We then correlate these parameters with their rheological behaviour with the aim of optimizing their healing ability. Finally, carefully chosen formulations of materials are subjected to magnetic induction healing and are mechanically tested for their properties to be compared with those of the original nanocomposites.

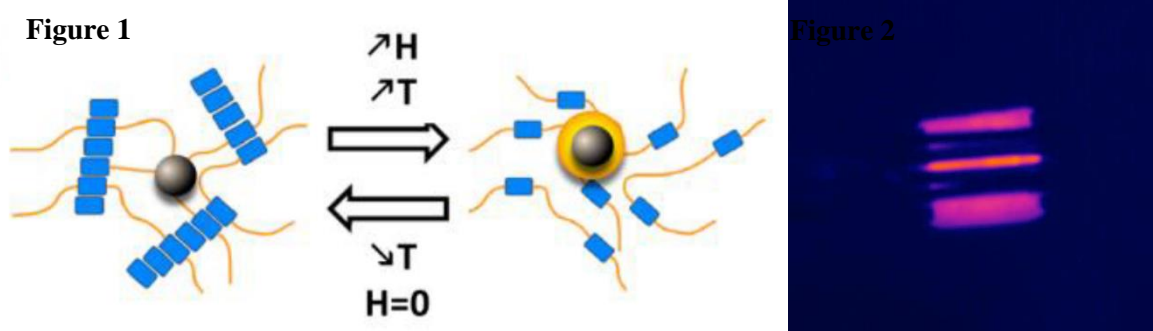


Figure 1. Schematic representation of a smart rubber made of a thermoplastic elastomer and responsive nanofillers.

Figure 2. Thermal imaging of cylindrical nanocomposite placed at the centre of a coil and submitted to an oscillating magnetic field.

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- [3] Bayerl, T., Duhovic, M., Mitschang, P., & Bhattacharyya, D. (2014). The heating of polymer composites by electromagnetic induction - A review. *Composites Part A: Applied Science and Manufacturing*, 57, 27-40.

Thematic Session: Nano for Imaging, diagnosis and therapy

Keywords: Smart microgels, gold nanoparticles, fluorescence probes, photoacoustic imaging, Raman imaging, phototherapy

Versatile Design of Multifunctional Microgels from Molecular, Nano- and Microscale Building Blocks for Biomedical Applications

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Abstract. The development of hybrid microgels based on the integration of inorganic nanoparticles into polymeric particles has stimulated worldwide efforts in recent years due to their promising biomedical applications as smart therapeutic system and bioimaging agents^{1,2}. In this talk, we describe an innovative modular strategy to obtain multifunctional smart hybrid particles based on the self-assembly of different building blocks (stimuli-responsive microgels, gold nanoparticles and fluorescent dyes) that could be compared to the assembly of lego® bricks (Fig. 1). The final hybrid networks display intense Raman signatures due the presence of the gold nanoparticles (Au NPs) trapped within the polymer matrix, which strongly enhance the vibrational signals of the dyes. The nanohybrids thus act as surface-enhanced Raman spectroscopy (SERS) tags for bioimaging. Moreover, the Au NPs trapped within the particles are also valuable light-to-heat plasmonic converters for biomedical hyperthermia. Besides, the combination of both Au NPs and dyes offers

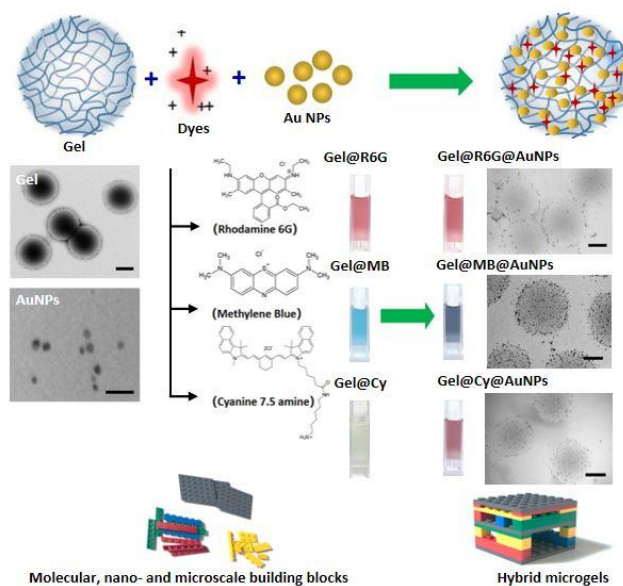


Figure 1. Smart combination and assembly of cationic molecular linkers (fluorescent dyes), negatively charged inorganic NPs (Au NPs) and polyanionic microgels. Scale bar = 200 nm except for AuNPs (scale bar = 20 nm).

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added-value property for photoacoustic imaging. Such hybrid particle thus not only combine the remarkable physico-chemical features of each component but also display synergetic properties that open promising prospects for a broad range of biomedical applications, including photoacoustic, Raman imaging and phototherapy.

References:

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Thematic Session: Nanomaterials and nanocomposites

Keywords: Graphene, functionalization, polymer blends, percolation, electrical conductivity

Control of graphene localization in co-continuous PMMA/PS polymer blends via chemical modification for electrical applications

Thibaut LALIRE¹, Belkacem OTAZAGHINE¹, Claire LONGUET¹, Aurélie TAGUET¹

1. *Polymers Composites and Hybrids (PCH), IMT Mines Ales, Ales, France*

Nanocomposites containing polymer matrix and graphene appear to be one of the most innovative electrical conductive materials. However, the difficulty to disperse graphene and exfoliate it in polymeric phase forces to incorporate high amounts of graphene to obtain high electrical property. The challenge is to control graphene exfoliation and localization in immiscible polymer blends, in order to reduce its amount while having an improvement of the electrical conductivity.

By using polymer blends and controlling the localization of graphene in the blend, the percolation threshold can be decreased [1]. In this context, the present study is focusing on the chemical modification of graphene in order to improve and localize its dispersion into polymer blends. PMMA/PS co-continuous blend was prepared by melt mixing. The continuous interface, which separates the two polymers, will be the future location of graphene to form a percolated network. To exfoliate the graphene and guide the platelets at the interface of the blend during the compounding, oxidation treatments followed by grafting reactions, with PS based copolymers, were performed. As exfoliated graphene grafted with PS (GO-g-PS) has more affinity with PS, it was first dispersed in PMMA, and then PS was added during melt mixing. Hence, the GO-g-PS functionalized graphene migrated to the interface during the process.

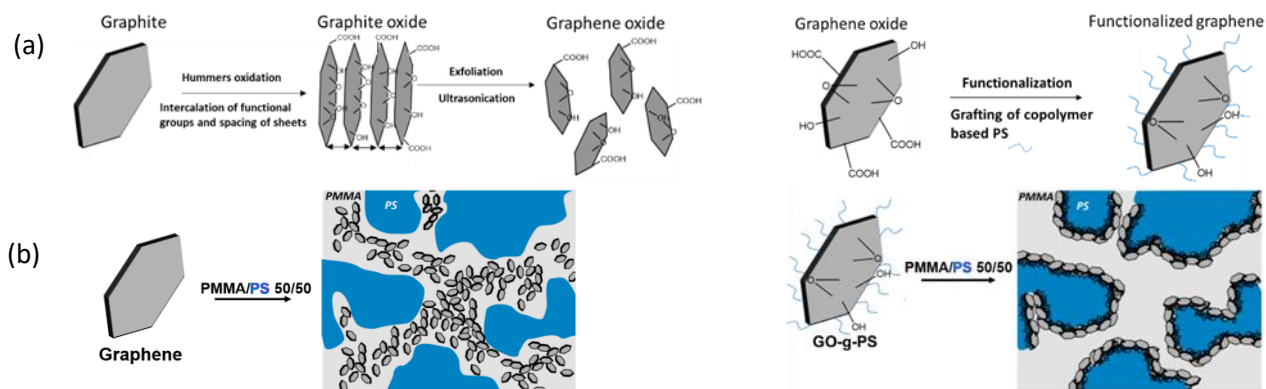


Figure 1 – (a) Scheme of the graphene oxidation and functionalization, (b) Scheme of the pure and functionalized graphene localized in one phase and at the interface of the polymer blend, respectively

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Thematic Session: *Multifunctional nanocomposites*

Keywords: Spin crossover, actuators, nanocomposites, nanoparticles

Controllable, resilient and efficient artificial muscles based on spin-crossover/polymer nanocomposites

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The development of artificial muscles is a rapidly growing field of research and concerns flexible and soft materials able to deform themselves to move or to adapt their shape to accomplish specific tasks. The development of new versatile materials is thus essential for this field. Spin crossover (SCO) materials have been investigated before as the basis for actuators due to the fact that they present a reversible phase transition accompanied by a significant volume change [1]. The nanocomposite approach, where nanoparticles of SCO complexes are dispersed in a polymeric matrix, has allowed for the elaboration of conductive actuators [2], micro electromechanical cantilevers [3] and 3D printed actuators [4]. In the present work, we highlight the development of a highly controllable, electrically driven SCO polymeric actuator. We use a nanocomposite approach to confer a polymer matrix with novel conductive and actuating properties, and through careful tuning of the morphology of the nanocomposite, amplify the effect of the volume change of the SCO complexes.

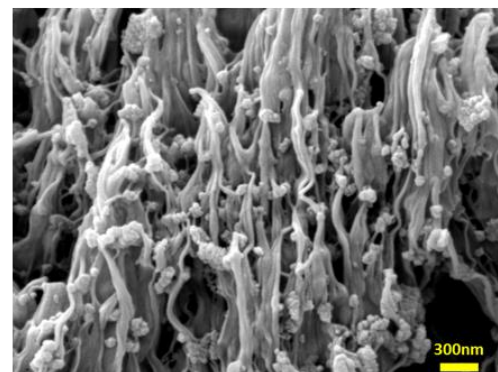
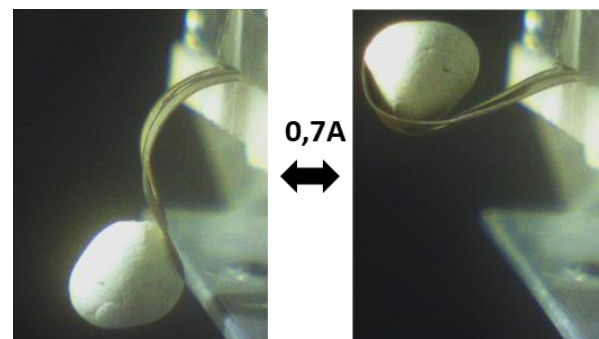


Figure 1. Electrically driven actuation of a spin crossover artificial muscle lifting a mass equivalent to 800% of the actuators weight (up). SEM imagery of the cross section of a SCO/polymer nanocomposite showing the spherical complex nanoparticles embedded in the polymer fibers.

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Acknowledgment: This work was supported by the Federal university of Toulouse/Région Occitanie (PhD grant of MPB)

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Thematic Session: (Nano for Imaging, diagnosis & therapy)

Keywords: (polymers, hybrid assemblies, gold nanoparticles and metallic ions)

Gold nanoparticles-Gadolinium ions-Polymers Hybrid Assemblies

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The spontaneous assembly of double hydrophilic block copolymers induced by the complexation of metal ions, represents a simple approach to access nanometric-sized Hybrid Polyionic Complexes (HPICs) colloids. HPICs formed by the addition of Gd^{3+} trivalent ions to a double hydrophilic block copolymer poly(acrylic acid)-*b*-poly(ethylene oxide) (PEO_{6k}-*b*-PAA_{3k}) have been developed in the team and used as a contrast agent for Magnetic Resonance Imaging. [1]

We investigated the possibility of extending this strategy to systems including a third component, namely gold nanoparticles.

We have shown that the assembly process is sensitive to the local environment around the nanoparticles and depends of the amount of Gd^{3+} ions and of polymer. The formation of the objects was studied by UV-Vis, MET, DLS, NTA spectroscopy. The findings presented here may assist in the design of optimized nanoscale assembly as multifunctional nanoplatform allowing the combination of multiple-modal imaging techniques with great potential for precision theragnostic nanomedicines.

References :

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Nanoscale Mechanical and Electrical Characterization of the Interphase in Polyimide/Si₃N₄ Nanodielectric Materials

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Abstract:

Nanodielectrics, which are composed of nanofillers embedded in a polymer matrix, present attractive properties for a lot of applications as electrical engineering or power electronic. Indeed, for a low amount of nanofillers, the nanodielectric presents improved properties compared to the bare matrix. This phenomenon was attributed to the formation of an interphase area around nanofillers with properties different from the matrix and the filler ones [1]. In this context, the determination of the interphase properties appears crucial to control the nanodielectric specifications.

In this study, interphase properties in a polyimide/silicon nitride (PI/Si₃N₄) nanocomposite are investigated. For that, three modes derived from Atomic Force Microscopy (AFM) are used: the Peak Force Quantitative Nanomechanical (PFQNM) to probe the interphase thickness [2], the Electrostatic Force Microscopy (EFM) to probe the interphase dielectric permittivity and the Kelvin Probe Force Microscopy (KPFM) to follow the injected charge dynamic in the interphase region [3]. Measurements are performed on an isolated nanoparticle protruding on the surface.

According to results, the interphase presents a higher Young modulus and a lower dielectric permittivity than the PI matrix, which indicates that polymer chains are well organized or movement are restricted at the interphase. Moreover, according to KPFM measurement the interphase induces a charge cloud spreading and a charge decay increase after injection. This could imply that the interphase presents a higher electrical conductivity than the matrix one. The correlation between these nanoscale results and the macroscopic properties modification is a primordial step in the way to understand nanodielectrics behavior for a given application.

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