

# ADVANCES AND APPLICATIONS IN CARBON RELATED NANOMATERIALS: FROM PURE TO DOPED STRUCTURES INCLUDING HETEROATOM LAYERS



2019, Dec 09 -- Dec 13

## Organizers:

R. Arenal (LMA - INA, **chairman**)  
C. P. Ewels (Nantes U.)  
D. Golberg (Queensland University of Technology)  
V. Meunier (Rensselaer Polytechnic Institute)  
A. Rubio (U. País Vasco - Fritz Haber Institut - Max Plank Gesellschaft)

**ThermoFisher**  
SCIENTIFIC

 *applied  
sciences*



 **araid**  
FUNDACIÓN AGENCIA ARAGONESA  
PARA LA INVESTIGACIÓN Y EL DESARROLLO



## Schedule of HeteroNanoCarb-2019

### Monday 9<sup>th</sup> December 2019

15:30/16:00	Departure Bus from Barcelona Downtown/Airport <a href="http://benasque.org/2019heteronanocarb/#bus">http://benasque.org/2019heteronanocarb/#bus</a>
~20:30	Arrival Bus to Benasque
21:00	Welcome cocktail

### Tuesday 10<sup>th</sup> December 2019

### Wednesday 11<sup>th</sup> December 2019

### Thursday 12<sup>th</sup> December 2019

8:45 - 8:55	Remarks - Announcements				
8:55-10:35	Session I	8:45-10:40	Session IV	8:45-10:40	Session VII
10:35-11:00	Coffee Break	10:40-11:05	Coffee Break	10:40-11:05	Coffee Break
11:00-13:00	Session II	11:05-13:15	Session V	11:05-13:00	Session VIII
13:00-18:30	Mini Workshops	13:15-18:30	Mini Workshops	13:00-18:30	Mini Workshops
18:30-20:25	Session III	18:30-20:20	Session VI	18:30-20:10	Session IX
20:25-21:55	Poster session / Cocktail	20:20-21:50	Poster session / Cocktail	21:00-...	Conference Dinner

### Friday 13<sup>th</sup> December 2019

8:45	Departure Bus to Barcelona Airport/Downtown <a href="http://benasque.org/2019heteronanocarb/#bus">http://benasque.org/2019heteronanocarb/#bus</a>
13:00-14:00	Arrival Bus to Barcelona Airport

Tuesday 10<sup>th</sup> December 2019

8:55 – 10:35	Session - I	Chairs: R. Arenal & O. Stephan
Invited Speaker	8:55 – 9:30	<b><i>Defects in 2D Metal Dichalcogenides: Doping, Alloys, Vacancies and Their Effects in Magnetism, Electronics, Catalysis, Optical Emission and Bio-Applications</i></b> Mauricio Terrones <a href="mailto:mut11@psu.edu">mut11@psu.edu</a>
	9:30 – 9:45	<b><i>Phonons in low-dimensional materials</i></b> Vincent Meunier <a href="mailto:meuniv@rpi.edu">meuniv@rpi.edu</a>
	9:45 – 10:00	<b><i>DFT Modelling of carbon nanomaterials</i></b> C. P. Ewels <a href="mailto:chris.ewels@cncrs-imn.fr">chris.ewels@cncrs-imn.fr</a>
Invited Speaker	10:00 – 10:35	<b><i>Stability of edge magnetism against disorder in MoS2 nanoribbons with zigzag edges</i></b> Péter Vancsó, Imre Hagymási, Pauline Castenetto, Philippe Lambin <a href="mailto:vancso.peter@energia.mta.hu">vancso.peter@energia.mta.hu</a>
10:35 – 11:00		COFFEE BREAK
11:00 – 13:00	Session - II	Chairs: V. Meunier & M. Mayne-L'Hermite
Invited Speaker	11:00-11:35	<b><i>New optical effects in 2D materials as probed by electron and photon spectroscopy in a Scanning Transmission Electron Microscope</i></b> Luiz Galvao Tizei, Alberto Zobelli, Steffi Woo, Jean-Denis Blazit, Marcel Tencé, Mathieu Kociak, Odile Stéphan <a href="mailto:odile.stephan@u-psud.fr">odile.stephan@u-psud.fr</a>
	11:35-11:50	<b><i>Piezo-doping of bilayer graphene and mechanical layer decoupling: an in-situ Raman spectroscopy of 12C/13C bilayer graphene at high pressure</i></b> A. Forestier, F. Balima, C. Bousige, D. Machon, M. Kalbac, and A. San Miguel <a href="mailto:colin.bousige@univ-lyon1.fr">colin.bousige@univ-lyon1.fr</a>
	11:50-12:05	<b><i>Raman mapping analysis of liquid-exfoliated few-layer nanomaterials</i></b> Aline Amorim Graf, Matthew J. Large, Sean P. Ogilvie, Manoj Tripathi, Alice A. K. King, Alan B. Dalton <a href="mailto:a.amorim-graf@sussex.ac.uk">a.amorim-graf@sussex.ac.uk</a>
	12:05-12:20	<b><i>Characterization of Atomically Precise Graphene Nanoribbons by Raman Spectroscopy</i></b> J. Overbeck, G. Borin Barin, C. Daniels, M. Perrin, O. Braun, P. Ruffieux, V. Meunier, R. Fasel and M. Calame. <a href="mailto:jan.overbeck@empa.ch">jan.overbeck@empa.ch</a>
Invited Speaker	12:20-12:55	<b><i>GO-ING ON WITH GRAPHENE OXIDE</i></b> Wolfgang K. Maser, A.M. Benito <a href="mailto:wmaser@icb.csic.es">wmaser@icb.csic.es</a>

Tuesday 10<sup>th</sup> December 2019

18:30 – 20:25	Session - III	Chairs: C. Ewels & M. Terrones
Invited Speaker	18:30-19:05	<p><b><i>Theory of defect ionization in 2D semiconductors and prediction of the double layer honeycomb structure</i></b>            Damien J. West  <a href="mailto:westd2@rpi.edu">westd2@rpi.edu</a></p>
	19:05-19:20	<p><b><i>Bottom-up fabrication of graphene nanoribbons: from molecules to devices</i></b>            Gabriela Borin Barin, Maria El Abbassi, Jan Overbeck, Juan Pablo Llinas, Colin Daniels, Rimah Darawish, Oliver Braun, Mickael Perrin, Akimitsu Narita, Klaus Müllen, Vincent Meunier, Jeffrey Bokor, Michel Calame, Pascal Ruffieux, Roman Fasel  <a href="mailto:gabriela.borin-barin@empa.ch">gabriela.borin-barin@empa.ch</a></p>
	19:20-19:35	<p><b><i>Preparation of 2H-MoTe2 films with high crystalline quality and large area by molecular beam epitaxy</i></b>            Trung T. Pham, Roshan Castelino, Alex Felten, and Robert Sporken  <a href="mailto:trung.phamthanh@unamur.be">trung.phamthanh@unamur.be</a></p>
	19:35-19:50	<p><b><i>Iodine-Chlorine complexation in intercalated Graphite for positive Graphenium production</i></b>            Xiaoyang CHE, Ferdinand HOF, Alain PENICAUD, Emmanuel PICHAUT, Anthony IMPELLIZZERI, Chris EWELS  <a href="mailto:xiaoyang.che@u-bordeaux.fr">xiaoyang.che@u-bordeaux.fr</a></p>
Invited Speaker	19:50-20:25	<p><b><i>Visualization of multifractal superconductivity in a two-dimensional transition metal dichalcogenide in the weak-disorder regime</i></b>            Miguel M. Ugeda  <a href="mailto:mmugeda@dipc.org">mmugeda@dipc.org</a></p>
20:25-21:55	Poster Session	Cocktail

Wednesday 11<sup>th</sup> December 2019

8:45 – 10:40	Session - IV	Chairs: D. West & M. Ugeda
Invited Speaker	8:45 – 9:20	<b>Aerosol-assisted CCVD process: an up-scalable one-step method for the production of versatile VACNT carpets</b> Martine Mayne-L'Hermite <a href="mailto:martine.mayne@cea.fr">martine.mayne@cea.fr</a>
	9:20 – 9:35	<b>Lightweight Cu/Carbon Nanotube composites as promising future Cu substitutes</b> Rajyashree Sundaram, Guohai Chen, Takeo Yamada, Don Futaba, Kenji Hata, Atsuko Sekiguchi <a href="mailto:atsuko-sekiguchi@aist.go.jp">atsuko-sekiguchi@aist.go.jp</a>
	9:35 – 9:50	<b>Base washing functionalised nanotubes with copper hydroxide for hybrid film fabrication</b> Peter Lynch, Sean Ogilvie, Mathew Large, J. Salvage, Alan Dalton <a href="mailto:p.j.lynch@sussex.ac.uk">p.j.lynch@sussex.ac.uk</a>
	9:50 – 10:05	<b>Conventional and nitrogen doped vertically aligned carbon nanotubes for energy storage</b> Corentin QUERNE, Philippe BANET, Martine MAYNE-L'HERMITE, Pierre-Henri AUBERT, Mathieu PINAULT <a href="mailto:corentin.querne@cea.fr">corentin.querne@cea.fr</a>
Invited Speaker	10:05 – 10:40	<b>Characterizing Filling of Carbon Nanotubes by Optical Spectroscopy</b> S. Cambré, , J. Campo, S. van Bezouw, B. Botka, W. Van Werveke, W. Wenseleers, J. Obrzut, J.A. Fagan <a href="mailto:sofie.cambre@uantwerpen.be">sofie.cambre@uantwerpen.be</a>
10:40 – 11:05		COFFEE BREAK
11:05 – 13:15	Session - V	Chairs: S. Cambré & R. Arenal
Invited Speaker	11:05-11:40	<b>Perspective of 2D materials: Macroscopic and nanoscopic viewpoints</b> Reshef Tenne <a href="mailto:reshef.tenne@weizmann.ac.il">reshef.tenne@weizmann.ac.il</a>
	11:40-11:55	<b>Electron microscopy investigation of nanotubes from the misfit-layered compounds (La,Y)S-TaS<sub>2</sub></b> S. Hettler, M. Serra, R. Tenne, R. Arenal <a href="mailto:hettler@unizar.es">hettler@unizar.es</a>
	11:55-12:10	<b>Covalently incorporated photoactive dyes onto transition metal dichalcogenides</b> Ruben Canton-Vitoria, Ryo Kitaura, Nikos Tagmatarchis <a href="mailto:canton@eie.gr">canton@eie.gr</a>
	12:10-12:25	<b>Unique properties and performance evaluation for ultra- and nano-filtration membranes containing nanostructured carbon materials</b> Edward Nxumalo <a href="mailto:edwardnxumalo@gmail.com">edwardnxumalo@gmail.com</a>
	12:25-12:40	<b>Theoretical ab-initio study of graphene vacancies and pyridinic defects for gas separation</b> N. N. Lathiotakis, Z. G. Fthenakis, and I. D. Petsalakis <a href="mailto:lathiot@eie.gr">lathiot@eie.gr</a>
Invited Speaker	12:40-13:15	<b>Graphene-Based High Open-Circuit Voltage Heterojunction Solar Cell</b> Dieter M. Gruen, Hisham A. Maddah and Sanjay K. Behura <a href="mailto:dietergruen@comcast.net">dietergruen@comcast.net</a>

Wednesday 11<sup>th</sup> December 2019

18:30 – 20:20	Session - VI	Chairs: E. Obraztsova & R. Tenne
Invited Speaker	18:30-19:05	<b>MECHANISMS OF THE SP<sup>2</sup>-C TO SP<sup>3</sup>-C CONVERSION DURING THE LOW TEMPERATURE, LOW PRESSURE SYNTHESIS OF DIAMANE AND DIAMANOIDS FROM GRAPHENE</b> Fabrice Piazza, Pascal Puech, Iann Gerber, Kathleen Gough, Germercy Paredes, Marc Monthieux <a href="mailto:monthiou@cemes.fr">monthiou@cemes.fr</a>
	19:05-19:20	<b>DOPED DIAMOND INTERFACES: APPLICATION IN ENERGY AND BIONICS</b> Ahmed Farid Halima <a href="mailto:ahmed.f.halima@gmail.com">ahmed.f.halima@gmail.com</a>
	19:20-19:35	<b>Atomic configuration studies of n-type ultrananocrystalline diamond films</b> R. Arenal, F. Hage, Q. Ramasse and D.M. Gruen4 <a href="mailto:arenal@unizar.es">arenal@unizar.es</a>
	19:35-19:50	<b>FABRICATION OF BN COATED CARBON NANOSTRUCTURES USING ALD BASED POLYMER DERIVED CERAMICS ROUTE</b> C. Marichy, W. Hao, C. Journet <a href="mailto:catherine.marichy@univ-lyon1.fr">catherine.marichy@univ-lyon1.fr</a>
	19:50-20:05	<b>Assessment of charge transfer phenomena in nanostructured composite materials using photoelectrochemical methods.</b> Javier Hernández-Ferrer, Emin Istif, Alejandro Ansón-Casaos, Ana Santidrián, Ana M. Benito, Wolfgang K. Maser <a href="mailto:jhernandez@icb.csic.es">jhernandez@icb.csic.es</a>
	20:05-20:20	<b>Emulsion-templated graphene-silicone composites with robust exponential electromechanical response</b> Marcus O'Mara, Sean P. Ogilvie, Matthew J. Large, Aline Amorim Graf, Peter J. Lynch, Jonathan P. Salvage, Alice A. K. King, Alan B. Dalton <a href="mailto:mo264@sussex.ac.uk">mo264@sussex.ac.uk</a>
20:20-21:50	Poster Session	Cocktail

Thursday 12<sup>th</sup> December 2019

8:45 – 10:40	Session - VII	Chairs: T. Reiss & P. Ayala
Invited Speaker	8:45 – 9:20	<b>Synthesis of boron nitride single crystals under high pressure impurity and isotope control for their functionalization</b> Takashi Taniguchi <a href="mailto:taniguchi.takashi@nims.go.jp">taniguchi.takashi@nims.go.jp</a>
	9:20 – 9:35	<b>SYNTHESIS OF EXFOLIABLE HEXAGONAL BORON NITRIDE SINGLE CRYSTALS OF MILLIMETER SIZE</b> Catherine Journet, Y. Li, V.t Garnier, P. Steyer, B. Toury <a href="mailto:catherine.journet@univ-lyon1.fr">catherine.journet@univ-lyon1.fr</a>
	9:35 – 9:50	<b>HEXAGONAL BORON NITRIDE: AN EMERGING 2D MATERIAL FOR PHOTONIC AND OPTOELECTRONIC APPLICATIONS</b> Marie Krečmarová, R. Canet-Albiach, D. Andres-Penares, L. Fekete, P. Ashcheulov, A. Molina-Sánchez, J.P. Martínez-Pastor, J.F. Sánchez-Royo. <a href="mailto:Marie2.Krecmarova@uv.es">Marie2.Krecmarova@uv.es</a>
	9:50 – 10:05	<b>1T/2H mixed-phase few-layer MoS2 nanosheets vertically aligned on nitrogen-doped reduced graphene oxide as superior electrochemical ascorbic acid biosensor</b> He Li , Zhihao Yuan, Wei Li, Minfang Chen, Rony Snyders, Wenjiang Li and Carla Bittencourt <a href="mailto:li_wenjiang@163.com">li_wenjiang@163.com</a>
Invited Speaker	10:05 – 10:40	<b>OPTICAL PROPERTIES of MoS2, WS2 and GRAPHENE GROWN by CHEMICAL VAPOR DEPOSITION</b> P.V. Fedotov, F.D. Vasil'eva, P.V. Vinokurov, E.A. Obraztsova, V.R. Islamova, M.G. Rybin, S.A. Smagulova, E.D. Obraztsova <a href="mailto:elobr@mail.ru">elobr@mail.ru</a>
10:40 – 11:05		COFFEE BREAK
11:05 – 12:55	Session - VIII	Chairs: M. Monthieux & T. Taniguchi
Invited Speaker	11:05-11:40	<b>NO2 Sensitivity and Selectivity of Single-Walled Carbon Nanotube-Hybrids upon cluster filling</b> Paola Ayala <a href="mailto:paola.ayala@univie.ac.at">paola.ayala@univie.ac.at</a>
	11:40-11:55	<b>Carbon nanostructures-based aqueous bioinks</b> J. M. González-Domínguez, M. A. Álvarez, A. Baigorri, A. Ansón-Casaos, G. Huet, C. Hadad, A. Nguyen Van Lier, J. E. García-Bordejé, A. M. Benito, W. K. Maser <a href="mailto:jmgonzalez@icb.csic.es">jmgonzalez@icb.csic.es</a>
	11:55-12:10	<b>IN-SITU GRAPHENE OXIDE THERMAL ANALYSES VIA TEM/EELS: WATER DESORPTION, REDUCTION AND GRAPHITISATION</b> Mario Pelaez-Fernandez, A. Bermejo, A.M. Benito, W.K. Maser, R. Arenal <a href="mailto:mariopf@unizar.es">mariopf@unizar.es</a>
	12:10-12:25	<b>Nanomaterial Tissue Substrates to Probe Cellular Disease Mechanisms</b> Rhiannon W. Harries, P. Lynch, M. Large, S. Ogilvie, L. Woodbine, T. Simon, G. Giamas, Alan B. Dalton, Alice A. K. King <a href="mailto:R.W.Harries@sussex.ac.uk">R.W.Harries@sussex.ac.uk</a>
	12:25-12:40	<b>Mechanochemical synthesis of "Sweet green graphene"</b> Viviana Jehová González, Antonio M. Rodríguez, Ester

		Vázquez <a href="mailto:VivianaJ.Gonzalez@uclm.es">VivianaJ.Gonzalez@uclm.es</a>
	12:40-12:55	<b><i>P3HT aggregation tuned by synergic interaction with different carbon nanostructures</i></b> E. Colom, E. Istif, J.M. González-Domínguez, J. Hernández-Ferrer, A.M. Benito, W.K. Maser <a href="mailto:ecolom@icb.csic.es">ecolom@icb.csic.es</a>

Thursday 12<sup>th</sup> December 2019

18:30 – 20:00	Session - IX	Chairs: W. Maser & R. Arenal
Invited Speaker	18:30-19:05	<b><i>The Graphene Technology and Innovation Roadmap</i></b> Thomas Reiss <a href="mailto:thomas.reiss@isi.fraunhofer.de">thomas.reiss@isi.fraunhofer.de</a>
	19:05-19:20	<b><i>Recent advancements in S/TEM technology: Thermo Scientific Spectra”</i></b> Daniel G. Stroppa <a href="mailto:daniel.stroppa@thermofisher.com">daniel.stroppa@thermofisher.com</a>
Invited Speaker	19:20-19:55	... Alan Dalton <a href="mailto:A.B.Dalton@sussex.ac.uk">A.B.Dalton@sussex.ac.uk</a>
	19:55-20:00	<b><i>Concluding remarks</i></b>
21:00		<b><i>Congress Dinner</i></b>



# **ORAL PRESENTATIONS**

**TUESDAY 10th  
PRESENTATIONS**

# Defects in 2D Metal Dichalcogenides: Doping, Alloys, Vacancies and Their Effects in Magnetism, Electronics, Catalysis, Optical Emission and Bio-Applications

Mauricio Terrones<sup>1</sup>

<sup>1</sup> Department of Physics, Department of Chemistry, Department of Materials Science and Engineering and Center for 2-Dimensional & Layered Materials. The Pennsylvania State University, University Park, Pennsylvania 16802, USA

Semiconducting two-dimensional transition metal dichalcogenides (TMDs) such as MoS<sub>2</sub>, MoSe<sub>2</sub>, WSe<sub>2</sub>, and WS<sub>2</sub> hold great promise for many novel applications. Recent years have therefore witnessed tremendous efforts on large scale manufacturing of these 2D crystals. A long-standing puzzle in the field is the effect of different types of defects in their electronic, magnetic, catalytic and optical properties.

In this presentation an overview of different defects in transition metal di-chalcogenides (TMDs) will be presented [1,2]. We will define the dimensionalities and different atomic structures of defects, and discuss how these defects could be imaged with novel optical-driven techniques. We will emphasize doping and alloying in monolayers of MoS<sub>2</sub>, WS<sub>2</sub>, and WSe<sub>2</sub> and describe their implications in magnetism, as well as in electronic transport [3]. We will also describe the catalytic effects of edges, vacancies and local strain observed in Mo<sub>x</sub>W<sub>(1-x)</sub>S<sub>2</sub> monolayers by correlating the hydrogen evolution reaction (HER) with aberration corrected scanning transmission electron microscopy (AC-HRSTEM) [4]. Our findings demonstrates that it is now possible to use chalcogenide layers for the fabrication of more effective catalytic substrates, however, defect control is required to tailor their performance. By studying photoluminescence spectra, atomic structure imaging, and band structure calculations, we also demonstrate that the most dominating synthetic defect—sulfur monovacancies in TMDs, is responsible for a new low temperature excitonic transition peak in photoluminescence 300 meV away from the neutral exciton emission [5]. We further show that these neutral excitons bind to sulfur mono-vacancies at low temperature, and the recombination of bound excitons provides a unique spectroscopic signature of sulfur mono-vacancies [5]. However, at room temperature, this unique spectroscopic signature completely disappears due to thermal dissociation of bound excitons [5]. One-dimensional hetero-interfaces in TMDs will be shown by AC-HRSTEM in conjunction with their non-linear optical emission, constituting a new way to image 1D defects [6]. Finally, the electronic effects of C-H defects within TMDs will be discussed, as p-type doping could be controlled by the presence of C within TMDs [7].

## References:

- [1] Z. Lin, M. Terrones, et al. "Defect engineering of two-dimensional transition metal dichalcogenides". *2D Materials* **3** (2016) 022002.
- [2] R. Lv, M. Terrones, et al. "Two-dimensional transition metal dichalcogenides: Clusters, ribbons, sheets and more". *Nano Today* **10** (2015) 559-592.
- [3] F. Zhang, M. Terrones, et al. "One-Step Synthesis of Monolayer Vanadium-doped Tungsten Disulfide: A Room-Temperature Dilute Magnetic Semiconductor", *submitted* (2019).
- [4] Y. Lei, M. Terrones, et al. "Low temperature synthesis of heterostructures of transition metal dichalcogenide alloys (W<sub>x</sub>Mo<sub>1-x</sub>S<sub>2</sub>) and graphene with superior catalytic performance for hydrogen evolution". *ACS Nano*, **11** (2017), 5103-5112.
- [5] V. Carozo, M. Terrones, et al. "Optical identification of sulfur vacancies: Bound excitons at the edges of monolayer tungsten disulfide", *Sci. Adv.* **3** (2017), e1602813
- [6] B. R. Carvalho, M. Terrones, L. M. Malard, et al. "Imaging of 1D defects in monolayer dichalcogenides", *submitted* (2019).
- [7] F. Zhang, M. Terrones, et al. "Carbon Doping of WS<sub>2</sub> Monolayers: Band Gap Reduction and P-type Doping Transport", *Sci. Adv.* **5** (2019), eaav5003.

## **Phonons in low-dimensional materials.**

Vincent Meunier

Rensselaer Polytechnic Institute

2D materials (2DMs) such as graphene, transition metal dichalcogenides (TMDs) and black phosphorus have attracted significant attention as emerging low-dimensional materials. These materials feature an array of properties that offer many promises in terms of potential electronic and optoelectronic applications. Many characterization techniques have been employed to improve the understanding of these materials, to establish their crystal structure, purity, number of layers, and internal configurations. In particular, Raman spectroscopy, has demonstrated that structural vibrations can be used as reliable indicators of the structural properties of 2DMs.

Due to the emergence of new properties, the interpretation of experimental features requires a dedicated modeling effort based on quantum-mechanics. In this talk, I will overview how quantum mechanical properties and non-resonant Raman scattering are combined to determine the fundamental structural properties in a broad array of 2D materials. I will discuss the importance of low-frequency modes in the study of layer-layer interactions in 2DMs, and how relative twisting angles between layers can be determined by monitoring relative shifts in Raman active mode. If time permits, I will also explain how vibrational signatures can be exploited to understand in-plane anisotropy in phosphorene.

# Novel Carbon Nanostructures through HRTEM and Molecular Dynamics

Chris EWELS<sup>a</sup>, Irene Suarez-Martinez<sup>b</sup>, Edward Goldwyn<sup>c</sup>, Mildred Quintana<sup>d</sup>, M. I. Heggie<sup>e</sup>

<sup>a</sup> IMN, CNRS / Université de Nantes, 2 Rue de la Houssiniere, BP32229, 44322 Nantes, France

<sup>b</sup> Nanochemistry Research Institute, Department of Physics and Astronomy, Curtin University, Perth, Australia.

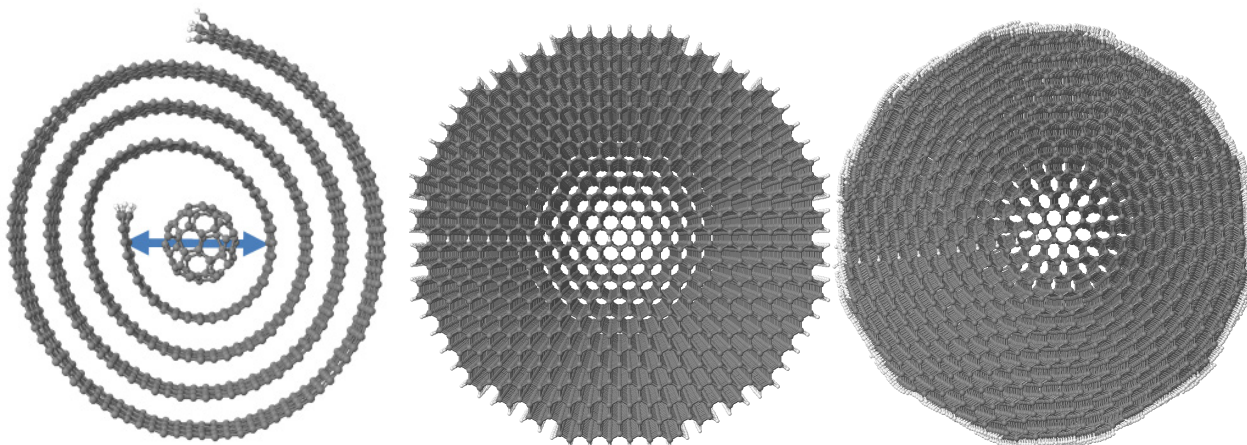
<sup>c</sup> Goldwyn Productions Ltd, London, UK

<sup>d</sup> Instituto de Física, UASLP Universidad Autónoma Metropolitana, San Luis Potosí Area, Mexico

<sup>e</sup> Black Dog Bytes, Devon, UK / University of Loughborough, Loughborough, UK

e-mail: [chris.ewels@cnrs-imn.fr](mailto:chris.ewels@cnrs-imn.fr)

We are interested in exploring the wealth of “non-standard” and often low-symmetry carbon nanoforms that exist, many of which involve mechanical deformation of sp<sup>2</sup> sheets of graphitic carbon under the influence of external stimuli, such as surface absorbed pi-stacked molecular species, or internal stacking forces. In this poster we discuss two such species, the spontaneous formation of carbon nanoscrolls when graphene and fullerenes are mixed<sup>1</sup>, and the structure of screw dislocations in graphite. Such large scale problems can be addressed using realistic interatomic potentials such as AIREBO<sup>2</sup>, in this case within the LAMMPS molecular dynamics package<sup>3</sup>, and compared directly with experimental HRTEM images.



**Figure:** (left) Fullerene encapsulated in carbon nanoscroll (now obtained experimentally in the group of Mildred Quintana), and screw dislocation in graphite (centre) before relaxation, (right) after geometrical optimisation.

## References

<sup>1</sup> E. Goldwyn, I. Suarez-Martinez, J. Rio, Y. Sayed-Ahmad Baraza, M. Quintana, C. P. Ewels, in preparation (2018)

<sup>2</sup> S. J. Stuart *et al.*, *J. Chem. Phys.* **112**, 6472 (2000).

<sup>3</sup> S. Plimpton, Fast Parallel Algorithms for Short-Range Molecular Dynamics, *J Comp Phys*, **117**, 1-19 (1995), [lammps.sandia.gov](http://lammps.sandia.gov)

## Stability of edge magnetism against disorder in MoS<sub>2</sub> nanoribbons with zigzag edges

Péter Vancsó<sup>1\*</sup>, Imre Hagymási<sup>2</sup>, Pauline Castenetto<sup>3</sup>, Philippe Lambin<sup>3</sup>

1. *Hungarian Academy of Sciences, Centre for Energy Research, Institute of Technical Physics and Materials Science, 2DNanoelectronics Lendület Research Group 1121 Budapest, Hungary*
2. *Max Planck Institute for the Physics of Complex Systems, Nöthnitzer Straße 38, Dresden, Germany*
3. *University of Namur, Department of Physics, 61 rue de Bruxelles, 5000 Namur, Belgium*

MoS<sub>2</sub> nanoribbons with zigzag edges show ferromagnetic properties based on previous density functional (DFT) calculations [1] similarly to graphene nanoribbons. This magnetism is associated with the metallic edge states, where the edge sulfur atoms play an important role. However, investigation of the role of disorder on the magnetic properties is still lacking due to the computational costs of these methods. In this work we provide a study of the magnetic properties of several nanometer long MoS<sub>2</sub> ribbon with zigzag edges by using tight-binding (TB) and Hubbard Hamiltonians [2]. Our results reveal that proper tight-binding (TB) parameters for the edge atoms are crucial to obtain quantitatively the metallic states and the magnetic properties of MoS<sub>2</sub> nanoribbons. The large-scale magnetic calculations based on the Hubbard model predict low domain-wall energies along the ribbon edges, which are also sensitive to the presence of edge disorder. Our results give an insight into the magnetic properties of MoS<sub>2</sub> nanoribbons in large-scale systems and can also provide valuable information for spintronic applications.

[1] Y. Li et al., J. Am. Chem. Soc. (2008) 130, 16739–16744.

[2] P. Vancsó et al., Phys. Rev. Mater. (2019) 3, 094003.

## New optical effects in 2D materials as probed by electron and photon spectroscopy in a Scanning Transmission Electron Microscope

Odile Stéphan, Laboratoire de Physique des Solide, Université Paris-Sud/Paris-Saclay  
Bâtiment 510, Orsay, France

T: +33 169155369, odile.stephan@u-psud.fr

Luiz Galvao Tizei, Alberto Zobelli, Steffi Woo, Jean-Denis Blazit, Marcel Tencé, Mathieu Kociak  
Laboratoire de Physique des Solide, Université Paris-Sud/Paris-Saclay  
Bâtiment 510, Orsay, France

Scanning transmission electron microscopy (STEM) and associated imaging and spectroscopic modes is a very powerful and versatile technique for providing structural, chemical and electronic information of materials with very high spatial resolution. Recently the electron microscopy community has enjoyed great successes in STEM aberration correction and electron-beam monochromation for Electron Energy-Loss Spectroscopy (EELS). Atomically-resolved spectroscopy is now “routinely” achieved and a new access to a full range of optical excitations such as phonons, plasmons or excitons is provided. More exciting applications will emerge from the combination of such extraordinary instrumental progress with conceptual and methodological advances and complementary instrumental developments. At Orsay, some progress has been made in this direction, exploiting the combination of photon and electron beams (development of a light injection/detection system) inside the STEM. Nanometer-resolved Cathodoluminescence experiments are now available in a last generation microscope equipped with an electron monochromator providing a 5 meV energy resolution in EELS spectroscopy for a combined use of CL and EELS performed both at high spectral and spatial resolution. Derived from the quantum optics community, Hanbury Brown Twiss experiments have also been developed to detect the emission properties of individual quantum emitters in materials and entering the field of quantum nanooptics with free electron beams. When performed in the context of a STEM, such “optical” measurements can be coupled to state of the art “conventional” STEM measurements such as high ultra-high-resolution imaging, elemental and spectroscopic fingerprints mapping down to the atomic scale for an exploration of the structure / properties relationship in novel materials.

Some examples will be given here when exploring in 2D materials this intimate link between the crystal structure (including that of optical-active defects) and the optical properties. This comprises:

- the role of single dopants (Cr atoms) in WSe<sub>2</sub> crystals [1]
- optical properties and single photon emitters in h-BN [2] and dichalcogenides
- stacking effects on excitons in h-BN [3] and the appearance of new excitonic effects in dichalcogenide double layer systems
- strong coupling effects between plasmon and phonon modes in h-BN coupled to silver nanorods [4].

Références:

[1] Interplay Between Cr Dopants and Vacancy Clustering in the Structural and Optical Properties of WSe<sub>2</sub> [Ho. Ching-Hwa; Chen, Wei-Hao; Tiong, Kwong K.](#); et al., *ACS NANO* 11 (2017) 11162

[2] « Bright UV single photon emission at point defects in h-BN », R. Bourrellier et al. *Nano letters* 16 (2016) 4317-4321

[3] « Nanometric Resolved Luminescence in h-BN Flakes: Excitons and Stacking Order » R. Bourrellier, et al. , *ACS Photonics* 1 (2014) 857-862

[4] L. Tizei et al, unpublished

## Piezo-doping of bilayer graphene and mechanical layer decoupling: an *in-situ* Raman spectroscopy of $^{12}\text{C}/^{13}\text{C}$ bilayer graphene at high pressure

A. Forestier,<sup>1</sup> F. Balima,<sup>1,2</sup> C. Bousige,<sup>3</sup> D. Machon,<sup>1,4</sup> M. Kalbac,<sup>5</sup> and A. San Miguel<sup>1</sup>

<sup>1</sup> Institut Lumière Matière, Univ. Lyon 1, CNRS, Villeurbanne, France

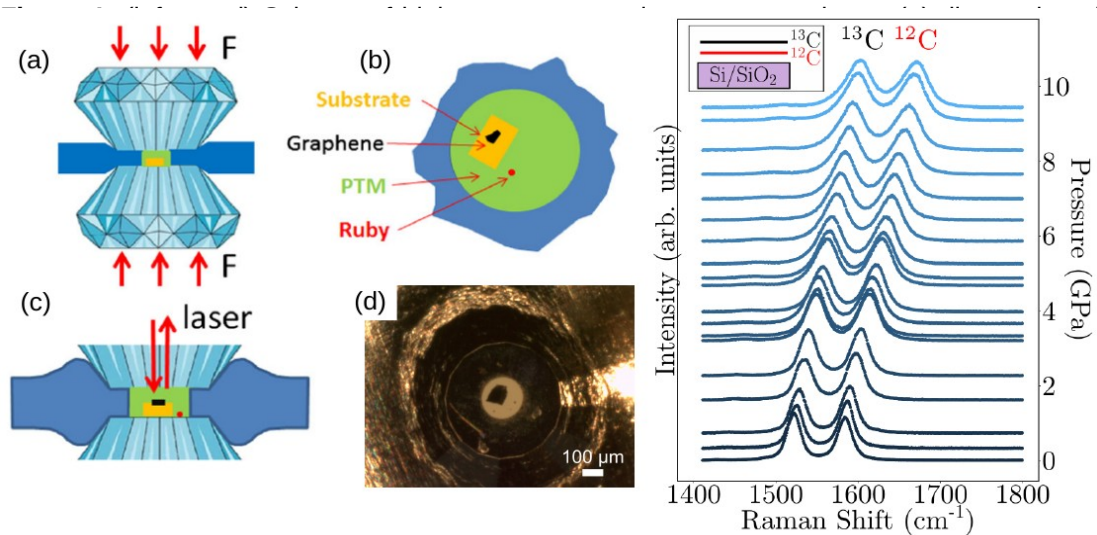
<sup>2</sup> Institut de Chimie de la Matière Condensée de Bordeaux, CNRS, Pessac, France

<sup>3</sup> Laboratoire des Multimatériaux et Interfaces, Univ. Lyon 1, CNRS, Villeurbanne, France

<sup>4</sup> Lab. des Nanotechnologies et Nanosystèmes, Univ. Sherbrooke, Sherbrooke, Canada

<sup>5</sup> Heyrovsky Institute of Physical Chemistry, Prague, Czech Republic

Stress and doping effects in graphene-based systems are in general not easy to disentangle. This is particularly true in high-pressure experiments where both effects are exacerbated through high mechanical stress and heightened electronic interactions with the environment. By studying the response of isotopically labeled bilayer graphene (il-BLG) with Raman spectroscopy and using various pressure transmitting media, we have been able to clearly separate mechanical and doping effects. Raman spectroscopy is a technique of choice for the study of carbon systems and especially graphene. It allows measuring very precisely the strain in a graphene layer, and even give information on the charge concentration in it. When graphene is submitted to very high pressure (GPa range) in a diamond anvil cell (Fig. 1), its strain is dictated by the substrate volume reduction by adhesion [1,2].



[3] A. Forestier *et al.*, submitted

[2] D. Machon *et al.*, J. Raman Spectrosc. 49 (2018) 121



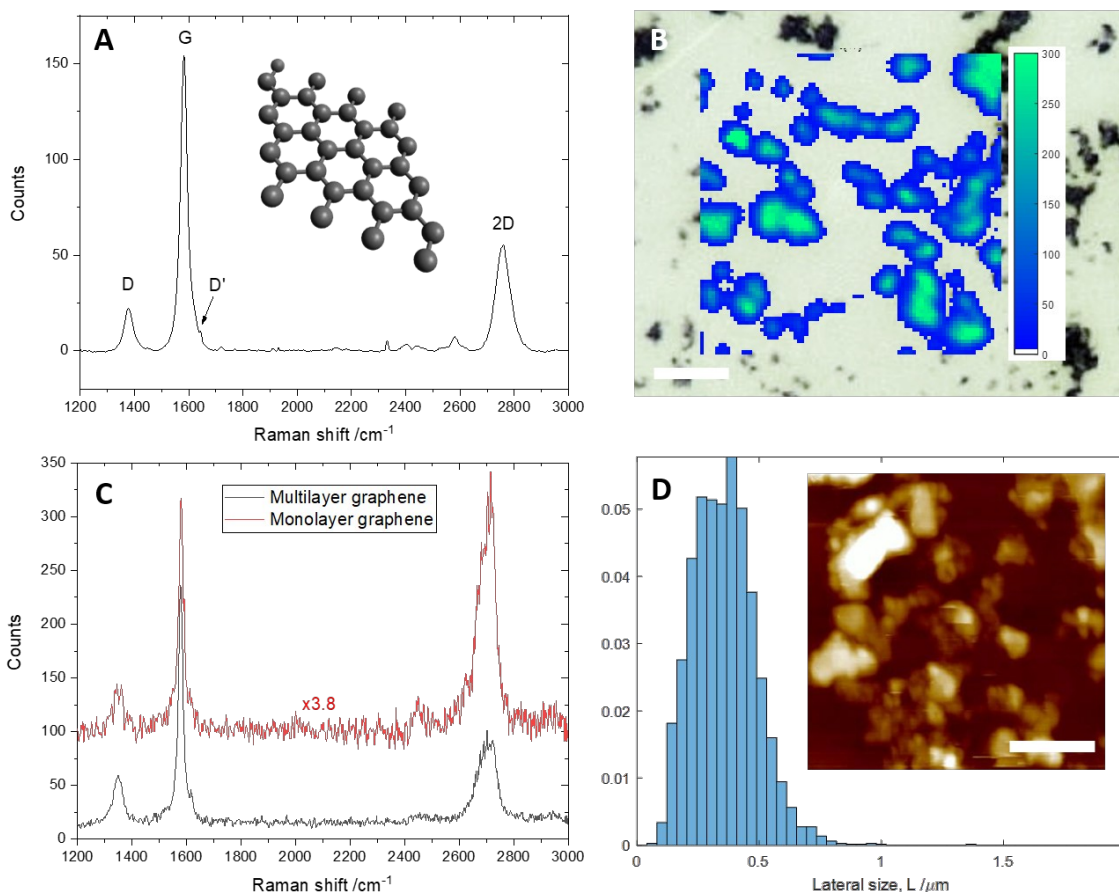
## Raman mapping analysis of liquid-exfoliated few-layer nanomaterials

Aline Amorim Graf<sup>1</sup>, Matthew J. Large<sup>1</sup>, Sean P. Ogilvie<sup>1</sup>, Manoj Tripathi<sup>1</sup>, Alice A. K. King<sup>1</sup>, Alan B. Dalton<sup>1</sup>

<sup>1</sup> University of Sussex, Brighton, East Sussex, United Kingdom

*a.amorim-graf@sussex.ac.uk*

Liquid phase exfoliation (LPE) is a powerful, efficient, and scalable method for producing industrial quantities of few-layer nanomaterials. Most variations on the process necessarily produce a distribution of particle size and thickness. Although centrifugation-based size selection can separate particles approximately by layer number, robust methods are necessary to characterise this particle size distribution. Raman spectroscopy has demonstrated itself to be a powerful non-destructive tool, as it facilitates characterisation of the thickness and length distributions of nanosheets through use of metrics. It is noted that single Raman spectra, collected at low magnification, are often used as “representative” of a particular material sample. It is observed that many of these spectra are indistinguishable on cursory inspection; in the case of graphene, spectra with near-identical 2D/G ratios, D/G ratios, and 2D lineshapes are presented from multiple sources. Larger multilayer particles should have higher Raman cross-sections than smaller monolayers. As such, it is postulated that low-magnification spectra will be dominated by contributions from the thickest, largest particles in the distribution present. To investigate this phenomenon an analysis based on high-magnification Raman mapping of LPE nanomaterials deposited onto substrate is presented.



## Characterization of Atomically Precise Graphene Nanoribbons by Raman Spectroscopy

J. Overbeck<sup>1,2,3</sup>, G. Borin Barin<sup>1</sup>, C. Daniels<sup>4</sup>, M. Perrin<sup>1</sup>, O. Braun<sup>1,2</sup>, P. Ruffieux<sup>1</sup>, V. Meunier<sup>4</sup>, R. Fasel<sup>1</sup> and M. Calame<sup>1,2,3</sup>.

Graphene nanoribbons (GNRs) exhibit an electronic bandgap due to the lateral confinement of charge carriers and edge effects. They can be fabricated by bottom-up on-surface synthesis from molecular precursors resulting in atomically precise structures [1]. This approach promises tunable optical and electronic properties [2]. We use Raman spectroscopy to characterize different types of GNRs and investigate their properties directly after growth and after transfer to electronic device substrates. We employ large area Raman mapping on optimized substrates with interference enhancement, to investigate reveal less intense geometry dependent Raman modes [3]. In particular, we show that a longitudinal compressive mode (LCM) can be used to investigate the length of bottom-up synthesized GNR and probe their interaction with different types of substrates [4].

[1] Cai, J. et al. (2010), *Nature* 466, 470–473

[2] Chen, Y.-C et al. (2013), *ACS Nano* 7, 7, 6123–6128

[3] Overbeck, J. et al. (2019), arXiv:1907.01797

[4] Overbeck, J. et al. (2019), *ACS Nano*, doi: 10.1021/acsnano.9b05817

1) Empa, Swiss Federal Laboratories for Materials Science and Technology, 8600 Dübendorf, Switzerland

2) Swiss Nanoscience Institute, University of Basel, 4056 Basel, Switzerland

3) Department of Physics, University of Basel, 4056 Basel, Switzerland

4) Department of Physics, Rensselaer Polytechnic Institute, Troy, New York 12180, USA

## GO-ING ON WITH GRAPHENE OXIDE

Wolfgang K. Maser, A.M. Benito  
Instituto de Carboquímica (ICB-CSIC)  
C/Miguel Luesma Castán 4, Zaragoza, Spain  
wmaser@icb.csic.es

Graphene oxide (GO) is an elusive but highly fascinating tunable nanostructure [1, 2, 3]. Dispersible in aqueous solutions, it can be easily processed into macroscopic functional materials such as papers, aerogels and thin films for different kinds of applications [1-9]. Equally, it can be used as versatile platform for the formation of functional hybrid optoelectronic materials.

GO-ing on with GO research, we will present our latest findings on the use of GO as unique interface layer [10-12]. We will demonstrate that GO can be employed in a controllable way to enable or block charge transfer in optoelectronic device structures. Emphasis is given on the unique and highly dynamic charge-transfer interface interactions established with conjugated polymers [13,14] facilitating improved thin film operation of interest for optoelectronic device structures.

### References

- [1] A. Tararan, A. Zobelli, A.M. Benito, W.K. Maser, O. Stéphan, *Chem. Mater.* 28, (2016) 3741.
- [2] M. Peláez-Fernández, A. Bermejo-Solis, A.M. Benito, W.K. Maser, R. Arenal (submitted).
- [3] L. Serrano-Luján, S. Víctor-Román, C. Toledo, O. Sanahuja-parejo, A.E. Mansour, J. Abad, A. AMassian, A.M. Benito, W.K. Maser, A. Urbina, *SN Applied Science* 1, (2019), 179.
- [4] J.D. Núñez, A.M. Benito, S. Rouziere, P. Launois, R. Arenal, P.M. Ajayan, W.K. Maser, *Chem. Sci.* 8 (2017) 4987
- [5] J.D. Núñez, E. Paineau, A.M. Benito, W.K. Maser, P. Launois, *J. Appl. Cryst.* 40, (2017) 876
- [6] S. Rouzière, P. Launois, A.M. Benito, W.K. Maser, E. Paineau, *Carbon* 137, (2018) 379
- [7] E. García-Bordejé, S. Víctor-Román, OI Sanahuja, J. Sánchez-García, A.M. Benito, W.K. Maser, *Nanoscale* 10, (2018) 3526
- [8] V. Roddríguez-Mata, J.M. González-Domínguez, A.M. Benito W.K. Maser, E. García-Bordejé, *ACS Appl. Nano Mater.* 2 (2019), 1210
- [9] S. Nufer et al., *ACS Appl. Nano Mater* 1 (2018) 1828)
- [10] J. Hernández-Ferrer, A. Ansón-Casaos, S. Víctor-Román, A. Santidrián, A. M. Benito, W.K. Maser, *J. Electroanal. Chem.*, 828, (2018), 86.
- [11] J. Hernández-Ferrer, A. Ansón-Casaos, S. Víctor-Román, O. Sanahuja-Parejo, M.T. Martínez, B. Villacampa, A.M. Benito, *Electrochim. Acta* 298, (2019), 279
- [12] S. Víctor-Romá, E. García-Bordejé, J. Hernández-Ferrer, J.M. González-Domínguez, A. Ansón-Casaos, W.K. Maser, A.M. Benito, *Catal. Today* (2019): 10.1016/j.cattod.2019.05.049
- [13] E. Istif, J. Hernández-Ferrer, E. Urriolabeitia, A. Stergiou, N. Tagmatarchis, G. Fratta, J.M. Large, A.B. Dalton, A.M. Benito, W.K. Maser, *Adv. Funct. Mater.* 28, (2018), 1707548
- [14] E. Palacios-Lidón, E. Istif, A.M. Benito, W.K. Maser, J. Colchero, *Nanoscale*, 11, (2019), 11202

Acknowledgement: Funding by EU (Project H2020-ITN 2014 642742), Spanish MINEICO (Project ENE2016-79282-C5-1-R, AEI/FEDER) and Government of Aragon (DGA-T03-17R, FEDER, UE), is gratefully acknowledged.

## BOTTOM-UP FABRICATION OF GRAPHENE NANORIBBONS: FROM MOLECULES TO DEVICES

Gabriela Borin Barin<sup>1</sup>, Maria El Abbassi<sup>2</sup>, Jan Overbeck<sup>2</sup>, Juan Pablo Llinas<sup>3</sup>, Colin Daniels<sup>5</sup>, Rimah Darawish<sup>1</sup>, Oliver Braun<sup>2</sup>, Mickael Perrin<sup>2</sup>, Akimitsu Narita<sup>4</sup>, Klaus Müllen<sup>4</sup>, Vincent Meunier<sup>5</sup>, Jeffrey Bokor<sup>3</sup>, Michel Calame<sup>2</sup>, Pascal Ruffieux<sup>1</sup>, Roman Fasel<sup>1</sup>

<sup>1</sup>Nanotech@surfaces Lab, Empa, Dübendorf Switzerland

<sup>2</sup>Transport at nanoscale interface Lab, Empa, Dübendorf, Switzerland

<sup>3</sup>Dept. of Electrical Eng. and Comp. Sciences, UC Berkeley, USA

<sup>4</sup>Max Planck Institute for Polymer Research, Mainz, Germany

<sup>5</sup>Dep of Physics, Appl. Physics and Astronomy, Rensselaer Polytechnic Institute, Troy, USA

[gabriela.borin-barin@empa.ch](mailto:gabriela.borin-barin@empa.ch) /+41 79 9161340

Atomically precise graphene nanoribbons (GNRs) exhibit a sizeable bandgap, which is inversely proportional to their width<sup>1</sup>, and thus potentially overcome many of the limitations of graphene in electronic device applications. Despite their exceptional properties, significant challenges remain for GNR fabrication, processing and characterization. Bottom-up synthesis of graphene nanoribbons is most commonly performed under ultra-high vacuum conditions, which is one of the bottlenecks in the further technological advancement of this material. Additionally, little is known about the stability of ultra-narrow GNRs under ambient conditions or during device processing. In this work we focused on 9- and 5-atom wide armchair GNRs (9-AGNR and 5-AGNR, respectively) grown under ultrahigh vacuum conditions on Au(111) and on vicinal gold surfaces Au(788), which promotes GNR's unidirectional growth on the narrow (111) terraces along the step edges, fig.1a. We first investigate the role of halogen functionalization of the precursor monomer in the final GNR length. Using different precursor monomers and synthesis protocols we show an increase in the average length for the 9-AGNR from 15 nm to 45 nm<sup>2</sup> and for the 5-AGNRs from 10 nm to 30 nm. GNRs grown on Au(111) substrates were transferred using a polymer-free<sup>3</sup> method. Raman spectra indicate no significant degradation of GNR quality, reveal a homogeneous GNR distribution on the target surface and also showed GNRs had remarkably stability under ambient conditions tracked over a 2-year period<sup>3</sup>. GNRs grown on Au(788) were transferred via electrochemical delamination method<sup>4</sup>, fig. 1b, and Polarized Raman of the G mode showed that GNRs retain their orientation after transfer with maximum Raman intensity along the ribbon axis and minimum intensity perpendicular to it, fig. 1c. These process steps allowed us to integrate both 9- and 5-AGNR into short channel field-effect transistors. Using the 9-AGNR we demonstrate FETs with high on-current  $I_{on} > 1 \mu\text{A}$  at  $V_d = -1 \text{ V}$ , high  $I_{on}/I_{off}$  ratios of  $\sim 10^5$  and 10% device yield<sup>5</sup>. In a next step, aligned 9-AGNR-FET devices were produced using graphene electrodes, and a performance of  $I_{on} > 6 \mu\text{A}$  at  $V_d = 0.1 \text{ V}$  and high  $I_{on}/I_{off}$  ratios of  $\sim 10^4$  was observed along with an increase of device yield to 80-100%, fig. 1d. GNR devices using 5-AGNRs as channel material and graphene as electrodes showed a linear IV curve at room temperature. The metal-like behavior was observed for all 31 devices investigated at RT. GNR devices measured at 13 K, showed single-electron transistor behavior, with addition energies of about 100 meV.

In this work we explore all the steps from growth to device integration of bottom-up graphene nanoribbons. We believe that this work is very relevant to the themes of the conference especially regarding the growth of nanocarbons their characterization and transport properties.

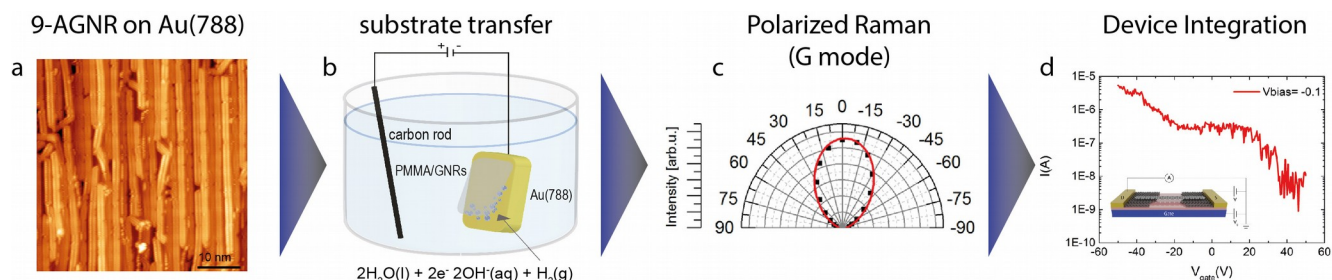


Figure 1. a) STM of 9-AGNR on Au(788), b) electrochemical delamination transfer, c) Raman Polar plot of G mode for 9-AGNR and d) I-V curve of 9-AGNR

1. J. Cai *et al*, Nature, 466, 470-473, 2010 / 2. M. Di Giovannantonio *et al*, ACS Nano, 12, 74-81, 2018 / 3. G. Borin Barin *et al*, ACS Applied Nanomaterials, 2, 2184-2192, 2019 / 4. B.V. Senkovskiy *et al*, Nano Letters, 17, 4029-4037, 2017 / 5. J.P. Llinas *et al*, Nature Comm, 8, 633, 2017

## Preparation of 2H-MoTe<sub>2</sub> films with high crystalline quality and large area by molecular beam epitaxy

Trung T. Pham, Roshan Castelino, Alex Felten, and Robert Sporken  
Namur Institute of Structural Matter (NISM), Department of Physics, University of Namur,  
61 Rue de Bruxelles, B-5000 Namur, Belgium  
E-mail: trung.phamthanh@unamur.be

### ABSTRACT

Besides graphene, layered transition metal dichalcogenides (TMDs) are part of the family of 2D materials that have recently revealed interesting physical phenomena [1-3]. TMDs are materials with a general chemical formula, MX<sub>2</sub> where M is a transition metal atom (Mo, W, Ta, etc.) and X is a chalcogen atom (S, Se, or Te). A single layer of TMDs consists of three atomic layers formed by one layer of M atoms sandwiched between two layers of X atoms. Unlike graphene, these materials can exist in more than one structural phase such as hexagonal (2H), octahedral (1T), monoclinic (1T') and orthorhombic (1T<sub>d</sub>) structures [4] in which the semiconducting 2H phase is thermodynamically stable while the metallic 1T phase, under ambient conditions spontaneously relaxes into semi-metallic 1T' or T<sub>d</sub> phase [5, 6]. For some TMDs such as MoTe<sub>2</sub>, the distorted 1T phase (1T') can be stabilized at room temperature. According to literature, monolayer semiconducting TMDs show sizable direct band gap [7], quantum confinement effects [8], large exciton binding energies [9] and large valley polarizations [10] and so on, which are very promising for applications in electronics and optoelectronics. Although MoTe<sub>2</sub> is the least studied TMD, it has some unique properties that make it attractive for research on 2D materials. 2H-MoTe<sub>2</sub> is one of the semiconducting TMDs with the smallest bandgap [11]. Single layer films and those that are a few atomic layers thick have a direct bandgap close to 1 eV, similar to the width of the indirect bandgap of Si, making it more attractive not only for controllable ambipolar field-effect transistors (FETs) but also for optoelectronic applications ranging from the visible to the near-infrared part of the spectrum [11,12]. Therefore, the controllable synthesis of large-area lateral growth of uniform mono- and double-layer 2H-MoTe<sub>2</sub> is highly desirable for device fabrication. Up to now, unfortunately it still maintains challenging although there have recently been several attempts to grow and transfer MoTe<sub>2</sub> on various substrates using different methods. In this talk, we present here results which demonstrate the direct growth of large area and high crystalline 2H-MoTe<sub>2</sub> films on graphene terminated 6H-SiC(0001) substrates by using molecular beam epitaxy with appropriate conditions. We present furthermore scanning tunneling microscopy (STM) images together with diffraction patterns and X-ray photoemission spectroscopy/scanning tunneling spectroscopy (XPS/STS) spectra which establish unambiguously the 2H-MoTe<sub>2</sub> nature of the films. Our study indicates that control of MBE conditions can be used to synthesize stoichiometric, high crystalline, and phase stabilized 2H-MoTe<sub>2</sub> films.

- [1] N.Choudhary, M.A. Islam, J.H. Kim, T.J. Ko, A. Schropp, L. Hurtado, D. Weitzman, L. Zhai, and Y. Jung, *Nanotoday* **19**, 16-40 (2018).
- [2] W. Choi, N. Choudhary, G.H. Han, J.Park, D. Akinwande, and Y.H. Lee, *Materials Today* **20**, 116-130 (2017).
- [3] D. Jariwala, V. K. Sangwan, L.J. Lauhon, T.J. Marks, and M.C. Hersam, *ACS Nano* **8**, 1102-1120 (2014).
- [4] A. V. Kolobov and J. Tominaga, *Two-Dimensional Transition-Metal Dichalcogenides* **165**, 226 (2016).
- [5] R. Wang, Y. Yu, S. Zhou, H. Li, H. Wong, Z. Luo, L. Gan, and T. Zhai, *Advanced Functional Materials* **28**, 1802473 (2018).
- [6] X. Yin, C. S. Tang, D. Wu, W. Kong, C. Li, Q. Wang, L. Cao, M. Yang, Y.H. Chang, D. Qi, F. Ouyang, S.J. Pennycook, Y.P. Feng, M.B.H. Breese, S.J. Wang, W. Zhang, A. Rusydi, A. T. S. Wee, *Advanced Science* **6**, 1802093 (2019).
- [7] W. Zhang, Z. Huang, W. Zhang, Y. Li, *Nano Research* **7**, 1731-1737 (2014).
- [8] J. A. Schuller, S. Karaveli, T. Schiros, K. He, S. Yang, I. Kymissis, J. Shan, R. Zia, *Nature Nanotechnology* **8**, 271 (2013).
- [9] J. J. Pei, J. Yang, T. Yildirim, H. Zhang, Y. R. Lu, *Advanced Materials* **31**, 1706945 (2019).
- [10] Q. Zhang, S. A. Yang, W. Mi, Y. Cheng, U. Schwingenschlogl, *Advanced Materials* **28**, 959 (2016).
- [11] Y. Bie, G. Grosso, M. Heuck, M. M. Furchi, Y. Cao, J. Zheng, D. Bunandar, E. Navarro-Moratalla, L. Zhou, D. K. Efetov, T. Taniguchi, K. Watanabe, J. Kong, D. Englund, P. Jarillo-Herrero, *Nature Nanotechnology* **12**, 1124 (2017).
- [12] Y. Li, J. Zhang, D. Huang, H. Sun, F. Fan, J. Feng, Z. Wang, C. Z. Ning, *Nature Nanotechnology* **12**, 987 (2017).

## **Iodine – Chlorine complexation in intercalated Graphite for positive Graphenium production**

Xiaoyang Che<sup>1</sup>, Ferdinand Hof<sup>2</sup>, Alain Penicaud<sup>2</sup>, Emmanuel Pichaut<sup>2</sup>, Anthony Impellizzeri<sup>1</sup>, Christopher P. Ewels<sup>1\*</sup>

<sup>1</sup> Institut des Materiaux Jean Rouxel (IMN)-UMR6502, 2 Rue de la Houssiniere, BP32229, 44322 Nantes (France)

<sup>2</sup> Centre de Recherche Paul Pascal (CRPP)-UMR5031, 115 Avenue du Dr Albert Schweitzer, 33600 Pessac (France)

Graphite-based intercalation is an excellent way to enhance the surface and electronic properties of graphene. Depending on the chemical nature of the intercalant compounds used, it is possible to obtain graphene layers that are positively charged (graphenium) or negative (graphenide). The homo-halogen compounds such as Br<sub>2</sub>, I<sub>2</sub> are good electrons accepters and have been extensively studied in this context. In contrast the hetero-halogens compounds, notably ICl have received much less attention, even though the intercalation of ICl into graphite is spontaneous and the graphite staging can reach stage-I. In this talk I will present our recent work with the ICl-graphite system. Experimental characterisation of graphite-ICl interaction compounds by Raman spectroscopy and Transmission Electron Microscopy (TEM) shows unexpected richness and complexity in the halogen behaviour. The Raman G peak is in good agreement with stage-I intercalation graphite. The low frequency Raman spectroscopy reveals several vibration modes, indicating the transformation of ICl to other species. Our first principle studies confirm that ICl intercalation is thermodynamically favourable and drives expansion along the graphene stacking direction. However the calculations demonstrate the instability of interlayer ICl with spontaneous transformation into I<sub>x</sub>Cl<sub>y</sub> charge transfer species responsible for strong p-doping. We determine relevant reaction pathways, both in the bulk and on graphene surfaces. Calculated vibrational frequency indicated the experimental low frequency Raman shifts correspond to the presence of various halogen complexes, such as iodine chains and I<sub>x</sub>Cl<sub>y</sub>.

# Visualization of multifractal superconductivity in a two-dimensional transition metal dichalcogenide in the weak-disorder regime

Miguel M. Ugeda<sup>1,2\*</sup>

<sup>1</sup>Donostia International Physics Center (DIPC), 20018 San Sebastián, Spain.

<sup>2</sup>Centro de Física de Materiales CFM/MPC (CSIC-UPV/EHU), 20018 San Sebastián, Spain.

\*mmugeda@dipc.org

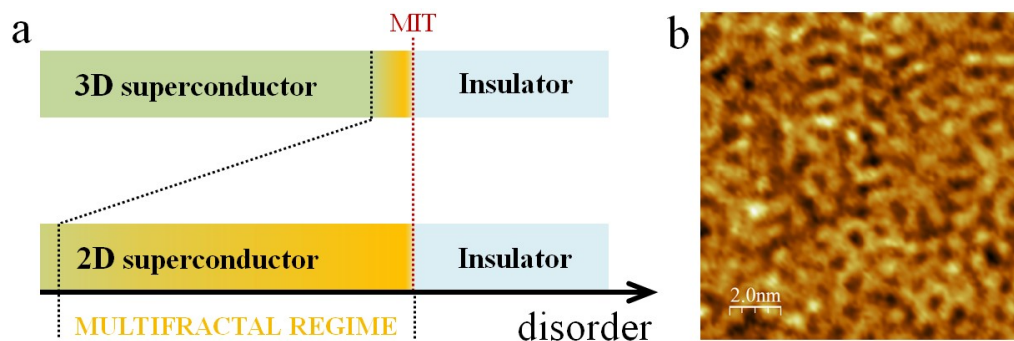
Eigenstate multifractality is a distinctive feature of non-interacting disordered metals close to a metal-insulator transition, whose properties are expected to extend to superconductivity. While multifractality in three dimensions (3D) only develops near the critical point for specific strong-disorder strengths, multifractality in quasi-two dimensional (2D) systems with spin-orbit coupling is expected to be observable even for weak disorder. Here we investigate the impact of multifractality on the superconducting state [1] of an intrinsic weakly disordered single-layer of NbSe<sub>2</sub> by means of low-temperature scanning tunneling microscopy/spectroscopy (STM/STS) [2]. The superconducting gap, characterized by its width, depth and coherence peaks amplitude, shows characteristic spatial single-wavelength modulation nearly coincident with the periodicity of the quasiparticle interference pattern observed at the Fermi energy. Spatial inhomogeneity of the superconducting gap width, which is proportional to the local order parameter in the weak disorder regime, shows a characteristic log-normal statistical distribution as well as a power-law decay of the two-point correlation function, in agreement with our theoretical model. This novel state is universal and governs the properties of even weakly disordered 2D superconductors with spin-orbit coupling. This offers a novel platform to tune and ultimately control superconductivity in novel 2D quantum materials. Lastly, I will briefly discuss our most recent results regarding the fate of the superconducting and charge density wave states of single-layer NbSe<sub>2</sub> on different substrates studied at 340 mK.

## References

[1] M. M. Ugeda, et al., Nature Physics 12, 92 (2016).

[2] C. Rubio-Verdú, et al, submitted (2019).

## Figures



**Figure 1.** a. Sketch of the extent of the multifractal regime in the superconducting state in 3D and 2D. b. Spatial distribution of the superconducting order parameter in a 12 nm x 12 nm region of single-layer NbSe<sub>2</sub>.

**WEDNESDAY 11th  
PRESENTATIONS**



## **Aerosol-assisted CCVD process: an up-scalable one-step method for the production of versatile VACNT carpets**

Martine Mayne-L'Hermite

NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay 91191 Gif-sur-Yvette France  
(email: martine.mayne@cea.fr)

Vertically Aligned Carbon Nanotubes (VACNT) are seen as potential candidates for many applications in different fields (energy, environment, electrical or thermal transport,...)i, ii. Since the demand of such materials is increasing, the development of controlled, cheap and versatile processes transferred to industry is necessarily required.

Nowadays, there are mainly two routes based on chemical vapour deposition (CVD) process to get such networks that can be composed of single-walled or multi-walled CNTs. The two-step route involves a preliminary deposition of a metal catalyst film on a dedicated substrate before CNT growth resulting in the rapid formation of multi-walled (MW) or single-walled (SW) VACNT iii. This process allows advantageously a precise control of nanotube diameter distribution and the production on large substrates, but catalyst preparation and sample handling are considered as the main drawback for a low-cost industrial production. On the contrary, the one-step route relying on the simultaneous feeding of the reactor with both the catalyst and the carbon precursor iv,v,vi and enabling the continuous formation of multi-walled VACNT is referred as a cheapest method compatible with an industrial operation.

This communication addresses this context with a special focus on the Aerosol-Assisted Catalytic Chemical Vapour Deposition (AA-CCVD) process, a one-step process that we are developing since several years. A summary of our approach based on fundamental studies of CNT growth that fed our developments towards up-scaling, and recent transfer at the industrial scale for commercial applications through roll to roll production, will be first presented.

Then, we will report the versatility of such a process in terms of control of VACNT characteristics, which is crucial for the consideration of a wide range of applications. The catalyst and carbon precursor content, the carrier gas nature, the synthesis temperature are among the most important parameters playing on the purity, chemical composition, length, diameter, structure and density of CNT in the VACNT carpets. Representative studies demonstrating either the effect of the carrier gas nature (mainly H<sub>2</sub> and NH<sub>3</sub>) on CNT or N-doped CNT composition, diameter and density, or the influence of the catalyst precursor content on the purity and structure of CNT will be reported. In addition, we will demonstrate how this process is adjustable for VACNT growth on various substrates vii.

Finally, VACNT processing for energy storage and electricity transport will be developed. Supercapacitor electrodes are prepared through a versatile approach lying on the use of raw VACNT carpet or VACNT carpet covered with a pseudo-capacitive material (electronic conducting polymer (ECP) or metal oxide). One main challenge was to grow VACNT on current collector compatible with a commercial application. Therefore, developments on aluminium substrates at temperatures lower than the aluminium melting point, were performed, demonstrating that it is possible to get VACNT with such a one-step CCVD process and to transfer it on industrial equipment viii. The performances of the resulting supercapacitor devices are promising as compared to activated carbon. Prototype devices prepared from VACNT synthesized at laboratory scale or on an industrial production line (Roll to Roll process) exhibit similar performances. Generation of CNT fibres from VACNT spinning process will also be illustrated with a special focus on the preparation process and on the measurement of their electrical properties in comparison with the ones of individual carbon nanotubes.

1 Y. Lan et al., *Advances in Physics*, 2011.

2 W. Shi et al., *Green Chem.*, 2018.

3 K. Hatta et al., *Nano Letters*, 2009.

4 C. Singh et al., *Carbon*, 2003.

5 M. Pinault et al., *Nano Lett.*, 2005.

6 C. Castro et al., *Carbon*, 2013.

7 M. Delmas et al, *Nanotechnology*, 2012.

8 F. Nassoy et al., *Nanomaterials*, 2019.

## Lightweight Cu/Carbon Nanotube composites as promising future Cu substitutes

*Rajyashree Sundaram, Guohai Chen, Takeo Yamada, Don Futaba, Kenji Hata, Atsuko Sekiguchi*

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan

We present high-performance copper-matrix carbon nanotube (Cu/CNT) composites as promising materials to fulfil a growing demand for lightweight electrically conducting Cu-substitutes [1-4]. We prepared Cu/CNT micropillars and macrowires as additions to planar Cu/CNT microlines and macrosheets we previously reported [5-7]. Compared to copper, our Cu/CNT composites are at least 2/3rd as light with competitive electrical conductivities, thermal- and current-stabilities as well as mechanical performances. Our composite electrical conductivities are  $1-3 \times 10^5$  S/cm (vs.  $5.9 \times 10^5$  S/cm for Cu) with temperature coefficients of resistivity (TCR) as low as  $4.4 \times 10^{-4}$  /K (~10% Cu-TCR) and current carrying capacities (CCC) > Cu. Our Cu/CNT show coefficients of thermal expansion (CTE) ~ 4-7 ppm/K closer to Si-CTE (~3 ppm/K) and lower than Cu-CTE (~17 ppm/K). With mechanical strengths ~ 300 MPa, our Cu/CNT composites are as robust as commercial Cu wires. We observe that Cu/CNT performances depend on Cu spatial distribution and CNT attributes, indicating prospects for tuning properties.

In terms of applications, lightweight conducting Cu/CNT wires could replace heavy copper electrical wiring in aircrafts and automobiles to achieve better fuel efficiencies and reduced CO<sub>2</sub> emissions. In electric vehicles with higher amounts of Cu than regular automobiles, lighter Cu/CNT wires could help with weight-reduction essential for increased travel range per charge. Cu/CNT's temperature-stable electrical conductivity (TCR < Cu) makes it a more reliable conductor than Cu for high-temperature operation e.g., in motor windings. Further, our Cu/CNT microstructures with better thermal and current-stability than copper (CTE ~ Si and CCC > Cu) could serve as superior interconnects with reduced delamination and current-failure, enabling smaller and more powerful electronics.

### **References:**

- [1] Sundaram R, Sekiguchi A, Sekiya M, Yamada T, Hata K, Royal Soc. Open Sci., 5(11) (2018), 1-21.
- [2] Sundaram R, Yamada T, Hata K, Sekiguchi A, Sci. Rep., 7(1) (2017), 9267.
- [3] Sundaram R, Yamada T, Hata K, Sekiguchi A. Mater. Tod. Commun., 13 (2017), 119.
- [4] Sundaram R, Yamada T, Hata K, Sekiguchi A. Jpn. J. Appl. Phys., 57(4)(2018), 04FP08.
- [5] Subramaniam C, Yamada T, Kobashi K, Sekiguchi A, Futaba DN, Yumura M, Hata K, Nat. Commun., 4(2013), 2202.
- [6] Subramaniam C, Yasuda Y, Takeya S, Ata S, Nishizawa A, Futaba D, Yamada T, Hata K, Nanoscale, 6(5) (2014), 2669.
- [7] Subramaniam C, Sekiguchi A, Yamada T, Futaba DN, Hata K, Nanoscale, 8(7)(2016), 3888.

## Base-washing functionalised nanotubes with copper hydroxide for hybrid film fabrication

Peter Lynch<sup>1</sup>, Sean Ogilvie<sup>1</sup>, Matthew Large<sup>1</sup>, Jonathan Salvage<sup>2</sup>, Alan Dalton<sup>1</sup>

<sup>1</sup>University of Sussex, Brighton, United Kingdom

<sup>2</sup>Brighton University, Brighton, United Kingdom  
p.j.lynch@sussex.ac.uk

Carboxylic acid functionalised carbon nanotubes (CNTs) are widely used as they allow for dispersion in aqueous and other polar media. These tubes have poly-aromatic compounds adhered to the surface of the nanotube in addition to functional groups in the structure of the tube<sup>1</sup>. Base washing is an established route to removing these additional compounds<sup>2</sup>. In this presentation the use of copper hydroxide, dispersed as a high aspect ratio material in liquid, is added to nanotube dispersions. The hydroxide groups on the surface of the copper hydroxide interact with the functionalities and cause immediate flocculation. Raman analysis of the flocculent reveals significant reduction in the D peak suggesting that these poly-aromatic compounds have been removed. By adjusting the mass ratios of the two materials, as well as the size of the copper hydroxide, results in films of different electrical properties. Analysis of percolation and network segregation will be used to optimise the material for use as a surfactant-free material in a non-enzymatic glucose sensor.

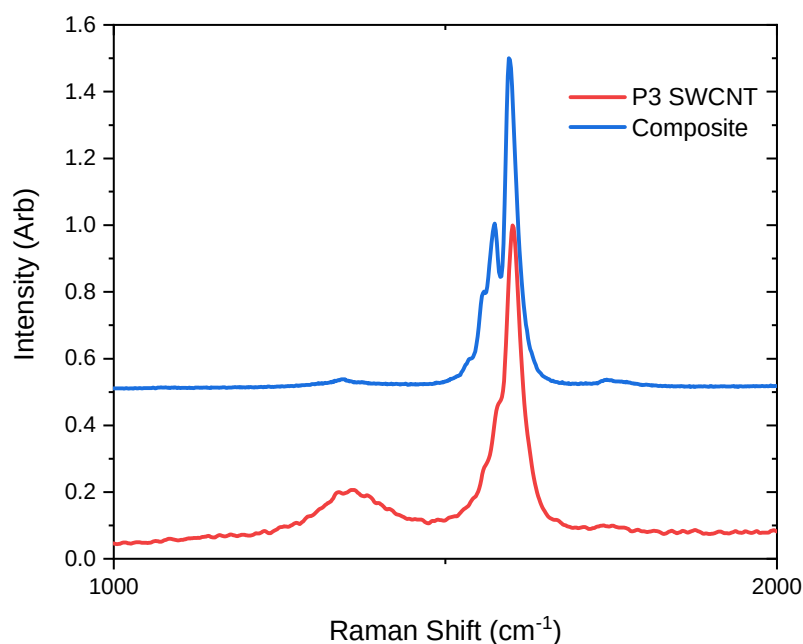


Figure 1-Effect of addition of Cu(OH)<sub>2</sub> nano-cuboids to functionalised carbon nanotubes. Red = before, blue = after

### References

- (1) Gotovac, S.; Yang, C. M.; Hattori, Y.; Takahashi, K.; Kanoh, H.; Kaneko, K. Adsorption of Polyaromatic Hydrocarbons on Single Wall Carbon Nanotubes of Different Functionalities and Diameters. *J. Colloid Interface Sci.* **2007**.
- (2) Fogden, S.; Verdejo, R.; Cottam, B.; Shaffer, M. Purification of Single Walled Carbon Nanotubes: The Problem with Oxidation Debris. *Chem. Phys. Lett.* **2008**.

## Conventional and nitrogen doped vertically aligned carbon nanotubes for energy storage

C. Querne<sup>a,b\*</sup>, P. Banet<sup>b</sup>, M. Mayne-L'Hermite<sup>a</sup>, P.-H. Aubert<sup>b</sup>, M. Pinault<sup>a</sup>

<sup>a</sup>NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay 91191 Gif-sur-Yvette France

<sup>b</sup>LPPI (EA 2528), Université de Cergy-Pontoise, 95000 Cergy-Pontoise France

(\*email : corentin.querne@cea.fr)

Owing to their surface area, anisotropy and good electrical conductivity, Vertically Aligned Carbon Nanotubes carpets (VACNT) and their combination to electronic conducting polymer (ECP) are promising materials for ultracapacitor electrodes. To fabricate low cost, highly conducting and light electrodes, we have adjusted a single-step process, namely the Aerosol Assisted Catalytic Chemical Vapor Deposition operated at low temperatures (580 to 615°C), to synthesize VACNT on aluminium current collectors, which is compatible with industrial requirements [1], [2]. This method provides quite long, dense and clean VACNT. In addition, we have also developed an easy method based on electrodeposition of ECP (poly(3-methylthiophene) on VACNT, to improve the capacitance [3]. Homogenous deposition of ECP was achieved all along the thickness of the carpet by pulsed chronoamperometric method. The energy was increased up to 52Wh/kg owing to the nanostructuring of the ECP. To improve supercapacitor's performances, one route consist in enhancing the potential window of the devices and the capacitance of the electrodes. Hence, one approach is to dope with heteroatoms carbon nanotubes in the VACNT. Nitrogen doping should provide potentialities to increase the capacitance owing to the oxidation of the nitrogen sites inserted in the graphitic walls but also by increasing the specific surface because of the bamboo shape of N@VACNT [4]. The growth of nitrogen doped VACNT was achieved at 850°C on Si substrates by using ethylenediamine as nitrogen and carbon source. Such carpets exhibit a low density of  $4 \cdot 10^{10}$  NTC/cm<sup>2</sup> of few walled "bamboo" shaped nanotubes, and the nitrogen content is 4.5%at. First electrochemical characterizations, using an ordinary electrolyte (TEABF<sub>4</sub> in acetonitrile), show a capacitive storage with a capacitance of 12.6 F/g.

[1] M. Pinault et al, *Nano Lett.*, vol. 5, n° 12, p. 2394-2398, 2005.

[2] M. Delmas et al, *Nanotechnology*, vol. 23, n° 10, p. 105604, 2012.

[3] S. Lagoutte et al, *Electrochimica Acta*, vol. 130, p. 754-765, 2014.

[4] W.-Q. Han et al, *Appl. Phys. Lett.*, 2000

## Characterizing Filling of Carbon Nanotubes by Optical Spectroscopy

S. Cambré<sup>1</sup>, J. Campo<sup>1</sup>, S. van Bezouw<sup>1</sup>, B. Botka<sup>1</sup>, W. Van Werveke<sup>1</sup>, W. Wenseleers<sup>1</sup>

J. Obrzut<sup>2</sup>, J.A. Fagan<sup>2</sup>

<sup>1</sup>University of Antwerp, Department of Physics, Antwerpen, Belgium

<sup>2</sup>National Institute of Standards and Technology, Materials Science and Engineering Division,  
Gaithersburg Maryland US,

presenting author: sofie.cambre@uantwerpen.be

Single-walled carbon nanotubes (SWCNTs), conceptually formed as a rolled-up sheet of graphene, exhibit unique, remarkably diverse electronic and optical properties that depend critically on their exact chiral structure. Since all carbon atoms reside at their surface, these structure-dependent properties are extremely sensitive to their external and internal environment. For example, filling of the endohedral cavity of the carbon nanotubes results in characteristic shifts and broadening of both the radial breathing mode vibrational frequency and the optical transitions, making optical spectroscopy one of the key techniques to investigate the filling of SWCNTs. [1-4]

The encapsulation of molecules in SWCNTs often leads to new functionalities. For example, when encapsulating water molecules in sufficiently narrow SWCNTs, we have previously shown that a single file of water molecules will be formed, in which new quasi-phase transitions of the molecular dipole moments in the one-dimensional array can occur.[5] The 1D hollow structure of the SWCNTs can also be exploited to induce a unique head-to-tail order of asymmetric dipolar dye molecules, resulting in nanohybrids with a giant 2<sup>nd</sup>-order nonlinear optical response, [6] and in addition, the encapsulation of organic dye molecules can be used to photosensitize the SWCNTs, by energy transfer from the dyes to the SWCNTs after optical excitation.[7]

In this paper, I will mainly discuss the specific and tuneable modification of the optical properties of SWCNTs through the direct encapsulation of more than 30 different guest molecules with widely varying dielectric constants. The spectroscopic analysis of these filled SWCNTs, in comparison to empty SWCNTs, demonstrates that the general effect of filler static dielectric constant on the SWCNTs' optical properties corresponds to a monotonic red shifting of the optical transitions with increased magnitude for higher dielectric constants. In addition to these spectral shifts, the filling also reveals a general increase of fluorescence intensity with lower dielectric constants.[8]

### References:

- [1] W. Wenseleers *et al*, *Adv. Mater.* 19, 2274 (2007)
- [2] S. Cambré *et al*, *Phys. Rev. Lett.* 104, 207401 (2010)
- [3] S. Cambré *et al*, *Angew. Chem.* 50, 2764 (2011)
- [4] S. Cambré *et al*, *ACS Nano* 6, 2649 (2012)
- [5] X. Ma *et al*, *Phys. Rev. Lett.* 118, 027402 (2017)
- [6] S. Cambré *et al*, *Nature Nanotechnol.* 10, 248 (2015)
- [7] S. van Bezouw *et al*, *ACS Nano* 12, 6881 (2018)
- [8] J. Campo *et al*, in preparation

## **Perspective of 2D materials: From macroscopic to nanoscopic viewpoints**

R. Tenne, Department of Materials and Interfaces, Weizmann Institute, Rehovot 76100, Israel

Like many other materials disciplines, serious research on 2D materials (layered compounds) started some 100 years ago, when scientific tools like XRD, spectroscopy and transport measurements became accessible to researchers. In the early years, most of the investigated 2D-materials, were either naturally occurring materials, like graphite, molybdenite, chrysotile, etc. or could be synthesized by the simple techniques available at these times. Following WWII, and particularly in the late 50's and 60's of the last century, research of 2D materials has expanded dramatically and became the mainstay of science. With the advent of new synthetic techniques, classification of 2D materials into different classes and different optical and electrical properties was advanced. Many physio-chemical phenomena were systematically investigated including charge density waves, intercalation, superconductivity in anisotropic materials, catalysis and more. A few technologies were also commercialized, like catalysts and intercalation batteries in the late 70's and new opportunities in photovoltaic research were offered. The discovery of carbon fullerenes and nanotubes in the late 80's and beginning of the 90's and those based on 2D materials, like  $WS_2$  and  $MoS_2$ , started the rush into the golden age of nano 2D-materials. Concomitantly, DFT and other theoretical models became inseparable from the main-course of research in this area. The discovery of graphene and later on the beyond graphene analogues has led to the observation of intriguing physical properties and new conceptual breakthroughs in device technology of nano-2D materials.

In the remaining time of my talk, I will deliberate on late advances in the research of inorganic nanotubes from 2D-materials and their technological implications.

# Electron microscopy investigation of nanotubes from the misfit-layered compounds (La,Y)S-TaS<sub>2</sub>

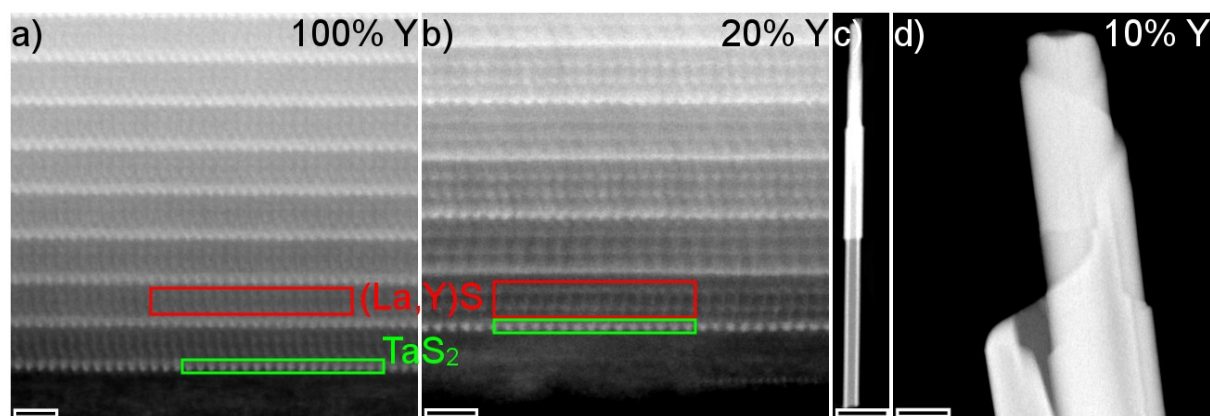
Hettler S<sup>1</sup>, Serra M<sup>2</sup>, Tenne R<sup>2</sup>, Arenal R<sup>1,3,4</sup>

1. Laboratorio de Microscopías Avanzadas, Instituto de Nanociencia de Aragón, Universidad de Zaragoza, Zaragoza, Spain
2. Department of Materials and Interfaces, Weizmann Institute, Rehovot 76100, Israel
3. ARAID Foundation, Zaragoza, Spain
4. Instituto de Ciencias de Materiales Aragón, CSIC-U. Zaragoza, 50009 Zaragoza, Spain

\*E-mail for correspondence: [hettler@unizar.es](mailto:hettler@unizar.es)

**Keywords:** misfit-layered compounds, electron microscopy, EELS, nanotubes

Nanotubes (NTs) based on misfit-layered compounds (MLC) [1] are studied intensively since the synthesis allows to reach a high NT yield [2]. MLC consist of two different layered oxides or chalcogenides which are stacked alternatively along the c direction. In case of chalcogenide MLCs the stack is composed of a metal chalcogenide (MX) and a transition-metal dichalcogenide (TX<sub>2</sub>). MLC-NTs are promising for applications, e.g. in the field of thermoelectricity, due to the complementary properties of the two layered compounds [3]. Only recently, an improvement of the synthesis process of MLC-NTs allowed to introduce additional elements to form quaternary compounds starting from LaS-TaS<sub>2</sub> [4]. Here we present an analysis of the novel family (La,Y)S-TaS<sub>2</sub> by electron microscopy. We applied imaging by high-resolution (scanning) transmission electron microscopy ((S)TEM), electron diffraction (ED), energy-dispersive x-ray spectroscopy and electron energy-loss spectroscopy (EELS) to profoundly analyse the NTs. NTs were successfully synthesised for Y percentages up to 100% with the NT yield showing two maxima at 10% (global) and 80%. The aspect ratio (length/width) of the NTs lies between 10 and 20 with NT lengths of up to 15 µm. Fig. 1a and b show two STEM images revealing the repeating layers of 2x (La,Y)S and TaS<sub>2</sub>. EELS and ED results suggest a homogeneous and in-phase substitution of La by Y only negligibly changing the lattice parameter of the material. Besides NTs (Fig. 1c), also scrolls are found as visible in the STEM image in Fig. 1d. In conclusion, we were able to prove by in-depth EM analysis the successful synthesis of a novel family of MLC-NMs that has never been synthesized before [5].



**Figure 1:** STEM images of different (La,Y)S-TaS<sub>2</sub> NTs with different percentages of Y. Scale bars are (a,b) 1 nm, (c) 500 nm and (d) 200 nm.

## References

- 1 - G.A. Wiegiers (1996). *Prog Solid State Ch* **24**, 1–139.
- 2 - G. Radovsky et al. (2011). *Angew Chem Int Edit* **50**, 12316–12320.
- 3 - M. Serra, R. Arenal, R. Tenne, (2019). *Nanoscale* **11**, 8073-8090.
- 4 - G. Radovsky et al. (2016). *J Mater Chem C* **4**, 89–98.
- 5 - Research supported by the Spanish MINECO (MAT2016-79776-P, AEI/FEDER, EU), Government of Aragon through project DGA E13\_17R (FEDER, EU) and European Union H2020 programs “ESTEEM3” (823717), Flag-ERA GATES (JTC – PCI2018-093137).

## Covalently incorporated photoactive dyes onto transition metal dichalcogenides

Ruben Canton-Vitoria,(1,2) Ryo Kitaura,(2) Nikos Tagmatarchis(1)

1- Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, 116 35 Athens, Greece.

E-mail (R. Canton-Vitoria): [canton@eie.gr](mailto:canton@eie.gr)

2- Department of Chemistry, Nagoya University, Nagoya 464-8602, Japan.

Exfoliated semiconducting transition metal dichalcogenides (TMDs), MoS<sub>2</sub> and WS<sub>2</sub> were covalently functionalized with four different photoactive dyes, pyrene<sup>i</sup>, quantum dots (QDs)<sup>ii</sup>, zinc phthalocyanine (ZnPc)<sup>iii</sup> and porphyrin (H<sub>2</sub>P)<sup>iv</sup> through 1,2-dithiolane addition. The newly synthesized hybrids were characterized by spectroscopic, thermal and electron microscopy imaging methods. Based on steady-state and time-resolved photoluminescence spectroscopy assays, appreciable electronic interactions at the excited state between the photoactive pyrene and MoS<sub>2</sub> and WS<sub>2</sub>, within the MoS<sub>2</sub>-pyrene and WS<sub>2</sub>-pyrene hybrids, were identified. On the other hand, excited state events, investigated by femtosecond transient absorption spectroscopic studies, revealed ultrafast energy transfer from photoexcited QDs to both MoS<sub>2</sub> and WS<sub>2</sub>. Furthermore, upon MoS<sub>2</sub> photoexcitation, charge-transfer from an exciton dissociation path of MoS<sub>2</sub> to QDs, within MoS<sub>2</sub>-QDs, was observed. However, such process in WS<sub>2</sub>-QDs was found to be absent. Recently, ZnPc functionalized MoS<sub>2</sub> resulted on different photochemical events in MoS<sub>2</sub>-ZnPc, namely bi-directional electron-transfer leading to MoS<sub>2</sub><sup>•-</sup>-ZnPc<sup>•+</sup> charge-separated state. Finally, H<sub>2</sub>P functionalized MoS<sub>2</sub> showed a complex ping-pong energy-transfer mechanism, namely from the H<sub>2</sub>P to MoS<sub>2</sub> and back to the porphyrin. The present work highlights the importance of TMD-derived donor-acceptor hybrids in light energy harvesting and optoelectronic applications.

### Acknowledgements

We are indebted to our collaborators Dr. W. K. Maser, Dr. C. P. Ewels, Dr. R. Arenal, Dr. C. Bittencourt, Dr. A. Dalton, Prof. A. Sastre, Prof. H. Shinohara, Prof. F. D'Souza, Prof. D. M. Guldi, and their groups for their continuous support. This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 642742 and Japan Society for the Promotion of Science (JSPS) postdoctoral fellowship grant agreement No P19368.

<sup>i</sup> (a) R. Canton-Vitoria, Y. Sayed-Ahmad-Baraza, M. Pelaez-Fernandez, R. Arenal, C. Bittencourt, C. P. Ewels, N. Tagmatarchis, *npj 2D Mater. Appl.* **2017**, *1*, 13. (b) R. Canton-Vitoria, Y. Sayed-Ahmad Baraza, S. Nufer, R. Arenal, C. Bittencourt, A. Brunton, A. Dalton, C. P. Ewels, N. Tagmatarchis, Submitted, **2019**.

<sup>ii</sup> L. Vallan, R. Canton-Vitoria, H. B. Gobeze, Y. Jang, R. Arenal, A. M. Benito, W. K. Maser, F. D'Souza, N. Tagmatarchis, *J. Am. Chem. Soc.* **2018**, *140*, 13488-13496.

<sup>iii</sup> R. Canton-Vitoria, H. B. Gobeze, V. M. Blas-Ferrando, J. Ortiz, Y. Jang, F. Fernández-Lázaro, Á. Sastre-Santos, Y. Nakanishi, H. Shinohara, F. D'Souza, N. Tagmatarchis, *Angew. Chem. Int. Ed.* **2019**, *58*, 5712.

<sup>iv</sup> R. Canton-Vitoria, T. Scharl, A. Cadranell, R. Arenal, D. M. Guldi, N. Tagmatarchis, Submitted, **2019**.



## **Unique properties and performance evaluation for ultra- and nano-filtration membranes containing nanostructured carbon materials**

Edward Nxumalo

Nanotechnology and Water Sustainability Research Unit, College of Science, Engineering and Technology, University of South Africa, Roodepoort 1709, South Africa, Email add:

[nxumaen@unisa.ac.za](mailto:nxumaen@unisa.ac.za)

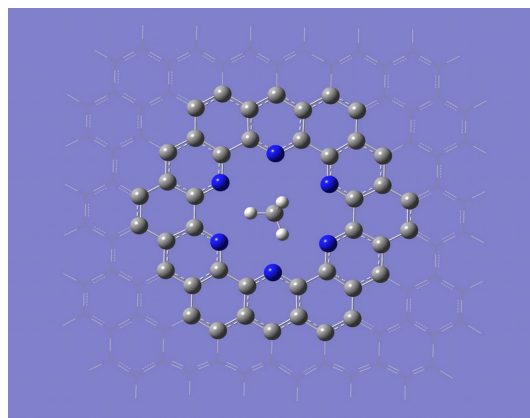
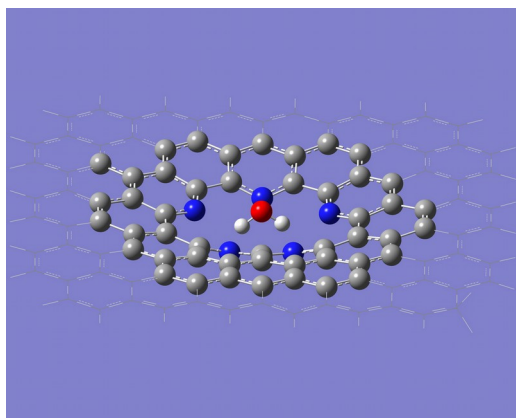
This presentation discusses PES membranes containing nanostructured carbon materials that displays attractive features for ultra- and nano filtration processes. The methods of fabrication entail a non-solvent induced phase separation process using non-solvent additives. The results show that the finger-like, fully sponge-like and macrovoid-free morphology of PES membranes could be achieved as the content of carbons in the casting solutions was varied and as non-solvents are added in solution. The formation of strong hydrogen bonding interactions between different species significantly affected the structures. Microscopic analysis, mechanical strength, permeability, flux recovery ratio and rejection studies are carried out. The fabricated flat-sheet membranes display attractive features for use as membranes in pre-treatment stages.

## Theoretical ab-initio study of graphene vacancies and pyridinic defects for gas separation

N. N. Lathiotakis, Z. G. Fthenakis, and I. D. Petsalakis

*Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Vass. Constantinou  
48, 11635 Athens, Greece*

Porous graphene has been predicted theoretically to be an ideal membrane for gas separation with high selectivity in several cases of different molecules. In the present work, we apply DFT approximations in the study of the energy barriers for the permeation of molecules of interest through pores in single-layer graphene that have been made by Carbon vacancies alone as well as pyridinic defects of several shapes and sizes. For our study, the gaussian 16 computer code is used, with recent DFT functionals, like MO6-2X. Several kinds of graphene flakes are considered either directly passivated with Hydrogen or extended through the ONIOM method and the environment of the pore has been optimized during simulations. The permeation of molecules of interest, like (He, H<sub>2</sub>O, CH<sub>4</sub>, CO<sub>2</sub>, CO, N<sub>2</sub>) is studied and the difference in energy barriers is highlighted demonstrating the potential of these systems for gas separation applications.



## Graphene-Based High Open-Circuit Voltage Heterojunction Solar Cell

Dieter M. Gruen

Argonne Distinguished Fellow, Emeritus and Dimerond Technologies

Hisham A. Maddah and Sanjay K. Behura,

Department of Chemical Engineering, University of Illinois in Chicago

Photovoltaics would rapidly become the major technology for global energy generation if single junction solar cells could achieve conversion efficiencies several times higher than current technologies. The present work finds inspiration in that vision.

A graphene shell/ZnO nanowire core radial heterojunction solar cell that displays an exceptionally large open-circuit voltage of 2.4 V under AM 1.5G illumination has been discovered and is described here. The wavelength independence of the photocurrent in the range 200-1100 nm is evidence that excitons originate in graphene rather than ZnO which, because of its 3.37 eV bandgap, cannot absorb light in the visible region of the spectrum. Further evidence for this conclusion is provided by the fact that the ratio of photocurrents at AM 1.5G illumination versus illumination at a selected monochromatic wavelength is closely similar to the ratio of the three order of magnitude difference in the respective light intensities.

A primary reason for the large open-circuit voltage is likely to be the built-in potential that arises from a work function difference due to contact of n-type ZnO with graphene acting as an electron acceptor. This reasoning is supported by the observation that the work function of ZnO increases very substantially as a consequence of making contact with an organic molecular semiconductor electron acceptor (1).

A lifting of the G peak degeneracy is seen in Raman spectroscopy. Presumably this could originate from two effects acting synergistically. The first is strain stemming from the fact that graphene surrounds nanowires having a very small radius of curvature. The second is symmetry-breaking as a result of an attractive 1 eV van der Waals potential that density functional calculations predict to exist between graphene and the zinc terminated (001) growth face of the nanowires (2). Importantly, this interaction is responsible for the opening of a small band-gap in graphene.

ZnO nanowires on Zn foil were synthesized with well-known hydrothermal growth techniques. Various traditional methods such as drop, dip and spin coating were used to surround the nanowires with graphene oxide (GO) followed by thermal reduction to rGO. A variety of techniques were employed to apply electrodes such as Ti/Au and Ag.

Future work will focus on series resistance, coating uniformity, recombination kinetics as well as other aspects traditionally related to increasing the photocurrent levels of the solar cells.

---

(1) R. Schlesinger et al, Phys. Rev. B 87, 155311(2013)

(2) K. Larson et al, RSC Adv. 5, 65719 (2015)

## MECHANISMS OF THE $sp^2$ -C TO $sp^3$ -C CONVERSION DURING THE LOW TEMPERATURE, LOW PRESSURE SYNTHESIS OF DIAMANE AND DIAMANOIDS FROM GRAPHENE

Fabrice Piazza, Nanoscience Research Laboratory, Pontificia Universidad Católica Madre y Maestra  
Autopista Duarte km 1 1/2, Apartado Postal 822, Santiago, Dominican Republic

T: (+1) 809-580-1962, ext. 4081, fpiazza@pucmm.edu.do

Pascal Puech, Centre d'Elaboration des Matériaux et d'Etudes Structurales (CEMES), CNRS, Université de  
Toulouse, France

Iann Gerber, Laboratoire de Physico-Chimie des Nano-Objets (LPCNO), CNRS, INSA, Université de Toulouse,  
France

Kathleen Gough, Department of Chemistry, Universidad de Manitoba, Winnipeg, Canada  
Germercy Paredes, CEMES, CNRS, Université de Toulouse, France / NRL, PUCMM, Dominican Republic  
Marc Monthieux, CEMES, CNRS, Université de Toulouse, France

Since 2009 and until very recently, diamanes, which constitute new synthetic nanoforms after fullerenes, nanodiamonds, carbon nanotubes and graphene, were hypothetical materials of possibly great interest in various applications such as nanoelectronics, quantum information processing and nanomedicine. We studied the hydrogenation of few-layer graphene (FLG) by the chemisorption of H generated from the dissociation of  $H_2$  in a hot filament reactor at low temperature (below 325 °C) and low pressure (50 Torr), and the subsequent conversion of the FLG structure into crystalline  $sp^3$  material. Fourier Transform Infrared (FTIR) microscopy was used to track the C-H stretching band. One single component attributed to  $sp^3$ -C-H mode was detected showing that only  $sp^3$ -C is bonded to H, and that one single hydrogen is involved in this bonding. UV and visible Raman spectroscopy and mapping were also used to track the structure conversion and the dimensions of the converted domains. Raman peaks from crystalline  $sp^3$ -C were detected, as well as other peaks, yet to explain, but already evidenced in the literature dealing with other carbon materials. Combined data show that hydrogenated, nanosized, crystalline  $sp^3$ -bonded carbon materials were obtained over large surface areas up to  $\sim 1700 \mu m^2$ , strongly suggesting that the  $sp^3$ -C materials obtained are ultrathin films with basal planes hydrogenated. Crystalline  $sp^3$ -C/graphene hybrids were also obtained from the partial conversion of FLG [1]. Meanwhile, low voltage (5 keV) electron diffraction showed that the C  $sp^2$ - $sp^3$  conversion comes along the frequent occurrence or slightly twisted domains.

In order to understand the conversion mechanisms accounting for all the Raman, FTIR, and electron diffraction data, the experimental results were compared to a stacking sequence model (Figure 1) and subsequent predictions from Density Functional Theory calculations [2]. As soon as the number of graphene layers in the starting FLG is higher than 2-3, the  $sp^2$ -C to  $sp^3$ -C conversion can only be partial, due to the prevalence of the Bernal stacking in the FLG material. The partial  $sp^2$ -C to  $sp^3$ -C conversion generates couples of slightly twisted, superimposed coherent domains (TCD), presumably because of stress relaxation. Therefore, in the partially converted FLG, TCDs come with the occurrence of (i) a  $sp^3$ -C layer sandwiched between the highly hydrogenated  $sp^3$ -C surface and the underneath unconverted graphene layer(s); (ii) a twisted bilayer graphene feature located at the interface between the upper diamanoïd domain and the non-converted graphenic domain underneath. Both are responsible for specific Raman signatures which are consistent with what is found in both the experimental spectra and the literature data.

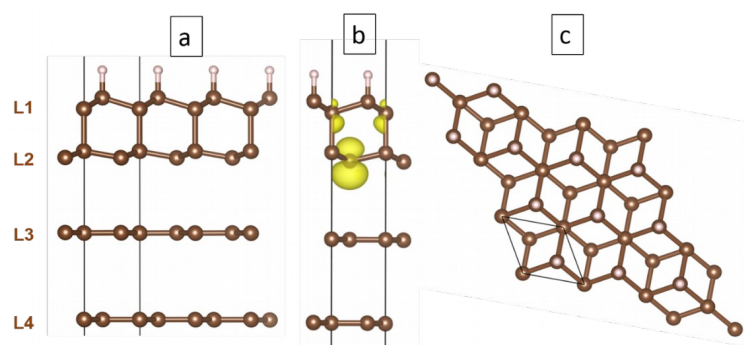


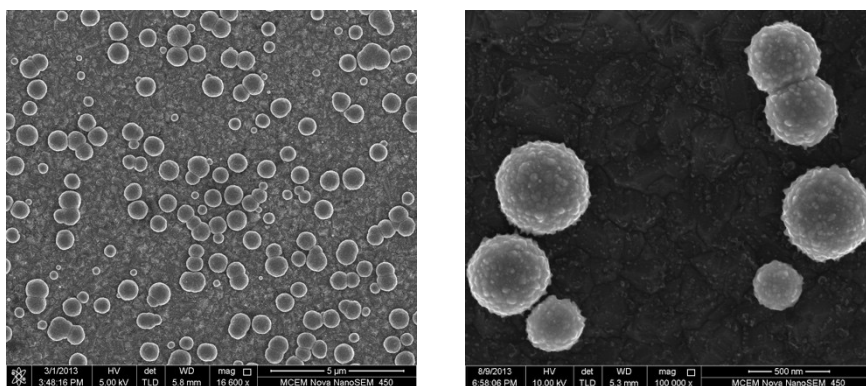
Figure 1 – Example of a diamanoïd/graphene hybrid stacking sequence. (a) and (b) are two side-views and (c) is a top view of the partially hydrogenated FLG used in DFT calculations with a ABBA (most stable) stacking. The projected structure is that of the face centered cubic of diamond. In (b) is shown how the  $p_z$  orbitals are preferably oriented towards the layer underneath (L3). The black lines delimitate the primitive cell.

[1] Piazza F., Gough K., Monthieux M., Puech P., Gerber I., Wiens R., Paredes G., Ozoria C. (2019) Low temperature, pressureless  $sp^2$  to  $sp^3$  transformation of ultrathin, crystalline carbon films. **Carbon** 145, 10-22.

[2] Piazza F., Monthieux M., Puech P., Gerber I. (2020) Towards a better understanding of the structure of diamanoïds and diamanoïd/graphene hybrids. **Carbon** 156, 234-241.

## DOPED DIAMOND INTERFACES: APPLICATION IN ENERGY AND BIONICS

Ahmed Farid Halima, Monash University  
13 Rainforest Walk Clayton VIC 3800 Australia  
T: +61410013007, [ahmed.f.halima@gmail.com](mailto:ahmed.f.halima@gmail.com)  
Douglas R MacFarlane, ARC Centre of Excellence for Electromaterials Science (Monash University)



Current challenges facing functional materials in electrochemical applications (including photoelectrocatalysis, sensors, bionics) are limitations associated with interfacial stability under kinetic or thermodynamic influences. This leads to compromising efficiency and catalytic activity driving redox chemistry, as well as physical properties that are essential for optoelectronic systems. Doped Diamond doesn't only combine these facets with its superlative properties, but also retains robustness and chemical inertness in extreme conditions. Moreover, access to high energy electrons from Diamond facilitates solvated electrons, which are especially useful for high overpotential redox reactions due to the high electron affinity. This work presents progress with modified Diamond materials with inherently stable interfacial thermodynamics for exceptionally sensitive biological components, and on the other hand, highly active interfaces as required for competing photoelectrochemical processes. Two research investigations are presented for nanofabrication and characterization of Diamond interfaces for a) bionic eye research conducted at The University of Melbourne, Australia, and b) renewable energy research conducted at Monash University, Australia. The presented results demonstrate the ability to tune and optimize physico-chemical properties of stable doped Diamond interfaces to facilitate a wide range of functionality in these important applications. This research is presented from an electrochemical perspective, where thermodynamic and kinetic properties are investigated with respect to morphological and composition analysis of Doped Diamond electrocatalytic interfaces. This research promotes Diamond-based interfaces with tunable physico-chemical properties as high-performance components in renewable energy applications.

*Figure 1 – Electrochemically stable Diamond interfaces with functional Pt catalysts for energy conversion*



## Atomic configuration studies of n-type ultrananocrystalline diamond films

R. Arenal<sup>1,2</sup>, F. Hage<sup>3</sup>, Q. Ramasse<sup>3</sup> and D.M. Gruen<sup>4</sup>

1. Laboratorio de Microscopias Avanzadas (LMA), Instituto de Nanociencia de Aragon (INA), Universidad de Zaragoza, Calle Mariano Esquillor, 50018 Zaragoza, Spain. Email: arenal@unizar.es
2. ARAID Foundation, Calle Mariano de Luna, 50018 Zaragoza, Spain.
3. SuperSTEM Laboratory, Daresbury WA4 4AD, U.K.
4. Materials Science Division, Argonne National Laboratory, Illinois 60439, USA.

Ultrananocrystalline diamond (UNCD) film is a crystalline diamond film consisting of 3-5 nm randomly oriented diamond crystallites surrounded by 0.2-0.3 nm wide grain. These films possess exemplary mechanical, electronic and optical properties [1,2]. Under normal process conditions, these UNCD films are highly electrically insulating, but they can become highly conducting when Ar is substituted in the synthesis gas with some of N<sub>2</sub> [1, 5]. In this contribution, we have revisited, using aberration corrected microscopes and combining HR(S)TEM and EELS, the structure and local composition of these n-type UNCD films [3-5].

n-type UNCD films are composed by elongated diamond nanocrystals (called nanowires (NWs) [3]). The formation of these NWs starts to appear when the N<sub>2</sub> content in the gas phase reaches about 10% in volume. From these studies, we concluded that the insulator-metal transition of these films is strongly correlated with the formation of these diamond NWs. Indeed, these NWs are enveloped by a sp<sup>2</sup>-based carbon layer that seems to provide the conductive path for electrons, see Fig. 1 [3-5]. Thus, here we will present the atomic structure studies and local EELS analyses developed on these complex films [5]. In summary, these studies elucidate crucial questions concerning the local composition (atomic configuration) of these NW. This detailed knowledge is essential for better understanding the outstanding properties of such NW.

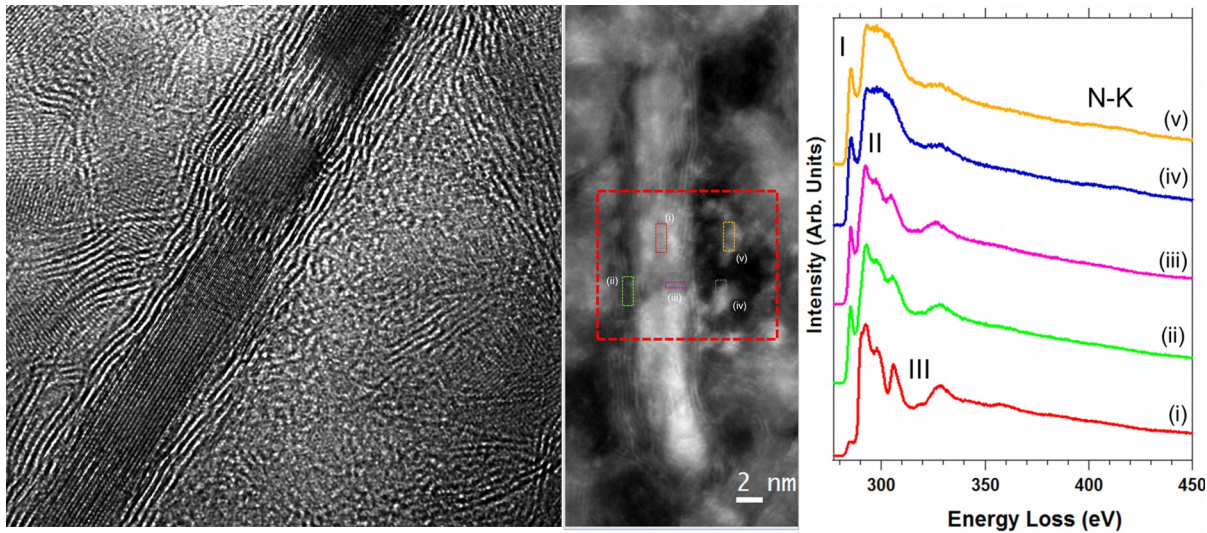


Figure 1 – **Left:** HRTEM micrograph of a diamond NW and the UNCD matrix. **Middle:** HAADF-STEM image of another diamond NW as well as the UNCD matrix. A SPIM-EELS has been recorded in the red marked area of the HAADF image. **Right:** EEL spectra extracted from the squared regions marked in the HAADF image.[5]

### References

- [1] O.A. Shenderova & D.M. Gruen, UNCD: synthesis, properties & applic. William Andrew. (2012).
- [2] R. Arenal, Review paper, to be submitted.
- [3] R. Arenal, P. Bruno, D.J. Miller, M. Bleuel, J. Lal, D.M. Gruen, Phys. Rev. B 75, 195431 (2007).
- [4] R. Arenal, O. Stephan, P. Bruno, D.M. Gruen, Appl. Phys. Lett. 94, 111905 (2009).
- [5] R. Arenal, F. Hage, Q.M. Ramasse and D.M. Gruen, to be submitted.

[6] R.A acknowledges the funding from the Spanish MICINN (MAT2016-79776-P) and from the EU H2020 programs Flag-ERA (JCT, PCI2018-093137, MICINN) and "Graphene Flagship" Grant Agreement 785219.

## FABRICATION OF BN COATED CARBON NANOSTRUCTURES USING ALD BASED POLYMER DERIVED CERAMICS ROUTE

Catherine Marichy, Univ Lyon, Laboratoire des Multimatériaux et Interfaces, UMR CNRS 5615  
6 rue Victor Grignard, Villeurbanne, France

T: +33-472-431-701, Email address: catherine.marichy@univ-lyon1.fr

Wenjun Hao, Univ Lyon, Laboratoire des Multimatériaux et Interfaces, UMR CNRS 5615, France

Catherine Journet, Univ Lyon, Laboratoire des Multimatériaux et Interfaces, UMR CNRS 5615, France

Search and development of sustainable energy as well as environment issues are two of the most important current concerns. In particular, applications in corrosive and/or high temperature treatment such as in heterogeneous catalysis need support with excellent thermal stability and chemical inertness. Boron Nitride (BN) seems thus an excellent candidate; however it is an electrical insulator. Carbon nanotubes, despite their excellent electric properties, suffer of instability under reaction condition at high temperature (>300 °C) especially, if the targeted reactions are partial oxidations. Deposition of a very thin BN coating appears an elegant approach to prevent the CNT oxidation while preserving its electric properties [1,2] and access to a support allowing for instance heterogeneous catalysis/electrocatalysis even at high temperature (e.g. 400-700 °C). Nevertheless, fabrication of such hetero-structures requires a synthetic approach capable of controlling the size and morphology of the desired materials. Atomic Layer Deposition (ALD) has demonstrated to be an effective approach for surface modification and fabrication of carbon based heterostructures.[3] Currently, BN coating of carbon material by ALD has been poorly investigated. Based on polymer derived ceramic chemistry, a novel two-step ALD approach for BN has been recently reported.[4] Due to its low deposition temperature and non-corrosive precursors, it has been successfully used for BN deposition onto various substrates such as inorganic and polymer nanostructures.[5]

Herein coating of various carbon nanostructures is reported using this new ALD process. As inertness of highly graphitic carbon inhibits the initiation of ALD growth, use of amorphous and graphitized carbon substrates allows studying the impacts of the crystalline nature of the substrate on the coating in terms of growth and structure. The obtained BN coated carbon materials are characterized by advanced electron microscopy and related techniques. As a function of the degree of graphitization, nucleation delay and impact on the crystalline quality (amorphous, turbostratic, hexagonal phase) of BN films are observed. Finally, potential of such coating to improve the oxidation resistance of carbon material is demonstrated.

### References:

- 1- Liew K.M., Yuan J., *Nanotechnology*, **2011**, 22 (8), 085701.
- 2- Jing L., Tay R.Y., Li H., Tsang S.H., Huang J., Tan D., Zhang B., Teo E.H.T., Tok A.I.Y., *Nanoscale*, **2016**, 8 (21), 11114.
- 3- Marichy C., Pinna N., *Coordination Chemistry Reviews*, **2013**, 257, 3232.
- 4- Hao W., Marichy C., Brioude A., *ChemNanoMat.*, **3**, **2017**, 656.
- 5- Hao W., Marichy C., Journet C., Brioude A., *Enviro. Science Nano.*, **4**, **2017**, 2311.



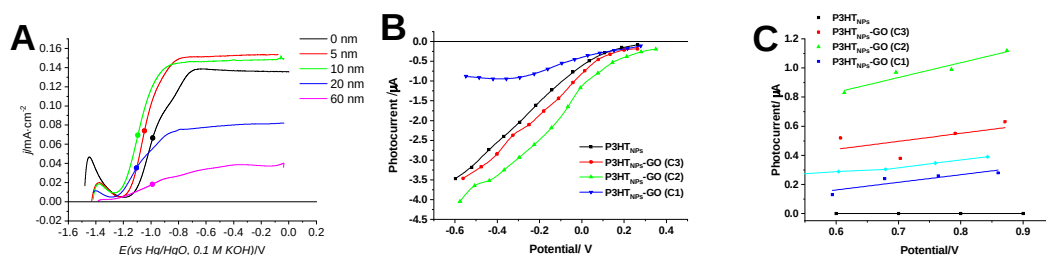
## Assessment of charge transfer phenomena in nanostructured composite materials using photoelectrochemical methods.

Javier Hernández-Ferrer\*, Emin Istif, Alejandro Ansón-Casaos, Ana Santidrián, Ana M. Benito, Wolfgang K. Maser.

Instituto de carboquímica-CSIC, c/ Miguel Luesma Castán 4, 50018 Zaragoza, Spain

\*corresponding author: jhernandez@icb.csic.es

Photoelectrochemistry is a valuable technique for the study of intrinsic electronic properties of a great variety of nanostructured semiconductor materials, such as conductive polymers or metal oxide nanoparticles. It is also a highly valuable implement to assess charge and/or energy transfer phenomena between the mentioned semiconductors and carbon nanomaterials (GO, CNTs), unveiling their role as charge acceptors/donors, blockers/transporters, sensitizers/conditioners, or even as photoelectroactive materials for themselves, thus allowing the tuning of optoelectronic properties of composite materials, for their future application in fields related to energy and environment, such as water splitting, solar cells or water remediation. This versatility makes photoelectrochemistry a key tool in the field of carbon nanoscience and nanotechnology [1-4].



**Figure 1.** Photoelectrochemical properties of TiO<sub>2</sub>/electrochemically reduced GO (A) and P3HT/GO composites in the photocathodic (B) and photoanodic (C) branch.

### References

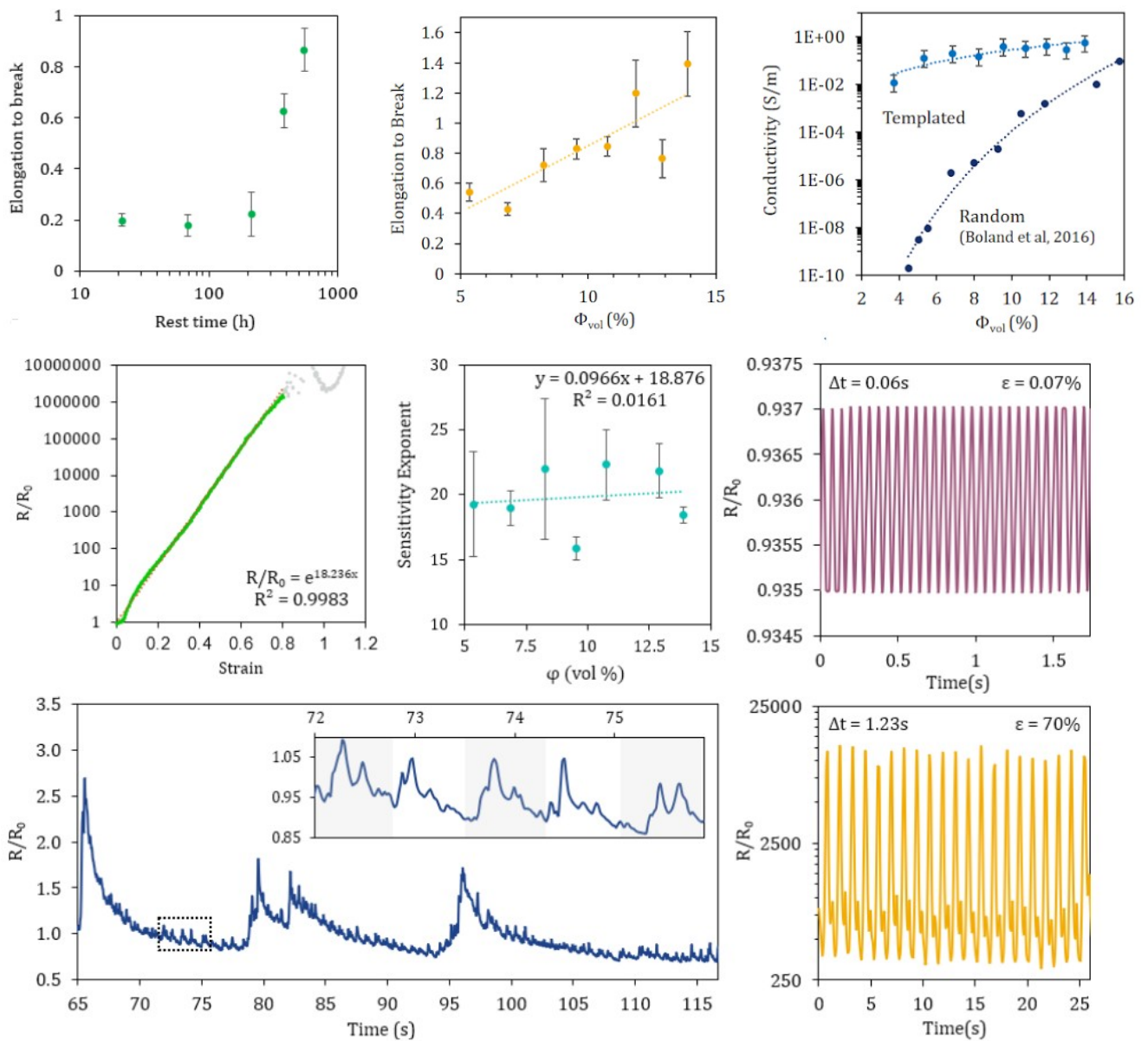
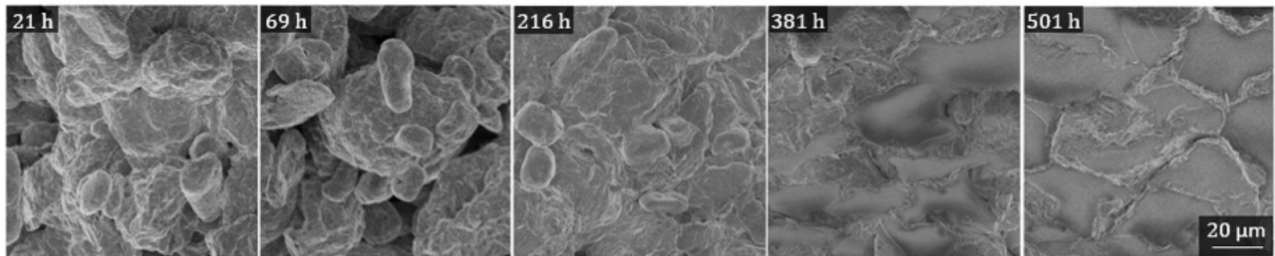
1. Istif, E., Hernández-Ferrer, J., Urriolabeitia, E.P., Stergiou, A., Tagmatarchis, N., Fratta, G., Large, M.J., Dalton, A.B., Benito, A.M., Maser, W.K. *Advanced Functional Materials* 28, Article number 1707548 (2018)
2. Hernández-Ferrer, J., Ansón-Casaos, A., Víctor-Román, S., Sanahuja-Parejo, O., Martínez, M.T., Villacampa, B., Benito, A.M., Maser, W.K. *Electrochimica Acta* 298, 279-287 (2019)
3. Hernández-Ferrer, Ansón-Casaos, A., Víctor-Román, S., Santidrián, A., Benito, A.M., Maser, W.K. *Journal of Electroanalytical Chemistry* 828, 86-90 (2018)
4. Santidrián, A., González-Domínguez, J.M., Díez-Cabanes, V., Hernández-Ferrer, J., Maser, W.K., Benito, A.M., Ansón-Casaos, A., Cornil, J., Da Ros, T., Kalbáč, M. *Physical Chemistry Chemical Physics* 21, 4063-4071 (2019)

**Acknowledgements.** MINEICO (project ENE2016-79282-C5-1-R, AEI/FEDER, UE), European Union (H2020-MSCA-ITN-2014-ETN 642742), Gobierno de Aragón (Grupo Reconocido DGA T03\_17R, FEDER, UE).

# Highly-sensitive exponential gauge factor strain sensors based on graphene-silicone emulsion composites

Marcus O'Mara<sup>1</sup>, Sean P. Ogilvie<sup>1</sup>, Matthew J. Large<sup>1</sup>, Aline Amorim Graf<sup>1</sup>, Peter J. Lynch<sup>1</sup>, Jonathan P. Salvage<sup>2</sup>, Alice A. K. King<sup>1</sup>, Alan B. Dalton<sup>1</sup>

<sup>1</sup>Physics and Astronomy, University of Sussex, Brighton, UK  
<sup>2</sup>Pharmacy and Biomolecular Sciences, University of Brighton, Brighton, UK



**THURSDAY 12th  
PRESENTATIONS**

## Synthesis of boron nitride single crystals under high pressure impurity and isotope control for their functionalization

Takashi Taniguchi  
National Institute for Materials Science  
1-1 Namiki Tsukuba 305-0044 Japan

**Email:** Taniguchi.takashi@nims.go.jp

Hexagonal boron nitride BN (hBN) and cubic BN (cBN) are known as the representative crystal structures of BN. The former is chemically and thermally stable, and has been widely used as an electrical insulator and heat-resistant materials. The latter, which is a high-density phase, is an ultra-hard material second only to diamond. The color of the cBN crystals were always amber or brownish so far which is attributed by carbon and oxygen impurity. After some struggles for high pressure and high temperature (HPHT) solution growth, we could find suitable solvent of Ba-BN system which gave us almost colorless cBN with band-edge nature[1]. At the same time, high purity hBN crystals were recovered in the same HPHT capsule and their attractive potential as a wide-band gap material was realized. It is emphasized that hBN crystals exhibits superior properties as ultra violet light emitter[2] as well as a substrate of graphene devices[3]. While the current subject is to realize how the major impurities such as carbon and oxygen affect the properties of hBN and cBN, some progress for the realization for the application of 2D's substrates and photonic materials have been achieved.

Another issue is to fabricate fine hBN crystals with high quality via conventional route. Although high pressure synthesis process has an advantage to use reactive alkali-base solvent such as Ba-BN, search for the alternative synthesis route without pressure is important for the practical application of hBN. Since hBN is thermodynamically stable at high temperatures and at atmospheric pressure, it should be possible to obtain high-quality hBN crystals at atmospheric pressure by using an appropriate solvent. Ni or Co-base metal base solvents seem useful to obtain high quality hBN crystals, though the yield of the crystals is less than those of high pressure process.

While the current subject is to realize how the major impurities such as carbon and oxygen affect the properties of hBN and cBN, some progress for the realization for the application of 2D's substrates and photonic materials have been achieved. Also, controlling of boron and nitrogen isotope ratio ( $^{10}\text{B}$ ,  $^{11}\text{B}$  and  $^{15}\text{N}$ ) in hBN and cBN crystals can be now carried out by metatheses reaction under HPHT.

In this paper, our recent studies on hBN and cBN single crystals growth under HP with respect to impurity / isotope controls and their functionalizations will be reported.

### [References]

- [1] T.Taniguchi, K.Watanabe, J.Cryst.Growth , **303**,525 (2007).
- [2] K.Watanabe,T.Taniguchi,A.Niiyama,K.Miya, M.Taniguchi, Nature Photonics **3**, 591 (2009).
- [3] C.R. Dean, A.F. Young, I. Meric, C. Lee, W. Lei, S. Sorgenfrei, K Watanabe, T. Taniguchi, P. Kim, K.L.Shepard, J. Hone, Nature Nanotechnology, **5**,722 (2010).

## SYNTHESIS OF EXFOLIABLE HEXAGONAL BORON NITRIDE SINGLE CRYSTALS OF MILLIMETER SIZE

Catherine Journet, Univ Lyon, Laboratoire des Multimatériaux et Interfaces, UMR CNRS 5615, UCBL  
6 rue Victor Grignard, Villeurbanne, France

T: +33-472-433-564, Email address: catherine.journet@univ-lyon1.fr

Yangdi Li, Univ Lyon, Laboratoire des Multimatériaux et Interfaces, UMR CNRS 5615, UCBL and Laboratoire  
Matériaux Ingénierie et Science, UMR CNRS 5510, INSA Lyon

Vincent Garnier, Laboratoire Matériaux Ingénierie et Science, UMR CNRS 5510, INSA Lyon

Philippe Steyer, Laboratoire Matériaux Ingénierie et Science, UMR CNRS 5510, INSA Lyon

Bérangère Toury, Univ Lyon, Laboratoire des Multimatériaux et Interfaces, UMR CNRS 5615, UCBL

Prompted by the rising star of graphene, 2D nanomaterials are now a hot issue in the scientific world. Among them, the hexagonal boron nitride (hBN) nanosheets (BNNSs), consisting of thin atomic layers made of boron (B) and nitrogen (N) atoms covalently bounded, is particularly relevant. BNNSs have shown to be excellent gate dielectric supports for graphene and other two-dimensional materials owing to their atomically smooth surface, high thermal conductivity and stability combined with high mechanical strength. Compared with conventional SiO<sub>2</sub> substrate, lattice matching and absence of dangling bonds make BNNSs and graphene excellent pairing materials and give incentive to develop various Van der Waals hetero structures. However, it must be pointed out that such applications cannot be put into use without high purity large BNNSs.

In order to achieve high quality and large BNNSs, we propose a novel synthesis way by the Polymer Derived Ceramics (PDCs) route involving polyborazylene as precursor, combined with sintering technique [1]. This promising approach allows synthesizing pure and well-crystallized h-BN single crystals of millimeter size, which can be easily exfoliated into BNNSs with lateral size over hundreds of microns [2]. Here we present recent investigations on how to optimize processes, considering the influences of both sintering temperature (1200°C to 1950°C) and crystallization promoter ratio (0 to 10 wt %) on hBN. Structural studies were led by TEM and Raman spectroscopy. Both methods evidence a very high crystalline quality attested by the FWHM value, 7cm<sup>-1</sup>, as one of the best reported in literature. More original characterizations were carried out by cathodoluminescence and XPS to prove the high BNNSs purity from both structural and chemical points of view. As a final application purpose, further physical measurements have confirmed that derived BNNSs exhibit an interesting dielectric constant of 3.9 associated with a dielectric strength of 0.53 V/nm.

### References

[1] S. Yuan, S. Linas, C. Journet, P. Steyer, V. Garnier, G. Bonnefont, A. Brioude, B. Toury, *Sci. Rep.*, **6** (2016) 20388

[2] Y. Li, V. Garnier, C. Journet, J. Barjon, A. Loiseau, I. Stenger, A. Plaud, B. Toury, P. Steyer, *Nanotechnology*, **30** (2019) 035604

# HEXAGONAL BORON NITRIDE: AN EMERGING 2D MATERIAL FOR PHOTONIC AND OPTOELECTRONIC APPLICATIONS

Marie Krečmarová, Instituto de Ciencia de Materiales, Universidad de Valencia (ICMUV),  
c/ Catedrático José Beltrán, 246980 Paterna (Valencia), Spain  
+34 963 544 858, Marie2.Krecmarova@uv.es

Rodolfo Canet-Albiach, Instituto de Ciencia de Materiales, Universidad de Valencia (ICMUV), Valencia, Spain,  
Daniel Andres-Penares, Instituto de Ciencia de Materiales, Universidad de Valencia (ICMUV), Valencia, Spain,  
Ladislav Fekete, Institute of Physics, Academy of Sciences Czech Republic v.v.i., Prague, Czech Republic,  
Petr Ashcheulov, Institute of Physics, Academy of Sciences Czech Republic v.v.i., Prague, Czech Republic,  
Alejandro Molina-Sánchez, International Iberian Nanotechnology Laboratory (INL), Braga, Portugal,  
Juan P. Martínez-Pastor, Instituto de Ciencia de Materiales, Universidad de Valencia (ICMUV), Valencia, Spain,  
Juan F. Sánchez-Royo, Instituto de Ciencia de Materiales, Universidad de Valencia (ICMUV), Valencia, Spain.

Hexagonal boron nitride (hBN) is a wide band gap 2D layered material with outstanding physical properties for wide range of applications at nanoscale. For instance hBN as an electrical insulator with optical transparency at broad spectrum of wavelengths is an attracting material for fabrication of new optoelectronic nano-devices by formation of 2D van der Waals heterostructures with another 2D semiconductors. Moreover, due to its high chemical stability, hBN is also an ideal material for the passivation of air-unstable 2D materials, such as black phosphorus or halide perovskites, to protect them against ambient degradation. Another promising properties of hBN are recently discovered quantum defects with visible photoluminescence (PL) at room temperature, which is promising for development of new quantum computing, photonic and sensing nano-devices. However an integration of few-layer thick hBN into nano-devices based on 2D materials requires fast and non-destructive techniques to quantify their thickness. First, we demonstrate experimentally and theoretically thickness estimation of few-layer hBN on SiO<sub>2</sub>/Si substrates by optical contrast (OC) and micro-Raman spectroscopy, which was also measured by atomic force microscopy. Low OC of hBN was enhanced by using illumination of near-monochromatic light. We verified that the OC technique is fast and accurate for the thickness determination of hBN exhibiting a linear dependence with the thickness of nanosheets up to around 50 monolayers. Contrary micro-Raman spectroscopy exhibits a weak thickness-dependence. Experimentally and theoretically (ab initio calculations), the frequency of the E<sub>2g</sub> phonon mode increases as the number of hBN monolayers reduces, but only below 3–4 monolayers (see Figure 1). Then we applied few-layer thick hBN as a protective layer of air-unstable 2D halide perovskites. The hBN encapsulated perovskites crystals show long-term stability and resistance to a higher laser power irradiation. Finally, we engineered quantum colour defects in hBN nano-crystals (see Figure 2). Majority of quantum emitters have zero phonon line at wavelengths between 550 – 650 nm. Charge state manipulation of the quantum emitters by a cationic charged polymer for instance, which results in quenching of the PL, can be then used for nano-sensing applications.

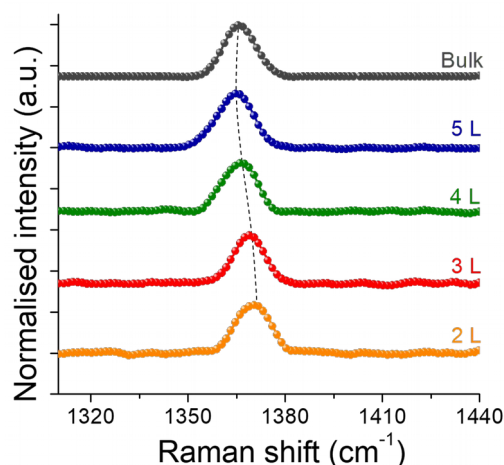


Figure 1 – Normalized Raman spectra of hBN crystals with thickness varying from 2 to 5 layers and bulk (Nanomaterials 2019, 9, 1047).

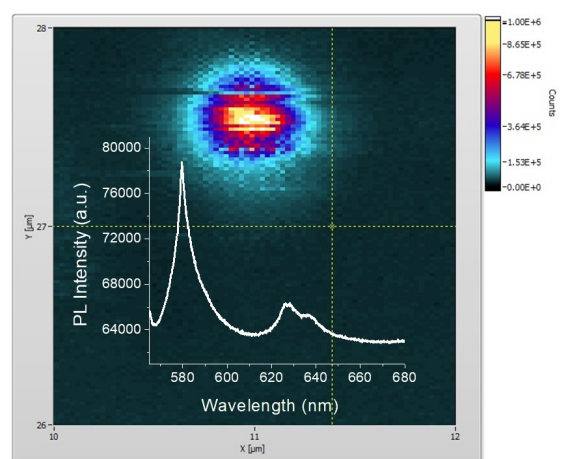


Figure 2 – PL map and spectra (inset) of a quantum emitter in hBN crystal with zero phonon line at 580 nm.



# 1T/2H mixed-phase few-layer MoS<sub>2</sub> nanosheets vertically aligned on nitrogen-doped reduced graphene oxide as superior electrochemical ascorbic acid biosensors

He Li<sup>a</sup>, Zhihao Yuan<sup>a</sup>, Wei Li<sup>a</sup>, Minfang Chen<sup>a</sup>, Rony Snyders<sup>b,c</sup>, and Wenjiang Li<sup>a\*</sup>

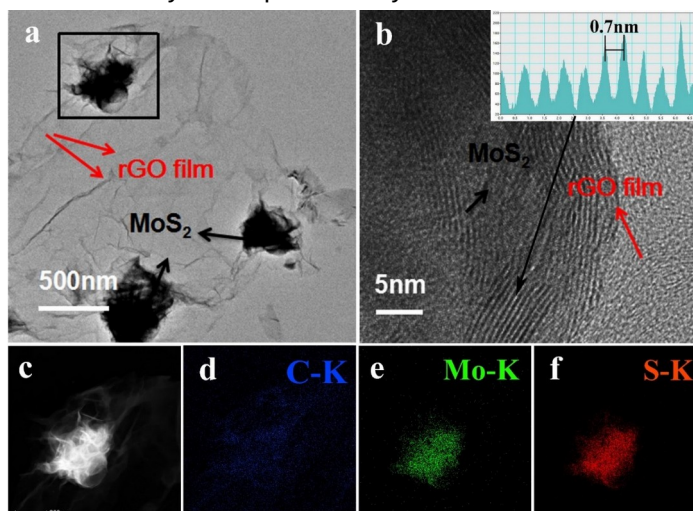
<sup>a</sup>Key Laboratory of Display Materials & Photoelectric Devices, School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, PR China.

<sup>b</sup>Chimie des Interactions Plasma-Surface, University of Mons (UMONS), 20 Place du Parc, 7000 Mons, Belgium.

<sup>c</sup>Materia Nova Research Centre, 1 Avenue Nicolas Copernic, B 7000 Mons, Belgium.

## Abstract

Here, molybdenum disulfide nanosheets vertically aligned on nitrogen-doped reduced graphene oxide support composite (MoS<sub>2</sub>@NG) were constructed via a surfactant-free hydrothermal route for electrochemical ascorbic acid (AA) biosensors (Fig.1). As-prepared MoS<sub>2</sub>@NG composite could own highly exposed catalytic edge sites, excellent conductivity and fast electron mobility by reason of unique structure and properties, including 1T/2H mixed phase, low agglomeration/restacking and rich defect, which endows MoS<sub>2</sub>@NG composite superior electrocatalytic oxidation activity towards AA. Modified glassy carbon electrode with MoS<sub>2</sub>@NG composite using drop casting presents the highly selective detection for AA despite various interference species with a low detection limit (3.5 μM, S/N=3), high sensitivity (340.5 μA·mM<sup>-1</sup>·cm<sup>-2</sup>) and two wide linear ranges (from 10 μM to 1000 μM and from 1000 μM to 6000 μM) as well as ideal stability and reproducibility.



**Fig. 1.** (a) TEM, (b) HRTEM, (c) STEM images and (d-f) corresponding EDX elemental mapping of C, Mo, S of MoS<sub>2</sub>/rGOA.

## OPTICAL PROPERTIES of MoS<sub>2</sub>, WS<sub>2</sub> and GRAPHENE GROWN by CHEMICAL VAPOR DEPOSITION

P.V. Fedotov<sup>1,2</sup>, F.D. Vasil'eva<sup>3</sup>, P.V. Vinokurov<sup>3</sup>, E.A. Obraztsova<sup>1,4</sup>, V.R. Islamova<sup>1,2</sup>, M.G. Rybin<sup>1,2</sup>, S.A. Smagulova<sup>3</sup>, E.D. Obraztsova<sup>1,2\*</sup>

<sup>1</sup> A.M. Prokhorov General Physics Institute, RAS, 119991 Moscow, 38 Vavilov street, Russia

<sup>2</sup> Moscow Institute of Physics and Technology, 141701 Dolgoprudny, Russia

<sup>3</sup> Ammosov North-Eastern Federal University, 677000, Yakutsk, Russia

<sup>4</sup> Shemyakin and Ovchinnikov Institute of Bioorganic Chemistry, RAS, 117871 Moscow, Russia

Last decade there is a growing interest to layered dichalcogenides of transition metals. Among them MoS<sub>2</sub> and WS<sub>2</sub> are the most interesting and often used ones. Bulk crystals of MoS<sub>2</sub> and WS<sub>2</sub> are semiconductors with the indirect gaps of 1.2 eV and 1.3 eV, correspondingly [1]. With the layer number decrease there is a transition from an indirect-gap to a direct-gap semiconductor with the increased gap value. The direct-gap provides a high absorption coefficient and an efficient generation of electron-hole pairs upon photoexcitation. These properties are promising for optoelectronic applications.

In this work the films of MoS<sub>2</sub>, WS<sub>2</sub> and graphene were grown by chemical vapor deposition (CVD) technique (Fig.1). Transition from islands (of 800 nm on SiO<sub>2</sub>) to the continuous film were controlled by deposition time. The Raman and Photoluminescence studies were performed [2]. The Raman spectra [2] (and especially their low-frequency part) were very informative for the layer number estimation (Fig.2). The properties of heterostructures MoS<sub>2</sub>-graphene and WS<sub>2</sub>-graphene were investigated.

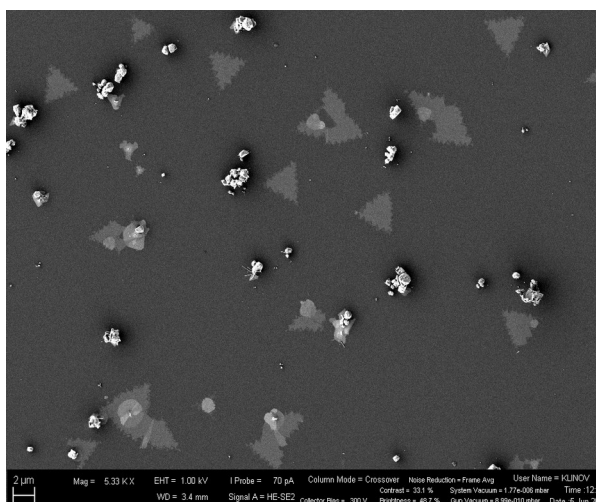


Fig. 1. SEM image of WS<sub>2</sub> island-film.

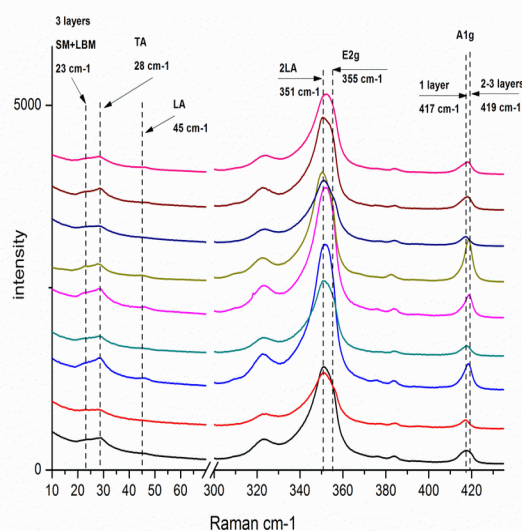


Fig.2. Raman spectra of 1-3 layer WS<sub>2</sub> islands.

The work was supported by RFBR projects 19-32-50034 and 18-29-19113.

### References

1. W.Zhao, R.M. Ribeiro, M. Toh, et al. , *Nano Let.* 13 (2013) 5627.
2. E.A. Obraztsova, A.V. Osadchy, et al., *Phys. Stat. Sol. B* 245 (2008) 2055.



## **NO<sub>2</sub> Sensitivity and Selectivity of Single-Walled Carbon Nanotube-Hybrids upon cluster filling**

Paola Ayala, Faculty of Physics, University of Vienna  
Boltzmannngasse 5, Vienna, Austria  
T: +431427772626, paola.ayala@univie.ac.at

The properties of single-walled carbon nanotubes provide them with enormous potential as gas sensors and it is therefore not surprising that a great number of studies have been published over the last two decades in the field. However, true effectiveness of these materials can truly be expected if their interaction with the sensing targets is controlled and their recovery is granted. In this presentation we will aim at understanding the role of impurities and the use of raw nanotube samples for sensing purposes. Conclusive answer can only be given if ultra-clean SWCNT samples are used. We have conducted a careful experimental and theoretical investigation of the adsorption of O<sub>2</sub>, NO and NO<sub>2</sub> molecules onto SWNTs to shed light on the nature of adsorption and its effect on their electronic properties of SWNTs. It will then be shown how metallicity-sorting and the further use of carbon nanotube hybrids are able to unfold two major challenges: tuning the gas-tube interaction and achieving desorption of gases at ambient temperature. By means of X-ray photoelectron spectroscopy (XPS), the dynamics of the molecular oxygen-SWCNTs interaction was followed. Using time resolved photoemission we observed that in semiconducting nanotube hosts the chemical potential is pinned inside their energy gap shifted to the onset of the conduction band when nanotubes filled with nanoclusters are used. This remarkably reveals that having a metal cluster filling could represent a key to high sensitivity with a very effective desorption at ambient temperature.

## **Carbon Nanostructures-based aqueous bioinks**

J. M. González-Domínguez,<sup>1\*</sup> M. A. Álvarez,<sup>1</sup> A. Baigorri,<sup>1</sup> A. Ansón-Casaos,<sup>1</sup> G. Huet,<sup>2</sup> C. Hadad,<sup>2</sup> A. Nguyen Van Lier,<sup>2</sup> J. E. García-Bordejé,<sup>1</sup> A. M. Benito,<sup>1</sup> W. K. Maser<sup>1</sup>

- 1) Group of Carbon Nanostructures and Nanotechnology, Instituto de Carboquímica ICB-CSIC, C/Miguel Luesma Castán 4, 50018, Zaragoza, Spain
- 2) Labroatory LG2A, Chemistry Department, Université de Picardie Jules Verne, Amiens, France.

In the present work, the most recent progress in our laboratories will be presented, regarding the synthesis, characterization and applications of conductive inks made with carbon nanostructures (carbon nanotubes and graphene derivatives). Our main approach is to develop aqueous systems, capable of acting as precursors of conductive thin films, under a sustainability scope, by employing 'green' nanomaterials as dispersing agents coming from renewable sources. The main focuses are cellulose or chitin nanocrystals, and silk fibroin, which are able to generate stable aqueous bioinks in combination with carbon nanomaterials and several processing techniques (namely, dispersion, centrifugation or autoclave treatments). The processing, characterization and use of these inks will be discussed, as well as some application aspects in the energy and biomedicine fields.

# IN-SITU GRAPHENE OXIDE THERMAL ANALYSES VIA TEM/EELS: WATER DESORPTION, REDUCTION AND GRAPHITISATION

Mario Pelaez-Fernandez<sup>1</sup>, Alba Bermejo Solis<sup>1</sup>, Ana M. Benito<sup>2</sup>, Wolfgang K. Maser<sup>2</sup>, Raul Arenal<sup>1,3,4</sup>

<sup>1</sup> Instituto de Nanociencia de Aragón, Universidad de Zaragoza, Spain

<sup>2</sup> Instituto de Carboquímica, Zaragoza, Spain

<sup>3</sup> Fundación ARAID, Zaragoza, Spain

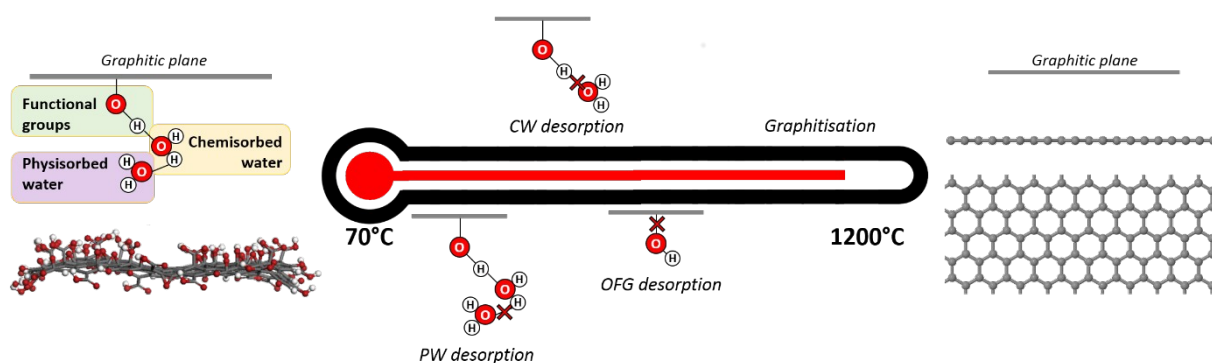
<sup>4</sup> Instituto de Ciencias de Materiales Aragón, CSIC-U. Zaragoza, Spain

Email: [mariopf@unizar.es](mailto:mariopf@unizar.es)

For the last fifteen years, graphene oxide (GO) has become a material of great importance within the subject of chemically modified graphene (CDG)[1] for its vast potential applications[2]. However, both the chemical structure of Graphene oxide and the diverse processes taking place in thermal reduction of GO into reduced graphene oxide (RGO) are still not completely clear despite the sizable amount of studies concerning this issue[2].

TEM and EELS, using a sample holder capable of heating samples up to 1200°C within the TEM, is a unique and extensive technique for the analysis of the reduction of GO. Using this technique, we can measure, simultaneously and *in situ*, four main properties essential to this analysis at several intermediate temperatures and under high vacuum: the oxidation rate [3], its thickness [4], its mass density [5] and its sp<sup>2</sup>-sp<sup>3</sup> bond ratio [6].

This study presents an analysis of GO by studying all of the aforementioned properties in two different studies: a first one heating up to 300°C to better understand the physisorbed and chemisorbed water desorption, and a second one up to 1200°C focused on the desorption of various oxygen functional groups; as well as the graphitisation of GO. Our results will be compared with previous studies on the matter.



## References

1. Dreyer, D. R. The chemistry of graphene oxide.
2. K. P. Loh *et al*, Nat. Chem, 2(12), 1015–1024.
3. L. Grade & F. Javier, Advanced methods for Electron Energy Loss Spectroscopy core-loss analysis.
4. T. Malis *et al*, Journal of Electron Microscopy Technique, 8, 193-200
5. K. Gross *et al*, Nanotechnology 27(36), 1-10
6. L. Lajaunie *et al*, Carbon 112, 149-161
7. This work was supported by the Spanish MINECO (MAT2016-79776-P, AEI/FEDER, EU), and European Union H2020 programs Marie Skłodowska-Curie “Enabling Excellence” (642742), “ESTEEM3” (823717), Flag-ERA GATES (JTC - PCI2018-093137) and Graphene Flagship (785219).

## Nanomaterial Tissue Substrates to Probe Cellular Disease Mechanisms

Rhiannon W. Harries<sup>1</sup>, Matthew Large<sup>1</sup>, Sean Ogilvie<sup>1</sup>, Lisa Woodbine<sup>2</sup>,  
Thomas Simon<sup>3</sup>, Georgios Giamas<sup>3</sup>, Alan B. Dalton<sup>1</sup> and Alice A. K. King<sup>1</sup>

<sup>1</sup>Department of Physics and Astronomy, University of Sussex, Brighton, UK

<sup>2</sup>Genome Damage and Stability Centre, University of Sussex, Brighton, UK

<sup>3</sup>Department of Biochemistry and Biomedicine, University of Sussex, Brighton, UK

r.w.harries@sussex.ac.uk

How the structure of cells alters and develops in response to the substrate and its neighbours is critical in the development of tissue architecture and plays a significant role in cancer metastasis. Increasingly, the role of the topographical and mechanical properties of the cell surroundings are being identified as key to a cell's structural dynamics and mobility, with cells sensing hardness, elasticity and stability at the nanoscale. Due to this complex response, nanomaterials are becoming increasingly important for development of tissue scaffolds. By controlling the nanoscale structure and chemistry of a substrate, it is possible to identify specific cellular responses. The use of synthetic nanomaterial substrates for cell growth is an exciting area of interdisciplinary research. Langmuir film creation is a powerful tool for obtaining monolayer nanomaterial films, with fine control over the surface coverage, and selection of the nanomaterial dictating chemistry, elasticity, etc.

Using various liquid-phase exfoliated nanomaterials, the pressure-area isotherm has been used to select repeatable surface coverage, thereby tuning the substrate properties to identify cellular responses to substrate cues. MoS<sub>2</sub> follows specific uptake pathways, only identified through substrate interaction rather than media exposure, which dictate the fate of the MoS<sub>2</sub> within the cell, and the platelet persistence in daughter cells. Graphene has been demonstrated to induce vessel formation in glioblastoma cells *in vitro*, a known mechanism of disease progression *in vivo*. In this way, these nanomaterials provide key insights into mechanistic understandings of important cellular processes for disease investigation and potential therapeutics.

## MECHANOCHEMICAL SYNTHESIS OF “SWEET GREEN GRAPHENE”

V. J. González<sup>1\*</sup>, A. M. Rodríguez<sup>1</sup>, E. Vázquez<sup>1,2</sup>

<sup>1</sup> Instituto Regional de Investigación Científica Aplicada (IRICA), UCLM, 13071 Ciudad Real, Spain.

<sup>2</sup> Facultad de Ciencias y Tecnologías Químicas, UCLM, Avda. Camilo José Cela S/N, 13071, Ciudad Real, Spain.

e-mail: vivianaj.gonzalez@uclm.es

First isolated in 2004, graphene has sparked a great scientific interest thanks to its peculiar mechanical and electronic properties, which promise to upgrade many technologies, from microelectronics to biosensing and nano-medicine.[1] Among the many molecules that have been proposed as exfoliating agents of graphite, only a few ones successfully exfoliate and stabilize graphene in aqueous media.[2]

Mechanochemistry has gained increasing importance in diverse fields of chemistry,[3] principally in the exfoliation and functionalization of nanomaterials like graphene, it has also many advantages such as shorter reaction times, higher product yields and the elimination of (harmful) organic solvents.

Here we report the development of an environmentally friendly, cheap and simple approach for the synthesis of aqueous soluble few-layer graphene, useful for biological purposes. We propose that different carbohydrates behave as melamine in a micro-solvation model where the interplay between non-covalent interactions, provides the necessary thermodynamic driving force to stabilize the graphene-water dispersions.[2] The prepared graphene have been characterized by TEM, X-ray diffraction, TGA, Raman spectroscopy. This study aims to use carbohydrates as exfoliating agents and open up new possibilities for preparing graphene materials, in large-scale, for biological applications.

### References

- [1] (a) K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, *306*, 666-669. (b) K. S. Novoselov, V. I. Fal'ko, L. Colombo, P. R. Gellert, M. G. Schwab, K. Kim, *Nature* **2012**, *490*, 192-200; (c) V. Palermo, *Chem. Commun.* **2013**, *49*, 2848-57.
- [2] A. M. Rodríguez, A. B. Muñoz-García, O. Crescenzi, E. Vázquez, M. Pavone *Phys. Chem. Chem. Phys.*, **2016**, *18*, 22203- 22209.
- [3] D. Tan, et al., *Chem. Commun.*, **2016**, *52*, 7760-7781.

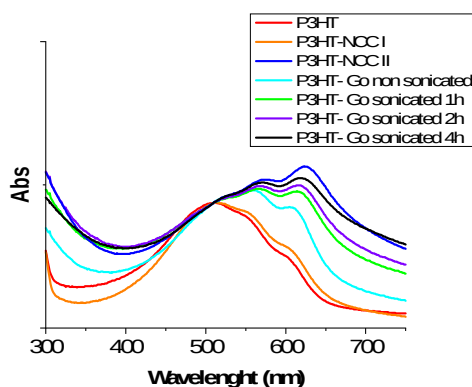
## P3HT aggregation tuned by synergic interaction with different carbon nanostructures

E. Colom, E. Istif, J.M. González-Domínguez, J. Hernández-Ferrer, A.M. Benito, W.K. Maser  
Instituto de Carboquímica, ICB-CSIC, C/ Miguel Luesma Castán, 4. 50018-Zaragoza, Spain  
[ecolom@icb.csic.es](mailto:ecolom@icb.csic.es)

Poly(3-hexylthiophene) (P3HT) is one of the most popular conductive polymers for optoelectronic applications. [1] Their device operation critically depends on the nanocrystalline domain structure, i.e. the aggregate structure acquired by the polymer chains. Most common aggregates' distribution corresponds to H-aggregates, which implies charge transfer across the chains compared to those acquiring a J- aggregate structure with favorable charge transport along the chains. [2]

We recently have shown that strong interactions between P3HT and water-dispersible graphene oxide can be obtained upon the formation of P3HT nanoparticles in aqueous dispersions. [3,4] These interactions enable a significant modification of the internal structure of P3HT aggregates towards a structure predominated by J-aggregates.

Following this approach, in this work we have synthesized P3HT nanoparticles by the re-precipitation method in the presence of various types of water-soluble carbon nanostructures. Under scrutiny are graphene oxide flakes of different sizes, as well as nanocrystalline cellulose of type I and II. Of all the nanostructures exploited, the rarely investigated nanocrystalline cellulose of type II, [5] exhibits significantly enhanced synergetic interface interactions with P3HT nanoparticles. This finding not only reveals a great potential towards improved thin film optoelectronic device structures, but even more underlines value of nanocellulose II for the development of green inks of photoactive polymers, ready to be used for printed electronics.



**Fig.1.** Normalized UV spectra with aggregates formation with different nanostructures.

### References

- [1] Al-Ibrahim, M *et al.* *Solar Energy Materials and Solar Cells* **2005**, *85* (1), 13-20.
- [2] Spano, F *et al.* Expanded Theory of H- and J-Molecular Aggregates: The Effects of Vibronic Coupling and Intermolecular Charge Transfer *Chem. Rev* **2018** *118* (15) 7069-7163.
- [3] Istif, E. *et al.* Conjugated Polymer Nanoparticle–Graphene Oxide Charge-Transfer Complexes. *Advanced Functional Materials* **2018**, *28* (23), 1707548.
- [4] Palacios-Lidón, E. *et al.* Key to electronic interface interactions with graphene oxide as revealed by KPFM. *Nanoscale* **2019**, *11* (23), 11202-11208
- [5] González-Domínguez, J.M. *et al.* Unique properties of non-mercerized type –II cellulose nanocrystals as biocompatible dispersants. *Biomacromolecules* **2019**, *20* (8), 3147-3160

Acknowledgement: Funding by EU (Project H2020-ITN 2014 642742), Spanish MINEICO (Project ENE2016-79282-C5-1-R1 (AEI/FEDER, UE), contract BES2017-080020 including FSE, UE, contract IJCI-2016-27789) and Government of Aragon (DGA-T03-17R and FEDER, UE).

## **The Graphene Technology and Innovation Roadmap**

*Dr. Thomas Reiss, Fraunhofer Institute for Systems and Innovation Research ISI, Karlsruhe, Germany*

Graphene and related 2D materials (GRM) have the potential for enabling innovations in many important sectors of the economy such as energy, communication, machinery, automotive, medical devices, or aerospace. However, bringing a new material to market is challenging, since innovation does not evolve in a vacuum or proceed in a simple linear mode from basic research to applied research, to development, to design, to production until marketing. Innovation processes are characterised by intense interactions and feedbacks between a diverse set of actors and activities; innovation is a systemic process. Therefore, creating an innovation ecosystem and providing holistic innovation support are key factors facilitating the commercialisation of GRM.

A crucial requirement is the identification and characterisation of strategic target areas for GRM enabled innovation via roadmaps. Another important factor is the creation and improvement of trust and confidence in these new materials among end user industries. For that purpose, it is crucial to provide testing and validation services based on state of the art metrology, to develop standards and to communicate the outcomes transparently.

We are elaborating and updating regularly the Technology and Innovation Roadmap (TIR) of the Graphene Flagship. It is based on the insights of scientists and industrial experts on both technological potential and commercialization. Key elements of the roadmapping process are the identification of important market needs, the elaboration of value chains addressing these markets, and the identification of stakeholders from research and industry who are working on different levels of the value chain. Together with these stakeholders, specific value chain roadmaps are elaborated.

The lecture will introduce this approach to a holistic innovation support, provide an overview of markets for GRM, discuss the current version of the TIR and present in more detail selected value-chain roadmaps for promising applications of GRM.

The main conclusion is that GRM will not be used by industry because they hold scientific and technological promises. Rather, GRM need to provide functionalities, which provide solutions to currently unsolved problems. In addition, creating an innovation ecosystem for GRM is crucial.

### **References:**

T. Reiss, K. Hjelt, A.C. Ferrari: Graphene is on track to deliver on its promises. *Nature Nanotechnology* **2019**, DOI: [10.1038/s41565-019-0557-0](https://doi.org/10.1038/s41565-019-0557-0).

## Recent advancements in S/TEM technology: Thermo Scientific Spectra

Daniel G. Stroppa, Thermo Fisher Scientific

Analysis of functional nanomaterials often requires a combination of imaging, spectroscopy and diffraction techniques with high spatial resolution, therefore transmission electron microscopy (TEM) has been a fundamental characterization technique to support materials sciences research and applications. Recent developments significantly enhanced the analysis possibilities of high-end TEM microscopes, making them multifunctional tools that can accommodate a wide range of samples and address their structure, chemical composition and diverse properties at the atomic scale. Though the spatial resolution, stability and ease-of-use have continuously increased in recent years due to multiple advances in TEM hardware and software, challenges related to preparation and damage-free analysis of functional nanomaterials became increasingly evident and constitute a major challenge in the characterization of materials science specimens. This talk will provide an overview of the state-of-the-art technologies developed by Thermo Fisher Scientific to enhance the TEM analysis of beam-sensitive samples. These include improvements on the electron optics to achieve sub-Å resolution with low accelerating voltages down to 30kV and newly developed detectors capable of generating high-contrast and chemical-sensitive images at atomic resolution with beam currents lower than 1 pA.

**Keywords:** TEM, atomic resolution, beam-sensitive samples.



# **POSTER PRESENTATIONS**

## Control of Exciton-Polariton Interactions in Size-Dependent WS<sub>2</sub> Nanotubes

Sudarson. S. Sinha<sup>1</sup>, Alla. Zak<sup>2</sup>, Rita Rosentsveig<sup>1</sup>, Iddo Pinkas<sup>3</sup>, and Reshef Tenne<sup>1\*</sup>, Lena Yadgarov<sup>1</sup>

<sup>1</sup>Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 7610001, Israel

<sup>2</sup>Faculty of Sciences, Holon Institute of Technology, Holon 5810201, Israel

<sup>3</sup>Department of Chemical Research Support, Weizmann Institute of Science, Rehovot 7610001 Israel

\* Presenting Author; [reshef.tenne@weizmann.ac.il](mailto:reshef.tenne@weizmann.ac.il)

### Abstract

Multiwall WS<sub>2</sub> nanotubes (and fullerene-like nanoparticles thereof) are currently synthesized in large amounts, reproducibly. Other than showing interesting mechanical and tribological properties, which offer them myriad of applications, they were recently shown to exhibit remarkable optical and electrical properties, including quasi-1D superconductivity; electroluminescence and a strong bulk photovoltaic effect. Here we show that, using a simple dispersion-fractionation technique, one can control the diameter of the nanotubes and move from pure excitonic to polaritonic features. While nanotubes of average diameter >80 nm can support cavity modes and scatter light effectively via a strong coupling mechanism, the extinction of nanotubes with smaller diameter consists of pure absorption. The experimental work is complemented by finite-difference-time-domain (FDTD) simulations, which shed new light on the cavity mode-exciton interaction in 2D materials. Furthermore, transient absorption experiments of the size-fractionated tubes fully confirm the steady-state observations. Moreover, we show that the tools developed here are useful for size control of the nanotubes, e.g. in manufacturing environment. The tunability of the light-matter interaction of such nanotubes offers them intriguing applications such as polaritonic devices, in photocatalysis and for multi-spectral sensors.

## Development of nanocomposite based graphene/TiO<sub>2</sub> photocatalyst for high photocatalytic degradation of antibiotic drugs

Majid Jahdi<sup>1</sup>, Shivani B. Mishra<sup>1</sup>, Edward N. Nxumalo<sup>1</sup>, Sabelo D. Mhlanga<sup>2</sup>, Ajay K. Mishra<sup>1\*</sup>

1. Nanotechnology and Water Sustainability Research Unit, College of Science, Engineering and Technology, University of South Africa, Florida, 1709, Johannesburg, South Africa
2. DST/Mintek Nanotechnology Innovation Centre, Council for Mineral Technology (MINTEK), Private Bag X3015 Randburg, 2125, South Africa

\*Corresponding author email: mishrak@unisa.ac.za; Tel: +2711 670 9702

### Abstract

The outstanding and promising properties of the nanocomposites based titanium dioxide (TiO<sub>2</sub>) have stimulated a great interest in the design of high-performance photocatalysts that might be integrated in diverse applications including water cleaning. The properties of TiO<sub>2</sub> can be improved by doping its lattice with suitable elements to make an efficient nano-structured photocatalyst that can effectively purify water. On the other hand, graphene oxide with its excellent properties makes it the best candidate to incorporate TiO<sub>2</sub>. Our work focuses on the development of nanocomposites with high photocatalytic activity in the visible and near-infrared regions. Meanwhile, an antibiotic drug is used to evaluate the photocatalytic performance of the synthesized nanocomposites. TiO<sub>2</sub> based nanocomposites were characterized by X-ray diffraction (XRD), ultraviolet-visible (UV-Vis) spectroscopy, scanning electron microscopy (SEM)/energy-dispersive spectroscopy (EDS), and transmission electron microscopy (TEM). The XRD analysis indicated that the crystalline form of the TiO<sub>2</sub> based nanomaterials is a single anatase phase. Moreover, TEM images revealed that the nanoparticles supported on the graphene oxide sheets were almost squares and compressed tetragonal shapes with an average size of 10-20 nm. Doping TiO<sub>2</sub> with metallic and non-metallic ions supported on graphene oxide is an efficient strategy to achieve high photocatalytic activity toward antibiotic drugs under solar light irradiations.

**Key words:** Nanocomposites; Titanium dioxide; Graphene oxide; Doping; Photocatalyst; Antibiotic drugs.

## Exciton Diffusion in hBN-encapsulated Monolayer TMDs

○Takato Hotta<sup>1</sup>, Shohei Higuchi<sup>1</sup>, Yosuke Uchiyama<sup>1</sup>, Ruben Canton-Vitoria<sup>1</sup>, Keiji Ueno<sup>2</sup>, Kenji Watanabe<sup>3</sup>, Takashi Taniguchi<sup>3</sup>, Hisanori Shinohara<sup>1</sup> and Ryo Kitaura<sup>1</sup>

<sup>1</sup> Department of Chemistry, & Institute for Advanced Research, Nagoya University, Nagoya 464-8602, Japan

<sup>2</sup> Department of Chemistry, Saitama University, Saitama 338-8570, Japan

<sup>3</sup> National Institute of Materials Science, Tsukuba 305-0044, Japan

Optical responses from low-dimensional systems, such as transition metal dichalcogenides (TMDs), are dominated by the excitonic effect even at room temperature due to the strong coulomb interaction between electrons and holes. In response to optical excitation of TMDs, a series of responses, including creation, diffusion and radiative recombination of excitons, occurs in the optical excitation of TMDs, and the exciton diffusion is one of the important processes for understanding optical properties of TMDs. However, to investigate intrinsic exciton diffusion in TMDs, extrinsic effects, such as substrate effects, need to be suppressed. In this work, we have conducted systematic investigations of exciton diffusion in hBN-encapsulated monolayer TMDs.

We have fabricated high-quality hBN-encapsulated TMDs with (1) the all-dry transfer method and (2) the dry-transfer combined with nano-squeeze method [1]. In the nano-squeeze method, contaminants between hBN layers and a TMD are removed through sweeping the surface of samples by AFM tip in the contact mode. Fig. 1 shows an optical microscope image of the fabricated hBN-encapsulated monolayer MoS<sub>2</sub>. The monolayer MoS<sub>2</sub> was grown directly onto a hBN substrate, and a hBN flake was transferred on it to form the hBN-encapsulated structure. The Red flame in Fig.1 corresponds to the region treated with the nano-squeeze method, where no bubbles can be seen. Fig. 2 (a) and (b) show an image of excited laser spot and a PL image of excitonic emission of hBN/MoS<sub>2</sub>/hBN, respectively. As clearly seen in the line profile shown in Fig. 2 (c), the PL image is larger than the image of laser, which clearly demonstrates the diffusion of excitons.

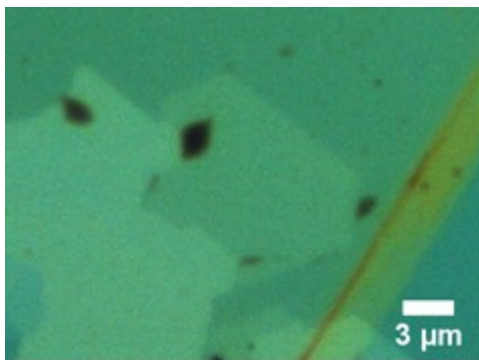


Fig. 1 An optical microscope image of the fabricated hBN/MoS<sub>2</sub>/hBN structure. Red flame corresponds to a region cleaned with AFM.

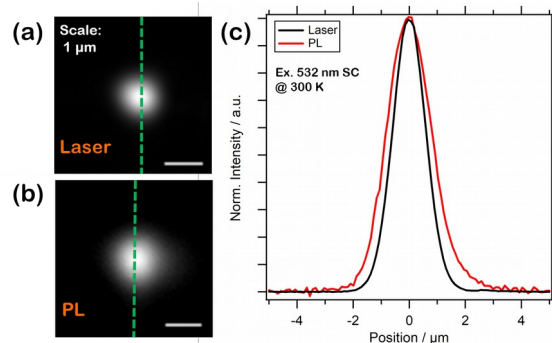


Fig. 2 (a) and (b) Images of excitation laser (532 nm) spot and PL of excitonic emission (1.88 eV) at 300 K. (c) line profiles of laser (black) and PL (red) intensity along green lines in Fig 2 (a) and (b)

[1] M. R. Rosenberger, et. al., ACS Appl. Mater. Interfaces 10, 10379-10387 (2018).

Corresponding Author: R. Kitaura Tel: +81-52-789-3660, Fax: +81-52-747-6442,

E-mail: r.kitaura@nagoya-u.jp

## FUNCTIONALIZING VERTICALLY ALIGNED CARBON NANOTUBES WITH OXYGEN GROUPS THROUGH LOW ENERGY ION IMPLANTATION

Selene Acosta, Chimie des Interactions Plasma-Surface, CIRMAP, University of Mons, 7000 Mons, Belgium.  
+32 489 41 56 68, acostaselene93@gmail.com

Juan Casanova, MINOS Group, Universitat Rovira i Virgili, Tarragona, Spain.

Eduard Llobet, MINOS Group, Universitat Rovira i Virgili, Tarragona, Spain.

Ayrton Sierra, Research Group on Carbon Nanostructures (CARBONNAGE), University of Namur, 5000 Namur, Belgium.

Jean-François Colomer, Research Group on Carbon Nanostructures (CARBONNAGE), University of Namur, 5000 Namur, Belgium.

Mildred Quintana, Centro de Investigación en Ciencias de la Salud y Biomedicina, Universidad Autónoma de San Luis Potosí., San Luis Potosí, México.

Carla Bittencourt, Chimie des Interactions Plasma-Surface, CIRMAP, University of Mons, 7000 Mons, Belgium. Carbon nanotubes (CNTs), due to their unique chemical and electronic properties, are good candidates to be used in electronic devices. CNT properties can be altered and tailored through changes of their surface chemistry by functionalization. Functionalization of CNTs has been achieved via different techniques such as wet chemistry functionalization, surface plasma treatment, simultaneous functionalization during synthesis and ion implantation. In order to obtain an optimal tailoring of the CNT chemical and electronic properties, the functionalization technique used must be fully controlled. In this direction, low kinetic energy ion implantation, unlike to other techniques, is a clean, efficient and site-selective post-growth technique that allows functionalizing with precise ion dose control adjusting the quantity and energy of ions arriving at the sample surface. In addition, this technique has a low impact on the structure of the nanomaterials due to reduced ion back-scattering.

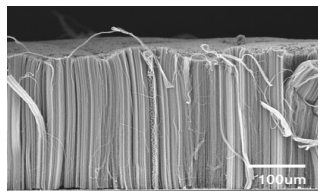


Fig 1. SEM image v-CNTs

In this work, vertically aligned multi-walled carbon nanotubes (v-CNTs) were functionalized with oxygen groups using low kinetic energy ion implantation. We aim at obtaining tailored v-CNTs to be used as an active layer in chemical sensors. Vertically aligned nanotubes were used because they have unidirectional electron transport which facilitates the transducer operation. Besides, their vertical geometry avoids the use of wet-chemistry preventing contamination of the CNTs walls in the engineering of the active layer in the transducer.

v-CNTs were prepared by thermal catalytic chemical vapor deposition (CVD). The v-CNTs functionalization was performed using a Tectra plasma source as ion source. The implantation parameters were: implantation time (1, 2.5, 5 and 10 minutes) and ion energy (0, 0.5, 1, 1.5 and 2 kV). The v-CNT morphology was characterized before and after oxygen ion implantation using scanning electron microscopy (SEM), we observed that the ion implantation does not affect the alignment of v-CNTs. The amount and the chemical bonding configuration of the oxygen atoms at the v-CNT surface were evaluated through X-ray photoelectron spectroscopy. We observed that the oxygen content increases for increasing ion implantation time. When only the ion energy was varied the oxygen content remains constant. The C1s XPS spectra can be reproduced using three components assigned to: epoxy configuration of oxygen (-O-), carbonyl configuration of oxygen (C=O) and carboxyl configuration oxygen (O-C=O) respectively centered at 286.6 eV, 288.3 eV and 289.8 eV of binding energy.

The carbonyl oxo-group due to its reactivity is expected to have an important participation in chemical sensing as well as in further functionalization of the v-CNTs, hence it is important to relate the amount of this oxo-group at the v-CNT surface and the parameters used for ion implantation. We observed that the relative amount of C=O increases from 5 to 12 % as the treatment time increases. On the contrary, when the ion energy is varied: at 0 kV the amount of C=O was 4% and increased to 8 ± 1 % for 0.5, 1, 1.5 and 2 kV. Therefore, changing the ion implantation parameters we can fine-tune the amount of each oxo-groups at the CNT-surface. We will discuss the effect of low kinetic energy oxygen ion functionalization of v-CNTs on the detection of NO<sub>2</sub> and NH<sub>3</sub>.

Bittencourt, C., Navio, C., Nicolay, A., Ruelle, B., Godfroid, T., Snyders, R., ... & Suarez-Martinez, I. (2011). Atomic oxygen functionalization of vertically aligned carbon nanotubes. *The Journal of Physical Chemistry C*, 115(42), 20412-20418.

TECTRA. PLASMA SOURCES. <https://tectra.de/sample-preparation/plasma-sources/>

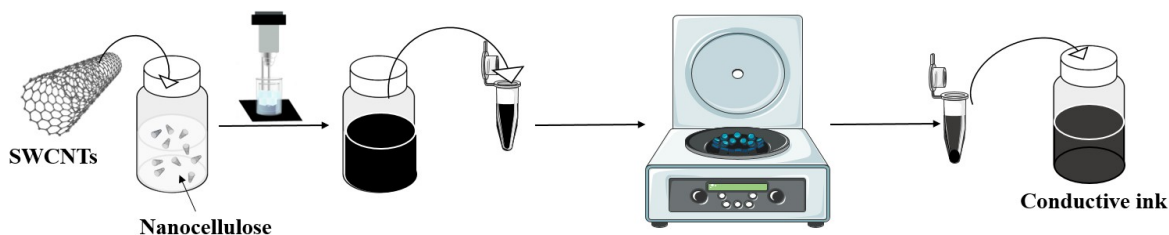
## Fabrication of thin conductive films made up of SWCNT aqueous inks through green approaches.

Miguel A. Álvarez-Sánchez<sup>1</sup>, José Miguel González-Domínguez<sup>1</sup>, Alejandro Ansón-Casaos<sup>1</sup>, Ana M. Benito<sup>1</sup>, Wolfgang K. Maser<sup>1</sup>

<sup>1</sup>Instituto de Carboquímica, CSIC, Miguel Luesma Castán 4, E-50015, Zaragoza, Spain.  
maalvarez@icb.csic.es

Conductive inks development is currently a field of study for electronic applications, including energy devices and sensors, where metal nanoparticles (MNPs) have most commonly been used. However, MNPs present important disadvantages, typically the scarcity of noble metals (Au, Ag, Pt) and the easy oxidation of the rest (Cu, Al). Carbon nanomaterials, such as single-walled carbon nanotubes (SWCNTs), are regarded as an alternative for the fabrication of conductive inks, because of their properties: electronic and thermal conductivity, 1D structure, surface functionalization, and the dispersion in many surfactants and some organic solvents, which are unfortunately highly toxic and unsustainable.<sup>1</sup>

New biofriendly and sustainable dispersing agents are on demand, and also the use of water as the liquid medium for conductive inks. Nanocellulose, an emerging 'green' nanomaterial, possesses many desirable features: hydrophilicity, sustainability, abundance and excellent performance as dispersing agent, which makes it a promising candidate as an alternative to toxic surfactants and hazardous organic solvents.<sup>2</sup> Herein, we report the facile, non-toxic and environmentally friendly fabrication of aqueous and stable conductive inks made up of SWCNTs, using nanocrystalline cellulose as dispersant agent (Figure 1).<sup>3</sup> The conductive ink was deposited by optimized spray coating techniques to fabricate the thin films, which were characterized in terms of electrical properties.



**Figure 1.** Fabrication of conductive inks made up of SWCNTs and Nanocellulose as dispersant agent.

### References

1. K. Pan, et al. *Nature Communications*, 9, 5197 (2018)
2. A. Hajian, et al. *Nano Lett*, 17, 1439-1447 (2017)
3. J. M. González-Domínguez et al. *In revision* (2019)

**Acknowledgements:** Spanish MINEICO (Project ENE2016-79282-C5-1-R, AEI/FEDER, UE) and Government of Aragon (Grupo de Referencia DGA-T03\_17R, FEDER, UE)

# Growth of Transition-metal-dichalcogenide-based two-dimensional superstructures with Cold-walled Metal-Organic CVD

○Satoshi Iida<sup>1</sup>, Takato Hotta<sup>1</sup>, Ruben Canton-Vitoria<sup>1</sup>, Kenji Watanabe<sup>2</sup>, Takashi Taniguchi<sup>2</sup>, Hisanori Shinohara<sup>1</sup>, and Ryo Kitaura<sup>1</sup>

<sup>1</sup>Department of Chemistry, Nagoya University, Nagoya 464-8602, Japan

<sup>2</sup>National Institute for Materials Science, Tsukuba 305-0044, Japan

Since the discovery of graphene, two-dimensional (2D) materials have been attracting considerable attention. Recent research on 2D heterostructures, including heterostacks and heterojunctions, has clearly demonstrated the possibility of emergence of novel properties in these heterostructures<sup>1</sup>. In this work, we have focused on growth of a new type of heterostructure, 2D superlattices (2D-SLs), where periodic junctions of different 2D materials form novel 2D superstructures. To fully explore the possibility of 2D-SLs, development of a highly-controllable crystal growth method is indispensable. For this purpose, we have focused on Metal-Organic Chemical Vapor deposition (MOCVD), in particular, a cold-wall type MOCVD. In this poster, results on MOCVD growth of transition metal dichalcogenides ( $WS_2$  and  $MoS_2$ ) and 2D-SLs composed of  $WS_2$  and  $MoS_2$  are shown.

Figure 1 shows an AFM image of a 2D-SL composed of  $WS_2$  and  $MoS_2$ . For the growth of 2D-SLs, we have developed an automatic valve control system that enables us to perform automatic switch of the source supply. The triangle contrasts correspond to a crystal of 2D-SL, and wide (narrow) contrasts seen in the crystal correspond to  $WS_2$  ( $MoS_2$ ) monolayers: widths of each  $WS_2$  ( $MoS_2$ ) region are 70 (10) nm. Figure 2 is typical Raman and PL spectrum of  $WS_2$ - $MoS_2$  2D-SLs, respectively. These spectra are consistent to the formation of 2D-SLs composed of monolayer  $WS_2$  and  $MoS_2$ . We are, now, working on optimization of growth condition and investigation of atomic structure at interfaces of  $WS_2$  and  $MoS_2$ .

[1] A. K. Geim. *et al.*, Nature **499**, 419-425 (2013).

Corresponding Author: R. Kitaura Tel: +81-52-789-2477, Fax: +81-52-747-6442, E-mail: [r.kitaura@nagoya-u.jp](mailto:r.kitaura@nagoya-u.jp)

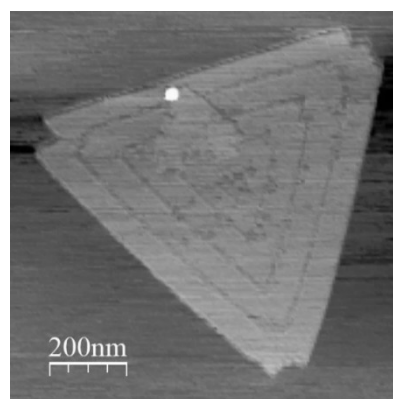


Fig. 1 An AFM image of a  $WS_2$ - $MoS_2$  superlattice

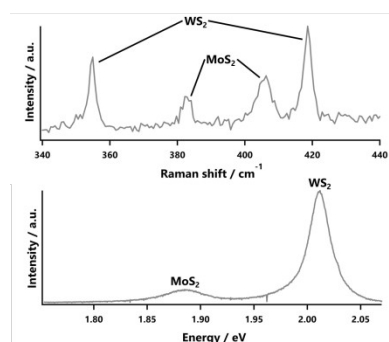


Fig. 2 A typical Raman and PL spectrum of a  $WS_2$ - $MoS_2$  superlattice measured at room temperature.

# Hydrogels with magnetic properties as 3D culture media systems.

Viviana Jehová González<sup>a</sup>, Jesús Herrera<sup>a,b</sup>, M<sup>a</sup> del Pilar Prieto<sup>b</sup>, Ester Vázquez<sup>a,b</sup>.

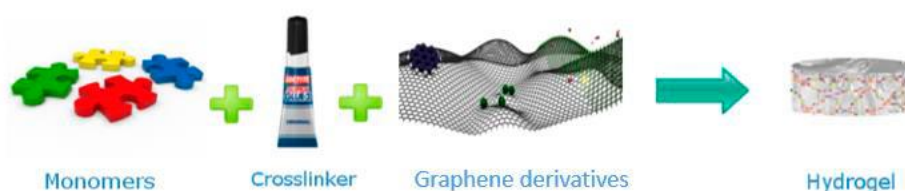
<sup>a</sup> Instituto Regional de Investigación Científica Aplicada (IRICA), UCLM, 13071 Ciudad Real, Spain.

<sup>b</sup> Department of Organic Chemistry, Faculty of Chemical Sciences and Technologies, Castilla-La Mancha University, Camilo José Cela Avenue, S/N, 13071, Ciudad Real, Spain Tel: 926-295300

VivianaJ.Gonzalez@uclm.es, jesus.herrera@uclm.es

**Key Words:** hydrogels • magnetic nanoparticles • graphene • culture media

Hydrogels are physically or chemically crosslinked hydrophilic 3D polymer networks, which absorb and retain large amounts of water, though not soluble in it, with maintenance of shape [1]. Our research group has a large experience synthesizing hydrogels (Figure 1). It is well known that hydrogels can store drugs inside and, depending on the structure and composition, they can deliver the drug in response of a certain stimulus [2]. In this communication, we show the synthesis of hybrid hydrogels prepared in the presence of Co and Fe Nanoparticles and also with Few Layer Graphene (FLG) and Graphene Oxide (GO). These hydrogels will be applied to the design of scaffolds for 3D cell cultures. The presence of nanoparticles makes them sensitive to magnetic stimulus which will be used to deliver grown factors (GF), that are a soluble-secreted signaling polypeptides capable of a wide variety of processes related to migration, proliferation and cellular differentiation. Furthermore, graphene is expected to contribute to the mechanical, electrical and thermal properties, and at the same time, cellular adhesion can be increased.



**Figure 1. Synthesis scheme of a hydrogel.**

## References

[1] Jagur-Grodzinski, J. Polymeric Gels and Hydrogels for biomedical and Pharmaceutical Applications. *Polym. Adv. Technol.* **2010**, *21*, 27-47.

[2] Merino, S.; Martín, C.; Kostarelos, K.; Prato, M.; Vázquez, E. Nanocomposite Hydrogels: 3D Polymer-Nanoparticle Synergies for On-Demand Drug Delivery. *ACS Nano* **2015**, *9*, 5, 4686-4697.



## Optimizing Bacterial Cellulose Production Towards Materials for Water Remediation

Víctor Calvo<sup>1</sup>, Javier Torrubia<sup>2</sup>, Domingo Blanco<sup>2</sup>, Enrique García-Bordeje<sup>1</sup>, Wolfgang K. Maser<sup>1</sup>, Ana M. Benito<sup>1</sup>, Jose M. González-Domínguez<sup>1\*</sup>

- 1) Group of Carbon Nanostructures and Nanotechnology, Instituto de Carboquímica ICB-CSIC, C/Miguel Luesma Castán 4, 50018, Zaragoza, Spain
- 2) Department of Animal Production and Food Science, Veterinary Faculty, Instituto Agroalimentario de Aragón (IA2), C/ Miguel Servet 177, 50013 Zaragoza, Spain

Cellulose is a renewable alternative to mass consumption plastics, but its manufacture by the classical methods is not sustainable due to the use of large amounts of strong acids, bases and/or organic species (e.g. ionic liquids) in its production, generating many residues. Bacterial cellulose (BC) has a simpler processing because it is much more cleanly generated. In this work, BC hydrogels, stemming from *Komagateibacter xylinus* bacteria, has been optimized in terms of bacterial culture and subsequently tailored in their physical properties after drying, giving rise to aerogels and xerogels. These are compared in order to ascertain how the bacterial culture conditions (pH, carbon and nitrogen sources) and the raw hydrogels processing determine their thermal stability, crystallinity index, swelling ratio and flammability. The most notable results are the influence of the drying method on the swelling ratio and the carbon source on the thermal stability. It is possible to control the BC hydrogel properties by rationally selecting the appropriate drying method. In this regard, the aerogels (obtained by lyophilisation) have a much larger sorption capacity and a higher porosity, whereas xerogels (obtained by drying in open air) are more compact, as observed by SEM. Contrary to the aerogels, the BC xerogels are non-flammable. The pH of the culture medium does not have a great influence on the thermal stability of the xerogels and aerogels, but it is important for the hydrogel production rate and slightly influences the CI. The carbon source has a greater influence in the thermal stability of the final materials. Fructose provides a higher thermal stability; however, its dry materials are flammable; glucose and saccharose show an inverse trend as compared to fructose. The advantage of glucose over the fructose and saccharose is its somewhat faster production rate.

Finally, a feasible application of BC aerogels is presented by treating contaminated water and by capturing water within a nonpolar solvent, taking advantage of the dry BC sorption capacity. The accomplishment of a sorption test demonstrates that BC aerogels, once optimized in production and physical properties, can be applied as an efficient sorbent, taking advantage of their porosity and hydrophilic character. There are other possible implementations, such as filters to purify water, with critical implications in human safety and defence against chemical threats.

# Plasmonic Behaviour Of High Aspect Ratio Au Nanostructures Via Low-Loss EELS And NMF

Mario Pelaez-Fernandez<sup>1</sup>, Daniel Funes-Hernando<sup>2</sup>, Jean-Luc Duvail<sup>2</sup>, Raul Arenal<sup>1,3,4</sup>

<sup>1</sup> Laboratorio de Microscopias Avanzadas (LMA), Inst. Nanociencia de Aragon (INA), Univ. Zaragoza, Zaragoza - Spain <sup>2</sup> Institut des Matériaux Jean Rouxel, CNRS – Université de Nantes - France

<sup>3</sup>Instituto de Ciencia de Materiales de Aragón (ICMA), Zaragoza-Spain

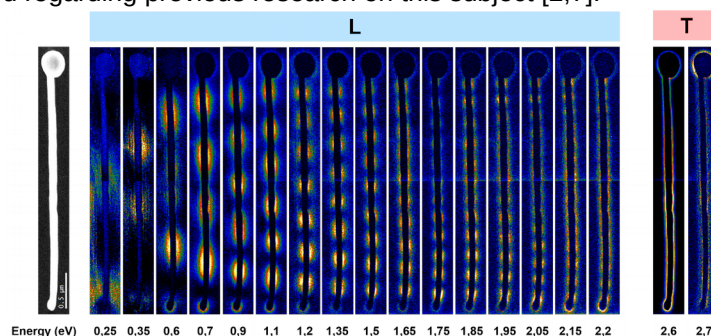
<sup>4</sup>Fundación ARAID, Zaragoza, Spain

mariopf@unizar.es

The field of plasmonics, and especially the plasmonics of metal nanostructures, has been a hot spot in solid state physics for some years now. The interest for these structures comes mainly from their various applications, ranging from devices [1] to Raman resonance-related applications [2]. Electron energy loss spectroscopy (EELS) allows spatial and structural mapping of these nanostructures [3], including but not limited to their plasmonic behavior, and with a resolution going down to the nanometric level, as well as a very high spectral resolution.

The object of our study is the plasmonic behaviour of these high aspect-ratio nanostructures, namely a high aspect-ratio nanowire [5] and a half-dumbbell. As promising as high aspect-ratio nanostructures are for this subject, studying the plasmonic behavior of these nanostructures at the nanoscale using EELS is still very challenging. Due to their high aspect ratio, their plasmonic resonance components are tightly packed in energy [4], which results in a double handicap: on the other hand, the different plasmonic features overlap, greatly difficulting the analysis. On the other hand, these features go down to such low energies it is virtually impossible to find a common area to extract the background from.

By using a custom background removal procedure, as well as Non-negative Matrix Factorisation (NMF) [6] for an optimal decomposition of the different plasmonic features, we can analyse these features accurately and gain a bigger understanding of their properties. Results will be deeply discussed regarding previous research on this subject [2,7].



**Figure 1.** Plasmonic analysis of half-dumbbell system obtained by background extraction and NMF decomposition: from left to right: (i) STEM HAADF image of half-dumbbell. (ii) NMF longitudinal and transversal components corresponding to longitudinal modes in ascending order of resonance energy.

## References

1. A.S.Maier, Plasmonics: Fundamentals and Applications, Springer (2007).
2. L. Billot. et al. Chem. Phys. Let. 422 (2006) 303–307
3. J. Nelayah, et al., Nature Physics, 2007; 3.
- 4 P. Jain, et al., Chem. Phys. Let. 487(2010), 153-164
5. D. Funes-Hernando, et al– Nanoscale, 2018, 10, 6437– 6444
6. O. Nicoletti et al., Nature 502, 80–84 (2013)
7. D. H. Park, et al., Chem. Soc. Rev., 2010, 39, 2439–2452
8. This work was supported by the EU Marie Skłodowska-Curie “Enabling Excellence” project 642742. R.A. gratefully acknowledges the support from the Spanish MINECO through project grant MAT2016-79776-P (AEI/FEDER, UE)

## Quaternary $\text{Ln}_x\text{La}_{(1-x)}\text{S-TaS}_2$ nanotubes (Ln=Pr, Sm, Ho, and Yb) as a vehicle for improving the yield of misfit nanotubes

M. Serra,<sup>1,2</sup> L. Lajaunie,<sup>3,4</sup> M. B. Sreedhara,<sup>1</sup> Y. Miroshnikov,<sup>1</sup> I. Pinkas,<sup>5</sup>, J. J. Calvino,<sup>3,4</sup> A. N. Enyashin<sup>6\*</sup> and R. Tenne<sup>1\*</sup>

<sup>1</sup>Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

<sup>2</sup>Department of Physical Chemistry, Center for Biomedical Research (CINBIO) Universidad de de Vigo, 36310 Vigo, Spain

<sup>3</sup>Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, Campus Río San Pedro S/N, Puerto Real 11510 Cádiz, Spain

<sup>4</sup>Instituto Universitario de Investigación de Microscopía Electrónica y Materiales (IMEYMAT), Facultad de Ciencias, Universidad de Cádiz, Campus Río San Pedro S/N, Puerto Real 11510 Cádiz, Spain

<sup>5</sup>Department of Chemical Research Support, Weizmann Institute of Science, Rehovot 76100, Israel

<sup>6</sup>Institute of Solid State Chemistry UB RAS, 620990 Ekaterinburg, Russian Federation

### Abstract

The non-stoichiometric misfit layered compounds (MLC) of the general formula  $((\text{MX})_{1+y})_m(\text{TX}_2)_n$  (abbreviated herein as MX-TX<sub>2</sub>) have been investigated quite extensively over the last 30 years. Here MX is a monoatomic slab of a material with distorted rocksalt structure and TX<sub>2</sub> is a layered compound with hexagonal (octahedral) coordination between the metal T atom and the chalcogen X atom. Recognizing the mismatch between the two (MX and TX<sub>2</sub>) sublattices, nanotubes from the MLC of different compositions were described in the past. In particular, semimetallic nanotubes belonging to the family LnX-TaX<sub>2</sub> with Ln= rare earth atom and X=S, Se, Te have been studied in the past. While some of them, like LaS-TaS<sub>2</sub> were obtained with moderately high yields, others like YbS-TaS<sub>2</sub> were scarce. In the present study, a new strategy for promoting the yield of such MLC nanotubes by alloying the LaS sublattice with another Ln atom is proposed. Detailed transmission electron microscopy investigation of the (mixed)  $\text{Ln}_x\text{La}_{(1-x)}\text{S-TaS}_2$  (Ln= Pr, Sm, Ho, Yb) nanotubes show clearly that the substituting Ln atom resides in the rocksalt LaS sublattice of the nanotubes. Raman measurements show distinct differences between mixed tubes with open-shell (Pr, Sm, Ho) and close-shell (La, Yb) rare-earth atoms. Density functional calculations show that the interplay between two important factors determine the enhanced stability of the mixed nanotubes- the size and electronic structure of the substituting rare-earth atom. The smaller is the substituting rare-earth atom (larger Z number), the more dissimilar it is to the original La atom. This dissimilarity enhances the incommensurability between the  $\text{Ln}_x\text{La}_{(1-x)}\text{S}$  and the  $\text{TS}_2$  subunits, promoting thereby the stability of the mixed MLC. However, the electronic structure of the Ln atom was found to play a more significant role. The MLC lattice of the LaS-TaS<sub>2</sub> is electron-rich and consequently the  $4d_z^2$  level of Ta is full. The unoccupied  $4f$  levels of the substituent open-shell atoms (Pr, Sm, Ho), which are positioned below the Fermi level, serve as electron acceptors. Consequently, the Ln substitution is found to enhance the stability of the mixed lattice and nanotubes thereof. This strategy can be employed for enhancing the yield of these and other misfit nanotubes using different substituents of the right size and energy profile.

## Reduced graphene oxide aerogels with unidirectional porosity as structured support for electrocatalysis

Clara Carrera, Javier Hernández-Ferrer, José Miguel González-Domínguez, Alejandro Ansón-Casaos, Ana M. Benito, Wolfgang K. Maser, Enrique García-Bordejé.

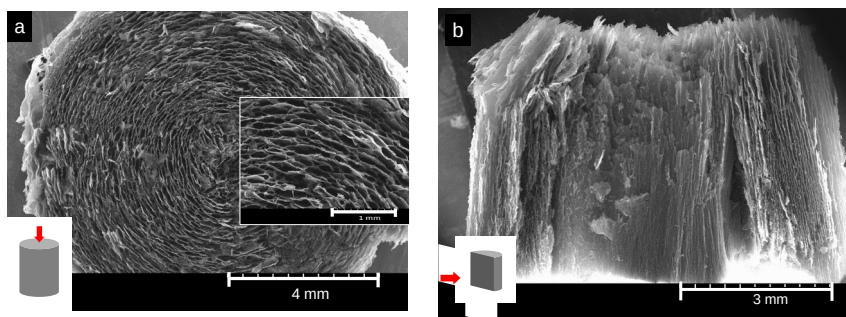
Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán 4, Zaragoza, Spain, +34976733977, [ccarrera@icb.csic.es](mailto:ccarrera@icb.csic.es), [jegarcia@icb.csic.es](mailto:jegarcia@icb.csic.es)

3-D graphene structures have been thoroughly studied in order to translate the properties of individual graphene nanosheets into the macroscale by the assembly of graphene building blocks with control over the porous structure and functionalities. 3D graphene aerogels have some interesting properties such as high specific surface area, open porous network for ion transport, flexibility, tough mechanical strength and conductive framework which lend them high potential for wide application fields such as supercapacitors, oil-water separations, sorbents, chemical reactor and solar cells [1].

One way to prepare 3D aerogels is gelation of GO dispersions under hydrothermal conditions [2]. Upon hydrothermal treatment, the functional groups of GO nanosheets are removed by reduction resulting in a decrease of hydrophilicity and loss of surface charges, which leads to the crosslinking of rGO nanosheets and ultimate phase separation.

Herein, we have achieved a control over the orientation and size of the pores in graphene aerogels as a way of prepare aerogels of unidirectional pores (Figure 1) [3] by modifying the hydrothermal synthesis conditions (pH, time, and freezing method). Moreover, the pH of the initial solution has a profound impact on the reduction degree and morphology of the individual graphene nanoplatelets. [2]

Previously, the group has tested the aerogels for water remediation [2] and as supercapacitors [5]. In this work, the materials have been used as platinum nanoparticles support and tested for hydrogen evolution reaction (HER).



**Figure 1.** Microscopy images of aerogels of unidirectional pores: transversal cut (a) and longitudinal cut (b).

### References

- [1] V. Chabot, D. Higgins, A. Yu, X. Xiao, Z. Chen, J. Zhang, *Ener. Environ. Sci.*, 7, 1564 (2014).
  - [2] E. Garcia-Bordeje, S. Victor-Roman, O. Sanahuja-Parejo, A.M. Benito, W.K. Maser, *Nanoscale*, 10, 3526 (2018).
  - [3] V. Rodríguez-Mata, J.M. González-Domínguez, A.M. Benito, et al., *ACS Applied Nano Materials*, 2, 1210 (2019).
  - [4] Roldan, L.; Benito, A. ; Garcia-Bordeje, E., *J. Materials Chemistry A*, 3, 24379 (2015).
  - [5] V. Rodríguez-Mata, J. Hernández-Ferrer, C. Carrera, A. M. Benito, W. K. Maser and E. García-Bordejé, *Energy Storage Materials*, 2019, in press, DOI: <https://doi.org/10.1016/j.ensm.2019.09.012>.
- Aknowledgements.** MINECO (project ENE2016-79282-C5-1-R, AEI/FEDER, UE)), Gobierno de Aragón (Grupo Reconocido DGA T03\_17R, FEDER, UE)).

## The surface chemistry of graphene oxide: Enhancing the performance of ZnO – GO photocatalysts

S. Victor-Román<sup>1</sup>, E. García-Bordejé<sup>1</sup>, J. Hernández-Ferrer<sup>1</sup>, J.M. González-Domínguez<sup>1</sup>, A. Ansón-Casaos<sup>1</sup>, A.M.T. Silva<sup>2</sup>, W.K. Maser<sup>1</sup>, A.M. Benito<sup>1</sup>

<sup>1</sup>Instituto de Carboquímica (ICB-CSIC), C/Miguel Luesma Castán 4, 50018 Zaragoza, Spain

<sup>2</sup>LSRE-LCM, Faculdade de Engenharia, Universidade do Porto, 4200-465 Porto, Portugal

abenito@icb.csic.es

We demonstrate that the surface chemistry of graphene oxide (GO) is of critical importance for the photocatalytic performance of semiconducting metal oxides such as TiO<sub>2</sub> or ZnO. To this end we employ GO with distinct and well-defined oxidation degree for the preparation of ZnO-GO hybrid materials. We show that the surface chemistry of GO is key for facilitating favorable interface interactions. This results in a lowering of the alignment of energy levels at the ZnO-GO interface and enables the transfer of photo-excited electrons from ZnO to GO. The remaining positive charge at the valence band of ZnO then easily can promote oxidation reactions with the analyte and/or the solvent. In this way, GO reduces the recombination rate of the photogenerated electron-hole pair and enhances the photocatalytic activity of ZnO. We show that by solely controlling the oxidation degree of GO and by optimizing the loading fraction highly efficient ZnO-GO photocatalysts can be prepared. Most favorable conditions are achieved for intermediate oxidation degrees of GO. Optimized ZnO-GO hybrids thus reveal photocatalytic degradation of methylene blue at conversion rates of up to 80%, within times as short as 70 minutes at concentrations as low as 0.045 mg/mL, accompanied by a good recyclability behavior. The results are of general character and extendable to semiconducting metal oxides used in photocatalysis [1].

### References

1. S. Victor-Román, E. García-Bordejé, J. Hernández-Ferrer, J.M. González-Domínguez, A. Ansón-Casaos, A.M.T. Silva, W.K. Maser, A.M. Benito, *Catalysis Today* 2019. DOI: 10.1016/j.cattod.2019.05.049

**Acknowledgements:** Spanish MINEICO (Project ENE2016-79282-C5-1-R, AEI/FEDER, UE and FPI Grant BES2014-068727) and Government of Aragon (DGA-T03-17R, FEDER, UE), is gratefully acknowledged.

## Transmission electron microscopy investigation of graphene oxide flakes

S. Hettler<sup>1</sup>, D. Sebastian<sup>1</sup>, M. Peláez-Fernández<sup>1</sup>, A.M. Benito<sup>2</sup>, W.K. Maser<sup>2</sup>, R. Arenal<sup>1,3,4</sup>

1. Laboratorio de Microscopías Avanzadas, INA-U. Zaragoza, Zaragoza, Spain

2. Instituto de Carboquímica (ICB-CSIC), U. Zaragoza, 50018 Zaragoza, Spain

3. ARAID Foundation, Zaragoza, Spain

4. Instituto de Ciencias de Materiales Aragón, CSIC-U. Zaragoza, 50009 Zaragoza, Spain

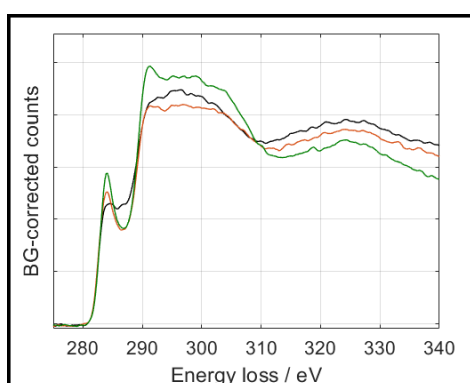
\*E-mail for correspondence: [hettler@unizar.es](mailto:hettler@unizar.es)

**Keywords:** graphene oxide, transmission electron microscopy, electron energy-loss spectroscopy

A significant amount of research has been done on (reduced) graphene oxide ((r)GO) due to its controllable properties and because it is widely used as a starting point for graphene production and functionalization [1]. Although the chemical model of GO is very complex [2], it is well established that its properties are mainly controlled by the different functional groups present, the percentage of incorporated oxygen and the ratio between  $sp^2$  and  $sp^3$ -hybridized C bonds [3].

Here we present our experimental results on transmission electron microscopy (TEM) investigation of GO acquired with an image-corrected FEI Titan<sup>3</sup> operated at 80 kV. Using TEM imaging, electron diffraction and electron energy-loss spectroscopy (EELS), GO can be characterized in detail and properties such as composition, size, thickness or fraction of  $sp^2$ -hybridized C bonds can be determined with high spatial resolution. Three EEL spectra showing the background-corrected C-K edge of different GO flakes are depicted in Figure 1. The C-K edge exhibits a sharp pre-peak at 285 eV, whose intensity corresponds to the fraction of  $sp^2$ -hybridized C bonds, followed by a set of peaks associated to different oxidized functional groups and a broad peak starting at 290 eV. While the black line shows a spectra of a highly oxidized flake (17 %), the red and green curve were obtained from flakes with a low oxygen content.

In summary, TEM-EELS is highly suited for an in-depth analysis of GO. The obtained information on structure, composition and alien material present in the GO allows to better understand the macroscopic properties of GO and its use in applications [4].



**Figure 1.** Comparison of EEL spectra of GO flakes with different ratio between  $sp^2$  and  $sp^3$ -hybridized C bonds.

## References

- 1.- S Mao, H Pu and J Chen, Graphene oxide and its reduction: modeling and experimental progress, *RSC Adv.* **2** 2643–62
- 2.- DW Boukhvalov, M Katsnelson, Modeling of graphite oxide, *J Am Chem Soc* **130** 10697–701 (2009).
- 3.- K Gross et al, Electrical conductivity of oxidized-graphenic nanoplatelets obtained from bamboo: effect of the oxygen content, *Nanotechnology* **27** 365708 (2016).

4 - Research supported by the Spanish MINECO (MAT2016-79776-P, AEI/FEDER, EU), Government of Aragon through project DGA E13\_17R (FEDER, EU) and European Union H2020 programs "ESTEEM3" (823717), Flag-ERA GATES (JTC - PCI2018-093137) and Graphene Flagship (785219).