

Conférence annuelle sur la recherche des **matériaux fonctionnels**



Advanced Materials Annual Conference

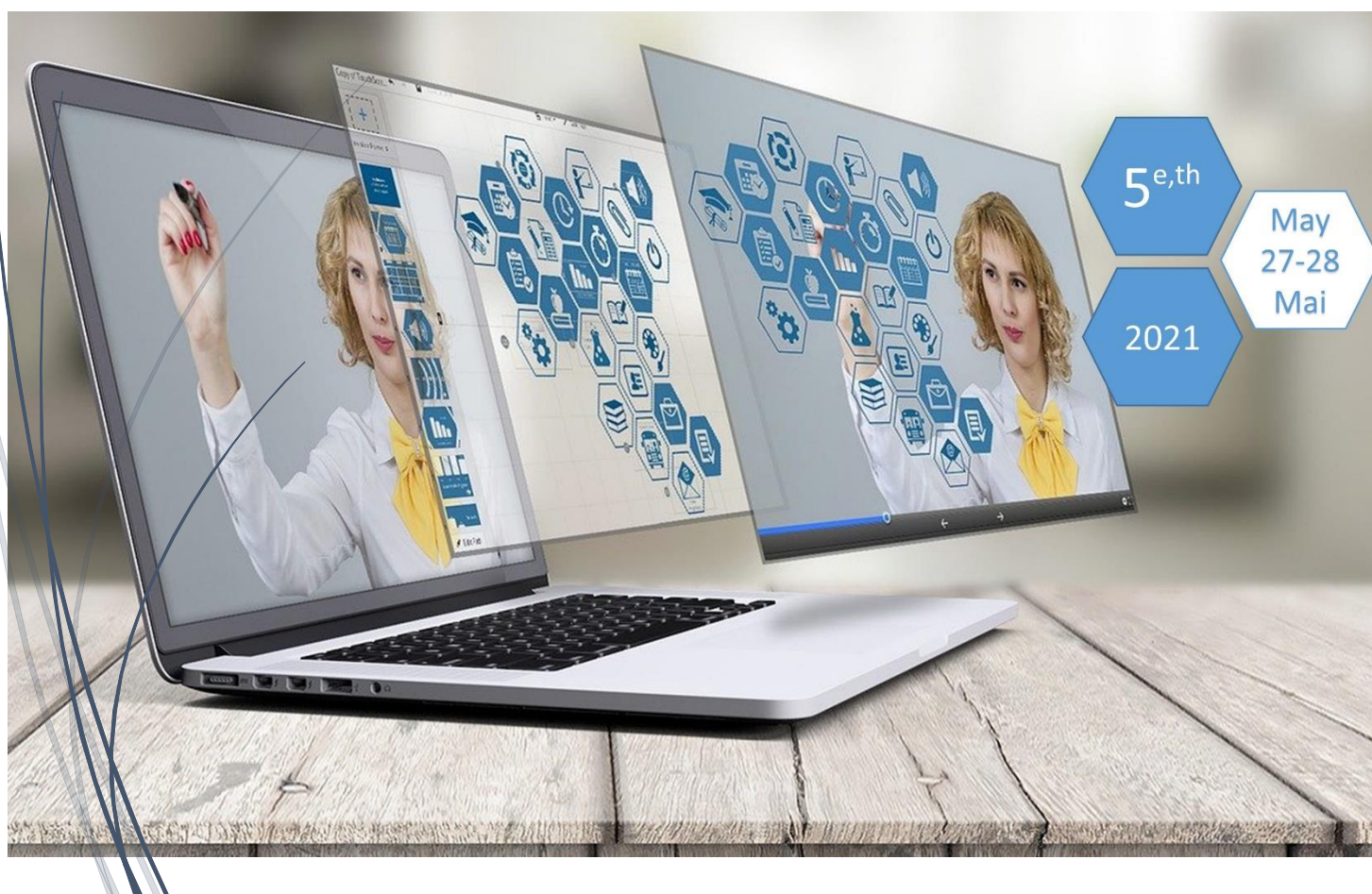


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Horaire

Jeudi 27 mai, 2021

9h00- 9h30 : Mots de bienvenue

Theo van de Ven, *McGill*, directeur du CQMF

9h30-10h15 : Conférence plénière **Élodie Boisselier**, Université Laval, Québec- *Matériaux fonctionnels à base d'or pour le traitement des maladies oculaires*

10h15-11h00 : Conférence plénière **Prashant Kamat**, Université de Notre Dame, Indiana- *Conversion de l'énergie lumineuse avec des nanostructures semi-conductrices : Des points quantiques aux pérovskites.*

11h00-11h20 : Pause-café/Expo virtuelle

11h20-11h35 : Présentation SFR commandite **Platine**, **David Polcari**, directeur des affaires Québec – *Progrès des techniques de caractérisation des surfaces en 3D*

11h00-12h05 : Séances thématiques AM

12h05-12h25 : Lunch

12h25-12h55 : Lunch&learn SFR webinaire, **S.H. Lau**, applications scientifiques - *Repousser les limites de la chimie, des états de valence et de l'imagerie structurale.*

13h00-13h45 : Conférence plénière, **Ian Manners**, Université de Victoria, Colombie Britannique - *Auto-assemblage contrôlé d'amphiphiles polymères pilotés par la cristallisation*

13h45-14h00 : Présentation Perkin Elmer commandite **OR**, **Brian Wong**, applications scientifiques- *Analyse des gaz émanants : techniques couplées*

14h00-14h30 : Séances thématiques PM

14h30-15h00 : Pause-café/Expo virtuelle

15h00-16h00 : Présentation Blue Solution commandite **OR**, **Olivier Rynne**, Concepteur Electrochimie et Matériaux - Vers la batterie tout-solide du futur 

15h15-16h00 : Séances thématiques PM (suite)

16h00-16h30 : Session d'affiches Partie 1/ Expo virtuelle

16h30-17h00 : Session d'affiches Partie 2

17h00-17h30 : Session d'affiches Partie 3

17h30-18h00 : Session d'affiches Partie 4

Horaire

Vendredi 28 mai, 2021

9h20 : Bienvenue aux participants

9h30-10h15 : Conférence plénière **Xia Li**, Université Concordia, Québec- *Développement de batteries de nouvelle génération, sécuritaires et performantes*

10h15-11h00 : Conférence plénière **Bart Kahr**, Université New York, New York- *Croissance de cristaux hélicoïdaux et transport de charges.*

11h00-11h20 : Pause-café/Expo virtuelle

11h20-12h20 : Séances thématiques AM

12h20-13h00 : Lunch

13h00-13h45 : Conférence plénière, **Julia R. Greer**, Caltech, Californie - *Matériaux par le Design: 3D Méta-matériaux nano-architecturés*

13h45-14h30 : Séances thématiques PM

14h30-15h00 : Pause-café/Expo virtuelle

15h00-16h00 : Séances thématiques PM (suite)

16h00-16h30 : Remise des prix par SFR et mot de clôture

Conférences plénières / Plenary lectures

Functional gold-based materials for the treatment of eye diseases



Élodie Boisselier

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Faculty of Medicine, Université Laval*

Résumé/Abstract

A large number of drugs are administrated on different mucosal surfaces, such as the ocular mucosa. However, due to the poor mucoadhesion of the current formulations, their bioavailability is often very low. The development of efficient mucoadhesive drug delivery systems is thus crucial for improving the performance of these drugs. We investigated the mucoadhesive properties of gold nanoparticles. The different techniques used to study the gold nanoparticles strongly highlighted their mucoadhesive properties, which can be modulated through the use of peripheral thiol groups. Moreover, for their use in nanomedicine, gold nanoparticles need to be ultrastable. We developed a new synthesis leading to their resistance against ultracentrifugation, heat treatments, autoclave sterilization, salts exposure and freeze-drying cycles. Their cytotoxicity was also assessed with human corneal epithelial cells and human tissue engineered corneas at different doses. Eventually, since it is known that gold nanoparticles have good drug encapsulation properties, it should be possible to produce gold nanoparticles for drug delivery that are highly mucoadhesive and that would improve the medication thanks to their longer residence time on their mucous target. In particular, medication for ocular diseases, requiring topical application on the corneal mucosa, might be enhanced. Due to their unique properties, gold nanoparticles have thus a great potential to be used as drug delivery system for various eye diseases.

Light Energy Conversion with Semiconductor Nanostructures: From Quantum Dots to Perovskites.



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Résumé/Abstract

Semiconductor nanostructures with tunable photoresponse can capture the visible and near IR photons quite effectively. By controlling the size and composition one can tune the photoresponse of semiconductor nanostructures in the entire visible region. Assembling these nanostructure assemblies on electrode surfaces in a controlled fashion is an attractive approach for designing next generation solar cells. The key advantage of semiconductor nanostructures lies in designing thin film solar cells with low temperature processing. These advantages significantly decrease the energy payback time since less energy is consumed (and hence a lower carbon footprint) during their manufacture.

The early studies which focused on the synthesis of semiconductor quantum dots and elucidation of charge carrier dynamics have led to the evolution of high efficiency metal halide perovskite solar cells. In the present talk light induced charge carrier generation and transport across interfaces which are important in the operation of solar cells will be discussed. Photoinduced segregation in mixed halide perovskite has a direct influence on decreasing the solar cell efficiency as segregated I-rich domains serve as charge recombination centers.⁵ Recent developments in utilizing semiconductor quantum dots in light energy conversion will be discussed.

Additional Readings

- [1] Manser, J. S.; Christians, J. A.; Kamat, P. V., Intriguing Optoelectronic Properties of Metal Halide Perovskites. *Chem. Rev.* **2016**, *116*, 12956–13008.
- [2] Kamat, P. V. Semiconductor Surface Chemistry as Holy Grail in Photocatalysis and Photovoltaics. *Acc. Chem. Res.* **2017**, *50*, 527-531.
- [3] Brennan, M. C.; Draguta, S.; Kamat, P. V.; Kuno M. K. Light-Induced Anion Phase Segregation in Mixed Halide Perovskites ACS Energy Lett., **2018**, *3*, 204–213
- [4] DuBose, J. T.; Kamat, P. V., Probing Perovskite Photocatalysis. Interfacial Electron Transfer between CsPbBr₃ and Ferrocene Redox Couple. *The Journal of Physical Chemistry Letters* **2019**, *10*, 6074-6080.
- [5] Kamat, P. V.; Kuno, M., Halide Ion Migration in Perovskite Nanocrystals and Nanostructures. *Accounts of Chemical Research* **2021**, *54* (3), 520-531.

Controlled Self-Assembly of Polymeric Amphiphiles Driven by Crystallization



Ian Manners

Department of Chemistry, University of Victoria, Canada

Résumé/Abstract

Molecular, and more recently, macromolecular synthesis has evolved to an advanced state allowing the creation of remarkably complex organic molecules and well-defined polymers with typical dimensions from 0.5 nm - 10 nm. In contrast, the ability to prepare materials in the 10 nm – 100 micron size regime with controlled shape, dimensions, and structural hierarchy is still in its relative infancy and currently remains the virtually exclusive domain of biology.

In this talk recent developments concerning a promising “seeded growth” route to well-defined 1D and 2D nano- and microparticles termed “living” crystallization-driven self-assembly (CDSA), will be described. Living CDSA can be regarded as a type of “living supramolecular polymerization” that is analogous to living covalent polymerizations of molecular monomers but on a much longer length scale (typically, 10 nm – 5 microns). Living CDSA also shows analogies to biological “nucleation-elongation” processes such as amyloid fiber growth.

The building blocks or “monomers” used for living CDSA consist of a rapidly expanding range of crystallizable amphiphiles such as block copolymers, homopolymers with charged termini, or planar π -stacking molecules with a wide variety of chemistries. The seeds used as “initiators” for living CDSA are usually prepared from preformed polydisperse 1D or 2D micelles by sonication.

Recent results indicate that living CDSA is scalable, which will help enable applications in areas such as optoelectronics, catalysis, and biomedicine, and recent examples of work by our group and our collaborators in these areas will be discussed.¹⁻⁴

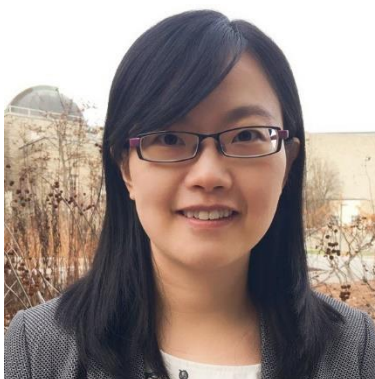
1. Jin, X.-H.; Price, M.B.; Finnegan, J.R.; Boott, C.E.; Richter, J.M.; Rao, A.; Menke, M.; Friend, R.H.; Whittell, G.R.; Manners, I. *Science*, 2018, 360, 897.

2. Cai, J.; Li, C.; Kong, N.; Lu, Y.; Lin, G.; Wang, X.; Yao, Y.; Manners, I.; Qiu, H. *Science*, 2019, 366, 1095.

3. Tian, J.; Zhang, Y.; He, Y.; Jin, X.-H.; Pearce, S. Eloi, J.-C.; Harniman, R.L.; Alibhai, D.; Ye, R.; Phillips, D.L.; Manners, I. *Nat. Chem.*, 2020, 12, 1150.

4. Street, S.; He, Y.; Jin, X.; Hodgson, L.; Verkade, P.; Manners, I. *Chem. Sci.*, 2020, 11, 8394.

Development of Safe and High Performance Next Generation Batteries



Xia Li

Department of Chemical and Materials Engineering, Concordia University

Résumé/Abstract

Among the various energy storage devices, lithium-ion batteries, with their high energy density, scale flexibility, and low maintenance cost, have been successfully applied in our daily life. However, the intrinsic limitation of safety and energy densities of battery materials make the conventional lithium-ion batteries approaching a bottleneck in the near future. Therefore, Dr. Xia Li's research focuses on the development of next-generation batteries beyond conventional Li-ion batteries to overcome the challenges in practical application. In this talk, Dr. Li will present her research on how to understand and design the key materials in next-generation batteries, such as lithium-sulfur batteries and all solid-state batteries.

Helicoidal Crystal Growth and Charge Transport



Bart Kahr

Molecular Design Institute at New York University, NY, USA

Résumé/Abstract

Crystals are straight, by definition. They have sharp edges and flat faces. They are polyhedra. However, molecular crystals that twist as they grow are common, a fact poorly recognized. More than one third of simple molecular crystals are capable of forming twisted morphologies including aspirin, paracetamol, coumarin, DDT, malic acid, and many other common, long-studied molecular materials. The growth and micromorphologies of twisted crystals are discussed. Simulations aimed at understanding when and why crystals sacrifice their long-range translational symmetry will be presented. Meanwhile, crystal twisting introduces a new dimension to materials design. Plastic electronic devices, e.g. foldable LCD screens, smart phones, computers, and solar panels, may depend on organic crystals that carry electricity. We investigate the role twist on the propagation of charge in organic semiconductors. Is charge mobility greater or lesser in a twisted crystal than in its straight configuration? Answers to this question will be provided.

A. G. Shtukenberg, Y. Yang, X. Zhu, B. Kahr, Common occurrence of twisted molecular crystal morphologies from the melt, *Cryst. Growth Des.* **2020**, *20*, 6186-6197. 10.1021/acs.cgd.0c00908
A. G. Shtukenberg, Yu. O. Punin, A. Gujral, B. Kahr, Growth actuated bending and twisting of crystals, *Angew. Chem. Int. Ed.* **2014**, *53*, 672–699. doi: 10.1002/anie. 201301223

Materials by Design: Three-Dimensional (3D) Nano-Architected Meta-Materials



Julia R. Greer

California Institute of Technology, CA, USA

Résumé/Abstract

Creation of extremely strong and simultaneously ultra lightweight materials can be achieved by incorporating architecture into material design. In our research, we design and fabricate three-dimensional (3D) nano-architected materials that can exhibit superior and often tunable thermal, photonic, electrochemical, biochemical, and mechanical properties at extremely low mass densities (lighter than aerogels), which renders them useful, and often enabling, in many technological applications. Dominant properties of such meta-materials are driven by their multi-scale nature: from characteristic material microstructure (atoms) to individual constituents (nanometers) to structural components (microns) to overall architectures (millimeters and above).

Our research is focused on fabrication and synthesis of nano- and micro-architected materials using 3D lithography, nanofabrication, and additive manufacturing (AM) techniques, as well as on investigating their mechanical, biochemical, electrochemical, electromechanical, and thermal properties as a function of architecture, constituent materials, and microstructural detail. The focus of this talk is on additive manufacturing via function-containing chemical synthesis to create 3D nano- and micro-architected metals, ceramics, multifunctional metal oxides (nano-photonics, photocatalytic, piezoelectric, etc.), shape memory polymers, etc., as well as demonstrate their potential in some real-use biomedical and sensing applications. I will describe how the choice of architecture, material, and external stimulus can elicit stimulus-responsive, reconfigurable, and multifunctional response.

1. Xia, X., Afshar, A., Yang, H., Portela, C.M., Kochmann, D.M., Di Leo, C.V., Greer, J.R. "Electrochemically Reconfigurable Architected Materials" *Nature*, 573 (7773) 205 (2019).
2. Narita, K., et al. "3D Architected Carbon Electrodes for Energy Storage" *Advanced Energy Materials*; 11 (5) (2021)
3. Yee, Daryl W.; Citrin, Michael A. et al. "Hydrogel-Based Additive Manufacturing of Lithium Cobalt Oxide" *Advanced Materials Technologies* 6 (2) (2021)
4. Yee, D., Lifson, M., Greer, J.R. "Additive Manufacturing of 3D Architected Multifunctional Metal Oxides" *Advanced Materials* 31, 1901345 (2019).
5. Vyatskikh, A., Ng, R. C., Briggs, R., Greer, J.R. "Additive Manufacturing of High- Refractive-Index, Nanoarchitected Titanium Dioxide for 3D Dielectric Photonic Crystals" *Nano Letters* 20 (5) (2020)
6. Portela, C. Vidyasagar, A., Greer, J.R., Kochmann, D. "Extreme mechanical resilience of self-assembled nano-labyrinthine materials" *Proceedings of the National Academy of Sciences, USA* 117 (11) (2020)
7. Portela, C.M., et al "Supersonic Impact Resilience of Nano-architected Carbon" *Nature Materials* (accepted, 2021)
8. L. R. Meza, S. Das, J. R. Greer "Strong, Lightweight and Recoverable Three-Dimensional Ceramic Nanolattices" *Science* 345, 1322-1326 (2014) à

Séances thématiques présentations étudiantes

Parallel student presentations

Unravelling phase separation behavior of A-D-A conjugated oligomers in supported lipid bilayers

Aya Sakaya, Yuxuan Che, Ghufra Rafique, Hanadi F. Sleiman, Dmitrii F. Perepichka, Gonzalo Cosa*

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Abstract— Interfacing electronic materials with living organisms presents tremendous benefits to the field of health sciences, such as for the development of diagnostic tools, sensors, and biomedical devices. We propose the use of acceptor-donor-acceptor (A-D-A) conjugated oligomers as transmembrane molecular wires that electrically connect the cell interior to its exterior. The A-D-A oligomers employed in this study demonstrated a remarkable photo-induced phase separation from their surrounding lipid membrane. In this work, the photophysical properties and photostability of these A-D-A oligomers are assessed in supported lipid bilayers, and the molecular mechanism behind the ensuing phase separation is investigated. We show that the phase separation of these A-D-A oligomers is singlet oxygen mediated and dependent on the structure of the acceptor end groups. We stipulate that singlet oxygen is leading to the formation of lipid hydroperoxides and to the oxidation of the A-D-A oligomers, resulting in unfavorable mixing of the newly formed products.

Novel synthesis pathway of carbon nanohorns by inductively coupled plasma

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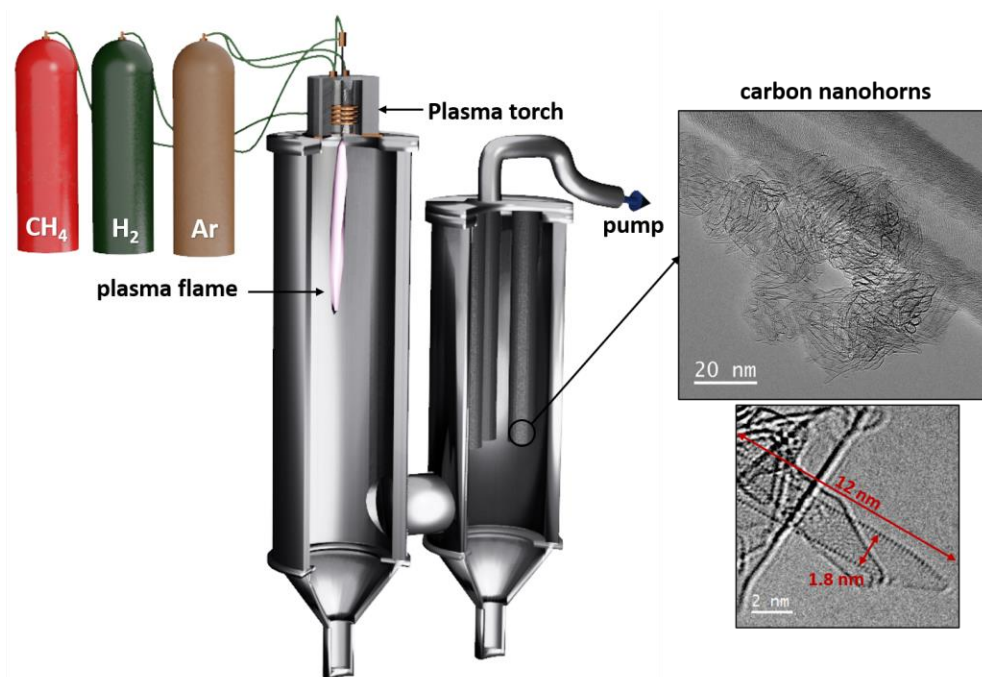
Christian Ricolleau

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Abstract—

Carbon nanohorns (CNHs) are conical structures that are closed on one side by a fullerene hemisphere with a diameter between 2 nm for the top and 5 nm for the base with 50 nm of length for ‘dahlia-like’ aggregates. Currently, there are three main CNHs synthesis pathway: (i) by CO₂ laser ablation method, (ii) by direct current (DC) arc-discharge and (iii) by direct vaporization of graphite. Contrary to carbon nanotubes (CNTs), all these syntheses of CNHs do not require any catalyst. Here, we present a novel pathway for the synthesis of CNHs in a reactor by using inductively coupled thermal plasma (ICTP) and gaseous precursors. Thermal plasma synthesis is known for the synthesis of different carbon allotropes such as carbon nanoflakes, carbon nanotubes, fullerenes, or graphitic capsules. We will discuss the impact of various parameters such as pressure, precursor composition on the CNHs formation affecting the carbon nanostructures formed. The various morphologies were determined by TEM and aberration-corrected HREM. In some cases, molecular dynamics combined to multi-slice simulation helped assess the size, orientation and the nature of defects found in these CNTs.

Keywords— carbon, nanohorns, plasma, synthesis, microscopy



Aptamer-based biosensors and T-cell inhibitors development for costimulatory molecules in Rheumatoid Arthritis

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Abstract— Rheumatoid Arthritis (RA) is a chronic inflammatory disease that causes local inflammation in synovial joints (synovitis), resulting in the erosion of bones and the destruction of joints. The inflammation process in RA involves T-cell activation through two signals. One of these signals is the costimulatory pathway (CP) (CD28-B7), where the cluster of differentiation (CD80 and CD86) proteins interact with the CD28 and activate T-cells. CTLA-4 is another co-stimulatory protein that interacts with the same antigens, i.e., CD80 and CD86, which results in an adverse immune response. CD80, CD86, and CTLA-4 could be considered as potential biomarkers for RA and other inflammatory diseases. The detection and measurement of costimulatory molecules in different biological fluids are commonly carried out using an immunoassay-based technique, such as Enzyme-linked Immunosorbent Assay (ELISA). Aptamer-based biosensor methods are fast, sensitive, relatively inexpensive, and do not require animals for antibody production. Herein, we develop aptamers (single-stranded DNA, ssDNA)- based biosensors for CD80/CD86 and CTLA-4 biomarkers for RA diagnosis, prognosis, and treatment monitoring. The systematic evolution of ligands by exponential enrichment (SELEX) was performed to select the specific aptamers for CD80 and CD86, and next, for CTLA-4. The selected aptamers will be used as the recognition elements for developing electrochemical-based biosensors. On the other hand, the selected aptamers for CD80 and CD86 will be further studied to evaluate their T-cell inhibition effect by blocking (CP) (CD28-B7) using multiple reaction monitoring liquid chromatography-mass spectrometry method (MRM) LC-MS/MS. Target proteins' signature peptides were determined using standard proteins analyzed on the high-resolution mass spectrometry (HR-LC-MS) and synthesized as standard material for (MRM) LC-MS/MS method development.

Keywords—*Rheumatoid Arthritis; Biomarkers; Costimulatory pathway; Aptasensor; Multiple Reaction Monitoring*

Fluorescence spectroscopy to confirm a photobattery concept : study of the electronic transfer implied

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Abstract— An all-in-one photobattery will be presented as a portable device that couples lithium-ion batteries and a dye-like sensitized solar cell. Fluorescence spectroscopy was used to demonstrate the feasibility of the all-in-one device along with electrochemical testing.

Keywords— Dye-sensitized solar cell, lithium-ion battery, photobattery, electronic transfer, quenching

I. INTRODUCTION

Addressing the current global energy consumption needs and reducing the carbon footprint that is associated with the use of primary non-renewable energy resources are key challenges of the 21st century. Solar energy is among the best suited candidates to that end. This is in part because it can contribute to lowering greenhouse emissions. However, the energy provided by the sun is intermittent and then must be stored for use during dark periods. Devices that convert, store, and deliver the stored energy during dark periods are therefore of importance.

II. CONCEPT

To date, proven technologies with high energy density along with a long cycle life, lithium-ion batteries have been chosen

and successfully coupled to silica-based solar cells such as photovoltaic panels. To expand upon these proven solar-battery technologies and move towards self-sustaining and portable energy devices, we merged a lithium-ion battery with a photoactive organic dye. The working principle of this all-in-one device is based on a new photo-electrode, thus allowing the energy harvesting from sun light with the organic dye and the direct storing as chemical energy courtesy of redox reactions that are specific to the lithium-ion battery.

III. EXPERIMENTAL

Both steady-state and time-resolved emission quenching measurements will be presented as sound evidence for electron transfer between the constitutional “solar” and “battery” components. Electrochemical studies will also be presented to show the performance of the modified electrode and the compatibility of its components. Towards this end, galvanostatic cycling with various photo-cathode architectures with the dye along with post-cycling chemical analyses of the different photoactive and battery components will be presented. Replacing conventional battery solvents with environmentally benign water will also be illustrated.

Morphology and surface chemistry engineering the novel MoSe₂/Mo₂C hybrid electrocatalysts for high-performance hydrogen evolution reaction

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Abstract— For more energy-efficient and economical hydrogen production, highly active noble metal-free hydrogen evolution catalysts are a priority for all. Here, we address these challenges by exploring the roles of the morphology and the surface chemistry of the electrocatalysis for hydrogen evolution reaction. The model electrocatalyst that will be presented is molybdenum diselenide (MoSe₂) microspheres modified by molybdenum carbide (Mo₂C) nanoparticles. A comparison between pure MoSe₂, pure Mo₂C and MoSe₂-Mo₂C electrodes shows that the MoSe₂-Mo₂C hybrid electrocatalyst is highly active for hydrogen evolution with low onset overpotentials of 67 mV in acidic medium (figure 1). Based in our data, it can be concluded that the hybrid nanostructured material could improve the surface-active area which yields to a higher hydrogen evolution reaction (HER) catalytic activity. The present study provides a simple and effective way for the exploration of efficient Mo-based HER catalysts.

Keywords —Hybrid; molybdenum diselenide ; molybdenum carbide; hydrogen evolution reaction

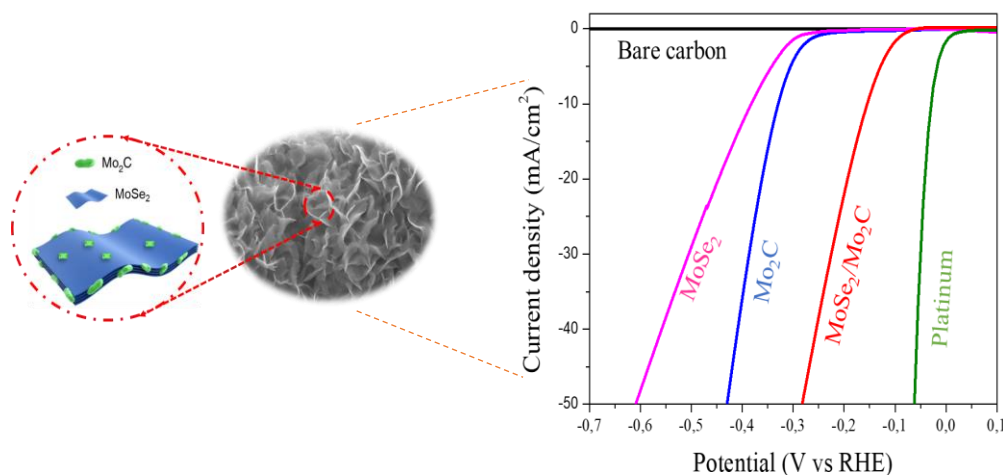


Figure 1: Electrochemical measurements of MoSe₂, Mo₂C, MoSe₂/Mo₂C products: Polarization curves

Stable and Porous 2D Layered structures of Mixed-Linkers Coordination Polymers for Gas Sorption Studies

Layered structures of flexible mixed-linkers metal-organic frameworks termed IRHs-(4 and 5) (IRH= Institut de Recherche sur l'Hydrogène) were synthesized and fully characterized. The two isostructural materials characterized by single-crystal X-ray diffraction exhibited the features of HOFs and MOFs. Their structures are formed by coordination and hydrogen bonds that link the transition metal macrocycles and the tetratopic acid to a 2D sheet which are further packed to form a 3D structure with 1D microchannels. Remarkably, IRHs-(4 and 5) as-synthesized contain DMF in the channels that can be exchanged with DCM and afterward removed from the framework by heating without losing the single-crystallinity. This enabled an easy elucidation of the structural transformations by single-crystal and powder X-ray diffractions. Experimental studies of single-component adsorption isotherms of pure CO₂, CH₄, and N₂ gases have been investigated for all activated IRHs. Based on the obtained adsorption isotherms, theoretical calculations using Ideal Adsorbed Solution Theory (IAST) has been performed to predict the selectivity of equimolar CO₂/CH₄ and CO₂/N₂ (1:1) binary mixtures. The simulations predicted outstanding selectivity for CO₂/N₂ than CO₂/CH₄ at low pressures, reaching 185 for IRH-4 and 130 for IRH-5 at 1 bar.

Use of azulene based polymers in graphene dispersion for printed electronics

Guillaume CHAMELOT

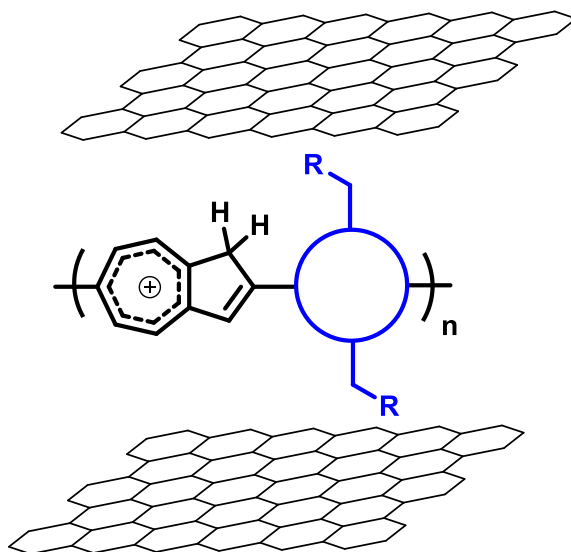
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Organic semiconductors for printed electronics have been intensively studied over the last decade for a wide range of applications, including organic solar cells, RFID tags or OLEDs. One of the most used materials for printed electrodes is silver nanoparticles due to their high conductivity and processability. However, silver nanoparticles suffer from poor chemical stability, toxicity, and high price. Thus, the development of new materials for ink formulation is needed to make printed electronics a viable alternative to traditional fabrication methods. In this regard, graphene inks, which consist of stable dispersions of graphene flakes in a solvent, offer several advantages such as good chemical stability and low environmental impact. However, the conditions used for the preparation of graphene dispersions are not ideal for printing as it often involved the use of high boiling point, toxic solvent like NMP and DMF. When these solvents are replaced by low boiling point solvents, the use of a significant amount of non-conducting surfactants such as polyvinyl alcohol (PVA) or sodium cholate is necessary to stabilize the colloidal suspension, decreasing the conductivity values of the resulting printed graphene film.

To overcome these issues, we propose to use water-soluble π -conjugated polymers to stabilize graphene. More precisely, we aim to synthesize azulene-based polymers with different co-monomers containing solubilizing groups in lateral chains. We expect the enhancement of the π - π interactions to provide stable suspensions that exhibit, once printed, sufficient conductivity values to enable its use as electrode material in printed electronics.



Graphene; liquid phase exfoliation; polymers; conductive ink

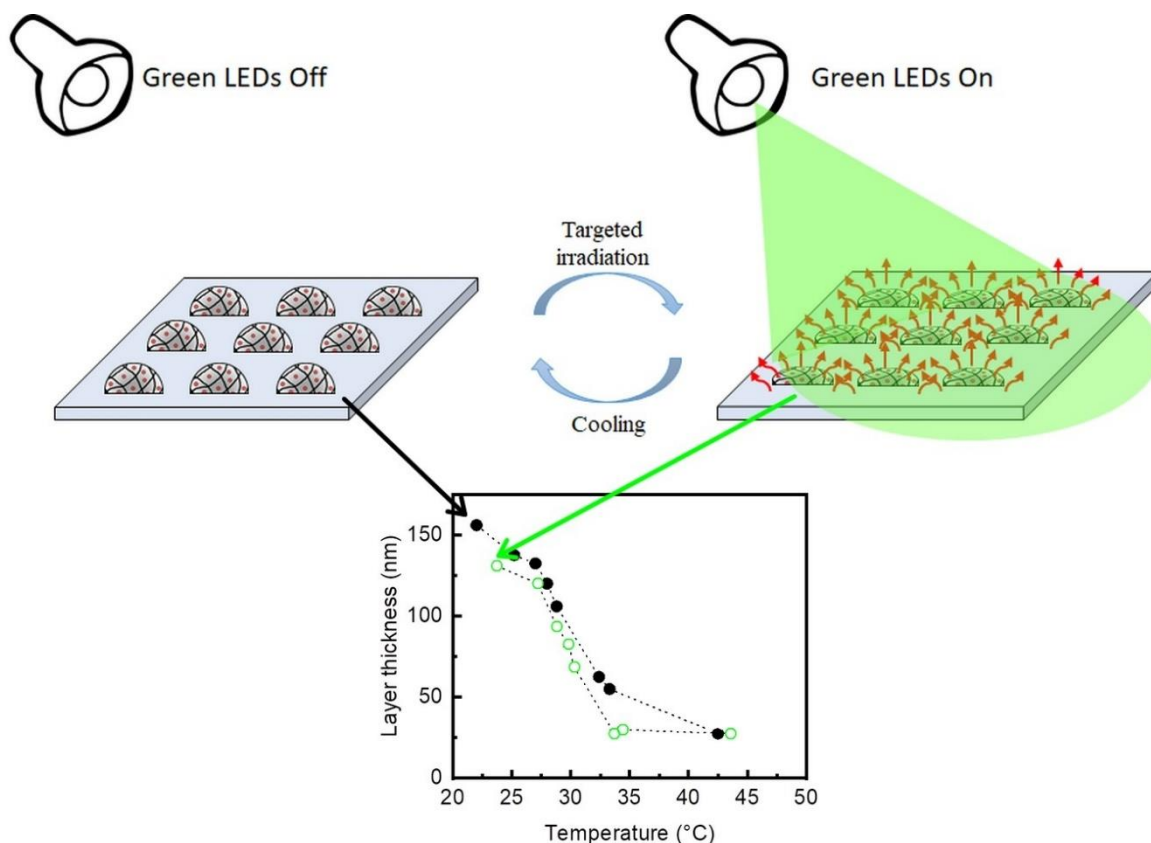
Enhanced Swelling Using Photothermal Responsive Surface-Immobilized Microgels

Charly Ou^{1a}, Suzanne Giasson^{1a,1b*}

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Abstract :

Unprecedented quantitative assessment of the swelling behavior of surface-immobilized photothermal responsive microgels (PTRM) will be presented. Controlling the swelling behavior of thermo-responsive hydrogel using light provides an interesting non-contact way to tune surface properties. The PTRM consist of gold nanoparticles (AuNPs) embedded in thermo-responsive microgels. The dual responsive behavior of the microgels was investigated in aqueous suspensions using Dynamic Light Scattering and on surfaces using the Surface Forces Apparatus. This talk will show how the photo-induced swelling response of PTRM coatings can be enhanced compared to that in suspension. Such enhanced photo-induced swelling provides a very useful tool for the design of responsive surfaces to be used at sub-microscale such as in micro- and nano-fluidic devices.



Modified hairy nanocrystalline celluloses as photobactericidal nanofillers for food packaging application

Photobactericidal hairy nanocrystalline celluloses

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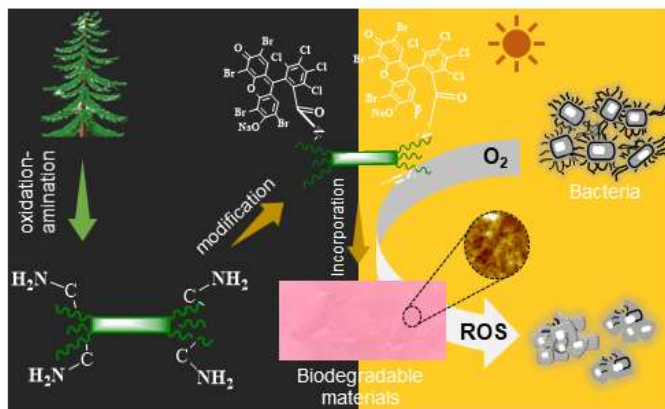
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Abstract— Due to a soaring population growth, reliable access to safe food has turned into a global challenge. One of the most effective strategies for controlling foodborne pathogens is to develop antimicrobial materials/surfaces that are in a direct or an indirect contact with foods. However, the extensive use of the antibacterial substances such as antibiotics, fungicides, antiviral drugs, etc., has become a great threat to human health due to the emergence of antimicrobial-resistant bacterial strains. As an alternative to the conventional antimicrobial agents to eliminate/reduce bacteria, we developed a photobactericidal hairy nanocrystalline cellulose as a bionanofiller for engineering self-disinfecting food packaging. A new version of hairy nanocellulose functionalized with a high density of primary amine groups called ANCC was for the first time synthesized. Rose bengal (RB), as a natural photosensitizer, was then covalently linked to ANCC via an aqueous-based bioconjugation reaction, as confirmed by ^{13}C nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopies. Antibacterial effect of RB-ANCC conjugate was evaluated against two major foodborne pathogens, namely *Listeria monocytogenes* and *Salmonella enterica* serotype Typhimurium. RB-ANCC conjugate inactivated over 80% of both pathogens upon normal light irradiation. A remarkable photo-inactivation of *S. Typhimurium* was achieved using RB-ANCC in which cases free RB had no effect. We then selected two model materials (i.e., cellulose-based film and electrospun nanofibers) to incorporate RB-ANCC for further evaluating antimicrobial activity. It was identified that the activity was due to a combination of photodynamically generated reactive oxygen species by RB and an electrostatically-induced cell wall disruption by cationic ANCC. The developed RB-ANCC conjugate processed via green chemistry is regarded as a promising photobactericidal nanofiller and can be potentially used for food packaging.

Keywords— aminated hairy nanocrystalline cellulose; rose bengal; DMTMM coupling; photobactericidal; electrospun nanofibers; cellulosic films



Thermal annealing Effects on the Electrical Characteristics of Back-Gated tungsten diselenide Field-Effect Transistors (FET-WSe₂)

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Abstract— In this work, field effect transistors based on multilayers of tungsten diselenide were fabricated using gold / chromium (Au / Cr) as the metal contact in order to study the influence of the indisputable environmental effects on their electrical performance and therefore on the WSe₂ channel properties. These devices are characterized before and after thermal annealing (annealing under vacuum 10⁻⁵Torr at 400K) and at different measurements temperatures (ranging from 300K up to 10K) using a Physical Property Measurement System (PPMS). The results show that these FET-WSe₂ transistors exhibit n-type transport and the thermal annealing effected remarkably improved their characteristics. Indeed, electronic mobility increased by more than 5*10³ times upon annealing at 400 K in vacuum. This enhancement could be attributed to the removal of absorbed moisture and solvent molecules (oxygen, hydrogen and fictitious carbon).

Keywords— field effect transistors; WSe₂; thermal annealing; mobility; I_D-V_G characteristics; n-type transport.

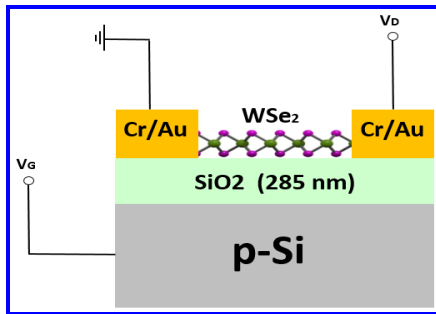


Fig1: Schematic representation of WSe₂ FET with highly p-doped silicon as the back gate

Recently the physics of charge transport in transition-metal dichalcogenides TMDs has been much studied since they are two-dimensional. Indeed, with two-dimensionality, we can observe quantum confinement effects on charge transport [1], which is very exciting. However, because they are so thin they are also prone to degradation by adventitious contaminants (oxygen, water, carbon). Hence, studying the effects of undesired environmental effects on their electrical performances can be very important to understand if something can be done to prevent such issues. Tungsten diselenide (WSe₂) is one of the most attractive two-dimensional transition

metal dichalcogenides due to its interesting electronic and mechanical properties which makes it a competitor to channel materials already studied in the field of electronics [2]. In the table1 are presented the characteristic parameters of FET-WSe₂ without and after (1st and 2nd) thermal annealing at 400K. A clear improvement in transistor performance is noticed following annealing. indeed, electronic mobility increased by more than 5*10³ times after second annealing, this increase is thought to be due to the rearrangement of WSe₂ atoms under the effect of thermal energy (removal of absorbed moisture and solvent molecules) [2,3]. The interface properties between the WSe₂ and the silicon dioxide SiO₂ seemed to be improved.

Table1: Device parameters FET1 – WSe₂

Parameter at 300 K	Before 1 st annealing	After first annealing (3 h)	After second annealing (14.5h)
$\mu_e(\text{cm}^2\text{V}^{-1}\text{s}^{-1})$	$2.4 * 10^{-3}$	9.14	14.15
$I_{ON}/I_{OFF}(\text{electron})$	$2.35 * 10^2$	$3.52 * 10^4$	$1.36 * 10^6$
$V_{th} \text{ (V)}$	-4.13	4.26	7.15
Subthreshold swing $S: \text{ (V/dec)}$	18,91	6.12	2.94
interface trap densities $D_{it} \text{ (eV}^{-1} \text{cm}^{-2})$	$2.41*10^{13}$	$7.75*10^{12}$	$3.68*10^{12}$

The Subthreshold swing $SS = dV_G / d \log(I_D)$ is 18.91V/dec and 2.94 V/dec without and after annealing (2nd annealing) respectively. The decrease in SS result from a decrease of the trap density at the WSe₂ / dielectric interface [4] implying a lower trap density when the device is annealed [2], which is in good agreement with the increase in electron mobility.

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Simple fabrication of Bioglass-Poly (lactic-co-glycolic acid) composite scaffolds with dual scale porosity: Effect of matrix microporosity on the bioactivity of the scaffold

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Abstract— Scaffold porosity plays an important role in bone tissue engineering as macropores promote cell migration and flow of nutrients and micropores promote protein adsorption and cell adhesion. Currently, there are no methods that can create dual scale porosity without complex, multi-step processes.

In our study, we developed a simple solvent casting and porogen leaching technique to prepare a macroporous (250-355 μm) Bioglass-Poly(lactic-co-glycolic acid)(BG-PLGA) composite scaffold with intrinsic micropores (1-10 μm) in the PLGA matrix using paraffin microspheres as a porogen and CitriSolv as the leaching solvent instead of hexane, the solvent usually used in this process. Micropores were formed only in the scaffolds leached with CitriSolv (C scaffolds) and not in those leached with hexane (H scaffolds). We compared C and H scaffolds to evaluate the effect of matrix microporosity on the bioactivity of the BG-PLGA composites by simulated body fluid (SBF) immersion tests and cell assays on both scaffolds.

We observed apatite formation on both scaffolds after 3 days of immersion in SBF, and larger apatite deposition on C after 7 and 14 days SBF immersion compared to H scaffolds. We could explain this because the microporous PLGA phase increases the surface area of the scaffold, leading to faster and larger apatite deposition and thus higher bioactivity of the composite scaffold. Microporosity in C scaffolds also enhanced protein adsorption onto the scaffolds. Both scaffold types supported cell adhesion, proliferation and differentiation, but cells cultured on C scaffolds produced thicker and more extensive extracellular matrix.

These results highlight PLGA leaching with CitriSolv as a simple and effective method to produce dual porosity scaffolds including both macropores and micropores that are excellent candidates for bone tissue engineering, as their greater bioactivity, protein adsorption and cellular matrix coverage as a result of high surface area are likely to lead to faster bone integration upon implantation.

Keywords—*microporosity; composite; bioactivity; scaffold; Bioglass; tissue engineering*

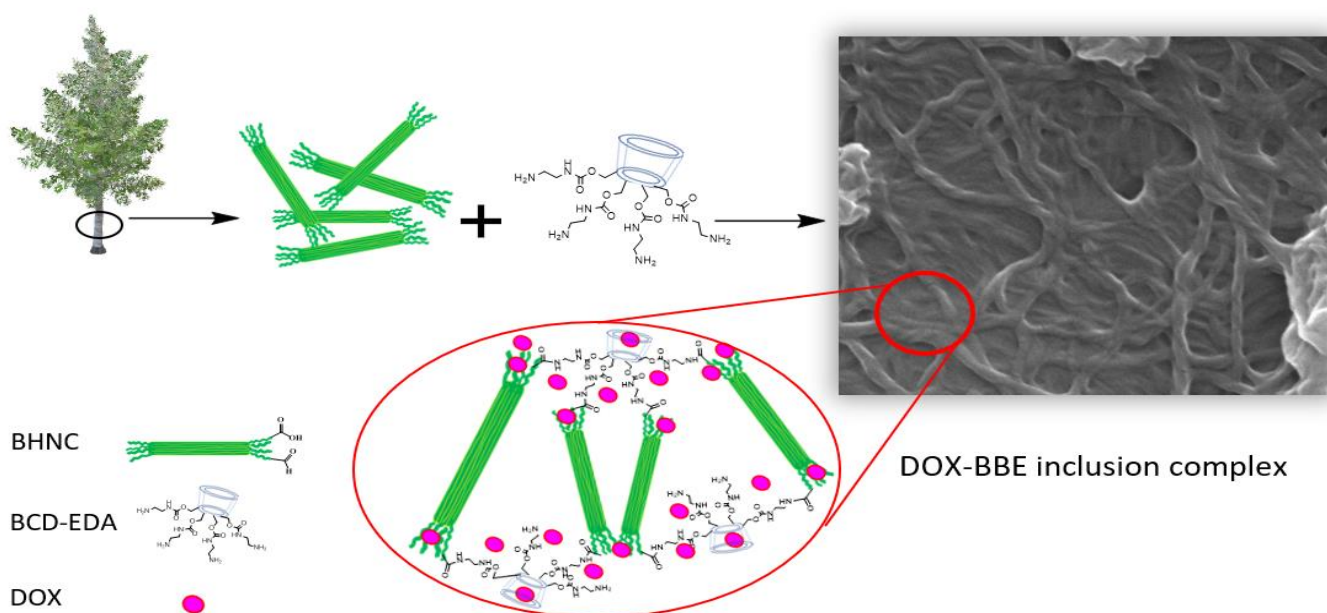
Polymer-based Beta-Cyclodextrin and Bifunctional Hairy Nanocellulose as biocompatible nanocarriers for Anti-Cancer Drug Delivery

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Abstract— Cellulose is the most abundant renewable biomaterial on earth and beta-cyclodextrin (BCD) is among the most commonly used biocompatible drug encapsulation agents. Combining these bio-organic materials is a very powerful approach to greatly enhance the bioavailability of many drugs. These systems also allow for optimal selective drug release profiles, high biocompatibility, as well as “green nanomedicine” approaches that are eco-friendly in their synthesis and have minimal ecological toxicity. In the present work, we designed a new type of green and biopolymer-based drug carrier which is polymerized by crosslinking beta-cyclodextrin ethylene diamine (BCD-EDA) with bifunctional hairy nanocellulose (BHNC). BHNC contains, besides aldehyde groups, carboxyl groups which can react with amino groups in BCD-EDA. Firstly, the crosslinker BCD-EDA was obtained through a simple nucleophilic substitution reaction between beta-cyclodextrin carbonyl imidazole (BCD-CI) and ethylene diamine (EDA). Secondly, BHNC was functionalized with the crosslinker BCD-EDA through a facile nucleophilic substitution crosslinking reaction of the BHNC activated carboxyl groups by the amines of BCD-EDA. We refer to the polymerized highly crosslinked BHNC-BCD-EDA network as BBE. Various ratios of BCD-EDA and BHNC were polymerized with the help of DMTMM as an activator, which resulted in different morphological shapes of BBE, and thus in different release profiles and pH-responsiveness. Unlike other polymer-based BCDs, these new types of crosslinked polymer were prepared in a green and safe solvent (water) and with very short reaction times and at low temperatures. Finally, the BBE polymers were tested as biocompatible nanocarriers for controllable doxorubicin (DOX) delivery. These hyper crosslinked polymers show a high capacity for loading DOX with extended drug release. Furthermore, breast cancer cell cultures show lower cell viability when DOX was loaded in various BBEs than control samples or DOX alone, indicating that our DOX-BBE drug delivery systems are better anticancer agents than DOX alone.

Keywords — drug delivery system, Beta-cyclodextrin, bifunctional hairy nanocellulose, extended drug release, biocompatible, biodegradable, green nanomedicine, Doxorubicin, hyper crosslinked polymer.



PANI@Multimodels Pores MOF-808 Composite for Supercapacitor Electrodes with High Longevity

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Abstract

Metal-organic frameworks (MOFs) are a combination of organic ligands and metal ions or clusters to form multidimensional porous networks.[1] Among their potential applications, they emerge as promising alternative electrode materials to overcome the disadvantages of low energy density.[2] Although the potential of MOFs that lies in their adjustable pore structure, morphology, crystallinity, and high surface areas, they lack on conductivity. [3] In this context, composites with conductive matrices, including conductive polymers, have proved to enhance the electrochemical properties of MOFs and their structural stability in the long-term cycling process compared to the pristine MOF. In this work, we have chosen MOF-808 as porous material because of its resistance to strong acidic media in a post-synthetic modification process.[4] As a conductive agent, we have selected polyaniline (PANI) due to its high stability and facile synthesis.[5] The new obtained composite (PANI@MOF) is supposed to increase the charge transport properties. The synthesized new material has been characterized by FTIR, powder XRD, UV-Vis, SEM and TEM. Cycling voltammetry was performed to calculate capacitance and cycling stability. Among the series of composites with different ratios of MOF:PANI the 60: 1 composite shows the highest capacity as well as longevity up to 10,000 cycles.

Keywords: Defective MOF-808, PANI, High longevity, electropolymérisation,

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Physicochemical and Electrochemical Characterization of Salt-in-Water and Water-in-Salt Potassium and Lithium Acetate Electrolytes

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Abstract— Effect of salt concentration from dilute to highly concentrated in potassium and lithium acetate electrolytes on their physicochemical and electrochemical properties has been studied.

Keywords—Acetate-based electrolytes; Water-in-salt; Salt-in-water; Physicochemical; Electrochemical

Electrolytes are an important part of any electrochemical technology (e.g., energy storage systems and electrocatalysis), which can impact their overall safety, capacity, and cost.¹ Highly concentrated “water-in-salt” electrolytes gained significant attention for developing aqueous batteries due to their enhanced electrochemical potential window, energy density, and life-span on par with commercially available non-aqueous batteries.² In case of non-fluorinated salts, such as acetate-based ones, the electrolytes are also eco-friendly.³ The main interest in these electrolytes arise from minimal free water molecules, which cause the electrochemical stability window of aqueous electrolyte to expand from 1.23 V (theoretical) to above 3.0 V.⁴ Here, physicochemical and electrochemical properties of potassium and lithium acetate electrolytes from dilute (1 molal) to near saturation as well as a mixed potassium/lithium acetate with $\text{Li}_{0.2}\text{K}_{0.8}\text{OAc} \cdot 1.3\text{H}_2\text{O}$ composition are studied. Using cyclic voltammetry and electrochemical impedance spectroscopy, it is found that electrochemical stability window increases with concentration and reaches about 2.9 V for the dual cation water-in-salt electrolyte. The capacitance of highly oriented pyrolytic graphite electrode at the potential of zero charge (PZC) is about $4 \mu\text{F cm}^{-2}$ and not affected by the electrolyte concentration. However, increasing the acetate salt concentration causes the PZC to shift to more negative values. Ion transport properties and electron transfer kinetics in the acetate-based electrolytes are also investigated using ferricyanide and ferrocene methanol redox probes. Both diffusion coefficient and electron transfer for ferricyanide ions decrease with increase in concentration of electrolyte (e.g. 4 orders of magnitude when the concentration changes from dilute acetate electrolyte to the dual cation water-in-salt electrolyte). High viscosities (about 400 mPa s in mixed cation water-in-salt electrolyte compared to ca. 1 mPa s for a dilute single cation electrolyte) could partially contribute to the decrease. It is also possible that other factors like interactions of ferricyanide ions with water, electrolyte ions and electrode play a role.

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Plasma thinning of black phosphorus large flakes

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Abstract— The growing interest over the 2D materials has led to the discovery of exfoliated black phosphorus (bP), a semiconductor with a thickness-dependent bandgap. The direct bandgap energy varies from 0.3 eV for bulk materials to 1.9 eV for the monolayer of black phosphorus. The fabrication of a thin layer bP is, however, difficult because the bP flakes photo-oxidize in air into phosphoric acid with kinetic that gets faster for thinner layers¹. Inspired by a new method to produce thin layers of black phosphorus using oxygen plasma, we work to optimise the process for making large few-layered bP². Using ICP-RIE oxygen plasma, exfoliated flakes of black phosphorus were etched in a controlled way and Raman spectroscopy was used to evaluate the quality of the flakes after plasma treatments. The results show no sign of degradation of the bP crystal structure after the plasma treatment. Here we show that the method can be adapted to produce high quality thin flakes of black phosphorus towards incorporation into electronic and optoelectronic applications.

Keywords —*black phosphorus; 2d semiconductor; plasma thinning*

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Bimodal functionalized nanoparticles selective to cell receptor density

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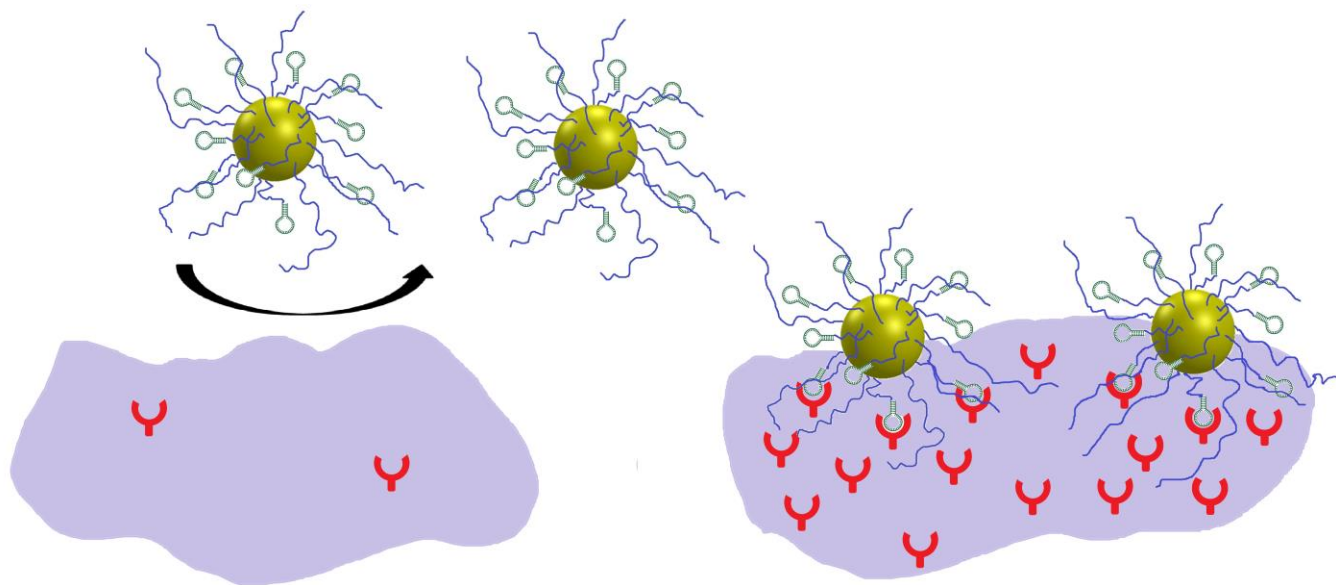
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Abstract - The selectivity of interactions between functionalized nanoparticles and cell surfaces of different receptor densities plays an essential role in differentiating healthy cells from affected cells. We developed a nanoplatfrom based on gold nanoparticles functionalized with mixed polymer-brush layers (containing a shorter functionalized chain and a longer unfunctionalized chain) for a selective adsorption on receptor surfaces. The effect of the molar ratio and the relative length of the polymers on the selectivity of nanoparticle/receptor surface interaction was investigated. We will show how the selectivity can be improved by adjusting these two parameters.

Keywords: *Selectivity, cell receptor, targeting, bimodal functionalization, nanoparticles*



Charge transport and trapping in meniscus-sheared TIPS-pentacene:polystyrene transistor devices

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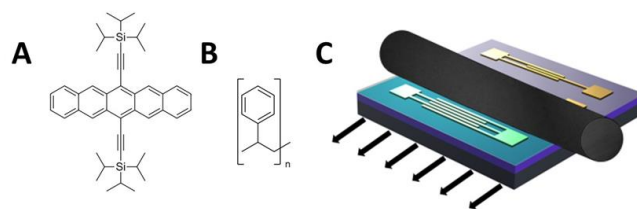
Organic semiconductors, i.e. small conjugated molecules and conjugated polymers, have received wide interest for application in electronics thanks to their facile large-scale fabrication, solution processability, flexibility, and tunable optical properties. Many reports have highlighted how structural and morphological properties of organic semiconductors depend on processing conditions, which therefore play a crucial role in defining the performances of electronic devices such as organic field-effect transistors (OFETs) [1]. In OFETs, the semiconductor-dielectric interface plays a critical role given that charge transport occurs at the said interface (within few nanometers). Crucial electrical parameters such as mobility, I_{ON}/I_{OFF} and threshold voltage directly depend on the density of traps at this interface. It was recently demonstrated that using blends of semiconductors with insulating polymers, such as polystyrene, can lead to considerable passivation of interfacial traps on SiO₂ [2]. This, in turn, considerably improves device performances, and has the advantage of being done in a single step of solution processing.

Here, we have fabricated and studied OFETs whose active layer is a TIPS-pentacene/polystyrene blend deposited, at ambient conditions, on a SiO₂ dielectric by a bar-assisted solution shearing technique, which is a relatively new method that has been shown to produce high-performance devices. At room temperature, our devices allow for low-power operation, displaying relatively low threshold voltage ($\sim -3V$) and subthreshold swings ($< 1V/decade$), values from which we extracted interfacial trap densities in the $10^{11}cm^{-2}$ range. All of our devices have hole mobilities well above $1 cm^2V^{-1}cm^{-1}$ at room temperature, which is among the best values reported for TIPS-pentacene.

Further, we have conducted the first temperature-dependent charge transport characterization for TIPS-pentacene OFETs processed in this manner. In addition to resolving the evolution of interfacial trap density with temperature, the study of the temperature-dependence of mobility allows us to extract apparent activation energies for charge transport

around 15 meV, a value much lower than those reported in prior work for TIPS-pentacene devices ($> 25 meV$). The careful analysis of contact resistance effects reveals that, as processed, TIPS-pentacene intrinsically exhibits a decrease of the mobility with temperature ($d\mu/dT < 0$) at least in the 200-300 K range, and that the measured activation energy originates from charge injection at contacts.

Overall, our study demonstrates that TIPS-pentacene blended with polystyrene and processed via meniscus shearing results in high performance devices, featuring low trap densities and shallow trapping energies. The temperature-dependent characterization together with the comparison with other works suggest that the performances could even be further improved, notably for applications in low power consumption. These results pave the way towards low-cost and easily scalable device solutions for organic electronics.



A. TIPS-pentacene B. Polystyrene C. Schematic of the bar-assisted meniscus shearing (BAMS) deposition method

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Graphene Oxide/Elastin Multilayered Membranes for Bone Regeneration

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Abstract— Bone regeneration remains a great challenge due to the complexity of tissue repair. A common strategy for repairing bone defects is to employ a bone implant¹. However, conventional bone substitutes such as metals, ceramics, polymers, and their composites fail to provide mechanical properties matching the native bone and biological activity for bone regeneration.

Many naturally occurring composite materials have developed hierarchical architecture with superior mechanical properties during the evolutionary process. Nacre, as an example, has an excellent combination of strength and toughness due to its “brick-and-mortar” layered structure, which consists of highly aligned aragonite platelets connected by organic layers in between the platelets². Compositional and structural similarities shared by nacre and bone make nacre-like composites promising materials for bone regeneration. Graphene oxide (GO) is an ideal candidate for “bricks” due to its two-dimensional structure, along with the outstanding ultimate strength and Young’s modulus³⁻⁵. An advantage of GO for bone regeneration is that it can stimulate the osteogenic differentiation of bone marrow mesenchymal stem cells (BMSCs)⁶. However, current nacre-like GO composites mainly focused on strength and toughness enhancement instead of exploring their potential as bone implants. As for the choice of “mortar”, it varied from synthetic polymers^{7, 8} to natural polymers such as silk fibroin^{9, 10}, chitosan¹¹⁻¹³, and cellulose^{14, 15}. Elastin, as a polymeric extracellular matrix protein, has rarely been explored as the “mortar” phase. Previous studies showed that elastin acts as the apatite nucleator in vascular calcification, suggesting that it may promote mineralization during bone regeneration¹⁶⁻¹⁸.

In this work, we fabricated a nacre-like GO/elastin membrane with GO as the “brick” and elastin as the “mortar” by a simple evaporation approach. GO/elastin membrane showed improved water stability and hydrophilicity compared with pristine GO. The achieved membrane has a comparable tensile strength (93.2 ± 9.6 MPa) and Young’s modulus (13.4 ± 0.4 GPa) with native bone. Furthermore, the incorporation of elastin promoted the mineralization process and enhanced the proliferation and osteogenic differentiation of mouse BMSCs compared with pristine GO membranes. These results suggest that the nacre-like GO/elastin membrane is a promising material for biomedical applications in bone regeneration, including bone implants, barrier membranes for guided bone regeneration, and coatings for implant materials.

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Electrochemically grown porous electrodes to improve charge injection in organic field-effect transistors

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Abstract— In this work, we present a novel way of improving organic field-effect transistors (OFET) performances by electrochemical growth of a porous Au layer on pre-deposited 30-nm thick Au source and drain electrodes. The study compares the electrical performances of p-type OFETs using an isoindigo-based semiconducting polymer with either (standard) flat vs electrochemically-grown porous electrodes.

Keywords—porous electrodes, organic field-effect transistor, device characterization, contact engineering, semiconductors.

OFETs have garnered significant attention for flexible and large-area electronics thanks to their expected low-cost fabrication, allowed by the solution-processability of its semiconductor part. Alongside the increasing focus on molecular design and device structure optimization, the charge carrier mobility, which represents a central figure-of-merit of OFETs, has greatly improved in the past years^{1, 2, 3}. In spite of such progress on improving charge carrier mobility, one of the biggest hurdles in the field is to optimize charge carrier injection at the electrode/semiconductor interface by reducing the so-called contact resistance (R_c). In OFETs, R_c can be around hundreds of $k\Omega \text{ cm}^{-1}$ which implies that the injection in these devices is not ohmic⁴⁻⁶. As the device current has an exponential dependence from contact resistance, a minor enhancement of injection can lead to a considerable improvement of OFET performance.

In this study, we employ an electrochemical method to grow porous electrodes on pristine gold flat electrodes. The dynamic hydrogen bubble template (DHBT) method is proved to increase the roughness factor described as the active surface area divided by the geometrical area. It has been used for different applications such as sensors, microbatteries, catalysis^{7,8}. The DHBT method increases the thickness (t) of the electrodes while keeping the same channel width (W).

According to the equation below, the increase in cross sectional area results directly in increased current density.

$$I_{DS} = J_{DS} * (W * t) \quad (1)$$

with t being the electrode thickness, and I_{DS} and J_{DS} being the current and the current density of the device. Higher currents as a result of a lower contact resistance could be observed in devices with electrochemically-grown porous electrodes (Fig.1). While the DHBT method has been used only for Au in this work, it can be extended to other metals. As such, this work paves the way for a simple way of implementing high performing organic devices.

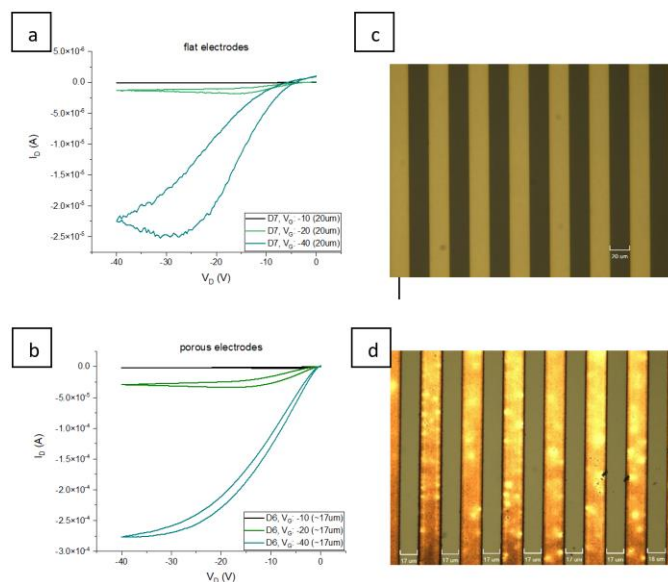


Fig.1 Output curves of an isoindigo polymer-based OFET with a) flat, b) porous electrodes. Optical microscope images of c) flat, d) porous OFET electrodes.

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Design and Development of a Reinforced Tubular Electrospun Construct for Deep Flexor Tendon Repair

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Abstract—The repair of traumatic and degenerative ruptures of deep flexor tendons remains one of the most intriguing topics in hand surgery. Current treatment methods fail in efficient repair of the injured tendon, and are mainly challenged in attaining sufficient mechanical strength and in limiting adhesion and inflammation issues. This research aims at developing a more potent solution for deep flexor tendon repair by combining a mechanical (improved mechanical properties) and biological approach (incorporation of bio-active compounds). A reinforced, multi-layered electrospun tubular construct is developed, composed of three layers: an inner electrospun layer containing an anti-inflammatory component (Naproxen), a middle layer of braided monofilament as reinforcement and an outer electrospun layer containing an anti-adhesion component (hyaluronic acid, HA).

In a first step, a novel acrylate endcapped urethane-based precursor (AUP) is developed and characterized by measuring molar mass, acrylate content and thermo-stability. The AUP material is benchmarked against commercially available poly(ϵ -caprolactone) (PCL). Next, the materials are processed into multi-layered, tubular constructs with bio-active components (Naproxen and HA) using electrospinning. *In vitro* assays using human fibroblasts show that incorporation of the bio-active components is successful and not-cytotoxic. Moreover, tensile testing using ex vivo sheep tendons prove that the developed multi-layered constructs fulfill the required strength for tendon repair (i.e. 2.79 - 3.98 MPa), with an ultimate strength of 8.56 \pm 1.92 MPa. In conclusion, by combining a mechanical approach with the incorporation of bio-active compounds (biological approach), this solution shows its potential for application in deep flexor tendon repair.

Keywords—biomaterials; biomaterial processing; drug-loaded electrospun construct; tendon repair

I. INTRODUCTION

The repair of traumatic and degenerative ruptures of deep flexor tendons remains one of the most intriguing topics in hand surgery. Current treatment methods fail in efficient repair of the injured tendon, and are mainly challenged in attaining sufficient mechanical strength and in limiting adhesion and inflammation issues. This research aimed at developing a more robust solution for deep flexor tendon repair by combining improved mechanical properties and the incorporation of bio-active compounds. A reinforced, multi-layered electrospun tubular construct was developed, composed of three layers: an inner electrospun layer containing an anti-inflammatory component (Naproxen), a middle layer of braided monofilament as reinforcement and an outer electrospun layer containing an anti-adhesion component (hyaluronic acid, HA).

II. MATERIALS AND METHODS

In a first step, a novel acrylate endcapped urethane-based precursor (AUP) with a poly(ϵ -caprolactone) (PCL) backbone was developed. The material synthesis occurred through a two-step process: (i) a PCL diol (MM 2000 g·mol⁻¹) was linked to isophorone diisocyanate (IPDI), and (ii) an acrylated oligomeric ethylene oxide (EO) end capping agent was then added to the intermediate product.[1] All materials were purchased from Sigma-Aldrich, Diegem, Belgium.

The developed AUP material was characterized by measuring molar mass (MM) and acrylate content through proton nuclear magnetic resonance (¹H-NMR) spectroscopy (Bruker WH 500 MHz) and thermo-stability by thermogravimetric analysis

(TGA) (TA Instruments, Q50). The AUP material was benchmarked against commercially available PCL (Sigma-Aldrich, Diegem, Belgium). Next, the materials were processed into multi-layered, tubular constructs with bio-active components (1.47 wt% Naproxen and 0.99 wt% HA) (Fagron Belgium and Sigma-Aldrich, respectively) using an in-house developed electrospinning set-up (CFWF Ghent University).

The electrospun constructs were then biologically (i.e. *in vitro* assays using human fibroblasts via an MTS assay and Ca-AM/PI staining), physico-chemically and mechanically (i.e. degradation tests, suture retention and tensile properties using *ex vivo* sheep tendons) evaluated. Thereafter, the developed constructs were evaluated in a rabbit model with forty New Zealand rabbits.

III. RESULTS

The novel AUP material with a PCL backbone was synthesized and characterization by NMR enabled determination of the MM of the PCL diol ($1931 \text{ g}\cdot\text{mol}^{-1}$), the MM of the AUP ($3336 \text{ g}\cdot\text{mol}^{-1}$) and the acrylate content ($0.554 \text{ mmol}\cdot\text{g}^{-1}$). TGA analysis showed that the developed material is perfectly stable at body temperature, as the degradation onset point was located only at 357°C . Subsequently, PCL and an AUP/PCL blend were electrospun, whereby homogeneous fibers were obtained with an average diameter of $8.77 \pm 1.88 \mu\text{m}$ and $4.30 \pm 0.41 \mu\text{m}$, respectively. Based on the degradation study, none of the materials showed a statistically significant ($p < 0.05$) weight loss after 9 weeks. In a next step, a reinforced, multi-layered electrospun construct was developed with the addition of bio-active compounds (i.e. HA and Naproxen). *In vitro* assays using human fibroblasts showed that incorporation of the bio-active components was successful and not-cytotoxic. There was an indication of integration of the HA in the cells as well as good viability in the materials in which the bio-active compounds were included. The monolayered PCL showed an average suture retention strength of $0.50 \pm 0.09 \text{ MPa}$ while the monolayered AUP/PCL reached a significantly higher average strength of $0.79 \pm 0.17 \text{ MPa}$ ($p < 0.05$). The tensile testing of monolayered and multi-layered PCL and AUP/PCL repair constructs on *ex vivo* sheep tendons (Figure 1) resulted in maximal stresses of the monolayered PCL and AUP/PCL structures of respectively $0.39 \pm 0.10 \text{ MPa}$ and $0.27 \pm 0.11 \text{ MPa}$ and for the multi-layered PCL and AUP/PCL in maximal stresses of respectively $8.56 \pm 1.92 \text{ MPa}$ and $8.36 \pm 0.57 \text{ MPa}$. The *in vivo* study is still ongoing, but the results will be presented at the CBS conference.

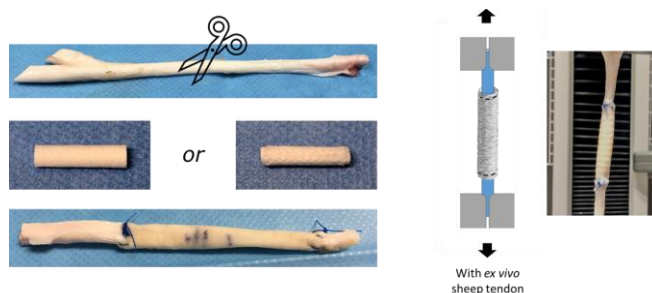


Figure 1 – Mechanical evaluation of drug-loaded or reinforced drug-loaded electrospun constructs for tendon repair. Set-up of tensile testing evaluation using *ex vivo* sheep tendons.

IV. DISCUSSION AND CONCLUSIONS

The aim was to develop a robust solution to repair deep flexor tendons, offering the injured tendon an excellent environment to heal faster and more efficiently. The developed tubular constructs have proven to be stable for at least 8 weeks, which corresponds to the healing time required for a lesioned tendon to pass to an advanced healing. Anti-adhesion (HA) and anti-inflammatory (Naproxen) were included as bio-active compounds. *In vitro* assays using human fibroblasts showed that incorporation of the bio-active components was successful and not-cytotoxic. Moreover, a slower leaching of HA in the AUP/PCL construct could be attributed to the more densely crosslinked network of AUP/PCL and was thus preferred over the PCL construct. With respect to the mechanical properties, tensile testing using *ex vivo* sheep tendons have proven that the developed multi-layered AUP/PCL constructs fulfill the minimal required strength for tendon repair (i.e. 4 MPa) [2], with an ultimate strength of $8.56 \pm 1.92 \text{ MPa}$. In conclusion, by combining a mechanical approach with the incorporation of bio-active compounds (biological approach), the proposed solution shows a strong potential for application in deep flexor tendon repair.

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Development of Main-Chain *N*-Heterocyclic Carbene-Based Metallopolymers as Precursors for Metallic Nanoparticles

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Abstract — *Recently, *N*-heterocyclic carbenes (NHCs) have emerged as excellent ligands to stabilize metal nanoparticles (NPs) thanks to their strong electron-donating characteristic.¹ Such functionalized metal NPs are formed by either top-down or by bottom-up approaches by reducing their corresponding metal complexes; however, the stability of these NPs in biological conditions remains limited.^{2,3,4} Herein, we aim to introduce a novel bottom-up strategy to form NHC-protected gold- and silver NPs by developing their corresponding poly(NHC-metal) precursors. Through this approach, we demonstrate that the resulting NPs are stabilized by a polymeric NHC network on the surface leading to their higher resistance to not only the biological thiols but also to other harsh conditions. In addition, we indicate that this methodology results in the formation of nanoparticles that are larger than those fabricated using their small molecule analogs. The catalytic activities of these materials will be discussed.*

Keywords—*AuNPs; AgNPs; *N*-heterocyclic carbenes; nanoparticles; poly(NHC-metal); bottom-up*

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Room temperature ppb-level H_2S gas sensor based on $MoSe_2-Mo_2C$ nanocomposites

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Abstract—Hydrogen sulfide (H_2S) produced from the degradation of domestic human waste and some industrial activities, can cause serious health problems even in low concentrations (1). Owing to their advantages of robustness, fast response, good recovery, metal oxide-based gas sensors have been widely used for the detection of H_2S (2). However, their working principle requires the sensor to be heated at high temperature, resulting in major drawbacks concerning its working principle. For these reasons, recent studies have suggested alternative sensing materials for the development of gas sensors operating at low temperature. TMDs, such as $MoSe_2$ have been used as sensitive material for the detection of various toxic gases (3). Some researchers have found that the modification of TMDs surfaces by chemical doping or hybridization with other conductive material improve the adsorption of gas molecules by enhancing its surface activity [4]. This study focuses on the development of $MoSe_2-Mo_2C$ based low cost and flexible gas sensor for the hydrogen sulfide detection at room temperature. A novel material with Mo_2C nanoparticles modified $MoSe_2$ ($MoSe_2/Mo_2C$) was synthesized by hydrothermal method then calcinated at $780^\circ C$. The sensing film was produced by drop casting the dispersed material on top of screen-printed carbon electrodes on a flexible polyethylene terephthalate substrate. It is found that the Mo_2C nanoclusters change the surface chemistry of the $MoSe_2$ and enhance its gas sensing properties. Compared to pristine $MoSe_2$ as the sensing material, $MoSe_2-Mo_2C$ based sensor exhibits a much higher performance, in which the sensitivity has been increased by up to 6 times in the presence of 100 ppb of H_2S . The improved sensitivity could be attributed to the increase of adsorption site in the material induced by the incorporation of Mo_2C facilitating the charger transfer process. The new sensor possesses good linearity and high sensitivity between 100 ppb and 1 ppm, with good stability and a full recovery at room temperature (Fig.1). This suggests that $MoSe_2-Mo_2C$ appear as a potential candidate for developing high performance nanoelectronic devices.

Keywords— H_2S gas sensor, $MoSe_2-Mo_2C$, room temperature

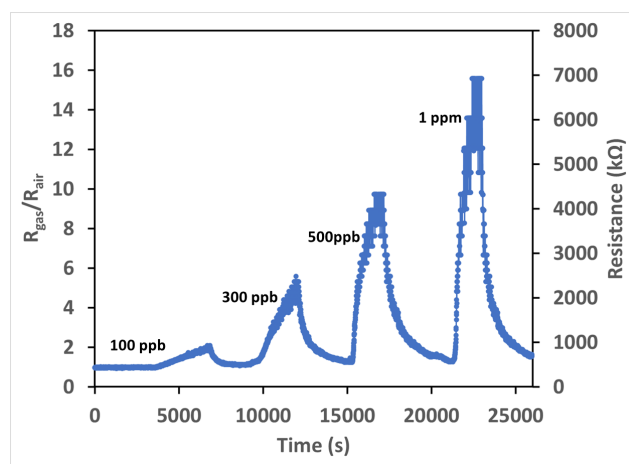


Fig. 1. Sensor response (R_{gas}/R_{air}) and resistance sensor to various concentrations of H_2S at room temperature

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Preparation of Yolk-Shell nanoparticles with a gold core and CO₂-responsive polymer shell as an efficient and easily recyclable catalyst

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Gold nanoparticles are good heterogeneous catalysts, but they tend to aggregate and are difficult to handle. In order to solve this problem, Yolk-Shell nanoparticles, of Au @ void @ PDEAEMA configuration were synthesized (PDEAEMA is poly (N, N-diethylaminoethyl methacrylate)). Due to its specific structure, the polymer shell prevents aggregation of gold nanoparticles while leaving its surface accessible to reagents. The rate of the catalytic reaction can be further regulated by controlling the diffusion of molecules through the CO₂-sensitive PDEAEMA shell by switching the latter between a hydrophilic state by bubbling CO₂, and a hydrophobic state by bubbling N₂. In addition, under its hydrophobic state, the nanoparticles agglomerate which allows easy recycling. The synthesis of the polymer shell was carried out by precipitation polymerization using Au @ SiO₂ nanoparticles as a matrix. Then, selective removal of the silica inner shell produces the Yolk-Shell Au @ void @ PDEAEMA nanoparticles. The shape and size of the nanoparticles were characterized by TEM, the CO₂-sensitive behavior of the outer layer was characterized by UV-Vis spectrometry and DLS. The catalytic activity of yolk-shell nanoparticles and the controlled catalysis were characterized by UV-Vis spectrometry using the catalytic reduction of p-nitrophenol.

Auto-assemblage de nanoparticules métalliques à l'aide de la technique Langmuir-Blodgett

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Les nanoparticules (NPs) métalliques possèdent des propriétés physicochimiques et optiques uniques qui les rendent très intéressantes pour diverses applications. De plus, il est plus avantageux de les utiliser sous forme de matériaux nanostructurés puisqu'ils présentent des propriétés optiques amplifiées par rapport aux NPs individuelles.¹ Cependant, la fabrication d'un matériau peu coûteux comportant des nanostructures métalliques hautement ordonnées à grande échelle demeure toujours un défi.² Dans ce contexte, les approches ascendantes basées sur l'auto-assemblage restent attrayantes, malgré leur tendance à présenter une plus grande hétérogénéité que les approches descendantes.³

*Dans le cadre de ce projet, la technique Langmuir-Blodgett est utilisée pour la préparation de films minces nanocomposites. L'objectif principal de cette étude est d'investiguer l'assemblage de différentes populations de NPs avec le poly(styrène-*b*-2-vinylpyridine) (PS-*b*-P2VP) pour l'obtention de nanostructures cœur-satellite. Plus précisément, basé sur la méthode d'auto-assemblage déjà développée dans notre laboratoire⁴, ce copolymère dibloc est utilisé pour son habileté à former un arrangement périodique, et ainsi permettre d'orienter les NPs métalliques de manière ordonnée à grande échelle. Tout d'abord, des nanoparticules fonctionnalisées de compositions métalliques variées sont préparées. Dans un deuxième temps, les NPs mélangées avec le PS-*b*-P2VP sont assemblées à l'aide de la technique Langmuir-Blodgett. Ces assemblages sont observés par microscopie électronique à transmission (MET). Finalement, d'autres caractérisations supplémentaires sont effectuées afin de comprendre les propriétés d'auto-assemblage. L'étude démontre que l'assemblage de NPs avec le PS-*b*-P2VP à l'aide de la technique Langmuir-Blodgett est une avenue prometteuse pour le développement de nanostructures cœur-satellites ordonnées à grande échelle et bon marché.*

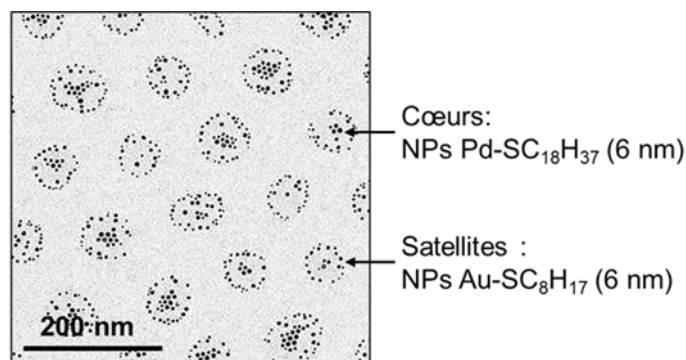


Figure 1. Image MET de nanostructures cœur-satellite composées de NPs et de PS-*b*-P2VP.

Auto-assemblage, nanoparticules plasmoniques, copolymères blocs, nanostructures métalliques

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Fonctional suprastructures from self-assembling perylene diimide-peptide conjugates

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Abstract— As one of the most important class of dyes, perylene diimide (PDI) derivatives are intensively studied owing to their excellent chemical robustness, photostability, and interesting optoelectronic properties.¹ Therefore, PDIs are widely applied and used in various biomedical and technological fields. However, the control of their molecular self-assembly into highly ordered supramolecular structures remains a challenge.² In this study, we took advantage of the high aggregation propensity of amyloid peptides to design nanofilaments functionalized with PDI. The amyloidogenic domain of the islet polypeptide (IAPP), i.e., the segment 20-29 (I₂₀₋₂₉), was used as the self-assembling core, which was attached to the PDI moiety by a flexible hexyl spacer. Mono- (PDI-I₂₀₋₂₉) and bis-PDI functionalized peptide (PDI-[I₂₀₋₂₉]₂) derivative were synthesized on solid support. Self-assembly of these novel conjugates was studied by their dispersion in aqueous buffer and rotary agitating them at room temperature. Self-assembly process was followed by measuring their UV-vis absorbance, fluorescence emission and circular dichroism (CD) spectroscopy as well as by atomic force microscopy. These analyses revealed that both PDI-peptides self-assembled into long, unbranched, and linear filaments with a cross- β -sheet quaternary organization. The UV-vis absorbance spectra exhibit a clear signature of H-aggregates for both assemblies. Overall, this study reveals that defined nanostructures functionalized with PDI can be obtained from amyloid peptide building blocks, opening the door to novel applications in bioimaging, photodynamic therapy and bioelectronic.

Keywords— *Self-assembly; perylene diimide; peptide; supramolecular; amyloid filaments.*

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Fonctional suprastructures from self-assembling perylene diimide-peptide conjugates

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Abstract— As one of the most important class of dyes, perylene diimide (PDI) derivatives are intensively studied owing to their excellent chemical robustness, photostability, and interesting optoelectronic properties.¹ Therefore, PDIs are widely applied and used in various biomedical and technological fields. However, the control of their molecular self-assembly into highly ordered supramolecular structures remains a challenge.² In this study, we took advantage of the high aggregation propensity of amyloid peptides to design nanofilaments functionalized with PDI. The amyloidogenic domain of the islet polypeptide (IAPP), i.e., the segment 20-29 (I₂₀₋₂₉), was used as the self-assembling core, which was attached to the PDI moiety by a flexible hexyl spacer. Mono- (PDI-I₂₀₋₂₉) and bis-PDI functionalized peptide (PDI-[I₂₀₋₂₉]₂) derivative were synthesized on solid support. Self-assembly of these novel conjugates was studied by their dispersion in aqueous buffer and rotary agitating them at room temperature. Self-assembly process was followed by measuring their UV-vis absorbance, fluorescence emission and circular dichroism (CD) spectroscopy as well as by atomic force microscopy. These analyses revealed that both PDI-peptides self-assembled into long, unbranched, and linear filaments with a cross- β -sheet quaternary organization. The UV-vis absorbance spectra exhibit a clear signature of H-aggregates for both assemblies. Overall, this study reveals that defined nanostructures functionalized with PDI can be obtained from amyloid peptide building blocks, opening the door to novel applications in bioimaging, photodynamic therapy and bioelectronic.

Keywords— *Self-assembly; perylene diimide; peptide; supramolecular; amyloid filaments.*

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Mechanically and electrically tunable PEDOT:PSS composites containing bacterial protein nanofibers

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PEDOT:PSS is a widely used biocompatible conductive polymer used for bioelectronics applications. It has previously been combined with biopolymers or proteins, which have led to an enhanced conductivity due to a synergistic change in microscale morphology of the polymer. Here, we have used PEDOT:PSS and curli fibers, a class of bacterial proteins produced by *E. coli* bacteria, which exhibit stiffness, genetic tunability and resistance to environmental stresses such as heat, to prepare a protein-polymer composite. The curli-PEDOT:PSS can self-heal with water-stimulation and have its mechanical and electrical properties tuned by changing the ratio of protein:polymer composition. We optimized the composite preparation process using different mixing strategies and thermal processing of the curli fibers, followed by drop-casting onto a substrate. We characterized the conductivity, the morphology, and the chemical composition of composite films with curli fiber content ranging from 0 to 100% (w/w). We also studied their swelling and elastic properties of the films. We found that films containing 60% (w/w) curli fibers exhibited the highest conductivity at ~9 S/cm.

P3HT-FxTCNQ: Integer-charge transfer is governed by doping-related broadening of the density of states

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Molecular doping is a major route for enhancing the conductivity of organic semiconductors. Therein, two competing mechanisms have been identified – integer and fractional charge transfer. The former is beneficial to the generation of mobile holes in the semiconductor. It is generally expected that a high dopant electron affinity promotes integer charge transfer, while fractional charge transfer is the result of strong coupling between the frontier molecular orbitals of dopant and host. In the present study, we investigate how the width of the density of states (DOS) in the host, is influencing the doping process.

We study the prototypical conjugated polymer poly(3-hexylthiophene) (P3HT) p-doped with tetracyanoquinodimethane (TCNQ) derivatives of different electron affinities at 2% dopant ratio. We determine the involved energy levels through cyclic voltammetry (CV), probe the percentage of ionized dopants through Fourier-transform infrared (FTIR) spectroscopy, and measure the resulting conductivities. We compare our experimental results with the percentage of ionized dopants and the hole densities in the P3HT matrix resulting from varied widths of the P3HT HOMO-DOS as calculated via a semi-classical computational approach.

We confirm that only the electron affinity of F4TCNQ is greater than the ionization energy of P3HT and find that TCNQ and FTCNQ exhibit significantly weaker but essentially identical electron affinities. However, while TCNQ only undergoes fractional charge transfer, almost 90% of FTCNQ is ionized, as inferred from FTIR spectra. Accordingly, P3HT conductivities are enhanced for F4TCNQ and FTCNQ doping but, surprisingly, even reduced for TCNQ doping. We turn to our computational results to understand this remarkable discrepancy between TCNQ and FTCNQ. While for TCNQ the doping behavior is well reproduced if the recently reported width of the P3HT HOMO-DOS is used, it must be broadened by almost one order of magnitude to yield the ionization percentage found with FTCNQ. Thus, we reason that the dopants exhibit significantly different tendencies to cause energetic disorder in the host matrix and, therefore, broadening of the P3HT HOMO-DOS. We argue the permanent dipole in FTCNQ to be the driver behind this tendency.

Our study demonstrates that electron affinities alone are not sufficient to define the strength of molecular dopants and their capability to perform integer charge transfer with organic semiconductors.

Perylene Diimide-Tagged *N*-Heterocyclic Carbene-Stabilized Gold Nanoparticles: How Much Ligand Desorbs from Surface in Presence of Thiols?

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Abstract: *N*-heterocyclic carbenes (NHCs) have recently emerged as viable alternatives to commonly used thiols to stabilize a variety of metal surfaces and nanoparticles.¹ In this context, thanks to their biocompatibility and novel optical properties, NHC stabilized gold nanoparticles (AuNPs) have been extensively studied.² It has been shown that such materials exhibit improved stabilities in acidic and basic solutions, high temperatures, electrolyte solutions, cell culture media, and to some extent to nucleophilic thiols.³ Despite intense efforts, shedding light on the true stability of NHC-functionalized AuNPs to thiols has been an ongoing challenge. Herein, we introduce the development of a water-soluble azide decorated NHC-stabilized “clickable” AuNPs. Optically active perylene diimide (PDI)-tagged AuNP hybrids nanomaterials are then obtained using “click” chemistry between these AuNPs and an alkyne-decorated PDI derivative. The extent of NHC desorption from AuNP surface in presence of glutathione is then quantified using fluorescence spectroscopy, unveiling the true stability of NHC moieties as ligands to stabilize AuNPs.

Keywords: “Clickable” gold nanoparticles, *N*-Heterocyclic carbenes, Perylene diimide, Stability, Glutathione

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Highly Selective CO₂ Capture Under Ambient Conditions Using A Tunable Microporous Metal-Organic Framework

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Abstract: The exponential exploitation of fossil fuel resources during the last century has resulted in harmful effects on the globe and many consequences have been observed at several environmental, and climatic levels; including global warming, the spread of pollution, climate change, and furthermore.¹ Scientist have linked the environmental issues observed to the excessive concentration of carbon dioxide (CO₂) in the atmosphere.² Metal-organic framework (MOF)-based materials is a new class of porous coordination polymers, widely studied over the past decades for their high surface areas, chemical tunability, and stability, which makes them very promising for several applications.³ MOFs have attracted a lot of attention for CO₂ capture, separation, and conversion. The functionalization of these materials involves high CO₂ selectivity and efficient catalytic conversion.⁴ In this perspective, we report the successful synthesis and characterization of novel MOFs termed IRHs based on nitrogen-rich cyamelurate, and neodymium metal ions, with a pre-programmed pore structure, as well surface and internal texture chemistry. We were successfully able to tune the MOF pores opening and its surface polarity to enhance the selective uptake of quadripolar gas molecules (CO₂) rather than nonpolar gas molecules (H₂, N₂, CH₄), which provides promising potential in CO₂ capture and separation.

Keywords: Metal–Organic Frameworks, CO₂ capture, adsorption, IRHs, selectivity

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Designing Nanostructures for Broadband Solar Photon Harvesting for Photocatalytic Reactions

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Abstract—Broadening photon absorption into the longer visible wavelength and even near-infrared (NIR) ranges represents a unique opportunity of improving the use of solar energy in various fields. Recent advances in nanomaterials open a new door in realizing this goal. Herein, I will present some of our recent work on the design and synthesis of broadband solar light absorbing materials. One example is our synthesized nanocomposites based on plasmonic Au nanoparticles (NPs) and in-situ synthesized lanthanide-doped NaYF₄ on g-C₃N₄. It showed enhanced ultraviolet-, visible- and NIR-light photocatalytic activity in the degradation of organic pollutants. To utilize solar energy more efficiently and cost-effectively, a 0D/2D heterojunction based on NIR-responsive quantum dots loaded g-C₃N₄ nanosheets was constructed, which showed a record NIR photocatalytic activity. In addition, a completely metal-free 2D/2D heterojunction of black phosphorus/g-C₃N₄ was synthesized. The 2D/2D heterojunction showed high activity and long-term stability in solar H₂ evolution. I will also present our preliminary try on the synthesis of ultrastable plasmonic Cu NPs and their applications in solar vapor generation. In addition

to yielding novel and interesting materials and properties, the current work also provides physical insights that can contribute to the future development of broadband solar absorbing materials and their applications in environmental remediation and green fuel production.

Keywords—broadband; photocatalysis; nanocomposites; g-C₃N₄; Au NPs; quantum dots; black phosphorus

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Liquid Crystalline Diels-Alder Dynamic Network: Form Room-Temperature Programmable Actuator to Self-sustained Soft Robot

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Liquid crystalline networks (LCNs), processing both anisotropic property and elasticity, are considered to be an ideal material system for the soft robots, thanks to their ability to macroscopically and reversibly stimuli-responsive deformation upon the liquid crystal-isotropic phase transition.^[1] However, the cross-linked structure makes the LCN have some inborn defects such as weak recyclability, limit size, and especially the difficulty to change actuation behavior as well as original shape, which restricted the practical application. Herein, by incorporating the thermal dynamic Diels–Alder (DA) bonds, we fabricated a novel smart material named liquid crystalline Diels-Alder dynamic network (LCDAN). Taking advantage of mild reaction conditions and suitable kinetic of DA reaction, LCDAN can be programmed or reprogrammed to 3D structured (such as various origamier, 3D solid shaped actuators and light-fueled macro-walkers) at room temperature. The fibrous and tuber actuators were also prepared by directly drawing LCDAN melt and solution casting, which cannot be achieved with previous.^[2] In addition, since the LCDAN exhibit unprecedented easy for actuator programming, the fibrous and spring soft robot with highly tunable light-fueled self-sustained locomotion can be fabricated by carbon nanotube doped LCDANs. The fiber and spring actuators can self-roll on multiterrains, including sand, water and human hand. Particularly, the spring actuator can directly self-roll under natural sunlight on a dark grey paper and pass through a narrow gap encountered in motion via significant body size change.

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Investigation of Extrinsic Disorder on the Magnetoresistance of Gated Single-layer Graphene

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Graphene represents the thinnest electronic material in two dimensions, and it is a monolayer of carbon atoms arranged in a hexagonal honeycomb fashion. Single-layer graphene has a linear band structure at low energies and such a physical peculiarity leads to a zero-electron and zero-hole effective mass and makes it differ from other conventional two-dimensional materials.¹⁻³. However, the influence of charge impurities and other sources of extrinsic disorder that are invariably present were studied extensively on the charge transport properties of graphene-based devices, but their impact has not been investigated on magnetoresistance of graphene. The origin of these adventitious charged impurities has been ascribed to charged impurities adsorbed at the graphene/silicon dioxide interface. The presence of such impurities is fully adventitious and can be controlled only to a certain extent unlike the case of macroscopically induced-disorder or defects,⁴⁻⁶ nitrogen dopants incorporated within the graphene lattice,⁷ and induced strain through a terraced SrTiO₃ substrate.⁸ In addition to the charge impurities, random strain fluctuation could be another source of adventitious disorder for high-quality exfoliated graphene on SiO₂/Si⁺ substrates.^{9, 10}

Here, firstly we evaluate the level of adventitious extrinsic disorder on the bare exfoliated graphene on SiO₂ by two manifestations of the presence of adventitious extrinsic disorder which are minimum conductivity (σ_0) and root-mean-square fluctuations in the carrier density (n^*). (The n^* has been shown to directly correlate to the mobility, as proved by previous works).⁹ Then we investigated the impact of such a disorder on Gr's MR as a function of gate voltage in wide range of temperature (50 K to 300 K) and magnetic field up to 9 T. We demonstrate that single-layer graphene transistors with a low density of extrinsic disorder feature a larger magnetoresistance (MR) than those with high density. Importantly, in gated single-layer devices with low density of charged impurities, we find that MR peaks at gate voltage values far from the charge neutrality point not only at low temperature but also at room temperature; in particular, MR approaches 800 % at room temperature and 1,400 % at 50 K in such devices. Our work indicates that the initial value of the minimum conductivity σ_0 at room temperature along with n^* which affect the mobility must be looked at in order to select the most promising devices with low level of extrinsic disorder for magnetosensing.

Keywords— Graphene, interfacial disorder, gate-tunable magnetoresistance, magnetic-field sensor, charged impurities, low-power device

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Stability Criteria and Instability Mechanism of sI and sII Methane and Carbon Dioxide Hydrates

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Abstract— Clathrate hydrates, also known as gas hydrates, are crystalline solids that resemble ice and consist of water molecules forming hydrogen-bonded cages and encapsulating various gas molecules (e.g., methane and carbon dioxide) [1]. This unique lattice structure brings the features of high storage capacity and stability. Due to the high heating value of methane gas, the amount of energy in natural hydrates is more than twice the amount found in all other available hydrocarbons combined. As at least 85% content of hydrates is water, gas hydrates share significant similarities with hexagonal ice, such as the elastic moduli, under standard conditions [2]. However, due to the presence of the guest molecules, some material properties of gas hydrates have different performances under a pressurized and high-temperature environment. For example, the abrupt climate changes (e.g., global warming) would lead to unexpected hydrates' destabilization, followed by gas emissions, which brings a significant threat to society. Thus, we will explore the hydrates' physical properties under non-standard conditions and investigate the structural stability in terms of temperature and pressure to relieve this issue. This work aims to determine the hydrate's structural strength and then further explore its instability or fracture mechanism, which involves using density functional theory and molecular dynamics to simulate the hydrates' performance under pressure and high-temperature conditions.

Keywords—*gas hydrates; methane; carbon dioxide; stability;*

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Structural and optical properties of crystalline blends of α -sexithiophene and para-sexiphenyl

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Abstract— Earlier reports indicated that organic semiconductor blends can exhibit opto-electronic properties significantly different to the pristine materials, where intermixture on the molecular scale is promoted by a similar molecular shape. Similarly sized rod-like conjugated molecules such as α -sexithiophene (6T) and para-sexiphenyl (6P) are thus expected to form mixed crystals in equimolar blends, where a spectral overlap between the 6P fluorescence and 6T absorption might give rise to resonant energy transfer between the species. In marked contrast to H-type aggregation found for 6T bulk crystals, isolated monolayers of 6T and 6T monolayers sandwiched between 6P multilayers have been reported to show pronounced green (instead of red) fluorescence, which has been attributed to J-type aggregation. Here, we investigate whether these altered optical properties of 6T translate from the monolayer to a bulk blend with 6P. Using synchrotron grazing-incidence X-ray diffraction we find that vacuum co-deposited films of 6T+6P indeed form crystalline blends on the molecular scale in standing and lying molecular orientation, as induced by different substrates. We find a mixed crystal structure very similar to that of pure 6P. For the standing film, neighbouring layers are not in crystalline correlation with each other, however, with the layers being still crystalline in-plane showing a molecular herringbone arrangement. By correlating the optical properties of the pure and mixed systems using absorption and photoluminescence spectroscopy we identify the green emission known from 6T monolayers to prevail in the blend. Our analysis indicates the formation of aggregates which are promoted by the molecular arrangement in the mixed crystal structure and highlights that the remarkable optical properties of 6T/6P heterostacks translate into mixed crystalline films. This study underlines that tuning the opto-electronic properties of organic semiconductors by blending species of similar shape but distinct opto-electronic properties is a promising pathway to achieve altered material properties.

Keywords —*photoluminescence; vacuum deposition; rod-like molecules; crystal structure; GIXRD*

Developing Effective Diagnostic Tools Using Carbon Dots

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Fluorescent imaging probes serve as a unique diagnostic tool for bioimaging and nanomedical applications offering high sensitivity particularly in their ability to image cells and tissues, as well as for the study of biological processes. These tools are becoming crucial for early detection and disease diagnostics especially with an increase in numbers of an aging population and the requirement for more efficient health care. Recent advancements in the field of nanomaterials have propelled research groups into investigating these nanoparticles for various biological applications including drug delivery, biosensing and bioimaging.^{1, 2} Indeed, several nanomaterials including polymer dots, quantum dots and lanthanide-doped upconverting nanoparticles have been investigated for these applications and more recently carbon dots, which have garnered significant attention.³ These carbon-based nanoparticles are interesting as they can be prepared from simple synthetic routes using inexpensive precursors, offer low cytotoxicity and good biocompatibility, as well as possess tunable optical properties.⁴ Their inherent fluorescent nature not only allows for fluorescence imaging, but also for sensing environmental changes (i.e. temperature and pH), which can provide additional insights in diagnostics. In this work, dual-fluorescing carbon dots are synthesized using a one-step microwave-assisted reaction. The carbon dots' physico-optical properties are thoroughly studied in order to shed light on their fluorescence mechanism. The fluorescence of the carbon dots is tailored through manipulation of key synthesis parameters to determine their underlying effect on the resultant optical signature. In addition, our results showcase that both the pH and the temperature of the media can be monitored through a ratiometric approach with the changes in fluorescence signatures in both the blue and red regions of the spectrum. We exploit these phenomena to develop a temperature- and pH-sensor inside living cells.

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Spectrally Pure Red and Strong UV Emissions by Lithium Based Upconverting Nanoparticles

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The unique ability of rare earth doped nanoparticles (RENPs) to convert low energy light into higher energy light by a process called upconversion, have made them ideal candidates for theranostic (therapy + diagnostic) applications in the biomedical field. Previously, optically triggered drug release inside deep tissue was severely hindered. Specifically, the high energy blue light needed to trigger the photochemical processes lacked the capability to penetrate deep into the tissue to induce the drug release, whilst the low energy red light had some penetration depth but not the required energy. When RENPs are irradiated with near infrared (NIR) light, they are able to upconvert a part of the energy provided into UV due to a sequential absorption of two or more photons, which can then be used to trigger the photochemical processes for drug release. RENPs also have intense emissions in the NIR region, that allows for deep tissue imaging as well. Thus, the emission spectra of current RENPs are known to have a spread of different peaks of different intensities between the UV and NIR regions. Isolating these peaks allows for the creation of spectrally pure nanoparticles, which have only one intense peak at a particular wavelength, to create specific RENPs for targeted applications.

One common type of theranostic RNP which has seen frequent use in research today is the LiYbF_4 doped nanoparticle with Tm^{3+} . Here we prepare a series of samples consisting of $\text{LiYbF}_4: \text{Tm}^{3+}(0.5\%)$, co-doped with all other rare-earth ions at a dopant concentration of 0.5% for each of them. Their upconversion spectra were acquired and analyzed for spectral purity. After which three co-doping ions, Pr^{3+} , Dy^{3+} , and Nd^{3+} , were shown to have spectrally pure red emissions when doped in $\text{LiYbF}_4: \text{Tm}^{3+}$. Other ions, namely, Eu^{3+} , and Tb^{3+} showed promising, high intensity UV light emission as well, though they were not spectrally pure. These co-doping ions underwent a concentration study, increasing the concentrations of the ions of interest from 0.5% to 1%, 2%, and 5%, to further isolate them as candidates for either red spectral purity or strong UV emission.

Poly(ϵ -caprolactone)/L-Ascorbic Acid Blends: Miscibility and Morphology Development

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Abstract— Blends of Poly(ϵ -caprolactone) (PCL) and L-Ascorbic Acid (AA) were prepared via solution casting into thin films. The addition of AA in the PCL matrix was intended to increase the biodegradation rate of the biopolymer (~50% in 4 years). Therefore, low amounts of AA were chosen (1, 2 and 5 wt%). The miscibility and morphology of the blends were investigated by means of polarizing optical microscopy (POM) and atomic force microscopy (AFM). We have demonstrated that the two crystallizable materials form an immiscible blend where nanometric particles and micrometric crystals of AA are confined in the PCL matrix. When 1 or 2 wt% ascorbic acid is included in the PCL matrix, the AA phase tend to uniformly disperse in the form of small particles with dimensions close to the nanometric range (~100 nm). The AA nanoparticles modified the crystallization behavior of PCL by increasing the nucleation density (smaller spherulites). When 5 wt% of AA was included, micrometric crystals of AA were also seen in the PCL matrix that have even stronger effect on the final morphology of the material: The AA microcrystals act as nucleating sites for PCL spherulites to grow. The trans-crystalline regions around the AA microcrystals were developed in advance of the bulk PCL spherulites resulting in a unique spherulite morphology. The composition of the AA microcrystals was investigated via Photo induced force microscopy (PiFM). PiFM images allowed us to differentiate the regions where PCL and AA are more present. While confirming the immiscibility of the blend, it was revealed that PCL penetrated into the porous AA microcrystals. A few points of interest were chosen on the surface of the AA crystal and inside the PCL matrix to record the local IR spectra. The recorded IR spectra on three different points on the surface of AA showed a lot of spectral variations in the form of absent peaks or different peak intensities. There are different theoretical ascorbic acid structures based on the orientations of their alcoholic hydrogen atoms and the presence of hydrogen bonding: A, B, C and dimer. However, the comparison of the data with the literature showed no correlation between spectral variations of the PiFM results and the assigned vibrational modes of AA structures. The difference in the IR spectra were then concluded to most likely be due to the different crystalline orientations of the AA crystals.

Keywords — Poly(ϵ -caprolactone); L-Ascorbic Acid; Crystallization; Polymer spherulite; Miscibility

Operando Observation of Li^+ in Li-ion Batteries

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Abstract— What if you could see inside a Li-ion battery while you operate it? This is the concept behind “operando” methodologies which allow researchers to experimentally observe fundamental processes that occur within batteries during charge and discharge.

One of the most important requirements of modern battery systems for automotive electrification is the ability for fast charge. The speed at which we can charge a battery is often limited by how fast Li-ions can travel from one electrode to the other (solution-phase) or how fast Li can diffuse within the active material (solid-phase).

Our team developed a new methodology employing synchrotron X-ray fluorescence to gain valuable information about the solution-phase mass transport in Li-ion batteries during (dis)charge. This work can validate the predictive power of established pseudo two-dimensional (P2D) models in order to improve their accuracy in addition to serving as a screening technique for new composite positive electrode architectures.

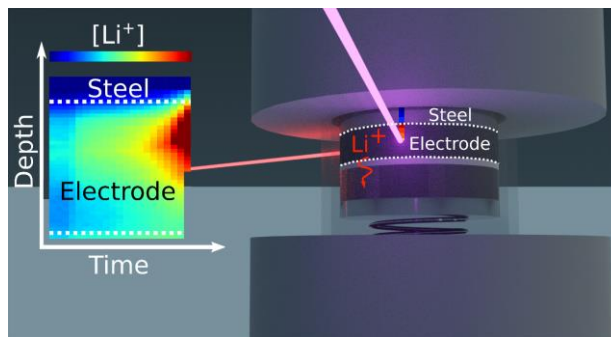


Figure 1: Representation of operando X-ray fluorescence measurement on a Li-ion cell and heatmap of obtained Li^+ concentration

Keywords (optional)— Li-ion Battery, X-ray Fluorescence, Synchrotron, Operando

References (optional):

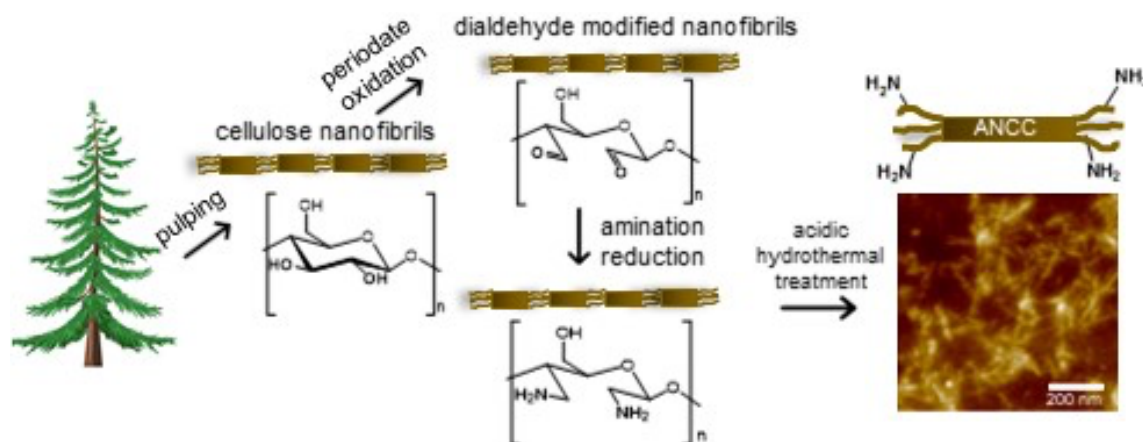
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Paper Title: Fabrication and characterization of aminated nanocrystalline celluloses

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Abstract—Hairy nanocellulose (HNC) consists of a crystalline rod-like body and amorphous cellulose chains (“hairs”) at both ends, on which various functional groups can be accommodated. Primary amines are very accessible and can easily form chemical and physical bonds which are important in various chemical applications such as drug delivery, wastewater treatment, packaging engineering, etc. Here we functionalized HNC with reactive primary amine groups and we refer to this new member as hairy aminated nanocrystalline cellulose (ANCC). We hypothesized that a two-step oxidation-reductive amination of cellulose fibers followed by hydrothermal treatment would result in the formation of rod-like hairy ANCC, and that the positively charged ANCC would exhibit antibacterial activity towards foodborne bacterial pathogens. Dialdehyde modified cellulose (DAMC) was prepared by periodate oxidation of cellulose and subsequently the aldehyde groups of DAMC were converted into primary amines using ammonia and sodium borohydride, which yielded diamine modified cellulose (DAMMC). DAMMC fibers were subjected to an acidic hot-water treatment to isolate amine-functionalized hairy nanocellulose. To examine the morphology and dimensions of ANCCs, images were taken using atomic force microscopy and transmission electron microscopy. Conductometric titration and electrophoretic light scattering were employed to provide the charge density of ANCCs. To confirm the formation of amine groups on ANCC, Fourier transform infrared (FTIR), solid carbon-13 nuclear magnetic resonance (NMR) and X-ray photoelectron (XPS) spectroscopies were employed. Antibacterial activity of ANCC was assessed by the well-established cell counting method. It was observed that ANCCs have needle-like morphology with a width of ~5 nm and a length ~120 nm. The amine content and ζ -potential of ANCC were obtained as ~ 5.5 mmol g⁻¹ and ~ +34 mV at pH 3, respectively. Spectroscopical analysis confirmed the introduction of surface primary amine groups qualitatively and quantitatively. ANCC showed certain bactericidal activity, against Gram-negative species due to their thinner and penetrable cell wall.



Keywords (optional)—component; formatting; style; styling; insert (hairy nanocrystalline cellulose; primary diamine modification; oxidation-reductive amination; hydrothermal treatment; antibacterial property)

Soft Actuators of Porous Liquid Crystalline Polymer Networks

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Abstract:

As a class of stimuli-responsive polymers, liquid crystalline networks (LCN) possess interesting properties like controllable shape change and locomotion under the effect of stimuli such as light, heat, humidity, and electric field. These properties make them promising candidates for making soft robots, actuators and energy generators. In the present work, porous LCN actuators were prepared using a template method, and investigated for actuator application. The porosity makes the initially hydrophobic LCN behave like a hydrogel, capable of absorbing a large amount of water and swelling up to ten times of the initial sample size. When the amount of absorbed water is relatively small (about 100% swelling ratio), the porous LCN displays anisotropic swelling in water and, in the same time, the retained uniaxial alignment of mesogens ensures thermally induced shape change associated with LC-isotropic phase transition. Upon further absorption of water, the swelling of the porous LCN becomes isotropic. Combining the actuation mechanisms characteristic of LCN (order-disorder phase transition) and hydrogel (water absorption), such porous LCN actuators can be explored for versatile stimuli-triggered shape transformations.

Drug loading and delivery studies using gold nanoparticles as new ophthalmic drug vectors

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Abstract—Gold nanoparticles are novel drug vectors showing promising drug loading and delivery abilities. They are ultrastable and mucoadhesive: they can adhere to ocular proteins and keep their structural integrity while delivery drugs to the corneal cells. This systematic study of their drug loading and release capacity is a step to show light on their potential use for future ophthalmologic treatments.

Keywords—drug vectors; gold nanoparticles; ultrastability; mucoadhesion; eye drops; drug delivery systems

I. BACKGROUND

Eye drops represent 90% of all ophthalmic treatments currently used. There is only 0.02% of eye drops therapeutic molecules that reach the eye anterior chamber despite their high concentration. The tear film efficiently protects the cornea, reducing access to the target. Thereby, the increase of the drug bioavailability and efficiency must come from the mucoadhesion optimization of the drug delivery system. The goal was thus to study the gold nanoparticles ability to load and release two specific ophthalmic drugs, flurbiprofen and ketorolac. They are two nonsteroidal anti-inflammatory drugs, typically used in post-surgical cataract treatments.

II. EXPERIMENTAL SECTION

A. Drug Loading

Drug loading kinetics were measured using UV-visible spectroscopy to determine optimal loading parameters. Plasmon bands first derivatives analysis were possible because of the localized surface plasmon resonance effect of the gold core. Drug loading quantification was performed with an immunoprecipitation protocol followed by a high-performance liquid chromatography analysis. Gold nanoparticles to drugs ratios of 1:10, 1:20, 1:50 and 1:100 were used for all drug loading experiments. Flurbiprofen and ketorolac were loading for 3 or 10 days.

B. Drug Delivery

The drug release was measured using an *in vitro* model based on dialysis bags coupled with UV-visible spectroscopy. Passive and active drug delivery were studied. The dialysate was changed every 8 hours for active delivery experiments to mimic the tear film renewal. The same gold nanoparticles to drugs ratios and drug loading times previously tested were used for delivery experiments.

III. RESULTS

A. Drug Loading

Two saturating points appeared during the drug loading kinetics measurements for the two therapeutic molecules, displaying the gold nanoparticles loading ability with both molecules. Drug loading percentages were shown to be linked to the nanoparticle:drug ratio. Hydrophobic molecules displayed a higher loading trend than hydrophilic ones.

B. Drug Delivery

During release studies, passive or active, drug delivery percentages were higher with hydrophilic molecules than hydrophobic molecules. However, forced delivery allowed higher drug concentrations to be measured in dialysate by UV-visible spectroscopy.

IV. CONCLUSION

Based on these preliminary results, gold nanoparticles are a promising drug delivery system for ketorolac and flurbiprofen. This nanotechnology demonstrated its drug loading and release abilities with hydrophobic and hydrophilic anti-inflammatory drugs. Further experimentations are needed to fully showcase the impact of experimental parameters on drug administration tuning and the potential of gold nanoparticles to improve the medication in ophthalmology.

Synthesis and Characterization of Shape and Size-Tunable Fluorescent Carbon Nanoparticles (CNPs) by dispersion polymerization of *sp*-carbon rich precursors

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Abstract

Carbon nanoparticles (CNPs) have emerged as one of the most promising nanomaterials due to their distinct optoelectronic properties for a diverse range of applications in the area of electronics, energy conversion/ storage, and bio-imaging. The properties of photoluminescence, photostability, and low toxicity makes them a potential candidate for various applications. The uniqueness in terms of functions and properties of the CNPs gets more interesting as it changes distinctly with a change in the shape, size, and dimensionality of these nanoparticles. Despite several advantages and unique properties, the transformation from laboratory to industrial products has been slow for carbon nanoparticles because of the difficulty in synthesizing and in controlling the size of CNPs. The synthetic methods reported until now involves high-temperature ($>100\text{ }^{\circ}\text{C}$) processes which often results in uncontrolled shape, size, polydisperse and chemically inert nanoparticles, increasing the difficulty to modulate their morphological, optical, and electronic properties. Thus, the development of low temperature and controlled synthesis method is desirable.

This work is focused on the development of a low-temperature synthetic method for the preparation of fluorescent carbon nanoparticles allowing precise control over the shape, size, and properties by dispersion polymerization of *sp*-carbon rich precursors. These *sp*-carbon rich precursors (butadiyne and acetylene) tend to become thermodynamically unstable when polymerized to long polyyne chains and decompose inside the reaction mixture to give CNPs. Hence, these polyyne intermediates provide us with the control over the size and shape of CNPs during the reaction and in turn, over their properties for further modulations and functionalization. The shape- & size-tunable nanoparticles were synthesized in a single step with dispersion polymerization by Glaser-Hay coupling. The shape and size of the resulting carbon nanoparticles are controlled by changing different reaction parameters such as temperature, monomer loading, reaction concentration, and pressure. The control over the different reaction parameters allows us to obtain monodisperse CNPs in spherical and tubular shapes with a size in the range of 25 nm to 250 nm. The use of low-temperature methods ($\text{RT} < T < 70\text{ }^{\circ}\text{C}$) also allows us to overcome the limitations associated with current methods. After isolation, CNPs were characterized by microscopy techniques to analyze the shape and size of the nanoparticles. The nanoparticles were further characterized to by various techniques for chemical composition, structure, morphology, and optical properties. The functionalization and graphitization of CNPs were performed with UV-photochemical irradiation and microwave heating resulting in blue fluorescence in CNPs.

Architecture at the nanoscale and its application for developing thicker low tortuosity electrodes

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Abstract:

Li-ion batteries offer one of the most promising alternatives to fossil fuels evidenced by their mainstream integration in electric vehicles, which is demonstrated by the 250% growth in market value of electrical cars between 2015 to 2020. However, more than 30% of the battery electrode components are materials like the current collector that does not get directly involved in charge storage[1]. One solution to this problem could involve developing thicker free-standing electrodes, but these electrodes suffer from extremely high ionic resistances due to high tortuosity of electrode [2].

Herein, we employed magnetic fields to template the orientation of graphite mixed with graphene flakes in the fabrication of 300 micron thick anodes. Raman spectroscopy and X-Ray diffraction facilitated monitoring the diamagnetic particles as they responded to the magnetic stimulus. Finally, half-cells constructed using the magnetically templated electrodes underwent charge-discharge cycling to assess their electrochemical performance. Our methodology demonstrated a 38% enhancement in the specific charge compared to an amorphous porous electrodes at a rate of 1C.

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2. Lin, F et al. Advanced Materials, 29(1), p.1604453.

The Electrochemical Stability Window of LAGP and LATP Solid Electrolytes for All-Solid-State Li Batteries

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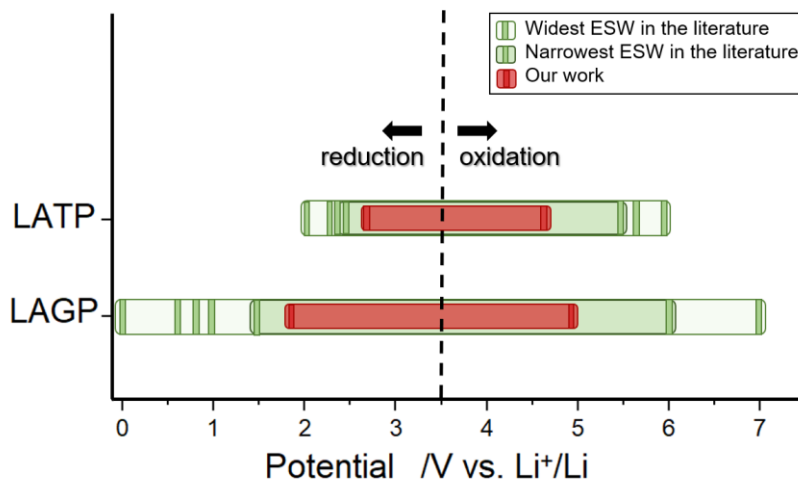
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Abstract—All-Solid-State Lithium Batteries (ASSLBs) are promising since they may enable the use of high potential materials as positive electrode and lithium metal as negative electrode. This is only possible through solid electrolytes (SE) stated large electrochemical stability windows (ESW). Nevertheless, reported values for these ESWs are very divergent in the literature. Establishing a robust procedure to accurately determine SEs' ESWs has therefore become crucial. Our work focuses on bringing together theoretical results and an original experimental set up to assess the electrochemical stability window of the two NASICON-type SEs $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) and $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP). Using first principles, we computed thermodynamic ESWs for LATP and LAGP and their decomposition products upon redox potentials. The experimental set-up consists of a sintered stack of a thin SE layer and a SE-Au composite electrode to allow a large contact surface

between SE and conductive gold particles, which maximizes the redox currents. Using Potentiostatic Intermittent Titration Technique (PITT) measurements, we were able to accurately determine the ESW of LATP and LAGP solid electrolytes. Finally, we attempted to characterize the decomposition products of both materials upon oxidation. The use of an O_2 sensor coupled to the electrochemical setup enabled us to observe operando the production of O_2 upon LAGP and LATP oxidations, in agreement with first-principles calculations. This presentation aims at providing a method to accurately determine the ESWs of solid electrolytes, considered a key parameter to a successful material selection for ASSLBs.

Keywords—Electrochemical Stability Window (ESW), NASICONs, Potentiostatic Intermittent Titration Technique (PITT), Spark Plasma Sintering (SPS), solid electrolyte, all-solid-state battery, Grand Potential Phase Diagram (GPPD).

Graphical abstract



Conductive metal-organic frameworks with molecularly defined M-O₄ active sites as highly active biomass valorization electrocatalyst

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Abstract— The electrochemical oxidation of biomass platform 5-hydroxymethyl furfural (HMF) to 2,5-furandicarboxylic acid (FDCA), is an important reaction in the emerging area of renewably powered biomass valorization. To this end, to render these systems economically competitive, the efficiency of catalytic systems still needs to be improved. In the electrochemical HMF oxidation reaction (HMFOR), the utilization of well-defined active sites is critical for fundamental insights into their function and subsequently rationally turning them to maximize catalytic activity. Heterogeneous catalysis of HMF conversion, however, often feature poorly defined catalytic surfaces, hampering the community's complete understanding of the reaction mechanism. Herein, we report the use of reticular chemistry to design a conductive metal organic framework-based electrocatalytic model system with well-defined M-O₄ active sites to better understand the HMROR reaction mechanism. The activity of MOFs bearing Ni-O₄ (Ni-CAT) and Co-O₄ (Co-CAT) active sites was analyzed with electrochemical and operando spectroscopic techniques to elucidate the reaction mechanism occurring on the surface. Electrochemical experiments reveal that Co has better onset potential than other reported onset potential, while the Ni-CAT has faster kinetics that will efficiently transfer HMF to FDCA.

Also, Ni-CAT exhibits efficient charge transfer properties and intrinsically high kinetic towards HMFOR. It achieved FDCA yields of 98.7% with 86.8% faradic efficiency.

Infrared spectroscopy captures the surface-bound aldehyde group as the key intermediate in the catalytic cycle, which forms once M(II/III) oxidation occurs. This work illustrates the advantage of utilizing molecularly defined active sites coupled with operando spectroscopy to provide fundamental insights into a variety of electrosynthetic reactions and paves the way for future catalyst design.

Keywords—*electrochemistry; electrocatalysts; renewable energy; metal-organic framework*

Présentation par affiches / Poster abstracts

Demonstration of catalysis using nanofurnace

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Chemical looping is a chemical process that performs a specific reaction in 2 or more steps. For instance, the reverse water-gas shift reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) can be separated into two sub-reactions that rely on oxygen-deficient catalyst: the first is a reduction step that generates oxygen vacancies and refills during reoxidation. The separation of the reactants in two subreactions for the WGS reaction improves the selectivity by avoiding methanation.

A conventional furnace is common to heat a reactor but is non-specific because energy is wasted to heat non-catalytic mass (support, tube, gas). Alternatively, magnetic induction generates heat where needed, especially if the catalyst is susceptible to magnetic heating, such as ferrites. This strategy concentrates the heat on the catalyst and is likely to improve the energy efficiency of the reaction.

Here, we propose to use nickel ferrite as both catalyst and inductor for chemical looping for WGS. The experimental setup is composed of a magnetic coil that stimulates the catalyst incorporated in pellets placed inside a tubular reactor. We compare the conversion and catalytic performance to an equivalent conventional heat source. Following a reduction step to create oxygen vacancies at 410°C over a H_2 flow, the catalyst converted CO_2 to CO [1.62 moles CO/g cat] with an efficiency of 83.4 % at 420°C . Simultaneous feeding achieved an efficiency of 99% with < 8.1% of CH_4 demonstrating that induction heating is promising.

Heat loss from the existing magnetic reactor design created peripheral zones of the catalyst bed that are were not active and over-reduced central parts. Further work is needed for a better design of the reactor, the catalyst bed, and the catalyst itself. Heat management and magnetic coupling with an intelligent coil configuration will also be important. We also propose to evaluate the energy efficiency to develop the technology to a point where it becomes suitable for industrial use. Furthermore, we intend to explore the concept of nanofurnace working with susceptor and catalyst in close vicinity to maximize heat efficiency in catalytic conditions.

Keywords—Nanoparticles; Chemical looping; Magnetic induction

References (optional):

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Effect of N₂ plasma surface modification over the adhesion of FEP films

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Abstract— Among all the polymers, fluorinated ethylene propylene (FEP) stands out among others because of its processability, thermal stability, strong chemical inertness, and low surface energy. However, for some specific applications, it is necessary to modify their surface to increase adhesion with specific targets (*e.g.* adhesives, materials). These modifications are usually carried out by the deposition of thin-film coatings, the grafting of specific functional groups, as well by changing the roughness. These improvements are usually made at the end of the fabrication process to enhance or to induce a specific physicochemical behavior on materials. In this context, modification by plasma is a highly versatile and efficient technique used to change a wide variety of substrates (*e.g.* polymers, ceramics, metals) without affecting the bulk properties. In addition, this approach avoids the typical problems encountered with wet chemical techniques such as the presence of residual solvents on the surface or the swelling of substrates. Consequently, we present a plasma surface modification method to treat FEP films employing a dielectric barrier discharge at atmospheric pressure of N₂. This reactor allows moving the polymer film up to 5 m/min through the discharge thanks to a roll-to-roll system. As the aim of this project is to improve the adhesion properties of FEP films with adhesives, the characterization of the surface was being carried out by X-ray photoelectron spectroscopy (XPS) and the adhesion was evaluated by peel test with acrylic adhesive. The surface modification was carried out keeping the same conditions (*i.e.* same N₂ flow, frequency, voltage, power, gas gap) and moving the film through the discharge at speeds from 0.5 to 5 m/min. Results show that plasma treatment produces a decrease in the atomic percentage of fluorine, an increase in the atomic percentage of carbon, and introduces nitrogen and oxygen-containing functionalities (C=O, N-C=O, C-O, C-N) on the FEP surface. The modification gives a large rise of the adhesion with acrylic adhesive from 114 ± 58 g/cm (untreated) to a maximum of 2102 ± 484 g/cm at 0.5 m/min. This increase in the adhesion is related to the functional groups introduced in the surface and the defluorination of the FEP surface which depends on the plasma exposition time of the film and can be controlled by changing the line speed.

Keywords: *Atmospheric pressure nitrogen plasma; fluorinated ethylene propylene; adhesion.*

Catalytic Conversion of Polysulfides by Atomic Layer Deposited Titanium Nitride for High-Rate Lithium Sulfur Batteries

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Abstract— In this study, a novel catalyst material titanium nitride (TiN) for sulfur cathodes is developed via atomic layer deposition (ALD). The synthesized ALD-TiN catalyst shows controllable ultrafine particle size (< 2 nm) and uniform distribution at nanoscale in the carbon matrix. Combined with electrochemical analysis and multiple post characterization techniques, ALD-TiN demonstrates excellent catalytic effect to facilitate the nucleation and deposition of Li_2S , which effectively suppresses the dissolution and shuttle of polysulfides. The as-prepared sulfur cathodes with the assistance of TiN catalyst exhibit excellent cycling performance at high rate (4 C) and deliver 200% higher discharge capacity than the pristine S-C cathodes.

Keywords (optional)—*Atomic Layer Disposition, sulfur cathode, titanium nitride, cycling, discharge, capacity*

Fabrication of the aqueous self-lubricating coatings containing PEG-PDMS copolymers

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Icephobic coatings is considered as one of the effective solutions to protect the infrastructures subjected to harsh cold-weather environments. Inspired by ice skating, the aqueous self-lubricating coatings have got great interest in developing a cost-effective anti-icing method. In this paper, at first the aqueous self-lubricating coatings have been fabricated by adding polydimethylsiloxane-poly (ethylene glycol) (PEG-PDMS) copolymers into a PDMS matrix. Then, wettability, morphology and topography of the fabricated coatings were analysed using goniometer, scanning electron microscopy (SEM) and atomic force microscopy (AFM). Furthermore, icephobic characteristics of the samples were studied by differential scanning calorimetry (DSC), push-off test, and centrifugal test. Blending PEG-PDMS in the elastomeric matrix can enhance the effective contact area between water droplet and the coating; because water molecules would readily spread on the surface, as a result of the formation of hydrogen bonds between them and the hydrophilic functional groups. Increase in the percentage of such groups can heighten ice delay time and reduce ice adhesion strength, probably owing to the formation of quasi liquid-like layer. Although, immiscibility of PEG-PDMS copolymer within PDMS matrix can interfere wettability and icephobic characteristics of the coatings, and an optimized copolymer content of 5% can result in to achieve a durable icephobic aqueous self-lubricating coating.

Conductive stretchable fibers by electrospinning

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Abstract

Efficient synthetic methods for preparing conjugated organic materials have provided the means to tailor material's properties. Devices prepared from such active materials have the benefit of improved performance. Most organic electronics, however, are reliant on the intrinsic high conductivity of doped PEDOT to enable the operation of devices. While continuous thin films of this conductive polymer on device electrodes are possible by spincoating, the films are typically brittle. Therefore, they cannot be used *as-is* in stretchable and bendable electronics. To address this short-coming, we examined a method to prepare fibers whose conductivity would be consistent regardless of applied stress and strain. Ultimately, this would yield stretchable and bendable electrodes. It will be presented that such conductive electrodes can be prepared by a combination of electrospinning and vapor phase polymerization. The effect of different polymer carriers on the fiber's morphology and conductivity along with the fiber's capacity to sustain applied stresses and strains will also be presented. It will also be presented that the fibers can be used in stretchable transistors.

Keywords : *Stretchable Transistors, Electrospinning, Organic Electronics*

Liesegang Patterns of Copper Aspartate Coordination Polymers

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Self-assembly of metal ions and amino acids to form coordination polymers is well known.¹ In 2009, Amabilino *et al.* described the formation of copper aspartate nanofibers using slow polymerization at the interface between an organic solvent containing aspartic acid and an aqueous phase containing Cu²⁺ (**Figure 1a**).²

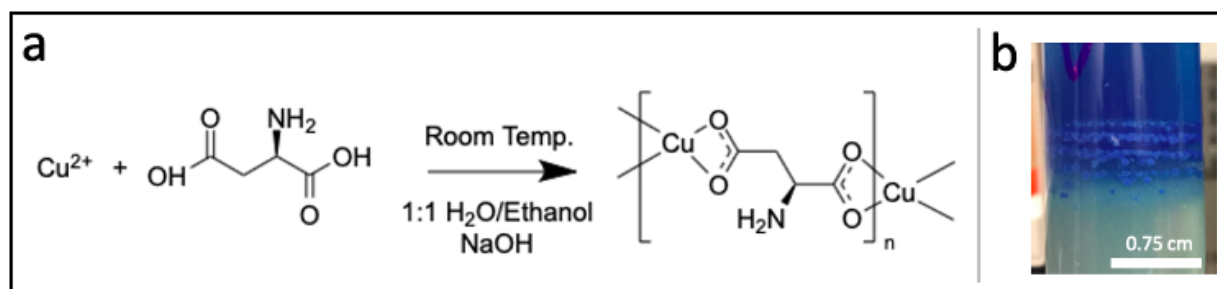


Figure 1. (a) General scheme for the formation of copper aspartate coordination polymer. (b) Spherulitic copper aspartate displaying Liesegang banding

Crystal growth in gels is dominated by diffusion and often leads to high quality single crystals.³ Herein, we demonstrate the formation of copper aspartate in agar gel which leads to coordination polymers with spherulitic morphology. Remarkably, crystallization of copper aspartate in gel also displayed Liesegang banding (**Figure 1b**). This phenomenon results in a series of repeating concentric bands.⁴ Various parameters for coordination polymer growth were investigated, including amino acid and Cu²⁺ concentration, copper ion source and solvent. The coordination polymers were characterized by scanning electron microscopy, circular dichroism, powder X-ray diffraction and light microscopy. Our goal is to optimize crystal growth, to understand the mechanism of Liesegang ring formation, and to investigate the role of chirality on the copper aspartate self-assembly. Future work includes lanthanide amino acid-based coordination polymers grown in gel to investigate the influence of chirality on luminescence.

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New carbon allotropes from azulene

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For decades, electronics have been implanted in everyday life and been gaining in importance every day. Due to its presence in all sectors of activity, dependence on the production of electronic devices is increasingly strong. At present, these are mostly made from silicon or metal oxides. This poses a problem since the production of such materials can be expensive and energy consuming. In addition, it does not allow flexible and lightweight devices to be made, which are becoming more and more popular for portable applications. To overcome these problems, researchers are moving towards alternative semiconducting materials. Among them, carbon materials have the advantage of being inexpensive, particularly abundant and allowing the production of flexible devices. While their performances does not currently match that of silicon or metal oxides, those predicted for optimized systems are superior. Among the carbon materials there are graphene nanoribbons (GNRs). These materials are promising for various applications ^[1] such as Organic Field-Effect Transistor (OFET), Organic Light-Emitting Diode (OLED), Organic Solar Cell (OSC), surfactant for graphene dispersion and in conductive electrode material since they possess very high charge carrier mobility values.

In this presentation, we will show our most recent efforts towards the synthesis of a new kind of GNR possessing 5- and 7-membered rings. To obtain these GNRs, azulene, a molecule formed of a 5 and 7 carbon ring fused, has been used as the main building block ^[2]. Using azulene should allow a new edge structure, low band gap and charge carrier properties intrinsic to azulene structure ^[3]. Synthesis and characterization of new azulene-based nanographene will be discussed.

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Analysis of phase-enabled metal-organic framework homojunction for highly selective CO₂ photoreduction by Transmission Electron Microscope

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Abstract— Conversion of clean solar energy to chemical fuels is one of the promising and up-and-coming applications of metal–organic frameworks. However, fast recombination of photogenerated charge carriers in these frameworks remains the most significant limitation for their photocatalytic application. Although the construction of homojunctions is a promising solution, it remains very challenging to synthesize them. Herein, we report a well-defined hierarchical homojunction based on metal–organic frameworks via a facile one-pot synthesis route directed by hollow transition metal nanoparticles. The homojunction is enabled by two concentric stacked nanoplates with slightly different crystal phases. Moreover, we demonstrate the imaging capabilities of electron energy loss spectroscopy (EELS) in the low/core-energy-loss region, reporting the direct image of two concentric stacked nanoplates by using non-negative matrix factorization performed within EELS dataset.

Transamination-based dynamic combinatorial chemistry of zwitterionic quinones

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Dynamic Combinatorial Chemistry (DCC) is simply combinatorial chemistry under thermodynamic (and/or kinetic control).¹ DCC is a method for devising intricate chemical systems which obey the general principles of a basic evolutionary mechanism proposed by Darwin: natural selection. A wide variety of complex compounds crafted *via* DCC under reversible conditions constitute the dynamic combinatorial library (DCL). Described herein is the first example of a precipitation-induced DCL of zwitterionic quinones, where the interconversion of the equilibrating species occurs at room temperature with no catalyst.² The transamination equilibria are shifted by changes in the nature of the reaction solvent. High resolution mass spectrometry (HRMS), ¹H NMR spectroscopy and scanning tunneling microscopy (STM) were employed to investigate the kinetics of this reversible adaptive system both in solution and at the liquid-solid interface.

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Dye encapsulation in Carbon NanoHorns (CNH)

Study by simulation and Raman scattering signal of encapsulated dye in CNHs

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Keywords: *atomistic modeling, encapsulation, dyes, carbon nanohorns, Raman spectroscopy, probes*

Raman nanoprobe were recently proposed to detect cancer cells or allergens. These probes are composed of a dye encapsulate in carbon nanotubes (CNTs) or carbon nanohorns (CNHs) which are functionalized to be specific to the chosen target. When the dye is confined inside the tube or the horn, its Raman signal is significantly increased but the exact reason for this amplification is still open to debate. Questions also arise on the configuration of the dye inside and around the capsules. Here, we will present a combined work of simulation and experimental work to clarify the Raman amplification phenomena and offer some insight on the process of encapsulation.

For a complex system such as the Raman probe, deducing the theoretical Raman scattering from simulations is challenging. Here, we propose to evaluate the Raman polarizability of the system in order to deduce the Raman intensity. The calculations were recently launched with *Orca* on a Compute Canada server.

The behavior of dye encapsulation mechanism is then investigated by molecular dynamics and by high-resolution transmission electron microscopy (HR-TEM). First, we constructed an atomistic model of the system (CNHs + dye) then geometry optimization and dynamics calculations run using *Forcite* module. With these first results, we report a deformation of the CNH shell that will be more investigate in the future. Subsequent simulations will demonstrate the influence of the solvent, dye nature, dye molecule position around the CNHs and graphene pattern on the dye stabilization from either side.

We will conduct a series of experiments on encapsulation to confirm the trends observed from molecular dynamics. In particular, we expect to relate the Raman amplification with the dye concentration and the impact of CNH oxidation during the encapsulation procedure.

Lithium Detection in Li-ion Battery Electrolytes Using Pt/Ga Microelectrode

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Abstract

During lithium ion battery charge/discharge cycles, lithium ions are continually exchanging between cathode and anode materials *via* the liquid electrolyte. Therefore, Li^+ ion detection is critical to determining reactive heterogeneity and the properties of the mass transport at the interface of the electrode and solution. The main goal of this work is to develop a technique for detecting the quantity of Li^+ ions transport in the electrolyte of the battery, which pass through the porous network of the cathode material.

A Pt/Ga microelectrode was developed as a scanning electrochemical microscopy (SECM) probe that could provide spatial resolution in combination with anodic stripping voltammetry (ASV) or square wave voltammetry (SWV). ASV based calibration Li^+ curves are reproducible within $\pm 7.5\%$ confirming the suitability of the Pt/Ga electrode as a local Li^+ sensor. Using SWV, the linear regime of the sensor is 0.3-5 mM with a calculated 77 μM limit of detection. In the future Pt/Ga electrode will be used in SECM, a powerful tool for recoding the *in situ* electrochemical behavior of the chemical species, the quantity of Li^+ in the solution of battery electrolyte.^{1,2}

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Synthèse par évaporation thermique de couches minces de pérovskites sans plomb pour cellule tandem

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Abstract — Dans le contexte énergétique et climatique actuel, l'utilisation de l'énergie solaire pour l'industrie photovoltaïque représente une solution viable et durable. Toutefois, les cellules solaires les plus commercialisées souffrent de grandes pertes en efficacité dues à des limites théoriques. Actuellement, une des solutions les plus étudiées sont les cellules tandem pérovskites/silicium. Bien qu'elles aient fait leur preuve en termes d'efficacité, ces cellules souffrent d'instabilité lorsqu'exposées aux conditions ambiantes ou à la lumière. De plus, elles possèdent une concentration non négligeable en complexe de plomb hautement soluble dans l'eau, ce qui nuit grandement à leur commercialisation. Dans ce travail, nous proposons d'utiliser la méthode de synthèse de couches minces par évaporation thermique afin de contrôler précisément l'épaisseur, la cristallinité, l'absorption, les bandes d'énergies, la morphologie et la mobilité des couches de type $\text{Ag}_x\text{Bi}_y\text{I}_{x+3y}$. Nous démontrons aussi comment les conditions ambiantes lors du recuit thermique influencent la stabilité des couches en fonction du mode d'évaporation. Il s'agit donc des premiers pas vers la fabrication d'une cellule tandem pérovskite sans plomb/silicium stable.

Pushing the Envelope in Chemical, Valence States & Structural Imaging

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Summary

X-ray synchrotron techniques have enabled breakthrough research in a variety of fields, spanning from alternative energy research, catalysts, nanomaterials to biomedical science. Synchrotron beamline X-ray techniques have several inherent advantages over their laboratory equivalent. Advantages include their massively higher source brilliance, energy coherence, tuneability and sub-micron resolution capabilities. This has led to oversubscription and the immense competition in acquiring beamtime. In spite of the growth of these techniques at synchrotron facilities, efforts toward developing higher sensitivity laboratory X-ray capabilities have progressed relatively slowly due to bottlenecks in X-ray optics and low brightness laboratory X-ray sources. We have developed a breakthrough laboratory microfocus X-ray source with user selectable or tunable energy which has significantly higher brightness/flux than conventional micro focus &/or rotating anode sources. Coupling this patented source with our novel double-paraboloidal X-ray mirror lenses, we introduced to the research community a suite of laboratory X-ray instrumentation with performances close to their synchrotron equivalent. These include XAS (X-ray Absorbance Spectrometry with XANES & EXAFS); microXRF (X-ray fluorescence microscopy) and micro to nano X-ray tomography. In this presentation, we will describe some of these commercialized synchrotron-like laboratory techniques and review their applications. The power of X-ray absorption spectroscopy with sub-eV resolution in its ability to track valence states and bond length changes is crucial for our understanding of in operando of charge-discharge cycle of batteries; the aging of catalysts and processes in a variety of novel advanced materials will be discussed. Scan times are in minutes to hours. The role of micro/nanoXRF for mapping chemical composition down to ultratrace levels and that of the novel X-ray Microscope in the imaging of hard to soft materials will also be shown. In the area of micro and nanotomography, the power of tunable energies to enhance contrast in imaging of soft materials and biological materials will be highlighted. All these novel X-ray techniques are complementary. They form part of the essential components in the emerging field of correlative and functional microscopy, tying structural information from optical and electron microscopy with elemental, chemical states and 3D volumetric data in applied research.

Printed Flexible Chemiresistive pH Sensor for Smart Bandages

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By using printed electronic fabrication methods, we can develop chemiresistive sensors which will be a key component of our smart medical bandage system. Bandages with embedded sensors can help determine the health of damaged tissue cells and the status of the bandage itself by detecting the pH of the fluid analyte from the wound. One of the most important parameters that changes in wounds in different states is pH and could help bring added value to patients and health actioners in identifying the onset of infection.

In this project, a screen-printed flexible chemiresistive sensor based on polyaniline (PANI) and single walled carbon nanotubes (SWCNT) on PET substrates are presented. Chemiresistive sensors operate in the presence of a chemical target based on electrical changes in resistance. For the first layer, silver contacts are screen printed on a cleaned PET substrate. For the active layer, a combination of SWCNT and PANI have been used for proton sensing. Firstly, SWCNT has been drop-casted between the electrodes and a conductive network can be formed due to SWCNT's high aspect ratio and high conductivity. Secondly, PANI, a conductive polymer, has been investigated as the sensing layer since it is hydrogen sensitive through protonation/deprotonation and is therefore appropriate for pH sensing. Finally, a mixture of SWCNT and PANI is used as the sensing layer. The chemiresistive sensor can monitor the changes in the resistance of nanocomposite films (SWCNT, PANI) in different ranges of pH.

Moreover, pH sensors have the potential for different applications, for instance: They play a critical role in monitoring the quality of water by measuring the alkalinity and acidity and can also be used as an indicator for increasing pollution. Additionally, pH sensors are used in agriculture to detect soil alkalinity or acidity as soil pH is an important factor that effects the plant quality. Finally, pH sensor can also be used as an indicator in food packaging as well. It can indicate the food quality throughout the supply chain, ensuring it is safe for the consumer.

Synthesis and Characterization of Amphiphilic Janus Dendrimers with Aggregation-Induced Emission Properties

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Abstract— Janus dendrimers, unlike conventional dendrimers, provide asymmetry and can impart significantly different chemical and/or physical properties. This leads in their applications as drug carriers, substrates for self-assembly to access various nanostructures, and biologically active molecules and excipients, such as antibacterial and penetration enhancers.¹ The broken symmetry offers new and efficient characteristic properties to form complex self-assembled materials, such as cubosomes, tubular vesicles, helical ribbons and bilayered vesicles (also known as dendrimersomes), which provide morphological monodispersity and long term stability in various media.² In addition, the dendritic peripheral groups can be used to attach various functional molecules to Janus dendrimers. Here, we present the synthesis and characterization of amphiphilic Janus dendrimers with aggregation-induced emission (AIE) properties via the attachment of tetraphenylethylene (TPE) moieties, a known molecule to efficiently undergo AIE³, to dendritic backbone. Both amphiphilic nature of our Janus dendrimers and their AIE properties unite the drug delivery aspect of their corresponding potential nanomaterials with their inherent diagnostic capabilities into one theranostic system.

Keywords—Janus dendrimers; Tetraphenylethylene; Dendrimersomes; Aggregation Induced Emission; Theranostic

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Electrochemically Driven C-N Bond Formation from CO₂ and Ammonia at the Triple - Phase Boundary

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Abstract

CO₂ electroreduction reaction (CO₂RR) is a promising method to produce fuels or useful chemicals in a clean and sustainable way. Electricity can be derived from the conversion of other clean energy sources, such as solar or wind, and the extra electricity can be converted into chemical fuels and stored in the form of chemical bonds. The consumption of CO₂ can also release greenhouse effect, thus this reaction has the potential to solve energy crisis and environmental problems. Various products (carbon monoxide, methanol, methane, ethanol, ethylene, n-propanol) can be produced by CO₂RR, but products with heteroatoms like acetamide or urea are more valuable than these products. Recently, nitrogen source (such as N₂ or ammonia) was added into CO₂RR system and products with C-N bonds were obtained, but the mechanism of the formation of C-N bonds is still unclear.

Herein, we combine electrochemical method with in-situ spectroscopy to reveal the intermediate of the reaction, and propose the possible reaction pathways. Cu or CuO nanoparticles (NPs) commercial powder was used as electrocatalyst, CO₂ and NH₄OH was used as the precursor, acetamide and formamide were observed as the final products with heteroatom. Electrolysis experiment shows that formamide is preferential to be formed on Cu catalyst, while CuO is more likely to produce acetamide. The faradaic efficiency (FE) is maximum for the formation of acetamide at -1.8V, which is 0.63%. While for Cu, the formation of formamide reaches maximum (3.78% FE) at -2.0V. As the formation of acetamide and acetate share the same intermediate, the production of formamide and formate may also undergo the same reaction pathway at the initial stage of the reaction. In-situ infrared (IR) spectroscopy was conducted to prove this speculation.

Keywords—CO₂ reduction reaction, carbon-nitrogen bonds formation, electrosynthesis, in-situ infrared spectroscopy

Fabrication of Liquid-Infused Textured Surfaces With Icephobic Characteristics

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Liquid-infused surfaces (LIS) and liquid-infused textured surfaces (LITS) were successfully fabricated to study the effect of the creating texture and lubricant infusion on ice adhesion, ice nucleation and long-term durability of such surfaces. The purpose was to merge the textured morphology and slipperiness in a lubricant infused silicone elastomer through replication method. The results showed that the designed slippery surfaces can decrease ice adhesion strength (less than 20 kPa) in four order of magnitude compared to the pristine surface. The heat insulation effect of lubricant could also influence the ice nucleation temperature. Indeed, in comparison with micro-textured samples without lubricant (-13.97 °C), increasing the lubricant percentage at both viscosity of 50 and 500 cSt, resulted in reduced ice nucleation temperature to near -22 °C. The micro-texturing of surface played an important role in controlling the presence of oil on the surface and it could enhance the durability of anti-icing results. The micro-textures could also reduce the rate of oil depletion by blocking them in the surface. So, for long-term applications, the designed lubricant infused surfaces could show more durable and stable anti-icing results in comparison with smooth lubricant infused surfaces.

Directing the Chirality of Epsomite Crystals with Chiral Additives

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Chirality is a geometric property of a molecule being non-superimposable with its mirror image. A remarkable manifestation of chirality results when achiral molecules crystallize to form enantiomorphic crystals (*e.g.* left- and right-handed crystals of quartz). When this occurs, one expects a stochastic distribution of left- and right-handed crystals (*i.e.* 50:50).¹ Epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) is a chiral sulphate mineral made up of achiral building blocks.^{2,3} Remarkably, a non-stochastic chiral distribution of epsomite was first reported by Dufet (1904) and Pocklington (1906) and recently confirmed in our lab (52 right-handed crystals out of 60 crystals).^{2,4}

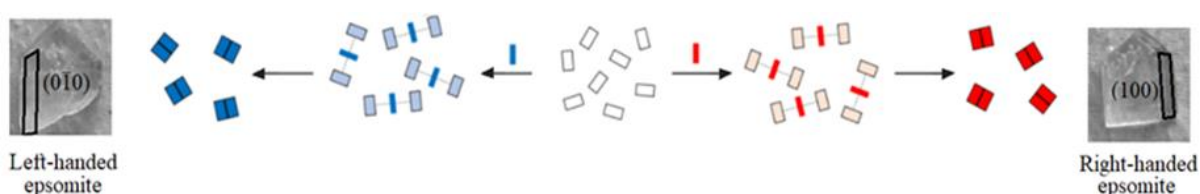


Figure 1. Chiral additives directing the crystal chirality of epsomite.

Epsomite can be resolved according to their distinguishable morphologies by identifying either the (0 $\bar{1}$ 0) or the (100) face in left- or right-handed crystal, respectively (Figure 1). The absolute configuration of epsomite was determined from the Flack parameter obtained by single crystal X-ray diffraction of each enantiomorph. Right-handed crystals predominantly form at 0.06 M of D- or L-asparagine (21 right-handed crystals out of 25 crystals and 30 right-handed crystals out of 35 crystals, respectively). In the presence of L-asparagine at 0.18 M, on the other hand, the number of left-handed epsomite crystals increased (15 left-handed crystals out of 28 crystals). This study suggests the possibility of directing the chiral crystallization of epsomite with chiral additives. More experiments for the chiral crystallization of epsomite with chiral additives are ongoing.

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Ultrastable Plasmonic Cu-Based Core–Shell Nanoparticles

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Abstract—Cu is the cheapest plasmonic metal showing plasmonic resonance in the visible region, which makes it highly attractive in various fields (e.g., sensing, surface-enhanced Raman scattering, and photocatalysis). However, its poor chemical stability severely restricts its application. Herein, we develop a seed-mediated approach to synthesize ultrastable Cu-based nanoparticles (NPs) stabilized with a thin, completely covered shell. By precisely controlling the reaction conditions, we are able to achieve uniform plasmonic Cu–Au core–shell NPs with significantly enhanced chemical stability even in a harsh environment in the presence of a strong oxidizing acid (HNO_3) solution. In-depth characterizations and analysis allow us to identify the critical role of the external crystalline Au layer, as compared to the AuCu alloy layer, in achieving superior stability. Furthermore, a deeper understanding of the plasmonic spectra was obtained by correlating the theoretical calculations on NPs of different core–shell dimensions with experimental results. Transient absorption measurements reveal that the plasmon dynamics and the heat transfer coefficients are not affected with the shell formation. As a proof of concept, these NPs demonstrate high photothermal efficiency and chemical stability for solar steam generation. This work offers a general strategy for the synthesis of ultrastable cost-effective, plasmonic Cu-based NPs, which show great potential in catalysis, electronics, and optics.

Comment peut-on fabriquer des feuilles à partir des fibres phosphorylées hautement chargées

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Abstract— La forte augmentation de la charge anionique des fibres lignocellulosiques après la phosphorylation conduit à une répulsion entre les fibres modifiées. Dans ces circonstances, les fibres phosphorylées présentent une forte affinité pour les surfaces métalliques, ce qui cause des problèmes de qualité de mise en forme du matériau et l'adhésion de la feuille aux différentes pièces de la machine à papier.

Nous avons utilisé comme support les fibres de pâte à papier issues du procédé kraft. Ces fibres sont très abondantes, faciles à modifier chimiquement et adaptées à plusieurs utilisations dans différents domaines des produits celluloseux fonctionnels. Les feuilles fabriquées à partir des fibres phosphorylées seront utilisées dans l'emballage alimentaire, la fabrication des matériaux de construction et également comme membranes filtrantes de l'eau et de l'air.

La stratégie expérimentale a consisté à synthétiser des esters de phosphate à longues chaînes carbonées, puis à les greffer par voie chimique sur les fibres lignocellulosiques. Le couplage a été réalisé dans un mélange d'esters de phosphate et d'urée. Les fibres obtenues ont été caractérisées par spectroscopie infrarouge, RMN et le taux de phosphore déterminé par spectrophotométrie UV-visible.

Pour réduire la charge anionique des fibres phosphorylées, plusieurs solutions sont évaluées. Dans un premier temps, nous avons utilisé des agents de rétention classiques (coagulants et floculants cationiques), non pas pour augmenter la rétention des fines ou des charges minérales, mais afin de favoriser la formation de microflocs pouvant être agglomérés et ainsi obtenir une bonne uniformité de formation de la feuille. Nous avons évalué les effets de ces additifs sur l'indice de formation des feuilles préparées pour contrôler le degré de floculation et l'uniformité de la distribution des fibres dans la feuille. Les résultats préliminaires démontrent que l'utilisation d'un système de rétention permet d'améliorer significativement l'indice de formation de la feuille (diminution de IFK=136 à 33). Des valeurs proches de celles des fibres de pâte kraft non modifiées (IFK de 20-30) ont été obtenues. Par contre, certaines propriétés mécaniques sont affectées négativement.

Keywords— Fibre lignocellulosique, phosphorylation, fibre phosphorylée, répulsion électrostatique, procédé kraft, esters de phosphate, agent de rétention.

Defluorination of the fluoropolymer surfaces for composite materials in the industrial market

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Abstract— Fluoropolymers are suitable for many applications, including textile, building, and biomedical materials. They are mainly used for their chemical inertness and low friction coefficient. However, their low surface energy leads to poor adhesion during the assembly with other materials for many applications. Among the different techniques used to enhance the adhesion of polymers, atmospheric pressure discharges (APD) remain fast and cheap methods that are suitable for industrial applications. The highly energetic species present in the ionized gas allow the breaking of molecular bonds at the film surface and favor the recombination with polar free radicals from the discharge. Although this approach has been proven to be efficient, understanding the chemical and physical processes leading to these results remains not yet fully understood. In this study, we performed the modification/defluorination of the fluoropolymer surfaces at atmospheric pressure using an inert N₂ plasma treatment equipped with a roll-to-roll system. The effect of the discharge on Ethylene tetrafluoroethylene (ETFE) was studied through a detailed surface analysis before and after each treatment. The characterization of the extreme surface was carried out by X-ray photoelectron spectroscopy (XPS). This work aims to show the effect of the precursor amount on the defluorination of the surface; meanwhile, the power control system will be characterized to have the most efficient surface defluorination. The proposed method to control the power is using the duty cycle (DC) to control the overheating and avoid polymer damage. The surface modification was carried out keeping the same conditions (i.e. same total N₂ flow, frequency, gas gap) and moving the film through the discharge at speed close to the industry condition. Results show that with changing the duty cycle from 10% to 80% with different powers (constant voltage), the lower amount of precursor (1.5%) could defluorinate the surface continuously by adding the carbon(%) on the surface from the precursor (increase of C/F from 0.85±0.01 (untreated) to 1.2±0.02). At the same time, the C/F increased by 3% precursor, but after 40% DC, the C/F ratio was constant. Therefore, a 1.5% precursor chose to evaluate the effect of duty cycle vs power because of stronger defluorination. The same power was applied by 20%, 30%, and 40% DC. The results showed that 40% DC could reach higher defluorination (C/F) while it could reach higher power at the same voltage compare to other duty cycles. These promising results constitute the first step toward a better understanding of the fundamental defluorination induced by this relatively new approach.

Keywords: *Atmospheric pressure nitrogen plasma; fluorinated ethylene propylene; power, organic precursor, duty cycle.*

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Multiresponsive hierarchical microgels: towards an independent tuning of swelling and surface properties

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Stimuli-responsive polymer coatings can be used as functional elements in nanotechnologies such as valves in microfluidic devices, as membranes in biomedical engineering, as substrates for culture of biological tissues or substrates of low friction. However, such coatings usually suffer from major shortcomings such as lack of selectivity and poor environmental stability. The talk will present a new generation of multi-responsive hierarchical and hybrid coatings aiming to overcome some of these limitations. A hierarchical polymer coating, consisting of two-dimensional thermo-responsive microgel arrays and surface-functionalized with non-responsive or pH-responsive polymers, was developed to tune independently the surface chemistry and the swelling behavior of the coating using different stimuli. The talk will report results showing how the characteristic dimensions (i.e. layer thickness) can indeed be controlled without affecting the surface properties (i.e. adhesion) of the functionalized microgel arrays. The responsiveness of the hierarchical coatings was investigated using the Surface Forces Apparatus allowing adhesion, friction, and layer thickness to be accurately determined under different stimuli.

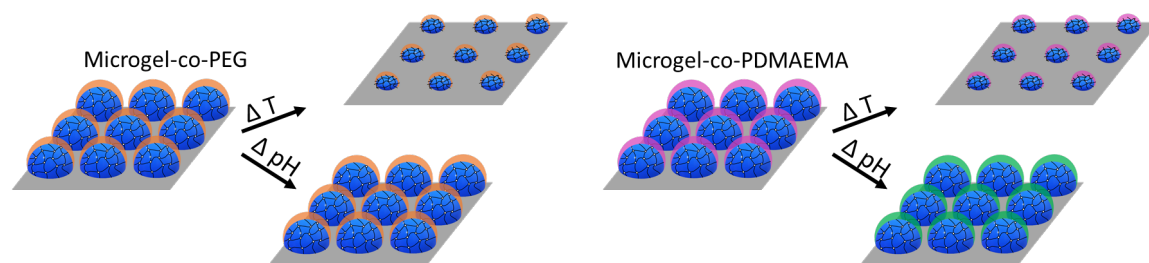


Photo-induced Force Microscopy Characterization of 2D Materials Grafted with Diazonium Salt

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Surface science and surface functionalization are important and well-studied realms. Modifications of surfaces imply critical changes of existing physical and chemical properties. Concrete examples of surface modifications are common in the field of material science. Simply modifying surfaces leads to characterization studies, with aims of better understanding the induced morphological changes effects. For instance, diazonium salts were grafted on conductive surfaces allowing sequential binding of specific antibodies and the target analyte, enabling sensing capabilities¹⁻³. Diazonium salts are known to bind via two different routes, spontaneously or electrochemically. On naturally reducing substrates (metals or conductive material), diazonium salts are known to graft spontaneously without additional driving force. Conversely, on rather dielectric material (for example SiO₂) additional treatment necessitates the successful binding of the aryl derivative. Such as the inclusion of mechanical defects or chemical etching. Aside substrate effects, layer thickness is a major determinant of the grafting method. Previously published work demonstrated the ability to confirm the functionalization by indirect or direct chemical and microscopical surface characterization techniques. These techniques were Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, polarization-modulation infrared reflectance spectroscopy, surface-enhanced Raman spectroscopy, Raman spectroscopy, scanning-tunneling, atomic force and transmission electron microscopy. Undoubtedly, these techniques ably demonstrated the success in functionalizing with the aryl derivatives. However, in terms of resolution and sensitivity, aside the surface-enhanced Raman spectroscopy, all are limited to a bulk sample response and therefore provide null data on the distribution at the molecular scale. Herein, a novel and innovative technique countering the previously stated shortcomings is introduced, the photo-induced force microscopy (PiFM), to characterize the resulting surface grafted molecules. Exploiting the induced dipole-moment at the tip-sample interaction area upon infrared irradiation, this technique resolves sub-10 nm features. In addition to localized chemical information, the photo-induced force microscope provides high-quality atomic force microscopy images accompanied with corresponding chemical mapping at selected wavenumbers of interest⁴⁻⁶. In this work, a sample application covers the comparison of spontaneous modification of four in-house ambient stable transition metal dichalcogenides (TMDCs), MoS₂, MoSe₂, WS₂ and WSe₂ on a dielectric growth wafer SiO₂ and the electrochemical modification on glassy carbon and gold electrode surfaces. To the best of our knowledge, we will show the first systematic 2D materials (TMDCs) surface characterization by PiFM obtained through a prominent thin-layer functionalization on the edges and defect sites of the grown material. As a control experiment, thin layers are electrochemically grafted on two different well-known substrates (glassy carbon and gold), in two different solutions, using two different diazonium salts.

Keywords: Diazonium salt grafting, photo-induced force microscopy, transition metal dichalcogenide, spontaneous grafting, electrochemical grafting, topography, infrared spectroscopy

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Exploring the potential of activated carbon nanoparticles as high solar absorption material to augment light-heat conversion ratio for solar desalination applications

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Abstract — Clean water is the most important need of inhabitants, however, increasing population and industrial growth is generating huge stress on the available water resources. On Earth, more than 95 % of available water resources are saline water in seas/oceans, and the existing desalination technology for converting saline water into freshwater like multi-stage flashing, reverse osmosis, and multi-effect desalination requires large amount of energy for its operation. Because of water scarcity and existing high energy usage desalination methods, solar-based water desalination using solar still (SS) is considered the most sustainable and cheapest method for converting brackish water into fresh water in an arid and remote area with abundant availability of solar energy. However, the major drawback of SS is lower water yield and different techniques have been investigated to improve its yield. Different improvement approach has been developed by the researchers such as utilization of sensible and latent heat energy storage materials. However, the stability of nanoparticle in base fluid (latent heat storage) and low-thermal conductivity of material (sensible heat storage) were the major constraint for these approach. In this view, the present experimental work synthesized an excellent solar absorption material i.e, activated carbon nanoparticles using dead *Kigelia Africana* leaves for improving the solar-thermal conversion and augmenting the water evaporation rate to achieve high yield. The pyrolysis of dead crushed leave powder in a muffle furnace at 500°C was carried out to achieve the nanoparticles. Fig. 1 depicts the SEM image of synthesized activated carbon nanoparticle. Thereafter, novel black paint was prepared with dispersion of 5 wt. % activated carbon nanoparticle in black paint with homogeneous mixing using the magnetic stirring. Afterward, this paint was used to absorb maximum solar radiation and augmented the solar thermal conversion efficiency.

To explore the solar - thermal conversion behaviours of the paint, comparative study of solar still with only black paint coated absorber and black paint with 5 wt. % activated carbon dispersion mixture were carried out under Indian climatic conditions and performance analysis, water analysis were performed. Result depicted that usage of carbon in black paint significantly improved the solar absorption behavior, leading to water productivity enhancement of 14%, as compared to the

conventional solar still with only black paint coated absorber. In addition, the water quality of the distilled water generated using the solar based conversion process was well in range as defined by WHO. It is concluded that the low cost synthesized carbon from bio-waste is excellent material for light-heat conversion and this will pave the path in improving the performance of solar desalination unit.

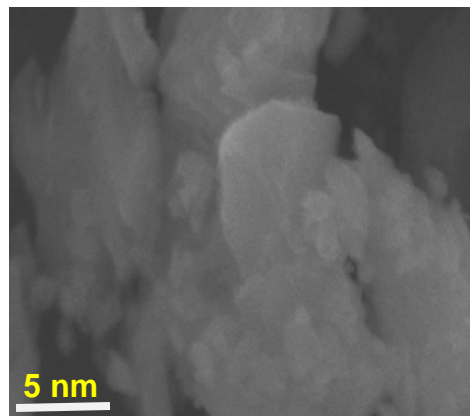


Fig. 1. SEM image of activated carbon nanoparticles

Keywords — Activated carbon nanoparticle, Solar-thermal conversion, Sustainable water generation, Thermal performance

Solution and Mechanochemical Synthesis of a New Class of Salicylic Acid-Based Metallohelicates

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Abstract— *The versatility and relevance of metallohelicates in the field of supramolecular chemistry have contributed significantly towards our understanding of self-assembly, molecular recognition, interactions with biologically relevant molecules, catalysis, and design of therapeutics.¹⁻³ Studies on helicates, however, have largely focused on cationic and neutral systems, specifically their ability to encapsulate other molecules or be templated by anions in solution. Studies on the preparation of new anionic helicates are scarce, and solvent-free routes to their synthesis are extremely poorly investigated.*

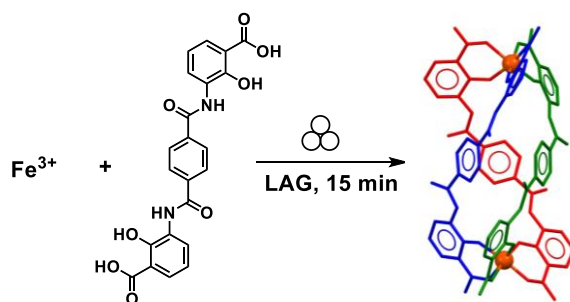


Figure 1. General scheme for the mechanochemical synthesis of Fe-based helicates

Herein, we disclose the design, as well as solution- and mechanochemistry-based syntheses, of a new class of anionic helicate units assembled from divalent and trivalent metal cations in the presence of a ligand derived from industrially relevant components: terephthalic and salicylic acids (Figure 1). We demonstrate the nuances of their self-assembly in the presence of various inorganic and organic cations. We further discuss the implications on the discovery of new solid and functional materials, as well as the implications on opportunities for the rapid, inexpensive, and environmentally-friendly design and synthesis of helicate-based materials.

Keywords (optional)—*helicate; supramolecular chemistry; self-assembly; mechanochemistry*

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Implementation of DFT calculations for the rational design of novel catalysts

Simulation of the catalyst $\text{Ce}_6\text{O}_{13}/\text{Cu}(111)$ and its synthetic process

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Keywords: *Methanol; catalyst; DFT; Quantum Espresso; simulation; optimization; synthetic process.*

The classical trial-and-error methodology to develop new catalysts consumes a great amount of time and resources and requires a lot of luck. Multiple factors need to be considered to develop an efficient and durable catalysts adapted to a given process: crystalline phase, composition, exposed facets, size, support, presence of promoters, etc. The number of possibilities increases exponentially with all the available parameters and along with it, the difficulty to successfully develop a new catalyst. Rational design has emerged as a new method to streamline the development of catalysts thanks to simulations and modelling that considerably reduce the parameter space and help select potential candidates.

Different levels of approximation exist to simulate molecular system such as quantum, or atomistic approaches. The Density Functional Theory (DFT) approach is a powerful quantum method to model reactions taking place at the catalyst's surfaces. Different codes exist, Quantum ESPRESSO (opEn-Source Package for Research in Electronic Structure, Simulation, and Optimization) that is considered in our calculations, is based on the use of plane wave basis sets and pseudopotentials.

Here, we explore DFT calculations in the framework of a model reaction: the synthesis of methanol. The validation step consists of reproducing the reactional pathway and energy as those published by Graciani et al. for the activity $\text{Ce}_6\text{O}_{13}/\text{Cu}(111)$ with Quantum ESPRESSO. This project is thus divided into two parts: the catalyst's modelization and optimization, and the synthetic process's reproduction.

The final structure of the catalyst's system is found to be slightly different from the one obtained by Graciani et al. Indeed, if the nanocluster of Ce_6O_{13} is similarly centered on the surface of $\text{Cu}(111)$ to avoid edge effects that were preventing the system's optimization, there is a minor difference in the number of layers composing the copper substrate. Graciani et al. only allowed the first two layers of $\text{Cu}(111)$ in contact with the nanocluster to move freely and froze the two last but we decided to keep only two layers of $\text{Cu}(111)$ instead of four in order to alleviate the time computing.

Simulation of the synthetic process begins by putting a molecule of CO_2 and three molecules of H_2 above the surface of the catalyst. These molecules are placed far enough from the catalyst to be free of any interaction with it during the system's optimization. The total energy of this system, once it is optimized, is considered as ground zero for the evaluation of the total energy of the system. Hence, the differences of the system's energies between the different steps of the synthetic process can be compared to those of Graciani et al.

The next step of this project is to simulate the rest of the synthetic process using Quantum ESPRESSO and to compare the results with the conclusions stemming from this article.

Electrospun cellulose acetate/chitosan nanofibers: an efficient adsorbent resulted from intermolecular interaction study for humic acid removal

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Abstract— Humic substance is a ubiquitous class of natural organic matter (NOM) in soil and aquatic ecosystems, which severely affects the terrestrial and aquatic environments as well as water-based engineering systems. In our previous work, the adsorption of humic acid (HA) on self-assembled monolayers with different functional groups (OH-SAMs, CH₃-SAMs, NH₂-SAMs, and COOH-SAM) has been reported, where amino groups exhibited superior adhesion energy towards HA, followed by methyl groups and hydroxyl groups. Therefore, in this work, chitosan (CS) and cellulose acetate (CA) derived from waste materials were selected to fabricate electrospun nanofibers containing -NH₂ and -CH₃ groups for the removal of HA from aqueous solutions. The effect of CA/CS ratios on the structure and adsorption performance of electrospun nanofibers was investigated in detail. The results revealed that all the samples (CA/CS=3:1, 1:1, 1:3) showed the high adsorption capacities (> 152 mg/g) towards HA at pH 4. It was because of the abundant functional groups on the surface of nanofibers. Especially, the CA/CS 1:1 sample had a uniform fibrous morphology with the average diameter of 335±242 nm, which led to the highest tensile strength of 2.97±0.59 MPa and adsorption capacity of 184.72 mg/g. The adsorption of HA onto CA/CS nanofibers was non-spontaneous and exothermic in nature. It followed the pseudo-first-order kinetic model and was primarily driven by electrostatic interaction. The adsorption isotherm was better fitted by Langmuir model. Therefore, this work demonstrates the feasibility to use intermolecular interaction mechanisms to guide the design of functional materials. Moreover, it provides a biodegradable efficient adsorbent that is promising for the applications in water treatment.

Keywords— *electrospinning, adsorption, cellulose acetate, chitosan, humic acid*

We would like to acknowledge financial support from the Fonds de Recherche du Quebec - Nature et Technologies (266796), Natural Sciences and Engineering Research Council of Canada (250374), Natural Sciences and Engineering Research Council of Canada Discovery Launch Supplement (250531), and McGill University Academic Startup Grant (130209). F.W. would like to thank the China Scholarship Council (CSC No. 201808515185) for financial support.

Controllable synthesis and development of one-dimensional oriented CdS-based nanoarray photoanodes for efficient solar hydrogen evolution

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Abstract: Photoelectrochemical (PEC) water splitting for hydrogen evolution is a highly efficient and eco-friendly technology towards solar energy conversion, but the question still how to build an available PEC system with satisfied photoconversion efficiency. Photoactive materials as the basic component for PEC systems, have been extensively studied due to their distinct structure features. Among them, cadmium sulfide (CdS), especially one-dimension (1D) oriented CdS nanoarray has attracted considerable attention and is regarded as a promising candidate for PEC hydrogen production due to its suitable narrow bandgap (2.4 eV), excellent electrical/optical properties, larger aspect ratio and confined charge transfer path for lower carrier loss. However, bare CdS nanoarray photoanode suffers from serious surface charge recombination, photo-corrosion, and low quantum efficiency which is greatly limiting its practical application. Here, the rational design of CdS-based nanojunctions, like plasmon-enhanced, Z-scheme and p-n scheme heterostructure, will be employed to overcome these drawbacks through coupling 1D CdS with other components. In current work and as proof of concept (Figure 1), a novel ternary hierarchical photoanode with oriented 1D nanostructure has been successfully prepared via decorating gold nanoparticles (Au NPs) and carbonized Polydopamine (CPDA) film onto CdS nanorod arrays (CdS/CPDA/Au). A variety of material characterization and PEC measurements demonstrates that the fabricated CdS/CPDA/Au photoanode presents higher photoconversion efficiency, better photostability and lengthened electron lifetimes.

Keywords: CdS-based photoanodes, carbon coating, graphene-like, plasmon-enhanced photoelectrocatalysis, hydrogen evolution.

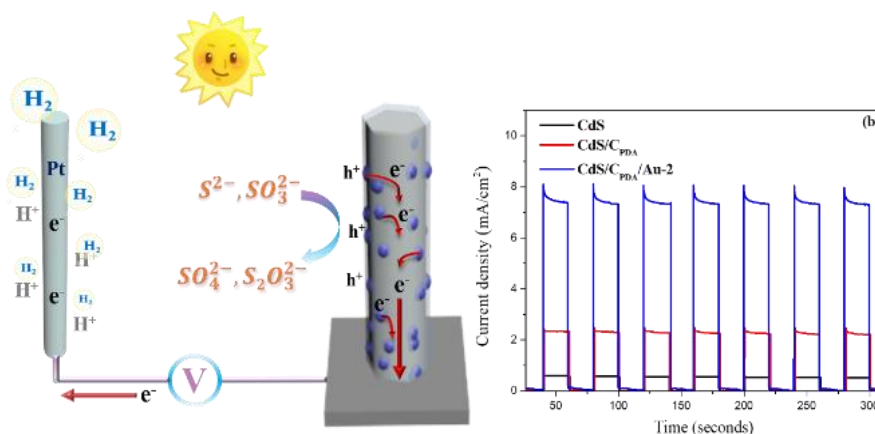


Figure 1. The possible mechanism sketch of PEC hydrogen generation over 1D-oriented CdS/CPDA/Au photoanode and its transient photocurrent response

Étude du comportement de gouttelette d'eau sur des surfaces micro structurées

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Résumé

Le résumé suivant porte sur le travail de recherche intitulé : Étude de l'impact de gouttelette d'eau sur des surfaces micro structurées. C'est une étude qui consiste à fabriquer différents modèles de surfaces micro structurées à base de polymère et de métal (le Kapton et l'aluminium). Cette différence entre ces modèles est définie par la variation de la distance entre les trous ainsi que les diamètres des trous. Une approche mécanique sera adoptée pour créer la texture de la surface grâce à une machine à commande numérique. Une réplique des motifs est faite grâce au moulage par compression en utilisant une machine à compression. Le caoutchouc de silicone est utilisé comme matériau de base. En fait, cette réplique des textures nous permet d'étudier et d'observer le comportement dynamique des gouttelettes d'eau sur les différents motifs des surfaces créées. La variation de la vitesse d'impact et le diamètre ainsi que la micro structure de la surface de la gouttelette d'eau et leur impacts sur le comportement de gouttelette d'eau seront étudiées. Cet impact est enregistré par une caméra à haute vitesse qui est connectée à un ordinateur. Cette recherche permettra de montrer quelles microstructures sont appropriées pour avoir des surfaces hydrophobes et/ou superhydrophobes avec des comportements de rebondissement. De plus, nous avons montré comment les conditions de gouttelettes d'eau (taille, vitesse d'impact etc.) affectent sur le comportement de ces surfaces. Il convient de noter qu'en utilisant une méthode industriellement applicable pour produire ces surfaces (usinage en utilisant une machine à commande numérique). Cette étude peut ouvrir de nouvelles voies dans la fabrication de surfaces hydrophobes et/ou superhydrophobes à l'échelle industrielle.

Mots clés : Mouillabilité, rugosité, micro structure, rebondissement, déposition, comportement, machine à commande numérique, réplique et moulage par compression.

Development of a dual capsule self-healing silicone composite using poly(melamine-urea-formaldehyde) shells

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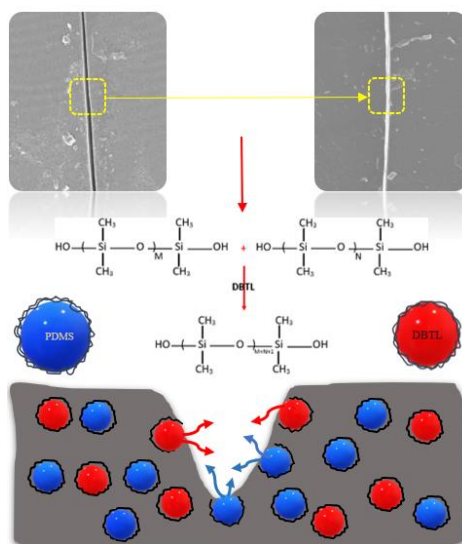
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This study aims to develop microcapsules that can be used as room-temperature self-healing agents in silicone-based matrices. A reactive silanol-terminated polydimethylsiloxane (PDMS) as the healing agent, was selected to ensure the homogeneity of the polymeric matrix and encapsulated in poly(melamine-urea-formaldehyde) shells through an in-situ emulsion polymerization technique. Dibutyltin dilaurate (DBTL) was encapsulated as the catalyst within the same type of polymeric shell. The synthesized microcapsules were characterized using Fourier-transform infrared spectrometry, optical microscopy, scanning electron microscopy, and differential scanning calorimetry. The analyses confirmed that the spherical microcapsules with an average size of 56 μm for PDMS-MUF microcapsules and 42 μm for DBTL-MUF microcapsules, with a shell wall thickness of 100–200 nm, and good thermal stability. Therefore, the two-component self-healing silicone composite was successfully developed using 10:1.2 wt.% PDMS:DBTL microcapsules within the silicone matrix. Scanning electron microscopy (SEM) confirmed the self-healing ability of the silicone matrix by observing the successful healing of microcracks at room temperature.

Keywords Self-healing; Smart materials; Microencapsulation; in situ polymerization; Polydimethylsiloxane (PDMS); Poly(melamine-urea-formaldehyde) shell.



Development of an icephobic organosilane-based coating for application in condensing environments

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Abstract— Icing is a very important problem with disastrous consequences in common infrastructure including marine ones. In the last decades, the development of icephobic surfaces; more advantageous, are gaining much importance over traditional de-icing techniques. However, although icephobicity can be achieved with superhydrophobic surfaces, these later may be ineffective in environments with high humidity like river and sea areas. Due to condensation, the adhesive strength of the ice on superhydrophobic surfaces increases. In this contribution, the targeted strategy proposed, involves the development of hydrophobic coating with high icephobic potential to reduce the adhesion strength of the ice and delay the freezing time of impactful droplets. To meet this objective, the good adhesion of epoxies to metal substrates, the good reactivity of amino silicones and their ability to give hydrophobic epoxy resins with organosilanes as a surface energy modifying agent and water absorption barrier, were considered. Knowing that hydrophobicity of a surface is intrinsically linked to its surface energy, additives containing several -CH_x and -CF_x groups based on silicone or fluorocarbon are preferred. In the literature, several studies report the use of polydimethylsiloxane (PDMS) and polytetrafluoroethylene (PTFE) in the development of hydrophobic surfaces to achieve icephobicity [4] Therefore, the hydrophobic epoxy-silicone based coating developed with organosilanes as additives presents low ice adhesion strength with an ice Adhesion reduction Factor (ARF) greater than 5 on metallic substrates. In fact, ARF of 5.6 and 6.3 were observed respectively on aluminum and steel substrates. The freezing process was noticed to occurred with a delay of almost 30 minutes on the prepared surfaces with an appropriate amount of silane additive. Silicone contents in matrix induce the reduction of the elastic modulus (Young modulus) which means decreasing in ice adhesion strength [5]. Therefore, the mechanical properties are to be assessed by tensile testing based on ASTM D 2370. This study opens the door for the development of durable icephobic phobic surfaces, especially in high condensing environments.

Keywords— *Hydrophobic, icephobic, freezing delay, elastic modulus, Young modulus, adhesion reduction factor, marine, high humidity.*

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Thermal Properties of Structure I Hydrates Using Density Functional Theory and Phonon Calculations

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Abstract—Water and small gas molecules form inclusion compounds, or clathrates, under certain low temperature and high-pressure conditions. Previously examined due to their negative effects on flow assurance and petroleum extraction safety, gas hydrates are now examined as materials to separate flue gases, store natural gas and hydrogen, and as a potentially massive energy source in the form of continental and subsea reserves. The thermal properties and their underlying atomic sources are crucial to the development of gas hydrates as part of new green technologies and the development of knowledge related to their stability and formation yet remain limited and incomplete. By connecting density functional theory as implemented in the Vienna ab initio Simulation Package with phonon calculations as implemented in Phonopy, this work bridges the gap between theory and experiment by calculating the thermal properties of gas hydrates using atomic simulation and extending atomic phenomena to macroscale properties. The constant volume heat capacity, constant pressure heat capacity, the Grüneisen parameter, and the thermal expansion coefficient were calculated for hexagonal ice, empty sI hydrates, and methane, ethane, and carbon dioxide sI hydrates from 0 to 300 Kelvin. Compared to molecular dynamics, density functional theory found lower constant volume heat capacities for all structures. The constant pressure heat capacity at low temperatures calculated by this work replicated experimental values for all structures but deviations with experiment increased with temperature. The thermal expansion coefficient was underestimated by this work in all structures. When compared to methane and empty hydrates, carbon dioxide and ethane hydrates had markedly different thermal expansion behavior with much higher values. The Grüneisen parameter was overestimated for filled hydrates and ice in comparison to experimental values for hexagonal ice. This theoretical study adds to the basic material science and applications of gas hydrates to improve the database of properties that are of critical importance in energy security, environmental engineering and provides high quality data that can be used to optimize other simulation techniques, such as molecule dynamics.

Keywords—methane, renewables, hydrate, clathrate, computational, functional, phonon, thermal

Elucidation of a new complex pathway in 2D supramolecular polymerization of DNA-oligomer block copolymer amphiphiles

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Synthetically accessible two-dimensional (2D) nanomaterials are of great interest due to their prospective applications in electronics, catalysis, and biotechnology, and as membrane materials. One method of accessing these topologically planar structures is through the supramolecular polymerization of amphiphilic block copolymers (BCPs) via self-assembly in a selective solvent. The use of DNA-oligomer amphiphiles as the BCPs for construction of supramolecular 2D nanoarchitectures offers the unique opportunity to both introduce functional cores in these structures as well as functionalize the surface of the 2D material via complementary DNA base pairing or blunt end interactions. These DNA-based 2D nanostructures have not been widely explored, and the few studied thus far have been limited by a lack of control over their shape and size.

Our group has previously demonstrated the morphological tunability of supramolecular architectures comprising self-assembled DNA-oligomer amphiphiles leading to nanospheres/micelles (0D) and nanorods (1D). Here we report a complex hierarchical growth mechanism of 2D nanosheets obtained through the self-assembly of synthetic amphiphilic DNA-oligomers bearing π -conjugated chromophores in aqueous solution. We explore the effect of varying self-assembly parameters and amphiphile structure on the structural order and size of the nanosheets. The goal is to kinetically control the formation of the supramolecular architecture, allowing us to precisely tune the shape and size of the 2D assembly. This will enable the creation of synthetically accessible, well-defined, monolayered 2D DNA nanosheets – using a single type of block copolymer – that could potentially serve as economical alternatives to DNA-dense 2D DNA origami structures.

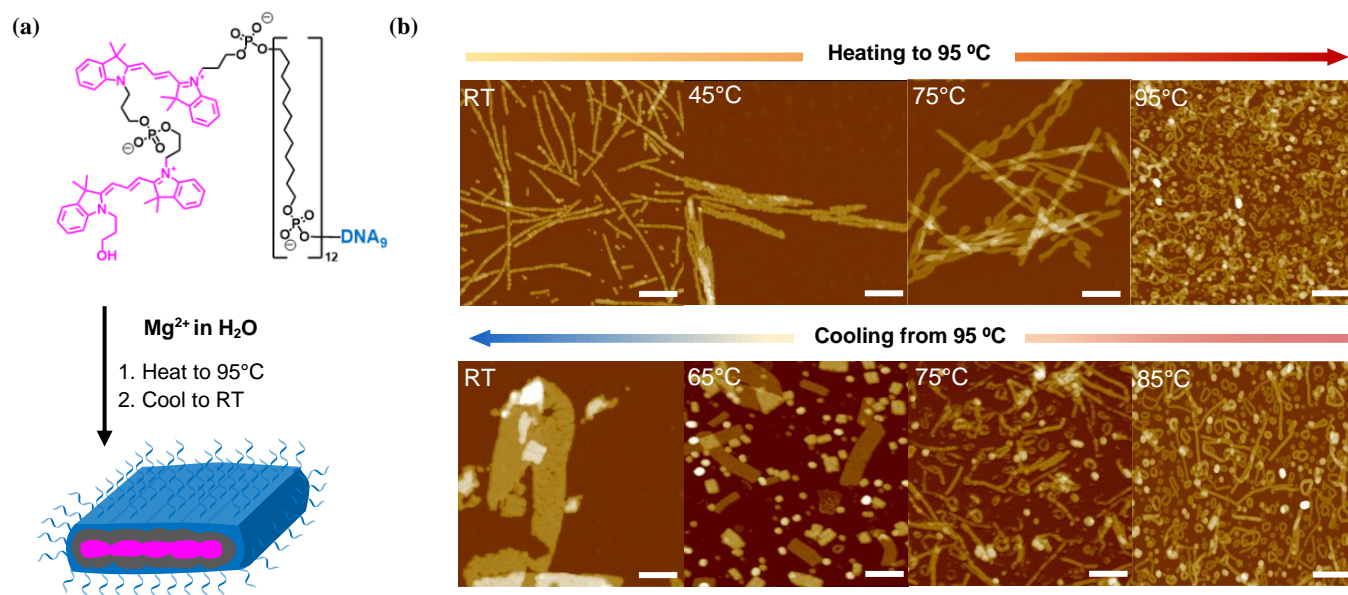


Fig. 1. (a) The block copolymer **Cy3₂-C12₁₂-DNA₉** ([2-Cy3]-[12-hexaethylene]-[9-mer DNA sequence]) undergoes cation-mediated self-assembly in aqueous solution upon annealing to form 2D nanosheets. (b) AFM images showing the kinetically trapped morphologies obtained during thermal annealing and cooling of **Cy3₂-C12₁₂-DNA₉** en route to the thermodynamic nanosheet structure. Scale bars: 250 nm.