

NANOMATERIALS FOR DEVICES

Italy/Canada Bilateral Workshop

Abstracts



September 10th-12th, 2018 – Montreal (Canada)

Scientific Committee

Giorgio Contini, ISM-CNR, Rome, Italy - giorgio.contini@ism.cnr.it

Federico Rosei, INRS, Montreal, Canada - rosei@emt.inrs.ca

Organizing Committee

Rufin Djaozandry, INRS, Montreal, Canada - rufin.djaozandry@emt.inrs.ca

Geneviève Goupil, INRS, Montreal, Canada - genevieve.goupil@emt.inrs.ca

Franca Rossi, ISM-CNR, Rome, Italy - franca.rossi@ism.cnr.it



CNR
Istituto di Struttura
della Materia



**CRSNG
NSERC**



INRS
UNIVERSITÉ DE RECHERCHE



*Ministero degli Affari Esteri
e della Cooperazione Internazionale*

Nanomaterials for Devices

Italy/Canada Bilateral Workshop

The Workshop covers a range of topics in the area of nanomaterials, from the design, to the synthesis, to the characterization of structure and properties and finally to their integration in devices. Both experimental and theoretical aspects are discussed.

Emphasis is given to new two-dimensional nanomaterials, as well as quantum dots and nanowires. These systems are being increasingly used in applications such as electronic and photonic devices, biomedical technologies and sensors. The Workshop aims at bringing together an outstanding and diverse group of scientists at the forefront of research on nanomaterials, with an interdisciplinary point of view. Researchers and students are encouraged to present posters on their activities.

The workshop is a bilateral project funded and sponsored by the Italian Ministry of Foreign affairs (MAECI) and the Natural Sciences and Engineering Research Council of Canada (NSERC) on the study of surface confined polymerization and it is organized by the Institute for the structure of matter (Giorgio Contini) – CNR and the Institut National de la Recherche Scientifique – INRS (Federico Rosei), jointly with the Embassy of Italy in Canada.

The Opening Keynote lecture is given by Professor John C. Polanyi from the University of Toronto, Nobel Laureate in Chemistry (1986).

INVITED SPEAKERS

Italy

- Fabio Beltram (Normale Univ.)
- Thomas M. Brown (Tor Vergata Univ.)
- Giovanni Comelli (Trieste Univ.)
- Luca Floreano (CNR, IOM)
- Stefan Heun (CNR, Nano)
- Alessandro Molle (CNR, IMM)
- Maurizia Palummo (Tor Vergata Univ.)
- Filippo Romanato (Padova Univ.)
- Anna Sgarlata (Tor Vergata Univ.)
- Valentina Tozzini (CNR, Nano)

Canada

- Marta Cerruti (McGill Univ.)
- Giovanni Fanchini (Western Ontario Univ.)
- Nazir Kherani (Toronto Univ.)
- Dongling Ma (INRS)
- Jean-François Morin (Laval Univ.)
- Jean Michel Nunzi (Queens Univ.)
- Emanuele Orgiu (INRS)
- Dimitrii Perepichka (McGill Univ.)
- John Polanyi (Toronto Univ.)
- Clara Santato (Polymtl)
- Mohamed Siaj (UQAM)
- Hanadi Sleiman (McGill Univ.)
- Thomas Szkopek (McGill Univ.)
- Fiorenzo Vetrone (INRS)

INDEX

PROGRAM	8
<u>INVITED SPEAKERS</u>	
SOMETHING NEW: NANO-MOLECULAR BEAMS GIVE SURFACE REACTION AT SELECTED IMPACT PARAMETERS	12
<i>J. Polanyi</i>	
GRAPHENE GROWTH ON NI(111).....	13
<i>G. Comelli</i>	
NANOSYSTEMS FOR BIOMEDICINE	14
<i>F. Beltram</i>	
TOWARDS GREENER ELECTRONICS	15
<i>C. Santato</i>	
NANOSTRUCTURED FLASH MEMORY DEVICES BASED ON RADICAL POLYMERS AND CARBON-BASED NANOMATERIALS	16
<i>G. Fanchini</i>	
OPTICAL RECTIFICATION AND HOT-ELECTRON PHOTO-DETECTORS	17
<i>JM. Nunzi</i>	
MATERIALS DESIGN THE TWO-DIMENSIONAL LEVEL: FROM XENES TO ANISOTROPIC MOS₂	18
<i>A. Molle</i>	
π-ELECTRON CONJUGATION IN 2D POLYMERS.....	19
<i>D. Perepichka</i>	
DEVELOPING HYBRID NANOSTRUCTURES FOR ENERGY AND BIOMEDICAL APPLICATIONS	20
<i>D. Ma</i>	
EPITAXIAL GROWTH OF GE-BASED NANOMATERIALS. FROM GESI TO NOVEL BIDIMENSIONAL SYSTEMS: GRAPHENE ON GE AND GERMANENE ON HOPG	21
<i>A. Sgarlata</i>	
NOVEL PHOTOCHEMICAL METHODS FOR THE PREPARATION OF NANOGRAPHENES AND GRAPHENE NANORIBBONS	22
<i>JF. Morin</i>	
GRAPHENE AEROGELS: FROM SELF-ASSEMBLY TO APPLICATIONS.....	23
<i>M. Cerruti</i>	
NOVEL 2D MATERIALS FOR OPTO-ELECTRONIC APPLICATIONS: INSIGHT FROM PARAMETER-FREE QUANTUM MECHANICAL METHODS"	24
<i>M. Palummo</i>	
NON-CLASSICAL LONGITUDINAL MAGNETO-RESISTANCE IN ANISOTROPIC BLACK PHOSPHORUS	25
<i>S. Heun</i>	
EFFICIENT HYDROGEN EVOLUTION BASED ON BIDDING-FREE MOLYBDENUM DISELENIDE CATALYST	26
<i>M. Siaz</i>	
CHEMICAL REACTIONS OF PORPHYRINS AT THE INTERFACE WITH TRANSITION METAL OXIDES.....	27
<i>L. Floreano</i>	

ENGINEERING NANOSTRUCTURED MATERIALS FORTUNABLE LIGHT-MATTER INTERACTIONS	28
<i>N. Kherani</i>	
NANOSTRUCTURED METASURFACE OPTICS FOR ORBITAL ANGULAR MOMENTUM SPECTROSCOPY	29
<i>F. Romanato</i>	
ION SENSITIVE GRAPHENE FIELD EFFECT TRANSISTORS : SATURATING THE PHYSICAL LIMIT TO POTENTIOMETRIC SENSING	30
<i>T. Szkopek</i>	
ELECTRON EXTRACTING NANOLAYERS IN PEROVSKITE & ORGANIC SOLAR CELLS.....	31
<i>T. M. Brown</i>	
LANTHANIDE-DOPED NANOPARTICLES.....	32
<i>F. Vetrone</i>	
HYBRID VAN DER WAALS HETEROSTRUCTURES.....	33
<i>E. Orgiu</i>	
GRAPHENE IMPERFECTIONS: DEFECTS OR EFFECTS?	34
<i>V. Tozzini</i>	
ASSEMBLING MATERIALS WITH DNA AS THE GUIDE.....	35
<i>H. Sleiman</i>	

POSTERS

HYDROTHERMAL GROWTH OF ZINC OXIDE NANO-RODS DOPED WITH MANGANESE	37
<i>R. Bagga</i>	
CARBON DOTS AS MATERIAL FOR SOLAR ENERGY HARVESTING DEVICES	38
<i>D. Benetti</i>	
WETTABILITY AND CHEMICAL AFFINITY OF CNC LATTICE PLANES	39
<i>C. Bruehl</i>	
SURFACE-MEDIATED ASSEMBLY, POLYMERIZATION AND DEGRADATION OF THIOPHENE-BASED MONOMERS	40
<i>F. De Marchi</i>	
TRANSFER OF A TWO-DIMENSIONAL POLYMERIC LAYER TO A DEVICE-SUITABLE SUBSTRATE FOR ITS UTILIZATION AS ACTIVE MEDIA	41
<i>D. Dettmann</i>	
CHALLENGES AND PERSPECTIVE OF ON-SURFACE ULLMANN POLYMERIZATION	42
<i>G. Galeotti</i>	
PREPARATION AND CHARACTERIZATIONS OF CH₃NH₃PBI₃ PEROVSKITE THIN FILMS FOR SOLAR CELLS APPLICATIONS	43
<i>S. Hariech</i>	
ELECTRONIC STRUCTURES OF 3P SUB-FAMILY GRAPHENE NANORIBBONS	44
<i>P. Ji</i>	
LIGHT-MATTER INTERACTION IN TERAHERTZ PLASMONIC NANOCAVITIES	45
<i>X. Jin</i>	
MODIFICATION OF THE SURFACE PROPERTIES OF TiO₂ FILMS USING AN N₂/N₂O DIELECTRIC BARRIER DISCHARGE PLASMA.....	46

Z. Matouk
nezhad

DEGRADATION ANALYSIS OF DYE-SENSITIZED SOLAR CELL PERFORMANCE UNDER THERMAL STRESS47
M. Mohammas

DETERMINING STRESSES IN SILICON-BASED MICRODEVICES USING FRACTOGRAPHY48
A. Moulins

EFFECT OF CHROMIUM DOPING ON THE FORMATION OF M2 PHASE OF VO₂ THIN FILMS DEPOSITED BY REACTIVE PULSED LASER ABLATION49
A. O. Suleiman

ELECTRONIC SHIELDS AND HUMIDITY SWITCHES MADE FROM COMPOSITES OF CARBON NANOTUBES AND NANOCELLULOSE50
T. G.M. van de Ven

SINGLE-PIXEL TERAHERTZ IMAGING USING A TIME-DOMAIN SPECTROSCOPY SETUP51
L. Zanotto

PROGRAM

September 10th 2018

8:30 am - 10:30 am **Registration and Refreshments**

10:15 am - 10:40 am **Opening remarks**

L.A. Giraldeau, DG of INRS

Claudio Taffuri, Italian Ambassador of Italy in Canada

Giorgio Contini and Federico Rosei

Session chair: Federico Rosei

10:40 am - 11:30 am	John Polanyi (Univ. of Toronto) <i>Something new: Nano-Molecular Beams give surface reaction at selected impact parameters</i>
---------------------	--

11:30 am - 12:00 am	Giovanni Comelli (Trieste Univ.) <i>Graphene growth on Ni(111)</i>
---------------------	--

12:00 pm - 1:30 pm **Buffet Lunch**

Session chair: Giorgio Contini

1:30 pm - 2:00 pm	Fabio Beltram (Normale Univ.) <i>Nanosystems for biomedicine</i>
-------------------	--

2:00 pm - 2:30 pm	Clara Santato (Polymtl) <i>Towards greener electronics</i>
-------------------	--

2:30 pm - 3:00 pm	Giovanni Fanchini (Western Ontario Univ.) <i>Nanostructured flash memory devices based on radical polymers and carbon-based nanomaterials</i>
-------------------	---

3:00 pm - 3:30 pm **Coffee Break**

Session chair: Giovanni Comelli

3:30 pm - 4:00 pm	Jean Michel Nunzi (Queens Univ.) <i>Optical Rectification and Hot-Electron Photo-detectors</i>
-------------------	--

4:00 pm - 4:30 pm	Alessandro Molle (CNR, IMM) <i>Materials design the two-dimensional level: from Xenon to anisotropic MoS₂</i>
-------------------	--

4:30 pm - 5:00 pm	Dimitri Perepichka (McGill Univ.) <i>π-Electron Conjugation in 2D Polymers</i>
-------------------	---

Session chair: Federico Rosei

5:00 pm - 5:10 pm	Robert Déziel (regional director, NSERC-CRSNG)
-------------------	---

5:10 pm - 6:30 pm	Panel Events: discussion with Industries Partners
-------------------	--

Participants	<i>Bioastra Technologies inc., Mrs Sumitra S Rajagopalan Sens Wear, Dr. Alireza Hassani Photon etc., Mr Sébastien Blais-Ouellette MPB Communications inc., Mr Emile Haddad</i>
---------------------	--

8:15 pm **Social Dinner**

September 11th 2018

Session chair: Fabio Beltram

10:00 am - 10:30 am	Dongling Ma (INRS) <i>Developing Hybrid Nanostructures for Energy and Biomedical Applications</i>
10:30 am - 11:00 am	Anna Sgarlata (Tor Vergata Univ.) <i>Epitaxial growth of Ge-based nanomaterials. From GeSi to novel bidimensional systems: Graphene on Ge and Germanene on HOPG</i>
11:00 am - 11:30 am	Jean-François Morin (Laval Univ.) <i>Novel Photochemical Methods for the Preparation of Nanographenes and Graphene Nanoribbons</i>

11:30 am - 12:00 am Coffee Break

Session chair: Dongling Ma

12:00 am - 12:30 am	Marta Cerruti (McGill Univ.) <i>Graphene aerogels: from self-assembly to applications</i>
12:30 am - 1:00 pm	Maurizia Palummo (Tor Vergata Univ.) <i>Novel 2D materials for opto-electronic applications: insight from parameter-free quantum mechanical methods"</i>

1:00 pm - 2:30 pm Buffet Lunch

Session chair: Maurizia Palummo

2:30 pm - 3:00 pm	Stefan Heun (CNR, Nano) <i>Non-Classical Longitudinal Magneto-Resistance in Anisotropic Black Phosphorus</i>
3:00 pm - 3:30 pm	Mohamed Sijaj (UQAM) <i>Efficient hydrogen evolution based on bidding-free molybdenum diselenide catalyst</i>
3:30 pm - 4:00 pm	Luca Floreano (CNR, IOM) <i>Chemical reactions of porphyrins at the interface with transition metal oxides</i>

4:00 pm - 4:30 pm Coffee Break

Session chair: Stefan Heun

4:30 pm - 5:00 pm	Nazir Kherani (Toronto Univ.) <i>Engineering Nanostructured Materials for Tunable Light-Matter Interactions</i>
5:00 pm – 5:30 pm	Filippo Romanato (Padova Univ.) <i>Nanostructured metasurface optics for Orbital Angular Momentum spectroscopy</i>
5:30 pm – 6:00 pm	Thomas Szkopek (McGill Univ.) <i>Ion Sensitive Graphene Field Effect Transistors: Saturating the Physical Limit to Potentiometric Sensing</i>

September 12th 2018

Session chair: Anna Sgarlata

10:00 am - 10:30 am	Thomas M. Brown (Tor Vergata Univ.) <i>Electron extracting nanolayers in perovskite & organic solar cells</i>
---------------------	---

10:30 am - 11:00 am	Fiorenzo Vetrone (INRS) <i>Lanthanide-Doped Nanoparticles</i>
---------------------	---

11:00 am - 11:30 am **Coffee Break**

Session chair: Dimitri Perepichka

11:30 am - 12:00 am	Emanuele Orgiu (INRS) <i>Hybrid van der Waals Heterostructures</i>
---------------------	--

12:00 pm - 12:30 pm	Valentina Tozzini (CNR, Nano) <i>Graphene imperfections: defects or effects?</i>
---------------------	--

12:30 pm - 1:00 pm	Hanadi Sleiman (McGill Univ.) <i>Assembling Materials with DNA as the Guide</i>
--------------------	---

1:00 pm – 1:10 pm **Concluding remarks and greetings**1:10 pm - 2:30 pm **Buffet Lunch**2:30 pm – 4:00 pm **Visit to INRS facilities**

INVITED SPEAKERS

Something new: Nano-Molecular Beams give surface reaction at selected impact parameters

K. Anggara, L. Leung, M. J. Timm, Z.Hu and J.Polanyi*

Lash Miller Chemical Laboratories, University of Toronto, Canada

Electron-induced chemical reaction at surfaces can give rise to selective bond-breaking, and to directional recoil of molecular fragments. Recent work has shown that these fragments can, in a favorable case, be collimated by underlying surface atoms giving rise to 'surface molecular beams'. The molecular beam can then be aimed to strike a second adsorbate molecule at a chosen impact parameter (chosen 'miss distance'). This is in contrast to gaseous crossed-beams that necessarily average from zero impact parameter to infinity. We describe some cases of electron-induced surface reaction for simple molecules, and report early results of 'Surface Aligned Reaction' at selected impact parameters.

Graphene growth on Ni(111)

G. Comelli

Department of Physics, University of Trieste and IOM-CNR TASC Laboratory, Trieste (Italy)

By means of joint Scanning Tunneling Microscopy (STM) experiments and Density Functional Theory (DFT) ab initio calculations, we have recently characterized the different chemisorbed configurations of epitaxial graphene coexisting on a Ni(111) single crystal surface [1], providing also an atomic scale description of the structure of their edges both during and post growth [2]. Here we demonstrate, both experimentally and theoretically, the catalytic role played by single metal adatoms during this spontaneous and technologically relevant growth process, which is crucial for the production of high quality graphene layers. The elusive catalytic action of individual Ni atoms at the edges of a growing graphene flake is directly captured by STM imaging at the ms time scale, thanks to the Fast-scan add-on module recently developed in our laboratory, that is capable of providing video rate STM movies of surface processes using a commercial STM system. DFT and force-field molecular dynamics calculations rationalize the experimental observations, yielding a full atomistic description of the growth mechanism [3], where the single atom Ni catalyst acts as a knitting needle, allowing new carbon stitches to be incorporated in the expanding graphene fabric. Our results represent a direct observation of a single atom catalyst at work during a surface catalysed process, providing straightforward evidence of the enhanced reactivity displayed by low-coordinated metal atoms in many model systems.

References:

- [1] F. Bianchini, L.L. Patera, M. Peressi, C. Africh, and G. Comelli, *J. Phys. Chem. Lett.* 51, 467 (2014).
- [2] L. L. Patera, F. Bianchini, G. Troiano, C. Dri, C. Cepek, M. Peressi, C. Africh, and G. Comelli, *Nano Lett.* 15, 56 (2015). [3] L.L. Patera, F. Bianchini, C. Africh, C. Dri, G. Soldano, M.M. Mariscal, M. Peressi, and G. Comelli, *Science* 359, 1243 (2018).

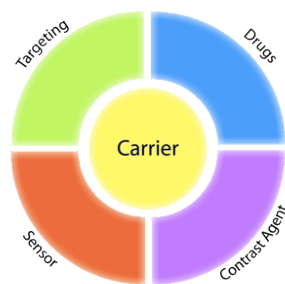
Nanosystems for biomedicine

F. Beltram

*Laboratorio NEST, Scuola Normale Superiore and Istituto Nanoscienze del CNR,
Pisa, Italy*

Nanotechnology was born as a result of the impressive technological advances driven by electronics, but has led to a set of methods and ideas drastically impacting other fields. In this presentation our increased ability to tailor nanosystem properties will be discussed as a means to design and produce multifunctional nanosystems of interest for biomedicine. These can provide a signal or a function dependent on the value of a specific biological parameter and can target specific subcellular domains. Importantly, they can be optimized also for the application to live organisms and are the enablers of *nanomedicine*.

Recent results will be discussed that highlight the impact of nanobiotechnology in this context with a particular emphasis given to methods suitable for *in vivo* studies that can be transferred to the biomedical world.



Schematic representation of the nanoprobe that will be discussed in this presentation.

Additionally I shall show that such nanotools can be integrated in lab-on-a-chip architectures to provide fast, automated diagnostic functions. In this context an on-chip pumping protocol based on surface acoustic waves will be shown also within complex fluidic networks. This approach eliminates the need for external pumps or fluidic circuitry and opens the way to fully stand-alone miniaturized fluidic chips.

Towards greener electronics

E. Di Mauro, C. Santato

Polytechnique Montreal, Montreal, Quebec, Canada

Electronics have become indispensable in our daily routine. A great part of the electronic equipment that surrounds us belongs to what is known as conventional electronics, based on inorganic materials such as silicon and gallium arsenide.

However, with the life of the electric and electronic equipment becoming shorter and shorter, two major issues arise for both the scientific community and municipalities: the increasing amount of Waste of Electrical and Electronic Equipment (WEEE) and the depletion of natural resources. Taking into account the definition of sustainability provided by the United Nations (the ability of satisfying one generation's needs without compromising the possibility of future generations to satisfy), those two issues point to the lack of sustainability in the electronics field of the current generation, at least so far. Consequently, great attention has been given to green (sustainable) electronics in the last years, having as core values (i) the use of abundant and low-cost precursors, leveraging on processing routes that (ii) lack toxic solvents as well as toxic waste and (iii) are low cost and (iv) involve biodegradable materials.

In this contribution, we will present our preliminary results on the biodegradability and compostability of organic electronic materials of interest for electronics and energy storage devices, focusing on the case of study of melanin biopigments used in transistors, batteries and supercapacitors [1].

References

[1] E. Di Mauro, R. Xu, G. Soliveri, C. Santato, Natural melanin pigments and their interfaces with metal ions and oxides: emerging concepts and technologies, *MRS Commun.* 7 (2017) 141–151. doi:10.1557/mrc.2017.33.

Nanostructured flash memory devices based on radical polymers and carbon-based nanomaterials

S. Ezugwu¹, J. A. Paquette², J. Park¹, D. Singh¹, J. B. Gilroy², G. Fanchini^{1,2}

¹ *Department of Physics & Astronomy, Western University, 1151 Richmond Street, London, Ontario, N6A 3K7, Canada*

² *Department of Chemistry, Western University, 1151 Richmond Street, London, Ontario, N6A 5B7, Canada*

In this talk, we will review the use of thin films of organic polyradicals – organic polymers with one unpaired electron per monomer [1] – for memory devices and other applications. Although memory devices based on radical polymers have been often proposed, their stability was frequently limited to a few writing cycles, despite the excellent quality of the active layer. To date, the most common nonvolatile memory components used data storage technology are devices that are writable once and readable multiple times (WORM). Memory components that are writable, readable and erasable multiple times (FLASH) are more attractive, but their costs are still high. [2] Here, design criteria for flash memory devices are given using a combination of Kelvin-probe force microscopy (KPFM), electrical transport and optical measurements. [3] As a case study, ultrathin devices in which the active layer is formed by a 10-nm homogeneous film of poly-[1,5-diisopropyl-3-(cis-5-norbornene-exo-2,3-dicarboxiimide) 6-oxoverdazyl] (P6OV) are presented. [4] We will show that high performance of these devices must be associated to the presence three tunable charge states in each monomer: positive, neutral, and negative. In the last part of our talk, as a complement of polyradical memory devices, we will present a very similar class of organic flash memory devices, based on “curved” carbon quantum dots containing fivefold and sevenfold aromatic carbon rings, in addition to sixfold rings typically featured by commonly synthesized sp^2 carbon-based nanomaterials, including graphene, carbon nanotubes, and flat and luminescent graphene quantum dots. Paramagnetic centers associated to fivefold and sevenfold rings are anticipated to be essential to memory effects and memory device operation from these systems. [5] We will demonstrate that careful engineering of the anode and cathode work functions, specifically aligning them with the negative and positive energy levels of polyradicals and carbon quantum dots, is vital to maximize the on/off current ratio and ensure flash operation in these devices based on organic neutral radicals in a nanostructured environment.

References

- [1] F. Xu, H. Xu, X. Chen, D. Wu, Y. Wu, H. Liu, C. Gu, R. Fu, D. Jiang, *Angew. Chem. Int. Ed.* **54**, 6814 (2015)
- [2] Y. Ji, J. Hu, M. Lanza, *IEEE Nanotechnol. Mag.* **9**, 12 (2015)
- [3] S. Ezugwu, J. A. Paquette, V. Yadav, J. B. Gilroy, G. Fanchini, *Advanced El. Materials* **2**, 1600253 (2016)
- [4] J. A. Paquette, S. Ezugwu, V. Yadav, G. Fanchini, J. B. Gilroy, *J. Polym. Sci., Part A: Polym. Chem.* **54**, 1803 (2016).
- [5] J. Park, H. Shah, V. Wong, P. Bazylewski, G. Fanchini, *Carbon*, to appear, (2018)

Optical Rectification and Hot-Electron Photo-detectors

S. M.A. Mirzaee and JM. Nunzi

Department of Physics, Engineering Physics and Astronomy, Queens University, Kingston, Ontario, Canada

There currently exists a significant demand for IR broadband photoresponsive devices for applications ranging from photovoltaics and renewable energy to photodetection for military and civilian purposes. When considering the effectiveness of those photosensitive devices, several factors must be considered including photoresponsivity, fabrication process, and cost. Moreover, the spatial resolution of IR photodetectors can be significantly improved by simultaneously sensing the intensity and polarization of the incident light.¹

Photodetection through conventional procedures is based on light absorption by a material with a matching bandgap. However, this approach limits the range of wavelengths that can be detected, it is not sensitive to polarization, and cannot be used accurately in the infrared range because of thermal noise.² Recent approaches have attempted to circumvent these limitations, optical rectification is one of them.³

Metal–semiconductor Schottky junctions have been reported as the most efficient structures to collect hot electrons⁴ and generate a signal in photodetectors. However, previously reported photodetectors based on this methodology can be very costly to fabricate, and are not suitable for large-scale fabrication. Herein, we demonstrate that ITO-Au nanostructures can indeed be used to fabricate a NIR photodetector⁵ using the rectification effect induced by dipole orientation in a thin-film.⁶

We review optical rectification principles and experiments and report on a hot electron-based photodetector device that is sensitive in the NIR range, sensitive to polarization, as well as easy and cost-effective to fabricate. The approach developed herein represents a significant milestone towards the development of energy conversion devices based on hot electrons and plasmonics, which could be beneficial in integrated optoelectronics.

References

- [1] Zhang, E.; Wang, P.; Li, Z.; Wang, J.; Song, C.; Huang, C.; Chen, Z.-G.; Yang, L.; Zhang, K.; Lu, S.; Wang, W.; Liu, S.; Fang, H.; Zhou, X.; Yan, H.; Zou, J.; Wan, X.; Zhou, P.; Hu, W.; Xiu, F., Tunable Ambipolar Polarization-Sensitive Photodetectors Based on High-Anisotropy ReSe₂ Nanosheets. *ACS Nano* 2016, 10, 8067-8077.
- [2] Mandal, P.; Sharma, S., Progress in plasmonic solar cell efficiency improvement: A status review. *Renew. Sustainable Energy Rev.* 2016, 65, 537-552.
- [3] Wen, L.; Chen, Y.; Liu, W.; Su, Q.; Grant, J.; Qi, Z.; Wang, Q.; Chen, Q., Enhanced Photoelectric and Photothermal Responses on Silicon Platform by Plasmonic Absorber and Omni-Schottky Junction. *Laser Phot. Rev.* 2017, 11, 1700059.
- [4] Lee, Y.K.; Lee, H.; Lee, C.; Hwang, E.; Park, J.Y., Hot-electron-based solar energy conversion with metal-semiconductor nanodiodes. *J. Phys. Cond. Matter* 2016, 28, 254006.
- [5] Mirzaee, S.M.A.; Lebel, O.; Nunzi, J.M., A Simple Unbiased Hot-electron Polarization-sensitive Near-Infrared Photo-detector. *ACS Appl.Mater.Inter.* 2018, 10, 11862.
- [6] Sentein, C.; Fiorini, C.; Lorin, A.; Nunzi, J.M, Molecular rectification in oriented polymer structures *Adv. Mater.* 1997, 9, 809.

Materials design the two-dimensional level: from Xenes to anisotropic MoS₂

A. Molle

CNR-IMM, via C. Olivetti 2, I-20864 Agrate Brianza (MB), Italy

Keywords: Xenes, two-dimensional materials, topological insulators, transition metal dichalcogenides, transistor, nanotechnology

The advent of two-dimensional (2D) materials inspired new paradigms in the research and technology forefronts. In between these avenues is the opportunity to engineer *ad hoc* physical properties and make them readily suitable for applications in nanotechnologies. In this framework, making adjustable 2D materials is an emerging route to reach a superior control of new functional properties. With this concept in mind, here I will consider two distinct cases, the epitaxial Xenes and the anisotropy design in MoS₂ nanosheets.

By close analogy with graphene, epitaxial Xenes are comprised of monoelemental atoms arranged in a honeycomb lattice. Unlike graphene, Xenes are epitaxially grown on substrates and exhibit a varying degree of buckling and/or puckering in the lattice structure [1]. Examples in this respect are silicene, germanene, stanene, borophene, epitaxial phosphorene, and recently synthesized antimonene and tellurene. Buckling in Xenes can be taken as a leverage to tune the electronic properties making it possible for Xenes to appear as semiconductors, semimetals, metals topological and trivial insulators. I will show the route and challenges for Xenes to be integrated in nanoelectronic devices aiming at topological field effect transistors. I will also envisage promising tips for the exploitation of selectively tailored Xenes for nanophotonics and plasmonics.

A different case of 2D materials design is the chemical vapour deposition (CVD) of MoS₂ nanosheets on nanostructured substrates. CVD is nowadays universally considered as the more viable technical path to achieve large-scale production of atomically thin transition metal dichalcogenides. I will show that MoS₂ growth can be conformally adapted to a unidirectional rippled substrate thus resulting in an anisotropically modulated MoS₂ nanosheet. Compared to the planar configuration, anisotropic MoS₂ exhibits phonon and electronic properties that are strongly morphology dependent. The so-induced morphological anisotropy is reflected in the anisotropy of the physical characteristics, such as the phonon spectrum and local charge fluctuations. Implications on the band-gap and exciton engineering will be discussed, and the potential for applications envisioned spanning from straintronics to light-harvesting [2].

- [1] A. Molle, J. Goldberger, M. Houssa, Y. Xu, S.-C. Zhang, and D. Akinwande, *Nature Mater.* 16, 163 (2017).
- [2] C. Martella, C. Mennucci, E. Cinquanta, A. Lamperti, E. Cappelluti, F. Buatier de Mongeot, and A. Molle., *Adv. Mater.* 30, 1705615 (2018).

π -Electron Conjugation in 2D Polymers

D. F. Perepichka

Department of Chemistry, McGill University (Canada)

One-dimensional conjugated organic polymers are important optoelectronic materials with tunable properties and myriads of applications. Two-dimensional (2D) inorganic materials, such as graphene, display a spectrum of unprecedented properties that fundamentally impact the solid state physics. It would thus be intriguing to be able to combine the *tunability* of an organic polymer and 2D electron confinement in a single material – a 2D π -conjugated polymer.^[1] The lecture will discuss how a 2D polymer network can be assembled from π -functional building blocks, and how the structure and connectivity of the latter define the properties of the material. It will present our approaches to growing such materials via surface-templated polymerization^[2] and through dynamic covalent polymerization in solution.^[3] The novel properties resulting from the π -electron delocalization (conjugation) in 2D systems will be also be discussed..

References

- [1] D. F. Perepichka, F. Rosei, *Science* **2009**, 323, 216. R. Gutzler, D. F. Perepichka, *J. Am. Chem. Soc.* **2013**, 135, 16585.
- [2] L. Cardenas et al. *Chem. Sci.* **2013**, 4, 3263; R. Gutzler et al. *Nanoscale* **2014**, 6, 2660; G. Vasseur et al. *Nat. Comm.* **2016**, 7, 10235.
- [3] M. R. Rao, Y. Fang, S. De Feyter, D. F. Perepichka, *J. Am. Chem. Soc.* **2017**, 139, 2421.

Developing Hybrid Nanostructures for Energy and Biomedical Applications

D. Ma

Institut National de la Recherche Scientifique (INRS)

With unique physical and chemical properties, and high potential for many important applications, nanomaterials have attracted extensive attention in the past two decades. In particular, due to their unique, size- and shape-tunable surface plasmon resonance, plasmonic nanostructures have recently been explored for enhancing the efficiency of solar cells and photocatalysis via improved light scattering, strong near field effect and/or hot electron injection. On the other hand, near infrared quantum dots (QDs) with size tunable bandgaps, broad absorption, narrow and bright emission, and high potential for multiple exciton generation represent a class of promising materials for new generations of solar cells and theranostic agents. Combination of different nanomaterials into a single architecture leads to even more promising, multifunctional nanomaterials. In this talk, I will present our recent work on the synthesis of nanomaterials (including plasmonic nanostructures and NIR QDs), and their assemblies as well as their applications in solar cells, solar fuel, photocatalysis and biomedicine [1-8]. Rational design of hybrid nanomaterials in order to maximize benefits is highlighted.

References:

- [1] J. Am. Chem. Soc., 2013, 135, 9616.
- [2] Adv. Energy Mater. 2018, 1703658.
- [3] Adv. Funct. Mater. 2018, 1706235 (Back Cover).
- [4] ACS Catalysis, 2017, 7, 6225.
- [5] Adv. Funct. Mater, 2015, 25, 2950 (Front Cover).
- [6] Adv. Funct. Mater. 2015, 25, 6650.
- [7] Adv. Funct. Mater., 2012, 22, 3914 (Highlighted by MaterialsViews).
- [8] Adv. Mater., 2012, 24, 6289 (Frontispiece Cover).

Epitaxial growth of Ge-based nanomaterials. From GeSi to novel bidimensional systems: Graphene on Ge and Germanene on HOPG

A. Sgarlata¹, M. Fanfoni¹, C. Goletti¹, B. Bonanni¹, M. De Crescenzi¹, L. Di Gaspare², M. De Seta², L. Persichetti², A. Notargiacomo³ and A. Balzarotti¹

¹ *Dipt. di Fisica, Università di Roma Tor Vergata, Via della Ricerca Scientifica 1, 00133 Rome, (Italy)*

² *Dipt. di Scienze, Università Roma Tre, Viale G. Marconi, 446- 00146 Rome, (Italy)*

³ *Institute for Photonics and Nanotechnology, CNR, Via Cineto Romano 42, 00156 Rome, (Italy)*

The history of the collaboration between the laboratory of Rome Tor Vergata and the INRS starts in 2003 [1] when together with one of us (F.R.), moved to Canada, by using step-bunched Si surfaces as templates, we demonstrated the self-assembly of an ordered distribution of Ge islands without lithographic patterning. The idea of that work was to exploit processes that naturally develop on the surfaces to produce new materials without introducing ex-situ fabrication processes that might favor the contamination affecting the quality of the samples on a "nano" scale. Based on the same idea we recently turned to the exploitation of novel two-dimensional materials that can be easily integrated with current generation of electronic technologies. Two specific Ge-based systems were investigated: Graphene on Ge and Germanene on HOPG

GRAFENE/Ge

Previous results have demonstrated the possibility of growing metal contamination-free high quality CVD graphene layers directly on Ge substrates representing a significant advancement toward the full compatibility with CMOS-technology. However, so as to enhance the graphene quality, the early stage of growth and the influence of temperature should be further investigated. Here we report our recent results concerning the first stages of growth with CVD method [2]. The nucleation of the small graphene domains is accomplished by the Ge surface proto-faceting that evolves in the characteristic Ge nano-faceting of single layer of graphene on Ge. The influence of deposition temperature on the crystallization process of graphene film is also investigated.

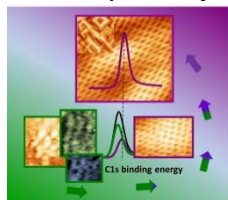


Figure 1: Scheme of the crystallization process of graphene on Ge(001) substrate.

GERMANENE/HOPG

The most obvious alternatives to graphene are "graphene-like" materials made of the group IV elements, i.e., silicon and germanium. In particular Germanene share several peculiar properties of graphene. We have recently demonstrated [3] that by depositing submonolayers of Ge on graphite at room temperature and subsequent annealing to 350 °C we obtain flat, two-dimensional germanium sheets showing a honeycomb lattice that matches that of germanene. Theoretical calculations agree well with our experimental findings measured by Scanning Tunneling Microscopy and Spectroscopy (STM/STS).

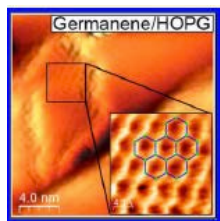


Figure 2: STM image of two-dimensional germanium sheets showing a honeycomb lattice

References

- [1] A. Sgarlata, P.D.Szkutnik,, A.Balzarotti, N.Motta and F.Rosei *Appl Phys Lett* **83**, 4002 (2003)
- [2] L. Di Gaspare, A.M.Scapparro, M.Fanfoni, L. Fazi, A.Sgarlata, A. Notargiacomo,V. Miseikis, C. Coletti, M.De Seta, *Carbon* **134**, 183 (2018)
- [3] L. Persichetti,F. Jardali, H. Vach, A. Sgarlata, I. Berbezier, M De Crescenzi and A. Balzarotti. *J. Phys. Chem.Lett* **7**, 3246 (2016)

Novel Photochemical Methods for the Preparation of Nanographenes and Graphene Nanoribbons

J.F. Morin¹, D. Miao¹, M. Daigle¹

¹ *Département de chimie and Centre de Recherche sur les Matériaux Avancés (CERMA), Université Laval, 1045 Ave de la Médecine, Québec G1V 0A6 (Canada)*

Atomically precise nanographenes and related structures have gained significant importance in several areas of chemistry and materials science due to their unmatched optoelectronic properties.[1] Yet, their full potential cannot be exploited as several types of very promising structures cannot be prepared efficiently due to the lack of synthetic methods. The central objective of our research program is to tackle this problem by developing innovative and versatile synthetic tools for the preparation of unprecedented, well-defined nanographenes (NGs), graphene nanoribbons (GNRs) and carbon allotropes with unique physical properties. In this presentation, we will show the most recent findings that we have made on a very promising photochemical reaction called the cyclodehydrochlorination (CDHC) to prepare NGs and GNRs.[2-4] In particular, we will demonstrate how the use of different benign catalysts can improve the efficiency of this reaction to prepare armchair GNRs that exhibit interesting electronic properties and how the reactivity of the polychlorinated precursors can be tuned by changing the reaction conditions. We will show how the photochemical CDHC reaction has been used to prepare low bandgap, one-dimensional carbon allotropes with exhibiting either aromatic or anti-aromatic character. Finally, we will present our most recent results about the selective dispersion of semiconducting single-wall carbon nanotubes (s-SWNTs) using well-defined GNRs to prepare GNR/s-SWNT nanocomposite for solar cells applications.

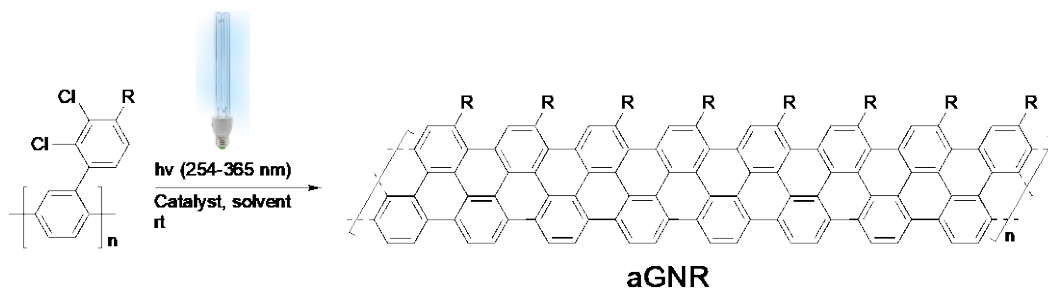


Figure 1. Synthesis of an armchair graphene nanoribbon from the CDHC reaction.

References

- [1] A. Narita, X.-Y. Wang, X. Feng and K. Müllen, *Chem. Soc. Rev.*, 44 (2015), pp. 6616-6643.
- [2] M. Daigle, A. Picard-Lafond, E. Soligo and J.-F. Morin, *Angew. Chem. Int. Ed.*, 55 (2016), pp. 2042-2047.
- [3] M. Daigle, D. Miao, A. Lucotti, M. Tommasini and J.-F. Morin, *Angew. Chem. Int. Ed.*, 56 (2017), pp. 6213-6217.
- [4] D. Miao, M. Daigle, A. Lucotti, J. Boismenu-Lavoie, M. Tommasini and J.-F. Morin, *Angew. Chem. Int. Ed.*, 57 (2018), pp. 3588-3592.

Graphene aerogels: from self-assembly to applications

M. Cerruti

Materials Engineering, McGill University, 3610 University Ave, Montreal, QC, Canada

Graphene aerogels are highly porous and light structures that maintain most of the exceptional mechanical and electrical properties of graphene in a substrate that can be handled and used in practical applications. This is possible because the graphene flakes do not excessively restack during aerogel formation.

In this talk we will explore how we can direct the self-assembly of graphene oxide flakes to generate graphene aerogels with different structures and mechanical properties, and generate materials with potential for applications as varied as sensing, pollutant absorption, photocatalysis, and cell culture.

Novel 2D materials for opto-electronic applications: insight from parameter-free quantum mechanical methods"

M. Palummo

INFN and Dipartimento di Fisica Università di Roma "Tor Vergata"

The use of emerging twodimensional and layered materials in technological applications presupposes a detailed knowledge of their chemical and physical properties. In this context abinitio theoretical methods and simulations are playing a fundamental role.

Among the large number of 2D materials discovered after graphene, of particular interest for optoelectronic applications is the family of Transition Metal Dichalcogenides (TMDs) [1,2] and more recently that one of 2D RuddlesdenPopper organiceinorganic halide perovskites (2DRPPs) [3].

The aim of my talk is to show how the use of parameterfree atomistic simulations can contribute to improve the microscopic understanding of the optoelectronic properties of these two classes of novel 2D materials and to predict new ones. I will show how abinitio DFT and postDFT calculations, based on ManyBody Perturbation Theory (MBPT), provide a very useful scheme to explain: i) the giant electronic bandgaps renormalization ii) the strong lightmatter interaction iii) the presence of strongly bound excitons. I will also discuss how to calculate in a fully abinitio framework the exciton radiative lifetimes [4] and the influence of electronphonon interaction on the electronic and optical spectra [5]. Finally for 2DTMDs I will show how doping and molecular functionalization can tune their optoelectronic properties [6].

References

- [1] M. Bernardi, C. Ataca, M. Palummo, J. C. Grossman Journal of Nanophotonics (2016)
- [2] M. Bernardi, M. Palummo, J. C. Grossman, Nano Letters (2013), 13(8), 3664
- [3] G. Giorgi, K. Yamashita and M.Palummo in preparation
- [4] M.Palummo, M. Bernardi, J.C. Grossman Nano Letters (2015) 15 (5),
- [5] A. MolinaSánchez, M Palummo, A Marini, L Wirtz Physical Review B 93 (15), 155435
- [6] G. Cicero, M. Palummo, J.C. Grossman in preparation

Non-Classical Longitudinal Magneto-Resistance in Anisotropic Black Phosphorus

F. Telesio,¹ N. Hemsworth,² W. Dickerson,² M. Petrescu,³ V. Tayari,² Oulin Yu,³ D. Graf,⁴ M. Serrano-Ruiz,⁵ M. Caporali,⁵ M. Peruzzini,⁵ M. Carrega,¹ T. Szkopek,² S. Heun,¹ and G. Gervais³

¹ NEST, Istituto Nanoscienze-CNR and Scuola Normale Superiore, I-56127 Pisa, Italy

² Department of Electrical and Computer Engineering, McGill University, Montréal, Québec, H3A 2A7, Canada

³ Department of Physics, McGill University, Montréal, Québec, H3A 2T8, Canada

⁴ National High Magnetic Field Laboratory, Tallahassee, FL 32310, United States

⁵ Istituto Chimica dei Composti OrganoMetallici-CNR, I-50019 Sesto Fiorentino, Italy

Resistivity measurements of few-layer black phosphorus (bP) in a parallel magnetic field up to 45 T are reported as a function of the angle between the in-plane field and the crystallographic directions of the bP sample, see Fig. 1. Both a transverse magneto-resistance (TMR, $\varphi = \pm 90^\circ$) and a classically-forbidden longitudinal magneto-resistance (LMR, $\varphi = 0^\circ$) are observed. Surprisingly, they are both found to be strongly anisotropic as well as non-monotonic with increasing field. While an explanation of the low magnetic-field behavior can be found in the strong (Anderson) localization framework, the strong *positive* LMR overcoming the TMR above ~ 30 T field is inconsistent with such scenario. Considering the known anisotropy of bP, whose zigzag and armchair effective masses differ by a factor of approximately seven, our experiments provide a key test for LMR scenarios based on an anisotropic Fermi surface, as proposed by Pal and Maslov [1].

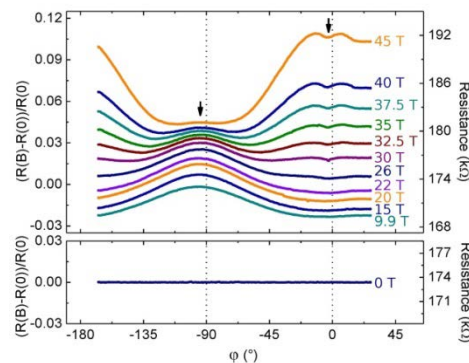


Fig. 1: Left: optical microscopy image of the device with labeling of source (S) and drain (D) contacts, top gates TG1 and TG2, as well as the definition of the angle φ as the angle between source-drain and the magnetic field (B) axis. Right top: Magneto-resistance, defined as $(R(B) - R(0)) / R(0)$, vs. the in in-plane angle of rotation φ at various magnetic fields is shown in left axis. The raw resistance value is displayed on the right axis. Right bottom: Zero-field resistance value measured versus in-plane rotation angle φ .

References

[1] H. K. Pal and D. L. Maslov, Phys. Rev. B **81**, 214438 (2010).

Efficient hydrogen evolution based on bidding-free molybdenum diselenide catalyst

S.Poorahong, X. Thai Tran and M.Siaj*

*Department of Chemistry and Biochemistry, Université du Québec à Montréal, Montréal
QC, H3C 3P8, Canada
siaj.mohamed@uqam.ca*

Design and development of inexpensive and highly efficient electrocatalysts for hydrogen production underpin several emerging clean-energy technologies. In this talk, we will present two novel strategies to synthesize molybdenum diselenide (MoSe_2) and used as a catalyst for hydrogen evolution reaction (HER). Both approaches are aiming to minimize the use of binder, conducting additives and transferring step when applying as an electrocatalytic material. The first method is based first on a co-electrodeposition followed by an etching step. In this approach a vertically aligned porous MoSe_2 on carbon surface was obtained. The second approach is solvothermal synthesis in which the graphene oxide@gelatin aerogel was first constructed and was used as a surface for the growth of MoSe_2 . The surface morphology and chemical composition of the synthesized materials were investigated by SEM, TEM, Raman spectroscopy, XPS and XRD. After characterizations, the materials were directly used as an electrode to evaluate their HER performance [1,2]. The as-prepared MoSe_2 exhibits an evident of HER enhancements in terms of reducing of onset overpotential, Tafel slopes and the increasing of cathodic current. The simplicity of the proposed strategy to prepare 3D binder-free MoSe_2 nanostructured on the conductive layer with an enhanced HER activity opens a new way to explore superior electrocatalysts for hydrogen evolution reaction.

References

- [1] X. T. Tran, S. Poorahong and M. Siaj. *RSC Advances*, **7** (82), 52345-52351 (2017)
- [2] S. Poorahong, R. Izquierdo and M. Siaj. *J. Mater. Chem. A*, **5** (39), 20993-21001 (2017)

Chemical reactions of porphyrins at the interface with transition metal oxides

L. Floreano

CNR-IOM, Laboratorio TASC, Trieste (Italy),

The in-vacuum metalation of free-base porphyrins (2H-Ps), either by metal deposition on a molecular layer or by atom extraction from a metallic substrate (self-metalation), is an effective alternative route to the conventional chemical synthesis of metallo-porphyrins (M-Ps), which represent the most widespread class of organic dyes at the basis of the natural life processes.[1] The highly polarizable and displaceable charge of the metal surface can support metallo-porphyrin complexes that would be unstable in both the gas and bulk phases. In particular, by self-metalation reaction one can achieve both ultra-high purity and long range ordering in the contact layer, which is highly desirable for the engineering of layered nano-architectures. The key mechanism for the metal incorporation into the porphyrin macrocycle is the recombination of the two pristine (pyrrolic) hydrogen atoms followed by desorption of a H₂ molecule. The substrate temperature required to activate hydrogen recombination and release depends on the degree of metal reactivity. It can be eventually lowered by pre-adsorption of dissociated oxygen, e.g. on copper, because it opens the alternative (more favorable) path of H₂O synthesis and release.[2]

For practical purposes, one would like to achieve a similar flexibility of tailoring the chemical modification of 2H-Ps also on native transition metal oxides (TMOs). In this regard, titanium dioxide is the TMO of choice because of its multiple applications in photocatalysis and photovoltaics. Porphyrins in the contact layer display a very rich phase diagram depending on temperature and coverage. 2H-Ps molecules deposited on the rutile TiO₂(110) surface display a high reactivity towards hydrogen capture from the surface and the topmost layer.[3] Most importantly, a self-metalation reaction sets in at temperatures as low as 80-100°C, a range easily reached by solar panels in working conditions, which opens the way to metal exchange reactions in porphyrin/TiO₂ archetypal devices.[4] The self-metalated molecules display an exceptional thermal stability up to 450-500°C, much higher than critical temperature of decomposition on metals (~300-350°C) and beyond the possible conformational changes of the porphyrin peripheral terminations (e.g. flattening of phenyls at ~300°C). The leitmotiv of these multiple reactions is the stability of the bond initially formed by the pristine pyrrolic terminations to two oxygen atoms underneath.[5] The hydrogen bonds are then replaced by oxygen bonding to the incorporated titanium atom, which also preserves the same oxidation state (Ti⁴⁺) of the substrate. The robustness of the macrocycle anchoring to titanium dioxide makes this hybrid interface a suitable candidate for catalytic applications in harsh environments.

References

- [1] J.M. Gottfried, *Surf. Sci. Rep.* 70, 259 (2015).
- [2] A. Verdini, *et al.*, *Chem. Eur. J.* 22, 14672 (2016).
- [3] G. Lovat, *et al.*, *Phys. Chem. Chem. Phys.* 17, 30119 (2015).
- [4] G. Lovat, *et al.*, *J. Phys. Chem. C* 121, 13738 (2017).
- [5] G. Lovat, *et al.*, *Nanoscale* 9, 11694 (2017).

Engineering Nanostructured Materials for Tunable Light-Matter Interactions

N. P. Kherani^{1,2}

¹ University of Toronto, Dept. of Electrical & Computer Engineering, Toronto, Canada

² University of Toronto, Dept. of Materials Science & Engineering, Toronto, Canada

Nanomaterials engineering presents a rich venue for the development of new materials with unique functionalities amenable to a variety of applications – computing, communications, sensing, and energy – to name a few. This abundance of possibilities arises from the fact that at the nanoscale, size shape and structure play a significant role in determining material properties and associated phenomena - in addition to composition.

This talk will highlight three recent studies in which we report on the potential of availing unique tunable light-matter interactions at the nano-length scale. These are:

- (i) The development of width-graded MIM nano-gratings which offer a novel and versatile paradigm for rainbow trapping which in turn opens the path to multiwavelength SERS; further, the new SERS platform is facile and low-cost *vis-à-vis* fabrication [1].
- (ii) The development of hitherto unrealized core-vest composite nanostructures (CVN) – which, unlike typical core-shells (wherein the core is fully encapsulated by the shell), the plasmonic core of the CVN selectively maintains physical access to its surrounding thereby enabling tailorable access pathways to the core and the shell [2].
- (iii) The modulation of optical properties of metallo-dielectric films on a compliant substrate via strain, resulting in a combination of scattering and surface plasmon excitations, that alter the film transmittance and reflectance [3].

References

- [1] Nastaran Kazemi-Zanjani, Moein Shayegannia, Rajiv Prinja, Arthur O. Montazeri, Aliakbar Mohammadzadeh, Katelyn Dixon, Siqi Zhu, Ponnambalam R. Selvaganapathy, Anna Zavodni, Naomi Matsuura, Nazir P. Kherani, “Multiwavelength Surface-Enhanced Raman Spectroscopy Using Rainbow Trapping in Width-Graded Plasmonic Gratings”, *Advanced Optical Materials* **6**(4) 1701136 (2018).
- [2] Arthur O. Montazeri, Yujin Kim, Yuan Sheng Fang, Navid Soheilinia, Gina Zaghi, J Kenji Clark, Roya Maboudian, Nazir P. Kherani, Carlo Carraro, “Scalable Super-Resolution Synthesis of Core-Vest Composites Assisted by Surface Plasmons”, *The Journal of Physical Chemistry Letters* **9**(4) 717-723 (2018).
- [3] J. Kenji Clark, Nazir P. Kherani, “Optical modulation using strain tunable metallo-dielectric films”, *Phys. Status Solidi A* **214**(6) 1600756 (2017).

Nanostructured metasurface optics for Orbital Angular Momentum spectroscopy

F. Romanato^(1,2,3,*), Ruffato^(1,2), M. Girardi^(1,2), M. Massari^(1,2), P. Capaldo⁽³⁾, G. Parisi⁽⁴⁾,
M. Zontin⁽⁴⁾,

⁽¹⁾ *Department of Physics and Astronomy ‘G. Galilei’, University of Padova, Padova, Italy*

⁽²⁾ *Laboratory for Nanofabrication of Nanodevices, Padova, Italy*

⁽³⁾ *CNR-INFM TASC IOM National Laboratory, Basovizza, Trieste, Italy*

⁽⁴⁾ *SM Optics – SIAE Group, Cologno Monzese, Milano*

The orbital angular momentum (OAM) of light has recently attracted increasing interest, both in academy and industry, due to the possibility offered by its potentially-unbounded state space to manipulate the phase structure and intensity distribution of light beams. Many applications have attracted increasing attention in a wide range of applications: particle trapping and manipulation, nanoscopy, black-hole physics and astronomy, security, and telecom, both in classical and quantum regime.

While several devices and techniques have been designed and experimentally tested for the generation and manipulation of OAM beams, covering a rather large range of complexity, efficiency, on the other hand the possibility to integrate and implement many optical operations is still lacking.

Here we present the design and fabrication of innovative optical architectures implementing the multiplexing and sorting of OAM beams with unprecedented levels of compactness and resolution. Samples have been nanofabricated as continuous phase-only diffractive optics with high-resolution electron-beam lithography and tested for the demultiplexing of optical vortex superposition, confirming the high efficiency and resolution.

We have also fabricated metasurfaces in silicon, where nanometric continuous gratings allow to generate birefringence effects and exploiting the Pancharatman-Berry phase delay as design control parameter. We will show how the metasurfaces can be organized in flat metalenses that represent the next frontier for robust industrial up-scalable, aberration-free, wide-bandpass micro optics.

The combination of the design criteria and of the fabrication method generates innovative sorters that are promising to ultimately achieve the required miniaturization and integration levels of high-fidelity OAM beam manipulation, and eventually inspire numerous applications that harness the intriguing properties of twisted light, both in classical and quantum regimes.

Ion Sensitive Graphene Field Effect Transistors : Saturating the Physical Limit to Potentiometric Sensing

T. Szkopek

McGill University, 3480 University Street, Montréal (Canada)

Ion sensitive field effect transistors (ISFETs) have been under development for decades [1], and indeed, the interaction of ions with semiconductor surfaces has been a subject of study since the invention of the transistor [2]. The applications of ion sensing are diverse, from genome sequencing [3] through to water quality monitoring. A key figure of merit for ISFETs is the minimum detectable change in ion concentration, which in the case of proton detection is expressed as the minimum detectable pH.

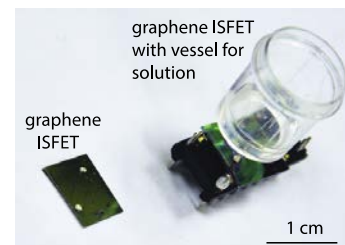


Fig. 1: a) Schematic and b) photograph of a graphene ISFET for pH sensing.

Minimizing the detection limit of an ISFET requires careful optimization of the ISFET structure, which can be achieved with graphene. High charge carrier mobility maximizes conductive gain. Quantum capacitance limited coupling between graphene and the active sensing layer maximizes the Fermi level shift within graphene in response to potential developed at the sensing layer. The potential developed in response to pH change (or pK in general) reaches the Nernstian limit of $kT/e \ln 10$ if the sensing layer functions as a good buffer for the analyte [4]. Finally, the noise in an ISFET is dominated by $1/f$ noise resulting from charge fluctuation at the sensing layer, which can be minimized by scaling the channel area to the cm x cm scale, made possible by large area chemical vapour deposition synthesis. These factors have enabled the graphene ISFET to reach a pH detection limit of 0.1 mpH [5,6], on par with spectroscopic titration methods. I will conclude my talk with future perspectives and opportunities for the development of graphene ion sensing methods.

References

- [1] P. Bergveld, *Sensors and Actuators B: Chemical* **88**, 1 (2003).
- [2] J. Bardeen, *Nobel Lecture* (1956).
- [3] J. M. Rothberg et al., *Nature* **475**, 348 (2011).
- [4] I. Fakih, S. Sabri, F. Mahvash, M. Nannini, M. Siaj, T. Szkopek, *Appl. Phys. Lett.* **105**, 083101 (2014).
- [5] I. Fakih, F. Mahvash, M. Siaj, T. Szkopek, *Phys. Rev. Appl.* **8**, 044022 (2017).
- [6] I. Fakih and T. Szkopek. *US patent application* 62/574,420.

Electron extracting nanolayers in perovskite & organic solar cells

J. Dagar¹, S. Castro-Hermosa¹, G. Lucarelli¹, A. Marsella¹,
T. M. Brown¹

¹ *CHOSE (Centre for Hybrid and Organic Solar Energy), Department of Electronic Engineering, University of Rome Tor Vergata, Via del Politecnico 1, 00133 Rome, Italy.*

Electron transport layers (ETLs) in emerging perovskite and organic semiconductor sandwich-structure solar cells play a huge role in their photovoltaic performance. Perovskite solar cells (PSC) have been attracting strong interest because of their rising efficiencies coupled with their processing via evaporation and printing techniques. Here we present research focused at developing device architectures and materials, including novel solution-processed transport layers, that produce devices with the highest performance reported for any PV technology under 200lx-400lx artificial indoor illumination, typically found in homes and offices. A thin MgO layer over a SnO₂ ETL enhanced efficiency by ~20%, reducing charge recombination with maximum power densities of MPD = 20.2 $\mu\text{W}/\text{cm}^2$ at 200 lx and 41.6 $\mu\text{W}/\text{cm}^2$ at 400 lx (and power conversion efficiencies, PCE, of 27%) reached. PCE of the same cell at 1 sun was 19.0% [1]. Efficient light harvesting by these perovskite solar cells under artificial light can power the future growing markets of indoor optoelectronics, including smart homes, autonomous indoor wireless sensor networks, and the internet of things.

Low temperature processing of films, including that of the TiO₂ mesoporous scaffold via UV-irradiation, enabled the development of PSCs on flexible substrates, avoiding deformation, not only on flexible PET films but also, for the first time, on paper substrates [2]. Cells on opaque paper, delivering a PCE of 2.7%, were obtained by developing a bottom Au/SnO₂ and a top window MoO_x/Au/MoO_x electrode stack as electron- and hole- extracting electrodes respectively. Paper represents a lightweight, flexible, inexpensive, ubiquitous, and environmentally friendly material, paving the way for integrating perovskite semiconductor technology with other electronic components on the same paper substrate.

The charge-extracting layers developed for PSCs were of the metal-oxide type. In organic solar cells, instead, we successfully incorporated biological deoxyribonucleic acid (DNA) as a nano-layer at the interface between the indium tin oxide (ITO) transparent electrode and the photoabsorbing polymer blend film. An initial strong improvement in open circuit voltage (from 0.39V to 0.73V) and power conversion efficiencies (PCE from 2% to 5%) was obtained by spin casting a 1-6 nm thick DNA electron extracting layer (EEL) [3]. Subsequently, we reached state of the art efficiencies of 8.3% by developing metal oxide/DNA composites as EELs leading to solar cells that are better than those with only metal oxide (i.e. ZnO) or DNA interlayers alone, and even with PEIE analogues [4]. DNA layers were deposited in benign water/alcohol solvents at room temperature. These results show that biological materials, in this case DNA, can modulate the photoresponse of bio-hybrid organic semiconductor devices even delivering uncompromising levels of performance.

References

- [1] J. Dagar, S. Castro, G. Lucarelli, F. Cacialli, T.M. Brown, *Nano Energy*, **49**, 290 (2018)
- [2] S. Castro-Hermosa, J. Dagar, A. Marsella, T.M. Brown, *IEEE El. Dev. Lett.*, **38**, 1278 (2017) [3]
- J. Dagar, M. Scarselli, M. De Crescenzi, T.M. Brown, *ACS Energy Lett.*, **1**, 510 (2016)
- [4] J. Dagar, G. Scavia, M. Scarselli, S. Destri, M. De Crescenzi, T.M. Brown, *Nanoscale*, **9**, 19031 (2017)

Lanthanide-Doped Nanoparticles

F. Vetrone¹

¹ *Institut National de la Recherche Scientifique, Centre Énergie, Matériaux et Télécommunications, Université du Québec, 1650 Boul. Lionel-Boulet, Varennes, QC, J3X 1S2 (Canada)*

In the last decade, the field of lanthanide-doped nanoparticles has progressed from the basic understanding of the photophysical properties governing their nanoscale luminescence to their use in a variety of applications, with considerable focus in biology and medicine. This interest stems primarily from the ability to stimulate these luminescent nanoparticles with near-infrared (NIR) light as well as their diverse emission wavelengths spanning the UV to the NIR regions. Therefore, with a single NIR excitation wavelength, it is possible to observe anti-Stokes emission, known as upconversion, or single photon (Stokes) NIR emission in the three biological windows (BW-I: 700-950 nm, BW-II: 1000-1350 nm, BW-III: 1550-1870 nm) where tissues are optically transparent. Here, we present methods for controlling the luminescence of these nanoparticles through core/shell nanostructures/nanoplatfroms and demonstrate how their various emissions could be harnessed for a multitude of applications.

Hybrid van der Waals Heterostructures

E. Orgiu^{1,2}

¹ *Laboratory of Molecular and Device Physics, Institut national de la recherche scientifique (INRS), EMT Center, 1650 Blvd. Lionel-Boulet Varennes J3X 1S2, (QC)*

² *Institut de chimie et ingénierie supramoléculaires, 8 allée Gaspard Monge, 6700 Strasbourg (France)*

The rise of graphene and related 2D materials makes it possible to form heterostructures held together by weak interplanar van der Waals (vdW) interactions. The incorporation of organic molecules within these systems holds an immense potential. Whilst nature offers a finite number of 2D materials, an almost unlimited variety of molecules can be designed and synthesized with predictable functionalities [1]. The possibilities offered by systems in which continuous molecular layers are interfaced with inorganic 2D materials to form hybrid organic/inorganic van der Waals heterostructures are emphasized. Similar to their inorganic counterpart, the hybrid structures have been exploited to put forward novel device architectures. Moreover, specific molecular groups can be employed to modify intrinsic properties and confer new capabilities to 2D materials. In particular, it is highlighted how molecular self-assembly at the surface of 2D materials can be mastered to achieve precise control over position and density of (molecular) functional groups, paving the way for a new class of hybrid functional. In particular, within such vdW heterostructures, currently assembled by mechanical superposition of different layers, periodic potentials naturally occur at the interface between the 2D materials. These potentials significantly modify the electronic structure of

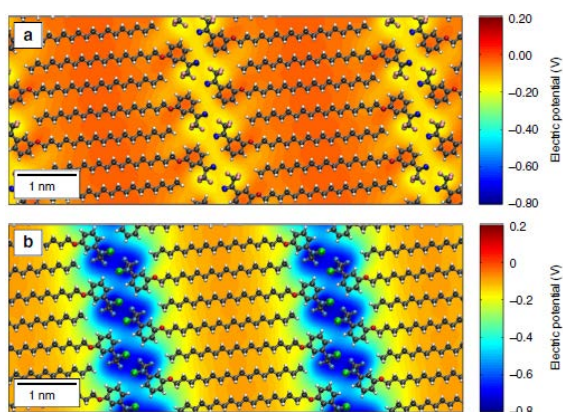


Fig. 1. Periodic potentials introduced by the supramolecular lattices. Calculated differential electrical potential induced by two different supramolecular lattices on graphene. The supramolecular lattice is superimposed for clarity. The electrical potential is periodically modulated, with negative values in the region below the molecular heads.

the individual 2D components within the stack and their alignment, thus offering the possibility to build up hybrid and novel materials with unique properties. In our work, we took a different approach by showing that pre-programmable periodic potentials arise in bi-layered structures formed by supramolecular lattices (SLs) over graphene, making them the hybrid equivalent of fully-inorganic vdW heterostructures. In particular, we employ a photoreactive molecule ideally suited to form a SL that induces a 1D-modulated gating effect on graphene with single domains extending over areas exceeding 10^4 nm^2 and stable at ambient conditions. The amplitude and sign of the potential can be modified without altering its periodicity by simply irradiating the photoreactive molecule in different solvents prior to the SL formation. Such a novel approach for tailoring the periodic potential is easily applicable to other 2D materials, highlighting the rich prospects that molecular design offers to create *ad hoc* heterostructures [2].

References

- [1] M. Gobbi, E. Orgiu, P. Samori *Adv. Mater.* **30**, 1706103 (2018)
- [2] M. Gobbi, .., E. Orgiu *Nature Communications* **8**, 14767 (2017)

Graphene imperfections: defects or effects?

V. Tozzini

Istituto Nanoscienze – Cnr, Lab NEST-SNS Piazza San Silvestro 12, 56127 Pisa Italy

All graphene amazing properties – large charge carriers mobility, extreme robustness combined with flexibility, broad band transmittance, huge surface to mass ratio, lubricity – rely on its being a perfect 2D crystal with the specific honeycomb symmetry[1]. However this status brings also some drawbacks [2]: its null density of states at the Fermi level limits its conducting properties; it is weakly interacting, which limits its potentialities as medium for gas storage. In addition, storage applications require building 3D media. On the other hand, perfect graphene is an ideal abstraction rather than a reality: epitaxially grown macroscopic 2D crystals display electronic doping, corrugations or localized defects [3], while using graphene flakes as precursors one can obtain nano-porous scaffolds with extremely complex and little ordered structure[4].

In this talk, it will be shown that the deviations from perfection of graphene are in fact opportunities to for specific applications. First, SiC supported epitaxial graphene will be examined. Density Functional Theory calculations show that the multi-stable corrugation of epitaxial monolayer graphene[5] and the steady-state rippling of its buffer carbon layer [6] could be exploited for chemical functionalization. Conversely, the quasi free-standing monolayer graphene obtained by H intercalation has with localized electronic states, with potential applications in optoelectronics[7,8]. Disordered graphene is more difficult to model. An algorithm to generate realistic models of graphene based scaffolds with given density, porosity and accessible surface is first illustrated and validated[9]. Adsorption of gases and electrolytes within these structures is subsequently simulated by means of Force Field based classical molecular dynamics, and its applications to hydrogen storage or for electrodes of batteries or supercapacitors is subsequently discussed.

This work was supported by EU-H2020, Graphene-Core1 (agreement No 696656) and Core2 (agreement No 725219), MCSA (agreement No 657070), by CINECA awards IsB11_flexogra (2015), IsC36_EIMaGRe (2015), IsC44_QFSGvac (2016), IsC44_ReIMCGr (2016) and PRACE “Tier0” award Pra13_2016143310 (2016).

References

- [1] Graphene-based technologies for energy applications, challenges and perspectives E Quesnel, et al 2D Materials 2, 030204 (2015)
- [2] T Cavallucci, K Kakhiani, R Farchioni, V Tozzini Morphing graphene-based systems for applications: perspectives from simulations GraphITA. Carbon Nanostructures., 87-111 (2017)
- [3] A Rossi, S Piccinin, V Pellegrini, S de Gironcoli, V Tozzini Nano-Scale Corrugations in Graphene: a Density Functional Theory Study of Structure, Electronic Properties and Hydrogenation JPC C 119 (14), 7900–7910 (2015)
- [4] G Mercier, A Klechikov, et al Porous Graphene Oxide/Diboronic Acid Materials: Structure and Hydrogen Sorption J. Phys. Chem. C 119, 49, 27179-27191
- [5] T Cavallucci, V Tozzini Multistable Rippling of Graphene on SiC: A Density Functional Theory Study JPC C 120, 7670 (2016)
- [6] T Cavallucci and V Tozzini Intrinsic structural and electronic properties of the Buffer Layer on Silicon Carbide unraveled by Density Functional Theory submitted; T Cavallucci, MsD Thesis, Supervisor: V Tozzini (2014)
- [7] T Cavallucci, Y Murata, M Takamura, H Hibino, S Heun, V Tozzini Unraveling localized states in quasi free standing monolayer graphene by means of Density Functional Theory Carbon 130, 466 (2018)
- [8] Y Murata, T Cavallucci, V Tozzini, et al Atomic and Electronic Structure of Si Dangling Bonds in Quasi-Free-Standing Monolayer Graphene Nano Research 11, 864–873 (2018)
- [9] In Silico design, building and deconstruction of nano-porous graphene scaffolds L Bellucci, and V Tozzini, in preparation

Assembling Materials with DNA as the Guide

Hanadi Sleiman¹

¹ *Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec, Canada H3A 0B8*

One of the challenges in nanoscience is the organization of functional components into deliberately designed patterns, and the ability to modify these patterns at will. Because of its molecular recognition specificity and structural features, DNA presents a unique opportunity to address this problem. A number of strategies for DNA construction have been developed, through weaving together DNA strands into tiles, or stapling a DNA strand into origami structures. Our group has been examining a different approach to build DNA nanostructures in which synthetic molecules are used to control and modify DNA self-assembly.

We will describe the use of this approach to generate 3D-DNA structures, such as DNA cages, nanotubes, sequence-controlled polymers and DNA-printed nanoparticles, with deliberate variation of geometry, size, single- and double-stranded forms, permeability and length. These structures are reconfigurable and molecule-responsive, e.g., cages and nanotubes can open and close on demand with specific DNA/RNA strands. The size-selective encapsulation of gold nanoparticles and small molecules within these host structures, and the release of this cargo when specific DNA strands are added will be shown. These compact 3D-DNA structures can travel across the plasma membrane of a number of mammalian cells and result in efficient gene silencing. The molecules shown here represent a new class of selective cellular probes and drug delivery tools, and can assist the development of nanoparticle devices.

We will discuss the use of these cages for the anisotropic organization of gold nanoparticles and hydrophobic polymers, thus defining new modes of protein-inspired interactions. Anchoring these structures on lipid bilayer membranes allows their potential use as light harvesting photosynthetic mimics.

Selected Recent References:

- [1] N. Seeman, H. Sleiman, "DNA Nanotechnology", *Nature Reviews Materials*, 2017, 17068
- [2] T. Trinh, C. Liao, V. Toader, M. Barlóg, H. S. Bazzi, J. Li, H. F. Sleiman, "DNA-Imprinted Polymer Nanoparticles with Monodispersity and Prescribed DNA-Strand Patterns" *Nature Chem.* 2018, 10, 184–192
- [3] N N. Avakyan, A. A. Greschner, F. Aldaye, C. J. Serpell, A. Petitjean, H. F. Sleiman, 'Reprogramming the assembly of unmodified DNA with a small molecule', *Nature Chem.*, 2016, 8, 368-376.
- [4] T. Edwardson, H. F. Sleiman, 'Transfer of molecular recognition information from DNA nanostructures to gold nanoparticles', *Nature Chem.* 2016, 8, 162-170

POSTERS

Hydrothermal Growth of zinc oxide nano-rods doped with manganese

R. Bagga, P. Bianucci, T. Vo Van

Department of Physics, Concordia University - Montreal, QC, Canada

We synthesised ZnO Nanorods arrays doped with and without Mn doping (at a 1% concentration of the precursor salts) by a hydrothermal method at low temperature [1]. They were characterised by scanning electron microscopy (SEM), Photoluminescence (PL) and electron paramagnetic (EPR) spectroscopy. SEM images shows that the introduction of the dopant does not preclude the formation of nanorods (Figure A and B). All samples produced broad band Photoluminescence (PL) emissions in the yellow-orange-red range, typically attributed to defects in the crystalline structure [2]. The PL spectra Figure D does not seem to show significant changes in the ratio of the near band edge emission and the defect emission with the Mn doping. From this, we infer that the crystal quality of the ZnO nanorods does not change with Mn doping. As it can seen in Figure D the EPR spectrum from the ZnO nanoparticles formed in the growth solution tells the presence of Mn in them.

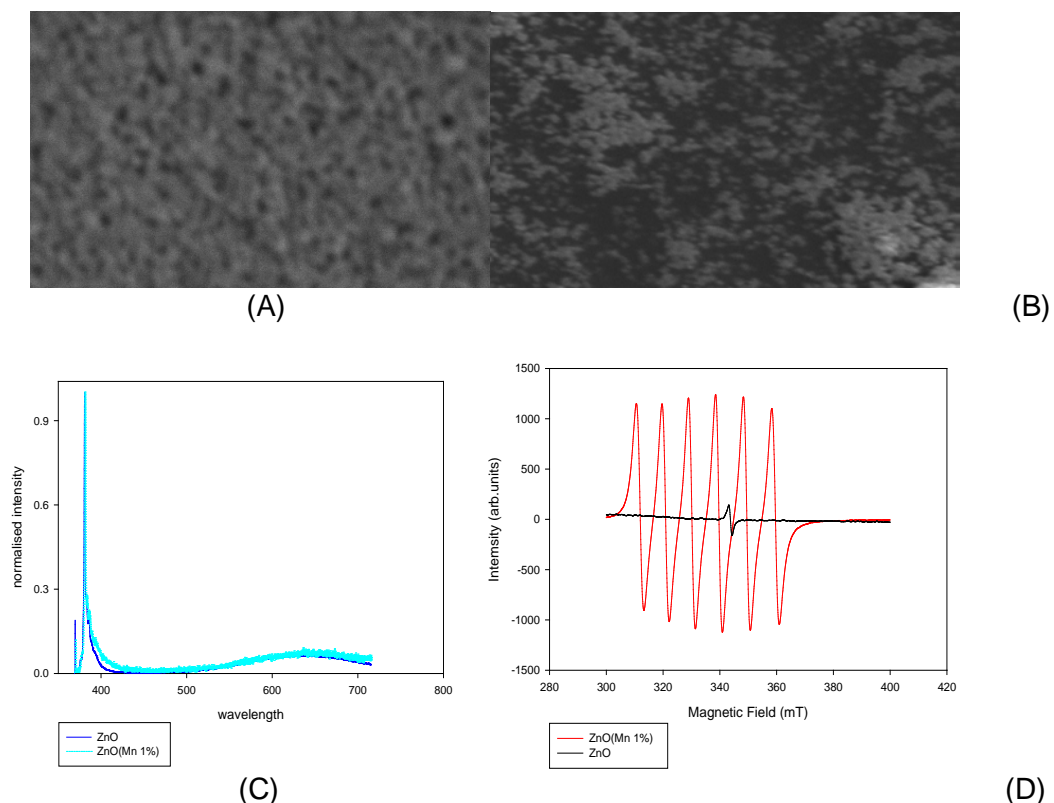


Figure 1: SEM image of (A) ZnO nanorods and (B) ZnO nanorods doped with 1% Mn (C) PL spectra of ZnO and Mn-doped ZnO nanorods (D) EPR Spectra of ZnO and Mn-Doped ZnO nanorods

1. A. Hassanpour, P. Guo, S. Shen, and P. Bianucci: The effect of cation doping on the morphology, optical and structural properties of highly oriented wurtzite ZnO-nanorod arrays grown by hydrothermal method. *Nanotechnology* **28**, 435707 (2017).
2. Fernanda C. Romeiro, Juliane Z. Marinho, Anielle Christine A. Silva, Nilo F. Cano, Noelio O. Dantas, and Renata C. Lima: Photoluminescence and Magnetism in Mn^{2+} -doped ZnO nanostructures grown rapidly by the microwave hydrothermal method. *J. Physical Chemistry C* 2013, 117,26222-26227

Carbon Dots as material for solar energy harvesting devices

D. Benetti¹, Y. Zhou¹, E. Jokar², H. Zhao¹, D. Ma,¹ A. Vomiero³, E. Diau², F. Rosei¹

1. INRS Centre for Energy, Materials and Telecommunications, 1650 Boulevard Lionel-Boulet, Varennes, Québec J3X 1S2, Canada.

2. Department of Applied Chemistry, Institute of Molecular Science and Center for Emergent Functional Matter Science, National Chiao Tung University, No.1001, Ta-Hsueh Rd., Hsinchu 30010, Taiwan.

3. Department of Engineering Sciences and Mathematics, Luleå University of Technology 981 87, Luleå, Sweden.

Generating power directly from solar radiation represents a promising opportunity towards addressing the increasing demand for clean energy, also reducing environmental impact caused by excessive carbon emissions. This challenge may be addressed by using carbon Dots (Cdots) which represent an emerging class of semiconducting nanomaterials. Cdots are exclusively composed of non-toxic elements (C, N and O) and can be synthesized in large quantities via a simple solvothermal approach. Compared to conventional semiconducting quantum dots (QDs), carbon dots (Cdots) have superior advantages of non-toxicity, environmental friendliness, low-cost and simple preparation using abundant carbon based feedstock. Exploiting the ability to tune the optical and electrical properties of Cdots by changing the synthetic methods, we synthesized different type of Cdots with absorption and emission spectra in the 380 - 650 nm range. Their ability to inject electrons/holes in different material, such as TiO₂ and Graphene Oxide, has been confirmed by photoluminescence (PL), transient PL decays and transient photovoltage (TPV) decays. The as-prepared Cdots are employed for realizing different devices such as Luminescent Solar Concentrator and Perovskite Solar Cells.

Wettability and chemical affinity of CNC lattice planes

C. Bruel, S. Queffelecoulou, J.R. Tavares,
P.J. Carreau, MC. Heuzey

*Department of Chemical Engineering, CREPEC, Polytechnique Montreal,
Montreal, QC, H3T 1J4, (Canada)*

Cellulose nanocrystals (CNCs) are biosourced, biodegradable and renewable nanomaterials whose mechanical properties –high Young modulus at a low density- are derived from their highly crystalline structure. In land plants, cellulose is present in its I_β allomorph: cellulose chains assemble in strong OH-O hydrogen bonded sheets, which then stack-up to form a layered structure whose cohesion is provided by weaker intersheet CH-O hydrogen bonds and van der Waals interactions. The extraction of these crystalline sections, usually through an acid hydrolysis, yields CNC particles. They display up to three different lattice planes at their surface, the dimensions and distribution of which are notably functions of the feedstock employed. CNC surfaces that are parallel to the cellulose sheets display hydrophobic C-H bonds, while surfaces intersecting the sheets display more hydrophilic -OH groups. It results into amphiphilic particles.

While this behavior had previously been predicted by numerical simulations of CNC structures, we aimed at validating this experimentally. Here, we investigated relationships between ramie- and wood-based CNC structures, as determined through X-ray diffraction (XRD) analysis and from their surface properties such as chemical affinity and wettability. The latter were assessed through sedimentation tests on CNC suspensions in 25 different organic solvents and advancing-receding contact angle measurements on thin films cast from CNC water suspensions, respectively. Wood-based CNCs displayed a more pronounced amphiphilic behavior than ramie-based ones. It resulted in stable suspensions in mildly non-polar solvents such as chloroform and dichloromethane, for the occurrence of a new pattern of structure organization during thin film casting, and for better resistance to film swelling.

Surface-mediated assembly, polymerization and degradation of thiophene-based monomers

F. De Marchi,¹ G. Galeotti,¹ M. Ebrahimi,² J. Lipton-Duffin,³ D. F. Perepichka,⁴ and F. Rosei¹

¹ INRS-EMT, 1650 Boulevard Lionel-Boulet, Varennes, (Canada)

² Technische Universität München, D-85748 Garching, (Germany)

³ Queensland University of Technology, 2 George Street, Brisbane, (Australia)

⁴ McGill University, 801 Sherbrooke Street West, Montreal, (Canada)

Ullmann coupling is commonly regarded as one of the most promising approach for the onsurface preparation of π -conjugated nanostructures. [1,2] In this surface catalyzed two-step reaction, thermal annealing triggers the transition of aryl halides into organometallic species or polymers. [3] While Ullmann reaction has been largely investigated, the realization of large ordered single domain structure is still an open challenge. So far, the choice of the building block was found to be pivotal to obtaining extended nanostructures with the wanted properties. In this aspect, sulfur containing molecules have been studied due to their promising electronic behavior, but have rarely produced successful nanostructure products. We have studied the adsorption of a thiophene-based prochiral molecule, tribromobenzoterthiophene (TBTTB), on three different surfaces with (111) orientation, with a combination of scanning tunneling microscopy (STM), X-ray photoemission spectroscopy (XPS) and density functional theory calculations (DFT). The Au, Ag and Cu surfaces have an increasing surface reactivity, and our data shows that while it was possible to form conjugated polymers on Au and Ag, on all surfaces the polymerization reaction was competing with the thiophene ring opening, therefore affecting the quality of the formed polymers. This study shows that reaction which involves high temperature and metallic surfaces are not suitable for sulfur-containing molecules, and different reaction pathways or precursors including N or O heteroatoms have to be preferred.

References

- [1] M. Di Giovannantonio; G. Contini. J. Phys. Condens. Matter **30**, 093001 (2018)
- [2] R. Gutzler; D. Perepichka. J. Am. Chem. Soc. **135**, 16585 (2013)
- [3] D. Perepichka; F. Rosei. Science **323**, 216 2009

Transfer of a two-dimensional polymeric layer to a device-suitable substrate for its utilization as active media

D. Dettmann^{1,2,3}, G. Galeotti^{1,2}, F. de Marchi¹, Ehsan Hamzehpoor⁴, D. F. Perepichka⁴, F. Rosei¹, G. Contini^{2,3}

¹ *Centré Énergie, Matériaux et Télécommunications, Institut National de la Recherche Scientifique, 1650 Boulevard Lionel-Boulet, Varennes, QC, J3X 1S2 (Canada)*

² *Istituto di Struttura della Materia, CNR, Via Fosso del Cavaliere 100, 00133 Roma (Italy)*

³ *Department of Physics, University of Rome Tor Vergata, Via della Ricerca Scientifica 1, 00133 Roma (Italy)*

⁴ *Department of Chemistry, McGill University, 801 Sherbrooke Street West, H3A 0B8 Montreal (Canada)*

Surface-confined polymerization is a powerful technique to obtain well-ordered covalent two-dimensional polymers [1]. However, up to this point, it requires substrates unsuitable to be employed in devices [2]. To exploit the unique properties of such tailored polymer networks, a reproducible transfer method has to be settled. To achieve this objective, well-established transfer protocols for graphene were applied to polymers formed by Oxygen bridged Triphenylamine (TBTANG), a triangulene based molecule with a heteroatom substitution in the center. Prior to transfer, structural quality is evaluated by Scanning Tunneling Microscopy (STM). The core, primary objective is to achieve a transfer protocol able to attain the transportation of the polymeric network on a device-suitable substrate while keeping the structural integrity leading to its utilization in applications such as organic field effect transistor [3], invisible electronics and sensors [4].

References

- [1] PEREPICHKA, Dmitrii F.; ROSEI, Federico. Extending polymer conjugation into the second dimension. *Science*, 2009, 323, 216.
- [2] DI GIOVANNANTONIO, Marco; CONTINI, Giorgio. Reversibility and intermediate steps as key tools for the growth of extended ordered polymers via on-surface synthesis. *Journal of Physics: Condensed Matter*, 2018, 30, 093001.
- [3] LLINAS, Juan Pablo, et al. Short-channel field-effect transistors with 9-atom and 13-atom wide graphene nanoribbons. *Nature communications*, 2017, 8, 633.
- [4] DONG, Jinqiao, et al. Ultrathin two-dimensional porous organic nanosheets with molecular rotors for chemical sensing. *Nature communications*, 2017, 8, 1142.

Challenges and perspective of on-surface Ullmann polymerization

G. Galeotti¹, F. De Marchi¹, M. Di Giovannantonio², M. Ebrahimi^{1,3}, J. Lipton-Duffin⁴, D. Perepichka⁵, G. Contini⁶, F. Rosei¹

¹INRS-EMT, Varennes (Canada), ²EMPA, Dübendorf (Switzerland), ³TUM, Garching (Germany), ⁴QUT, Brisbane (Australia), ⁵McGill, Montreal (Canada), ⁶ISM-CNR, Rome (Italy).

The realization of one-layer thick nano-devices is one of the great challenges of today nanotechnology. By exploiting the molecule-molecule and molecule-substrate interactions it is possible to create self-assembled 2D structures. Halogenated molecules can be further manipulated, and form extended π -conjugated polymer by Ullmann reaction. [1, 2]

Small differences in the self-assembling building blocks, such as the used substrate or halogen (Fig. 1), affect the reaction pathway as well as the final polymer structure. [3] In order to be able to engineer the polymerization result, it is necessary an increased understanding of the parameters that affect the process. During the last decade, our group used a combination of scanning tunneling microscopy, X-ray photoelectron spectroscopy and density functional theory to understand the role of all the parameters involved in the reaction, in addition to characterize the material properties, such as the band-gap and the k-dispersion. [4] In a recent paper we studied the reaction kinetic and mechanism involved in the polymerization of 1,4-dibromobenzene confined at the Cu(110) surface, [5] and new results show that the reaction mechanism is coverage dependent, opening new possibilities to the tailoring of the process.

By presenting our results, we will give a perspective on the state-of-the-art and challenges related to on-surface Ullmann reaction.

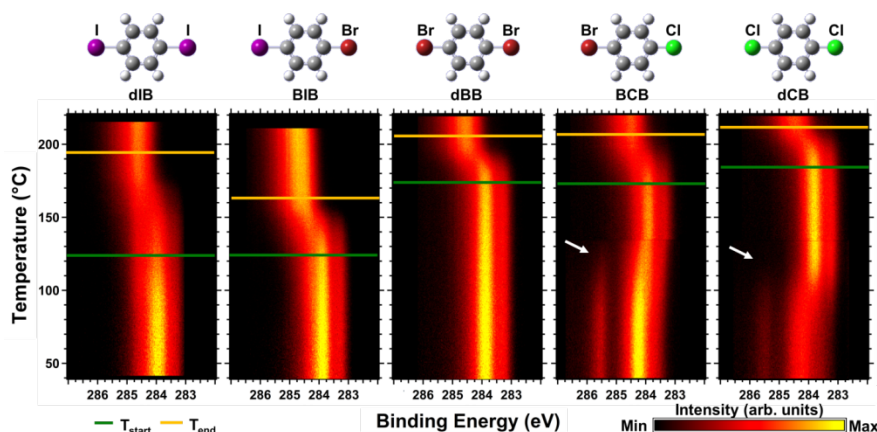


Fig. 1. Fast-XPS measurements of C 1s during annealing of various di-halobenzenes (a benzene with halogens in the 1,4 positions) dosed at room temperature on Cu(110). [3]

- [1] Perepichka, D. F.; Rosei, F., *Science*, **323** (5911), 216-217, (2009).
- [2] Gutzler, R.; Perepichka, D. F., *J. Am. Chem. Soc.*, **135** (44), 16585-94 (2013).
- [3] Galeotti, G.; et al., *Farad. Discuss.*, **204**, 453-469 (2017).
- [4] Vasseur, G.; et al., *Nat. Commun.*, **7**, 10235 (2016).
- [5] Di Giovannantonio, M.; et al., *J. Am. Chem. Soc.*, **138** (51), 16696-16702 (2016).

Preparation and characterizations of CH₃NH₃PbI₃ Perovskite thin films for solar cells applications

S. Hariech^{1*}, I. Menzri¹, J. Bougdira², M. Belmahi², M.S. Aida³, N. Attaf¹ and G. Medjahdi²

¹ Nanomaterials team for energy and environment, Unit of research Materials Sciences, Faculty of Sciences,

Department of Physics, Mentouri Brothers University, Constantine1-Algeria.

² Jean Lamour Institute, University of Lorraine, Vandœuvre Lès Nancy, France.

³ King Abdulaziz University, Jeddah, KSA.

*Corresponding author : Sana HARIECH

E. mail: sana.hariech@yahoo.fr

Our work has concentrated on the elaboration and characterizations of CH₃NH₃PbI₃, a type of organic-inorganic hybrid perovskite thin film by spin-coating deposition technique, in order to synthesis a series of these films. This series of samples was prepared on glass substrates by varying the rotation speed (1000 to 2000 rpm) and keeping the rotation time fixed (30 s). For this purpose, we used several characterization techniques which are: the X-rays diffraction (XRD) the UV-Visible spectrophotometry, the optical microscopy and the electrical characterization. The structural characterization reveals that the structure of the prepared perovskites films is tetragonal with preferential orientation in accordance with the plane (110). The optical characterization shows that these films have a fairly high absorbance in visible region and a direct band gap. The characterization I(U) shows that all elaborated films have a ferroelectric hysteresis behavior in the dark which it become Ohmic under illumination. It can be suggested that these properties make this type of perovskites films perfectly suitable for their use as absorbents films in solar cells fabrication and in other photovoltaic and microelectronics applications.

Keywords: Thin films, Spin-coating, Perovskites materials, organic-inorganic hybrid materials, Structural properties, Optical properties and electrical properties.

Electronic Structures of 3P Sub-Family Graphene Nanoribbons

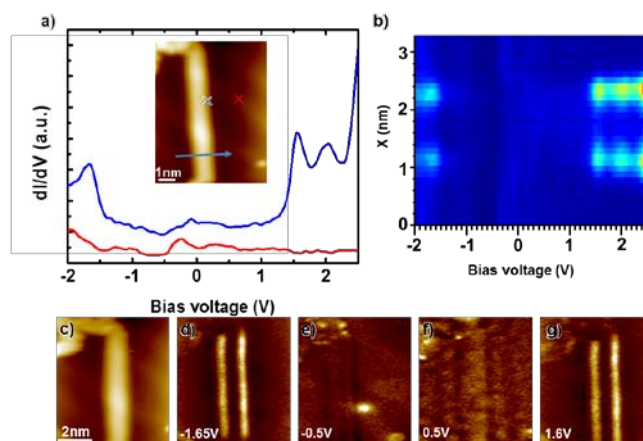
P. Ji,^{1,2} K. Sun,¹ H. Zhang,¹ L. Chi¹ and F. Rosei²

¹FUNSOM, Soochow University, Suzhou, China; ²Nanofemtolab, INRS-EMT, Varennes, Quebec, Canada

The structural boundary condition of graphene nanoribbons (GNRs) have drawn great attention in the last decade. According to edge structure, GRNs can be divided into zigzag and armchair GRNs, that present different and unique electronic and magnetic properties [1].

Based on the quantity of carbon atoms in the narrow dimension, Armchair GNRs can be classified into three families, 3P, 3P+1, 3P+2 (P is integer), respectively. In experimental regard, the electronic structures of 3P+1 and 3P+2 have already been characterized by scanning tunneling spectroscopy (STS). Herein, in order to complete the work of armchair GNRs, we characterized 3P family armchair GNRs by STS.

Atomically precise armchair GNRs of 3P family can be prepared through lateral fusing of poly-para-phenylene wires which are prepared via on-surface reaction of 4,4"-dibromo-p-terphenyl (DBTP) on Au (111). The electronic structures of 3P AGNRs are then investigated systematically through STS, showing a variation of band gaps that is in disagreement with the one previously reported for the 3P+1 family. Image charge corrections that can account for the difference between theoretical and



experimental results in 3P+1 family do not fit the 3P family, thus a more comprehensive explanation is necessary, in order to take in account of the substrate contribution.

Fig. 1. STS measurements and dI/dV mapping of 6-AGNR. a) dI/dV curves taken on the edge of ribbon (blue line) and bare Au (111) (red line). b) 2D dI/dV map consists of 32 dI/dV curves taken across the ribbon (blue arrow in figure a). c-e) Original STM image and constant bias dI/dV mapping of 6-armchair GNRs.

[1] L. Talirz, P. Ruffieux, R. Fasel, *Adv. Mater.*, **2016**, 28, 6222-6231.

Light-matter Interaction in Terahertz Plasmonic Nanocavities

Xin Jin¹, Andrea Cerea², Gabriele C. Messina², A. Rovere¹, R. Piccoli¹, R. Morandotti¹, F. De Angelis², A. Toma², L. Razzari¹

¹ INRS-EMT, 1650 Boul. Lionel-Boulet, Varennes, Quebec, J3X 1S2, (Canada)

² Istituto Italiano di Tecnologia, via Morego 30, 16163 Genova (Italy)

Recently, we showed how the phonon spectrum of nanocrystals can be drastically modified inside a terahertz (THz) plasmonic nanocavity, which in turn opens exciting perspectives for several applications in nanotechnology [1]. In a previous work, we also used a similar approach to demonstrate nanoantenna-enhanced terahertz spectroscopy [2], a technique capable of retrieving the spectroscopic information of few nano-objects. We believe that our findings can open a myriad of exciting perspectives as new opportunities to optimize nanodevices for light emission or charge transport, and the exploration of cavity nano-optomechanics at room-temperature as well.

References

- [1] Xin Jin, Andrea Cerea, Gabriele C. Messina, Andrea Rovere, Riccardo Piccoli, Francesco De Donato, Francisco Palazon, Andrea Perucchi, Paola Di Pietro, Roberto Morandotti, Stefano Lupi, Francesco De Angelis, Mirko Prato, Andrea Toma & Luca Razzari. *Nature Communications* **9**, 768 (2018)
- [2] Andrea Toma, Salvatore Tuccio, Mirko Prato, Francesco De Donato, Andrea Perucchi, Paola Di Pietro, Sergio Marras, Carlo Liberale, Remo Proietti Zaccaria, Francesco De Angelis, Liberato Manna, Stefano Lupi, Enzo Di Fabrizio, and Luca Razzari. *Nano Letters* **15**, 386 (2015)

Modification of the surface properties of TiO₂ films using an N₂/N₂O dielectric barrier discharge plasma

Z. Matouk, B. Torriess, R. Rincon, M. Chaker

*INRS, Centre Énergie Matériaux et Télécommunications, INRS, 1650 Lionel-Boulet,
Varennnes, Québec, J3X1S2, Canada*

Titanium dioxide (TiO₂) is one of the most studied transition-metal oxides which have been widely used in environmental application (photo catalysis), energy conversion (hydrogen production and solar cells), and energy storage (lithium batteries and super capacitors)... Recently, self-cleaning based on hydrophilicity of modified TiO₂ was reported as new application.

Dielectric barrier discharge (DBD) appears as an attractive solution to realise an atmospheric pressure cold plasma process suitable for all the surface treatments including thin film since it operate at low temperature .The synthesis of TiO₂ thin films made by injecting an aerosol suspension of nanocolloidal suspension of TiO₂ (size of about 20 nm) in isopropanol (IPA) into a dielectric barrier discharge generated in N₂/N₂O at atmospheric pressure (AP-DBD) was investigated. In this work, the focus is put on the influence of the voltage (3-8 kV) applied to the AP-DBD operated at 4 kHz on the wettability of the as-deposited TiO₂ thin films.

The TiO₂ films exhibited a significant change in its wetting property contact angle (WCA). Indeed, the WCA has reduced from 70° for the reference TiO₂ powder (without plasma) to considerable limits 5° for the 8 kV plasma deposited films. It is demonstrated that the hydrophilic property of plasma exposed TiO₂ films dependent mainly upon surface roughness and/or chemical composition. Scanning electron microscopy (SEM) images shows rugosity increasing when the voltage increases. The XRD pattern of the TiO₂ film displays the same anatase/rutile peak intensity ratio as compared to the TiO₂ powder. The size of anatase and rutile nanocrystals was found to be equal to (19.2±0.8) nm and (27.8±1.1) nm. However, a contribution of change in the surface states, to the hydrophilic property, is also observed. X-ray photoelectron spectroscopy (XPS) results show change in the surface states of titanium and oxygen by increasing the hydroxyl group (-OH) which tend to give more hydrophilic character to the films.

Degradation analysis of dye-sensitized solar cell performance under thermal stress

M. Mohammaznezhad, [a] G. S.Selopal, [a,b] Z.W. Wang,[b] Barry Stansfield,[a] H.Zhao, [c] and F. Rosei [a,b]

[a] *Institut National de la Recherche Scientifique, Centre Énergie, Matériaux et Télécommunications, 1650 Boul. Lionel Boulet Varennes, Québec, J3X 1S2, Canada.*

[b] *Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054, P. R. China.*

[c] *The Cultivation Base for State Key Laboratory & College of Physics, Qingdao University, No. 308 Ningxia Road, Qingdao 266071, P. R. China.*

Email: Mahyar.Mohammadnezhad@emt.inrs.ca

Dye-Sensitized Solar Cells (DSSCs), may become a viable alternative to silicon solar cells due to their simple and low-cost fabrication technology. The long-term thermal stability of DSSCs is a major challenge that needs to be addressed for this technology to become commercially viable. In this work, we investigate the degradation mechanisms of DSSCs under thermal stress (aging at 80 °C in the dark) as shown in Fig. 1. The results indicate a significant loss in photo conversion efficiency (PCE), dropping to 59% of their initial value. This degradation of cell performance is mainly associated with a dramatic reduction of the short circuit current density (J_{sc}) upon thermal aging. To understand the mechanism that underpin these changes in device performance under thermal stress, the cells were investigated using various techniques such as field emission scanning electron microscopy (FESEM), Raman spectroscopy and electrochemical impedance spectroscopy (EIS). Results of microstructural evaluation of the active layer as well as carrier dynamics (electron lifetime) after aging will be presented and discussed. In addition, desorption of dye molecules from the surface of the TiO_2 particles that can be considered as one of the most critical reasons for the degradation of DSSCs upon thermal aging, will be discussed based on Raman measurements.

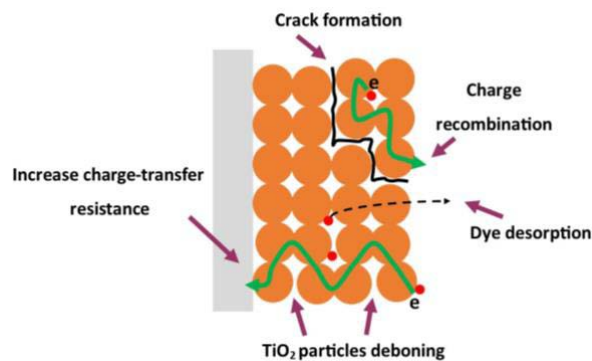


Fig. 1. Different possible degradation mechanisms of DSSCs under thermal stress

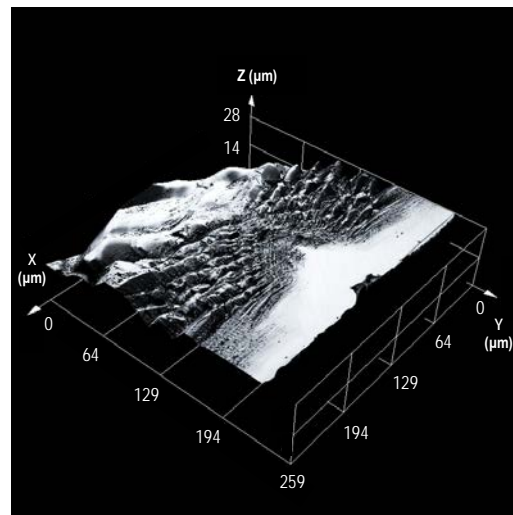
Determining Stresses in Silicon-based Microdevices Using Fractography

A. Moulines¹, G. Grosse¹, A. Esteves¹, R. Dugnani², R. Zednik¹

¹ *École de Technologie Supérieure, Université du Québec, Montréal (Canada)*

² *Joint Institute – UM-Shanghai Jiao Tong University, Shanghai (China)*

Silicon-based microdevices are already ubiquitous in our everyday lives; the single-crystals that are the fundamental building blocks of these devices occupy ever more restricted sub-micron geometries and are exposed to ever more complex mechanical stresses, directly affecting their mechanical and electrical properties[1]. These stresses occur during operation and processing, and include residual stresses within the material that can readily reach the GPa range[2]. However, unfortunately measuring these complex stresses at the sub-micron length-scale required is not possible using conventional characterization methods, severely restricting our understanding of the effects of mechanical stresses on material properties of single-crystal silicon. We therefore employ advanced fractographic techniques to correlate fracture features of single-crystal silicon and correlate them with mechanical properties. We evaluate the deviation of the crack-tip propagating on different crystallographic planes through height mapping contour methods. We thereby show how the characteristic “mirror region” can be used to determine the state of stress in silicon single-crystals at the sub-micron length-scale[3].



Deviation of the crack-tip propagating on different crystallographic planes produces a characteristic fracture surface in single-crystal silicon.

References

- [1] Uchida, K, R Zednik, Ching-Huang Lu, H. Jagannathan, J. McVittie, P.C. McIntyre, and others, “Experimental Study of Biaxial and Uniaxial Strain Effects on Carrier Mobility in Bulk and Ultrathin-Body SOI MOSFETs,” in IEDM Technical Digest. IEEE IEDM (2004)
- [2] Dugnani, R., and P. Verghese, “Failure Analysis of Modern Silicon Dice,” International Journal of Applied Ceramic Technology, 11 (2014)
- [3] Dugnani, R., and R. J. Zednik, “Flexural Strength by Fractography in Modern Brittle Materials,” Journal of the American Ceramic Society, 96 (2013)

Effect of chromium doping on the formation of M2 phase of VO₂ thin films deposited by reactive pulsed laser ablation

A. O.Suleiman¹, T. Hajlaoui¹, N.Emond¹, T. Bégin², M. Chaker³

^{1,3} *Institut National de la Recherche Scientifique, 1650 Lionel Boulet Varennes, J3X 1S2 QC (Canada)*

² *Polytechnique Montreal, 2900 Boulevard Edouard-Montpetit, Montréal, QC H3T 1J4 (Canada)*

Vanadium oxides especially those of magneli phases have been widely investigated for more than 5 decades due to their insulator to metal transition (IMT) [1]. Vanadium dioxide (VO₂) is characterized by the closest transition temperature to room temperature – $T_{IMT} \approx 68$ °C. More importantly, the IMT of VO₂ is characterized by contrast between the resistivity jump between the low temperature (monoclinic M1) and high temperature (tetragonal) rutile phases, estimated at more than 4 orders of magnitude for the bulk crystal. The transition temperature is accompanied by a strong change of the electrical and optical properties in the infrared region. The tunability of the transition temperature with donor- or acceptor-like dopants followed by control of phase transition from parameters like temperature, pressure, electric field etc. makes VO₂ suitable for various applications such as smart radiators, infrared uncooled bolometers, holographic storage systems, optical and electrical switches, etc.

The origin of its T_{IMT} however, has been a subject of debate and controversy as it is associated with either a Mott-Hubbard or Peierls transition [2]. Since VO₂ undergoes a structural transition from M1 to R phase, it was proposed that an intermediary structural phase(s) was necessary to have a better understanding of the driving force behind its transition.

Doping of VO₂ with chromium offers such intermediary structural phases such as M2 and M3. The low oxidation-state dopant, which through substitutional defect, introduces holes into the lattice, is known to increase the transition temperature of the parent material (VO₂). The increase in the transition temperature has been attributed to the tendency of the VO₂ system to remain semiconducting as a result of enhancement of the interactions between V atoms resulting from shortening of V-V bonds due to chromium substitution [3]. The Cr dopant is also capable of stabilizing different structural phases such as monoclinic M2 and M3 [4–6] at room temperature based on at. % of chromium.

References

- [1] F. J. Morin, Phys. Rev. Lett. **3**, 1 (1959).
- [2] A. L. Pergament, G. B. Stefanovich, and A. A. Velichko, J. on Selected Topics in Nano Electronics and Computing, **1**, 24 (2015).
- [3] M. Pan, H. Zhong, S. Wang, Z. Li, X. Chen, and W. Lu, Chem. Phys. Lett., **398**, 304 (2004).
- [4] M. Marezio, Phys. Rev. B, **91**, (1971).
- [5] J. B. Goodenough, J. Solid State Chem., **500**, 490 (1971).
- [6] C. Marini, E. Arcangeletti, D. Di Castro, L. Baldassare, A. Perucchi, S. Lupi, L. Malavasi, L. Boeri, E. Pomjakushina, K. Conder, and P. Postorino, Phys. Rev. B - Condens. Matter Mater. Phys. **77**, 1 (2008).

Electronic shields and humidity switches made from composites of carbon nanotubes and nanocellulose

T. G.M. van de Ven¹ and S. Safari²

¹ *Department of Chemistry and*

² *Department of Chemical Engineering*

^{1,2} *Pulp and Paper Research Centre*

Quebec Centre for Advanced Materials

McGill University, 3420 University Street, Montreal QC Canada

It has been long known that the electrical properties of cellulose are greatly influenced by adsorption of water vapor. Incorporating conductive nanofillers in a cellulose matrix is an example of an approach to tailor their characteristics for use in electronics and sensing devices. In this work, we introduce two new nanocomposites comprising carbon nanotubes (CNTs) and conventional or electrosterically stabilized nanocrystalline celluloses matrices. While conventional nanocrystalline cellulose (NCC) consists of a rigid crystalline backbone, electrosterically stabilized cellulose (ENCC) is composed of a rigid crystalline backbone with carboxylated polymers protruding from both ends. ENCC is a member of the family of hairy Nanocellulose [1]. By tuning CNT loading, we can tailor a CNT/NCC composite with minimal electrical sensitivity to the ambient relative humidity, despite the fact that the composite has a high moisture uptake [2]. The expected decrease in CNT conductivity upon water vapor adsorption, due to electron donation, is counterbalanced by an increase in the conductivity of NCC due to proton hopping at an optimum CNT loading (1–2%). Such composites can be used as shields for sensitive electronic devices. Contrary to the CNT/NCC composite, a CNT/ENCC composite at 1% CNT loading shows insulating behavior for relative humidities up to about 70%, after which the composite becomes conductive. This interesting behavior can be ascribed to the low moisture uptake of ENCC at low and moderate relative humidities due to the limited number of hydroxyl groups and hydrogen bond formation between carboxyl groups on ENCC, which endow ENCC with limited water molecule adsorption sites. Such CNT/ENCC composites can be used as humidity switches

References

- [1] T.G.M. van de Ven and A. Sheikhi, Hairy cellulose nanocrystalloids: A novel class of nanocellulose, *Nanoscale* **8**, 15101-15114 (2016)
- [2] S. Safari and T.G.M. van de Ven, Effect of water vapor adsorption on electrical properties of carbon nanotube / nanocrystalline cellulose composites, *ACS Applied Materials & Interfaces* **8**(14), 9483–9489 (2016)

Single-Pixel Terahertz Imaging Using a Time-Domain Spectroscopy Setup

L. Zanotto¹, R. Piccoli¹, J. Dong¹, H. Breitenborn¹, R. Naccache², R. Morandotti^{1,3,4},
L. Razzari¹

¹ INRS-EMT, 1650 Boulevard Lionel-Boulet, J3X 1S2, Varennes, Québec, Canada

²Department of Chemistry and Biochemistry, Concordia University, Montreal, Québec H4B 1R6, Canada

³National Research University of Information Technologies, Mechanics and Optics, 199034 St. Petersburg, Russia

⁴IFFS, University of Electronic Science and Technology of China, Chengdu, 610054 Sichuan, China

I. INTRODUCTION Terahertz radiation (0.1-10 THz) has attracted significant attention in the last years for many scientific and industrial applications [1]. Indeed, many materials such as cardboard, ceramic, plastic etc., are transparent to THz waves, and low-energy vibro-/rotational transitions of molecules are located in this region, thus enabling chemical recognition. Therefore, THz imaging represents a powerful tool for system inspection, security and material quality control [2]. However, the main constraints that hamper the wide industrial application of this technique are the long acquisition time required for a pixel-by-pixel scan of the object to be imaged through standard THz time-domain spectroscopy (TDS) setups [3] or, alternatively, the high cost of THz sensitive cameras. In recent years, different imaging approaches have emerged, based on the idea of imposing a spatial modulation on the THz light (pattern) propagating through (or reflected off) an object, and then collecting the overall THz radiation with a single-pixel detector (e.g., bolometer) [4,5]. The correlation between the patterns and the corresponding detector readings finally produces the image. This technique allows also to exploit compressive sampling algorithms, thus retrieving an N-pixels image, just recording M<N measurements [4]. In this study, we show some initial results regarding the implementation of single-pixel THz imaging, to be employed with standard THz -TDS setups.

II. EXPERIMENT In our configuration, 800-nm, 150-fs, 2.2 mJ, 1 kHz pump pulses are split into three lines: a pump beam (~48% of the laser power), a pattern generation beam (also ~48%) and a probe beam (~4%). The first beam generates THz pulses via collinear optical rectification in a 1-mm-thick ZnTe-crystal. The second one is shaped, by means of a Digital Micromirror Device, in a series of binary intensity patterns (~85% efficiency) and sent on a high-resistivity 0.5-mm-thick silicon plate. Here, the photo-excited carriers locally absorb the THz light (propagating through the plate) and thus transfer the patterns onto the THz beam. The so-generated THz patterns are then sent through the object to be imaged. The overall transmitted THz waveform is finally recorded by means of the probe beam via electro-optical sampling in a 1-mm-thick ZnTe crystal [1]. The image reconstruction is then obtained by summing up all the patterns, each one weighted by the integral of the corresponding THz waveform squared. The binary-patterns used are a set of Hadamard matrices [5], which are proven to be suitable for the implementation of compressive sampling algorithms (to increase the image acquisition speed), while guaranteeing an optimal SNR ratio.

References

- [1] S. L. Dexheimer, *Terahertz Spectroscopy, Principles and Applications*, CRC Press (2008)
- [2] J. B. Baxter et al., *Anal. Chem.* **83**, 12 (2011)
- [3] C. Jansen et al., *Applied Optics* **49**, 19 (2010)
- [4] R. I. Stantchev et al., *Sci. Adv.* **2**, e1600190 (2016)
- [5] D. Shrekenhamer et al., *Opt. Express* **21**, 12507 (2013)