3rd Edition
SMS
Smart Materials and Surfaces
EUROPE 2017
Conference

EUROPEAN GRAPHENE FORUM
EGF 2017

Smart Materials & Surfaces - SMS EUROPE 2017

European Graphene Forum - EGF 2017

Joint International Conferences

26th - 28th April, 2017

Paris - France

Book of Abstracts

Organizer:

SETCOR
Conferences & Exhibitions

TIME-RESOLVED PROFILOMETER

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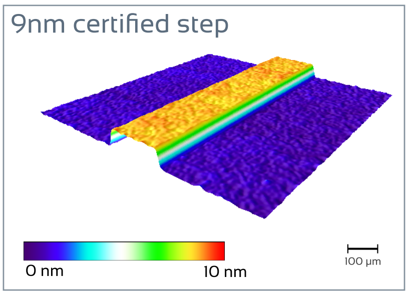
DIGITAL HOLOGRAPHIC MICROSCOPY

Digital Holographic Microscopes (DHM®) are the world fastest 3D optical profilometers.

Time is the 4th dimension of **4D topography**

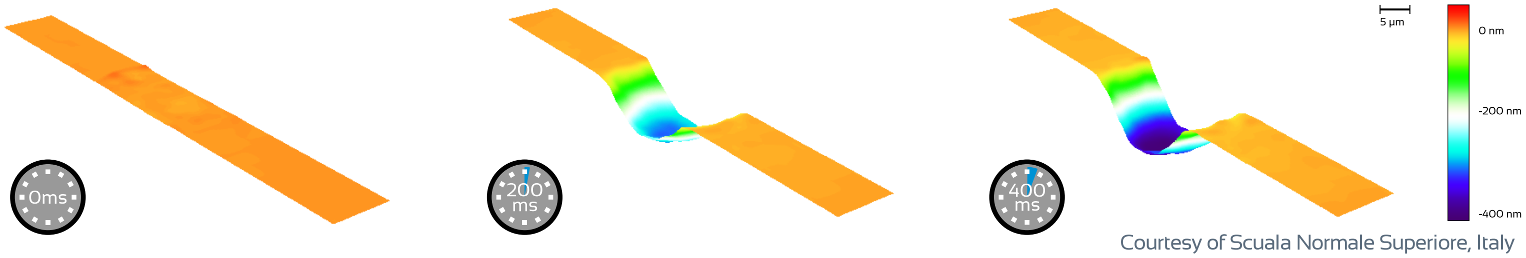
4D MEASUREMENT AT UNRIVALLED SPEED

- Strictly non-scanning acquisition
- 190 frames per second (1000 in option)
- Sub-nanometer vertical resolution



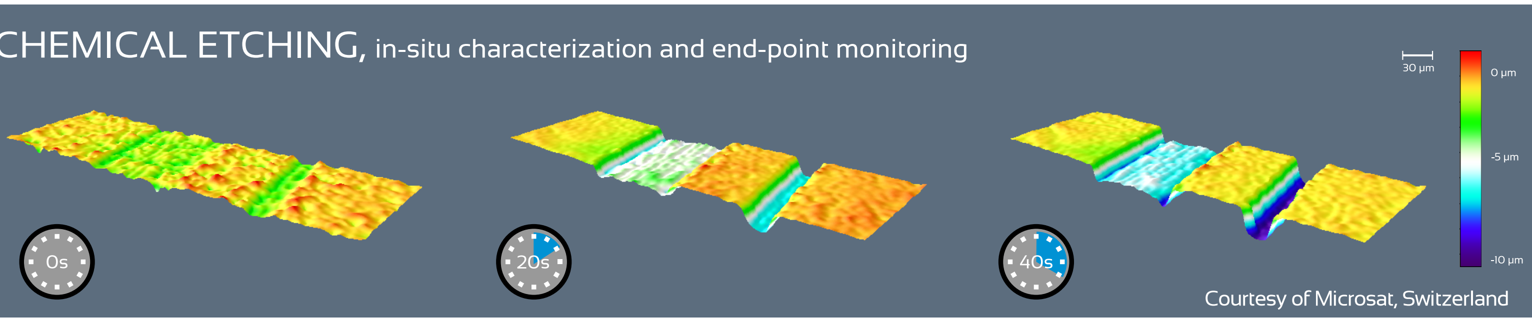
REAL TIME 3D TOPOGRAPHY

GRAPHENE MEMBRANE, mechanical deformation under vacuum



Courtesy of Scuala Normale Superiore, Italy

CHEMICAL ETCHING, in-situ characterization and end-point monitoring



Courtesy of Microsat, Switzerland

CHARACTERIZE SAMPLE CHANGES DUE TO :

- Thermodynamics parameters : pressure, temperature
- Surrounding gas and liquid : deposition, corosion
- Mechanic and electromagnetic forces
- Light irradiance

nature COMMUNICATIONS

New insights into photoactivated volume generation boost
surface morphing in liquid crystal coatings.

Danquing Liu & Dirk J.Broer

USER TESTIMONIAL

> *We are making surface structures that can be switched 'on' and 'off' by external means (at the frequency ranging from several Hertz to hundred Hertz). DHM has the unique possibility to measure real-time 3D topography in a non-contact and non-scanning manner while keeps the vertical resolution to sub-nanometers.*

Danqing Liu, Eindhoven University of technology

DIGITAL HOLOGRAPHIC MICROSCOPY

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European Graphene Forum - EGF 2017
Smart Materials and Surfaces - SMS EUROPE 2017
Joint Conferences Preliminary Program

26 - 28 April, 2017, Paris - France

	April 26th, 2017	
08:00-12:00	**Registration**	**Registration Area**
09:00- 10:30	**Plenary Session I - EGF 2017 / SMS EUROPE 2017**	**Amphitheatre G**
10:30-11:00	**Coffee Break / Poster Session I**	**Main Hall**
11:00-12:30	**Plenary Session I - EGF 2017 / SMS EUROPE 2017**	**Amphitheatre G**
12:00-14:00	**Lunch Break / Poster Session I**	**Restaurant / Main**
14:00-16:00	**SMS 2017 - Session I.A: Smart and functional materials**	**Room 908**
	EGF 2017 - Session I.B: Graphene and 2D Materials- Synthesis and functionalization	**Room 909/910**
	EGF 2017 - Session I.C: Graphene and 2D Materials - Characterization and Properties (Quantum transport, magnetism, spintronic, etc)	**Room 911**
16:00-16:30	**Coffee Break/ Poster Session I**	**Main Hall**
16:30-18:00	**SMS EUROPE 2017 - Session I.A: Smart and functional materials**	**Room 908**
	EGF 2017 - Session I.B: Graphene and 2D Materials- Synthesis and functionalization	**Room 909/910**
	EGF 2017 - Session I.C: Graphene and 2D Materials-Characterization and Properties (Quantum transport, magnetism, spintronic, etc)	**Room 911**
	April 27th, 2017	
09:00-10:30	**Plenary Session II - EGF 2017 / SMS EUROPE 2017**	**Amphitheatre G**
10:30-11:00	**Coffee Break / Poster Session II**	**Main Hall**
11:00-12:30	**Plenary Session II - EGF 2017 / SMS EUROPE 2017**	**Amphitheatre G**
	SMS EUROPE 2017 - Symposium on Functional Hybrid and Composite Materials	**Room 908**
12:00-14:00	**Lunch break / Poster session II**	**Restaurant / Hall**
14:00-16:00	**SMS EUROPE 2017 - Symposium on Functional Hybrid and Composite Materials**	**Room 908**
	SMS EUROPE 2017 - Session II.A: Bioinspired, Biomimetic and Bioactive biomaterials	**Room 909/910**
	EGF 2017 - Session II.B: Graphene and 2D Materials- Energy and environmental applications	**Room 911**
16:00-16:30	**Coffee Break / Poster Session II**	**Main Hall**
16:30-18:00	**SMS EUROPE 2017 - Symposium on Functional Hybrid and Composite Materials**	**Room 908**
	SMS EUROPE 2017 - Session II.A: Bioinspired, Biomimetic and Bioactive biomaterials	**Room 909/910**
	SMS EUROPE 2017 - Session II.C: New Materials for Energy and Environmental Applications	**Room 911**
	April 28th, 2017	
09:00-10:30	**EGF 2017 - Session III: Graphene and 2D Materials-Bioapplications**	**Room 908**
10:30-11:00	**Coffee Break**	**Main Hall**

April 26th, 2017
Plenary Session I: EGF 2017 / SMS EUROPE 2017

Amphitheatre G

Session Chairs:
Prof. Monica Craciun, Centre for Graphene Science, University of Exeter, UK
Prof. Maurizio Prato, University of Trieste, Italy

08:00-12:00 Registration

09:00-09:45	Functionalization and applications of graphene **M.Prato**	**Prof. Maurizio Prato**, University of Trieste, **Italy**
09:45-10:30	2D Nanomaterials: synthesis, processing, upscaling and applications **V. Nicolosi**	**Prof. Valeria Nicolosi,** Trinity college Dublin, **Ireland**

10:30-11:00 Coffee Break / Posters Session I

11:00-11:30	Graphene and Functionalized Graphene for Electronics, Photonics and Optoelectronics E Torres Alonso, I Amit, T. J Octon, N J Townsend, D Wehenkel, S Unal, ...and **M F Craciun**	**Prof. Monica Craciun**, Centre for Graphene Science, University of Exeter, **UK**
11:30-12:00	Competing structural orders at the interface between graphene and its substrate **J. Coraux**	**Dr. Johann Coraux,** Institut Néel, CNRS/ Grenoble Alpes University, **France**
12 :00-12:30	Automotive Structures based Graphene Nanocomposites **A. Elmarakbi**	**Prof. Ahmed Elmarakbi**, Sunderland University, **UK**

12:30-14:00 Lunch Break / Posters Session I

SMS EUROPE 2017 - Session I.A: Smart and functional materials

Conference Room 908

Session Chairs:
Dr. Johannes T. B. Overvelde, FOM Institute AMOLF, Amsterdam, Netherland

14:00-14:30	Rational design of reconfigurable prismatic architected materials **J.T.B. Overvelde**, J.C. Weaver, C. Hoberman and K. Bertoldi	**Dr. Johannes T. B. Overvelde,** FOM Institute AMOLF-Amsterdam, **Netherland**
14:30-15:00	Spatially Localized Self-Assembly Driven by Electrically Charged Phase Separation: Implications to Charged Polymeric Mixtures **A.Yochelis**	**Prof. Arik Yochelis**, Ben-Gurion University of the Negev, **Isreal**
15:00-15:15	Transparent icephobic coatings based on bio-epoxy resin **X.H.Wu** and Z. Chen	**Ms. Xinghua Wu**, Nanyang Technological University, **Singapore**
15:15-15:30	Shape Memory Polymer based 3D Printed Soft Robot for Industrial Applications **Y.S. Kim**, J.Z. Gul, H.B.Kim and K.H. Choi	**Mr. Jahan Zeb Gul**, Jeju National University, **Rep. of Korea**
15:30-15:45	Modeling of the thermo-mechanical behavior of a semi-crystalline thermoplastic shape memory polymer **R. Bouaziz**, F. Roger and K. Prashantha	**Mr. Rami Bouaziz**, Ecole des Mines de Douai, **France**
15:45-16:00	Unravelling the Photoinduced Ligand-to-Cluster Charge Transfer Process in Zr-Based MOFs: Toward better Photocatalysist. **M. Gutiérrez,** B. Cohen, F. Sánchez and A. Douhal	**Mr. Mario Gutiérrez Tovar**, University of Castilla-La Mancha, **Spain**

16:00-16:30 Coffee Break / Posters Session I

16:30-16:45	Untethered Manipulation of Helical Soft Robots **J. J. Wie**, J.E. Park, J. Jeon, J.H. Cho, K.H. Lee, M.R. Shankar and T.J. White	**Prof. Jeong Jae Wie**, Inha University, **Rep. of Korea**
16:45-17:00	Corrosion-Resistant Self-Healing Coatings A. Pastore, S. Dello Iacono, A. Martone and **E. Amendola**	**Dr. Eugenio Amendola**, Institute for Polymers,

		Composites and Biomaterials, CNR, **Italy**
17:00-17:15	Selective metallization of flexible substrates by inkjet printing with electroless copper plating **G. Barral**, N. Hanifi, R.Faddoul and P. Viel	**Mr. Geoffrey Barral**, Paris Saclay University, **France**

April 26th , 2017

EGF 2017 - Session I.B : Graphene and 2D Materials - Synthesis and functionalization

Conference Room 909/910

Session's Chairs:
Dr. Johann Coraux, Institut Néel, CNRS
Grenoble Alpes University, France

14:00-14:30	Graphite-to-Graphene: Total Conversion M. Buzaglo, I. Pri Bar, M. Varenik, L. Shunak, S. Pevzner and **O.Regev**	**Prof. Oren Regev**, Ben-Gurion University of the Negev, **Israel**
14:30-15:00	Impact of substrate on the thermal properties of graphene D. Pinho, **M. J. Pereira**, V. S. Amaral and R. Correia	**Prof. Maria R. Correia**, Aveiro University, **Portugal**
15:00-15:15	Scalable production of 2D materials based Heterostructures through green route **J. Kaur**, A. Vergara, M. Rossi, A. M. Gravagnuolo, M. Valadan, F. Gesuele, P. Giardina and C. Altucci	**Dr. Jasneet Kaur**, University of Naples, **Italy**
15:15-15:30	Interface Reactivity and Catalysis in Graphene on SiC to Unlock Exfoliation Mechanism by Electrochemical Bubbling Method **G. Rius**, E. Prats-Alfonso, R. Villa and P. Godignon	**Dr. Gemma Rius**, Barcelona Microelectronics Institute, **Spain**
15:30-15:45	Electrolytic phototransistor based on graphene-MoS2 van der Waals p-n heterojunction with tunable photoresponse **H.Henck**, D.Pierucci, Z.Ben Aziza, J.Chaste, E.Lhuilier and A.Ouerghi	**Mr. Hugo Henck,** Centre de Nanosciences et de Nanotechnologies (C2N), **France**
15:45-16:00	Position Controlled Nucleation of Single-Crystal Graphene on Cu D. Ding,1 P. Solís-Fernández,2 H. Hibino,3 and H. Ago 1,2*	**Mr Dong Ding**, Kyushu University, **Japan**
16:00-16:30	**Coffee Break / Exhibition / Posters Session I**	
16:30-16:45	Structure of water confined in nanocarbons - pressure enhancement effects **M.Sliwinska-Bartkowiak**, H.Drozdowski, K.Domin, M.Jazdzewska, Y.Long and K.E.Gubbins	**Prof. Malgorzata Sliwinska-Bartkowiak**, A.Mickiewicz University, **Poland**
16:45-17:00	Van der Waals pressure and its effect on trapped interlayer molecules **K. S. Vasu**, E. Prestat, J. Abraham, S. J. Haigh, A. K. Geim and R. R. Nair	**Dr. Vasu Siddeswara Kalangi**, University of Manchester, **UK**.
17:00-17:15	Large-Area 2D-0D Heterostructures via Langmuir-Blodgett Film Deposition **A. Black**, J. Roberts, M. Acebrón, R. Bernardo-Gavito, G. Alsharif, F. J. Urbanos, B. H. Juárez, D. Granados, B. J. Robinson, A.L. Vázquez de Parga and R. J. Young	**Mr. Andres Black**, Universidad Autonoma de Madrid, **Spain**
17:15-17:30	Tuneable Sieving of Ions Using Graphene Oxide Membranes **J. Abraham**, K. S. Vasu, A. K. Geim and R. R. Nair	**Mr. Jijo Abraham**, University of Manchester, **UK**
17:30-17:45	Comparison of green reductants for graphene fabrication via liquid chemical exfoliation process **V. Khranovskyy**, I. Shtepliuk, I.Wlasny, P. Kazmierczak, A. Wysmolek, Z. Klusek, K. Shavanova, Y.Ruban, A. Tencha and R. Yakimova	**Dr. Volodymyr Khranovskyy**, Linköping University, **Sweden**
17:45-18:00	Hydrogenation and fluorination of graphene via plasma: a possible route to open the gap **G. V. Bianco**, M. Losurdo, M.M. Giangregorio, A. Sacchetti, G. Pace, P. Capezzuto, and G. Bruno.	**Dr. Giuseppe Valerio Bianco**, Institute of Nanotechnology/ CNR-NANOTEC, **Italy**
18:00-18:15	Graphene-doped TiO2 nanotube composite for organic degradation under visible light S-R. Kim, **I.Ali**, K.Park and J-O. Kim	**Mr. Imran Ali**, Hanyang University, **Rep.of Korea**

18:15-18:30	A Novel Pt Nanoparticles Deposited and Tannic Acid-Reduced Graphene Oxide Nanocomposite for Glucose Oxidase Immobilization and its Application for Glucose Sensing Based on Direct Electrochemistry **B. Çakiroglu** and M. Özacar	**Mr Bekir Çakiroglu**, Sakarya University, **Turkey**
18:30-18:45	Direct growth of vertically oriented graphene nanowalls on multiple substrates by Low Temperature Plasma-Enhanced Chemical Vapor Deposition **A. Musheghyan-Avetisyan**, J. Marti-Gonzalez and E. Bertran-Serra	**Mrs. Arevik Musheghyan-Avetisyan**, Barcelone University, **Spain**

April 26th , 2017

EGF 2017 - Session I.C: Graphene and 2D Materials- Characterisation and Properties (Quantum transport, magnetism, spintronics, etc)

Conference Room 911

Session's Chairs:
Prof. Ahmed Elmarakbi, University of Sunderland, UK

14:00-14:15	Spectroscopic investigation of Ar/H2/CH4 induction thermal plasma for understanding synthesis of graphene nano-flakes **A. Mohanta**, B. Lanfant, M. Asfaha and M. Leparoux	**Dr. Antaryami Mohanta**, EMPA-Swiss, **Switzerland**
14:15-14:30	Surface-enhanced Raman Scattering Activities of Two Typies of Graphene/Ag Nanoparticls Hybrids **J. Zhang**, X.Y. Wang, T.C. Gong, J.M.Quan and Y.Zhu	**Prof. Jie Zhang**, Chong Qing University, **China**
14:30-14:45	Optical Characterization of Epitaxial Graphene with Confocal Laser Scanning Microscopy **R.E. Elmquist**, Y. Yang, V. Panchal, C-I. Liu, A. Rigosi and H-Y. Lee	**Dr. Rand Elmquist**, NIST, **USA**
14:45-15:00	Scanning photoemission imaging and spectromicroscopy: a powerfull tool to chemically characterize free standing graphene at the micro- and nano-scale **M. Amati**, H. Sezen and L. Gregoratti	**Dr. Matteo Amati**, Elettra - Soncrotrone Trieste S.C.p.A, **Italy**
15:00-15:15	Study on Thermal Stability of Multilayer Graphene with Metal Nanoparticle by Rapid Thermal Treatment in Oxygen Ambient **J.W. Lee**, S.W. Kim, Y.Il. Song and S.J. Suh	**Mr. Jung Woo Lee**, Sungkyunkwan University, **Rep. of Korea**
15:15-15:45	Graphene and Carbon related Materials: Photonics and Optoelectronics Applications **D-J. Liaw**, C-Y. Tsai, Q. Zhang, Y-C. Huang and Y-Z. Wang	**Prof. Der-Jang Liaw**, National Taiwan University of S&T, **Taiwan**
15:45-16:00	Use of moiré pattern from epitaxially grown graphene on Ir(111): Organization and magnetic properties of FePt nanoparticles **P. Capiod**, F .Tournus, L. Bardotti, G. Renaud and V. Dupuis	**Dr. Pierre Capiod**, Université Claude Bernard Lyon1, **France**
16:15-16:30	**Coffee Break / Exhibition / Posters Session I**	
16:30-16:45	Rise of Periodic Potentials in Hybrid van der Waals Heterostructures Formed by Supramolecular Lattices on Graphene **E. Orgiu**	**Dr. Marco Gobbi**, CNRS-Strasbourg University, France
16:45-17:00	Conductive Lightweight Composites of Polyetherimide with Graphene Nanoplatelets-Carbon Nanotube Hybrids H. Abbasi, **M. Antunes** and J.I. Velasco	**Dr. Marcelo Antunes**, UPC-Barcelona Tech, **Spain**
17:00-17:15	Precise electronic and valleytronic nanodevices based on strain engineering in graphene **N. Szpak** and T. Stegmann	**Dr. Nikodem Szpak,** University of Duisburg-Essen, Duisburg, **Germany**
17:15-17:30	Graphene and graphene-based composite materials for energy storage and thermal interfacing **X.W. Yuan** and S.L. Bai	**Dr. Xiaowen Yuan**, Massey University, **New Zealand**
17:30-17:45	Mechanical properties of Fe filled carbon nanotubes:a molecular dynamics approach **M. Kiwi**, V. Munizaga, R. Ramírez and G.García	**Prof. Miguel Kiwi**, Chile University, **Chile**
17:45-18:00	Gate tuneability of helicity dependent photocurrent in ABA- and ABC-stacked trilayer graphene **M. Eginligil**	**Prof. Mustafa Eginligil**, Nanjing Tech University, **China**

April 27th, 2017
Plenary Session II: EGF 2017 / SMS EUROPE 2017

Amphitheatre G

Session Chairs:
Prof. Eduardo Ruiz-Hitzky, Instituto de Ciencia de Materiales de Madrid, CSIC, Spain
Prof. Vladimir Falko, Manchester University, United Kingdom

09:00-09:45	New 2D semiconductor: atomically thin crystals of InSe **V. Falko**	**Prof. Vladimir Falko**, Manchester University, **United Kingdom**
09:45-10:30	Inorganic and hybrid nanomaterials: Integrative Approaches **C.Sanchez**	**Prof. Clément Sanchez,** University of Pierre and Marie Curie, Collège de France, CNRS, **France**
10:30-11:00	**Coffee Break / Posters Session II**	
11:00-11:30	2D dichalcogenide electronic materials and devices **A. Kis**	**Prof. Andras Kis**, EPFL-Lausanne, **Switzerland**
11:30-12:00	Advanced spintronics in graphene-Van der Waals heterostructures **B. van Wees**	**Prof. Bart Van Wees**, University of Groningen, **The Netherland**
12:00-12:30	2D materials and hybrids for novel photonic devices **G. Eda**	**Prof. Goki Eda**, University of Singapore, **Singapore**
12:30-13:00	Graphene MMICs for high data-rate communication **O. Habibpour**, N. Rorsman and H. Zirath	**Dr. Omid Habibpour**, Chalmers University, **Sweden**
12:30-14:00	**Lunch Break / Posters Session II**	

April 27th, 2017
SMS EUROPE 2017 - Session II.A: Bioinspired, Biomimetic and Bioactive biomaterials

Conference Room 909/910

Session Chairs:
Prof. Ester Vazquez, University of Castilla-la Mancha (UCLM), Spain
Prof. Maurizio Prato, University of Trieste, Italy

14:00-14:45	Graphene for Bioapplications: Preparation, Cytotoxicity and Integration in 3D-scaffolds **E. Vazquez**	**Prof. Ester Vazquez**, University of Castilla-la Mancha (UCLM), **Spain**
14:45-15:30	Development of Lipid Bilayer Platforms for Processing Cell Membrane Species **L. Chao**	**Prof. Ling Chao** National Taiwan University, **Taiwan**
15:30-15:45	Novel, precise approach in the research on biodistribution of ZnO-based nanoparticles **P. Kielbik**, J. Kaszewski, B. Dominiak, E. Wolska, M. A. Gralak , Z. Gajewski, M. Godlewski and M. M. Godlewski	**Ms. Paula Kielbik**, Warsaw University of Life Sciences – SGGW, **Poland**
15:45-16:00	Uptake and Release of Dyes for Photodynamic Therapy from Hy-drogels **S. Glass**, A. Schulze and B. Abel	**Ms. Sarah Glass**, Leibniz Institute for Surface Modification, **Germany**
16:00-16:30	**Coffee Break / Posters Session II**	
16:30-16:45	Wide Band-Gap Oxides Nanoparticles as Drug Carriers **W. Lipinski**, J. Kaszewski, Z. Gajewski, M. Godlewski and M. M. Godlewski	**Mr. Waldemar Lipinski**, Warsaw University of Life Sciences – SGGW, **Poland**
16:45-17:00	High-k Oxide Nanolayers for Biomedical Applications **I. Serafińska**, J. Kaszewski, R. Pietruszka, J. Cymerys, Z. Gajewski, M. Godlewski and M. M. Godlewski	**Ms. Izabela Serafinska**, Warsaw University of Life Sciences – SGGW, **Poland**
17:00-17:15	In-vivo analyses of the nanoparticle distribution by magnetic resonance **J. Olszewski**, K. Lorenc, K. Skierbiszewska, K. Siewruk, Z. Gajewski, M. Godlewski, J. Kaszewski and M. M. Godlewski	**Mr. Jarosław Olszewski,** Warsaw University of Life Sciences – SGGW, **Poland**

April 27th, 2017

SMS EUROPE 2017 - Symposium on Functional Hybrid and Composite Materials

Conference Room 908

Session Chairs:
Prof. Eduardo Ruiz-Hitzky, Instituto de Ciencia de Materiales de Madrid, CSIC, Spain
Dr. Francisco M. Fernandes, Pierre et Marie Curie University, France
Dr. Pilar Aranda, Instituto de Ciencia de Materiales de Madrid, CSIC, Spain

10:30-11:00	**Coffee Break / Posters Session II**	
11:00-11:30	Processing and fine characterization of nanoporous hybrid thin films and membranes **A. Ayral**	**Prof. Andre Ayral,** Institut Europeen des Membranes, Montpellier university, **France**
11:30-12:00	In-situ spectroscopic elipsometry for the fast development of functional thin films **C. Boissière**	**Prof. Cédric Boissière,** University Pierre et Marie Curie, CNRS, **France**
12 :00-12 :15	Deposition of Nanoporous Silica Layer on Particle Surface S. Bureekaew and **M. Ogawa**	**Prof. Makoto Ogawa,** Vidyasirimedhi Institute of Science and Technology, **Thailand**
12:15- 12:30	Synthesis, Mechanism and Functionalization of Bimodal Silica of SBA-15 Type **Y. Shchipunov**	**Prof. Yury Shchipunov**, Russian Academy of Sciences- Vladivostok, **Russia**
12:30-14:00	**Lunch Break / Posters Session II**	
14:00-14:30	Hybrid Biomaterials for Medicinal Applications **T. Weil**	**Prof. Tanja Weil**, Max Planck Institute for Polymer Research, **Germany**
14:30-15:00	Fabrication of 3D structured hybrid materials with nano second pulsed technology **T. Nakayama**	**Prof. Tadachika Nakayama,** Nagaoka University of Technology, **Japan**
15:00-15:15	Green foams based on clay-bionanocomposite materials M. Darder, B. Wicklein, F.M. Fernandes, A.C.S. Alcântara, R. F. Gouveia, P. Aranda, **E. Ruiz-Hitzky**	**Prof. Eduardo Ruiz-Hitzky,** Instituto de Ciencia de Materiales de Madrid, CSIC, **Spain**
15:15-15:30	Freeze casting hybrid living materials S. Christoph, T. Coradin and **F.M. Fernandes**	**Dr. Francisco M. Fernandes**, Pierre et Marie Curie University, **France**
15:30-15:45	Hybrid Layered Double Hydroxide/Sepiolite Heterostructures for Controlled Release Applications E.P. Rebitski, M. Darder, E. Ruiz-Hitzky, **P. Aranda**	**Dr. Pilar Aranda**, Instituto de Ciencia de Materiales de Madrid, CSIC, **Spain**
15:45-16:00	Chiral molecules based nano spintronics devices **S. Yochelis** and Y. Paltiel	**Dr. Shira Yochelis**, The Hebrew University of Jerusalem, **Isreal**
16:00-16:30	**Coffee Break / Posters Session II**	
16:30-17:00	Multimodal Metal Oxide Nanoparticles and their bio-interactions M. Lavenas, M. Simon, H. Seznec, J. Rocha, L.D. Carlos and **M-H. Delville**	**Dr. Marie-Helene Delville,** Bordeaux University, **France**
17:00-17:30	Multifunctional superstructures by hybridization of 2D solids Q. Evrard, G. Rogez and **P. Rabu**	**Prof. Pierre Rabu, CNRS** - IPCM of Strasbourg, **France**
17:30-17:45	Fluorescence emission properties of a neutral porphyrin loaded into a layered inorganic-organic monolith **K. Fujii**, J.P. Hill, H. Hashizume, S. Shimomura, K. Ariga and T. Ando	**Dr. Kazuko Fujii**, National Institute for Materials Science (NIMS), **Japan**
17:45-18:00	Synthesis of Manganese-Based Metal-Organic Frameworks **W.Tranganphaibul** and S. Bureekaew	**Ms. Wararat Tranganphaibul**, Vidyasirimedhi Institute of

		Science and Technology, **Thailand**
18:00-18:15	Crystal Engineering of Bimetallic Metal-Organic Frameworks based on MIL-101 **T. Tanasaro** and S. Bureekaew	**Ms. Thanadporn Tanasaro**, Vidyasirimedhi Institute of Science and Technology, **Thailand**
18:15-18:30	Brønsted Acid-Base Bifunctional Zr-Based Metal-Organic Framework **W. Pratanpornlerd** and S. Bureekaew	**Mr. Warat Pratanpornlerd**, Vidyasirimedhi Institute of Science and Technology, **Thailand**

April 27th , 2017
EGF 2017 - Session II.B: Graphene and 2D Materials- Energy and environmental applications

Conference Room 911

Session's Chairs:
Prof. Ahmed Elmarakbi, University of Sunderland, UK/ Prof. Maria R. Correia, University of Aveiro, Portugal

14:00-14:15	Binder-free metal loaded graphene aerogel for electro-oxidation of alcoholic fuels from a one-step, mild, and green preparation **C. H. A. Tsang** and D. Y. C. Leung	**Dr. Chi Him Alpha Tsang,** The University of Hong Kong, **Hong Kong**
14:15-14:30	Graphene/Fe3O4 Nanocomposite: Interplay between photo-Fenton type reaction, and carbon purity for the removal of methyl orange **A. Arshad** and J. Iqbal	**Ms. Aqsa Arshad**, International Islamic University, **Pakistan**
14:30-14:45	Development of graphene-modified yarns and woven fabrics for next-generation textiles **B. Weise**, G. Köppe, L. Völkel, G. Seide and M. Morgenstern	**Mr. Benjamin Weise**, RWTH Aachen, **Germany**
14:45-15:00	Influence of Dopant and Oxidant on the Electrochemical Properties of GNP/PANI Composites X. Zhao, **J. Pionteck** and O. Grätz	**Dr. Jürgen Pionteck**, Leibniz Institute of Polymer Research Dresden, **Germany**
15:00-15:15	Organic photovoltaic cells and modules with functionalized CVD-graphene as highly transparent conductive electrodes **L.La Notte**, E. Villari, A.L. Palma, A.Sacchetti, M.M. Giangregorio, G. Bruno, A. Di Carlo, G.V. Bianco and A. Reale	**Dr. Luca La Notte**, CHOSE - University of Rome Tor Vergata, **Italy**
15:15-15:30	Mass Transport Through 2D Materials Based Membranes **Y.Su** and R.R Nair	**Dr. Yang Su**, University of Manchester, **UK**
15:30-15:45	CO adsorption on graphene: A theoretical approach J. Wilson, **N. Faginas-Lago**, J. Vekeman, I.G. Cuesta, J. Sánchez-Marín and A. Sánchez de Merás	**Dr. M. Noelia Faginas Lago**, University of Perugia, **Italy**
15:45-16:00	Graphene-based batteries to improve the efficiency of the existing technologies G.T. Raquel, H. Martínez David and G. Bermúdez Lucia	**Dr. Raquel Gonzalez**, GrapheneTech S.L, **Spain**
16:15-16:30	**Coffee Break / Exhibition / Posters Session I**	

April 27th, 2017
SMS EUROPE 2017 - Session II.C: New Materials for Energy and Environmental Applications

Conference Room 911

16:30-17:00	2-Dimensional Electron Gases at Oxide Interfaces **F. Miletto Granozio**	**Dr. Fabio Miletto Granozio**, CNR-SPIN Unit of Naples, **Italy**
17:00-17:15	Preparation and characterization of Soundproofing PVP/Graphene electrospun mats **G.R.Del Sorbo**, G.Petrone, G.Tomaiuolo, A.Vergara, G.Ausanio, S.Guido, F.Marulo and F.Branda	**Dr Giuseppe R. Del Sorbo**, University Federico II of Naples, **Italy**
17:15-17:30	Comparison between flexible PZT and BTO piezoelectric films for mechanical energy harvesting **R. Seveno**, T. Dufay, B. Guiffard	**Dr. Raynald Seveno**, Bretagne Loire University, **France**

17:30-17:45	First-principles study of the transport properties in bulk and monolayer MX3 (M = Ti, Zr, Hf and X = S, Se) compounds **Y. Saeed**, A.Kachmar, and M.A. Carignano	**Dr. Yasir Saeed**, Hamad Bin Khalifa University (HBKU), **Qatar**
17:15-17:30	Enhancing CO2 adsorption of metal–organic activated carbon through APTES grafting and Co-NPs incorporation **N. Bouazizi** ,R. Bargougui, J. Vieillard, N. Mofaddel, O. Thoumire, G. Ladam, N. Brun, P. Fotsing, E. Djoufac Woumfo and F. Le Derf	**Mr. Bouazizi Nabil**, University of Rouen, **France**
17:30-17:45	Heteroatom doped graphene-semiconductor composites for CO2 photoreduction: Influence of sulfur and nitrogen species **L.M. Pastrana-Martinez**, M. Pedrosa, J.L. Figueiredo, J.L. Faria and A.M.T. Silva	**Dr. Luisa M Pastrana Martinez**, University of Porto, **Portugal**

April 28th , 2017

EGF 2017 - Session III: Graphene and 2D Materials- Bioapplications

Conference Room 908

Session's Chairs:

Prof. Ling Chao, National Taiwan University, Taiwan

09:00-09:15	Impact of Covalent Functionalization on the Aqueous Processability, Catalytic Activity, and Biocompatibility of Chemically Exfoliated MoS2 Nanosheets J.I. Paredes, **J.M. Munuera**, S. Villar-Rodil, L. Guardia, M. Ayán-Varela, A. Pagán, S.D. Aznar-Cervantes, J.L. Cenis, A. Martínez-Alonso and J;M. D. Tascón	**Mr. Jose Munuera**, INCAR-CSIC, **Spain**
09:15-09:30	Graphene oxide is trapped and degraded by primary human neutrophils and the degradation products are non-genotoxic **S.P. Mukherjee**, B. Lazzaretto, K. Bhattacharya, A. Gliga, B. Brandner, M. Fielden, A. Star, N. Lozano, K. Kostarelos and B. Fadeel	**Dr. Sourav Pr. Mukherjee**, Karolinska Institute, **Sweden**
09:30-09:45	Graphene Field-Effect Transistors for Biomedical Applications R. Campos, E. Fernandes, G. Machado Jr., P.D. Cabral, M.F. Cerqueira, J. Borme and **P. Alpuim**	**Dr. Pedro Alpuim**, INL - International Iberian Nanotechnology Laboratory, **Portugal**
09:45-10:00	Biocompatibility of silicone rubber/graphene-nanoplatelets composites with improved mechanical properties **A.Pinto**, S. Creason, Z. Wescoe, L. Zhen, R. Khalifehzadeh, M. Mecwan, C. Winston, F. Magalhães, I. Gonçalves and B. Ratner	**Mr. Artur M. Pinto**, University of Porto, **Portugal**
10:00-10:15	Mesenchymal stem cells coated with graphene oxide loaded with drugs for cancer therapy **S.Suryaprakash** and K.Leong	**Ms. Smruthi Suryaprakash**, Columbia University, **USA**
10:15-10:30	Copper Hydroxide Flower like Nanostructured decorated on Three Dimensional Graphene As Non-enzymatic Electrochemical Glucose Sensor **I. Shackery** and S. C. Jun	**Mr. Iman Shackery**, Yonsei University, **Rep. of Korea**
10:30-11:00	**Coffee Break**	

Posters Sessions

April 26th, 2017
Poster Session I: SMS EUROPE 2017

Main Hall

N.	Poster Title	Author/Affiliation/Country
1	Structural and Optical Properties of CuInS2 Nano-particles on TiO2 by Spray Pyrolysis **H-S. Jung** and G-C. Park	**Ms. Hyunsu Jung**, Mokpo National University, **Rep.of Korea**
2	Magnetically Active Helical Soft Robots **J. Jeon**, J. E. Park, J. H. Cho, K. H. Lee, J. J. Wie	**Mr. Jisoo Jeon**, Inha University, **Rep. of Korea**
3	Lattice Defects-Driven Magnetic Transformations in BiFeO3-Based Multiferroics **U. Khomchanka** and J. A. Paixão	**Dr. Uladzimir Khomchanka**, University of Coimbra, **Portugal**
4	Permanent Memory Effect of PDLCs devices: Effect of Glass Transition Temperature **A. Mouquinho** and J. Sotomayor	**Mrs. Ana Mouquinho**, NOVA University of Lisbon, **Portugal**
5	Development of a polymer-metal composite for dynamic-mask microstereolithography **B.Khatri**, A.Bhat and T. Hanemann	**Mr. Bilal Khatri**, IMTEK - University of Freiburg, **Germany**

April 26th, 2017
Posters Session I: EGF 2017

Main Hall

N.	Title	Author/Affiliation/Country
6.	Functionalization of graphene oxide with tetraethylene-pentamine (TEPA): CO2 capture application. **M.González-Barriuso**, C. Pesquera, F.González1, Á.Yedra and C.Blanco	**Mrs. Marina González-Barriuso**, Technological Centre of Components Foundation**, Spain**
7.	Growth of MoxW1-xSe2 Film with Tunable Band Gap via Metal-Organic Chemical Vapor Deposition **L. Yoo Been** and L. Jin Seok	**Ms. Yoo Been Lee**, Sookmyung Women’s University, **Rep. of Korea**
8.	Molecular Layer Deposition of Hybrid Organic-Inorganic Alucone Films Using Organic Precursors with Different Carbon Bond Order **U-J. Choi** and J.S. Lee	**Ms. Ui Jin Choi**, Sookmyung Women’s University, **Rep. of Korea**
9.	A New Approach to Graphene Manufacturing for Solid State Devices and Compound Heterostructure Applications S. Thomas, **I. Guiney** and C. Humphreys	**Dr. Ivor Guiney**, 2D Technologies Ltd.-Cambridge, **UK**
10.	Functionalization of reduced graphene oxide suspension by submerged plasma jet. **S. Vizireanu**, M.D. Ionita, S. D. Stoica, L. Carpen, M. Teodorescu, I. Ion, M. Ionita and G. Dinescu	**Dr. Sorin Vizireanu**, National Institute for Lasers, Plasma and Radiation Physics, **Romania**
11.	Role of hydrogen plasma post-treatment: etching behavior of vertically aligned graphene nano wall by electron cyclotron resonance plasma **J-H. Shin**, H.J. Park, Y-H. Jung, Y-S. Choi, Y.Il. Song and S.J. Suh	**Mr. Jin-ha Shin**, Sungkyunkwan University, **Rep.of Korea**
12.	Potentials for CH_4, H_2O, CO_2, N_2 and H_2 adsorption on graphene **J. Vekeman**, J. Wilson, I. Garcia Cuesta, N. Faginas Lago, J. Sánchez Marin and A. M. Sánchez de Merás	**Mr. Jelle Vekeman**, València University, **Spain.**
13.	TiO2-GO and TiO2-rGO Nanocomposites: Investigation on Structure, Morphology, Spectroscopic and Magnetic Studies **E. Kusiak-Nejman**, D. Moszyński, A. Wanag, J. Kapica-Kozar, Ł. Kowalczyk, R.J. Wróbel, A.W. Morawski and N. Guskos	**Dr. Ewelina Kusiak-Nejman**, West Pomeranian University of Technology, **Poland**
14.	XPS analyses of as-rubbed mono- and few layer graphene films obtained by the substrates rubbing method G. Shmavonyan, K. Hricovini, O. Heckmann, E. Boiakinov, W. Ndiaye, S. Vaiedelich and **M. C. Richter**	**Prof. Christine Richter**, Cergy-Pontoise University, **France**

April 27th, 2017
Poster Session II: SMS EUROPE 2017

Main Hall

N.	Poster Title	Author/Affiliation/Country
1.	Effect of Aluminium and Boron Ion Incorporation on Structure, Bioactivity and Mechanical Properties of Ordered Mesoporous Bioactive Glasses **O.Winter**, S. Melchers, T. Uesbeck, O. Lahayne, C. Hellmich, H. Eckert and D. Eder	**Mr. Oliver Winter,** Vienna University of Technology, **Austria**
2.	Tailoring of moisture management PLA fibers: Application of temperature and pH responsive nanogel **D. Štular**, B. Tomšič, B. Simončič, I. Jerman and M. Mihelčič	**Mrs. Danaja Stular**, University of Ljubljana, **Slovenia**
3.	Immobilization of titania nanoparticle into mesoporous silicas **K. Vibulyaseak** and M. Ogawa	**Mr. Kasimanat Vibulyaseak**, Vidyasirimedhi Institute of Science and Technology (VISTEC), **Thailand**
4.	Synthesis of new organic-inorganic hybrid - Physicochemical characterization and catalytic investigations **S. Dzwigaj**, K. Pamin, J.Połtowicz and S. Basąg	**Prof. Stanislaw Dzwigaj**, UPMC/CNRS- Sorbonne University, **France**
5.	Adsorption of indium ions from aqueous solution on layered silicates **N. Homhuan** and M. Ogawa	**Mr. Natthawut Homhuan,** Vidyasirimedhi Institute of Science and Technology (VISTEC), **Thailand**
6.	New dielectric properties in the hybrid DMAPbX3 (X=I and Br) perovskite A. García-Fernández, J. M. Bermúdez-García, **S. Castro-García**, A. L. Llamas-Saiz, R. Artiaga, J. López-Beceiro, M. Sánchez-Andújar and M. A. Señarís-Rodríguez	**Ms. Socorro Castro-Garcia**, University of A Coruña**, Spain**
7.	Evaporation of aromatic hydrocarbons from mesoporous silicas: Controlled release of aromatic hydrocarbons by the complexa-tion with mesoporous silicas **W. Reanthonglert**, K. Imwiset, S. Bureekaew, R. Yazawa and M. Ogawa	**Mr. Wichayut Reanthonglert**, Vidyasirimedhi Institute of Science and Technology (VISTEC), **Thailand**
8	Bioinspired Multifunctional Surfaces for Lab-on-Chip Applications **A.S. Moita** and A.L.N. Moreira	**Dr. Ana Moita**, Lisbon University, **Portugal**

April 27th 2017
Posters Session II: EGF 2017

Main Hall

N.	Title	Author/Affiliation/Country
8.	Dedicated functionalized graphene-based FET for highly sensitive detection of GQDs **J. Brndiarová**, M. Hulman, D. Gregušová, M. Bodík, P. Šiffalovič, V. Skákalová, Z. Markovič and K. Fröhlich	**Ms. Jana Brndiarova**, Slovak Academy of Sciences, **Slovakia**
9.	Disorder induced unusual quantum Hall effect in low p-doped epitaxial graphene **A. Nachawaty**, M. Yang, S. Nanot, B. Jabakhanji, W. Desrat, W. Escoffier and B. Jouault	**Ms. Abir Nachawaty**, Montpellier University, **France**
10.	The Effect of Oxygen Containing Functional Groups of Graphene-Oxide on The Morphology of Hydroxyapatite **S. Turk,** B. Cakiroglu, I. Aitinsoy, M. Ozacar and C. Bindal	**Mr. Serbülent Türk**, Sakarya University, **Turkey**
11.	Combination of Surface Charge and Size Controls the Cellular Up-take of Functionalized Graphene Sheets **Z. Tu,** M. Adeli and R. Haag	**Mr. Zhaoxu Tu**, Freie Universität Berlin, **Germany**

Oral Presentations Abstracts

Plenary Session I:
EGF 2017 / SMS EUROPE 2017

Synthesis and Applications of Functionalized Graphene

Maurizio Prato

Center of Excellence for Nanostructured Materials (CENMAT), INSTM UdR di Trieste, Dipartimento di Scienze Chimiche e Farmaceutiche, University of Trieste, Trieste, Italy
CIC BiomaGUNE, Parque Tecnológico de San Sebastián, Paseo Miramón, 182, 20009 San Sebastián (Guipúzcoa), and Ikerbasque Fdn. Sci., Bilbao, Spain

Abstract:

Following the production and characterization of graphene layers, much effort has been directed toward the chemical functionalization as a tool for tuning graphene chemical and physical properties. The chemical functionalization represents an important and versatile tool for tuning the chemical and physical properties of graphene, for example, rendering graphene dispersible in many solvents. We have recently reported the functionalization of graphene layers by condensation of a protected α-amino acid and paraformaldehyde, demonstrating that even if the reactivity of graphene differs from that of fullerenes and carbon nanotubes, the 1,3-dipolar cycloaddition can be efficiently performed and yields a highly functionalized material, taking place not just at the edges but also at the carbon-carbon bonds located in the center of graphene sheets.

During this talk, we will summarize our most recent results in the chemistry and applications of functionalized graphenes.

Keywords: functionalization, water splitting, neurons, biological applications.

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Acknowledgements

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Liquid-phase exfoliated two-dimensional nanosheets: processing and applications

Valeria Nicolosi

Trinity College Dublin, School of Chemistry, CRANN Institute, AMBER Centre, Dublin 2, Ireland, E-mail: nicolov@tcd.ie

Abstract:

Not all crystals form atomic bonds in three dimensions. Layered crystals, for instance, are those that form strong chemical bonds in-plane but display weak out-of-plane bonding. This allows them to be exfoliated into so-called nanosheets, which can be micrometers wide but less than a nanometer thick. Such exfoliation leads to materials with extraordinary values of crystal surface area, in excess of 1000 square meters per gram. This can result in dramatically enhanced surface activity, leading to important applications in microelectronics, energy storage and harvesting, composites, etc. Another result of exfoliation is quantum confinement of electrons in two dimensions, transforming the electron band structure to yield new types of electronic and magnetic materials. Exfoliated materials also have a range of applications in composites as molecularly thin barriers or as reinforcing or conductive fillers. Liquid phase exfoliation has been proved to be a cheap, scalable method for the mass production of 2D sheets [1-4]. This talk will first discuss the galaxy of existent layered materials, with emphasis on synthesis, liquid-phase exfoliation, and characterization, to finish off with some key applications recently developed in our laboratories, ranging from energy storage to composites [5-7].

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Graphene and Functionalized Graphene for Electronics, Photonics and Optoelectronics

E Torres Alonso[1], I Amit[1], T. J Octon[1], N J Townsend[1], D Wehenkel[1], S Unal[1], J Mehew[1], S F Ramadhan[1], G F Jones[1], T H Bointon[1], A De Sanctis[1], F Reale[5], F Bezares[2], D P Rodrigues[3], I de Schrijver[4], C D Wright[1], C Mattevi[5], H Alves[3], F H L Koppens[2], A Neves[1], S Russo[1], M F Craciun[1]*

[1]Centre for Graphene Science, CEMPS, University of Exeter, UK
[2]ICFO Institut de Ciencies Fotoniques, Mediterranean Technology Park, Barcelona, Spain
[3]CICECO, University of Aveiro, Aveiro, Portugal
[4]CenTexBel, Ghent, Belgium
[5]Department of Materials, Imperial College London, London, UK

Abstract:

Graphene is an emerging material for electronics, photonics and optoelectronics due to unique physical properties such as high electrical conductivity, optical transparency and mechanical flexibility. These properties can be further enhanced or tailored to fit specific device functionalities by means of chemical functionalization. A recent example of the potential of chemical functionalization is the intercalation of few-layer-graphene with $FeCl_3$ (dubbed GraphExeter)[1], developed by Prof Craciun's team at Exeter. In the past years our group demonstrated that this material is the best performing carbon-based transparent conductor[1], with resilience to extreme conditions[2] and potential for transparent photo-detectors[3], flexible photovoltaic and organic light emitting devices[4] and foldable light-emitting devices[5].

In this talk I will review our latest developments in the use of graphene and functionalized graphene for electronics, photonics and optoelectronics. I will present our recent studies on the use of high quality graphene for next generation light emitting devices and for flexible, wearable touch-sensors[6,7]. I will also present our recent demonstrationon of 2D heterostructures for video-frame-rate imaging applications[8], intelligent design of 2D devices[9] and GraphExeter photodetectors for high-definition sensing and video technologies.

Keywords: graphene, 2D heterostructures, photo detectors, flexible devices, light-emitting devices, touch-sensors, wearable electronics, smart textile, high-definition sensising, high-definitin videp imaging

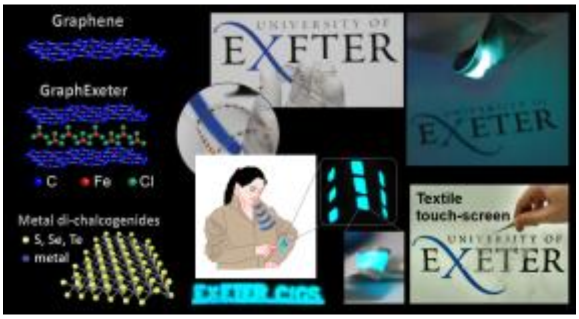

Figure 1: Figure illustrating different graphene and graphene related materials, i.e, few-layer graphene functionalized with FeCl3 and metal di-chalcogenides. These materials are used to build devices for various electronics and optoelectronics applications such as flexible and wearable, transparent touch sensors, foldable light-emitting devices, and wearable, textile based light-emitting devices.

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Competing structural orders in graphene on a substrate

J. Coraux[1,2,*]

[1] Univ. Grenoble Alpes, F-38000 Grenoble, France
[2] CNRS, Inst NEEL, F-38000 Grenoble, France

Abstract:

On-substrate bottom-up preparation is a mainstream route to large-area and high quality graphene. An interesting situation arises when the substrate is crystalline: two mismatched lattices (graphene & the substrate surface) are in contact. The system is here characterized by two different length-scales, in which case a rich of variety of structural phases is expected, as was extensively illustrated starting from the 70's in case of monolayered weekly bonded layers on graphite for instance. The structural orders each corresponding to a given structural phase are actually competing in such systems.

It is known that indeed, various coincidence lattices (referred to as moirés) are formed in graphene on metals.[1,2] In this presentation I will further explore the consequences of structural order competitions in these systems. First I will address the consequences of degenerate graphene-substrate binding configurations on the global (dis)order of the system.[3] Next, I will turn to the implications of coexisting, but non degenerate orders at the earliest stages of graphene growth, when small-sized graphene-like molecules with highly desirable structure form.[4]

The very recent results I will report on, obtained for graphene on a rhenium surface, rely on atomic-scale resolution scanning tunneling microscopy and extensive density functional theory calculations. They illustrate the link between the competition of different structural orders and the formation of topological structural defects, which are thought to host unique electronic properties.

Keywords: graphene, STM, DFT, rhenium, polycyclic molecules, topological defects, structure

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Automotive Structures based Graphene Nanocomposites

A. Elmarakbi

Automotive Compoistes Group, Faculty of Engineering and Advanced Manufacturing, University of Sunderland, Sunderland SR6 0DD, UK

Abstract:

The present initiative provides a summary overview on graphene related materials (GRMs) for automotive applications and investigates efficient ways to integrate graphene as polymer reinforcements within composite materials for energy-efficient and safe vehicles (EESVs). The automotive industry is a large and critical sector within the global economy. However, the global automotive industry is currently facing great challenges, such as responsibility for increasing annual CO_2 emissions, lack of strong decarbonisation targets, and safety issues. The development and manufacture of environmentally-friendly, EESV is a great solution to these challenges (Figure 1). The most effective way to enhance fuel consumption and to decrease CO_2 emissions is producing lighter vehicles. However, vehicle safety is usually compromised due to light-weighting. Due to the trade-off between light vehicles and safety standards, new directions need to be adopted to overcome safety issues. Several attempts have been made to strengthen vehicle structure to enhance crashworthiness, however, safety issues remain the main obstacle to producing lighter and greener cars. Therefore, the need to discover a new direction for greener and safer vehicles is urgent.

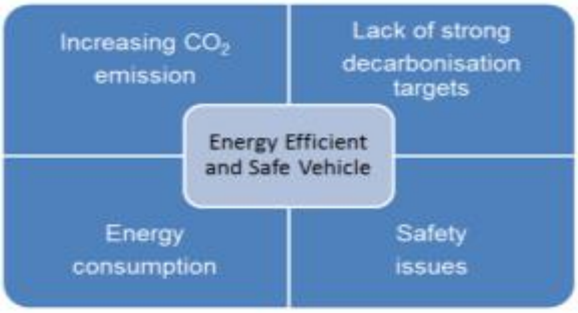

Figure 1: EESV and its compromising targets

Recently, graphene has attracted both academic and industrial interest because it can produce a dramatic improvement in properties at low filler content. Graphene is expected to have plenty of potential applications and the most immediate application for graphene-based products is to be used in composite materials. The particular example of polymer nano-composites or polymer matrix composites which incorporate nanoscale filler materials could be highlighted. Indeed, graphene-based polymers show substantial property enhancements at much lower loadings than polymer composites with conventional micron-scale fillers (such as glass or carbon fibres), which ultimately results in lower component weight and can simplify processing. Moreover, the multifunctional property enhancements made possible with nano-composites may create new applications of polymers. It has been found that by dispersing a small amount (%) of graphene in polymers, many properties of the resulting composites, such as tensile strength and elastic modulus, electrical and thermal conductivity, thermal stability, gas barrier, and flame retardance can be significantly improved. Based on these multifunctional properties, graphene/polymer composites are promising as both structural and functional composites that can be widely used in various important fields. The previous mentioned properties make graphene-based polymers and composites good candidate for structural materials, with integration of functionalities, within automotive sector. This initiative aims to analyse novel graphene-based composite materials and their potential applications in automotive industry. To this end, the utilisation of graphene in the fabrication of nano-composites with polymer matrices is investigated. Modelling, and design strategies are explored to enhance both vehicle and occupant safety; yet remain very light.

Keywords: Keywords: Automotive applications, Composite modelling and design, Energy efficient and safe vehicles, Graphene, Graphene composites

SMS EUROPE 2017 - Session I.A: Smart and functional materials

Rational design of reconfigurable prismatic architected materials

Johannes T.B. Overvelde,[1,2] James C. Weaver,[3] Chuck Hoberman,[3,4,5] Katia Bertoldi[2,6]
[1] University Name, Department of Nanobiotechnology, San Diego, USA
[2] State University of Campinas, UNICAMP, (Hemocentro), Sao Paulo, Brazil

[1]FOM Institute AMOLF, Designer Matter, Amsterdam, The Netherlands
[2]Harvard University, School of Engineering and Applied Sciences, Cambridge MA, USA
[3]Harvard University, Wyss Institute for Biologically Inspired Engineering, Cambridge MA, USA
[4]Hoberman Associates, New York, NY, USA
[5]Harvard University, Graduate School of Design, Cambridge MA, USA
[6]Harvard University, Kavli Institute, Cambridge MA, USA

Abstract:
Advances in fabrication technologies are enabling the production of architected materials with unprecedented properties. While most of these materials are characterized by a fixed geometry, an intriguing avenue is to incorporate internal mechanisms capable of reconfiguring their spatial architecture, therefore enabling tunable functionality. Inspired by the structural diversity and foldability of the prismatic geometries that can be constructed using the snapology origami-technique, here we introduce a robust design strategy based on space-filling polyhedra to create 3D reconfigurable materials comprising a periodic assembly of rigid plates and elastic hinges. Guided by numerical analysis and physical prototypes, we systematically explore the mobility of the designed structures and identify a wide range of qualitatively different deformations and internal rearrangements. Given that the underlying principles are scale-independent, our strategy can be applied to design the next generation of reconfigurable structures and materials, ranging from transformable meter-scale architectures to nanoscale tunable photonic systems.

Keywords: Metamaterials, architected materials, origami, reconfigurable, multifunctional.

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Figure 1: Prototype of a reconfigurable architected material with a single degree of freedom.

Spatially Localized Self-Assembly Driven by Electrically Charged Phase Separation: Implications to Charged Polymeric Mixtures

Arik Yochelis

Department of Solar Energy and Environmental Physics, Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, 8499000 Midreshet Ben-Gurion, Israel

Abstract:

Self-assembly driven by phase separation coupled to Coulombic interactions is fundamental to a wide range of applications, examples of which include soft matter lithography via di-block copolymers, membrane design using polyelectrolytes, and renewable energy applications based on complex nano-materials, such as ionic liquids. The most common mean field framework for these problems is the non-local Cahn-Hilliard (a.k.a. Ohta-Kawasaki) framework. Unlike the common investigations of spatially extended patterns, we describe the emergence of *spatially localized* states: (i) asymmetries in long-range Coulomb interactions that are manifested by differences in the dielectric response, and (ii) asymmetric short-range interactions that correspond to differences in the chemical potential between two materials phases. We show that counterintuitively, in one space dimension (1D) there is a multiplicity of coexisting localized solutions which appear as in dissipative systems. In addition, an analysis of 2D extension is performed and distinct instability mechanisms (related to extended and localized modes) of localized stripes are discussed with respect to model parameters and domain size. Finally, implications to localized hexagonal patterns are also made. The insights provide an efficient mechanistic framework to design and control localized self-assembly that might be a plausible strategy for low cost of nano-electronic applications, i.e., a rather simple nano-scale fabrication of isolated morphologies.

Transparent icephobic coatings based on bio-epoxy resin

X.H.WU, Z. Chen

School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore

Abstract:
Icephobic coatings, as a passive strategy for ice preventaion or delay, are essential for a series applications including solar cell, outdoor facilities, marine and aerospace structures [1, 2]. Till now, a lot of research work has been done on epoxy-based coatings which display excellent chemical and heat resistance, low adhesion, and good mechanical properties. The driving force for developing the icephobic bio-based epoxy coating comes from the growing awareness of toxic effect of bisphenol A (BPA) and greenhouse gas emissions. In this study, a commercial bio-epoxy and hydrophobic agent were used to fabricate water repellent coatings. The coating were prepared on bare glass slides and wood boards by spraying method. To obtain the optimum coating, three different hydrophobic interactions to bio-epoxy resins are formed. Ice adhesion, icing delay and ice accumulation properties of thease coatings were investigated in details. The optimum coating exhibits water contact angle larger than 90°, water sliding angle around 20° at room temperature, ice adhesion as low as 50 kPa, icing delay time larger than 600 seconds at -15 °C (Fig. 1). Moreover, The obtained coating exhibts transmittance as high as 95%, allowing coatings to be used in various applications where transparency is needed. The developed coating is green and has the potential to be biodegradable. It can be produced on an industrial scale by using known economical and viable processes and holds promise for a wide range of green chemistry applications.

Keywords: icephobic, transparent, bio-epoxy, ice adhesion, icing delay, water repellency, anti-icing.

Figure 1: Figure illustrating the ice accumultation results on a wood board with and with out our coating at -15 °C.

References:

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Shape Memory Polymer based 3D Printed Soft Robot for Industrail Applications

Young Su Kim,[1] Jahan Zeb Gul,[1] Hyeon Beon Kim,[1] Kyung Hyun Choi,[1]

[1] Jeju National University, Department of Mechatronics Engineering, Jeju, South Korea

Abstract:

Different situations such as having to realize a rapid escape or for food acquisition will require animals to either favor speed, agility or efficiency during locomotion. This change in locomotion characteristics may require changing gait, and there are often significant differences between the patterns of movement for the different gaits of an animal.This change in gait has been observed in many animals including quadrupedal animals, six-legged animals, flying animals and swimming animals. The goal of this research work is to design and fabricate a soft biomimetic frog bot for dynamic rowing in deep water. A soft biomimetic frog bot is designed and fabricated using multilayer composite of Polyurethane, Shape Memory Alloy (SMA) and Shape Memory Polymer (SMP) using additive manufacturing in order to investigate spectacular frog leg transformation. The SMA starts contraction at 70^0C and returns to relax position when temperature is lowered. Similarly the transition temperature of PLA based SMP is 70^0C. The complete frog is 3D printed using Polyurethane and SMP, SMA composite is embedded inside the legs of the frog bot. The fabricated frog softbot (Figure.1) is expected to exactly mimic the natural frog rowing. The individual configuration of multiple segments in leg of the frog was chosen based on a biological analysis of the movement of the different sections of the leg of the Xenopus laevis. The input power and temperature induced by BMF is also expected to be minimized because of this new composite properties. In conclusion, the fabrication of soft frog bot could be used to gain a deeper approach into the characteristics of the locomotion of frogs.

Keywords: shape memory alloy, shape memory polymer, biomimetic, under-water swimming, soft robot, xenopus laevis, 3D printing.

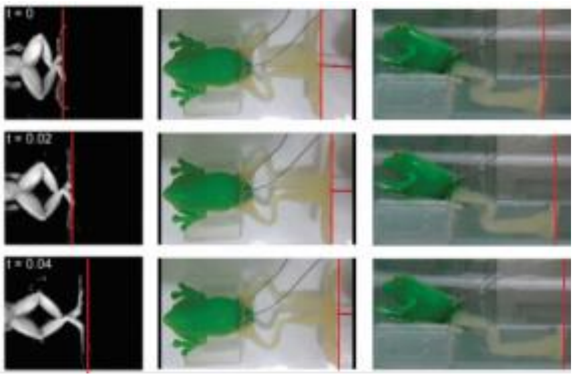

Figure 1: Images of SMP-SMA based frog softbot. Asynchronous kicks to show basic leg and foot motion, with the ventral and lateral view from the same sequence. Numbers indicate the timing (s) of the image relative to the start image Time lapse of real frog leg deformation in black.

Acknowledgements:
This work was supported by following:

1. BK21 plus program of the National Research Foundation (NRF) funded by the Ministry of Education of Korea (22A20152913424)
2. National Research Council of Science & Technology (NST) grant by the Korea government (MSIP) (No CRC-15-03-KIMM)

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Modeling of the thermo-mechanical behavior of a semi-crystalline thermoplastic shape memory polymer

R. Bouaziz[1], F. Roger[1] and K. Prashantha[1]

[1] Mines Douai, Department of Polymers and Composites Technology and Mechanical Engineering, 941 rue Charles Bourseul, CS 10838, F-59508 Douai France

Abstract:

The semi-crystalline thermoplastic shape memory polyurethane (TPU-SMPU) is a smart material which has the ability to return to its original shape after applying a large strain thermo-mechanical cycle (Figure 1) when it is stimulated by heating. This smart material has the advantage of recovering even after more than 100% of strain during several thermo-mechanical cycles. To explore the performance of a smart component in a mechanical system, it is mandatory to master the prediction of its behavior through a numerical model. In this paper, a constitutive model is proposed to describe its thermo-mechanical behavior and to predict the shape memory response. Uniaxial tensile tests at small strain rates were performed at 60°C in order to analyze the hyper-elastic response for each cycle. Relaxation tests were carried out at the end of the previous tensile loading to highlight the viscoelastic response during the shape memory cycle. These experimental data were, then, used in a curve-fitting algorithm employing least-squares optimization approach in order to identify the parameters of the proposed model. At last, the shape memory effect was investigated by means of free and constrained recovery experiments. The proposed model was then implemented into Comsol Multiphysics. It predicts quite well the experimental results in all cycles. In order to assess its predictability, this model was finally applied to the design of a 3D structure.

Keywords: semi-crystalline shape memory polyurethane, constitutive model, thermo-mechanical cycle, large deformation.

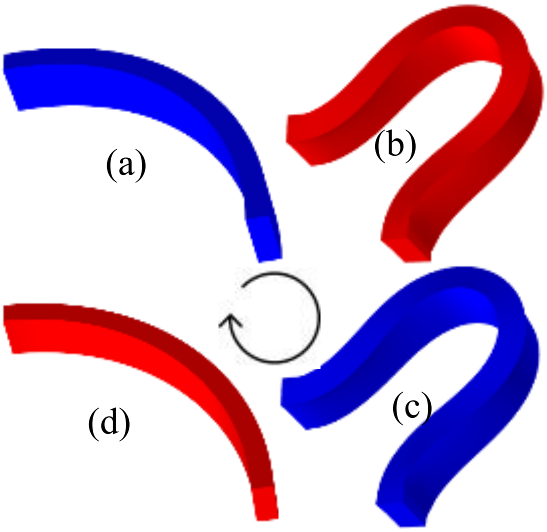

Figure 1: Shape memory cycle: (a) the original shape. (b) the deformed shape at 60°C. (c) the temporary shape obtained by cooling to 20°C. (d) the recovery shape obtained by heating up to 60°C.

Achnowledgement:

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Unravelling the Photoinduced Ligand-to-Cluster Charge Transfer Process in Zr-Based MOFs: Toward better Photocatalysist.

M. Gutiérrez,[1] B. Cohen,[1] F. Sánchez,[2] A. Douhal[1*]

[1] Departamento de Química Física, Facultad de Ciencias Ambientales y Bioquímica, INAMOL. Avenida Carlos III, S/N, Universidad de Castilla-La Mancha (UCLM), 45071, Toledo, Spain.
[2] Instituto de Química Orgánica, CSIC, Juan de la Cierva, 3, 28006 Madrid, Spain.

Abstract:

Understanding the photoprocesses that take place in Metal-Organic Frameworks (MOFs) is paramount for photonics and photocatalysis applications. For example, energy transfer process within MOFs containing fluorescent dyes has been used to get white light emitting materials.[1,2] On the other hand, Ligand-to-Cluster Charge Transfer (LCCT) in MOFs has been shown to play a key role in their photocatalytic activities.[3,4]

Herein, we show results of studies on LCCT from naphthalene and amino-naphthalene linkers to Zr metal-cluster parts in Zr-NDC and Zr-NADC MOFs. The LCCT occurs in ~60 fs for Zr-NDC MOF while it is in ~170 and 60 fs for Zr-NADC in N,N-dimethylformamide (DMF) and dichloromethane (DCM) suspensions (Figure 1), respectively. After the LCCT process, an (e^{-}-h^{+}) recombination from two different trap states of the Zr-cluster takes place from tens of nanoseconds (shallow trap states) to few microseconds (deep trap states). Moreover, we show that it happens in a dominant radiative way in DMF suspensions, while it becomes a non radiative event in a DCM one. We suggest that the electron donating ability of DMF favours the radiative pathways in contrast to the behavior in DCM. The LCCT process and the subsequent generation of the charge-separated state is further supported by the interaction of these MOFs with electron donor (N,N,N',N'-tetramethyl-p-phenylenediamine, TMPD) and scavenger (methyl viologen, MV^{2+}) compounds. Our results shed new light on the LCCT processes of MOFs opening the way to better design smarter materials based on these reticular structures for photocatalysis and H2 generation.

Keywords: Zr-MOFs, LCCT, spectroscopy, ultrafast photodynamics.

Acknowledges: MAT2011-25472, MAT2014-57646-P, and PEII-2014-003-P.

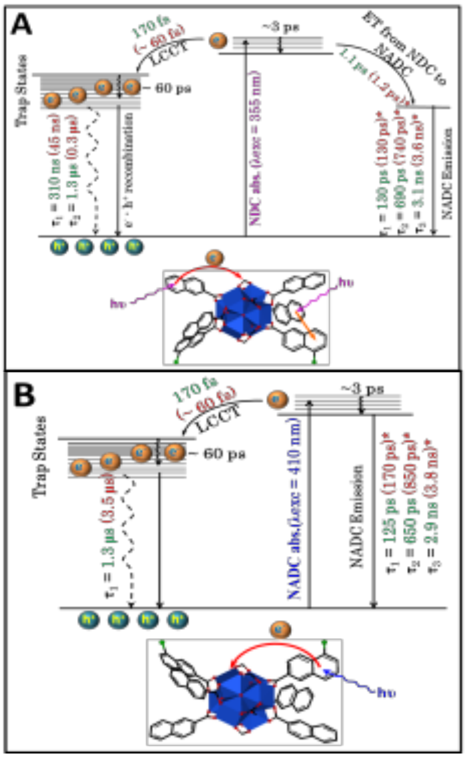

Figure 1: Illustration of the photoprocesses occurring within Zr-NADC in DMF and DCM suspensions, upon excitation at A) 355 and B) 410 nm .

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Untethered Manipulation of Helical Soft Robots

J. J. Wie,[1] J.E. Park,[1] J. Jeon,[1] J.H. Cho,[1] K.H. Lee,[1] M.R. Shankar,[2] T.J. White[3]

[1]Inha University, Department of Polymer Science and Engineering, Incheon, South Korea
[2]University of Pittsburgh, Department of Industrial Engineering, Pittsburgh, USA
[3]Air Force Research Laboratory, Materials and Manufacturing Directorate, Ohio, USA

Abstract:

Helical geometry is efficient for motility of soft robots, requiring a threshold moment only greater than rolling resistance. However, rolling motion of tethered helical robots cause entanglement of wires which limit the design and motion of robotic systems. To achieve untethered manipulation of soft robots, remote and wireless power supply is necessary. Toward this end, we utilized light and magnetic fields for light-responsive liquid crystalline polymer and magnet-responsive polymer composite, respectively. For photomotility, light-responsive azobenzene moiety is incorporated within liquid crystalline polymer networks (LCNs). [1] Here, the azobenzene-functionalized LCNs (azo-LCNs) are programmed to have twisted nematic geometry with offset angle between nematic director and film principal axis. Upon exposure to broadband ultraviolet–visible light (320–500 nm), initially flat azo-LCN films are deformed into helical robots and demonstrate directional motility originating from chirality and helix angle. The velocity of photomotility is governed by diameter of helix as well as film thickness and light intensity. For magnetomotility, magnetically active polymer composites are synthesized by inclusion of ferromagnetic iron particle into thermoset polymer matrix, polydimethylsiloxane (PDMS). By using two-step polymerization method, helical polymer composites are synthesized. When the magnetically active helical robots are driven by a constantly moving neodymium permanent magnet, magnetomotility of the robots is controlled by various parameters including magnitude of magnetic field and velocity of the magnet.

Keywords: soft robots, untethered robots, photomotility, magnetomotility, helical robots, stimuli-responsive polymers

Reference:

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Corrosion-Resistant Self-Healing Coatings

A. Pastore, S. Dello Iacono, A. Martone, E. Amendola

[1] National Research Council (CNR), Institute for Polymers, Composites and Biomaterials (IPCB), P.le E. Fermi 1 I-80055 Portici (NA) Italy

Abstract:

Self-healing polymers are a class of smart materials able to recover after sustaining damage. While the original approach of extrinsic self-healing process relies on monomer-filled capsules dispersed throughout the polymer matrix [1], a more innovative one is referred as intrinsic self-healing and uses homogeneous polymers containing Diels-Alder (D-A) precursors [2]. The reaction of a suitable diene/dienophile pair leads to monomers including D-A adducts, which could be directly incorporated in the polymer backbone. In such a way, the crosslinked resin overcomes the single-use limitation of traditional self-healing systems and can undergo multiple temperature-dependent healing cycles.

In this work, intrinsic self-healing epoxides containing D-A adducts, have been prepared [3]. The coexistence of thermally stable and thermo-reversible networks is required for the formation of a hybrid polymer architecture with robust self-healing capabilities and overall mechanical stability. The complete miscibility of all resin constituents allows the homogeneous distribution of different moieties in the resin network. The recovery capability of the resin has been verified by means of morphological observation, micromechanical and mechanical analysis.

The healing capability is very good in the case of damages and scratches which do not affect the whole sample thickness. Defects disappear after thermal healing (Figure 1), resulting in recovered resin.

In the case of substrate exposure through deep cuts (Figure 2, central image), substrate corrosion is evident in the left-hand side after 92 hours exposure in aqueous saline solution (5.0 % weight NaCl). Substrate protection is restored after healing (40 min @ 120°C), and corrosion is not evident after exposure in saline solution.

Thermal stimulus is able to trigger the r-DA reaction increasing local molecular mobility and activating the healing process. After complete recovery of morphological damage, a further thermal treatment promotes direct D-A recombination reaction and leads to network mending and thus restoring resin mechanical properties.

Nano-indentation and corrosion tests have been carried out to evaluate the healing efficiency of the coating material. Results reveal that a satisfactory morphological and mechanical recovery has been achieved suggesting very promising application in the field of corrosion-resistant protective coatings and adhesives.

Keywords: Diels-Alder, self-healing epoxy resin, corrosion resistance, nanoindentation

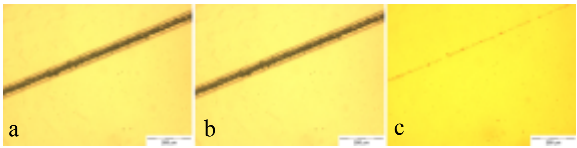

Figure 1: D-A epoxy resin, from left to right: a) scratched surface, b) surface after 5 minutes thermal treatment, c) surface after 30 minutes @ 120°C.

Figure 2: D-A epoxy coating on metal substrate, from left to right: damaged coating with oxidised substrate, damaged coating, healed coating.

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Selective metallization of flexible substrates by inkjet printing with electroless copper plating

G. Barral,[1,2,*] N. Hanifi,[2] R.Faddoul,[1] P. Viel,[2]

[1]Genes'ink, 24 av Gaston Imbert, 13 790 Rousset, France
[2]LICSEN, NIMBE, CEA, CNRS, Université Paris Saclay, CEA 91191 Gif-sur-Yvette Cedex, France

Abstract:

A new efficient approach for selective metallization of flexible substrates such as poly(ethyleneterephtalate) (PET) sheets has been developed (Figure 1). The method is based on the covalent grafting of a chelating polymer film poly-4-vinylpyridine (P4VP) able to complex metallic palladium ions which then serve as catalyst for a copper electroless plating step. A solution of P4VP containing the palladium ions (II) catalyst is firstly inkjet printed to form a metallization primer. This primer is then photo-grafted onto the surface using a flashlamp. By a photo-oxidation process, light allows the formation of free radicals on the P4VP layer in contact with the substrate. Thus, covalent adhesion between the substrate and the P4VP is achieved. A selective copper layer is finally grown on the activated primer by a copper electroless plating process. The grafted primer layer enhances the copper adhesion. A resistivity - measured with four probes - as low as 2.1 µΩ.cm (sheet resistance equivalent to 84 mΩ/□ for 250 nm thickness) is obtained, which is only 20% higher than the one of bulk copper. This new low-temperature process only requires a plating bath and is thus compatible with low-cost thermally unstable flexible polymer substrates and R2R printing processes. The final metallic layer notably shows a very good adhesion on PET substrate and good stability in ambient atmosphere.

This approach is a very attractive way to achieve localized plastic substrate (such as PET, Kapton) metallization under ambient conditions.

Due to the versatility of the process in terms of flexible substrate type, different applications can be targeted such as RFID, Plastronic, interconnects for flexible electronic.

Keywords: copper electroless plating, inkjet printing, printed electronics, flexible substrate, antenna

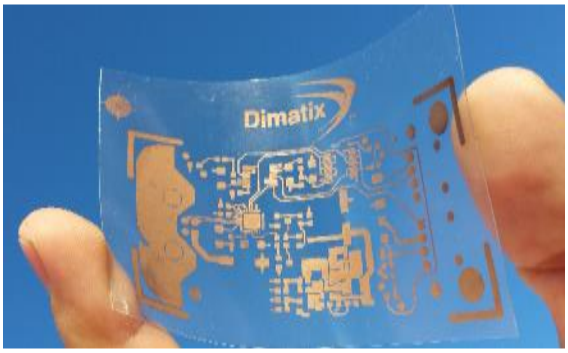

Figure 1: Copper patterns obtained on flexible substrate by electroless process after the primer printing, light-induced grafting and metallization steps.

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EGF 2017 - Session I.B: Graphene and 2D Materials - Synthesis and functionalization

Graphite-to-Graphene: Total Conversion

M. Buzaglo,[1] I. Pri Bar,[1] M. Varenik,[1] L. Shunak,[1] S. Pevzner,[3] O.Regev,[1,2*]

[1]Department of Chemical Engineering, [2]Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva, Israel [3]Department of Chemistry, Nuclear Research Center Negev, Israel

Abstract:

Graphene production has been intensively studied since its emergence in 2004, to accelerate its entrance to the application field in a reasonable price and quality. The most suitable methods for graphene mass production are top-down mechanochemical approaches, such as sonication and high-shear mixing. However, these techniques are limited to liquid medium, which requires graphene stabilization, solvent removal, and results in very low yields (<3%). Another top-down mechanochemical approach, ball milling, nowadays an established technique for producing nanomaterials, is a good candidate for generating the shear and impact forces needed to produce graphene from graphite. This method has been used to produce graphene from graphite in both wet (liquid media) and dry (solid media) milling. In these previous studies, the dry milling resulted in high content of amorphous carbon,[1] while the wet milling resulted in more crystalline products, but required extremely long milling procedures (milling time>20 hr.). Furthermore, in some cases, subsequent sonication was used to improve the relatively low yields.

In this study, graphite flakes were pre-mixed with a few solid diluents[2] to prevent re-aggregation of the obtained graphene sheets, and to minimize the formation of amorphous carbon during the dry milling process (>90% yield [3]). In the non-protected milling, there is a continuous fragmentation leading to amorphous carbon formation (Figure 1, right panel); while in a diluent-protected milling, the diluent adsorbs part of the impact forces, and therefore enables the exfoliation into graphene sheets (due to shear forces), followed by their fragmentation at higher milling energies (Figure 1, left panel). Next, all the diluent is completely removed via filtration with suitable solvents, to obtain the graphene product.

Keywords: Graphene, Ball-milling, Top-down synthesis, aromatic diluents

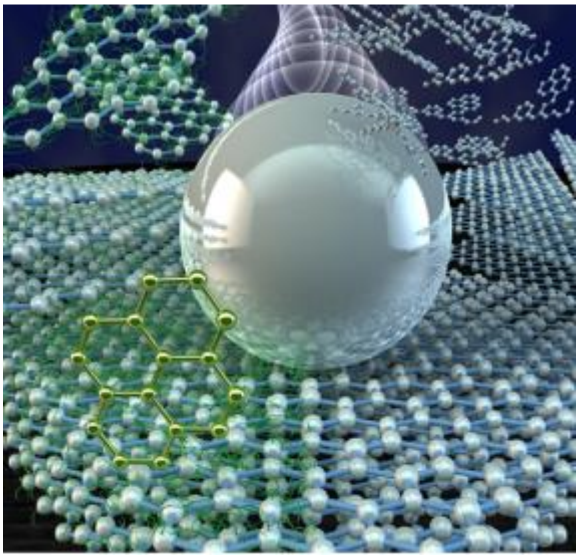

Figure 1: Schematic view of a *non-protected* (left panel) and a *diluent-protected* (right panel) milling of graphite flakes. Non-protected milling leads to amorphous carbon formation, and diluent (e.g., melamine, in green) - protected enables exfoliation into graphene sheets (upper left corner).

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Impact of substrate on the thermal properties of graphene

D. Pinho[1], M. J. Pereira[2], V. S. Amaral[2], R. Correia[3,*]

[1] Departamento de Física Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Aveiro, Portugal
[2] Departamento de Física & CICECO Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Aveiro, Portugal
[3] Departamento de Física & I3N Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Aveiro, Portugal (mrcorreia@ua.pt)

Abstract:

Graphene, a one atom thick layer of carbon atoms, raised much interest due to its outstanding physical properties allowing a wide variety of application uses in several fields of technology. Adding to its high charge-carrier mobility [1] and, since the first measurements of its thermal conductivity, graphene has displayed great potential uses for heat management purposes [2].

Being a 2D material, graphene's thermal properties can not be analysed as a regular bulk material, therefore, in order to overcome those challenges, aspects like the 2D hexagonal structure, influence of the substrate and the inapplicability of Fourier's law have to be taken into consideration. To counter this problem, several techniques have been used [3] to determine the thermal conductivity of graphene, the most utilized being Raman spectroscopy. For the case of graphene, its unique Raman features allow the possibility to quantify the thermal conductivity [2]. In this work, samples of commercial (Graphenea) CVD suspended graphene and graphene on top of SiO_2/Si and quartz substrates were studied using scanning thermal microscopy (SThM) and Raman spectroscopy.

The SThM analysis on the three samples displayed different thermal conductivity contrasts according to whether or not the graphene layer was suspended or supported by the substrate. In addition, the samples were also analysed by Raman spectroscopy as a function of incident laser power (0.1 to 4.4 mW) and temperature (20 to 200 ºC). In suspended graphene, the study with incident power, as well as with temperature, the G and 2D band frequencies were shown to have a linear behavior over the entire power and temperature range. Substantially different behavior was observed on the supported graphene and both the Raman and SThM analysis indicate that the substrate plays an important role in the thermal behavior of graphene. In this context, the evaluation of the thermal conductivity is quantitatively discussed. The results are promising regarding the discussion concerning the level of interaction graphene/substrate.

Keywords: graphene, thermal properties, thermal conductivity, Raman spectroscopy, scanning thermal microscopy.

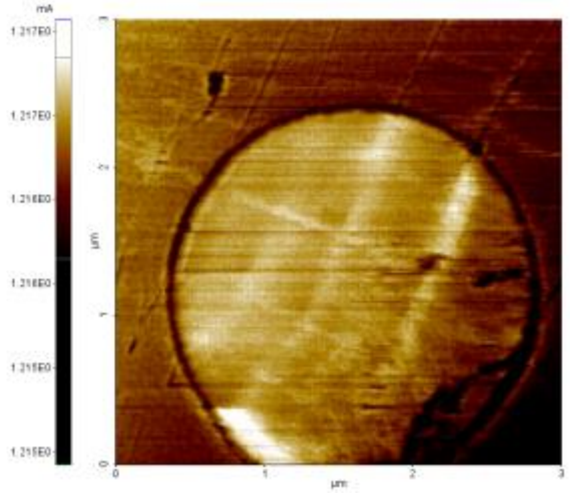

Figure 1: Thermal conductivity contrast of suspended graphene over a 2 μm hole.

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Scalable production of 2D materials based Heterostructures through green route

J. Kaur,[1*], A. Vergara[2], M. Rossi[3], A. M. Gravagnuolo[2], M. Valadan[1], F. Gesuele[1], P. Giardina[2] and C. Altucci[1]

[1] University of Naples Federico II, Department of Physics "Ettore Pancini", Naples, Italy.
[2]University of Naples Federico II, Department of Chemical Sciences, Naples, Italy.
[3]University of Naples Federico II, Dept. of Earth, Environment and Resources Sciences, Naples, Italy.

Abstract:

Two-dimensional crystals and based heterostructures are fetching great attention, due to their unique electronic and optical properties, in few-layered regime. In order to exploit the intriguing properties of these 2D structures, large scale production of high quality material, is an immediate impediment, which needs to be overcome to explore further their scope into promising applications. In this regard, liquid processing of 2D crystals such as graphene and MoS_2, offer relatively simple, reliable and cost-effective strategies for scalable production of few-layered 2D materials based dispersions. Herein, we produce liquid dispersions consisting of few-layered nanosheets of MoS_2 and graphene through a green route of production (1,2). In order to produce stable dispersions of graphene, hydrophobin Vmh2 is added during exfoliation, thus bio-functionalized nanosheets of graphene are produced, which are of high positive surface polarity. These graphene nanosheets are made to be in contact with negatively charged, exfoliated MoS_2 nanosheets, in presence of green solvents. An optimal film of 2D dispersions is drop-casted on the substrate, which is investigated through Raman and Photoluminecence spectroscopy and its surface morphology is analyzed through scanning electron microscopy with EDS measurements (Figure 1). Interestingly, realization of MoS_2/graphene heterostructures are exhibited through a significant upshift of 14 cm^{-1} in the Raman 2D peak of graphene, a shift of 1 cm^{-1} of A_{1g} peak of MoS_2, along with a strong quenching of the characteristic photoluminescence emitted from the monolayers of MoS_2, suggesting the occurrence of charge transfer process occuring between the MoS_2 and graphene nanosheets. This approach based on scalable green route of production of 2D materials based heterostructures offers economic and eco-friendly solutions to promote advanced applications in electronics and biomedical devices.

Keywords: MoS_2, graphene, hydrophobin, heterostructures, Liquid phase exfoliation, UV-visible absorption spectroscopy, Raman microscopy, Photoluminescence spectroscopy, Scanning electron microscopy (SEM).

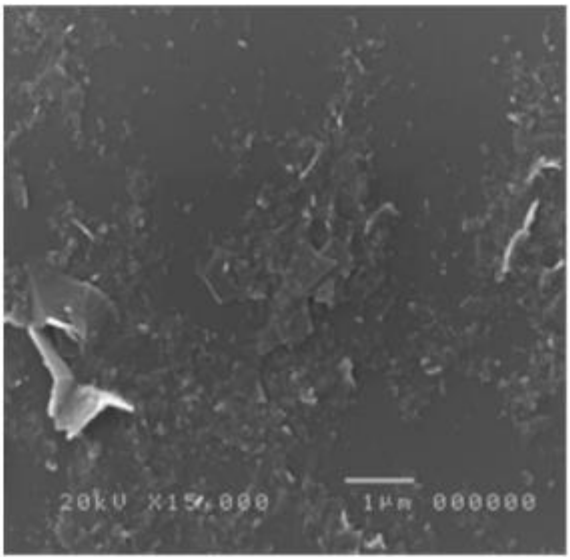

Figure 1: SEM image of the deposited heterostructure sample illustrating the bio-functionalized graphene nanosheets interfaced with smaller sized MoS_2 nanoflakes causing the interactions between the two oppositely charged layered structures.

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Interface Reactivity and Catalysis in Graphene on SiC to Unlock Exfoliation Mechanism by Electrochemical Bubbling Method

G. Rius,[1*] E. Prats-Alfonso,[2] R. Villa,[1,2] P. Godignon[1]

[1] Institut de Microelectrònica de Barcelona, IMB-CNM-CSIC, Campus UAB, Bellaterra, Spain
[2] CIBER-BBN, Barcelona, Spain

Abstract:

High quality graphene materials to be applied as elements of basic electronic components such as transistors, antennas, etc. are in high demand. Yet competitive, efficient, scalable and sustainable processing technologies are still missing. Precisely, reliable transfer methods for e.g. chemical vapor deposition graphene (CVD-G) and epitaxial graphene (EG) on SiC is a major drawback for the market development of graphene added-value products.

We have patented a novel procedure for the exfoliation of epitaxial graphene (EG) on SiC by an electrochemical cell-based method. Electrochemical bubbling typically uses the force exerted by gas bubbles generated at the graphene-substrate interface [1]. Detachement of EG from has been achieved i a cost efficient, one-step process (Fig. 1), overcoming complexity and limitations of the use of either an expensive stressor layer or an intermediate hydrogenation step [2]. Analogous to the conventional H_2 bubbling method used in CVD-G, same experimental approach has successfully applied to EG grown on the Si face of off-axis cut 4H-SiC. Highly doped SiC substrates to allow enough current flow at reasonable potential was required, and efficient voltages for EG delamination are 10-13 V. Graphene can be released just few seconds (Fig.1). An exemplary HRTEM image and diffraction pattern of exfoliated high quality EG is displayed in Figure 2.

To summarize this work, we have demonstrated that electrochemical cell method can be applied to transfer EG grown on SiC. In our presentation, we will present the procedure and results of its application. Experimental evidences of electrochemical as well as chemical-reaction mechanisms leading to physical detachment of EG from the buffer layer will be discussed. These include, e.g., SiC step reactivity (preferential bubble formation), leading to EG delamination as ribbons. Accordingly a model based on a combination of interlayer & graphene-SiC interface reactivity and catalytic capability to promote gas bubble formation and graphene-buffer layer bond breaking will be proposed with support and analogies to related methods in the literature.

Keywords: epitaxial graphene, SiC, buffer layer, electrochemical cell, bubble formation, step reactivity, chemisorption, exfoliation, delamination, gas intercalation, mechanical delamination.

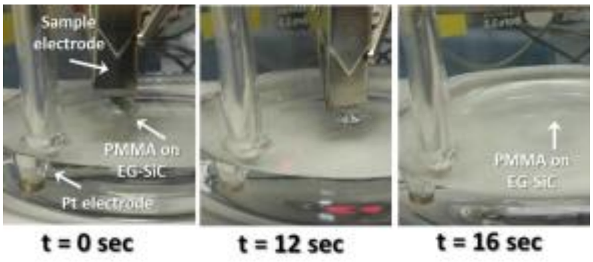

Figure 1: Setup & sequence of electrochemical delamination of EG in NaOH aqueous solution.

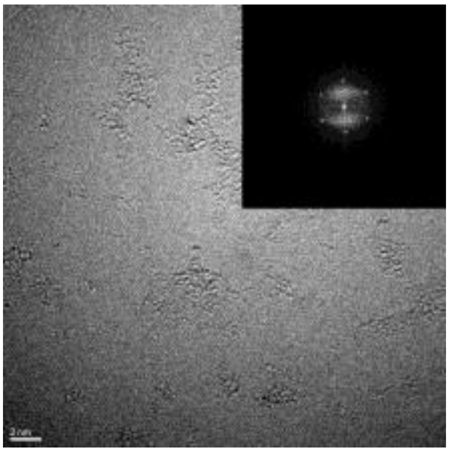

Figure 22: HRTEM and diffraction pattern of exfoliated EG, demonstrating its preserved crystal quality. Scale bar is 2 nm.

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Electrolytic phototransistor based on graphene-MoS2 van der Waals p-n heterojunction with tunable photoresponse

Hugo Henck[1,*] Debora Pierucci[1], Zeineb Ben Aziza[1], Julien Chaste[1], Emmanuel Lhuilier[2], and Abdelkarim Ouerghi[1]

[1] Centre de Nanosciences et de Nanotechnologies (C2N), Route de Nozay, 91460 Marcoussis, France
[2] Institut des Nanosciences de Paris, UPMC-CNRS UMR 7588, 4 place Jussieu, boîte courrier 840, 75252 Paris cedex 05, France

Abstract:

Van der Waals heterostructures (vdW) obtained by stacking 2D materials offer a promising route for next generation devices by combining different unique properties in completely new artificial materials[1–4]. In particular, vdW heterostructures combine high mobility and optical properties that can be exploited for optoelectronic devices[5]. We propose an approach for the fabrication of a p-n junction based on intrinsic n doped MoS_2 and p doped bilayer graphene hybrid interfaces. We demonstrate the control of the photoconduction properties using electrolytic gating which ensures a low bias operation. We show that by finely choosing the doping value of each layer, the photoconductive properties of the hybrid system can be engineered to achieve magnitude and sign control of the photocurrent. To understand the photoresponse of the system we use a combination of photoluminescence (PL), angle-resolved photoemission (ARPES) and ultraviolet photoemission (UPS) to probe the electronic structure and band alignment of the heterojunction. We additionally demonstrate that the magnitude and sign of the photoresponse can be controlled with Fermi level tunning. Finally, we provide a simple phase diagram relating the photoconductive behavior with the chosen doping, which we believe can be very useful for the future design of van der Waals based photodetectors.

Keywords: Graphene - Heterojunctions - Doping - Fermi levels - Electrolytes -

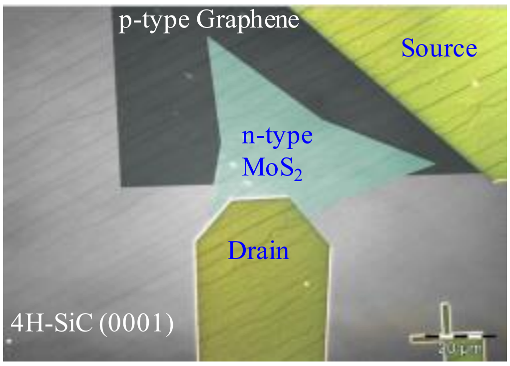

Figure 1: Optical image of a p-type epitaxial graphene/n-type MoS_2 p-n junction

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Position Controlled Nucleation of Single-Crystal Graphene on Cu

D. Ding,[1] P. Solís-Fernández,[2] H. Hibino,[3] and H. Ago [1,2*]
[1] Kyushu University, Interdisciplinary Graduate School of Engineering Sciences, Fukuoka, Japan
[2] Kyushu University, Global Innovation Center, Fukuoka, Japan
[3] Kwansei Gakuin University, School of Science and Technology, Hyogo, Japan

Abstract:

Synthesis of single-crystalline graphene is essential for high-performance electronic and photonic applications, as the presence of grain boundaries (GBs) degrades the physical and electrical properties of graphene.[1,2] One of the most promising approaches for the growth of graphene is the chemical vapor deposition (CVD) on Cu. However, graphene made by CVD is composed of merged small grains that nucleate all over the Cu surface, and hence the GBs are unavoidable. It is still a challenge to precisely control the position of the nucleation sites on Cu foil.

Here, we demonstrate a novel approach for the site selective nucleation of monolayer graphene on Cu foil.[3] The position of the nucleation site of graphene on the Cu can be effectively predetermined by controlling the local concentration of CH_4 with a perforated Ni foil mask (Figure 1a). This allows to grow a single and isolated monolayer graphene grain at the designated spot, which can then be grown up to mm size (Figure 1b,c). Predefined arrays of large isolated graphene grains can be grown by making multiple holes in the Ni mask. Moreover, this method can be exploited to directly grow patterned graphene on Cu in one step, avoiding any lithography post-process (Figure 1d). As a proof of concept, an array of graphene FETs has been successfully fabricated by this method. Finally, we show that the growth of bi-/few-layer graphene is totally suppressed in our system. Our strategy offers a simple, feasible, and low-cost way for controlling the graphene growth on Cu, which can be easily up-scaled for industrialization in semiconductor and transparent electrode fields in the near future.

Keywords: chemical vapor deposition, single-crystal graphene, crystal growth, field-effect transistors

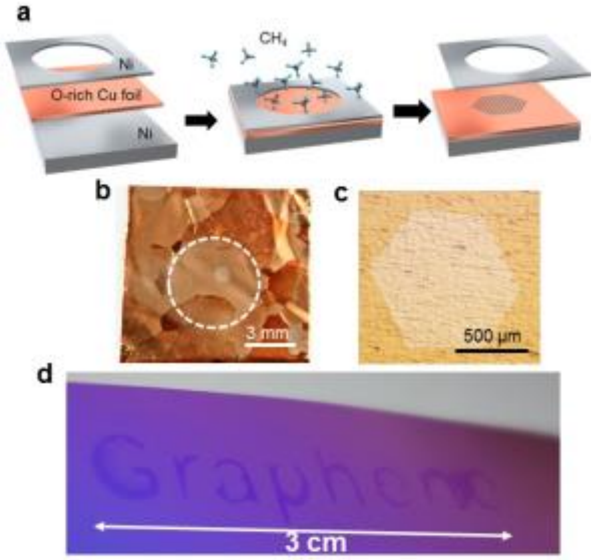

Figure 1: (a) Schematics of the production of a spatially controlled single-crystal graphene grain on Cu. The Cu is sandwiched between two Ni foils during the CVD. (b,c) As-grown, mm-sized single graphene grain obtained by using the method shown in (a). (d) Patterned growth of the word "Graphene" by using a corresponding Ni mask.

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Corresponding author: Hiroki Ago
(Tel&Fax: +81-92-583-8852
E-mail: ago.hiroki.974@m.kyushu-u.ac.jp)

Structure of water confined in nanocarbons - pressure enhancement effects

M.Sliwinska-Bartkowiak[1*], H.Drozdowski[1], K.Domin[1], M.Jazdzewska[1] Y.Long[2] and K.E.Gubbins[2]

[1]Faculty of Physics, A.Mickiewicz University, Poznan, Poland,
[2]Department of Chemical Engineering, North Carolina State University, Raleigh, USA

Abstract:
Phenomena that occur only at very high pressures in the bulk phase are often observed to occur in the confined phase at normal pressures (the pressure of the bulk phase in equilibrium with the confined phase) . Abundant experimental evidence suggests that adsorbates confined in nanoporous carbons exhibit high pressures, such as high pressure crystal structures, high pressure chemical reactions, and the deformation of pore walls due to the adsorbate. Also molecular simulation studies of the pressure tensor for simple adsorbates in carbon nanopores of slit, cylindrical and spherical geometries show that for modest bulk phase pressures the pressures parallel to the pore walls (tangential pressure) is of the order of GPa , while the pressure normal to the wall is of the order of about hundreds of MPa, and can be positive or negative depending on the pore size [1].

We report X-ray diffraction studies of water adsorbed in nanoporous activated carbon fibres (ACFs). The fibres are built of turbostratic nanoparticles separated by quasi two-dimensional voids, forming narrow slit-shaped pores. In order to determine the structure of water within the pores and its influence on the fibres' structure, mean interatomic and intermolecular distances have been estimated from the positions of the maxima of the normalized angular distribution functions obtained by X-ray diffraction [1]. We observe a significant changes in the interlayer distance of the carbon nanoparticles. The results suggest that very high pressures arise within the pores, about a few hundreds MPa, as has been observed in molecular simulations [1,2] .Such a results are confirmed by observation of high pressure forms of ice in cylindrical nanocarbons , using neutron diffraction method. [3] For water in cylindrical nanocarbons (CMK-3) we observe the existence of cubic ice, tetragonal : ice VIII and ice IX nanocrystal forms, while we find cubic ice in the case of multiwalled carbon nanotubes (MWCN) and CMK-3 mesopores [4]. These crystal forms, which occur in bulk water only at temperatures below 180 K in the case of cubic ice, and at pressures of hundreds or thousands of MPa in the case of ice VIII and IX, are stabilized by the confinement. Our observation of deformation of pore walls due to the adsorbate of water in ACF allow us to estimate experimentally the pressure normal to the pore walls as 377MPa The crystal forms of ice, observed in porous nanocarbons are typical for ice at pressures of hundreds or thousands of MPa

Keywords: nanoporous carbons, structures of confined ice, quasi-high pressure effects in carbon nanopores, X-ray diffraction and neutrons diffraction analysis,

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Van der Waals pressure and its effect on trapped interlayer molecules

K. S. Vasu[1*], E. Prestat[2], J. Abraham[1], S. J. Haigh[2], A. K. Geim[3] and R. R. Nair[1]

[1] School of Chemical Engineering and Analytical Science, University of Manchester, M13 9PL, Manchester. UK.
[2]School of Materials, University of Manchester, M13 9PL, Manchester. UK.
[3] School of Physics and Astronomy, University of Manchester, M13 9PL, Manchester. UK.

Abstract:
Van der Waals assembly of two-dimensional crystals continue attract intense interest due to the prospect of designing novel materials with on-demand properties. One of the unique features of this technology is the possibility of trapping molecules between two-dimensional crystals. The trapped molecules are predicted to experience pressures as high as 1 GPa. Here we report measurements of this interfacial pressure by capturing pressure-sensitive molecules and studying their structural and conformational changes. Pressures of 1.2 ± 0.3 GPa are found using Raman spectrometry for molecular layers of one-nanometer in thickness. We further show that this pressure can induce chemical reactions and several trapped salts are found to react with water at room-temperature, leading to two-dimensional crystals of the corresponding oxides. This pressure and its effect should be taken into account in studies of van der Waals heterostructures and can also be exploited to modify materials confined at the atomic interfaces.

Keywords: Van der Waals pressure, Heterostructures, Bubbles, Hydrolysis, 2D-Interfacial reactions,.

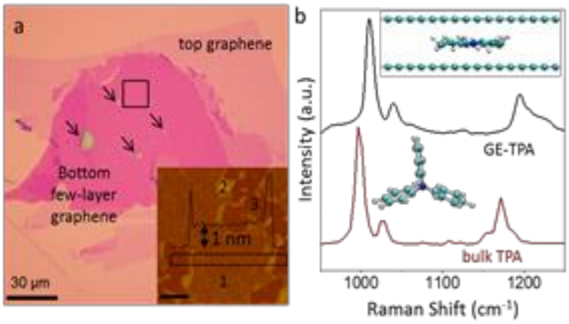

Figure 1: **Probing vdW pressure by Raman spectroscopy. a,** Optical micrograph of a graphene-encapsulated TPA on few-layer graphene placed on an oxidized Si wafer. **b,** Typical Raman spectra from macroscopic bubbles and regions such as 1. The bottom inset shows the standard molecular structure of TPA.

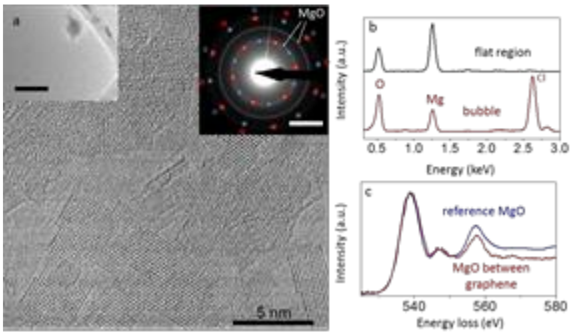

Figure 2: **TEM on graphene-encapsulated aqueous MgCl2. a,** High-resolution TEM image of MgO nanocrystal formed between two graphene layers. Diffraction pattern taken from a 1 μm-diameter flat area shows two hexagonal patterns (red and blue circles) from the top and bottom graphene layers, and diffraction rings corresponding to the {200} and {220} planes of polycrystalline MgO**.** Scale bar, 5 nm^{-1}**. b,** EDX spectra from a flat encapsulated region and from a large bubble. **c,** Oxygen-K edge spectrum from nanocrystals such as in (a) compared with the spectrum of bulk MgO from the EELS database (https://eelsdb.eu/spectra/magnesium-oxide-2).

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Large-Area 2D-0D Heterostructures via Langmuir-Blodgett Film Deposition

A. Black[1,2,*], J. Roberts[3], M. Acebrón[2], R. Bernardo-Gavito[3], G. Alsharif[3], F. J. Urbanos[1], B. H. Juárez[2,4], D. Granados[2], B. J. Robinson[3], A.L. Vázquez de Parga[1,2], R. J. Young[3]

[1]IMDEA Nanociencia, Madrid, Spain
[2] Departamento Física de la Materia Condensada, Universidad Autónoma de Madrid, Madrid, Spain
[3]Physics Department, Lancaster University, Lancaster, UK
[4]Departamento de Química Física Aplicada, Universidad Autónoma de Madrid, Madrid, Spain
[*]Contact: andres.black@uam.es

Abstract:

The integration of various low dimensional materials into large area, scalable, heterostructures is highly desirable. For example, 0D semiconducting nanocrystals (NCs) exhibit attractive optical emission and absorption properties, while single layer 2D graphene is ideally suited to act as a transparent electrode due to its superior electrical and mechanical properties.

The integration of silica encapsulated[1], 0D semiconducting NCs with 2D graphene grown by chemical vapor deposition (CVD) is presented in this work. Large area NC films were deposited onto graphene using the Langmuir-Blodgett (LB) method, a technique which allows for the deposition of nanomaterials on a liquid surface. The surface properties of the silica coated NCs necessitated the use of a novel electrospray method (Figure 1a) to successfully spread the NCs[2]. Large area graphene/NC/graphene (Gr/NC/Gr) heterostructures, seen in Figure 1b, were assembled after film deposition. Topographic, mechanical and electrical properties were investigated using scanning probe techniques and scanning electron microscopy. Photoluminescence (PL) and Raman measurements provided complementary optical and spectroscopic information.

The liquid employed in the LB trough was found to be critical for successful film transfer. By using dimethyl sulfoxide instead of water, continuous, homogenous films were obtained which maintained the optical properties of the NCs (Figure 1c). Raman measurements revealed a significant intensity enhancement of the top graphene sheets, along with additional characteristics attributed to the rippling and straining of the graphene on the NC film.

Keywords: graphene, nanocrystals, quantum dots, Langmuir-Blodgett, heterostructure

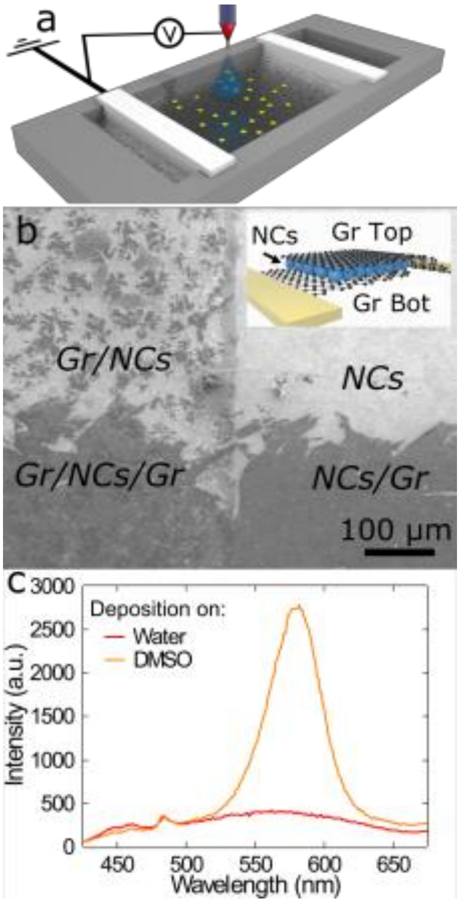

Figure 1: **a**. Schematic of a LB trough with electrospray spreading of nanostructures. **b**. SEM images and inset schematic of Gr/NC/Gr heterostructure. **c**. Ambient PL of Gr/NC/Gr heterostructure, excited at 405 nm.

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Tuneable Sieving of Ions Using Graphene Oxide Membranes

J. Abraham[1,2,3], K. S. Vasu [1,2] A. K. Geim[3] & R. R. Nair[1,2]

[1] National Graphene Institute, University of Manchester, Manchester, M13 9PL, UK.
[2] School of Chemical Engineering and Analytical Science, University of Manchester, Manchester, M13 9PL, UK.
[3] School of Physics and Astronomy, University of Manchester, Manchester M13 9PL, UK.

Abstract:
Graphene oxide membranes show exceptional molecular permeation properties, with a promise for many applications. However, their use in ion sieving and desalination technologies is limited by a permeation cutoff of ~9 Å, which is larger than hydrated ion diameters for common salts. The cutoff is determined by the interlayer spacing d ~13.5 Å, typical for graphene oxide laminates that swell in water[1]. Achieving smaller d for the laminates immersed in water has proved to be a challenge. Here we describe how to control d by physical confinement and achieve accurate and tuneable ion sieving. Membranes with d from ~ 9.8 Å to 6.4 Å are demonstrated, providing the sieve size smaller than typical ions' hydrated diameters(Figure 1). In this regime, ion permeation is found to be thermally activated with energy barriers of ~10–100 kJ/mol depending on d. Importantly, permeation rates decrease exponentially with decreasing the sieve size but water transport is weakly affected (by a factor of 2)[2] The latter is attributed to a low barrier for water molecules entry and large slip lengths inside graphene capillaries. Building on these findings, we demonstrate a simple scalable method to obtain graphene-based membranes with limited swelling, which exhibit 97% rejection for NaCl.

Keywords: Graphene oxide membrane,physical confinement, ion sieving, tunable d, energy barrier.

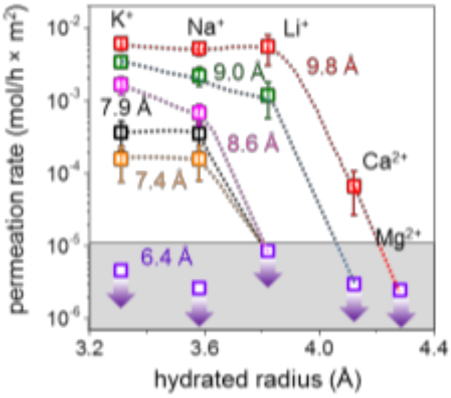

Figure 1: Permeation rates through PCGO membranes with different interlayer distances (colour coded). The salts used: KCl, NaCl, LiCl, CaCl2 and MgCl2. The hydrated diameters are taken from Ref. 32 (supplementary section 4). Dashed lines: Guides to the eye indicating a rapid cutoff in salt permeation, which is dependent on d. Grey area: Below-detection limit for our measurements lasting 5 days, with arrows indicating the limits for individual salts. The horizontal blue line indicates our detection limit for Cl- . Above the latter limit, we found that both cations and anions permeated in stoichiometric quantities. Error bars: Standard deviation.

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Comparison of green reductants for graphene fabrication via liquid chemical exfoliation process

Volodymyr Khranovskyy[1*], Ivan Shtepliuk[1], Igor Wlasny[2], Piotr Kazmierczak[2], and Andrzej Wysmolek[2], Zbigniew Klusek[3], Kateryna Shavanova[4], Yulia Ruban[4], Andrii Tencha[4]
and Rositsa Yakimova[1]

[1] Department of Physics, Chemistry and Biology (IFM) Linköping University, Linköping, Sweden
[2] Institute of Experimental Physics, Faculty of Physics, University of Warsaw, Warsaw, Poland
[3]Dept. of Solid State Physics, Faculty of Physics and Applied Informatics, University of Lodz, Poland
[4]National University of Life and Environmental Sciences of Ukraine, 03041 Kyiv, Ukraine

Abstract:

Modern liquid chemical exfoliation processes of graphene fabrication involves use of toxic and dangerous chemicals i. e. hydrazine for reduction purposes. These chemicals can be substituted by non-toxic, environment and human-friendly "green" chemicals, such as ascorbic acid (vitamin C), glucose, caffeic acid or even fruits juice extracts [1]. Their exact influence on the graphene oxide (GO) is not well known yet and deserves detailed study for future application in graphene industrial production [2].

For this purpose, we have synthesised GO by modified Hummers method and further treated it by various green reductants, engineering its surface (Fig.1). Raman spectra of GO has demonstrated both D and G bands, as well as 2D line, peculiar for 2D carbon materials. The presence of carbonyl (40%), carboxyl (17%), epoxy (3%) and oxygen substitution functional groups was identified and quantified on GO surface using XPS spectroscopy (Fig. 2). Upon GO reaction with diverse "green" reductants (Glucose, Vitamin C, Caffeic Acid and Blueberry juice) it was revealed that Vitamin C has the best reducing performance. It turned out, however, that it creates most defects in the reduced material, accordingly to the D/G lines ratio. While Glucose was observed to be the best green reductant in terms of least defects in rGO and best oxygen content decrease performance. Detailed data analysis allows us to claim that glucose as environmentally friendly and non-toxic "green" reductant can be used in the liquid chemical exfoliation processes for graphene production.

Keywords: green graphene synthesis; green reductants; surface chemistry of graphene; graphene oxide, reduced graphene oxide.

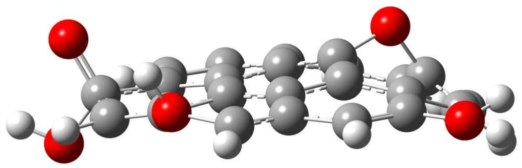

Figure 1: Schematic of simultaneous presence of different functional groups on Graphene Oxide: black balls - C atoms, grey – H, red – O.

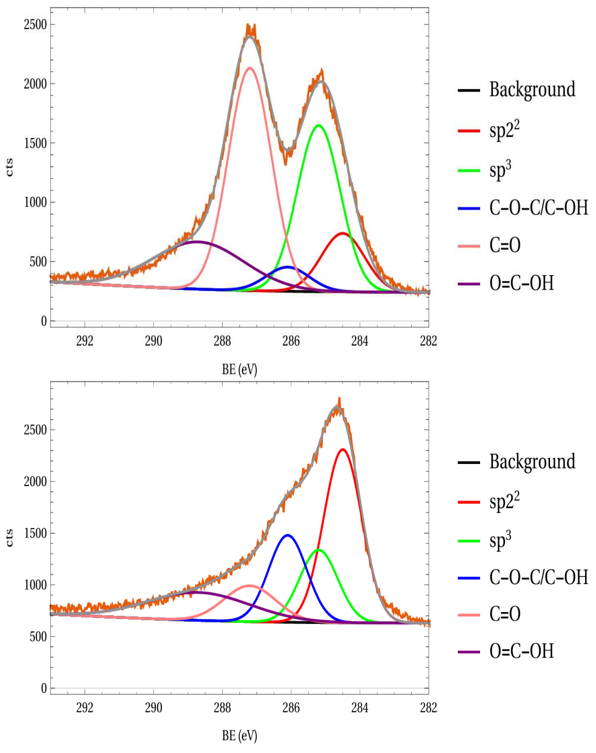

Figure 2: XPS data of functional groups available on Graphene surface before (top) and after reduction by glucose (bottom).

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Hydrogenation and fluorination of graphene via plasma: a possible route to open the gap

G. V. Bianco, M. Losurdo, M.M. Giangregorio, A. Sacchetti, G. Pace, P. Capezzuto, and G. Bruno.

[1] Institute of Nanotechnology, CNR-NANOTEC, Bari, Italy.

Abstract:

Theoretical studies have suggested that chemical functionalization is a promising route to open the gap on graphene, which plays an important role on widening its application. Several strategies have been proposed which include: (i) the controlled breaking of π conjugation in single layer graphene by tuning the functionalization coverage (fig. 1); (ii) the intralayer polarization of a graphene foil by asymmetrical functionalization of its sides with two different functionalization groups; (iii) the interlayer polarization between functionalized graphene foils stacked into specific architectures [1]. The successful exploitation of all these strategies require a chemical-modification methodology able to provide the full control of the graphene functionalization degree.

In this contribution, we demonstrate that plasma-chemistry is an effective route for the controlled functionalization of graphene aimed at the introduction of a gap. In particular, we show experimental results on the controlled hydrogenation and fluorination [2] of CVD graphene for the gap opening in single layer graphene (fig. 1) as well as in stacks of functionalized graphene foils. Data on the structural and transport properties of the fabricated systems based on chemical-modified graphene are reported. The potentiality of plasma-functionalization for experimentally pursuing the gap-opening strategies theoretically predicted is investigated and discussed.

Keywords: Graphene; plasma; functionalization; gap opening;

Acknowledgment: European Union's Horizon 2020 project "TWINFUSYON" (grant agreement N. 692034).

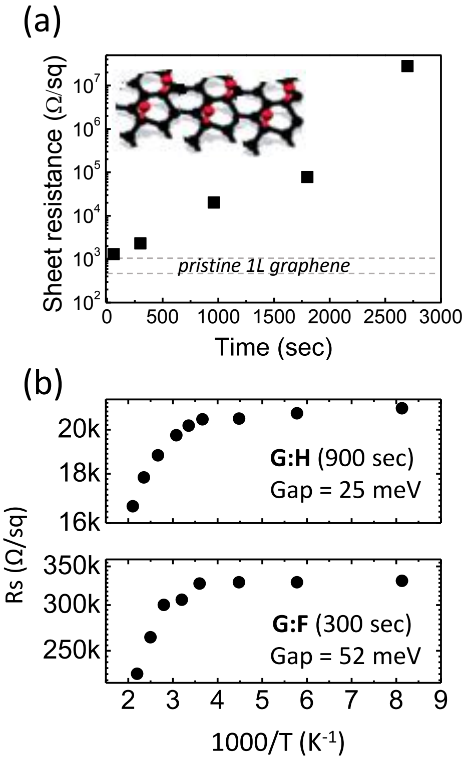

Figure 1: a) Evolution of the sheet resistance of hydrogenated graphene as a function of the plasma-treatment time; b) temperature dependence of the sheet resistance of hydrogenated (900 sec of plasma treatment) and fluorinated (300 sec) graphene. The estimated transport gap values are reported in the graphs.

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Graphene-doped TiO_2 nanotube composite for organic degradation under visible light

Seu-Run Kim,[1] Imran Ali,[1] Kyungmin Park,[1] Jon-Oh Kim,[1,*]

[1] Hanyang University, Department of Civil and Environmental Engineering, Seoul 04763, Korea

Abstract:

Photocatalyst is an environment-friendly process for organics removal from water in the presence of light as an energy. TiO_2 is a promising photocatalyst for its high photocatalytic activity, non-toxicity, low cost and high thermal stability [1]. Although, pure TiO_2 has band gap energy of 3.2 eV and has the absorption of light in UV region. So, the limitation of pure TiO_2 has less absorption of light in visible region. Recently, many visible light photocatalysts are being developed for the modification of TiO_2 and has focused on materials such as carbon, fullerene and graphene.

The objective of this study was to modify the TiO_2 nanotubes (TNT) with reduced graphene oxide (RGO) using electrochemical anodization. The RGO-TNT nanocomposites were synthesized using one-step, and two-step anodization methods. RGO was doped on TNT with different anodization voltages, times and RGO concentrations. The RGO-TNT composite was then evaluated for the degradation of MB under visible light. The synthesized catalyst was characterized by FE-SEM, XRD, AES, PL, UV-vis DRS and Raman. A recycling experiment was performed to check stability of nanocomposites.

RGO was synthesizeded from graphite powder using the modified Hummer's method [2]. The electrolyte solution for TNT anodization was ethylene glycol-DI water and NH_4F. The optimum synthesis conditions for one-step RGO-TNT was RGO 0.5 g L^{-1}, anodization at 48 V for 2 h. For two-step RGO-TNT, optimum synthesis conditions was RGO 0.5 g L^{-1}, anodization at 60 V for 1 min. The RGO doping can reduced recombination of e^- and h^+ in TiO_2. Thus, increased the formation of OH radicals and superoxides that degrade organics.

Keywords: graphene-TiO_2, nanocomposites, organic degradation, visible light, anodization.

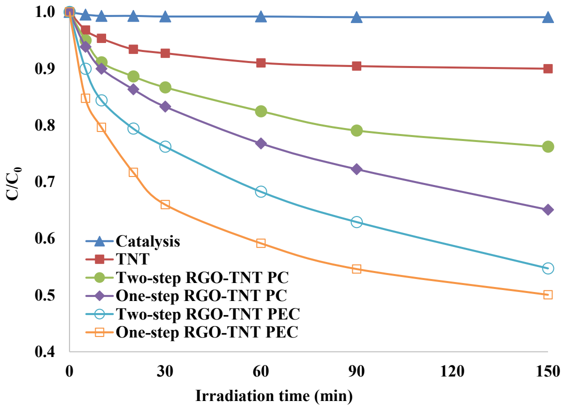

Figure 1: Photocatalytic degradation of organic under visible light by two-step and one-step RGO-TNT nanocomposite.

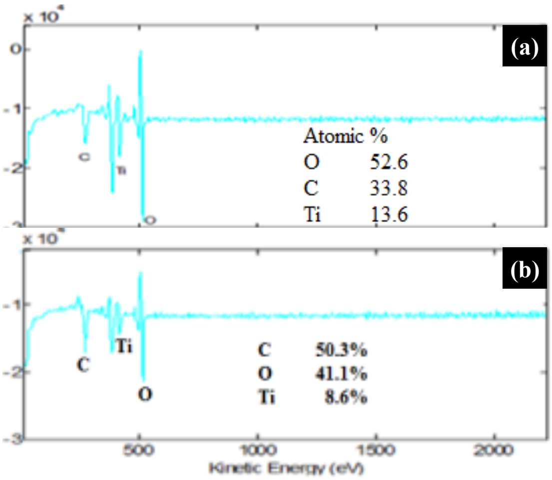

Figure 2: AES atomic% of RGO-TNT (a) two-step, and (b) one-step synthesis method.

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A Novel Pt Nanoparticles Deposited and Tannic Acid-Reduced Graphene Oxide Nanocomposite for Glucose Oxidase Immobilization and its Application for Glucose Sensing Based on Direct Electrochemistry

Bekir ÇAKIROĞLU,[1,*] Mahmut ÖZACAR,[1,2]

[1] Sakarya University, Biomedical, Magnetic and Semiconductor Materials Research
Center (BIMAS-RC), Sakarya, Turkey
[2] Sakarya University, Department of Chemistry, Sakarya, Turkey

Abstract:
Enzyme based electrochemical biosensors have been investigated for the rapid, facile, reliable measurements of biologically related analytes. For this purpose, graphene based biosensor systems are advantageous due to their excellent conductivity, high surface area for the immobilization, suitability for various binding methods. Metal nanoparticles can improve the electrical conductivity, and are extensively used in the biosensors. In this study, chemically reduced platinum nanoparticles deposited graphene nanocomposite was synthesized with environmentally friendly tannic acid (TA). TA not only reduced Pt^{4+} and graphene oxide but also deposited on the composite surface via strong π-π interactions by improving the glucose oxidase (GOx) immobilization via hydrogen bonds for the fabrication of glucose biosensor (Figure 1). The obtained system enabled GOx to realize direct electron transfer with the well defined redox peaks of FAD molecule, which is in the active site of GOx. The characterization methods, such as TGA, XRD, SEM, UV–Vis spectrophotometry, FTIR, Raman spectroscopy, and cyclic voltammetry revealed the stable graphene oxide structures, decent enzyme immobilization, well and uniform Pt Np deposition, and fast electron transfer between the electrode surface and GOx owing to the biocompatibility of nanocomposite. The constructed electrode is capable of being fabricated as a third generation glucose biosensor, and the procedure can be also extended to fabrication of other enzyme electrodes.

Keywords: reduced graphene oxide, tannic acid, direct electrochemistry, platinum nanoparticle, glucose biosensor, glucose oxidase.

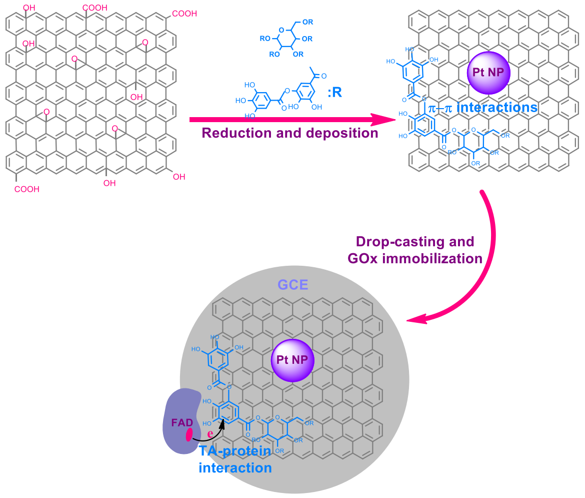

Figure 1: Schematic illustration of the assembly process of GOx-Pt NP-RGO/GCE.

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Direct growth of vertically oriented graphene nanowalls on multiple substrates by Low Temperature Plasma-Enhanced Chemical Vapor Deposition

Arevik Musheghyan-Avetisyan*, Joan Marti-Gonzalez and Enric Bertran-Serra
FEMAN Group, IN2UB, Dep Applied Physics, Universitat de Barcelona,
C/ Martí i Franquès, 1, 08028 Barcelona, Spain
amusheghyan91@ub.edu

Abstract

Vertical graphene (VG) is intrinsically graphene, but it also possesses unique structural features, i.e., being arranged perpendicularly to the substrate surface. Individual VG nanostructure usually has lateral and vertical dimensions of 0.1 to tens of micrometers and a thickness of only a few nanometers. Compared with the horizontally oriented graphene this type of graphene nanostructures attracts attention due to its high surface-area-to-volume ratio. Vertical graphene has a low operating temperature, which can be feasible for industrial applications, like supercapacitors, lithium-ion batteries, solar cells and sensors. For each application, high-quality GNWs should be grown on suitable substrate. For example, GNWs grown on Cu foil becomes an excellent electrode for supercapacitors, meanwhile, GNWs on dielectric (SiO_2) substrate could be used to fabricate gas or bio-sensors, also GNWs on semiconductor substrates could be used rather for potential application of solar cells. Plasma enhanced chemical vapor deposition (PECVD) for VG synthesis is a key method. PECVD offers the advantages of a low substrate temperature, higher growth selectivity, and better control in nanostructure ordering/pattering, due to the presence of energetic electrons, excited molecules and atoms, free radicals, photons and other active species in the plasma region, where occurs VG deposition. Depending the power frequencies of the plasma source they are different type of plasma such as, microwave (MW) plasma (2.45GHz), radio frequency (RF) plasma (13.56MHz), DC plasma and their combinations. In this study, we have used an inductively coupled plasma (ICP) configuration of the RF remote plasma enhanced chemical vapor deposition (PECVD) method. We have grown VG on top of Cu foil, Ni foil, c-Si substrate and silica substrate in the temperature range of 500-750ºC without any catalyst and post transfer. We have obtained VG on top of all substrates which we tested, but for each substrate, under the same preparation conditions, the morphology of VG nanostructures is different. The morphological and electrical properties of the obtained graphene nanowalls have been tailored by controlling the growth parameters, such as, plasma power, gas flow, temperature, pressure or cooling time. This unique three-dimensional graphene structure possessed high hydrophobicity and outstanding electron conductivity. The in-situ one step growth method indicates the great potential of using VG on supercapacitors. The present results of GNW show new evidences of its morphology, which have allowed us to propose an interpretation of its growth mechanism.

Keywords: Graphene nanowalls, Inductively Coupled Plasma Enhanced Chemical Vapor Deposition (ICP-PECVD), supercapacitors, Raman spectroscopy, Scanning Electron Microscopy (SEM).

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EGF 2017 - Session I.C: Graphene and 2D Materials - Characterisation and Properties (Quantum transport, magnetism, spintronics, etc)

Spectroscopic investigation of $Ar/H_2/CH_4$ induction thermal plasma for understanding synthesis of graphene nano-flakes

Antaryami Mohanta, Briac Lanfant, Mehari Asfaha and Marc Leparoux

EMPA – Swiss Federal Laboratories for Materials Science and Technology,
Laboratory for Advanced Materials Processing, Feuerwerkerstrasse 39, CH–3602 Thun, Switzerland

Abstract:
RF thermal plasma (ICP) has proved its potential for production of great variety of high purity ultra-fine nanoparticles, and has recently been employed for synthesis of graphene nano-flakes (GNF) by injecting CH_4 precursor into Ar/H_2 mixture plasma. However, $Ar/H_2/CH_4$ plasma has not been investigated in detail for understanding the growth process of GNF. We report synthesis of GNF in an RF ICP reactor with in-situ investigation of $Ar/H_2/CH_4$ plasma by optical emission spectroscopy (OES). OES spectra at different growth conditions are analyzed in order to understand the sequence of CH_4 dissociation and particle nucleation. Electron impact and dehydrogenation processes are primarily responsible for dissociation of CH_4. Emission spectra (Figure 1(a)) of $Ar/H_2/CH_4$ plasma are dominated by C_2 Swan system at lower pressures and by continuum emission from nanoparticles at higher pressures. Lower thermal gradient in plasma at lower pressures causes no production of GNF. In these conditions, C_2 species are believed to be converted into hydrocarbons by collision with the hydrogen molecules without producing any allotropes of carbon. The production of GNF is observed at higher pressures due to condensation of C_2 species caused by higher thermal gradient in plasma. Moreover, C_2 Swan band dominates at lower CH_4 flow rates and continuum emission band is pronounced at higher CH_4. Maximum production achieved at optimum growth condition is ~ 7 g/h. Number of layers of GNF is 11–12 for ≤ 1.5 slpm of CH_4 and 18–22 above 1.5 slpm. Observation of more layers of GNF with less production above 1.5 slpm of CH_4 is associated with higher monomer concentration and lower cooling rate at the point of nucleation. High resolution transmission electron microscopy image of synthesized GNF is shown in Figure 1(b). We will discuss in detail about the dissociation process of CH_4, formation of monomers and particle nucleation, and properties of GNF at different growth conditions. This study will be helpful to optimize growth parameters in different plasma based synthesis techniques to produce quality graphene and its derivatives with high yield.

Keywords: RF thermal plasma, Optical emission spectroscopy, Plasma synthesis of nanoparticles, Particle nucleation, Graphene, C_2 Swan band, Electron and dehydrogenation dissociation.

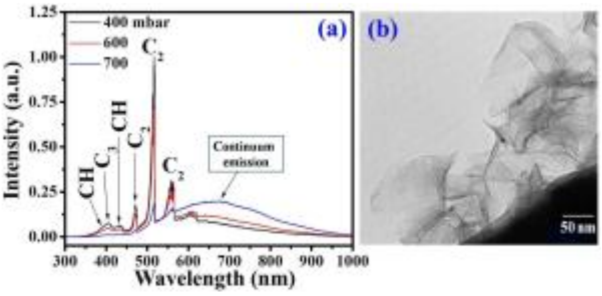

Figure 1(a): $Ar/H_2/CH_4$ plasma emission spectra at different pressures at 15 kW and CH_4 flow rate of 0.7 slpm. (b) HRTEM image of synthesized graphene nano-flakes.

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Surface-enhanced Raman Scattering Activities of Two Typies of Graphene/Ag Nanoparticls Hybrids

J. Zhang,[1*] X.Y. Wang[1], T.C. Gong[1], J.M.Quan[1], Y.Zhu[1]

[1] The Key Laboratory of Optoelectronic Technology & System, Education Ministry of
China, Chongqing University, Chongqing, 400044,China

Abstract:

This work aims to deeply investigate and analyze the properties of AgNPs and GE hybrid materials which have potential applications in SERS. Firstly, we synthesized two typies of surface-enhanced Raman scattering (SERS) substrates with hybridstructures including AgNPs underneath few-layer graphene (GE-AgNPs) and AgNPs on top of few-layer graphene (AgNPs-GE), by a convenient, environmental-friendly and low-cost method (Figure 1). Secondly, by studying local electric field properties of AgNPs and GE, the principles of the interaction between AgNPs and GE were analyzed theoretically and simulated with COMSOL. The influences of size and interparticle gap are discussed. Thirdly, we compared the effect of the enhancement of Raman signal and the stability, using rhodamine 6G (R6G) as probe molecules. In addition, the SERS substrates can be reused after being washed with sodium borohydride ($NaBH_4$) solution. Through experiments and theoretical analyses, the hybrid structure of AgNPs and GE is a potentially valuable and effective way to improve the performance of SERS substrates.

Keywords: Raman scattering; Graphene; Nanoparticles; Surface-enhanced Raman scattering.

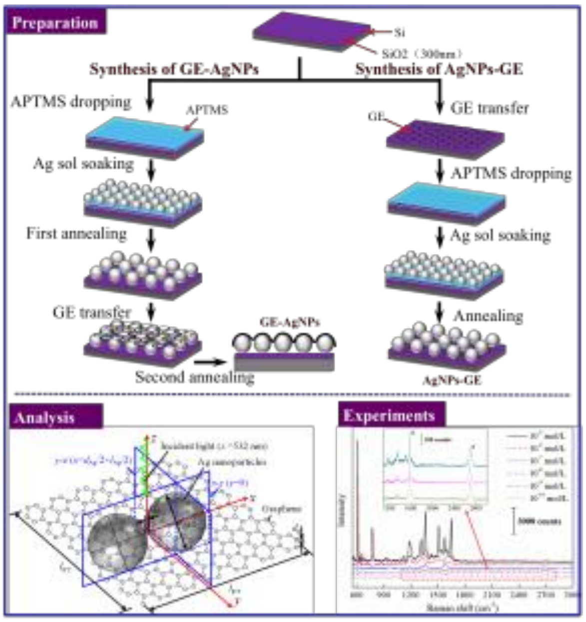

Figure 1: This figure shows the preparation of graphene (GE) and Ag nanoparticles (AgNPs). It also shows an analysis model of hybrid structures in our theoretical and simulational discuss. The Raman intensities of R6G (with concentration from 10^{-7} to 10^{-10} mol/L) are recorded with our samples as SERS substrates.

Acknowledgments:

We would like to thank Prof.H.F. Shi and D.P.Wei for graphene sample help. This research is funded by National Natural Science Foundation of China (No. 61376121), National, Natural Science Foundation of Chongqing (CSTC2015JCYJBX 0034) and National High Technology Research and Development Programof China (863 Program, No. 2015AA034801).

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Optical Characterization of Epitaxial Graphene with Confocal Laser Scanning Microscopy

Randolph E. Elmquist,[1*] Yanfei Yang,[1] Vishal Panchal,[1,2] Chieh-I Liu,[1,3] Albert Rigosi,[1] Hsin-Yen Lee[1]

[1] National Institute of Standards and Technology, Gaithersburg, MD 20899-8171, USA
[2] National Physical Laboratory, Hampton Road, Teddington, TW11 0LW, UK
[3] Graduate Institute of Applied Physics, National Taiwan University, Taipei 106, Taiwan

Abstract:
Wafer-scale epitaxial graphene (EG) could provide scalable integration for quantum Hall effect standards, electron optics and sensitive photon detectors. For large-scale integration to be possible the 2D graphene layer must have homogeneous carrier density and mobility, which requires careful control of defects and layer number. Optical microscopes can resolve the 2.3% adsorbtion of single-layer EG, but physical diffraction and depth of field effects limit the resolution and image quality, making it difficult to measure large-area optical uniformity at sub-micron scale[1]. Characterization of EG thus would benefit from high-speed automated imaging and a level of resolution not available using traditional microscopy techniques.

We present recent developments in rapid optical characterization of EG layer coverage at wafer scale using confocal laser scanning microscopy (CLSM), which acquires multiple images with resolution approaching 100 nm from selected depths, a technique described as optical sectioning. CSLM real-time image processing then combines the in-focus regions of each section into a single image, and can stitch many images to cover larger areas. For EG on SiC(0001), the controllable brightness of a 405 nm laser and a 12-bit photomultiplier sensor can provide clear delineation of layer number and SiC terrace structure over millimeter-scale regions. CSLM is complementary to atomic force techniques and Raman microscopy, and its use can provide detailed, large-scale characterisation that is predictive of electronic homogeneity[2]. We will describe how CSLM and other methods can help to optimize EG growth and make wafer-scale fabrication of EG-based devices more efficient.

Keywords: epitaxial graphene, transport mobility, carrier density, strain, Raman microscopy, quantized Hall effect

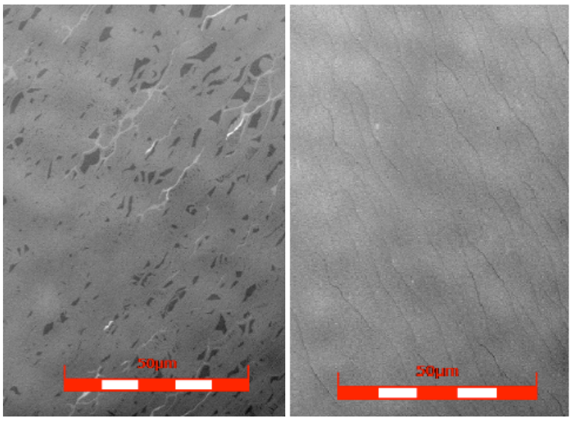

Figure 1: Confocal microscope images, laser wavelength 405 nm, showing EG samples on vicinal SiC(0001). The image at left shows uniform EG with darker interface-layer patches and lighter ribbons of multi-layer EG. At right, uniform monolayer EG and dark ribbons are SiC terrace boundaries.

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Scanning photoemission imaging and spectromicroscopy: a powerfull tool to chemically characterize free standing graphene at the micro- and nano-scale

M. Amati,[1,*] H. Sezen,[1]. L. Gregoratti,[1]

[1] Elettra – Sincrotrone Trieste S.C.p.A. di interesse nazionale, Trieste ITALY

Abstract:

Due to the relatively small size of thin (one or few layers) graphene flakes it is extremely difficult to study the behavior of free standing graphene with characterization techniques different from electron microscopies. In this work we present the capabilities of photoemission imaging and spectromicroscopy in the in the chemical investigation of graphene flakes at se micro- and nano-scale.

The Scanning PhotoEmission Microscope (SPEM), hosted at the ESCAmicroscopy beamline at the Elettra synchrotron light source, uses a direct approach to add the spatial resolution to photoemmision and characterize chemically surfaces at the submicron scale i.e. the use of a small focused x-ray photon probe to illuminate the sample[1]. The focusing of the x-ray beam is performed by using a Zone Plate and the sample surface is mapped by scanning the sample with respect to the focused beam. The x-ray beam can be downsized to a diameter of 120 nm which allows imaging resolution of less than 50 nm. The overall energy resolution is better than 200 meV.

Recent achievements in the chara cterization of graphene will be presented providing an overview of the capabilities of this powerful technique. For example in monitoring the fine tuning of graphene electronic properties, a key challenge for nano-device fabrication, by functionalizing the graphene with plasma based methods, leading to the grafting of atoms or molecules to the graphene lattice [2].

The unique capabilities of the SPEM allow also to highlight the effect of the substrate on the properties of the graphene and its effects on the functionalization, thanks to the possibility to characterize both free standing and supported graphene (see figure).

Keywords: XPS, microscopy, SPEM, 2D materials, Graphene, characterization,

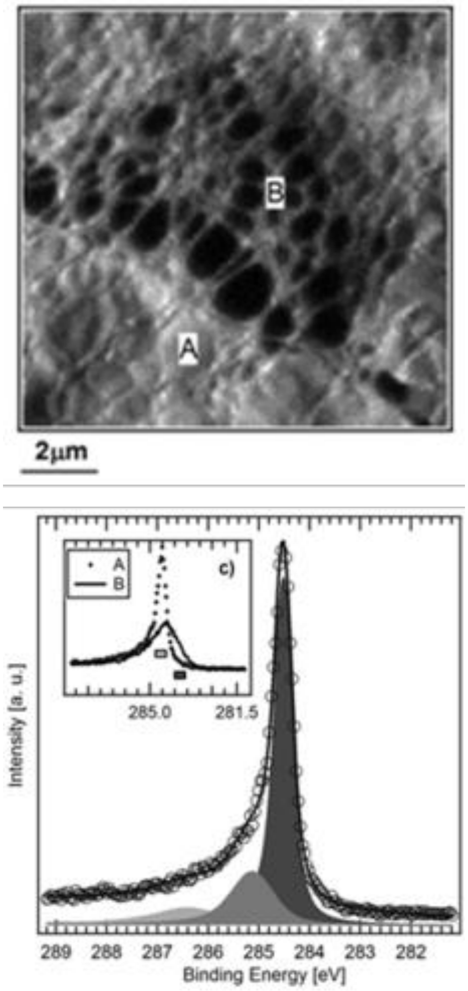

Figure: top: 12.8x12.8 μm^2 SPEM image : Lacey Carbon support partially covered by Gr flakes. bottom: C 1s representative of a suspended Gr flake (A) and the amorphous C support (B).

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Study on Thermal Stability of Multi-layer Graphene with Metal Nanoparticle by Rapid Thermal Treatment in Oxygen Ambient

Jung Woo Lee[1], Sun Woo Kim[1], and Young Il Song [1,2*], and Su Jeong Suh [1,2*]

[1]School of Advanced Materials Science and Engineering, Sungkyunkwan University, Rep. of Korea
[2]Advanced Materials and Process Research Center, Sungkyunkwan University, Rep. of. Korea

Abstract:
We have presented the effect of multi-layer graphene with metal particle by rapid thermal vapor in oxygen gas ambient. Multi-layer graphene coated copper nanoparticles (MGCNs) are produced by electrical explosion method in isopropylalchol liquid media. The obtained MGCNs have a layer spacing of 0.34 nm, are uniform in thickness, and usually consist multi-layer graphene shells tightly surround the core copper nanoparticles without obvious voids. This work introduce about fracture by tearing of multi-layer graphene structure and observation of oxidized copper metal particle of the MGCNs by thermal treatment in oxygen gas ambient at low temperature such as 25 ℃, 100 ℃, 200 ℃, and 300 ℃. The MGCNs were characterized with Raman to obtain graphene peak and variation depending on oxygen gas temperature. Transmittance electoron microscopy was used to confirm the images for effect of multi-layer graphene and copper nanoparticles phase by oxygen gas. The formation for the structure of copper nanoparticles were evidenced by the X-ray diffraction. X-ray photoelectron spectroscopy was used to measure for chemical bonding on multi-layer graphene surface depending on

Keywords: Multi-layer graphene, Graphene fracture, Wire explosion process, Metal nanoParticles, Thermal treatment oxygen gas

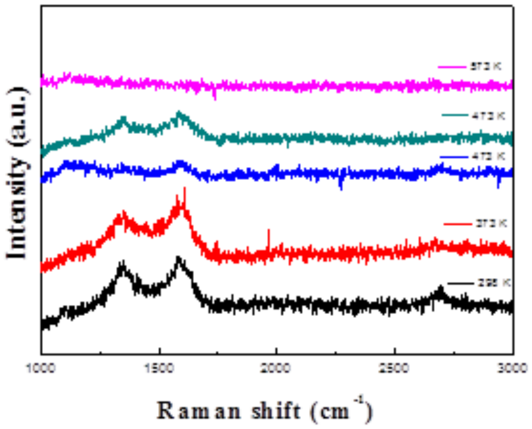

Figure 1: Raman analysis of Multi Layer Graphene Coated Copper nanoparticles depending on temperature in Oxygen gas.(black: Room temperature
red : 373 K, blue : 473 K, pink : 573 K).

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Graphene and Carbon related Materials: Photonics and Optoelectronics Applications

Der-Jang Liaw*, Chou-Yi Tsai, Qiang Zhang, Ying-Chi Huang and Yi-Ze Wang
Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, 10607
Taiwan, * liawdj@gmail.com; liawdj@yahoo.com.tw; liawdj@mail.ntust.edu.tw

Abstract:

Carbon-based polymeric nanomaterials including graphene, carbon nanotube, and fullerenes etc. boost as most promising materials for photonics and optoelectronics in the 21st century. Nanographenes prepared through a ‘‘bottom-up’’ chemically synthetic route with extended polycyclic aromatics possess well-defined structures and properties, which have potential applications in nanoelectronics, optoelectronics, and spintronics. Herein, nanographene-containing conjugated polymers and polynorbornenes (PNBs) were prepared *via* the Suzuki Coupling reaction and ring-opening metathesis polymerization (ROMP), respectively. Both polymers showed high thermal stability up to 300°C. The nanographene-containing conjugated polymer and PNB could be highly dispersed in cyclohexylpyrrolidone (CHP) through sonication, and exhibited intensive emission (485 and 465 nm) in photoluminescence-excitation (PLE) maps. The intensive and narrow emission of PNB is owing to the unsymmetrical structure of nanographene and electron donating group covalently bonded to nanographene. Monolayer graphene was prepared by chemical vapour deposition (CVD) and used as transparent electrodes. In addition, triarylamine-based conjugated polymers and polynorbornenes deposited on flexible monolayer graphene-based electrode for electrochromism. Moreover, triarylamine-based conjugated polymers were used for high selectivity of semiconducting single-walled carbon nanotubes (SWCNT). The selectivity of (6,5), (7,5), (9,5), or (8,7) nanotubes through polymer wrapping can be controlled by changing the main chain such as polytriarylamine or poly(triarylamine-fluorene), as well as adjusting the aliphatic side-chain length of polymers. Triarylamine-based amphiphilic conjugated polymer was prepared through Suzuki coupling reaction, and used as cathode and anode buffer layers for electronics including OLED and solar cells.

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Use of moiré pattern from epitaxially grown graphene on Ir(111) : Organization and magnetic properties of FePt nanoparticles

Pierre Capiod,[1] Florent Tournus,[1] Laurent Bardotti,[1] Gilles Renaud,[2] and Véronique Dupuis[1]

[1] Institut Lumière Matière, UMR5306 Université Lyon 1-CNRS, Université de Lyon, 69622 Villeurbanne cedex, France
[2] Commissariat à l'Energie Atomique, Institut Nanosciences et Cryogénie, Service de Physique des Matériaux et Microstructures, Nanostructures et Rayonnement Synchrotron, 17 Avenue des Martyrs, F-38054 Grenoble, Cedex 9, France

Abstract:

The FePt alloy, when chemically ordered in the L1 0 phase, is among the magnetic materials displaying the highest magnetic anisotropy constant (K around 7 MJ/m 3). Therefore it is a perfect candidate for ultra-high density magnetic storage applications, provided nanoparticles can be prepared in such a high anisotropy phase[1]. Another requirement for applications, as well as for fundamental studies, is to organize the magnetic nanoparticles in a 2D array. In parallel to investigations on chemically synthesized systems, a great effort is devoted to the bottom-up elaboration of nanomagnet arrays following a physical route.

In this context, one widely used path consists in using template surfaces with specific sites regularly distributed. Such a 2D lattice can be obtained with the moiré phenomenon, which appears when two crystalline structures of slightly different cell parameters are stacked. Thus, a graphene layer epitaxially grown by CVD on a Ir(111) surface displays a 2D spatial modulation corresponding to a hexagonal lattice of 2.5 nm cell parameter[2]. For the first time, we have characterized the organization and the magnetic properties of FePt nanoparticles on such a moiré pattern.**Keywords**: protein folding, nanoporous sol-gel glasses, silica-based biomaterials, circular dichroism spectroscopy, surface hydration, crowding effects, micropatterning, biomedical applications.

We will first describe the formation of graphene on Ir(111) by CVD, the synthesis and deposition of size se- lected (typically from 2 nm to 4 nm) FePt nanoparticles by Low Energy Cluster Beam Deposition (LECBD) on graphene/Ir(111) samples. We will discuss the organization of such particles on specific sites of the moiré lattice, as determined by grazing incidence x-ray scattering measurements (GISAXS technique) (figure 1) and x-ray diffraction performed at the European Synchrotron Radiation Facility (ESRF)[3]. The deposited nanoparticles are sensitive to the moiré pattern and we find that the resulting organization can be preserved up to temperatures around 700 K. Finally, we will report a clear evolution of the magnetic properties of the FePt nanoparticles induced by annealing (phase modification, anisotropy modification, interface effects between FePt and the graphene...) put into evidence by X-ray Magnetic Circular Dichroism (XMCD) measurements on the DEIMOS beamline at SOLEIL Synchrotron (figure 2). The magnetic properties will be compared to those of FePt diluted in an amorphous carbon matrix.

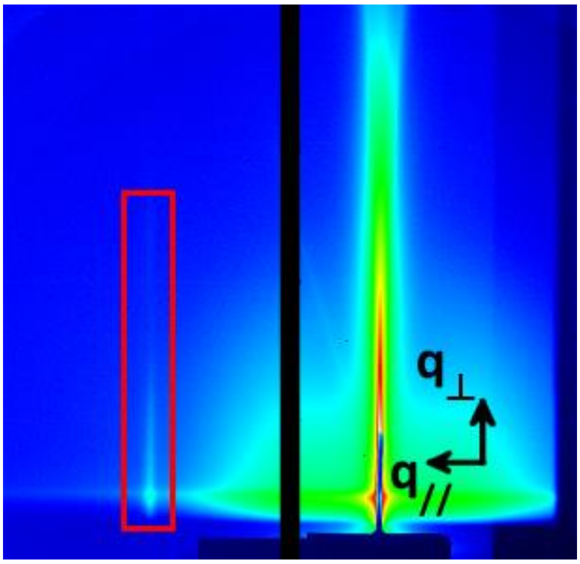

Figure 1: GISAXS pattern along the <100> direction of the moiré, of 2.2 nm diameter FePt nanoparticles on graphene/Ir(111) substrate. The correlation peak (highligthed in red) points out the organization of the nanoparticles on the surface.

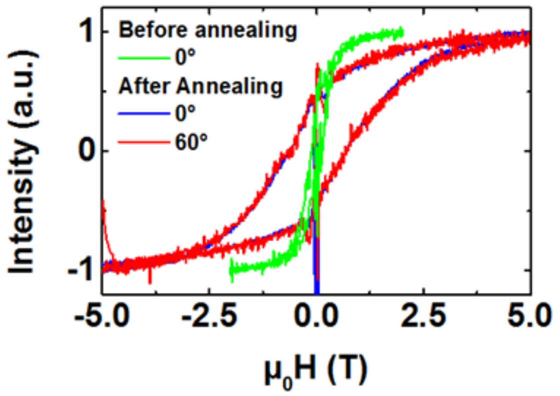

Figure 2: Hysteresis loops from XMCD measurements of the 2.2 nm diameter FePt nanoparticles sample for two x-ray incidence angles, before and after annealing at 600°C for 2 hours.

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Rise of Periodic Potentials in Hybrid van der Waals Heterostructures Formed by Supramolecular Lattices on Graphene

E. Orgiu,[1,2,*]

[1] INRS-EMT Centre, Montréal (QC), CA
[2] Institut de Science et d'Ingénierie Supramoléculaires, Université de Strasbourg, Strasbourg, France

Abstract:

Graphene and the two-dimensional (2D) van der Waals semiconductors represent the thinnest, air stable semiconducting materials known. Their unique optical, electronic and mechanical properties hold great potential for harnessing them as key components in novel applications for electronics and optoelectronics. However, the charge transport behavior in such semiconductors is more susceptible to external surroundings (e.g. gaseous adsorbates from air and trapped charges in substrates) and their electronic performance is generally different than the corresponding bulk materials due to the fact that surface and bulk coincide when going from 3D down to 2D. Interestingly, one can take advantage of the latter property by using ordered supramolecular layers in order to tune charge transport and optical properties of such 2D materials. Hence, the electrical properties of graphene can be strongly influenced by the presence of physisorbed molecules, which induce charge transfer and doping[1, 2]. In this context, supramolecular chemistry makes it possible to precisely tune the doping effect via the formation of ordered self-assembled monolayers (SAMs) of molecules embedding different functional groups[3].

In my presentation, I will give an example [4] of a more general physical scenario: the charge transport and the doping on graphene can be tuned through *ad-hoc* engineering of the supramolecular assemblies physisorbed on its surface. A very fine photoreactivity process allows to achieve molecules featuring the same assembly motif on the surface but different terminal groups which contribute to doping the graphene in a novel way.

This approach will give an easy example of all the potential hidden in van der Waals heterostructures composed of supramolecular lattices physisorbed onto graphene.

Keywords: Periodic Potentials, van der Waals Heterostructures, Charge Transport, Graphene Physics, Supramolecular Lattices.

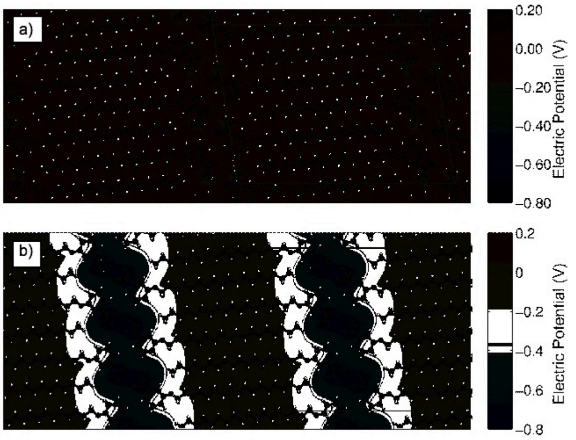

Figure 1: Calculated differential potential [V (z=8 Å) – V (z=0 Å)] induced by a SL of two different types of molecular building blocks (MBBs) (a) MBB-1 and (b) MBB-2 on graphene. SLs is superimposed for clarity. The potential is periodically modulated, with negative values in the region below the molecular heads. Carbon atoms are shown in grey, hydrogen in white, nitrogen in red, fluorine in light blue, chlorine in green.

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Conductive Lightweight Composites of Polyetherimide with Graphene Nanoplatelets-Carbon Nanotube Hybrids

H. Abbasi,[1] M. Antunes,[1,*] J.I. Velasco[1]

[1] Centre Català del Plàstic, Technical University of Catalonia (UPC · BarcelonaTech), Department of Materials Science and Metallurgy, Terrassa, Spain

Abstract:

Polyetherimide nanocomposites containing carbon-based nanoparticles such as graphene nanoplatelets (GnP) have shown promising properties for advanced applications, such as fuel cells or electromagnetic interference (EMI) shielding [1-2]. Nevertheless, there are still some issues that need to be addressed and that could further extend the applicability of these materials, such as their relatively high density or, in some cases, limited EMI shielding efficiency.

The present work considers the combination of two strategies to overcome these limitations: on the one hand foaming of the nanocomposites by means of water vapor-induced phase separation (WVIPS) and on the other the use of a hybrid nanofiller system based on graphene nanoplatelets (GnP) and carbon nanotubes (CNT). In terms of the first, we have already shown in a prior work [3] that the adition of GnP to PEI and foaming can lead to components with enhanced electrical conductivity, crucial in applications requiring high EMI shielding, especially those where EM absorption mechanism plays a key role, such as stealth technology. On the other hand, it has been shown that hybrid nanofillers based on GnP and conductive nanoparticles with a tubular-like morphology such as CNT may promote the formation of an efficient conductive GnP-CNT network (see Figure 1).

This work considers the preparation of nanocomposites based on PEI and different proportions of dispersed GnP and CNT (2.0/0.0, 15/0.5, 1.0/1.0, 0.5/1.5 and 0.0/2.0 wt.%, total amount: 2 wt%), their foaming by WVIPS and their characterization in terms of microstructure, cellular structure, thermal stability, dynamic-mechanical thermal behaviour and electrical conductivity.

Among the prepared lightweight nanocomposites, the one with 1/1 wt% proportion of GnP and CNT displayed the highest electrical conductivity, which was related to an optimum combination of cellular structure and formation of a highly effective conductive GnP-CNT network. Direct result of their properties, these lightweight nanocomposites with enhanced electrical conductivities are expected to find a broad range of applications, from electrostatic dissipation (ESD) to high performance electrical applications.

Keywords: graphene nanoplatelets, carbon nanotubes, hybrid nanofiller, nanocomposites, polyetherimide foams, electrical conductivity, EMI shielding.

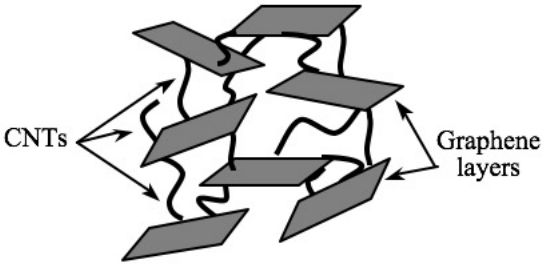

Figure 1: Scheme illustrating the conductive network formed in GnP-CNT hybrid nanofiller.

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Precise electronic and valleytronic nanodevices based on strain engineering in graphene

Nikodem Szpak[1], Thomas Stegmann[2]

[1]University of Duisburg-Essen, Duisburg, Germany
[2]Universidad Nacional Autonoma de Mexico, Cuernavaca, Mexico

Abstract:
Graphene based nano-devices can be made so small that quantum transport phenomena play a crucial role in their functionality. We will present several such systems and discuss the theoretical and numerical models which are helpful in the understanding and efficient prediction of their electronic properties.
As examples, planar graphene with out-of-plane deformations and bent carbon nanotubes will be discussed as deformation/pressure nano-sensors and valley filters/polarizers. Precise combination of the curvature, magnetic and the pseudo-magnetic fields enables to control the quantum transport in these systems and gives rise to phenomena such as directing and focusing of currents depending on the deformation, placement of contacts and valley polarization. They can be applied in new types of graphene based electronic and valleytronic nanodevices.

Keywords: Graphene, Valleytronics, Quantum Transport, Strain, Effective Gauge Fields, Curved Space.

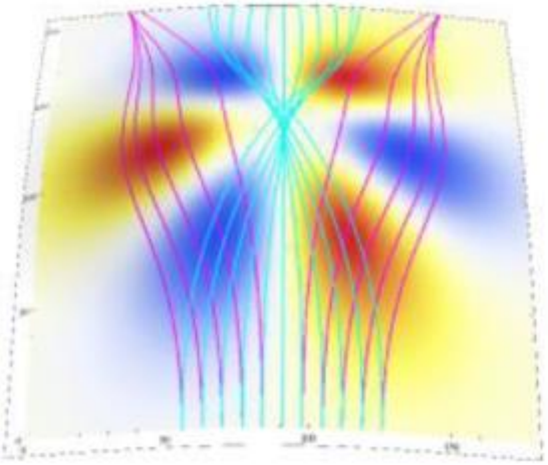

Figure 1: Theoretical model of current lensing and valley filtering based on classical trajectories

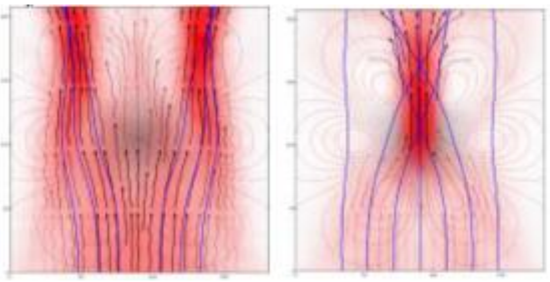

Figure 2: Numerical mo el of current lensing and valley filtering based on quantum transport calculations

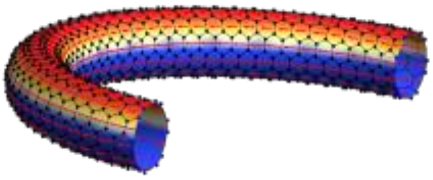

Figure 3: Artificial gauge fields due to strain in deformed carbon nanotubes also influence their current flow profiles and valley polarization

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Graphene and graphene-based composite materials for energy storage and thermal interfacing

X.W. Yuan,[1*] S.L. Bai[2]

[1] Massey University, School of Engineering and Advanced Technology, Auckland, New Zealand
[2] Peking University, Department of Materials Science and Engineering, Beijing, China

Abstract:

New sources of energy and various advanced energy storage systems are needed to address global energy depletion and environmental degradation [1]. In addition, the digitalization of industry has accelerated the demand for miniaturization and high power electronic devices, in particular commercial electrochemical electrodes have serious limitations. Development of the next generation of integrated circuits, three-dimensional integration, and ultrafast high-power density communication devices makes the thermal management demands an urgent task [2]. Thermal interface materials (TMS), applied between heat source and heat sink, are also essential elements of thermal management for electronic devices [3]. Conventional TIMs filled with thermally conductive particles require a high volume fraction of fillers (~50vol%) to achieve thermal conductivity of ~1-5 $Wm^{-1}K^{-1}$ at room temperature. To improve the thermal conductivity, conductive nanomaterials, such as carbon nanotubes have been used. However, such materials cannot be adopted practically mainly due to weak thermal coupling at the carbon nanotubes/matrix interface [2]. Graphene, a single-layered two-dimensional (2D) structure, is an excellent candidate due to its excellent mechanical, thermal and electrical properties. Graphene foam assembled from 2D graphene, graphene oxide or reduced graphene oxide sheets presents a macroscopic three-dimensional (3D) structure.

In this paper, we review the graphene based 2D and 3D structures for energy storage systems such as electrochemical capacitors, and also report the development of heat management graphene composite materials with graphene in a 2D structure (graphene sheets) and a 3D structure (graphene foam). The research focuses on the mechanical and thermal properties of novel graphene/polymer composites, addressing the heat dissipation issues due to the miniaturization and high power consumption of compact electronic devices; this is the key factor controlling the life span and computing power of electronic devices. The results show that the vertically aligned graphene sheet composites have excellent thermal and mechanical properties, and may be used for heat management of electronics. The microstructures of such composites are shown in Figure 1. A finite element model has been developed to predict the thermal conductivity of graphene foam filled polymer composites. The effect of graphene foam size, interfacial and contact resistance on the thermal conductivity was also investigated.

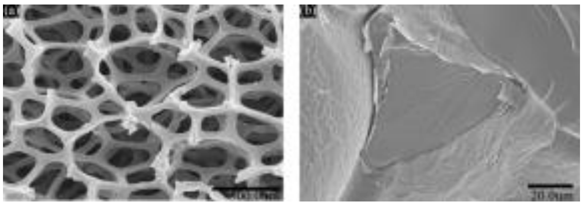

Figure 1: Scanning electron microscope (SEM) images of (a) graphene foam 3D network, and (b) graphene composites

Keywords: graphene, graphene/polymer composites, thermal interface materials, thermal and mechanical properties, electronic devices, heat management

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Mechanical properties of Fe filled carbon nanotubes: a molecular dynamics approach

M. Kiwi,[1,3]* Vicente Munizaga,[2] Ricardo Ramírez,[2,3] Griselda García[2]

[1] Depto. de Física, Facultad de Ciencias, Universidad de Chile,
Casilla 653, Santiago, Chile 7800024
[2] Facultad de Física, Universidad Católica de Chile,
Casilla 306, Santiago, CHILE 6904411
[3] Centro para el Desarrollo de la Nanociencia y la Nanotecnología,
CEDENNA, Avda. Ecuador 3493, Santiago, Chile 9170124.

Abstract:

Carbon nanotubes (CNTs) have been at center stage of science and technology for two decades. CNTs are quasi one-dimensional nanometric structures with superb mechanical, electrical, chemical, and thermal properties. Moreover, CNTs adsorb a wide variety of atomic and molecular species. Filling CNTs with different metals has also caught significant attention, as reviewed in 2014 by Monteiro et al.[1]

Fe-filled CNT's pose an interesting challenge from a basic viewpoint, underlined by the application they have found as magnetic force microscopy probes. Previously we presented an atomistic simulation, using classical MD, of the soldering process of two Fe filled CNTs.[2] Our work contributed to develop an understanding of the mechanisms that govern the dynamics of nano-soldering.

Here we report on their mechanical properties, which reveal the possibility of an Fe phase transition from bcc(111) to fcc(111) during the loading stage, on the basis of the results we obtained for the stress vs. strain relation, and the atomic pair distribution function. We also show that the deformation process of the Fe wire is influenced by temperature, and varies with the Fe crystal direction. However, it is almost independent of the strain rate that is applied, within the range we explored.

At low and intermediate temperatures the main energy release mechanism is the generation of dislocations and twin boundaries; these interact when they cross, but they do not interlock. When the temperature is large enough the response to the deformation is completely different, and no elastic response of the Fe@CNT system is observed.

Keywords: 2D systems, molecular dynamics, mechanical properties, iron filled carbon nanotubes.

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Gate tuneability of helicity dependent photocurrent in ABA- and ABC-stacked trilayer graphene

M. Eginligil [1*]

[1] Nanjing Tech University, Institute of Advanced Materials, Nanjing, CHINA

Abstract:

Helicity dependent photocurrent (PC) in single layer graphene (SLG) is the electric current generated by elliptically polarized light which is obliquely incident on to sample plane and there is a sign change of this PC upon reversal of light helicity. There are two major components of this PC, which are attributed to the linear photon drag effect (LPDE) and the circular photogalvanic effect (CPGE). Unlike SLG, band gap can open in bilayer graphene (BLG) by applying gate voltage (Vg). The PC of BLG as a function of light helicity and carrier density (by applying Vg) was recently studied. The PCs due to the LPDE and the CPGE for BLG showed features in common with SLG.

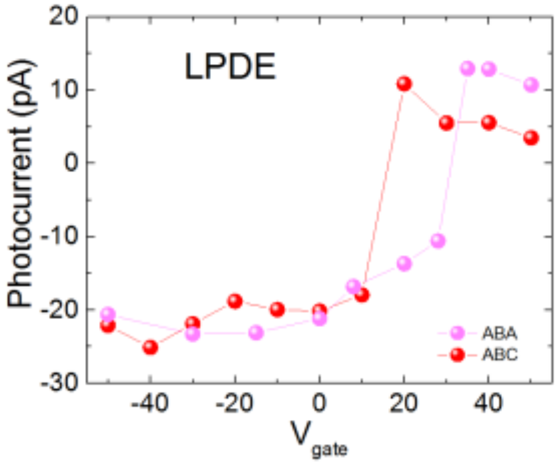

Figure 1: LPDE photocurrent in ABA- and ABC stacked TLG sample are similar.

Here we present helicity dependent PC data of trilayer graphene (TLG) ABA-stacked (which consists of SLG-like and BLG-like subbands) and ABC-stacked (approximately cubic band dispersion and band gap opening by gating). While the LPDE PC in TLG samples are similar as seen Figure 1 (also similar results were obtained for SLG and BLG); we noticed a large Vg dependence in the CPGE PC in ABC-stacked TLG (~15 pA), while the variation in the CPGE PC in ABA-stacked TLG is not that obvious (Figure 2). The large gate tuneability of the CPGE in ABC-stacked TLG reveals another potential application of graphene.

Keywords: graphene photoresponse, circular photogalvanic effect, trilayer graphene.

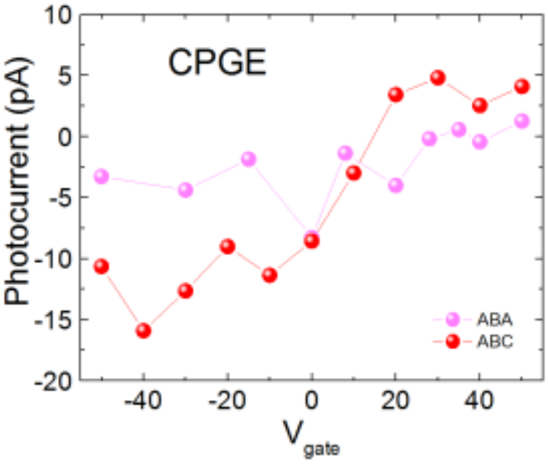

Figure 2: Large gate tuneability of the CPGE photocurrent in ABC-stacked TLG, while the variation in the CPGE photocurrent by varying the gate voltage in ABA-stacked TLG is negligible.

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Plenary Session II:
EGF 2017 / SMS EUROPE 2017

New 2D semiconductor: atomically thin crystals of InSe

Vladimir Falko

National Graphene Institute, the University of Manchester, Manchester, UK

Abstract:

We present the analysis of electronic band structure of InSe (and other III-VI semiconductors) films, from the stoichiometric mono- to N-layer films, and we describe the resulting optical properties of these 2D materials [1,2] and conduction/valence band parameters. This study is based on the ab initio DFT and related multi-orbital tight-binding model analysis of the electronic band structure and wave functions in the two-dimensional N-layer InSe crystals, and it is compared to the results of luminescence spectroscopy of this material. We show [1-3] that the band gap in InSe (and GaSe) strongly depend on the number of layers, with a strong (more than twice) reduction from the monolayer to crystals with N>6. We find that the conduction-band-edge electron mass in few-layer InSe is quite light (comparable to Si), which suggests opportunities for high-mobility devices and the development of nanocircuits. In contrast, the valence band in mono-, bi- and trilayer InSe is flat, opening possibilities for strongly correlated hole gases in p-doped films. We also propose a model to describe electronic properties of misaligned layers of InSe. Using the band structure and wave functions, we analyse optical transitions in thin films of InSe, identify their polarisation and compare the results of modelling to the measurements performed on hBN-encapsulated atomically thin InSe crystals.

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2D dichalcogenide electronic materials and devices

A. Kis

École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

Abstract:

The discovery of graphene marked the start of research in 2D electronic materials which was expanded in new directions with MoS_2 and other layered semiconducting materials. They have a wide range of promising potential applications, including those in digital electronics, optoelectronics and flexible devices. Combining 2D materials in heterostructures can increase their reach even further.

In my talk, I will present our recent efforts in growing 2D semiconducting transition metal dichalcogenides (TMDCs) and heterostructures using a variety of techniques such as CVD and MBE, starting from epitaxial growth of MoS_2 on sapphire with a high degree of control over lattice orientation. Next, I will show our work on atomically thin rhenium disulphide (ReS_2) liquid-electrolyte gated transistors with atypical behaviour at high charge densities related to the peculiar band structure of this material. I will finish by presenting new results on spin/valley transport in semiconducting monolayer TMDC materials.

Advanced spintronics in graphene-Van der Waals heterostructures

Bart van Wees[1]

[1] Zernike Institute for Advanced Materials, Nijenborgh 4.13, Groningen, The Netherlands

Abstract:

I will give an overview of the status of graphene spintronics, from both scientific as technological perspectives. In the introduction I will show that (single) layer graphene is the ideal host for electronic spins, allowing spin transport by diffusion over distances exceeding 20 micrometers at room temperature. I will show how by the use of carrier drift, induced by charge currents, effective spin relaxation lengths of 90 micrometer can be obtained in graphene encapsulated between boron-nitride layers[1]. This also allows for the controlled flow and guiding of spin currents, opening new avenues for spin logic devices based on lateral architectures.

By preparing graphene on top of a ferromagnetic insulator (yttrium iron garnet (YIG)) we have shown that we can induce an exchange interaction in the graphene, thus effectively making the graphene magnetic[2]. This allows for new ways to induce and control spin precession for novel applications. Finally I will show how, by using two-layer BN tunnel barriers, spins can be injected from a ferromagnet into graphene with a spin polarization which can be tuned continuously from -80% to 40%, using a bias range from -0.3V to 0.3V across the barrier[3]. Even higher polarizations are observed when using these tunnel barriers as (biased) detectors. These unique record values of the spin polarization are not yet understood, but they highlight the potential of Van der Waals stacking of graphene and related 2D materials for spintronics. I will conclude with a perspective of future developments of spintronics in graphene and transition metal dichalcogenide based Van der Waals systems.

Keywords: spintronics, spin transport, graphene, hexagonal boron nitride, ferromagnetic insulators, spin logic, Van der Waals materials

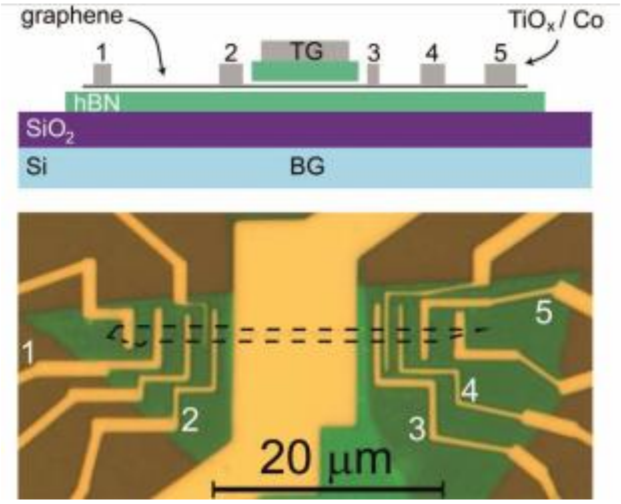

Figure 1: Cross section and top view of a dual gated BN encapsulated bilayer graphene spin valve device for the demonstration of carrier drift enhanced and controlled spin transport (from ref. 1)

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2D materials and hybrids for novel photonic devices

G. Eda,[1,2,3*]

[1] Department of Physics, National University of Singapore, Singapore 117542
[2] Department of Chemistry, National University of Singapore, Singapore 117543
[3] Centre for Advanced 2D Materials, National University of Singapore, Singapore 117546

Abstract:

Despite being only a few atoms thick, two-dimensional (2D) semiconductors such as monolayer MoS_2 and phosphorene exhibit unusually strong light-matter coupling mediated by tightly bound excitons - elementary excitation of solids consisting of a bound electron-hole pair. Unlike in conventional semiconductor quantum wells, excitonic effects dominate optical transitions in 2D semiconductors even at room temperature, allowing their exploitation for fundamental studies as well as practical device applications. Recent rapid progress in materials synthesis highlight the potential of 2D semiconductors for ultra-fast photo-detectors, flexible photovoltaic devices, chiral light emitters, single photon sources, and ultra-low threshold lasers. In this talk, I will disucss our recent findnigs on exciton relaxation dynamics in van der Waals hereostructures of 2D materials. Our experimnetal results show that excitonic dipole-dipole energy transfer in these heterostructures is among the fastest measured in nanomaterials, offering unique prospects for energy harvesting and optical conversion[1]. We further explore peculiar optical effects arising from strong exciton-plasmon coupling in 2D semiconductors hybridized with metal nanoparticles[2]. Finally, our recent efforts in realizing electro-optical devices based on van der Waals heterostructures will be discussed. I will share our views on the potential advantage of 2D semiconductors over other materials and discuss our outlook for further studies.

Keywords: 2D materials, photonic devices, exciton, plasmon, energy transfer, electroluminescence, photoluminescence spectroscopy, van der Waals heterostructure.

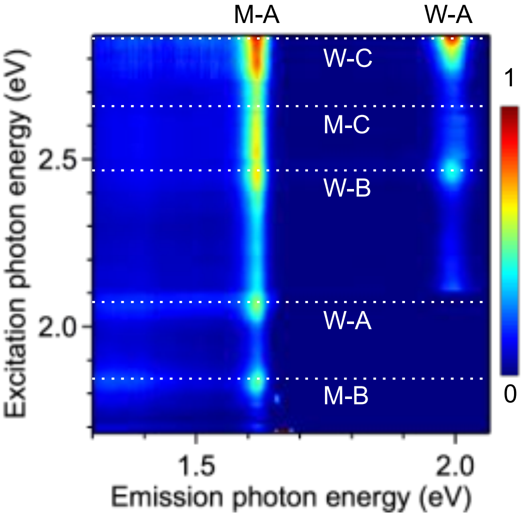

Figure 1: Photoluminescence excitation spectra of $MoSe_2/WS_2$ heterostructure demonstrating evidence of energy transfer.

References:

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Graphene MMICs for high data-rate communication

O. Habibpour, N. Rorsman and H. Zirath

Chalmers University of Technology, Department of Microtechnology and Nanotechnology, Göteborg, Sweden

Abstract:

We are developing monolithic millimeter wave integrated circuit (MMIC) based on hydrogen intercalated epitaxial graphene. This type of graphene exhibit a high carrier mobility (4000-5000 cm^2/Vs) at high carrier densities (0.8-1.2×10^{13} cm^2) resulting in a low sheet resistance (200-250 Ω/□) suitable for high frequency applications. We have developed graphene field effect transistors (G-FETs) on silicon carbide substrate (Figure 1a). The transistors exhibits very high transconductances (1000-1200 mS/mm). However, a poor saturation bahvaour of G-FETs (Figure 1b), which is due to lack of bandgap, limits maximum osciilation frequencies (f_{Max}). The lack of a bandgap is an advantage for the some applications where G-FETs operating in linear regions such as frequency mixers and power detectors. Therefore, we have focused on this type of devices. We have developed a compelet MMIC fabrication process. Figure 1c, shows the process chart including 3 ebeam-lithography steps and 10 photolithography steps as well as back side processing such as thinning substrate. The whole process can essentially well preserve the graphene transport properties. Figure 1d, illustrates fabricated MMIC [1]. The circuit is a single-ended resistive mixer on 70μm SiC based on a 250 nm G-FET. To assess the MMIC performance, the circuit is used to upconverd high data-rate (8-16 Gbps) modulated signals. Figure 1e shows the constellation of the retrieved data. As can be seen the constellation is not distorted suggesting that the mixer is highly linear.

Keywords: Millimeter-wave integrated circuit, high data rate communication,

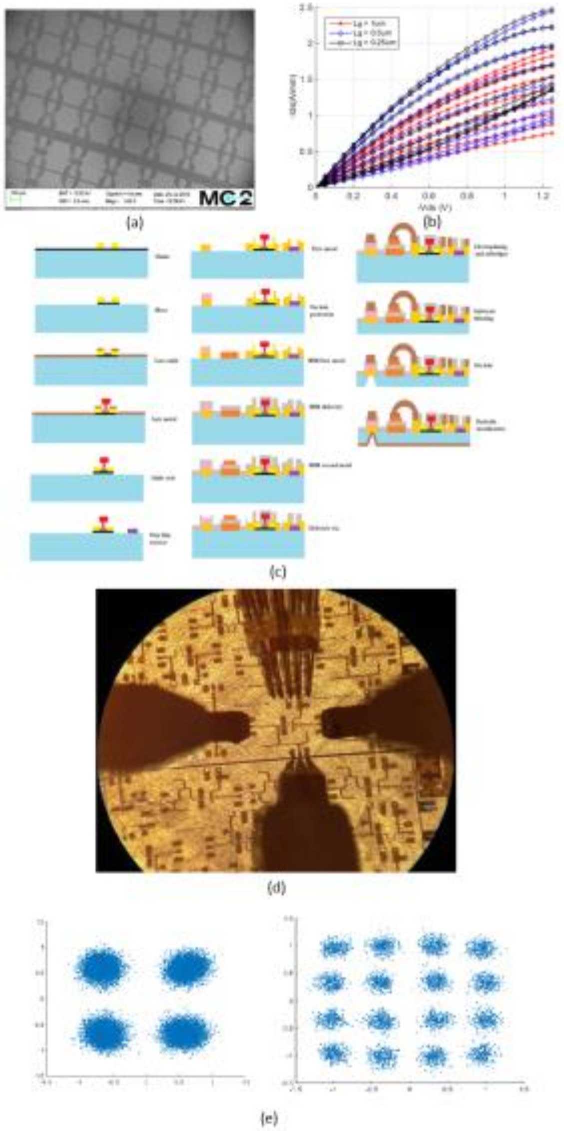

Figure 1: (a) Developed G-FET transistors, (b) Output characteristics of G-FETs, (c) MMIC fabrication process steps (d) Developed MMIC (e) I-Q constellation of upconverted 8 Gbps signal at 88 GHz

References:

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SMS EUROPE 2017 - Session II.A: Bioinspired, Biomimetic and Bioactive biomaterials

Graphene for Bioapplications: Preparation, Cytotoxicity and Integration in 3D-scaffolds

Ester Vázquez,[1,2,*]

[1] Instituto Regional de Investigación Científica Aplicada (IRICA), Universidad de Castilla-La Mancha, Ciudad Real, (Spain)
[2] Departamento de Química Orgánica, Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha, Ciudad Real, (Spain)

Abstract:
Graphene has emerged as a new material, with outstanding mechanical and electronic properties that will permit a broad range of applications, from microelectronics to composite or even medicine. Although there has been a huge effort directed in the area of nanomedicine, biomedical applications of graphene derivatives have, so far, mainly focused on graphene oxide and reduce graphene oxide. The main reason for this fact is the difficulty to obtain pristine graphene flakes, directly in water or in culture media, due to the intrinsic hydrophobicity of this material.

Our group have recently described an interesting approach for the preparation of stable dispersions of graphene in water, without detergents or any other additives, driven by an easy and eco-friendly ball milling approach.[1] These aqueous suspensions can be rapidly frozen and, subsequently, lyophilized giving rise to a very soft and low-density black powder.[2] Powders of graphene can be safely stored or shipped and they can be readily dispersed in culture media within the presence or absence of serum and antibiotics.

During this talk, we will discuss (i) optimized ways to generate graphene dispersions in culture media; (ii) studies of interaction of so-prepared solutions with cells. (ii) the use of graphene in polymeric 3D structures for drug delivery purposes[3] and for 3D cell culture media.

Keywords: graphene aqueous dispersions, 3D-scaffolds, cytotoxicity.

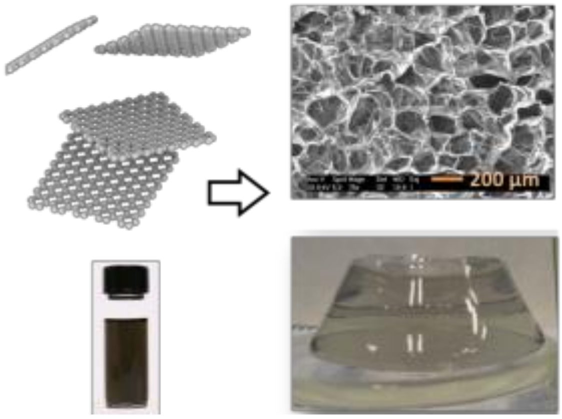

Figure 1: 3D-scaffolds from graphene water dispersions.

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Development of Lipid Bilayer Platforms for Processing Cell Membrane Species

Ling Chao

National Taiwan University, Department of Chemical Engineering, Taipei, 10617, Taiwan

Abstract:

Processing and handling membrane-bound species while maintaining intact structural information remains one of the largest bottlenecks to characterizing and understanding their structure-function behavior, even though membrane proteins are the major target for therapeutic development. Most of the problem stems from the requirement of protecting the delicate hydrophobic cores from water during processing to prevent denaturation and loss of function. A new direction is to carry out all of the necessary processing steps within a membrane environment such as a supported lipid bilayer, in which the hydrophobic cores of membrane species can be protected. We use various kinds of phase and barrier patterning techniques to construct several unit operation processes for separating membrane species in 2-D membrane platforms. The patterning techniques allow us to create phases and barriers at the desired locations of the membrane platforms, so that the extraction, filtration, and chromatography could be performed in the membrane. In addition, during many bio-assays, the samples would inevitably be exposed to air bubbles during the transport or reagent addition/exchange. Developing methods to form air-stable supported lipid bilayers is important for making robust platforms for handling membrane-bound species. We demonstrate using physical confinement instead of chemical modifications to create air-stable lipid membrane platforms. The physical confinement could trap some water above the lipid bilayers to prevent the air-water interface from directly contacting and peeling the lipid bilayers. We used two approaches, phospholipase A_2 (PLA_2) enzymatic reaction method and photolithography method, to generate obstacles for the physical confinement. Incorporating the built air-stable lipid bilayer platforms with some surface analytical tools could open the bottleneck of building highly robust in vitro cell-membrane-related bioassays.

Keywords: Supported lipid bilayers; patterning; separation processes

Novel, precise approach in the research on biodistribution of ZnO-based nanoparticles

P. Kielbik[1,2,*], J. Kaszewski[1,2,3], B. Dominiak[1,2], E. Wolska[3], M. A. Gralak[2], Z. Gajewski[1],
M. Godlewski[3], M. M. Godlewski[1,2]

[1] Warsaw University of Life Sciences, Veterinary Research Centre, Centre for Biomedical Research, Department of Large Animal Diseases with Clinic, Faculty of Veterinary Medicine, Warsaw, Poland
[2] Warsaw University of Life Sciences, Department of Physiological Sciences, Faculty of Veterinary Medicine, Warsaw, Poland
[3] Institute of Physics, Polish Academy of Sciences, Warsaw, Poland

Abstract:

Zinc oxide nanaopraticles (ZnO NPs) as a biodegradable material become very promising for numerous biomedical applications. Many studies have been conducted to assess their biodistribution and circlutaion in the living organism, however avaible reports present contradictory conslusions. Most of up-to date studies were based on measurement of total Zn concentration in analyzed organs using spectroscopy methods (AAS or ICP). However, this methodology does not answer the question whether measured zinc was present as NPs or ions. In our study we used ZnO NPs doped with Europim (ZnO:Eu) [1], which, when in NPs form, exhibit a red fluorescence following the excitation with appriopriate wavelength. ZnO:Eu NPs were orally administrated (IG, 90 mg/kg) to mice (n=35) and after different time points (3h, 24h, 7d, 14d, 1m) internal organs were collectes, for assesing a biodistribution of NPs. In addition AAS we also performed a quantitative scanning cytometry analyses. This comprehesive approach reflected more complete results on accumulation of NPs in organs and tissues. According to the results ZnO:Eu NPs are able to cross physiological barriers in the body and spleen as well as fat tissue were observed as a place of their accumulation. Liver and kidneys were designated for elimination of NPs from the organism [2]. Additionally we conducted an AAS analysis of the Zn level in the faeces. Results showed rapid Zn metabolism, with Zn levels returned to control level after just 4 days, in both single and multiple exposition.

Keywords: ZnO:Eu nanoparticles, biodistribution, nanoparticle circulation, biodegradation

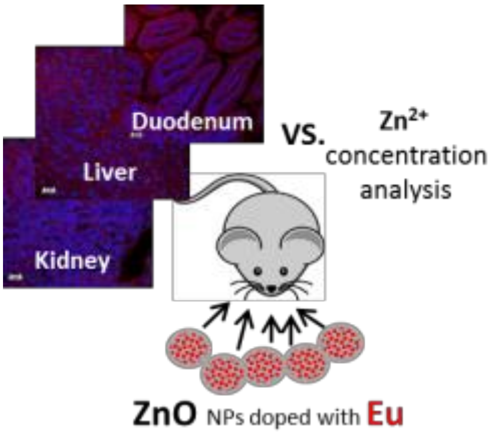

Figure 1: Following IG, the presence of ZnO:Eu NPs (red fluorescence) in the mouse organs was confirmed using AAS ans scanning cytometry methods. Scanning cytometry provided detailed intel on the distribution patterns of ZnO:Eu in NPs form, while AAS evaluation revealed a dynamic Zn metabolism in the tissues.

Acknowledgments:

NCN:DEC-2012/05/E/NZ4/02994; NCN:20/0139/N/ST3/04189; KNOW (Leading National Research Centre) Scientific Consortium "Healthy Animal—Safe Food", decision of Ministry of Science and Higher Education No. 05-1/KNOW2/2015

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Uptake and Release of Dyes for Photodynamic Therapy from Hydrogels

S. Glass,[1] A. Schulze,[1] B. Abel[1]

[1] Leibniz Institute for Surface Modification, Department of Chemistry, Leipzig, Germany

Abstract:

Hydrogels are water-swollen polymer networks that can be loaded with bioactive substances and drugs very easily. They are water absorbent and possess a high degree of flexibility [1].

Polyethylenglycol (PEG) hydrogels are a new and useful tool for drug delivery systems [2]. Therefore, they are of high interest for regenerative medicine applications [3]. The produced hydrogels should be used as wound patches for the regeneration of poorly healing lesions or the treatment of skin tumors. Drugs, used for photodynamic therapy (PDT), are immobilized and irradiated in order to produce singlet oxygen.

The polyethylenglycol diacrylate (PEGDA) hydrogels were prepared by photopolymerization (Fig. 1). The hydrogels were investigated by different analyzing methods e.g. scanning electron microscopy (SEM), infrared spectroscopy (IR), UV/VIS spectroscopy and dynamic mechanical analysis. Furthermore the swelling behavior and mesh size were determined.

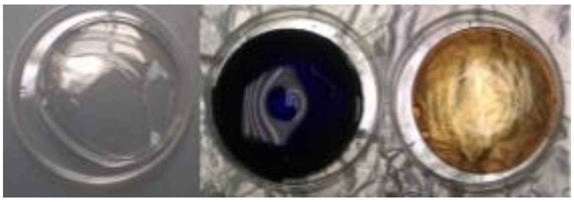

Figure 1 Fotograph showing three PEGDA hydrogels: pure hydrogel (left), hydrogel with methylene blue (middle) and with TMPyP (right).

Additionally the uptake and release of two dyes was analyzed. The first dye was methylene blue – one of the best known dyes for PDT [4]. The second dye was 5,10,15,20-Tetrakis(1-methyl-4-pyridinio) porphyrin tetra(p-toluenesulfonate) (TMPyP). Porphyrin dyes like TMPyP are typical photosensitizers for PDT. Uptake and release studies were performed through UV/VIS spectroscopy (Fig. 2).

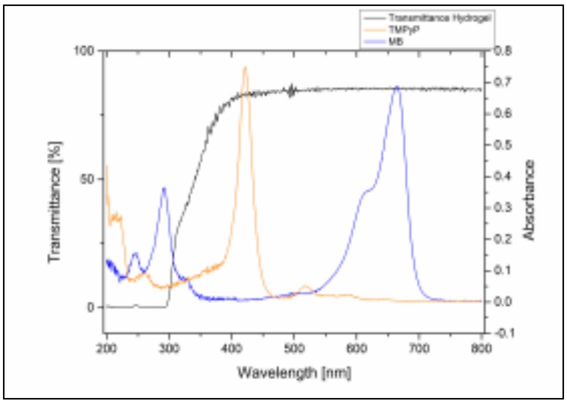

Figure 2 In this figure transmittance of hydrogel and the absorbance of the two dyes are compared.

The method shown here is be a simple and effective preparation strategy for wound gels, where different drugs can be incorporated, and which can be used for future medical applications.

Keywords: hydrogels, drug delivery, photodynamic therapy, transparent materials, biocompatibility, biomedical applications.

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Wide Band-Gap Oxides Nanoparticles as Drug Carriers

W. Lipinski[1], J. Kaszewski[2,3], Z. Gajewski[1], M. Godlewski[2], M. M. Godlewski[1,3]

[1] Warsaw University of Life Sciences – SGGW, Veterinary Research Centre, Biomedical Research Centre, Department of Large Animal Diseases with Clinic, Faculty of Veterinary Medicine, Poland
[2] Polish Academy of Sciences, Institute of Physics, Warsaw, Poland
[3] Warsaw University of Life Sciences – SGGW, Faculty of Veterinary Medicine, Poland

Abstract:

In recent years nanoparticles (NPs) gained many applications in almost every industry. However, in the field of medicine, although numerous possible applications, the use of NPs is still in the research phase. One of the most researched approach is the use of NPs as drug delivery system (DDS). Big advantage of using NPs in DDS is their throughout biodistribution [1] and possibility for surface modifications which could allow for targeted delivery of directed therapy.

In our research we focused on NPs from wide band-gap oxides doped with rare-earth metals made in Institute of Physics of Polish Academy of Sciences [2]. These NP's were prepared using microwave driven hydrothermal method and were fluorescent with excitation-emission range of 617 nm vs. 625-650 nm. They proved to be widely-distributed and nontoxic in the living organism. Furthermore, they exhibited key features that could prove to be of extreme usefulness in DDS. First of all, we determined that wide band-gap oxides NPs easily penetrate physiological barriers like intestinal barrier or blood-brain barrier. This opens up a possibility not only for targeting hard available sites like brain but also allows for oral administration instead of widely postulated intravenous administration. Secondly, they exhibit -OH groups on their surface which makes them an ideal target for surface modifications and orchestration with biomolecules.

The goal of presented study was to determine whether wide band-gap oxides NPs would act as efficient carriers for biomolecules. As an model of active substance we choose lectin from *Phaseolus vulgaris* (PHA), as it is not absorbed from the gastrointestinal tract *in substantia*. Y_2O_3 NPs doped with Tb^{3+} ions orchestrated with PHA by covalent bounding. NPs were administered via gastric gavage (IG) to adult mice. Mice were sacrificed after a period of 24h, 48h and 1 week. Afterwards, tissues were collected for analysis under confocal microscope and scanning cytometry.

We have found that Y_2O_3:Tb:PHA complexes were able to cross the intestinal barrier. Moreover, we have found considerable amount of modified NPs in the liver, kidney and the brain. We can conclude that orchestration did not alter the ability of NPs to penetrate physiological barriers. The analysis of biodistribution showed that the range of orchestrated NPs did not differ from that of unmodified ones. In 1 week samples we have found both free NPs and free lectin as well as NPs-lectin conjugates.

In conclusion we consider that wide band-gap oxides NPs are viable drug carriers especially for IG administered therapy.

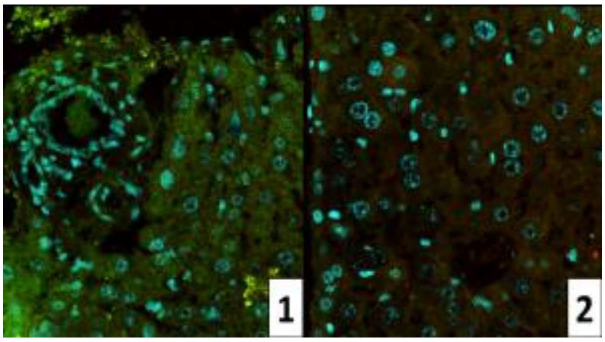

Fig. 1. Presence of Y_2O_3:Tb:PHA NPs in the liver, 1 week (1) ; 24h (2) sample. Fluorescence key: Blue – Nuclei; Green – Lectin; Red – NPs; Yellow – Conjugates NPs:Lectin (co-localization).

Keywords: Wide band-gap oxides, Lectin-orchestrated nanoparticles, Drug Delivery System.

Acknowledgments:

NCN DEC-2012/05/E/NZ4/02994
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High-k Oxide Nanolayers for Biomedical Applications

I. Serafińska[1,4,*], J. Kaszewski[1,3], R. Pietruszka[3], J. Cymerys[4], Z. Gajewski[1], M. Godlewski[3], and M. M. Godlewski[1,2]

[1]Veterinary Research Centre, Centre for Biomedical Research, Department of Large Animal Diseases with Clinic, Faculty of Veterinary Medicine, Warsaw University of Life Sciences – SGGW
[2]Department of Physiological Sciences, Faculty of Veterinary Medicine, Warsaw University of Life Sciences – SGGW
[3]Institute of Physics, Polish Academy of Sciences
[4]Department of Preclinical Sciences, Faculty of Veterinary Medicine, Warsaw University of Life Sciences – SGGW
*Ciszewskiego 8, 02-786 Warsaw, Poland

Abstract:

Atomic layer films, created layer by layer by atomic layer deposition (ALD), offer big promise in medicine. Nanolayers can easily intercalate the biosensing receptor biomolecules, are biocompatible, and provide a highly modifiable surface area. They could be utilized as aninterface between biological compound and inorganic material (metal, plastic). This solutions can be used for cell culture, tissue engineering or biomedical implants [1,2]. Using ALD, the finished products can be coated, even the highly developed surfaces.Unique technology of low-temperature coating of 3D structures by oxide nanolayers was developed in the Institute of Physics, PAS. This innovation opened the new way for application of nanotechnology and nanomaterials, enabling coating of perishable materials and biopolymers [2]. High-k oxide monolayers already proved their usefulness as antimicrobial materials and biosensors.

Coverslips were coated by different (biodegradable or bio-stable) high-k oxides by low temperature (below 100°C) ALD. Covered slides were then placed in Petri dishes and incubated with cell cultures. For the experiment both primary (mice's neurons and astrocytes) and fixed cell lines (Caco-2 and HaCaT) were used. For control the same cultures were incubated on uncoated coverslips.

Cultures were kept in standard growing conditions and monitored with JuliFl system for confluence and cell viability. After initial settling period cells were observed for 120-150 hours with image acquired every 2 hours. The dynamics of cell settling, growth and cell viability were assessed for indirect evaluation of the biocompatibility of high-k oxide nanolayers.

The cultures showed diverse growth according to the type of nanolayer. Cells adhered very quickly to biostable nanolayers, probably correlated to layer hydrophobicity. Caco-2 and HaCaT exhibited significantly faster growth than in the control group. Primary neuron culture settled effectively, but their further survival and growth depended strongly on the further bio-enrichment coating. Cells, which were incubated on biodegradable high-k oxide nanolayers, exhibited highly-significant drop in the adhesion, cell survival and growth.

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KNOW (Leading National Research Centre) Scientific Consortium “Healthy Animal—Safe Food”, decision of Ministry of Science and Higher Education No. 05-1/KNOW2/2015

Keywords: nanolayers, atomic layer deposition process, biomedical applications

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In-vivo analyses of the nanoparticle distribution by magnetic resonance

J. Olszewski[1], K. Lorenc[2], K. Skierbiszewska[2], K. Siewruk[2], Z. Gajewski[2], M. Godlewski[3],
J. Kaszewski[3], M. M. Godlewski[1,2]

[1]Veterinary Research Centre, Biomedical Research Centre, Department of Large Animal Diseases with Clinic, Faculty of Veterinary Medicine, WULS – SGGW, Warsaw, Poland,
[2] Department of Physiological Sciences, Faculty of Veterinary Medicine, WULS – SGGW
[3] Institute of Physics, Polish Academy of Sciences, Warsaw, Poland

Abstract:

Regardless of the great expand of nanoparticle (NPs)-related consumer products in recent years, relatively little is known on their interaction with living organism. New studies provided comprehensive proof of NPs absorption after gastrointestinal exposition [1]. Furthermore, the extent of NPs distribution in the organism and recirculation dynamics were also assessed.

Up to now, the greatest challenge for the assessment of NPs interaction with living organism was the fact that all analyses were done on isolated material (tissues or organs). Hereby, we present a novel approach to evaluate dynamics of NPs absorption, distribution and elimination based on the new generation of rare-earth-doped high-k oxide NPs with magnetic properties.

The aim of this study was to establish procedure for detection of NPs biodistribution with the use of magnetic resonance imaging in an *in vivo* rodent model.

During whole experimental procedure feed and water were provided *ad libitum* for animals. All procedures were conducted according to the EU and local directives.

Animals were divided into groups according to the type of used nanoparticles. Hafnium oxide nanoparticles doped with gadolinium (HfO:Gd) and hafnium oxide nanoparticles doped with iron (HfO:Fe) were used. Nanoparticle suspensions (10 mg/ml) were administered by gastric gavage.

GE MR Discovery mr750w 3.0T GEM Flex coil (GE Healthcare, Milwaukee, MI) unit was employed in the study.

Animals were anesthetized and imaged three times during the procedure. MR protocol consisted of T1 (3D IR-SPGR). T2-weighted images (3D FSE), SWI and SS-FSE.

The first examination was performed before administering nanoparticles. After that, either HfO:Gd or HfO:Fe NPs were administered and animals were investigated under magnetic resonance twice: 24 and 48 h after application.

Images were manually segmented into regions of brain, stomach, duodenum, left and right kidney, left and right testicle and urinary bladder. Data on each ROI were averaged and compared at each time point for particular organs.

Keywords: MRI, ferromagnetic nanoparticles, high-k oxides, *in-vivo* analysis

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NCN 20/0139/N/ST3/04189
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SMS EUROPE 2017 - Symposium on Functional Hybrid and Composite Materials

Depsotion of Nanoporous Silica Layer on Particle Surface

S. Bureekaew and M. Ogawa*

School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong, Thailand

Abstract:

After the successful preparation of mesostructured and mesoporous silica films on solid supports by the solvent evaporation method,[1,2] the preparation of mesoporous silica films have been extensively investigated partly due to the wide range of application of mesoporous silica films.[3] The deposition of mesoporous silica layer on powders have also been reported extensively. Here, we report the deposition of homogeneous nanoporous silica thin layer on a variety of solids surfaces with the emphasis on micrometer sized functional powders (oxide, hydroxide, inorganivc–organic hybrids, carbons and polymers).[4-9]

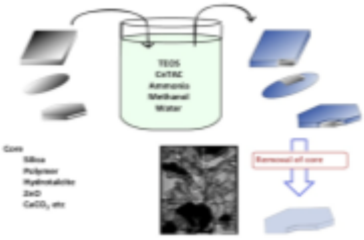

Figure 1: Schematic illustration of the formation of silica shell on the particle surface and the subsequent removal of the core.

The present reaction is very simple, where substrates (both plate and powder) were put into a homogeneous solution containing tetraethoxysilane, hexadecyltrimethylammonium chloride, methanol, water and ammonia. The present synthesis is a versatile method to prepare nanoporous silica thin layers on solid substrate especially when the reported procedure is not applicable; substrate with complex morphology and/or unstable in acidic solutions such as hydrotalcite and metal oxides. Mesoporous silica coating is regarded as a way to modify the surface property of powders as well as to impart new functions such as molecular sieving one on catalysts and adsorbents. Moreover, the surface modification of silica shell through grafting is possible to make the application of thecore-shell particles more versatile. The core-shell particle was also used as a precursor of hollow particles, which was prepared by the removal of the core.

Keywords: Mesoporous silica, Core-shell

References:

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Synthesis, Mechanism and Functionalization of Bimodal Silica of SBA-15 Type

Y. Shchipunov

Institute of Chemistry, Far East Department, Russian Academy of Sciences, Vladivostok, Russia

Abstract:

Template synthesis serves to increase and regulate silica porosity, while precursors allows manipulating the surface polarity and functionality. Here triblock copolymer P123, which widely applied to synthesize well-known SBA-15, was taken as the template. Our procedure was simplified by using silane with ethylene glycol residues instead of alcohols. *Monolithic* SBA-15 is prepared in *broad pH* and *temperature* ranges. Analysis of transmission electron microscope images led us to a novel mechanism in lieu of the previous one unchanged since 1992. It is reasoned that admixing of silica precursor into a solution of block copolymer triggers a set of transformations first of which is self-organization of initial spherical micelles into the hexagonal mesophase in which their subsequent unidirectional merging results in parallel alignment of cylindrical aggregates determining the final regular mesoporous structure of silica (Fig. 1) [1].

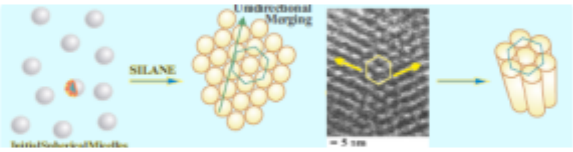

Figure 1: Evolution of template structure in the course of SBA-15 formation. Formed silica is not shown for simplicity.

Mixing of mentioned silane with a silica precursor containing covalently attached methyl group enabled us to introduce macropores. Hierarchical architecture of silica monoliths with a bimodal organization of periodic mesopores and bicontinuously arranged macropores was regulated by varying ratio of both the silanes as shown in Fig 2 [2].

The silica precursor with alkyl radical served also for regulating the hydrophobicity of synthesized silica [2,3]. It was made via the ratio of both precursors as well. The hydrophobic properties were caused by the alkyl radical coating the pore surface, as well as its surface morphology. It was demonstrated that the developed materials are promising as an oil adsorbent.

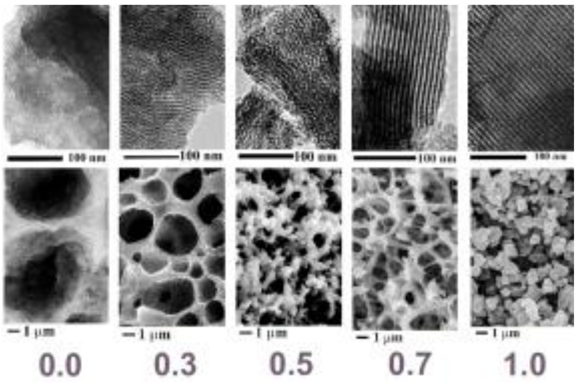

Figure 2: Change of regular mesoporosity (TEM images, upper row) and macroporosity (SEM images, bottom) with varying ratio of two silica precursors in the reaction media.

Keywords: block copolymer P123, sol-gel, bimodal silica, hydrophilic-hydrophobic porosity, oil absorbent.

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Hybrid Biomaterials for Medicinal Applications

Tanja Weil,[1,2,*]

[1] Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
[2] Ulm University, Albert-Einstein-Allee 11, 89081 Ulm, Germany

Abstract:
Efficient delivery of drug molecules in a living organism is of great importance for the therapeutic intervention of various diseases. Even though tremendous efforts have been made to design and synthesize more efficient transporter systems that operate in vivo, only few materials have made their way into clinical applications. Reaching the desired target structures e.g. inside the cells is not trivial and most likely, more synthetic efforts are needed to design more efficient transporter molecules.
Different concepts to design improved biomaterials will be presented that efficiently transport (1) clinically used viruses into their target cells, (2) cytotoxic proteins or drug molecules into tumor cells or modulate the viability of cells locally. The importance of controlling interactions of biomaterials with blood proteins, cell surface structures as well as cell organelles will be highlighted.

Keywords: biohybrid materials, polypeptide-copolymers, nanoparticle theranostics, drug delivery, gene transfection, phototoxic drugs, celltype-selective transport, tumor cell targeting.

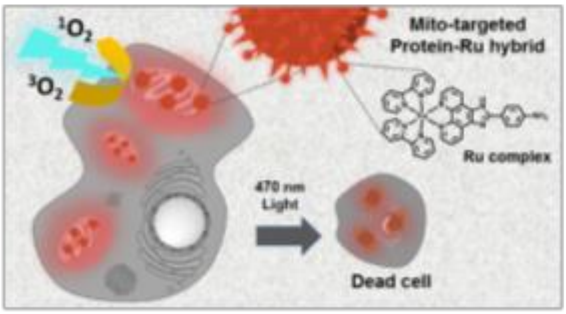

Figure 1: Figure illustrating celltype and mitochondria-selective transport of a phototoxic ruthenium drug by a tailored polymeric nanocarrier.

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Fabrication of 3D structured hybrid materials with nano second pulsed technology

T. Nakayama

Nagaoka University of Technology, Dept. of Mech. Eng., Nagaoka, Japan

Abstract:

The thermal management (thermal discharge) in compact devices has become an urgent issue as these devices become increasingly more compact. To overcome this problem, research is being conducted in materials that promote heat radiation. Materials conventionally used to dissipate heat include metals such as aluminum, copper, and, to some extent, silver, but they are problematic since it is not possible to insulate them. Consequently, manufacturers need to find inorganic substances that discharge heat to serve as next-generation heat-dissipating materials. Inorganic materials such as aluminum nitride and boron nitride have higher heat conductions than aluminum and copper and they also have the advantage of being electrical insulators". However, these inorganic materials are extremely brittle, which causes reliability problems when they are used in portable devices. Because of this, attention is currently focused on heat-dissipating materials that are composites of organic and inorganic materials (thermal interface materials; TIMs), since they provide a way to overcome the problem of reliability. These inorganic heat-dissipating materials are used as fillers and are dispersed within polymers. They are both pliant and maintain the thermal conducting and electrical insulating properties of the material. We have proposed a new method for realizing orientation that employs a nanosecond pulse power supply as a new way to achieve anisotropic structure control. This method permits characteristic structure control that cannot be realized using other orientation methods.

Keywords: nano second pulsed power, 3D micro structure control, BN, Polysiloxane, Thermal Interface Materials, Thermal conductivity

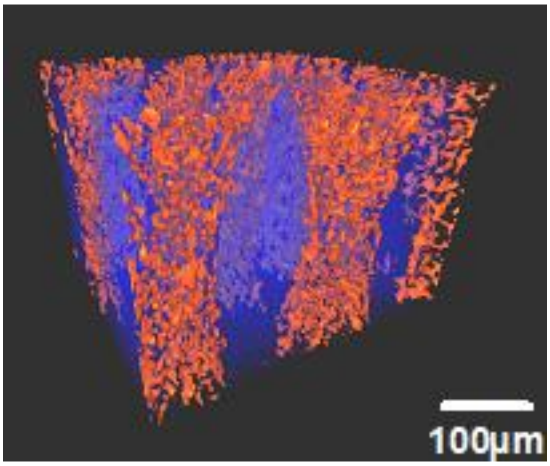

Figure 1: Micro Focous X-ray CT image of 3D structured BN/Polysiloxane Hybrid material by nano second pulsed power technology

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Green foams based on clay-bionanocomposite materials

M. Darder, B. Wicklein, F.M. Fernandes, A.C.S. Alcântara, R. F. Gouveia†, P. Aranda, E. Ruiz-Hitzky*
Instituto de Ciencia de Materiales de Madrid, CSIC, 28049 Madrid, Spain
†Laboratório Nacional de Nanotecnologia (LNNano), CNPEM, Campinas/SP (Brazil)
*e-mail: eduardo@icmm.csic.es

Abstract:

Composites resulting from the assembly between biopolymers and inorganic solids, such as clay nanoparticles, have been designated as "bionanocomposites" or "green nanocomposites" [1,2]. They can be conformed as cellular materials or foams, which are low-density macroporous solids produced under particular synthetic preparations and shaping procedures as for instance freeze-drying or supercritical drying processes. Taking into account the biological origin of the continuous phase, i.e. the matrix, they can be considered as bio-hybrid materials, at the frontier between life sciences, materials science, and nanotechnology.

Clay-based bionanocomposites represent an attractive field of research with the aim to develop novel hierarchical porous systems that bring out a broad range of advanced applications as functional materials. For instance, sepiolite is a natural fibrous clay that can be assembled to a great variety of biopolymers giving rise to bionanocomposites showing interesting characteristics in view to applications as diverse as biomedical aspects, energy generation and storage, or insulation.

A recent example of polysaccharide-based foams, involve the assembly of sepiolite with alginate and potato starch [3]. It is here observed that increasing amounts of the clay lead to smaller pore size in the foams, which seems to be related to a substantial increment in the mechanical properties of these materials. In addition, these bionanocomposite foams show an enhanced fire resistance and those containing an amount of sepiolite equal to or higher than 25% can be considered auto-extinguishable materials. Moreover, the crosslinking of alginate chains with calcium ions may enhance the mechanical properties of these bionanocomposite foams. Beside the robustness conferred by the clay fillers, as well as the developed porosity, another significant feature of these macroporous materials is the possibility of easy functionalization by further incorporation of nano-additives. Examples of this type of cellular materials are the tertiary systems generated by incorporation of carbon nanoparticles (carbon black, graphenes, CNTs…) into clay-based bionanocomposites, giving rise to conductive foams, which can be applied to develop biosensing devices and electrocatalytic reactors [4,5].

Keywords: bionanocomposites, biohybrids, foams, clays, sepiolite, polyssacharides.

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Freeze casting hybrid living materials

S. Christoph, T. Coradin, F.M. Fernandes

Sorbonne Universités, UPMC Univ Paris 06, CNRS, Collège de France, Laboratoire de Chimie de la Matière Condensée de Paris (LCMCP), 4 Place Jussieu, Paris, France

Abstract:

Microorganism-based biocatalytical platforms aim at providing domains such as environmental remediation, pharmaceutics synthesis, energy production and sensing with radically new, sustainable approaches[1]. In parallel, the rise of cell-based therapies in tissue engineering has stimulated the encapsulation of mammalian cells in order to efficiently preserve and deliver cellular therapeutic agents onto the target zones. All things considered, we witness a growing need to deliver and/or host metabolically active cells under easy to handle, stable and accessible materials.

From microencapsulation[2] to inkjet printing technology[3], a wide range of approaches have been proposed to address the need to formulate the new generation of cellularized materials. Here we will present recent results in the application of freeze casting, a materials processing technique we have adapted to produce metabolically active cell-containing hybrid materials with controlled morphology[4]

Our approach stands at the interface between standard cryopreservation techniques and commonly used ice templating techniques, providing solid-state cellularized materials with finely controlled macroporous morphology. Using a prokaryote (Pseudomonas aeruginosa) and an eukaryote (Saccharomyces cerevisiae) model microorganisms we show that ice templating of living cells in absence of commonly used cryoprotectants can be attained under specific processing conditions in the presence of different polysaccharide hydrocolloids. Moreover we focus on the interplay between the processing conditions, material morphology and cellular viability to discuss the application potential of freeze casting to the elaboration of cellularized materials. The implications of the silicification of the formed polysaccharide cellularized foams in terms of their stability, cell viability and morphology will be discussed in the context of environmental and biomedical fields.

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Hybrid Layered Double Hydroxide/Sepiolite Heterostructures for Controlled Release Applications

E.P. Rebitski, M. Darder, E. Ruiz-Hitzky, P. Aranda*

Instituto de Ciencia de Materiales de Madrid, CSIC, 28049 Madrid, Spain
*e-mail: pilar.aranda@csic.es

Abstract:

There is an increasing interest in the preparation of nanostructured materials based on the combination of diverse type of inorganic particulate solids with the aim to produce a new generation of functional materials for diverse applications. In this context, fibrous clays, sepiolite and palygorskite, have been used as nanoplatform of nanoparticles, as for instance metal oxides (e.g., TiO_2, Fe_3O_4,..), that provide photocatalytic, magnetic and other relevant properties [1]. The presence of hydroxyl groups (silanol groups) regularly distributed along the external surface of the sepiolite fibres allows the assembly to layered double hydroxides (LDH) nanoparticles in situ generated from the corresponding precursors [2]. The resulting materials show the simultaneous properties of the two nanoparticulated solids, for instance adsorption capacity towards cationic and anionic species, which could even result in synergistic effects [3]. The assembled LDH preserves its ion-exchange capacity which can be profited to incorporate anionic species useful for other applications. For instance, the herbicide 2-methyl-4-chlorophenoxyacetic acid (MCPA) can be easily intercalated into a Mg-Al LDH to produce hybrid materials of interest for controlled release applications. Moreover, the general synthesis procedure [2] allows to tune the sepiolite:LDH relative ratio, and even more, to co-precipitate the LDH in the presence also of anionic organic species to produce in a single step the formation of organic-inorganic hybrid LDH-sepiolite nanostructured materials, in which the organic species remain intercalated between the layers of the formed LDH. In this way, MCPA has been in situ co-precipitated with the MgAl-LDH in presence of sepiolite. Interestingly, the characteristics as well as the amount of associated MCPA in the MCPA-LDH/sepiolite hybrid materials prepared by this method are strongly influenced by the relative ratio of the three components in the reaction medium. This communication will discuss on diverse aspects of the formation of this type of hybrid materials, as well as on aspects related to the release of the herbicide also in comparison to that from the LDH alone. Furthermore, the prepared materials have been incorporated into beads formed by mixtures of zein and alginate biopolymers, a system that proved very effective in the controlled release of oral drugs [4], with the aim to produce a new generation of effective and tunable systems for controlled release of pesticides in soils.

Keywords: sepiolite, layered double hydroxides, MCPA herbicide, organic-inorganic hybrids, nanostructured materials, controlled release applications, bionanocomposites.

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Chiral molecules based nano spintronics devices

S. Yochelis, Y. Paltiel

The Hebrew University of Jerusalem, Applied Physics Dept., Jerusalem, Isreal

Abstract:

In recent years a new concept was developed in which spin current is produced by using the spin selectivity in electron transport through chiral molecules, termed Chiral-Induced Spin Selectivity (CISS).[1,2] The CISS effect allows realization of simple local and power efficient spintronics devices. Studying the CISS effect, we found that chiral molecules, especially chiral polyalanine alpha-helix molecules, can serve as very efficient spin filters at room temperature, with no need for a permanent magnetic layer. Recently, by utilizing this effect we demonstrated a simple magnetless optical and electrical magnetic memory[3,4], as well as local charge separation using a light induced configuration[5]. Moreover, we show that when chiral molecules are adsorbed on the surface of thin ferromagnetic film, they induce magnetization perpendicular to the surface, without the application of current or external magnetic field.

Taking this effect further we adsorbed the helical chiral molecules on top of a type II Nb superconductor to realize that the Nb surface is significantly altered upon adsorption. By applying scanning tunneling spectroscopy, we found that the singlet-pairing s-wave order parameter of the Nb is changed to a triplet p-wave symmetry at the Nb organic–molecules interface.[7] This may open a simple way to realize superconducting spintronics devices.

The combination of results point out that CISS-based devices has the potential to overcome the limitations of other magnetic-based memory technologies and to facilitate the fabrication of inexpensive, high-density memory and other spintronics elements.

Keywords: helical chiral molecules, self assembly, spintronics, superconductors, CISS effect.

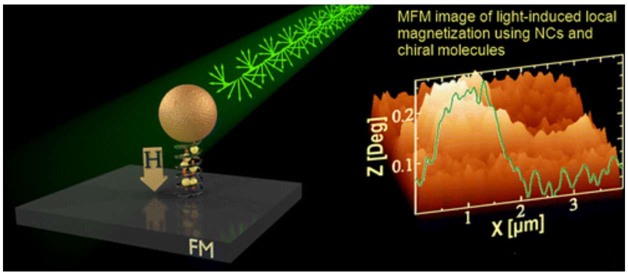

Figure 1: Figure illustrating an optical device based on the chiral induced spin selectivity (CISS) effect. On the right: magnetic phase image of a locally illuminated area, covered by helical molecules and CdSe NC, displays a highly localized magnetic response.

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Multimodal Metal Oxide Nanoparticles and their bio-interactions

Magali Lavenas, CNRS,[1,2] Marina Simon,[3] Hervé Seznec, [3] Joao Rocha[2], Luis D. Carlos[2] Marie-Hélène Delville, [1,2]

[1]Université de Bordeaux, ICMCB, Pessac, France
[2]Universidade de Aveiro, CICECO, Aveiro, Portugal
[3]CNRS, Université de Bordeaux, CENBG, UMR 5797, F-33170 Gradignan, France

Abstract:

Nanoparticles and their control are of great interest from both academic and industrial points of view, with numerous applications in domains such as medicine, catalysis and material sciences. This talk will stress on metal oxide nanoparticles (NPs) and two aspects: their use as multifunctional contrast agents[1-2] to help in therapy[3] but also their potential nanotoxicity. [4-5]

As multifunctional contrast agents, they can provide a multiple targeting and visualisation of organs or cells with both detectable changes in the MR signal intensity of the target tissue or organ by changing its MR relaxation properties and classical detectable optical signals for example. The development of biocompatible nanoparticles with an external shell of high-spin paramagnetic lanthanide contrast agents like gadolinium chelate, and europium fluorescent probes led to targeted imaging and gene therapy.

A second aspect of NPs is their nanotoxicology which also attracted the attention of public & governments worldwide. Scientists are concerned by addressing the special characteristics of NPs in terms of toxicology and more especially assessing their biological effects.

There is an urgent need to evaluate the risks of these particles to ensure their safe production, handling, use, and disposal. In particular, the behavior of NPs inside living cells is still an enigma, and no metabolic responses induced by these particles are understood so far.

With this respect, we have examined the potential toxicity due to exposure of TiO_2 NPs used in sunscreens & cosmetics. We applied an original imaging methodology (Ion Beam Analysis, TEM, & Confocal microscopy) to in vitro and in vivo studies, combining technologies for detection, tracking, and quantifying TiO2 NPs as well as the use of indicators for ion homeostasis, cell metabolism, or cell fate. [4-5]

Keywords: Multimodal Nanoparticles, imaging, nanotoxicologie, quantification biomedical applications.

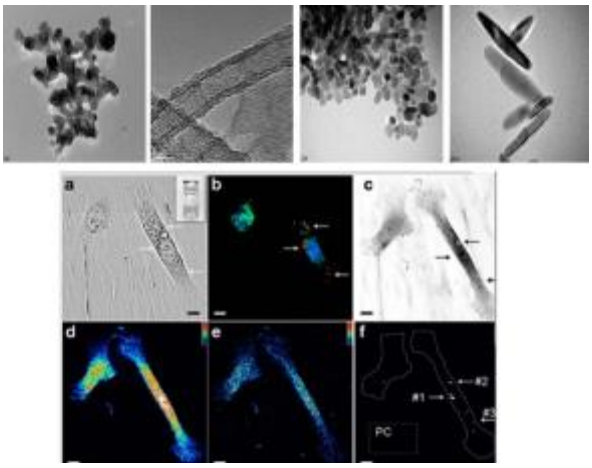

Figure 1: Figure illustrating various metal oxide NPs and their internalization and quantification in human cells.

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Multifunctional superstructures by hybridization of 2D solids

Q. Evrard,[1] G. Rogez[1] and P. Rabu[1*]

[1] Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504 CNRS, 23 rue du Loess, BP 43,
67034 Strasbourg Cedex 2, France.

Abstract:

Today, there is a great interest for the rational design of new materials with increasingly varied applications from electronics, catalysis, to biology and healthcare. The development of new multi-property devices led to explore new tracks for designing materials combining very different functional blocks within the same phase. Since the discovery of the outstanding electronic properties of the graphene derivatives, the research in the field of functional nanomaterials has been increasingly concerned with nanosheet-based multifunctional systems, with intensification of research in the field of layered materials.(1-3) Among possible chemical routes, the hybrid organic–inorganic approach is particularly well suited to promote multifunctionality. In this respect, transition metal layered hydroxides or oxides are very well adapted to functionalization with various molecules.(4, 5) Thanks to the multi-scale organization of their components and synergistic effects, such 2D structures may exhibit novel properties with tremendous potential in a broad field of applications (2).

In this paper, we will present recent progress in this field. We will describe some emblematic examples of layered hydroxide hybridization allowing better understanding of how to control their magnetic, optical and / or electrical properties. Then, going from hydroxides to layered oxides, we will present our latest results on the micro-wave assisted functionalization of layered materials (fig. 1).(6, 7) We will especially emphasize the possibilities offered by insertion/grafting chemistry for obtaining synergy at the organic-inorganic interface.

Keywords Hybrid organic-inorganic materials, 2D systems, hybridization techniques, magnetism, multifonctional materials.

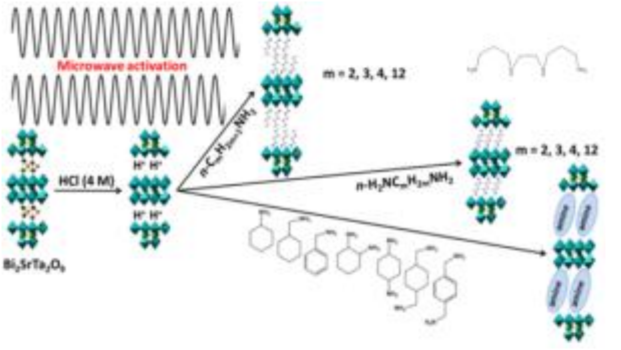

Figure 1: Example of efficient hybridization of layered oxides by a variety of amines opening the trail to multifunctionality.

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Fluorescence emission properties of a neutral porphyrin loaded into a layered inorganic-organic monolith

K. Fujii,[1] J. P. Hill,[2] H. Hashizume,[1] S. Shimomura,[1] K. Ariga,[2] T. Ando[1]

[1]Research Center for Functional Materials, National Institute for Materials Science (NIMS), Tsukuba, Japan
[2] WPI-MANA, NIMS, Tsukuba, Japan

Abstract:

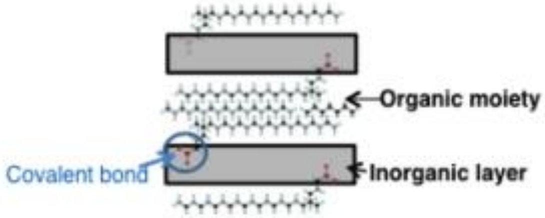
Porphyrins are an important class of pigments found in almost all living systems. Their most significant roles involve either absorption of incident light, as in the chlorophylls and photosynthesis, and electrochemical processes including catalysis. Of these properties, absorption of visible light by porphyrins has been investigated as a means of developing artificial light harvesting and photosynthetic systems. However, pigments contained in solution are usually not stable enough for applications due to photobleaching or other degradative processes. Therefore, it ought to be advantageous to prepare materials with the pigments included in the solid-state. Layered materials possess an interlayer space that provides an essential two-dimensional nanospace to immobilize the pigments in the solid-state. The immobilization of cationic and anionic pigments on the layered materials has been reported.[1, 2)] However, it is more difficult to fix pigments lacking charge onto the layered materials.

In this study we have investigated the preparation of composites by the immobilization of uncharged pigments on the layered materials. Further we have studied their emission. For this purpose, we have used a layered inorganic-organic monolith[3)] in which inorganic and organic moieties are covalently bound (Scheme 1).

The layered inorganic-organic monolith (A-Sm) was added into solutions of a neutral charged zinc porphyrin derivative (ZnTPPder) under several conditions in order to load ZnTPPder into A-Sm. Then ZnTPPder/A-Sm composite films were prepared.

UV-vis measurements revealed absorption peaks at around 430 and 500 nm for the ZnTPPder/A-Sm composite films. Emission peaks were observed for the ZnTPPder/A-Sm composite films. Based on these experimental results, we will discuss loading behavior of the neutral charged porphyrin on A-Sm.

Scheme 1: Schematic representation of the layered inorganic-organic monolith



Keywords: porphyrin, pigment, dye, layered inorganic-organic monolith, covalent bond between inorganic and organic moieties, layered materials, photosynthesis

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Synthesis of Manganese-Based Metal-Organic Frameworks

Wararat TRANGANPHAIBUL,[1*] Sareeya BUREEKAEW,[1]

[1] Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand

Abstract:

Metal-organic frameworks (MOFs) are a new crystalline porous materials which consist of metal ions or metal clusters coordinating with organic ligands.[1] Two new manganese (Mn^{II})-based metal-organic frameworks, namely $[Mn_2(adipate)_{0.5}(bpy)_2(ox)(H_2O)]\cdot 2(H_2O)\cdot(NO_3)$ (**1**) (adip = adipate, ox = oxalate and bpy = 4,4'-bipyridine) and $[Mn_4(formate)_3(BDC\text{-}NH_2)_{1.5}]$ (**2**) ($BDC\text{-}NH_2$ = amino benzene-1,4-dicarboxylate), have been solvothermally synthesized and characterized by single crystal XRD. Single crystal of **1** crystallized in the monoclinic $P2_1/c$ space group. This Mn-MOF contains half *adip*, two *bpy*, one *ox* and two metal atoms in an asymmetric unit. Mn ions bridged with dicarboxylate ligands to form 2D-sheets in the *bc* plane, and connected with *bpy* forming 3D framework ultimately. (Fig.1) Compound **2** crystallized in the monoclinic $C2/c$ space group, verifying by single-crystal X-ray diffraction. It contains 1D channel along the c axis which contains one and a half *BDC-NH_2,* three *formate,* and four metal atoms in an asymmetric unit. (Fig.2)

Keywords: manganese, synthesis, crystal structure, metal–organic frameworks

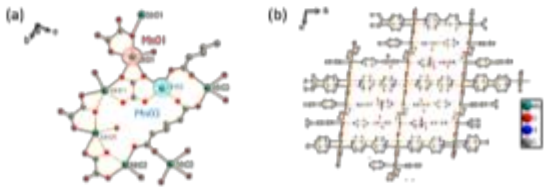

Fig. 1 (a) Two modes of Mn ion and crystal structure along a-axis (b) Crystal structure along b-axis of **1**

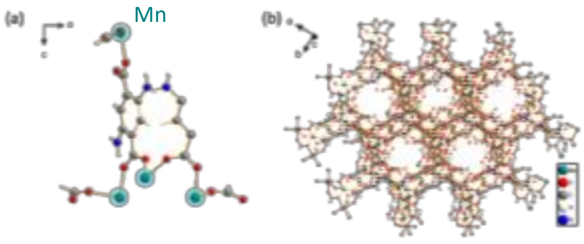

Fig. 2 (a) Asymmetric unit (b) Crystal structure along b-axis of **2**

References:

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Crystal Engineering of Bimetallic Metal-Organic Frameworks based on MIL-101

T. Tanasaro,[1*] S. Bureekaew,[1]

[1] Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand

Abstract:

MIL-101(Cr), $Cr_3X(H_2O)_2O[BDC]_3 \cdot nH_2O$ (X = Cl^-, OH; BDC = benzene-1,4-dicarboxylate), has been extensively studied due to its high thermal and chemical stability and its large cavities. In addition, MIL-101 presents coordinatively unsaturated sites (CUSs) which allow the strong interaction with guest molecules. As such, CUSs are considerably investigated to be active centers for being used in adsorption and catalytic applications. A mixed-metal approach is a versatile method for creating metal-organic frameworks (MOFs) with two or three different metals in the same framework. Based on this method, the mixed-metal MOFs with desired open metal sites would be achieved. In this work, the mixed-metal MIL-101(Cr, Fe) was synthesized through an environmental friendly hydrofluoric acid-free solvothermal method. The effects of the second metal (Fe) on the morphology and on H_2 adsorption property of mixed-metal MIL-101(Cr, Fe) were examined. The obtained materials were characterized by using Powder X-ray Diffraction (XRD), Scanning electron microscope (SEM), Energy-dispersive X-ray spectroscopy (EDS) and N_2 and H_2 adsorption. The EDS results show a good distribution of the Fe throughout the particles of obtained products. Moreover, the XRD results for mixed-metal materials are similar to that found for MIL-101(Cr). These results indicated a successful incorporating Fe into MIL-101(Cr) without damage its framework, and well dispersion of Fe. In contrast to MIL-101(Cr) with spherical shape (Figure 1a), the MIL-101(Cr, Fe) features an octahedral morphology as shown in Figure 1b. Interestingly, the particle size of mixed-metal MIL-101(Cr, Fe) increases as a function of the amount of Fe. By introduction of Fe, the morphology of MIL-101(Cr) changes and the H_2 adsorption property is significantly improved related to the amount of Fe. Overall, the mix-metal MIL-101(Cr, Fe) with controlled metal loading and morphology is successfully synthesized by using the mixed-metal approach.

Keywords: Metal-organic frameworks, HF-free, Morphology, Mixed-metal

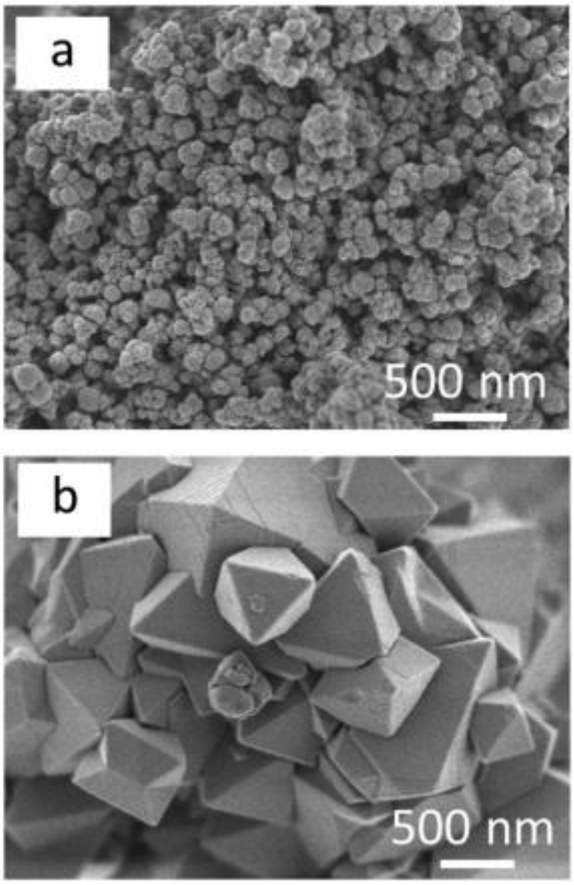

Figure 1: SEM images of (a) MIL-101(Cr) and (b) MIL-101(Cr, Fe)

References:

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Brønsted Acid-Base Bifunctional Zr-Based Metal-Organic Framework

W. Pratanpornlerd, S. Bureekaew,*

School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology,
Rayong, Thailand, 21210.

Abstract:

Metal-organic frameworks (MOFs) are one class of crystalline porous materials, which have received much interest due to their high crystallinity, high porosity with inherently structural tunability, and chemical functionalization. Design and synthesis of MOFs with multifunctionality have attracted attention because the combination of different functional groups potentially exhibits a synergistic effect, which is not found in mono-functional MOFs.[1,2] Herein, acid-base bifunctional MOF was successfully synthesized aiming to new applications such as gas separation, energy storage, sensing, and catalysis. Brønsted acid-base bifunctional UiO-66 (UiO-66-SO_3H-NH_2) was synthesized *via* one-pot procedure by using mixed ligands, 2-sulfonic benzenedicarboxylate (bdc-SO_3H) and 2-amino benzenetricarboxylate (bdc-NH_2). XRD patterns of the modified UiO-66 is similar to that found for the parent UiO-66 (Figure 1), indicating that the UiO-66-SO_3H-NH_2 shares the same structure as the parent UiO-66. IR and NMR results reveal the coexisting of bdc-SO_3H and bdc-NH_2 in UiO-66-SO_3H-NH_2. Note that the amount of acid-base functional groups in UiO-66-SO_3H-NH_2 can be precisely tuned. TGA result shows that the UiO-66-SO_3H-NH_2 is thermally stable up to 300 °C.

Keywords: multifunctional MOFs, acid-base bifunctional UiO-66.

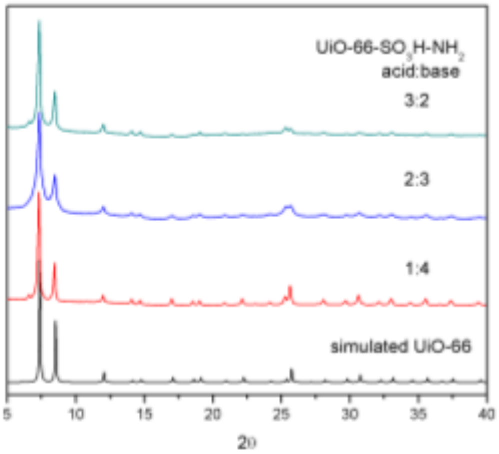

Figure 1: XRD patterns of parent UiO-66 and Brønsted acid-base bifunctional UiO-66 (UiO-66-SO_3H-NH_2) at various acid-base compositions.

References:

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EGF 2017 - Session II.B: Graphene and 2D Materials - Energy and environmental applications

Binder-free metal loaded graphene aerogel for electro-oxidation of alcoholic fuels from a one-step, mild, and green preparation

C. H. A. Tsang,[1]* D. Y. C. Leung,[1]

[1] The University of Hong Kong, Department of Mechanical Engineering, Hong Kong

Abstract:

Binder-free palladium loaded graphene aerogel on nickel foam (Pd/GA/NF) hybrid composite was successfully synthesized by a one-step, and green reaction under mild condition (Figure 1). The Pd particles size and overall loading (weight %) in the composite was controlled by the initial Pd concentration in the raw metal/graphene oxide mixture based on the electron microscopic characterizarion and X-ray fluorescence analysis. The hybrid composite was used as a binder-free anode for methanol and ethanol electrooxidation under room temperature. The cyclic voltammetry (CV) result showed that Pd/GA/NF exhibit strong electrocatalytic activity in ethanol and methanol oxidation, with a current density over 400 A g^{-1} and strong toxic tolerance ($I_f/I_b>2$) in both kind of reactions. However, its performance was strongly dependent on the loading of Pd in the electrode, it was especially obvious in methanol oxidation. Pd/GA/NF anode also showed superior stability in ethanol electrooxidation when compared to that in methanol electrooxidation throughout the 15 h CV operation (Figure 2). The peak current density in ethanol oxidation can keep almost constant over 500 cycles with low current density depreciation rate after 1000 cycles of operation when compared to that in methanol oxidation. This work provided an alternative way for the low cost fuel cell electrode, or even the fuel cell device parts production in the commercialization development.

Keywords: Graphene, aerogel, palladium, fuel cell, ethanol, methanol, nickel foam.

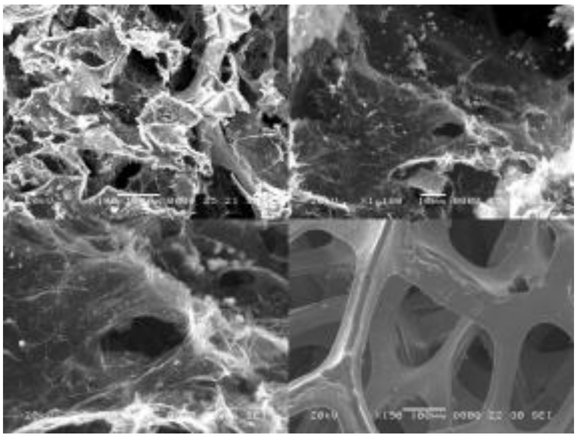

Figure 1: Microscopic images of Pd/GA/NF as catalytic electrode in alcohol electrooxidation, Pd/GA was covered on NF surface.

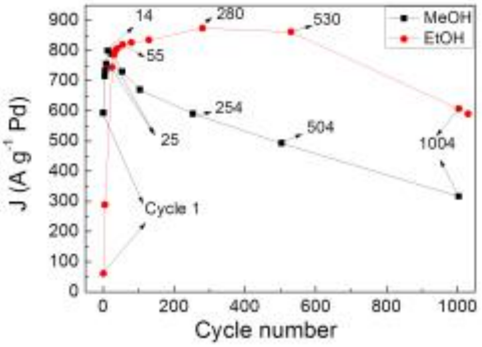

Figure 2: Figure illustrating the excellent electrocatalytic performance of the Pd/GA/NF as catalytic electrode in alcohol electrooxidation, especially the ethanol oxidation was showed the graphene aerogel high stability and activity.

References:

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Graphene/Fe_3O_4 Nanocomposite: Interplay between photo-Fenton type reaction, and carbon purity for the removal of methyl orange

A. Arshad,[1,2,*] J. Iqbal,[3]

[1] International Islamic University, Department of Physics, Islamabad, Pakistan
[2] Durham University, Department of Physics, Durham, United Kingdom
[3]Quaid i Azam University, Department of Physics, Islamabad, Pakistan

Abstract:

Graphene/Fe_3O_4 nanocomposite obtained via soft chemical method is characterized for its crystallinity, morphology, microstructure, optical properties and vibrational modes. Graphene sheets decorated with magnetite nanoparticles are employed to investigate their photocatalytic response against methyl orange. The study reveals that the conducting nature of graphene, engineered bandgap and photo Fenton like reaction synergistically govern the efficient photocatalytic activity of nanocomposite. Interestingly, it is observed that methyl orange can be completely removed i.e., upto 99.25% by graphene/Fe_3O_4 nanocomposite, whereas the removal efficiency is 43% for Fe_3O_4 nanoparticles, alone. The presence of graphene endows the delay in charge carriers' recombination, whereas, photo Fenton like reaction stimulates the generation of reactive oxygen species. This ultimately leads to the highly enhanced photocatalytic activity and complete removal of methyl orange. The magnetically separable photocatalyst presented in this work offers great prospects for fast and economical decontamination of dye polluted water.

Keywords: Graphene nanocomposites, magnetite, photocatalysis, waste water treatment, industrial dye removal.

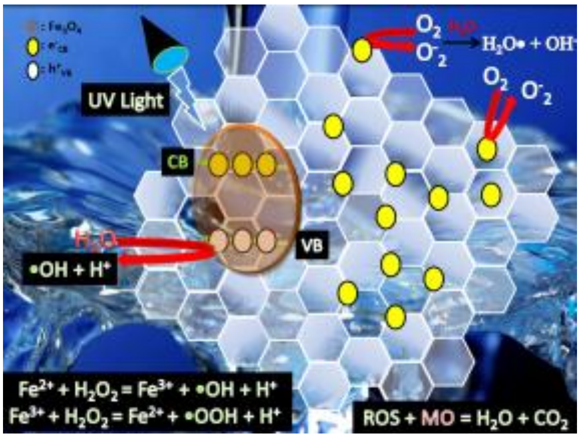

Figure 1: Schematic illustration of the fundamental process that governs the photodegradation of methyl orange in the presence of graphene/Fe_3O_4 nanocomposite.

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Development of graphene-modified yarns and woven fabrics for next-generation textiles

B. Weise,[1,*] G. Köppe[1], L. Völkel[1], G. Seide[1,2], M. Morgenstern[3]

[1] RWTH Aachen, Institut für Textiltechnik, Aachen, Germany
[2] Maastricht University, Aachen-Maastricht-Institute for Biobased Materials, Geleen, Netherlands
[3]RWTH Aachen, II. Institute of Physics B, Aachen, Germany

Abstract:

The modification of thermoplastic polymers by addition of graphene in the fibre spinning process opens a variety of new fields of fibre applications. For example, they could be used as electrically conductive filaments or as electrode materials for fibre-form batteries and supercapacitors. Several publications, especially in the wet-spinning process have been made underlining the great potential of graphene-based fibres [1,2]. However, the productivity of wet-spunning process (currently at a maximum of ~ 10 m/min) is very low, which limits the broader textile application extremely.

At ITA of RWTH Aachen, a novel route towards graphene-modified textiles has been developed by a melt-spinning approach. A multifilament melt spinning process at 1,400 m/min for polyamide containing 1 wt% of graphene has been developed successfully. An electrical conductivity of 10^{-5} S/m was measured and the filaments were processed into a woven fabric on an industrial-scale weaving machine.

The obtained woven fabrics were connected with an aluminium foil as current collector and a nonwoven diluted with supersaturated sodium sulphate solution as electrolyte. Thus, the realization of a textile supercapacitor with a gravimetric capacity of 1 F/g was successful. This offers potential for use of the textile structures as flexible, light-weight energy source for smart textiles in a new age of clothing.

In the talk, the recent advantages presented above as well as opportunities and challenges of research in cost-effective graphene fibres will be presented. An outlook about further research activities will be given.

Keywords: graphene, melt-spinning, polyamide-6, supercapacitor.

Figure 1: Photograph of graphene-modified polyamide-6 woven fabric

References:

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Influence of Dopant and Oxidant on the Electrochemical Properties of GNP/PANI Composites

X. Zhao,[1,2] J. Pionteck,[1*] O. Grätz[1,2]

[1] Leibniz Institute of Polymer Research Dresden, Department Functional Nanocomposites and Blends,
Hohe Str. 6, 01069 Dresden, Germany
[2] Technische Universität Dresden, Faculty of Science, Department of Chemistry and Food Chemistry,
Mommsenstr. 4, 01062 Dresden, Germany

Abstract:

Graphene-based materials are promising candidates for supercapacitor electrodes, which are urgently required due to the rapid growth of the hybrid electric vehicles and portable electronics. Graphene nanoplates (GNP) in combination with pseudocapacitors like transition metal oxides, hydroxides, or intrinsic conductive polymers electrodes with high capacitance can be generated. In such hybrid electrodes, graphene forms conductive channels for fast charge transfer while the reversible faradaic redox reactions at the electrode surface cause the high capacitance.[1]

Polyaniline is an easy to prepare and environmental stable intrinsic conductive polymer. Thus, GNP/PANI composites are promising candidates for supercapacitor electrodes. We prepared such composites in weight ratios of 1:1 and 1:10 via in-situ chemical polymerization of aniline using iron(III)chloride or ammonium persulfate (APS) as oxidant and dopant. The effects of the type and content of oxidant and dopant on the electrochemical properties of GNP/PANI composites were systematically investigated. It was observed that the dopant could strengthen the redox phenomenon, but its effect on the capacitance of GNP/PANI composites depend on the mass ratio of components. For the effect of oxidant, a $FeCl_3$ to aniline mass ratio of 2 is optimal for the electrochemical properties of both GNP/PANI (1:1) and (1:10) composites, and APS was better than $FeCl_3$ according to the magnitude of specific capacitance.

GNP/PANI (1:1) composites prepared with an APS to aniline ratio of 1 presents the best combination for obtaining high specific capacitance and good cycling stability.

As expected, PANI contributes more to the capacitance of composites, and graphene plays a more essential role in the rate capability of the composites.

Keywords: supercapacitor, graphene, polyaniline, composites, oxidant

References:

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Organic photovoltaic cells and modules with functionalized CVD-graphene as highly transparent conductive electrodes

Luca La Notte,[1] Enrica Villari,[1] Alessandro Lorenzo Palma,[1] Alberto Sacchetti,[2]
Maria Michela Giangregorio,[2] Giovanni Bruno,[2] Aldo Di Carlo,[1]
Giuseppe Valerio Bianco[2]* and Andrea Reale[2]*

[1] CHOSE (Centre for Hybrid and Organic Solar Energy), Department of Electronic
Engineering, University of Rome Tor Vergata, via del Politecnico 1, 00133 Rome,
[2] CNR-NANOTEC Institute of Nanotechnology, Apulian Graphene Lab, Department of
Chemistry, University of Bari, via Orabona 4, Bari, 70126, Italy.

Abstract:
One of the topics in Organic Photovoltaics (OPV) is the replacement of ITO as transparent conductive electrode[1]. Graphene is a promising candidate[2] but it needs low sheet resistance while maintaining high transparency, and wettability of the surface in order to be compatible with the typical solution processing of OPV. A five-layer (5L) graphene deposited on glass substrate by Chemical Vapor Deposition (CVD) has been properly functionalized to achieve the desired properties[3]. Two strategies have been applied: (i) the p-doping of the multilayer graphene by $SoCl_2$ treatment, thus reaching $25\Omega\square^{-1}$ and (ii) the decrease of contact angle from 90° to 58° by O_2-plasma oxidation. Inverted Polymer Solar Cells (PSCs) have been fabricated onto the modified graphene by using industry-compatible solvents for the deposition of the layers. The two distinct functionalization strategies of graphene have beneficial effects on the electrical parameters of the devices, leading to efficiency of about 4%, compared to the poor performance of pristine graphene (1%). A Nd:YVO_4 laser patterning has been implemented to properly design the layout of graphene film through an easy and scalable way. Notably, this has allowed the first application of graphene as electrode in organic photovoltaic modules ($5.6\text{x}5.6\text{cm}^2$), thus demonstrating the high uniformity of graphene over large areas.

Keywords: graphene, organic photovoltaics, electrode, CVD, polymer solar cells, ITO-free

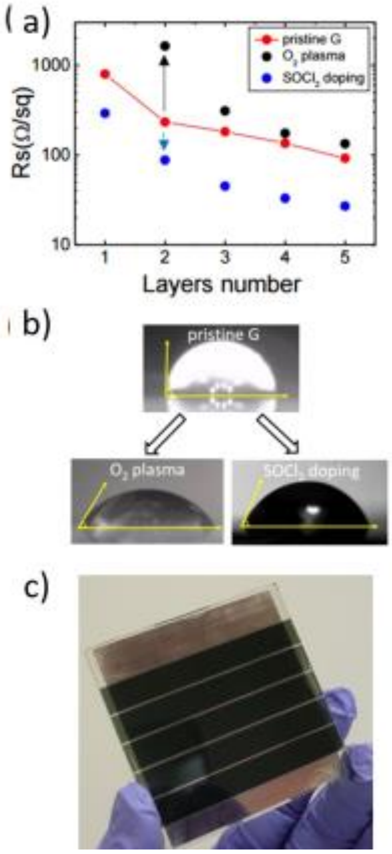

Figure: a) Sheet resistance and (b) water contact angle of multilayer CVD-graphene functionalized by O_2 plasma and $SOCl_2$ treaments. c) Photo of OPV module with laser-patterned graphene as transparent conductive electrode.

References:

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Mass Transport Through 2D Materials Based Membranes

Yang SU[1,2] Rahul R Nair[1,2]

[1] National Graphene Institute
[2] School of Chemical Engineering and Analytical Science. University of Manchester, M13 9PL, UK

Abstract:

Mass transport through nanometre-pore materials has been attracting unwavering interest due to fundamental differences in governing mechanisms at macroscopic and molecular scales, the importance of water permeation in living systems, and relevance for filtration and separation techniques. Graphene-based materials can have well-defined nanometer pores and can exhibit low frictional water flow inside them, making their properties of interest for filtration and separation[1,2]. In addition, recent developments in exfoliating and assembling other layered materials open the possibility of fabricating variety of membranes with different properties. In my talk, I will discuss our recent results on molecular and ionic mass transport of various 2D materials based membranes and its prospect for several applications[1,2,3].

Keywords: graphene, membrane, mass transport, water treatment, nanofiltration

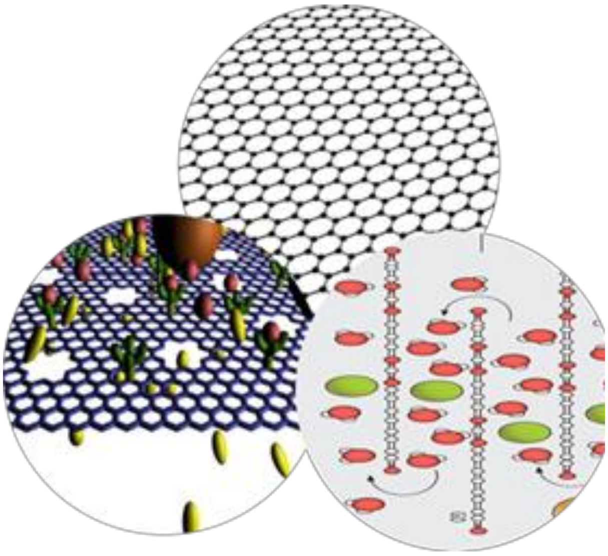

Figure 1: Various mass transport behaviours through 2D materials constructed membranes.

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CO adsorption on graphene: A theoretical approach

J. Wilson,[1] N. Faginas-Lago,[2] J. Vekeman,[1] I.G. Cuesta,[1] J. Sánchez-Marín,[1] A. Sánchez de Merás[1]

[1] Institute of Molecular Science, Universidad de Valencia, E-46980 Paterna, Spain
[2] Dipartimento de Chimica, Biologia e Biotecnologie, Università di Perugia, Perugia, Italy

Abstract:

The adsorption of gaseous molecules on surfaces of graphene is of high interest because of the potential ability to separate gases based on their adsorption energies. In this context, a multiscale modelling and simulation analysis of the adsorption of CO on graphene is presented here.

In the following, circumcoronene ($C_{54}H_{18}$) is used to represent graphene, and interaction energies are then calculated with carbon monoxide (CO) at several levels of approximation. Two different kinds of studies were done: first, the environment of three different sites of the circumcoronene molecule was investigated using the B97D [1] parameterization of the density functional and the TZVP one-electron basis set. It is concluded that there is little difference between the interaction energies of CO with the different sites of circumcoronene. The atom and bond sites are energetically comparable, while adsorption at the centre of the hexagon is slightly favoured (around 0.5 kJ/mol more stable). Contrarily, the orientation of the CO molecule relative to the circumcoronene plane was more important than the choice of site; the orientation with the strongest interaction energy is when CO approaches sideways and parallel to the plane (between 9.6-10.2 kJ/mol). The other two orientations, both where the molecule approached perpendicularly, interacted more weakly (between 6.1-7.0 kJ/mol). Additional calculations on $C_{54}H_{18}$/CO using B2PLYPD and SCSMP2 as well as CCSD(T)/ aug-cc-pVDZ calculations on $C_{24}H_{12}$/CO agree with those results.

Secondly, Improved Lennard-Jones potentials [2] for CO/CO and CO/graphene interactions were derived from the fitting of extensive grids of the corresponding B97D/TZVP data. Such potentials, that are rather similar to those previously proposed by Pirani and coworkers, were subsequently used in Molecular Dynamics simulations together with additional potentials from the literature representing the flexibility of graphene. The resulting MD simulations (Figure 1) show the formation of an adsorption layer on graphene of CO molecules in equilibrium with a gaseous phase. Interestingly there is a notable difference between the average number density peaks seen for the rigid and flexible case. For rigid graphene two sharp and well defined peaks are encountered, which represents the location of the adsorption layer. In the case of flexible graphene however each peak is split into two smaller sub-peaks, which are spread much more broadly.

Keywords: gas adsorption, coupled cluster calculations, DFT calculations, Molecular Dynamics.

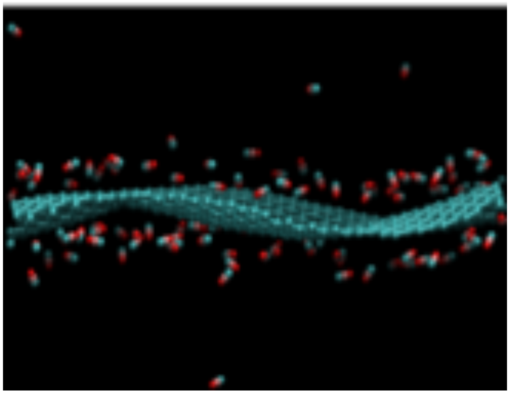

Figure 1: Snapshot of the Molecular dynamics simulation of the adsorption of CO on graphene.

References:

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Acknowledgment:

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Graphene-based batteries to improve the efficiency of the existing technologies

González Teresa Raquel,[1,*] , Hernández Martínez David[1] ,González Bermúdez Lucia,[1,]

[1] GrapheneTech S.L, Spain

Abstract:
Nowadays, we are in a society with a high technological development and a growing demand in electronic devices that requires batteries with better capacity, durability and shorter recharging rates.
To solve these challenges, the exploration of new materials with extraordinary properties, like graphene, is highly required. At this moment, there is an enormous interest in the use of graphene (1) (or graphene-based composites) for the development of next-generation batteries because of their attractive properties like flexibility, lightness and high conductivity.
In this context, GrapheneTech is focused on the incorporation of their products: high quality graphene nanoplatelets, to develop an anode with better performance than the conventional ones. In order to achieve this objective, GrapheneTech is developing a new composite film that can be used as battery anode. This new composite is formed by the combination of graphene with an ion-conducting polymer. Thanks to the presence of graphene, these films have high electrical conductivity, resulting in a greater and faster mobility of electrons through the electrodes. This can help to get batteries with shorter charging/discharging rates. On the other hand, polymers provide the ionic conduction to the films and improve mechanical properties such as elasticity and flexibility. In addition, the development of polymers with graphene as additive, to cover the battery cells will enable lighter and thinner materials reducing the weight of the batteries and increasing their performance

Keywords: Graphene nanoplatelets, conductivity, energy storage, flexible films.

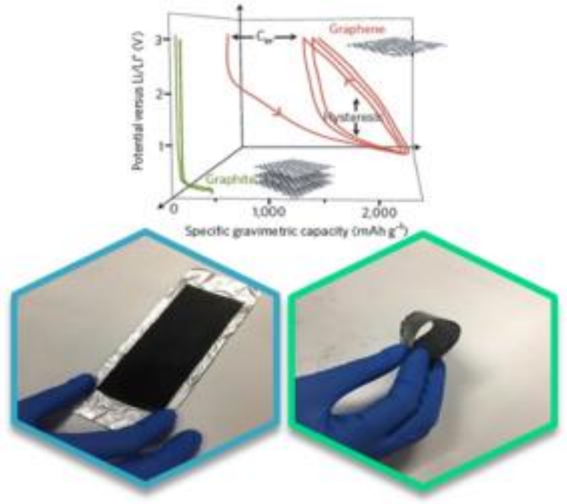

Figure 1: Figure illustrating a conductive flexible film sintetized in GrapheneTech. The film could be employed as an anode enhancing the ciclability and capacity of the batteries.

References:

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SMS EUROPE 2017 - Session II.C: New Materials for Energy and Environmental Applications

2-Dimensional Electron Gases at Oxide Interfaces

F. Miletto Granozio[1]

[1] CNR-SPIN Unit of Naples, Naples, Italy

Abstract:
2-Dimensional electron gases (2DEGs) at oxide interfaces have attracted a huge interest in the last decade. These heterostructures allow in fact to potentially combine features that are typical of 2D systems (as high mobility, large field effect tunability, Rashba type spin.orbit coupling and quantum transport) with a broad range of functional properties that are found in complex oxides systems (as superconductivity, magnetism, ferroelectricity, multiferroic behaviour) and are typically absent in simpler materials. The prototypical $LaAlO_3/SrTiO_3$ interface has been discovered in year 2004.[1] $LaAlO_3/SrTiO_3$ itself or some of its different variants, that have been engineered more recently, have been demonstrated to show field-tunable *a)* superconducting, *b)* magnetic, *c)* Rashba and *d)* Quantum Hall Effect behaviour.

In the course of this talk, the properties of the $LaAlO_3/SrTiO_3$ system and the origin of its metallic behaviour will be briefly discussed. The properties of a number of variants of the original system, realised in the CNR-SPIN laboratories and based on an atomic-level control of the growth process, will be presented. We will show in particular that a spin-polarised behaviour can be induced in the 2DEG by the introduction of two monolyaers of $EuTiO_3$ in the $LaAlO_3/SrTiO_3$ structure an that a colossal, repeatable ad non-volatile switching between a conducting and an insulating state can be induced in $LaGaO_3/SrTiO_3$ interfaces by the application of field effect and light.

Keywords: 2-Dimensional electron gases, oxide thin films, field effect devices, superconductivity, magnetism, photoconductivity.

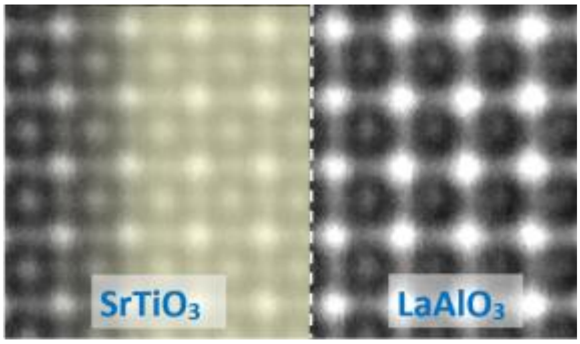

Figure 1: STEM picture of an atomically perfect $LaAlO_3/SrTiO_3$ interface. The region shaded in yellow mimicks the presence of the 2D electron gas.

References:

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Preparation and characterization of Soundproofing PVP/Graphene electrospun mats

G.R.Del Sorbo,[1]* G.Petrone[2], G.Tomaiuolo[1], A.Vergara[3], G.Ausanio[4], S.Guido[1], F.Marulo[2], F.Branda[1]

[1] University of Naples Federico II, DICMaPI, Napoli, Italy
[2] University of Naples Federico II, DII, Napoli, Italy
[3] University of Naples Federico II, DSC, Napoli, Italy
[4] University of Naples Federico II, DF, Napoli, Italy

Abstract:

Noise pollution is one of the most widespread irritations in modern society and constitutes real danger to the human health. The research on soundproofing materials has strong impact in both civil than industrial engineering.

Materials that have a high value of sound absorption coefficient are usually porous. Most of the porous sound-absorbing materials commercially available are fibrous. Electrospinning is an emerging technique that allows to produce fibers of diameter well below the micron size. It has recently been proposed in the field of sound absorption because, due to their low diameter, electrospun fibers possess high specific surface area which may be 100 to 10,000 times greater than traditional acoustical fibrous materials; as a consequence noise absorption is expected to rise just because of the high friction of the air molecules of sound waves with the electrospun fibers.

In the present work, light non-woven mats were successfully obtained by electrospinning polyvinylpyrrolidone (PVP) of high molecular weight (1300 KDa) added with graphene of three layers (so as proved by Raman and Atomic Force Microscopy) obtained through ultrasonication of graphite in low molecular weight PVP (10 kDa) alcoholic (ethanol) solution.

The sound absorption coefficients were measured with an impedance tube. When stacking thin electrospun disks on each other very high sound absorption coefficient α, close to unity, were measured in the frequency range 200-800 Hz, of high interest for the transportation industry, where traditional materials of similar thickness do exhibit much lower values (Figure 1). The effect of changing the graphene content on the fiber diameter and formation of electrospun mat on the target is reported.

Keywords: sound-proofing materials, electrospinning, exfoliated graphite, ultrasonication, Raman Spectroscopy, Scanning Electron Microscopy, Atomic Force Microscopy, Impedance Tube

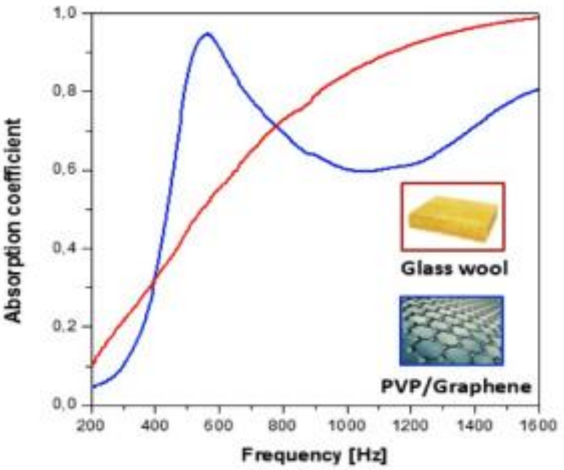

Figure 1: Sound absorption coefficient vs frequency for : PVP/graphene electrospun mat and glass wool.

References:

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Comparison between flexible PZT and BTO piezoelectric films for mechanical energy harvesting

R. Seveno, T. Dufay, B. Guiffard
Université Bretagne Loire, Université de Nantes, *IETR UMR CNRS 6164*, France

Abstract:
Due to the recent development of flexible perovskite-based thin films, the interest for this kind of material has increased, especially in the field of piezoelectricity and energy harvesting at low frequency. In order to anticipate some industrial developments, the fabrication process of these films has to be as simple as possible. In this aim, flexible lead zirconate titanate (PZT) films have been realized by a chemical solution deposition process (CSD) where no vacuum technique is needed[1]. These films exhibit good ferroelectric and piezoelectric properties[2], which allow to compete with polymeric piezoelectric films, such as polyvinylidene fluoride (PVDF) films, in flexible applications (Figure 1). However, the wide use of PZT films is limited by applications which require lead-free materials. In order to enlarge the panel of the flexible perovskite-based thin films, Barium titanate (BTO) films have been realized using a similar CSD process by using a metallic foil as substrate. Dielectric, ferroelectric and piezoelectric properties of both PZT and BTO films have been compared, as a function of process parameters. In a next step, these films have been encapsulated in a polyethylene terephthalate (PET) film in order to obtain a flexible piezoelectric generator. The harvested powers of both PZT and BTO films have been measured under mechanical stress at very low frequency ranging from 0.5 to 6 Hz and the optimization of the geometry of the generators has been discussed.

Keywords: flexible film, piezoelectricity, energy harvesting

Figure 1: Photograph of flexible piezoelectric generator based on PZT thin film deposited onto an aluminium foil and encapsulated in a double PET sheet.

References:

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2. R. Seveno, B. Guiffard, et J.-P. Regoin, « Ultra large deflection of thin PZT/aluminium cantilever beam », *Funct. Mater. Lett.*, vol. 08, nº 05, p. 1550051, oct. 2015.

First-principles study of the transport properties in bulk and monolayer MX_3 (M = Ti, Zr, Hf and X = S, Se) compounds

Y. Saeed*, Ali Kachmar, and Marcelo A. Carignano

Qatar Environment and Energy Research Institute (QEERI),
Hamad Bin Khalifa University (HBKU), Qatar Foundation, P.O. Box 5825, Doha, Qatar

Abstract:
Layered materials are the best candidates for thermoelectric application due to their in-plane low thermal conductivity that is a key property to achieve high efficiency. Owing to that, here we present our investigations on electronic as well as thermal transport of bulk and monolayer MX_3 compounds (M = Ti, Zr, and Hf and X = S and Se) based on density functional and semiclassical Boltzmann theories. The values of the bandgap are rather similar for bulk and the monolayer, with only a slight change in the shape of bands near the Fermi level that results in a different effective mass. We found that the monolayer MX_3 compounds are better thermoelectric materials than bulk. Also, the p-type monolayer of TiS_3 has a high power factor at 600 K that doubles its room-temperature value. The monolayer of the Zr/$HfSe_3$ compounds shows a promising behavior as a n-type thermoelectric materials at 600 K. In-plane tensile strain could be used to further tune the TE properties of the monolayers to obtain high-performance TE materials.

Keywords: Density functional theory, Thermoelectric materials, 2D materials, Bandgap, Density of states, Seebeck coefficient, Power factor, Energy harvesting, Heat energy into electrical energy, .

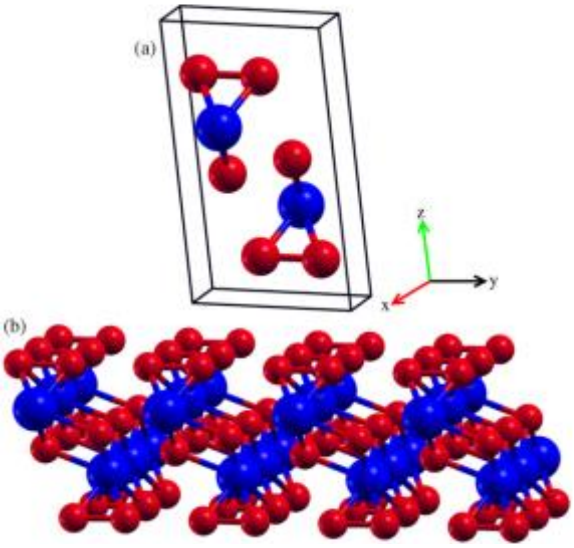

Figure 1: Crystal structures of bulk (a) and monolayer (b) MX_3, where M = Ti, Zr, or Hf and X = S or Se. M atoms are shown in blue and X atoms are shown in red.

References:

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Enhancing CO_2 adsorption of metal–organic activated carbon through APTES grafting and Co-NPs incorporation

N. Bouazizi ,[1*] R. Bargougui[1], J. Vieillard[1], N. Mofaddel[1], O. Thoumire[3], G. Ladam[3], N. Brun[4], P. Fotsing[2], E. Djoufac Woumfo[2], F. Le Derf[1]

[1] Normandie Univ, UNIROUEN, INSA Rouen, CNRS, COBRA (UMR 6014), 76000 Rouen, France.
[2] Laboratoire de Physico-Chimie des Matériaux Minéraux, Département de Chimie Inorganique, Faculté des Sciences, Université de Yaoundé I, B.P. 812 Yaoundé, Cameroun.
[3] Laboratoire de Biophysique et Biomateriaux (La2B - MERCI EA 3829), Université de Rouen, Centre Universitaire d' Evreux, 1 Rue Du 7ème Chasseurs, Evreux Cedex, 27002, France.
[4] Institut Charles Gerhardt, ENSCM, 34296 Montpellier Cedex 5, France.

Abstract:

The cocoa industry generates massive agricultural wastes which have currently no specific technical uses. Thus, the cocoa wastes, including shells, are usually left onto the field after the crop. This work was performed to upgrade this biomass. Firstly, cocoa shell was activated by hydrothermal treatment (AC) to increase its porosity. Then, the activated carbon was post functionalized with 3-aminopropyltriethoxysilane (APTES) grafting and cobalt nanoparticles incorporation (Co-NPs) (Figure 1). The effects of these modifications were evaluated on the surface functionalities and CO_2 adsorption behavior. The changes in textural, morphological and thermal properties were investigated in the presence of APTES/Co-NPs and in the absence of the surface modification. The analysis by scanning electronic microscopy demonstrates that the surface morphology was completely changed for the AC-APTES-Co, indicating good stability and uniform distribution of the Co-NPs on the surface. Surface charge densities have been studied by means of zeta potential measurements, indicating enhanced charge transfer. The retention capacity of CO_2 over the functionalized cocoa shell was also studied. The results demonstrated that both APTES attachment and Co-NPs insertion caused an increase in CO_2 retention capacity. The CO_2 adsorption capacity of AC-APTES-Co at 273 K and 1 atm, resulted in a CO_2 retention of 2.59 mmol/g, compared to 1.22 mmol/g for the activated carbon. Further investigations provided a correlation between the adsorption kinetics and the surface properties (chemical group and porosity).

Keywords: activated carbon; surface chemistry; 3-aminopropyltriethoxysilane; cobalt nanoparticles; CO_2 adsorption.

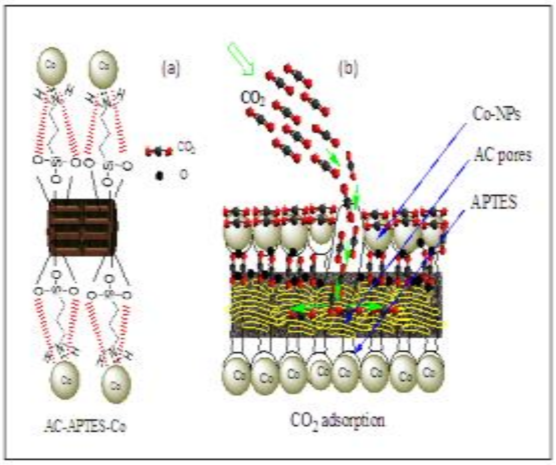

Figure 1: APTES/Co-NPs functionalized cocoa shell (a) and mechanism of CO_2 adsorption (b)

Heteroatom doped graphene-semiconductor composites for CO_2 photoreduction: Influence of sulfur and nitrogen species

L.M. Pastrana-Martinez, M. Pedrosa, J.L. Figueiredo, J.L. Faria, A.M.T. Silva

Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

Abstract:

The reduction of CO_2 into solar fuels by photocatalysis is far from being optimised, and there are still significant breakthroughs to be made before it can be accepted as a viable economical process. Recent interest is devoted to the synthesis of novel photocatalysts that can improve the CO_2 conversion rates and efficiencies compared to the state of the art values. In this context, graphene and graphene related materials (such as graphene oxide, GO, and reduced graphene oxide, rGO) have stimulated the interest for the design of high-performance photocatalysts to enhance the photoefficiency of the semiconductors in energy and environmental applications under visible light conditions [1]. It is noteworthy to mention that the presence of heteroatoms in graphene can change the properties of this carbon material, such as the electric conductivity (band-gap), thermal stability or chemical reactivity, improving the efficiency and selectivity and eliminating the need for noble metals in catalytic processes [2].

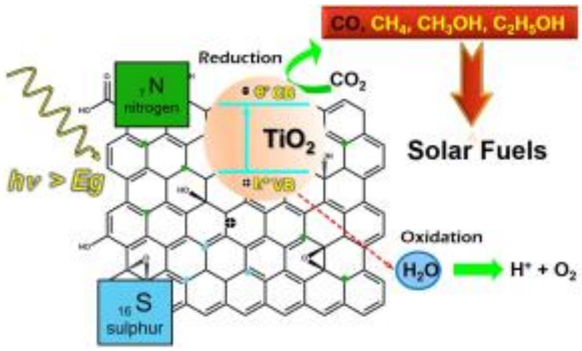

Figure 1: Schematic diagram of photoreduction of CO_2 catalyzed by heteroatom doped graphene-semiconductor composites.

In the present work, graphene-based materials were prepared both by Brodie and Hummers methods using graphite as starting material. Nitrogen-doped graphene derivatives were synthesized by annealing graphite oxide with NH_3 in a furnace and sulphur-doped graphene derivatives were synthesized by graphite oxide annealing with benzyl disulphide (BDS). A series of composites with the heteroatom doped graphene materials and titanium dioxide (TiO_2) were synthesized by the liquid phase deposition method at room temperature and applied to photoreduction of CO_2 with water under the irradiation of a Xe lamp. The influence of sulfur and nitrogen species on the photocatalytic performance of the heteroatom doped graphene-TiO_2 composites was assessed and discussed.

Keywords: heteroatom-doped graphene; TiO_2; photocatalysis; solar fuels; CO_2 conversion

References:

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Acknowledgments:

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EGF 2017 - Session III.A: Graphene and 2D Materials - Bioapplications

Impact of Covalent Functionalization on the Aqueous Processability, Catalytic Activity, and Biocompatibility of Chemically Exfoliated MoS2 Nanosheets

Juan I. Paredes,[1] José M. Munuera,[1] Silvia Villar-Rodil, [1] Laura Guardia, [1] Miguel Ayán-Varela, [1]
Ana Pagán, [2] Salvador D. Aznar-Cervantes, [2] José L. Cenis, [2] Amelia Martínez-Alonso, [1]
and Juan M. D. Tascón[1]

[1]Instituto Nacional del Carbón, INCAR-CSIC, Apartado 73, 33080 Oviedo, Spain
[2]Instituto Murciano de Investigación y Desarrollo Agrario y Alimentario (IMIDA), Calle Mayor 1, 30150 La Alberca, Spain

Abstract:

Chemically exfoliated MoS2 (ce-MoS2) has emerged in recent years as an attractive two-dimensional material for use in relevant technological applications, but fully exploiting its potential and versatility will most probably require the deployment of appropriate chemical modification strategies. Here, we demonstrate that extensive covalent functionalization of ce-MoS2 nanosheets with acetic acid groups (~0.4 groups grafted per MoS2 unit) based on the organoiodide chemistry brings a number of benefits in terms of their processability and functionality. Specifically, the acetic acid-functionalized nanosheets were furnished with long-term (>6 months) colloidal stability in aqueous medium at relatively high concentrations, exhibited a markedly improved temporal retention of catalytic activity to-ard the reduction of nitroarenes, and could be more effectively coupled with silver nanoparticles to form hybrid nanostructures. Furthermore, in vitro cell proliferation tests carried out with murine fibroblasts suggested that the chemical derivatization had a positive effect on the biocompatibility of ce-MoS2. A hydrothermal annealing procedure was also imple-mented to promote the structural conversion of the functionalized nanosheets from the 1T phase that was induced during the chemical exfoliation step to the original 2H phase of the starting bulk material, while retaining at the same time the aqueous colloidal stability afforded by the presence of the acetic acid groups. Overall, by highlighting the benefits of this type of chemical derivatization, the present work should contribute to strengthen the position of ce-MoS2 as a two-dimensional material of significant practical utility.

Keywords: MoS2, two-dimensional material, transition metal dichalcogenides (TMDs), colloidal dispersion, functionalization, metal nanoparticles, catalytic reduction

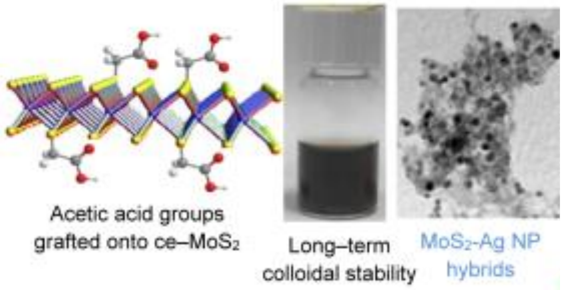

Figure 1: (From left to right) Structure of functionalized MoS2 nanosheets, long-term stable aqueous dispersion of the material, TEM image of MoS2-Ag NP hybrids.

References:

1. Juan I. Paredes, José M. Munuera, Silvia Villar-Rodil, Laura Guardia, Miguel Ayán-Varela, Ana Pagán, Salvador D. Aznar-Cervantes, José L. Cenis, Amelia Martínez-Alonso, and Juan M. D. Tascón, Impact of Covalent Functionalization on the Aqueous Pro-cessability, Catalytic Activity, and Biocompatibility of Chemically Exfoliated MoS2 Nanosheets, ACS Applied Materials and Interfaces, **2016**, *8* (41), 27974–27986.

Acknowledgements:

Financial support from the Spanish Ministerio de Economía yCompetitividad (MINECO) and the European Regional Development Fund (ERDF) through project MAT2011-26399 is gratefully acknowledged. Partial funding by Plan de Ciencia, Tecnología e Innovación (PCTI) 2013–2017 del Principado de Asturias and the ERDF (project GRUPIN14-056) is also acknowledged. J. M. M. and M. A.-V. are grateful to the Spanish Ministerio de Educación, Cultura y Deporte (MECD) and MINECO, respectively, for their pre-doctoral contracts.

Graphene oxide is trapped and degraded by primary human neutrophils and the degradation products are non-genotoxic

S.P. Mukherjee,[1]* B. Lazzaretto,[1] K. Bhattarcharya,[1] A. Gliga,[1] B. Brandner,[2] M. Fielden,[3] A. Star,[4] N. Lozano,[5] K. Kostarelos,[5] B. Fadeel[1]

[1] Nanosafety & Nanomedicine Laboratory, Division of Molecular Toxicology, Institute of Environmental Medicine, Karolinska Institutet, Stockholm, Sweden
[2] Materials and Surfaces, SP Technical Research Institute of Sweden, Stockholm, Sweden
[3] Department of Applied Physics, School of Engineering Sciences, Royal Institute of Technology, Stockholm, Sweden
[4] Department of Chemistry, University of Pittsburgh, Pittsburgh, PA, USA
[5] Nanomedicine Laboratory, Faculty of Biology, Medicine & Health and National Graphene Institute, University of Manchester, Manchester, United Kingdom

Abstract:

The biocompatibility of graphene oxide (GO), especially its interactions with the immune system, should be controlled for successful applications in medicine [1]. The innate immune system rapidly detects invading foreign materials and eliminates them, and neutrophils act as the first line of defense. Neutrophils can engulf and digest microbes or can release neutrophil extracellular traps (NETs) to digest microbes extracellularly or can release its secretory granules by degranulation which contains a diverse array of antimicrobial proteins and oxidative enzymes (e.g., myeloperoxidase (MPO), elastase etc.) for extracellular digestion. Here, we studied whether primary human neutrophils are capable of triggering NETs formation when in contact with endotoxin-free small and large GO flakes and whether it is capable of biodegrading them in purified NETs or upon degranulation. We have developed an interference-free method for endotoxin detection in GO and other nanomaterials using primary human macrophages and also devised a protocol for endotoxin-free synthesis of GO for safe biomedical applications [2]. The results confirmed that primary human neutrophils are capable of triggering NETs formation upon contact with endotoxin-free GO and that GO is efficiently enzymatically digested within 12 h of incubation in purified NETs. The degradation in NETs was MPO dependant. Degranulating neutrophils can also efficiently biodegrade small and large GO flakes within 6 h of incubation. We have also studied the toxicity and genotoxic potential of the partial enzymatic biodegradation products of GO following incubation with recombinant human MPO on primary human bronchial epithelial cells. The results confirmed that the degradation products are non-cytotoxic and do not cause any DNA damage as evidenced by the comet assay. Overall, the GO flakes can be efficiently enzymatically biodegraded by primary human neutrophils for effective clearance from the body for future biomedical applications and the partialy biodegradation products are non-genotoxic.

Keywords: Endotoxin detection in GO, endotoxin-free GO synthesis, GO biodegradation, primary human neutrophils, neutrophil extracellular traps, neutrophil degranulation, genototoxicity.

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Graphene Field-Effect Transistors for Biomedical Applications

R. Campos[1], E. Fernandes[1], G. Machado Jr.[1,2], P.D. Cabral[1,2], M.F. Cerqueira, J. Borme[1], P. Alpuim[1,2]

[1]INL - International Iberian Nanotechnology Laboratory, 4715-330, Braga, Portugal
[2] Department of Physics, University of Minho, 4710-057, Braga, Portugal

Abstract:

Biosensing systems became ubiquitous in recent years in medical and biomedical research, spanning a large range of health applications, from prognosis and/or diagnosis of diseases, to personalized medicine.

For specific target recognition biosensors based on graphene require surface functionalization. We immobilize probe molecules on CVD graphene surfaces for biorecognition of two important analyte types – antigens (proteins) and DNA. Electrolyte-gated field-effect transistors (FETs), with a receded, integrated gate architecture were fabricated at the 200 mm wafer scale.[1] The electrical signal is the shift in the Dirac point of the FET transfer curves, as a function of analyte concentration.

A graphene immuno-FET is developed by immobilization of antibodies to specifically detect the biomarkers related with the hemorrhagic transformation of ischemic stroke.[2] The probe immobilization is achieved via a pyrene-derivative linker, attached to the graphene surface via π-π interaction of the pyrene group and providing, at the other end of the molecule, a succinimidyl ester group that reacts with a primary amine from the protein antibody. The device was able to detect the biomarker (MMP-9) in concentrations down to 0.01 ng/mL, in a range up to 10 ng/mL. Compared with existing MMP-9 immunoassays our immuno-FET has similar or higher sensitivity and, because it is based on a much simpler label-free protocol than conventional methods, has a much shorter time to diagnostic.

The nucleic acid sensor is developed by immobilization of single-stranded DNA (25 nucleotides long) on the pyrene derivative-functionalized graphene transistor channel. Hybridization with complementary DNA (cDNA) was detected down to 1 aM, with a saturation attained at 100 fM and sensitivity to single nucleotide polymorphism (SNP).

These results open the possibility for fabrication of graphene sensors, using standard clean-room technology, with high sensitivity and low cost. Moreover the functionalization strategy shown here can be easily transferred to a broad range of probes for the detection of biomarkers in health, environment and food industries.

Keywords: graphene, transistor, proteins, DNA, biosensor.

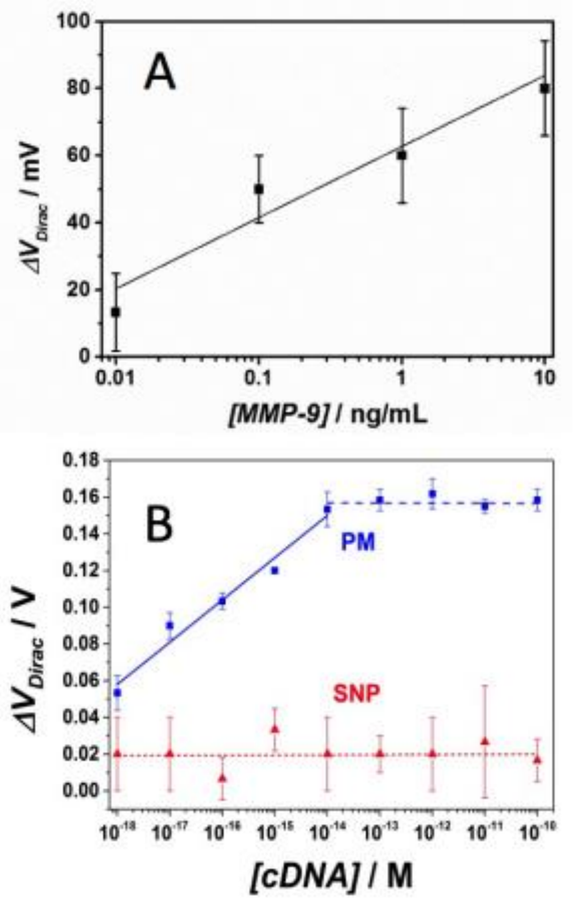

Figure 1: Callibration curves for A) an immune-FET and, B) a DNA-FET.

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Biocompatibility of silicone rubber/graphene-nanoplatelets composites with improved mechanical properties

A. Pinto[1,2,3,4], S. Creason[4], Z. Wescoe[4], L. Zhen[4], R. Khalifehzadeh[4], M. Mecwan[4], C. Winston[4], F. Magalhães[1,], I. Gonçalves[2,3,*], B. Ratner[4,*]
[1]LEPABE, Faculty of Engineering of University of Porto, Porto, Portugal

[2]INEB - Instituto de Engenharia Biomédica, Universidade do Porto, Porto, Portugal
[3]i3S - Instituto de Investigação e Inovação em Saúde, Universidade do Porto, Portugal
[4]UWEB - University of Washington Engineered Biomaterials, Seattle, WA, USA
*authors contributed equaly

Abstract

Introduction: There is a need to improve silicone rubber (SR) mechanical properties for some of its common applications, namely biomedical uses. The incorporation of several nanofillers have been tried for that purpose, like nanosilicas, nanoclays, and carbon black. However, a new class of carbon materials with superior potential for mechanical reinforcement is now available, graphene-based materials (GBMs) [1]. For that reason, SR/GNP composites production, mechanical characterization, and biocompatibility were studied.

Materials and methods: Graphene nanoplatelets (GNP) grades M15 and C750 (XG Sciences) with different dimensions were used. GNP-M, and C were oxidized by modified Hummers method [2]. Those materials are designated by GNP-M-ox, and C-ox. GNPs were dispersed in different amounts (0.25-5 wt.%) by mechanical mixing into Silastic MDX4-4210 elastomer (Dow Corning), the curing agent was added, the mixture cast on a mould, and cured at RT for 3 days. Dow Corning 360 Medical Fluid (Fluid) was used in a 1:1 ratio to modify silicone rubber (SR) viscosity with the purpose of trying to assist GNP-M 5 wt.% dispersion. Some samples were extracted (ex) for 24h with hexanes, acetone, methanol, ethanol, and gradually transferred to deionized water. Tensile properties of the samples (22 × 5 × 0.5 mm) were measured using an Instron motorized test frame, under water at 37 °C at a strain rate of 20 mm min^{-1}. Cytotoxicity was tested by direct contact with the materials, and performing the elution method according to ISO10993-5. Metabolic activity was evaluated performing the resazurin assay. Materials were tested for endotoxins, using Lonza's plus pyrogent kit.

Results and discussion: The mechanical properties of SR/GNP with lower loadings (0.25, 0.5, and 1 wt.%) were similar to the ones of unfilled SR. For SR/GNP-M 2, and 5 wt.% Young's modulus increased by 55, and 73%, respectively. Considering all the other samples, only SR/GNP-C-ox, and SR/GNP-M Fluid 5 wt.% presented relevant changes in mechanical properties. For the first, Young's modulus increased by 44%, however, elongation at break, and tensile stress, decreased by 40, and 41%, respectively. For the last, Young's modulus decreased by 50%, and elongation at break, and tensile stress, decreased by 35, and 77%, respectively. Extraction with solvents resulted in no differences in terms of mechanical properties. Cell morphology was normal for cells in direct contact with all the materials at 12, 24, 48, and 72h. Also, metabolic activity was always above the 70% toxicity limit defined by ISO-10993-05. In the live/dead assay few dead cells were observed for all materials at 48, and 72h. For cells in contact with 24h extracts of the materials, cell morphology was also normal at 12, 24, and 48h. All the materials were above the toxicity limit at 24, and 48h, presenting few cells stained red in the live/dead assay. The extracts of all the materials presented endotoxin levels below 0.06 EU, not causing limulus amebocyte lysate coagulation.

Conclusions: The incorporation of 2, and 5 wt.% GNP-M increased SR Young's modulus by 55, and 73%. Incorporation of 5 wt.% GNP-C-ox in SR or reducing SR/GNP 5 wt.% viscosity with a 1:1 ratio of Dow Corning 360 Medical Fluid decreases SR mechanical properties. Extraction with solvents resulted in no differences in terms of mechanical properties and *in vitro* biocompatibility. All the materials shown to be biocompatible *in vitro*.

Keywords: Graphene; Silicone rubber; Mechanical properties; Biocompatibility; *in vitro* assays.

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Mesenchymal stem cells coated with graphene oxide loaded with drugs for cancer therapy

S.Suryaprakash,[1] K.Leong [1]

[1] Columbia University in the City of New York, NY, USA

Abstract:

Graphene based systems have widely been used as a carrier for cancer therapy[1]. However most of the targeting is through passive targeting, stem cells such as mesenchymal stem cells on the other hand, have inherent tumor tropic properties that makes them an attractive cellular delivery vehicle for cancer therapy[2]. We have developed a new system where graphene oxide (GO) loaded with drugs is used to coat the surface of the mesenchymal stem cells, and the mesenchymal stem cells carries the GO-Drug composite directly to the site of tumor (Fig 1A). This system allows us to take advantage of MSCs unique tumor trophic properties, and simultaneously GO's ability to load a wide variety of drugs including proteins, nucleic acids, and small molecules.

We have shown that GO is not toxic to the MSC during long-term incubation. The GO can coat the surface of the MSC as demonstrated through scanning electron microscope, and fluorescent microscope (Fig 1B).

The GO coated MSC can successfully migrate towards the tumor cells within 24 hrs at a velocity equivalent to normal MSCs carrying the GO along with it(Fig 1C). GO loaded with doxorubicin (GO-DOX) and GO loaded with metoxantrone (MTX) were tested against a wide range of cancer drugs and were able to preferentially kill the cancer cells leaving MSCs unharmed. We then coated the MSC with GO-DOX and GO-MTX composite and co-cultured with LN18 a glioblastoma cell line. The co-culture of MSC carrying the drugs and cancer cells resulted in dose dependent killing of the LN18 cells demonstrating the killing efficiency.

MSC-GO is an efficient drug delivery system that can migrate towards the site of the tumor and deliver a wide range of therapeutics locally to kill the cancer cells. We plan to use to the system to test the efficacy in vivo in the future.

Keywords: Graphene oxide, cancer, stem cells, glioblastoma, cancer therapy, drug delivery

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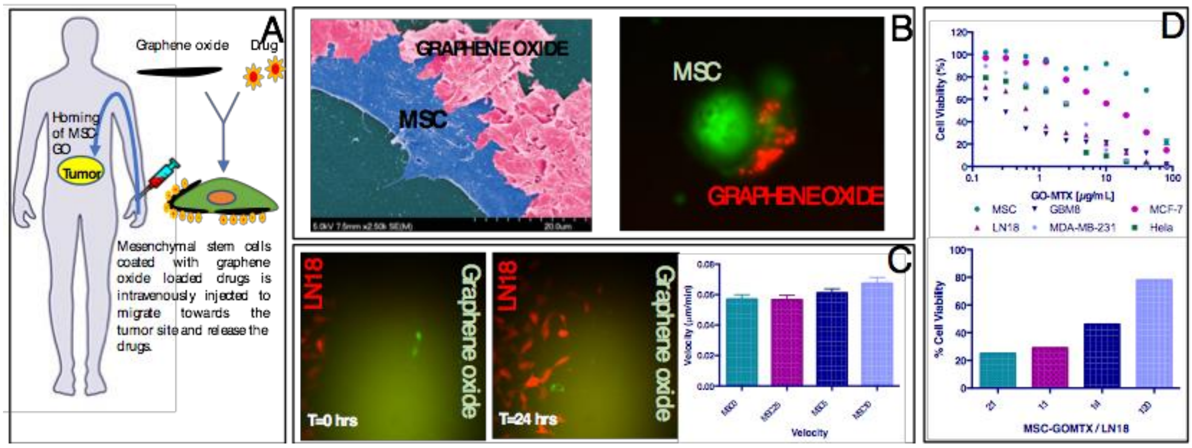

Figure 1: Figure (1A) MSC coated with graphene oxde loaded drugs migrate towards the site of tumor to release drugs locally. (1B) SEM and fluorescent images of GO coating on the surface of MSC. (1C) Migration of MSC coated with GO towards cancer cell in 24 hrs. (1D) Toxicity of GO-MTX on cancer cells and co-culture of MSC-GO-MTX with cancer cells showing dose dependent toxicity.

Copper Hydroxide Flower like Nanostructured decorated on Three Dimensional Graphene As Non-enzymatic Electrochemical Glucose Sensor

I. Shackery,[1] S. C. Jun,[1,*]

[1] School of Mechanical Engineering, Yonsei University, Seoul 120-749, Republic of Korea

Abstract:

The glucose sensing has wide range of application with significant role in clinical diagnostics, food industry and biotechnology [1]. The crucial importance of glucose sensors make it necessary to develop fast, accurate and reliable methods for glucose determination. The commercial glucose sensors are based on the enzymes which provide good selectivity and high sensitivity. But they are suffer from thermal and chemical instability, sensitivity to temperature, pH and humidity which comes from the nature of enzymes. Thus, to overcome above-mentioned drawbacks of enzyme based glucose sensors, several attempts have been done in order to achieve a simple, cheap, accurate and fast enzyme-free glucose sensor.

We report the synthesis of the flower-like nanostructure of copper hydroxide ($Cu(OH)_2$) on freestanding graphene pore structure (GPS) via a simple and cost-effective chemical bath deposition (CBD) method. The CBD is a facile method which provide relatively inexpensive, simple and convenient route for large area deposition. Meanwhile electrochemical sensors are simple, operative, sensitive, high time efficiency and reasonably inexpensive compare to other methods.

The structural and morphological characterization of $Cu(OH)_2$ reveals that, $Cu(OH)_2$ nano structure, consists of nanorods (diameter ~100 nm), are well covered over the porous graphene framework (Figure 1). The electrocatalytic activity of the nanocomposite, investigated by cyclic voltammetry (CV) and amperometric methods. The nanostructure morphology leads to be a high specific surface area, which provides the structural foundation for the high sensitivity. Significantly, $Cu(OH)_2$/GPS electrode showed the excellent sensitivity (up to 3.36 mA mM^{-1} cm^{-2}), low detection limit (1.2 µM), wide linear range (1.2 µM ~ 6 mM). The $Cu(OH)_2$/GPS exhibited good reproducibility and excellent selectivity toward usual interfering materials such as lactose, fructose, Acetaminophen, ascorbic acid, dopamine and urea in 1 M KOH aqueous electrolyte.

Keywords: Non-enzymatic glucose sensor, Graphene pore structure, Metal hydroxide, Bio sensing.

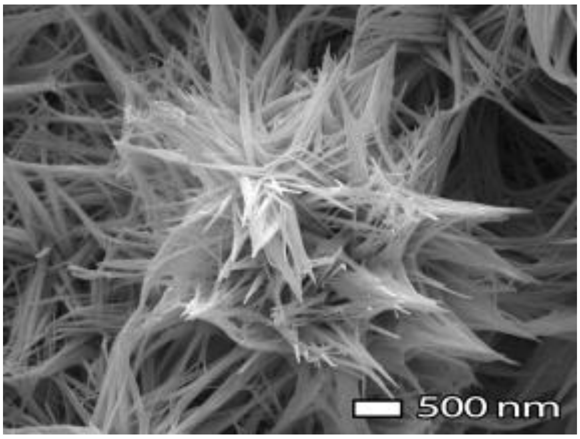

Figure 1: The SEM image of nanostructure copper hydroxide on graphene pore structure.

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Posters Abstracts

Poster Session I:
SMS EUROPE 2017

Structural and Optical Properties of $CuInS_2$ Nano-particles on TiO_2 by Spray Pyrolysis

Hyun-su Jung[1*], Gye-Choon Park[2]

[12]Mokpo National University, Department of Electrical Engineering, Muan,
Jeonnam, 534-729, South Korea

Abstract:

Copper Indium Disulfide ($CuInS_2$) which is one of $\mathrm{I\text{-}III\text{-}VI_2}$ chalcopyrite semiconductors possessing a direct band gap of 1.5 eV, has been attracted as a material for application of the photovoltaic solar cells. Titanium Oxide (TiO_2) which is a semiconductor material with a large bap gap of 3.2 eV, has been also widely used as a photocatalyst because of its high stability, favorable band gap energy, inexpensive cost and abundant availability. In this letter, $CuInS_2$ nano-particles deposited on TiO_2 porous film are applied for the use of the absorption layer of a composite solar cell, and the nano particles are prepared by using a method called the spray pyrolysis. Their material characteristics including structural and optical properties of $CuInS_2$ nano-particles on TiO_2 were analyzed as a function of its composition ratios of Cu:In:S. Crystalline structure, surface morphology and crystalline size were also investigated by X-Ray Diffraction(XRD), Field Emission Scanning Electron Microscope(FESEM), and High-Resolution TEM(HRTEM), respectively. On the other hand, optical property was characterized by an UV-Visible Spectrophotometer. As a result, it was found that the size of $CuInS_2$ nano-particles, which was formed at 300±5 ℃, was smaller than 16 nm from HRTEM analyses, and it was identified that the $CuInS_2$ particle size was increased as increasing the heat-treatment temperature and time. However, as the size of $CuInS_2$ nano-particle becomes smaller, optical absorption edge of ternary compound film tends to move to the blue wavelength band. It turns out that the optical energy-band gap of the compound films was ranging from 1.48 eV to 1.53 eV.

Keywords:

$\mathrm{III\text{-}VI_2}$ chalcopyrite semiconductor, $CuInS_2$, photocatalyst, TiO_2, absorption layer, composite solar cell, X-Ray Diffraction, Field Emission Scanning Electron Microscope, High-Resolution Transmission Electron Microscope, UV-Visable Spectrophotometer.

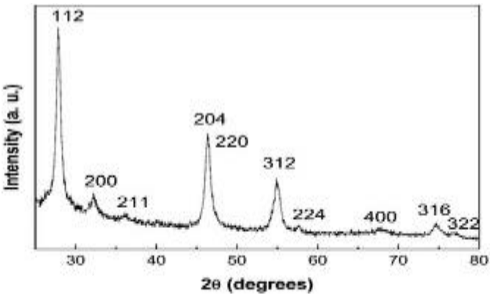

Figure 1 Measured XRD Patterns of $CuInS_2$ nanoparticles.

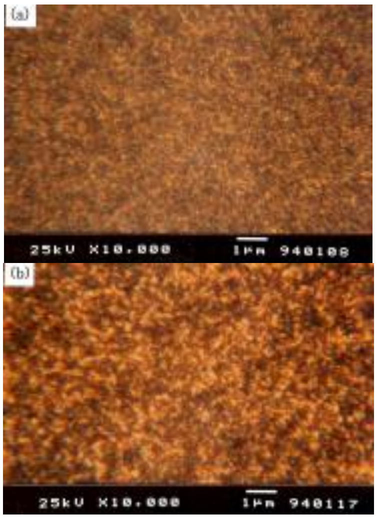

Figure 2. Top view images of $CuInS_2/TiO_2$ composite prepared by FESEM; (a) in situ deposition of $CuInS_2$ and (b) one hour heat-treatment after $CuInS_2$ deposition

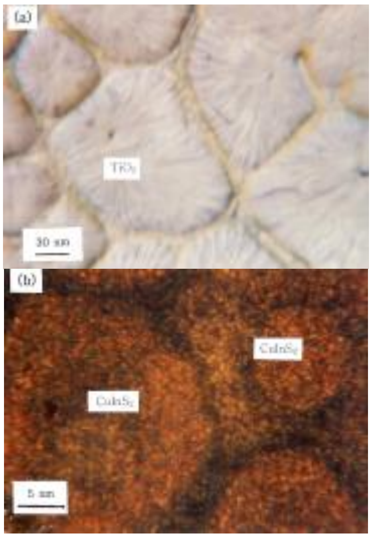

Figure 3. TEM images of (a) pure TiO_2 nanotube and (b) $CuInS_2$/ TiO_2 nano tube composite.

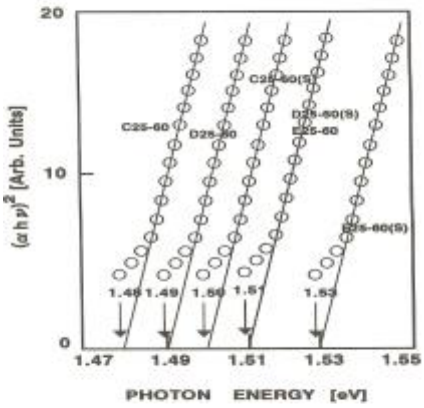

Figure 4. Energy band gaps of $CuInS_2$ according to Cu:In:S composition ratios.

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Magnetically Active Helical Soft Robots

J. Jeon, J. E. Park, J. H. Cho, K. H. Lee, J. J. Wie

Inha University, Department of Polymer Science and Engineering, Incheon, South Korea

Abstract:

Magnetically active soft robots are advantageous to achieve untethered manipulation of battery-free systems [1, 2] that can avoid on-board weight penalty [3] as well as distance and direction constraints originating from wire connections. In this work, we synthesized monolithic composite materials by incorporating magnetic iron particles into elastomeric polymer matrix, polydimethylsiloxane (PDMS). The magnetic polymer composites are processed into helical shapes by two-step polymerization of PDMS. Magnetic field is applied by a neodymium permanent magnet placed on a uniaxial moving stage. Displacement of magnet at constant velocity resulted in intermittent translational motility of helical soft robots via rotational motion. This intermittent motility of the soft robot was the consequence of force balance between magneto-generated stress-strain response and rolling friction. In this presentation, various parameters affecting magnetomotility of soft robots will be discussed.

Keywords: soft robot, magnetic field, helical robot, untethered robot, polymer composite, iron particles, magnetomotility.

Figure 1: (a) Monolithic composite helical soft robot by incorporating magnetic iron particles into elastomeric polymer matrix, PDMS (b) illustrating the magnetically helical soft robots

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Lattice Defects-Driven Magnetic Transformations in $BiFeO_3$-Based Multiferroics

U. Khomchanka,[1,*] J. A. Paixão[1]

[1] University of Coimbra, CFisUC/Department of Physics, Coimbra, Portugal

Abstract:
Multiferroics exhibiting magnetic and electric dipole ordering in the same phase are nowadays considered as having tremendous potential for application in spin-based electronics. Increasing attention is currently paid to perovskite-type bismuth ferrite ($BiFeO_3$) which remains an extremely rare example of a single-phase compound demonstrating magnetoelectric coupling at room temperature. Nevertheless, the cycloidal antiferromagnetic structure specific to this material limits its practical applicability. Partial replacement of Bi^{3+} with $A^{2+}=Ca^{2+}$, Sr^{2+} or Pb^{2+} is commonly considered as favoring the suppression of the cycloidal modulation. To reveal the reasons behind the doping-driven instability of the cycloidal magnetic order in the polar phase of $Bi_{1-x}A_xFeO_{3-x/2}$, synthesis and investigation of the crystal structure, microstructure, local ferroelectric and magnetic properties of the ceramic samples of $Bi_{0.9}Ca_{0.1}Fe_{1-x}Ti_xO_{3-\delta}$ (x=0.05, 0.1, 0.15) have been carried out. The Ti^{4+}-doped compounds have been found to be isostructural with the pure $BiFeO_3$. It has been shown that the pattern of changes in the lattice parameters of the samples can be interpreted as consistent with the doping-driven elimination of anion vacancies at $x \leq 0.1$ and the formation of cation vacancies at $x > 0.1$. The filling of oxygen vacancies suppresses a weak ferromagnetic contribution characteristic of the parent $Bi_{0.9}Ca_{0.1}FeO_{2.95}$. The appearance of cation vacancies restores the weak ferromagnetic phase. The key role of structural defects in the establishment of the weak ferromagnetic polar state has been confirmed by the observation of a correlation between the magnetic properties and the morphology / ferroelectric domain structure of the ceramics under study. These findings pave the way for understanding the conditions favoring the coexistence of spontaneous magnetization and polarization in $BiFeO_3$-based multiferroics.

Keywords: $BiFeO_3$, multiferroics, lattice defects, spin-cycloid instability, ferroelectric domains.

Permanent Memory Effect of PDLCs devices: Effect of Glass Transition Temperature

Ana Mouquinho*, João Sotomayor

LAQV-REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia,
Universidade NOVA de Lisboa, Quinta da Torre, 2829-516 Caparica, PORTUGAL
**a.mouquinho@campus.fct.unl.pt*

Abstract:
Among liquid crystal composite, polymer dispersed liquid crystal (PDLC) are promising materials for developed optical memory devices. They are polymer films with liquid crystal (LC) domains dispersed into them. Electro-optical effects in PDLCs films are made by changing the configuration of LC molecules in domains under the action of an electric field.

In OFF state the directors of LC domains are randomly aligned causing a mismatch between the effective refractive index of LC domains and the polymer matrix. In this way, the light incident to the PDLC surface is scattered and PDLC will appear in an opaque appearance. In the ON state the electric field reorients the LC molecules with their long axis parallel to the applied field (for nematic LCs having positive dielectric anisotropy). In this state, light incident normal to the film surface experiences refractive index $n_o=n_p$ and gets transmitted through the film[1].

However, this change could underlie two approaches types. In a traditional one based on the classical Fréedericksz effect, the LC alignment achieved will only persist so long as the field is applied, and when it is removed, the multi-domain texture will reappear. The scattering state always returns when the electric field is removed. This behavior makes these PDLC unsuitable for some applications. However this limitation might be overcome. The higher transparency obtained in the OFF state can permanently persists upon removal of the applied field giving rise to a permanent memory effect (PME). A schematic representation of PDLC film with permanent memory effect is shown in figure 1. For achieved this type of answer it is necessary a modification of the boundary surface anchoring on the LC domains surface. One way to modification of the interphase surface anchoring can be by selecting a thermoplastic polymer matrix.

Polymer around liquid crystal domains surface gets entangled liquid crystal molecules. When a voltage was applied to the PDLC, LC molecules reoriented along to the electric field. It is possible, that during this process, depending on the Tg of polymer matrix the configuration of polymer chain could change or remain unaltered[2,3,4].

If the T_g of polymer chain is lower than room temperature, surface structure of the polymer can be affected by the LC alignment. When the LC molecules reoriented along to the electric field easily force the polymer chain at boundaries to form a new conformation. In this way, even in boundaries LC molecules change their direction forcing polymer chain to form a new conformation. If this new polymer conformation is stable, the LC molecules do not tend to return to a random configuration when electric field is switched off and LC alignment is frozen. Therefore, the transmittance of PDLCs could not go back to its initial opaque state and a high transparency state is preserved giving permanent memory effect. If the T_g of polymer chain is to higher to move under temperature, the polymer chains tend to maintain the configuration even when the LC molecules reoriented with the electric field. When the electric field is removed the liquid crystal molecules tend to return to the random configuration by elastic forces that originate at the surface between LC and polymer and light will be scattered again.

In this way, with the selection of thermoplastic polymer matrix (among other factors) makes it possible to create PDLCs with permanent memory effect.

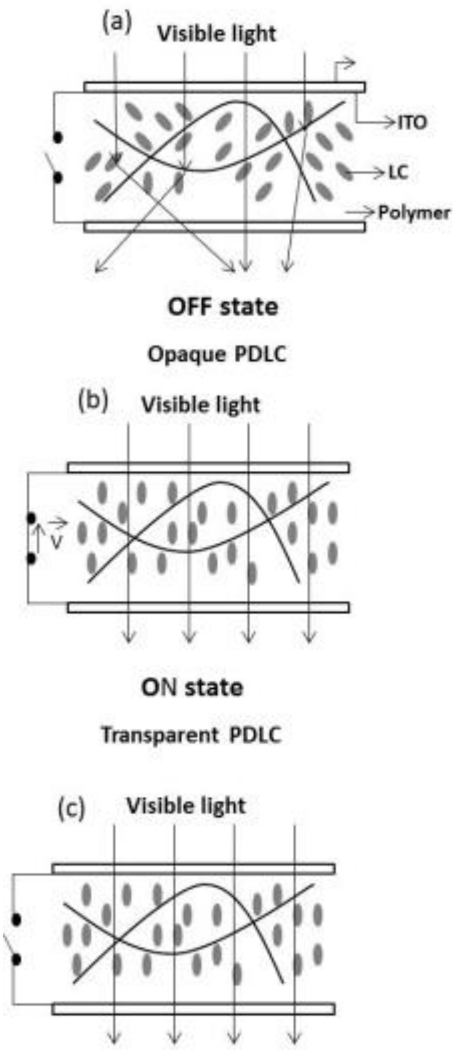

Figure 1: Schematic representation of the averaged molecular orientation of the liquid crystal within the microdroplets without electric field (a); (b) during application of an electric field and (c) after removal electric field for PDLCs films with permanent memory effect.

In this work we also have observed that polymer chain length affect the amorphousness and crystallinity of polymer (maintaining the number of functionalities). In this way the best molecular weight for polyethylene glycol di(meth)acrylate monomers to promote the permanent memory effect until 70% is between 875 and 1000g/mol. For longer polymer chains crystal aggregates by folded chains are formed resulting in semi-crystalline polymers [5] what cancels the permanent memory effect.

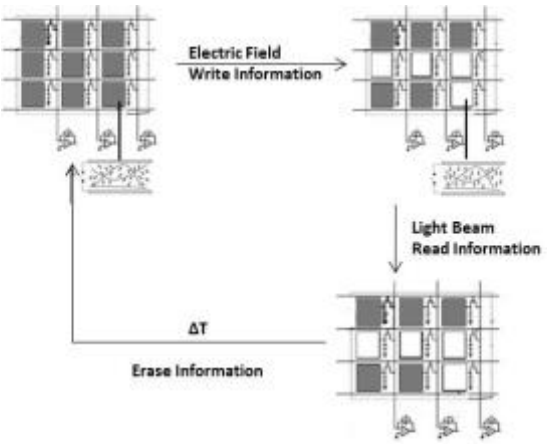

Figure 2 - Schematic description of optical data storage using PDLC with permanent memory

effect units.

PDLCs with permanent memory effect in addition to be more favorable energetically can be potential candidates for digital memory devices based on write-read-erase cycles. For this a pixel array is need where optical elements are form by PDLC units where voltage can be applicate to each unit independently. A robust representation of optical data storage in a PDLCs pixels array is shown in figure 2.

Keywords: Liquid Crystals, Permanent memory effect, multiplexed addressed, optical storage, smart windows.

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Development of a polymer-metal composite for dynamic-mask microstereolithography

B.Khatri[1], A.Bhat[1], T. Hanemann[1,2]

[1] University of Freiburg, IMTEK, Laboratory for Materials Engineering, Freiburg, Germany
[2] Karlsruhe Institute of Technology, Institute for Applied Materials, Karlsruhe, Germany

Abstract:
Dynamic-mask stereolithography (DMSL) has in recent years become a versatile additive rapid protoyping platform for the development of composite microstructures in a layer-by-layer manner, with applications ranging from micro-fabrication [1] [2] to RF antenna design [3]. The use of composite materials in DMSL has mainly been focused on ceramic-filled resins. We present a metal-filled composite material system developed for use with the B9Creator, a commercially available dynamic mask stereolithographic 3D printer. The material system comprises two acrylic comonomers (ethylene glycol dimethacrylate and bisphenol A ethoxylate diacrylate) combined with a radical photoinitiator (diphenyl (2,4,6-trimethylbenzoyl)phosphine oxide) and spheroidical copper micro-powder in ratios of 4.8 vol. % (28.2 wt. %) and 8.2 vol. % (41.4 wt. %). Test structures with feature sizes down to 200 µm with aspect ratios up to 7.5 could be reliably structured using these resins at a voxel resolution of 50 µm³. Tensile test specimens were printed using resins with and without the copper micro-powder which showed an overall decrease in the ultimate tensile strength and breaking strain from 928 MPa and 6.1 % for the pure resin to 577 MPa and 4.5 % for the 8.2 vol. % composite resin, respectively. The resin shows promise for the development of electrically conductive 3D printed structures, and combined with the achievable feature sizes, has potential as a manufacturing method for conductive microstructures such as micro-coils.

Keywords: Additive rapid prototyping, composite materials, stereolithography, metal micro-powder

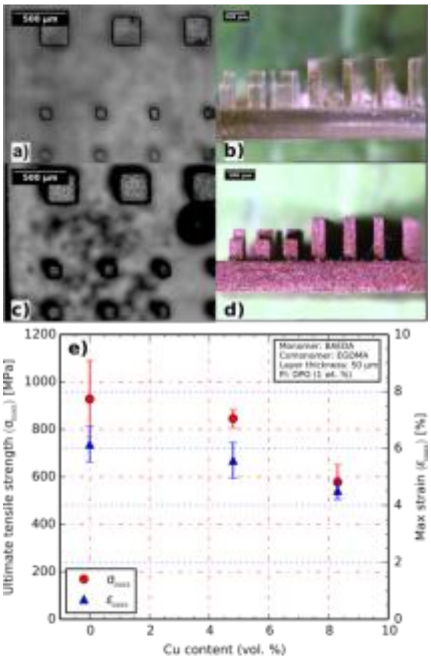

Figure 1: Test structures printed using (a), (b) the pure resin and (c), (d) using the polymer-metal composite resin. (e) Tensile behavior of the resin with increasing filler ratio.

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Poster Session I:
EGF 2017

Functionalization of graphene oxide with tetraethylenepentamine (TEPA): CO_2 capture application.

Marina González-Barriuso[1,2*], Carmen Pesquera[1], Fernando González[1], Ángel Yedra[2] and Carmen Blanco[1]

[1]Dept. Chemistry and Process & Resource Engineering, School of Industrial Engineering and Telecommunications, University of Cantabria, Av. de los Castros s / n, Santander 39005 Cantabria, SPAIN.

[2]Fundación Centro Tecnológico de Componentes. C / Isabel Torres, No. 1, in the Scientific and Technological Park of Cantabria, Santander 39011 Cantabria, SPAIN.

Abstract:

Fossil fuels are the first reason for climate change and global warming, due to CO_2 emissions. On the other hand, they are versatile energy sources. So, a balance between their drawbacks and benefits is needed.

In the latest years, plenty of works have been developed aimed at the solution of this problem. One of the strategies is reducing CO_2 emission. CO_2 reversible capture and storage, what it is known as carbon capture and conversion (CCC), can be the key to solve it. In this proposal, the gas is captured and stored for its later released and transformation, because in combination with hydrogen (or methane), CO_2 can be transform in high density fuels. These fuels are compatible with any energetic infrastructure of our days [1].

In this context, graphene and its derivatives are shown as the ideal materials for this kind of applications. The main reasons are its 2D structure, high specific surface, and the ability of modify its surface to give them the adequate selectivity.

In the present work amine-functionalized graphene oxide nanoparticles are synthesized. To do so, tetraethylenepentamine (TEPA) was used. The new amine groups ($-NH_2$-, –NH-) of the graphene oxide surface provide the material with a CO_2 chemisorption capability. This chemisorption is a reversible reaction between CO_2 molecules and the amine groups of the amino-functionalized graphene oxide surface for the formation of carbamates [2].

The characterization of the result amino functionalized graphene oxide was done by FT-IR spectrometry, DSC and TG as thermal analysis, mass spectrometry, elemental analysis, amount of NH_2- groups stimation. To evaluate its possible use as in CCC it was used CO_2 adsorption isotherms.

Keywords: graphene oxide, CO_2 capture, CO_2 adsorption, chemisorption, amino-functionalization, tetraethylenepentamine (TEPA).

Acknowledgements:

"Help Industrial Doctorate" granted by the University of Cantabria in its 2014 call associated with the project Nº 51.DI03.648 is gratefully acknowledged.

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Growth of $Mo_xW_{1-x}Se_2$ Film with Tunable Band Gap via Metal-Organic Chemical Vapor Deposition

Yoo Been, L., Jin Seok, L.,*

Sookmyung Women's University, Department of Chemistry, Seoul, Korea

Abstract:

Study of transition metal dichalcogenides (TMDC) are interested due to their optical, electronic properties. Synthesis of heterostucture TMDC like $Mo_xW_{1-x}S_2$ has researched variously. But, one of the spotlighted synthesis techniques, metal organic chemical vapor deposition (MOCVD) for synthesis TMDC materials and TMDC alloy films has not been reported yet.

Here, we present the report of synthesis continuous $Mo_xW_{1-x}Se_2$ films via metal organic chemical vapor deposition method using molybdenum hexacarbonyl ($Mo(CO)_6$), tungsten hexacarbonyl ($W(CO)_6$) and dimethyl selenide ($Se(CH_4)_2$) on silicon oxide wafer and characterized by atomic force microscopy (AFM). We observed two peaks of A_{1g} mode, main Raman modes of $MoSe_2$ and WSe_2, using micro-Raman spectroscopy and show tunable optical band gaps by photoluminescence measurements that they are detected different intensity and position, respectively. This study will attract us to discuss tunable band gap engineering applications that we have enlightened with continuous TMDC alloy.

Keywords: metal organic chemical vapor deposition, transitional metal dichalcogenides, tungsten diselenide, molybdenum diselenide, raman spectroscopy, photoluminescence, bandgap engineering, optical applications.

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Molecular Layer Deposition of Hybrid Organic-Inorganic Alucone Films Using Organic Precursors with Different Carbon Bond Order

Ui-Jin Choi, Jin Seok Lee*

Sookmyung Women's University, Department of Chemistry, Seoul, 140-742, Korea

Abstract:

Molecular layer deposition (MLD) is a method for obtaining conformal ultrathin organic films using vapor-phase organic precursors, while their composition and thickness can be controlled at the molecular level. This process is based on self-saturating reactions between the organic precursors and the substrate surface. Also, in comparison with solution-based technique, it allows epitaxial growth of molecular layer on substrate and is especially good for surface reaction or coating of nanostructures such as nanopore, nanochannel, nanowire array and so on.

In this study, we fabricated organic-inorganic alucone polymeric films through coupling reactions between trimethyl aluminum (TMA) and one of two diols with different carbon-carbon bond order as inorganic and organic precursors, respectively, by molecular layer deposition. Using ellipsometry, we confirmed linear growth of the films versus number of MLD cycles at all same temperature. The mass gains in alucone films grown with varying doses of TMA and organic diol were identified using in situ quartz crystal microbalance (QCM) technique. This presents different tendency of the mass gain of the films to reduce with increasing of the flexibility of organic precursors. And, surface potential of alucone films were investigated by ex situ analysis scanning kelvin probe microscopy (SKPM). Furthermore, all molecular geometries and doubling energies were predicted by performing density functional theory (DFT) calculations.

Keywords: Molecular layer deposition, doubling energies

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A New Approach to Graphene Manufacturing for Solid State Devices and Compound Heterostructure Applications

S. Thomas,[1,2,*] I. Guiney,[1,2], C. Humphreys,[1,2]

[1] University of Cambridge, Department of Materials Science and Metallurgy, Cambridge, UK
[2] 2D Technologies Ltd., Cambridge, UK

Abstract:

The extraordinary properties of graphene are well theorized and in many instances well demonstrated, at R&D level[1]. Graphene technologies are being constructed to the concept proof stage at increasingly impressive rates. The commercial realization of only a few could have incredible, world changing, impacts.

So where are the real world graphene devices? Enduring problems still persist for graphene, however wonderful its applications could be. Technology transfer from R&D to commercial proposition still has major barriers. The root problem, for the majority of applications, is still the lack of high quality graphene, producible on cost effective, commercially viable scales, delivering both performance and product value[2]. Raw material is still too small, non-uniform, poorly reproducible and contaminated to be successful on large scales. Further, as with all device materials, truly useful graphene needs to be available in formats and with properties suitable for the desired application. Currently repeatable, reliable functionalized graphene is proving difficult to consistently achieve.

We are developing new manufacturing techniques, focused on the issues barring commercial uptake of graphene. Our early work has yielded promising results, with graphene layers demonstrating comparable properties to current state of the art, best material and going a significant way to ameliorating the commercial exploitation issues.

The ability to directly form graphene on non-metalized, crystalline substrates has been the first key to our progress and while some issues still exist we have been able to show the potential of the approach. Our second achievement has been the ability to functionalize the graphene as it is produced, through highly co-ordinated stacking and/or doping. This has resulted in the capability to flexibly alter the properties of the material, allowing us to produce graphene with attributes that target the needs of the application.

Using this methodology we are starting to demonstrate the combination of our graphene and compound semiconductor materials, by forming the graphene directly on device heterostructures. We have shown promising, early stage results with graphene as a top-side, p-contact for Gallium Nitride (GaN) based LED's.

Although it is still early days our concept work is indicating this approach has the potential to address the graphene tech-transfer gap, particularly for solid state devices.

Keywords: graphene growth, graphene production, functionalized graphene, commercial graphene, graphene devices, manufacturing.

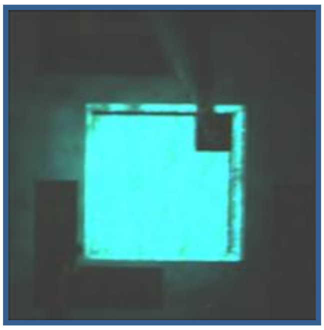

Figure 1: GaN/InGaN green LED structure with graphene top layer contact demonstrating good current spreading and high transmission intensity.

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Functionalization of reduced graphene oxide suspension by submerged plasma jet

S. Vizireanu[1], M.D. Ionita[1], S. D. Stoica[1], L. Carpen[1], M. Teodorescu[1], I. Ion[2], , M. Ionita[3], G. Dinescu[1]

[1] National Institute for Lasers, Plasma and Radiation Physics, Atomistilor Str. 409, Magurele, Bucharest, 077125, Romania
[2] National Institute for R&D in Electrical Engineering ICPE-CA, ,Carbon Materials Laboratory, Splaiul Unirii Nr.313 Bucharest Romania
[2] Advanced Polymer Materials Group, University Politehnica of Bucharest, 010737, Romania

Abstract:

Compared to the conventional methods as low pressure plasma and chemical routes plasma in liquid is a recent method which can be successfully applied for synthesis, functionalization and dispersion of nanomaterials. Functionalization by liquid plasma treatments is eco-friendly and can operate without surfactants or strong acids for modifying graphene suspensions.

Nitrogen incorporation in graphene presents a great interest because it changes the electrical conductivity and capacitance of nanostructured electrodes, which are key parameters for batteries and supercapacitors [1].

In the present report we have used a cold atmospheric plasma jet [2] submerged in a reduced graphene oxide suspension (Figure 1).

Figure 1: Image of plasma jet source submerged into liquid.

Previously, we have used the same technique for oxygen functionalization of carbon nanowalls (CNW) in water dispersion [3]. In the conditions tested before for graphene nano-sheets obtained through ultrasonication of vertically graphene nanowalls [3], oxygen atoms was successful embeded when we used plasma generated in argon-oxygen mixture, but not nitrogen incorporation, in spite of the inherent nitrogen plasma species provided by the liquid contact with the ambient atmosphere.

Herewith, for reduced graphene oxide (rGO) suspension, we managed to introduce nitrogen in the material, as observed in XPS survey spectra (Figure 2), by using submerged argon/nitrogen plasma.

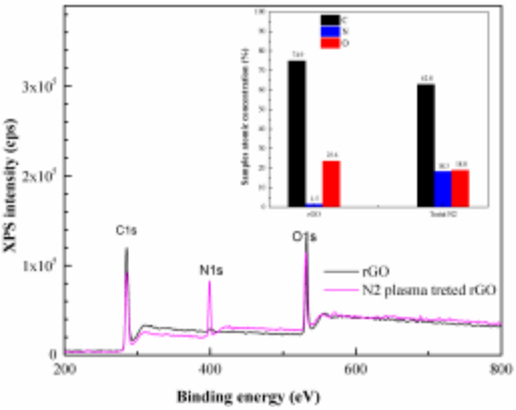

Figure 2: XPS survey spectra on dried suspension of untreated and plasma treated rGO suspension. The inset presents the relative atomic concentrations of C, N and O elements as bar diagram on rGO and Ar/N_2 plasma treated rGO suspension after samples dried on Si substrate.

The treatment was performed in the following conditions: submerged plasma gas mixtures Ar/N_2, gas flow ratio 4000/300 sccm, 100 W radiofrequency power, and 15-minute treatment time. The suspension was investigated by UV-Vis absorption spectroscopy, Dynamic Light Scattering-DLS for particle dimension and zeta-potential, pH, while the materials properties obtained after the suspension drying were characterized by SEM, TEM, Raman, FTIR and XPS methods.

The submerged plasma treatment in rGO suspension does not affect the graphene sheets integrity, morphology and structure. The characteristics of treated samples show nitrogen containing functional groups attached to graphene sheets, that prove the efficiency of the plasma in liquid procedure for functionalization of nanomaterials suspension.

Keywords: plasma in liquid, plasma modification, functionalization, nitrogen incorporation, reduced graphene oxide.

Acknowledgments:

This work has been financed by the National Authority for Research and Innovation in the frame of Nucleus programme-contract 4N/2016 and contract PN-III-P2-2.1-PED-2016-0287.

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Role of hydrogen plasma post-treatment: etching behavior of vertically aligned graphene nano wall by electron cyclotron resonance plasma

Jin-ha Shin1, HyunJae Park2, Yong-ho Jung2, Yong-sup Choi2, Young Il Song1,3,*, Su Jeong Suh1,3,*

[1]Department of Nanoscience, School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, Gyeonggi-do 440-746, Korea
[2]Plasma technology research center, Osikdo-dong 814-2, Gunsan-si, Jeollabuk-do, Korea
[3]Advanced Materials and Process Research for IT, Sungkyunkwan University, Suwon, Gyeonggi-do 440-746, Korea

Abstract:

Electron Cyclotron resonance plasma source is promising method for not even large scale but rapid and efficient to synthesize graphene. The aim of this research is to investigate role of hydrogen radical during in-situ hydrogen plasma post-treatment on vertically aligned graphene nano walls (GNW) grown in same ECR system. Vertically aligned GNWs were synthesized and post-treated by ECR system on various microwave power and synthesis time. GNWs synthesis process was carried out for two steps. For the first step to synthesize GNWs, H2 gas was injected into process chamber as carrier gas aiming to anneal the substrate, provide active defects, which promote graphene nucleation formation, and remove surface contaminations on substrate on surface. Reactive CH4 gas was then infused into processing chamber during discharging H2 plasma. H2 plasma etching process was proceeded ceasing CH4 gas.Characteristics of ECR plasma as microwave power difference and time variation were diagnosed by Langmuir probe. And by use of residual gas analyzer (RGA) and optical emission spectroscopy (OES), hydrogen and hydrocarbon radicals were investigated during etching process.To characterize number of layers and defects density of as-grown GNW and post-treated GNW, Raman spectroscopy was used. The morphologies and microstructures of GNW were characterized using field emission scattering electron microscopy (FE-SEM)

Keywords: Electron cyclotron resonance, plasma treatment, Hydrogen treatment, graphene, vertical alignment

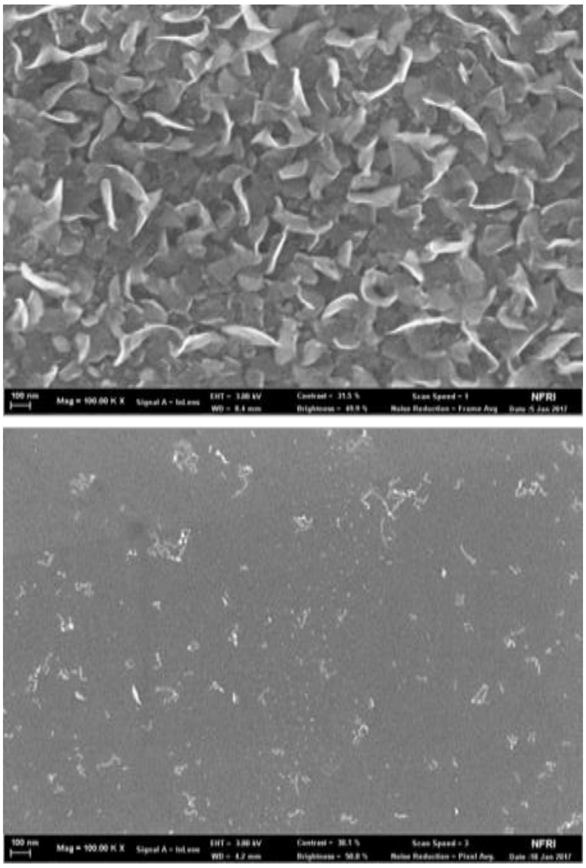

Figure 1: Top view of as deposited vertically aligned and H_2 plasma post-treated GNW by duration of time.

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Potentials for ch$_4$, h$_2$o, co$_2$, n$_2$ and h$_2$ adsorption on graphene

J. Vekeman[1], J. Wilson[1], I. Garcia Cuesta[1], N. Faginas Lago[2], J. Sánchez Marin[1], A. M. Sánchez de Merás[1]

[1] Instituto de Ciencia Molecular, Universitat de València, Cat. Jose Beltran Martinez 2, 46980 Paterna, Spain.
[2] Dipartimento di chimica, biologia e biotecnologie, università di Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy.

Abstract:
Graphene and its derivatives are widely investigated for their ability to adsorb small molecules through van der Waals interactions, possibly leading to new ways of natural gas storage. Furthermore, given the environmental issues of our time, hopes are that these materials could play an important role in capture and separation of greenhouse gases from gas mixtures. Methane and carbon dioxide are the two most important greenhouse gases and diminishing their presence in emissions is therefore a major challenge for the scientific community. Although a wide range of materials is being investigated for their capabilities to filter methane and carbon dioxide from common gas mixtures, previous results have shown graphene-derivatives to be promising candidates for this purpose. In order to provide a solid basis for research on a material and its derivatives, it is fundamental to well characterize the basis material first, in casu: graphene. A further advantage is the ease with which graphene can be modelled, while resulting potentials are likely to be transferable to more applicable derivatives. It is with this thought in mind that potentials for graphene in combination with small molecules like CH_4, H_2O, CO_2, N_2 and H_2 are presented here. In this work interaction energies for graphene-X and X-X (X being CH_4, H_2O, CO_2, N_2 or H_2) were calculated using the DFT-method with the B97D functional and a TZV2P basis set. The basis set superposition error was minimized by means of the counter-poise correction. The results were fitted to Improved Lennard-Jones[1] type potentials in order to get a set of parameters describing the dispersion interactions of interest. Aside from this, the parameters were also calculated from correlation formulae[2] at DFT, CC2, CC3 and CCSD level. This way we obtained the parameters of interest from different levels of theory to ensure an accurate potential energy. We aim at producing potentials that are on one hand very accurate, but on the other easily compatible with molecular dynamics. The resulting potentials were compared with energies from highly correlated ab initio methods in order to assure accuracy.

Keywords: graphene, DFT, CCSD(T), pairwise potentials, improved Lennard-Jones potential, methane, water, carbondioxide, hydrogen gas, nitrogen gas, van der Waals interactions, correlation formulae.

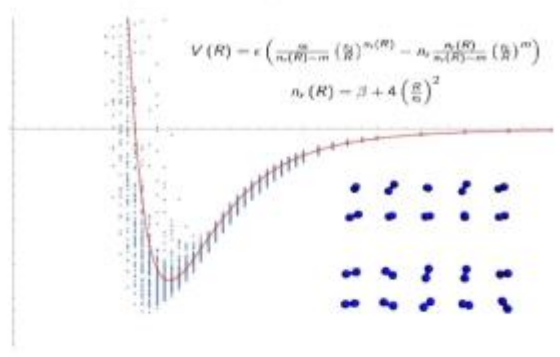

Figure 1: The improved Lennard-Jones potential is fitted to interaction energies calculated from a large amount of random geometries at DFT level in order to obtain accurate interaction potentials. nitrogen gas as example in the figure.

Acknowledgement: This work has the support of the European joint doctorate program on theoretical chemistry and computational modelling 642294-TCCM-MSCA-ITN-EJD within the framework of the innovative training networks of the Marie Skludowska-Curie actions.

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TiO_2-GO and TiO_2-rGO Nanocomposites: Investigation on Structure, Morphology, Spectroscopic and Magnetic Studies

E. Kusiak-Nejman,[1,*] D. Moszyński,[1] A. Wanag,[1] J. Kapica-Kozar,[1] Ł. Kowalczyk,[1] R.J. Wróbel,[1] A.W. Morawski,[1] N. Guskos,[2]

[1] West Pomeranian University of Technology, Szczecin, Faculty of Chemical Engineering, Institute of Inorganic Technology and Environment Engineering, Pułaskiego 10, 70-322 Szczecin, Poland
[2] West Pomeranian University of Technology, Szczecin, Institute of Physics, Al. Piastów 48, 70-311 Szczecin, Poland

Abstract:

Recently, the preparation of new graphene-TiO_2 nanocomposites with enhanced charge separation in electron-transfer, has been intensively studied [1]. Incorporation of GO or rGO into TiO_2 high charge carrier mobility due to the moving of TiO_2 generated electrons across the graphene sheets, which minimizes the electron-hole recombination and enhances the oxidative reactivity [2].

This study presents detailed characterization of TiO_2-GO and TiO_2-rGO nanocomposite photocatalysts preapared by hydrothermal metod.

SEM studies show difference between graphene oxide- (aggregated, crumpled, non-transparent) and reduced graphene oxide- (thin and transparent) TiO_2 nanocomposite photocatalysts (Fig. 1).

FTIR/DRS analysis (Fig. 2) allowes to find characteristic peaks of graphene oxide: epoxy stretching at 1229 cm^{-1} and alkoxy stretching vibration at 1059 cm^{-1}. However, in the spectrum of nanocomposites containing rGO, the epoxy bonds dissapear and the intensity of alkoxy bonds decrease. In addition, depending on the graphene form, the differences in the Ti-O and Ti-O-Ti positions are possible to observe (922cm^{-1} for TiO_2-GO and 902 cm^{-1} for TiO_2-rGO). XPS and EPR studies show the changes between GO and rGO modifiers as well as the medium (water or butyl alcohol) utilized in preparation step.

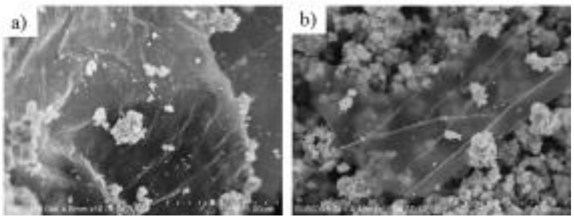

Figure 1: SEM images of (a) TiO_2-GO and (b) TiO_2-rGO obtained in the atmosphere C_4H_7OH

Keywords: nanocomposites, TiO_2, graphene oxide, reduced graphene oxide, XPS, EPR, TRMC

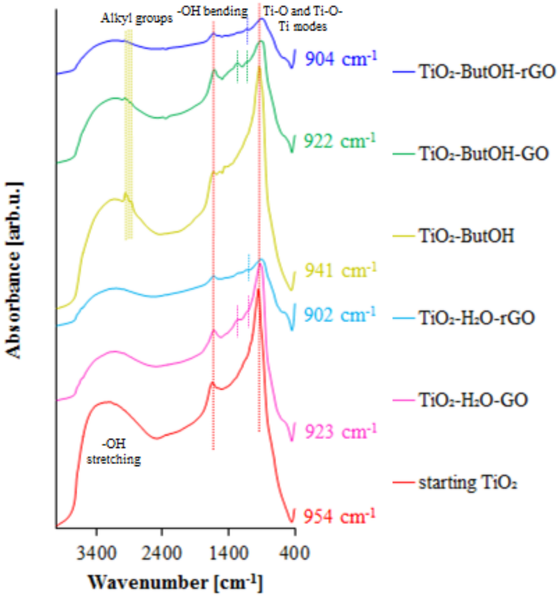

Figure 2: FTIR/DRS spectra of TiO_2-GO and TiO_2-rGO hybrid nanocomposites

Acknowledgments: This work was supported by grant Maestro 3 No. DEC-2012/06/A/ST5/00226 from the National Science Centre (Poland).

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XPS analyses of as-rubbed mono- and few layer graphene films obtained by the substrates rubbing method

G. Shmavonyan,[1]* K. Hricovini[2], O. Heckmann[2], E. Boiakinov[2], W. Ndiaye[2], S. Vaiedelich[3], M. C. Richter[2]

[1] National Polytechnic University of Armenia, Department of Microelecronics and Biomedical Devices, 105 Teryan street, Yerevan, 0009, Armenia
[2] Université de Cergy-Pontoise, Laboratoire de Physique des Matériaux et des Surfaces, 5 Mail Gay Lussac, 95031 Cergy-Pontoise, France
[3]Musée de la musique-Philharmonie, 221 avenue Jean -Jaurès, 75019 Paris, France

Abstract:
Graphene, a single layer of sp^2-bonded carbon atoms arranged in a honeycomb lattice, has attracted much attention as a promising material [1]. The elaboration of simple, fast and ecologically clean method for obtaining high quality and large size two-dimensional (2D) atomic materials on any substrate for industrial application is currently of high interest. High quality and large size samples of mono- and few layer (MFL) graphene, hexagonal boron nitride and other 2D material nanostripes, films and hybrid 2D heterostructures were obtained on different rigid and flexible inorganic and organic substrates by an extremely simple, fast, cost-effective, transfer- and chemical-free, reliable and industrially scalable method (substrates rubbing method) suggested recently [2]. In order to clarify the nature of carbon bonding and to reveal the presence of the contamination on the surface of as-rubbed MFL graphene films, as well as clarify how clean the rubbing proccess is, X-ray photoelectron spectroscopy (XPS) measurements on the rubbed samples are realized at room temperature and after annealing the sample up to 1050°C. MFL graphene films were obtained on SiO_2/Si substrates by a recently patented rubbing method [2]. Room temperature XPS spectra show that the samples have a detectable quantity of carbon contamination. The latter with native silicon oxide were removed by annealing, which allows avoiding the assymetric tail of the C1s spectrum, conditioned by native carbon. In combination with Raman spectra [2], the XPS results demonstrate that the observed sp^2 bond carbon peak is originating from MFL graphene. Thus, XPS analysis of as-rubbed MFL graphene films reveals that the rubbing performed by two substrates is a clean process as it is very fast and one-step and allows fabricating high quality 2D devices composed of 2D materials with clean surfaces and 2D hybrid heterostructures with clean interfaces. The quality of 2D devices can be improved by using a glovebox during rubbing.

Keywords: Graphene, two-dimensional atomic materials, mono- and few layer, substrates rubbing method, nanostripes, films, hybrid heterostructures, X-ray photoelectron spectroscopy.

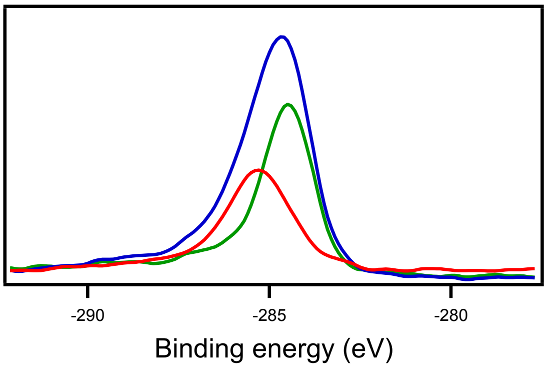

Figure 1: C1s XPS spectra (hν = 1285 eV) of two samples, one with MFL graphene on a SiO_2 (200 nm)/Si substrate (blue), the second sample is the naked substrate SiO (red); the difference spectrum (green) is centered at 284.5 eV and evidences pure sp^2 hybridized carbon atoms.

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Poster Session II:
EGF 2017

Dedicated functionalized graphene-based FET for highly sensitive detection of GQDs

J. Brndiarová,[1,*] M. Hulman,[1] D. Gregušová,[1] M. Bodík,[2]
P. Šiffalovič,[2] V. Skákalová[3], Z. Markovič[4], K. Fröhlich,[1]

[1] Slovak Academy of Sciences, Institute of Electrical Engineering, Bratislava, Slovakia
[2] Slovak Academy of Sciences, Institute of Physics, Bratislava, Slovakia
[3] Faculty of Physics, University of Vienna, Vienna, Austria
[4] Slovak Academy of Sciences, Polymer Institute, Bratislava, Slovakia

Abstract:
Graphene quantum dots (GQDs) have various important applications in bioimaging, drug delivery, LEDs light converters, photodetectors, solar cells, fluorescent material and biosensors fabrication. We present detection of GQDs by functionalized mechanically exfoliated graphene by means of FET. Graphene flakes were placed onto Si/SiO2 substrate and graphene FET was fabricated by optical lithography. Afterwards a controlled ozone treatment was utilized to create hydroxyl groups onto graphene surface in limited concentration to avoid a significant degradation of electron transport properties.Subsequently incubation in APTES solution was used to attach amino groups on the graphene surface. The affinity of negatively charged GQDs carboxylic groups towards the positively charged amino-functionalized graphene allows highly sensitive detectionbased on alteration of FET conductivity. In our contribution, properties of graphene FETs after APTES and GQD exposure were studied using Raman spectroscopy, scanning electron microscopy and atomic force microscopy. The graphene FET transfer and drain-source characteristics were measured for a control sample and the sample decorated with GQDs.

Keywords: back gated graphene field-effect transistor, bio-sensing, graphene quantum dots detection

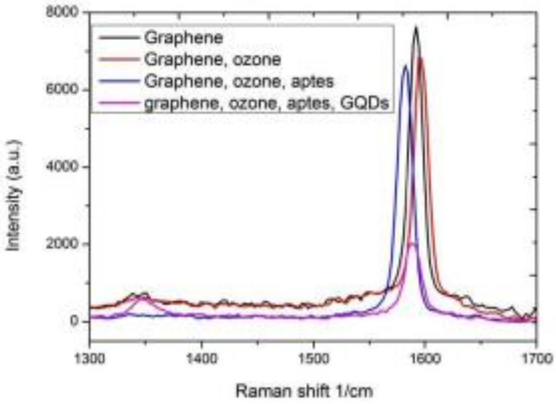

Figure 1: Raman spectrum of a monolayer graphene flake after controlled ozone treatment, incubation in APTES and GQDs. It displays shift of G peak after each step. Moreover, the comparison of graphene spectra before and after ozone treatment has proved no significant deterioration of graphene by controlled ozone treatment.

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Disorder induced unusual quantum Hall effect in low p-doped epitaxial graphene

A. Nachawaty, [1] M. Yang, [2] S. Nanot, [1] B. Jabakhanji, [3] W. Desrat, [1] W. Escoffier, [2] and B. Jouault [1]

[1]Laboratoire Charles Coulomb, UMR 5221 CNRS-Université de Montpellier, Montpellier, France.
[2]Laboratoire National des champs magnétiques intenses, INSA UPS, CNRS UPR 3228, Université de Toulouse, Toulouse, France.
[3]American University of the Middle East, College of Engineering and Technology, Egaila, Kuwait.

Abstract:

Graphene, a single layer of carbon atoms arranged in a honeycomb lattice, attracts a great interest due to his unique electronic properties. In particular, graphene allows the observation of an exceptionally robust quantum Hall effect [1]. In view of future applications, an industrial way to produce homogeneous graphene at the wafer scale is needed and the thermal decomposition of semi-insulating silicon carbide (SiC) appears promising [2]. In particular, on the Silicon-face of SiC, the graphene is very homogeneous but it is highly n-type doped because it forms on top of a buffer layer which acts as a reservoir charge. There is a charge transfer from the buffer layer to the graphene, which leads to a Fermi-level far from the Dirac point. It is interesting, for metrological applications, to test if the quantum Hall Effect is robust at very low magnetic fields [3]. Moreover most of the remarkable properties of graphene appear close to the Dirac point [4]. It is therefore crucial to control the carrier density. Here, we will present the method which we used to modulate the carrier density, the so-called "Corona Discharge" method [5]. Using this method, charge neutrality and p-doping were achieved from initially n-doped device. When lowering the temperature, for low p-doping device, the density decreases quadratically with temperature, in good agreement with theoretical predictions which take into account thermal excitation combined with electron-hole puddles induced by charged impurities. We deduce disorder amplitude of ~10 meV. At low temperature, under magnetic field, the Hall resistance decreases after reaching a maximum and shows a plateau value of $\approx h/e^2$ which indicates a change in majority carriers (figure 1). We will propose an explanation based on the presence of disorder near the charge neutrality point.

Keywords: epitaxial graphene, quantum Hall effect, metrology, electron-hole puddles

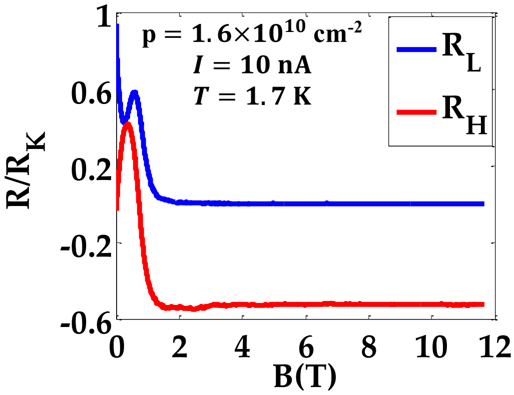

Figure 1: R_{xx} (blue) and R_{xy} (red) on an epitaxial graphene at 1.7 K measured using a current of 10 nA with carrier density equal to $\mathbf{1.6\times10^{10}}$ cm^{-2} obtained by classical Hall effect.

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The Effect of Oxygen Containing Functional Groups of Graphene-Oxide on The Morphology of Hydroxyapatite

S. TURK,[1,*] B. CAKIROGLU,[1] I. AlTINSOY[3], M. OZACAR[1,2], C. BINDAL[1,3]

[1]Sakarya University, Biomedical, Magnetic and Semi Conductive Materials Research Center (BIMAS-RC), Sakarya, Turkey
[2]Sakaray University, Science and Art Faculty, Department of Chemistry, Sakarya, Turkey
[3]Sakarya University, Faculty of Engineering, Department of Metallurgy and Materials Engineering, Sakarya, Turkey

Abstract:

Reduced graphene oxide–hydroxyapatite(GO-HAp) hybrid was synthesized via biomimetic mineralization of hydroxyapatite in SBF (Simulated Body Fluid) at different reducing reagent ratios. GO was prepared from pristine graphite by a modified Hummers and Offeman method. GO nanoparticles were reduced with different sodium borohydride ratios before soaking in SBF at 37 °C and pH 7.4 for biomimetic mineralization (Figure 1). In this study, the influence of reduction ratio of oxygen containing functional groups of GO on HAp morphology and size was investigated. The composites reduced at different grades were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, thermogravimetric analysis (TGA), and UV–visible spectrophotometry. The charge of functional groups, which influence the nucleation of HAp, was investigated by measuring the surface zeta-potential and wettability. Energy-dispersive X-ray spectroscopy (EDS) analysis revealed bone like hydroksyapatite Ca/P ratio. This study successfully addresses the relevance of the formation of hydroxyapatite by biomimetic minerization under the electrostatic interactions to the different amount of functional groups for bone tissue applications.

Keywords: Graphene oxide, hydroxyapatite, biomaterial, functional group, biomimetic mineralization

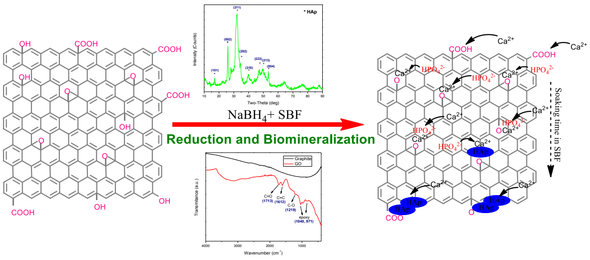

Figure 1. Reduction of some oxygen containing functional groups before soaking simulated body fluid, and biomineralization of bone-like hydroxyapatite by electrolytic interaction between calcium and phosphate ions and the functional groups on graphene oxide.

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Combination of Surface Charge and Size Controls the Cellular Uptake of Functionalized Graphene Sheets

Zhaoxu Tu,[1] Mohsen Adeli,[1,2,*] Rainer Haag,[1,*]

[1] Institut für Chemie und Biochemie, Freie Universität Berlin, Takustrasse 3, 14195, Berlin, Germany
[2] Department of Chemistry, Faculty of Science, Lorestan University, Khorram Abad, Iran

Abstract:

A fundamental issue for biomedical applications of graphene is the correlation between its physicochemical properties and cellular uptake mechanism.[1,2] However, such studies are challenging due to the intrinsic polydispersity of graphene.[3,4] In this work, a series of water soluble graphene sheets with the same polymer coverage, density of functional groups, and fluorescence intensity but three different sizes and surface charges were produced. We investigated the effect of the latter two factors and their combination on the mechanism of cellular uptake and intracellular pathways of these defined nanosheets. It was found that surface charge and size of the polymer-coated graphene sheets and the combination play a significant role in their cellular uptake mechanism. While positively ($-NH_3^+$) and negatively ($-OSO_3^-$) charged sheets showed an energy dependent uptake, their neutral analogs did not show any significant uptake. The cellular uptake efficacy of positively charged graphene sheets was independent of the size and occurred both through phagocytosis and clathrin-mediated endocytosis pathways. However, cellular uptake efficacy of graphene sheets with negative surface charge strongly depends on the size of the sheets. They crossed the membrane mainly through phagocytosis and sulfate-receptor mediated endocytosis. This study demonstrates that the impact of the size of graphene derivatives on their cellular uptake pathways highly depends on their surface charges and vice versa.

Keywords: Graphene, hPG, size, surface charges, cellular uptake, endocytosis pathway, inhibitors

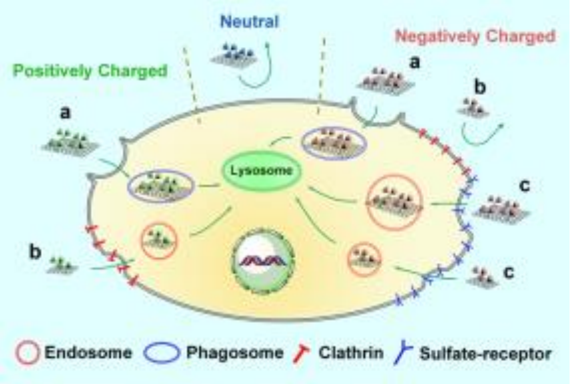

Figure 1: The cellular uptake mechanisms of graphene derivatives with different sizes and surface charges.

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Poster Session II: SMS EUROPE 2017

Effect of Aluminium and Boron Ion Incorporation on Structure, Bioactivity and Mechanical Properties of Ordered Mesoporous Bioactive Glasses

O.Winter,[1*] S. Melchers,[2] T. Uesbeck,[3] O. Lahayne,[4] C. Hellmich,[4] H. Eckert,[3,5] D. Eder[1]

[1] Technische Universität Wien, Institute of Materials Chemistry, Vienna, Austria
[2] University of Hannover, Insitute of Technical Chemistry, Hannover, Germany
[3] University of Münster, Institute of Physical Chemistry, Münster, Germany
[4] Technische Universität Wien, Institute of Mechanics and Structures, Vienna, Austria
[5] Instituto de Fisica de Sao Carlos, Universidade de Sao Paulo, Sao Carlos, Brazil

Abstract:
Mesoporous bioactive glasses (MBGs) are of high importance in the field of bone tissue engineering. Due to their excellent textural properties, e.g. high specific surface area and porosity, MBGs show several advantages compared to glasses prepared through a traditional melt-quenching process, such as an improved *in-vitro* bioactivity through the formation of a bonding layer of hydroxyapatite (HCA) when immersed in a simulated body fluid.[1]

Tailoring of *in-vitro* bioactivity and mechanical strength of MBGs by incorporation of additional oxides to the ternary SiO_2-CaO-P_2O_5-system is of high interest in latest research. Al_2O_3 and B_2O_3 are two oxides that have an influence on these two properties. While incorporation of Al_2O_3 has a positive influence on the mechanical strength and a negative influence on the *in-vitro* bioactivity[2], the reserve observation is true for B_2O_3.

We have synthesized a series of MBGs with different amounts of Al_2O_3 and B_2O_3 (0.5 – 15 mol-%) and investigated their influence on the mesostructre and textural properties with solid-state NMR, SEM, HRTEM and physisorption measurements. Moreover, we performed *in-vitro* bioactivity tests and ICP-OES measurements to correlate the formation of HCA with the changes in the glass structure.

Additionally, we performed nanoindentation measurements on the prepared glasses and we demonstrate that the incorporation of additional oxides can alter the mechanical properties of mesoporous bioactive glasses to make them more suitable for applications inbone tissue engineering .

Keywords: bioactive glasses, mesopores, solid-state NMR, bone tissue engineering, bioactivity, nanoindentation, mechanical properties, hydroxyapatite

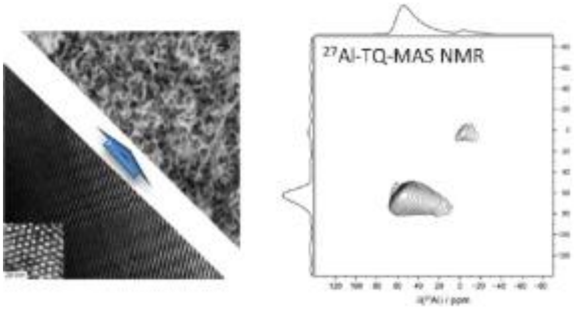

Figure 1: SEM image of Al_2O_3-doped MBG and ^{27}Al TQ-MAS NMR spectrum of Al_2O_3-doped MBG.[2]

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Tailoring of moisture management PLA fibers: Application of temperature and pH responsive nanogel

D. Štular,[1] B. Tomšič,[1,*] B. Simončič,[1] I. Jerman, [2] M. Mihelčič, [2]

[1] University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Textiles, Ljubljana, Slovenia
[2] National Institute of Chemistry, Ljubljana, Slovenia

Abstract:

Nanogel composed of (poly-NiPAAm) and chitosan (PNCS nanogel) exhibits both temperature and pH responsiveness, namely swelling when temperature and pH levels are below 32 °C and pH 6.5, and deswelling when temperature and pH level rises. Such properties make PNCS nanogel useful in various different applications. By applying PNCS nanogel to textile material, inteligent functional textile with moisture management properties can be tailored, since swelling of the nanogel restrain the moisture inside its structure and vice versa, allowing it to release into the sourroundings, when in shrunken state [1].

Poly(lactic acid) (PLA) is a biodegradable aliphatic polyester, produced from non-toxic renewable sources, such as fermentation of corn starch. Due to its renewability it is used in medicine and industry, replacing conventional polymers, based on petrol and chemicals [2]

This research aims to incorporate PNCS nanogel on to PLA fabric, in order to achieve pH and temperature responsiveness of the fabric with controlled thermoregulating abilities.

PNCS nanogel was synthesized by surfactant free dispersion copolymerization and applied to PLA fabric by pad-dry-cure procedure with 80 % wet pick-up (PLA_PNCS_N sample). Stimuli responsiveness was assessed by moisture content (*MC*) mesurements, where samples were preconditioned at 20- or 40 °C and 65 % R.H. for 24 hours, followed by drying of the samples to their constant weight at the temperature of 60 °C, i.e. bellow the glas transition temperature of PLA fibres. Untreated PLA fabric (UN_PLA sample) was used as control.

As depicted on figure 1, greater *MC* values were obtained for the treated sample, preconditioned at 20 °C, compared to UN_PLA sample. At this temperature PNCS nanogel was swollen, thus absorbing moisture from its environment. With the rise of preconditioning temperature to 40 °C, the hydrophobic character of poly-NiPAAm prevailed, thus PNCS nanogel shrunk and expelled water, reflecting in decreased moisture content values, compared to UN_PLA sample.

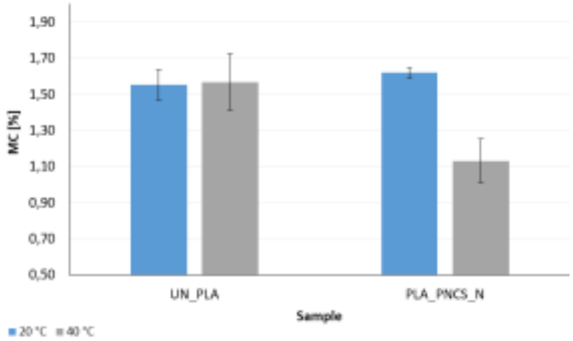

Figure 1: Moisture content (*MC*) of studied PLA samples, determined at 20 °C and 40 °C.

The results show, that by applying temperature and pH responsive PNCS nanogel to the PLA fibers, intelligent textile materials can be tailored, exhibiting controlled moisture management properties. Such textile composit can be used in medical applications for wound dressings, whereas nanogel can be exploit as a potential drug carrier.

Keywords: inteligent textiles, stimuli-responsive nanogel, poly-NiPAAm, chitosan, PLA fibers, thermoregulation.

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Immobilization of titania nanoparticle into mesoporous silicas

K. VIBULYASEAK* and M. OGAWA

School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology, 555, Payupnai, Wangchan, Rayong 21210, Thailand.

Abstract:

The hybridization of titania nanoparticles with porous silicas has been extensively investigated for the wide range of applications including those as photocatalyst. Periodic mesoporous silicas are promising scaffold to accommodate titania nanoparticles with controlled particle size due to the large BET surface area and narrow pore size distribution in the range of 2-10 nm. Titania nanoparticles supported in/on porous silicas are expected to show the improved catalytic performances if compared with un-supported titania nanoparticles due to the stability and the recyclability thanks to the supports. [1-2] In order to tune the performances more precisely, morphology, location and distribution of titania nanoparticles in/on the supports are important through the remaining nannospace design in addition to the nanoconfinement effects of the semiconductor particles.

Here, the immobilization of titania nanoparticles into the mespopore of SBA-15s (which have the BJH pore size of 5.5, 6.5 and 8.5 nm) was conducted.

SBA-15s were prepared by using a triblock copolymer (P123) as the template according to the reported method [3] and were used as support to accommodate titania nanoparticles. Titanium isopropoxide (TTIP) was used as the titania source and the reaction was conducted by simply mixing SBA-15 and TTIP at room temperature. Solid samples were characterized by nitrogen physisorption, X-ray fluorescence (XRF), inductively coupled plasma optical emission spectrometry (ICP-OES), UV-Vis absorption and Raman spectroscopies.

After the reaction of SBA-15 with TTIP, titania was immobilized in the mesopore of SBA-15 to give white powder. Nitrogen adsorption/desorption isotherms revealed the change in the porosity and the surface area of the SBA-15 by the immobilization of titania nanoparticles. The formation of titania nanoparticles and the crystallization to anatase during the heat treatment were confirmed by UV-visible absorption and Raman spectroscopies. The change in the nitrogen adsorption/desorption isotherms of a SBA-15 with the average pore size of 6.5 nm before and after the reaction with TTIP is shown in Figure 1. The BJH pore size decreased from 6.5 to 5 nm and the pore volume (derived from BET plot) was also decreased by the reaction with TTIP, indicating the successful immobilization of titania species in the mesopore. The thermal treatment of the sample to crystallize the titani nanoparticles in the mesopore was monitored by UV-Vis and Raman spectroscopies.

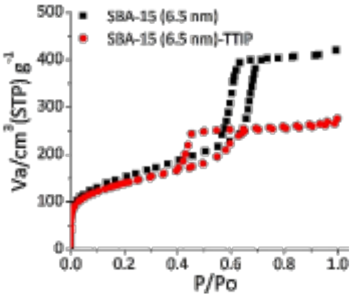

Figure 1: Nitrogen adsorption/desorp-tion isotherms of a SBA-15 before (black squares) and after (red circles) the reaction with TTIP.

Keywords: titania nanoparticle, photocatalyst, nanospace design, SBA-15

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Synthesis of new organic-inorganic hybrid - Physicochemical characterization and catalytic investigations

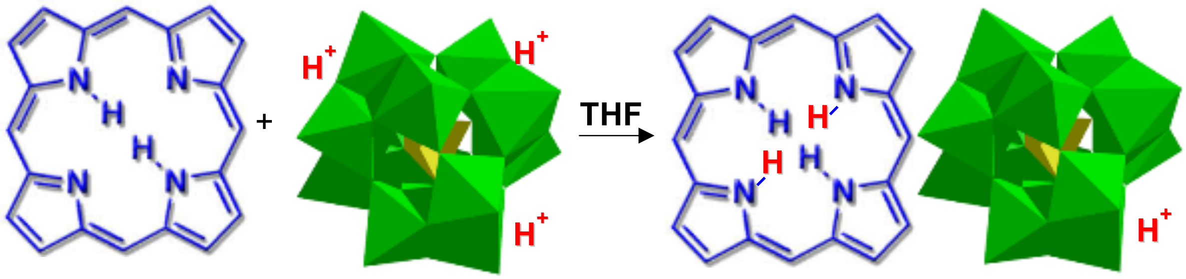
S. Dzwigaj,[1] K. Pamin,[2] J.Połtowicz,[2] S. Basąg,[3]

[1] Sorbonne Universités, UPMC, CNRS, UMR 7197, Laboratoire de Réactivité de Surface, Paris, France
[2] Jerzy Haber Institute of Catalysis and Surface Chemistry, PAS, Kraków, Poland
[3] Jagiellonian University, Department of Chemistry, Kraków, Poland

Abstract:
Through centuries people were fascinated with the possibilities of synthesis of new materials with extraordinary properties. New materials are practically needed in all domains of life and are often designed at the nano scale. Synthesis of organic-inorganic hybrids is one of the methods to obtain the new materials, usually with amazing properties [1]. Porphyrin ligands and heteropolyacids were selected as building blocks of new organic-inorganic hybrids. The properties of porphyrin ligands can be finely tuned by introduction of appropriate substituents that are necessary to achieve defined properties. Heteropolyacids were selected as inorganic building blocks because of their structural diversity and chemical composition variety. The aim of our study was the synthesis of new porphyrin-heteropolyacid hybrids by condensation of different porphyrin ligands with tungstophosphoric or molybdophosphoric acids.

The synthesis of new organic-inorganic hybrids was confirmed by different spectroscopic techniques like UV-Vis, FT-IR, ^{1}HNMR, differential scanning calorymetry DSC and cyclic voltammetry CV. The following organic-inorganic hybrids: mesityloporphyrin (TMP) and dichlorophenyl porphyrin (TDCPP) with tungstophosphoric or molybdophosphoric acids were synthesized and applied as catalysts in Baeyer-Villiger oxidation of cyclohexanone to ε-caprolactone with molecular oxygen. For the sake of comparison, the catalytic properties of parent heteropolyacids were also investigated.

Keywords: organic-inorganic hybrid, porphyrin-heteropolyacid hybrid, UV-Vis, NMR, FTIR spectroscopy, cyclic voltammetry, catalysis-oxidation processes, synergetic effects.



$H_3PW_{12}O_{40}$ + H_2TPP → $[H_4TPP^{2+}][HPW_{12}O_{40}^{2-}]$

Figure 1: Scheme illustrates the synthesis of the porphyrin ligand-heteropolyacid hybrid material. The essential step in the synthesis of new organic-inorganic hybrids is protonation of porphyrin ligand by reaction with heteropolyacid. As a result of this process two ions are formed: porphyrin cation and heteropoly anion. They are bound by electrostatic interactions forming organic-inorganic hybrid.

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Adsorption of indium ions from aqueous solution on layered silicates

N. Homhuan[1*] and M. Ogawa[2]

[1] School of Molecular science and engineering, Vidyasirimedhi Institute of Science and Technology,
Rayong, Thailand
[2] School of Energy science and engineering, Vidyasirimedhi Institute of Science and Technology,
Rayong, Thailand

Abstract:
The adsorption (ion exchange) of ions onto solids is a way for the concentration of toxic and noble ions from aqueous environments. In addition to the concentration of metal ions from environments, the adsorption was regarded as a way to prepare functional hybrids based on layered materials.[1-2] In the present study, the efficient concentration of indium(III) by the adsorption on layered silicates was investigated. Indium was selected as the target, because it is a rare and valuable element and is used in the wide range of applications. Na-magadiite (synthesized hydrothermally according to the previous publication[3]), a Na-montmorillonite (Kunipia-F purchased from Kunimine Industries Co., Ltd.) and a bentonite (obtained from Thai Nippon Chemical Co.) were used as the adsorbents in order to compare the adsorption capacity. The adsorption of indium onto the silicates were examined from the aqueous solution of indium chloride. The adsorption isotherms of In(III) for the layered silicates are shown in Figure 1. All the adsorption isotherms were classified as type H, which indicated the high affinity of In(III) and layered silicates. Na-magadiite adsorbed larger amount of In(III) than Kunipia-F and the bentonite. The maximum adsorbed amount of In(III) on magadiite was around 0.6 mmol/g silicate, which corresponded to the 90% of the ideal cation exchange capacity of magadite (2.2 meq/g silicate) derived from the chemical formula ($Na_2Si_{14}O_{29}$). The lamellar morphology of magadiite was preserved after the ion exchange with In(III), which was confirmed by SEM image in Figure 2. The reactions took only 10 minutes, which is an advantage for the practical application.

Keywords: Layered silicate, magadiite, ion-exchange, indium, adsorption isotherm, functional hybrids.

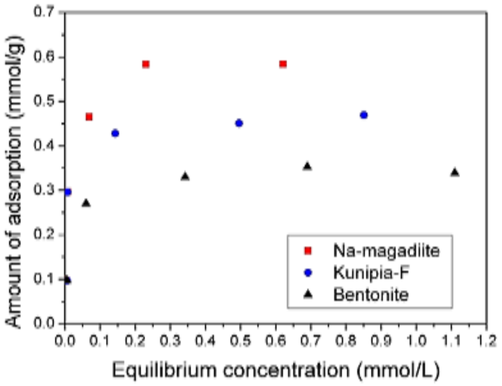

Figure 1: The adsorption isotherm of indium by Na-magadiite (red), Kunipia-F (blue) and a bentonite from Thai (black).

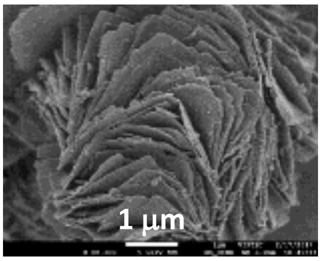

Figure 2: SEM image of In(III)-magadiite.

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New dielectric properties in the hybrid DMAPbX$_3$ (X=I and Br) perovskite

A. García-Fernández[1], J. M. Bermúdez-García[1], S. Castro-García[1], A. L. Llamas-Saiz[2], R. Artiaga[3], J. López-Beceiro[3], M. Sánchez-Andújar[1] and M. A. Señarís-Rodríguez[1]

[1] Grupo de Química Molecular e de Materiais, Centro de Investigacións Científicas Avanzadas (CICA), Departamento de Química Fundamental, Facultade de Ciencias, Universidade da Coruña, Campus de A Coruña, 15071 A Coruña, Spain.
[2] RIAIDT X-Ray Unit, University of Santiago de Compostela, 15782 Santiago de Compostela, Spain.
[3] Department of Industrial Engineering II, University of A Coruña. Campus Ferrol, 15403 Ferrol, Spain.

Abstract:

Along the half century, ABX$_3$ compounds with perovskite structure have been intensively and extensively studied in view of their structural richness and amazing variety of interesting functional properties, such ferroelectricity, ferromagnetism, magnetoresistance, superconductivity, multiferroicity, etc.[1] Traditionally, the studies on perovskite compounds have been focused on ceramic materials, mainly on transition metal oxides of general formula *ABX$_3$*, (A: alkali, alkaline earth, or lanthanide cations, B: transition metal cation, X: O).

Interestingly, in the last few years significant efforts have been devoted to the development of new members of the versatile family of the so-called perovskite-like organic-inorganic hybrid,[2] where the A- and/or X-site inorganic moieties of the conventional perovskites have been replaced by organic building blocks.

The organic-inorganic perovskites also display a structural richness and interesting functional properties, such as case of methylammonium lead triiodide perovskite, [CH$_3$NH$_3$]PbI$_3$, which is a very promising material for low cost and high efficiency photovoltaic applications[3] and the formate perovskite [(CH$_3$)$_2$NH$_2$][M(HCOO)$_3$] (with $M^{2+} = Mn^{2+}$, Co^{2+}, Ni^{2+} and Fe^{2+}), compounds which are specially interesting as type-I multiferroics.[4,5]

In this work, we have synthesized new organic-inorganic hybrid compounds of general formula DMAPbX$_3$, where DMA is the dimethylammonium cation and X are the I^- and Br^- anions. The crystal structure of these compounds have been elucidated by single crystal X-ray diffraction. Also, we studied the dielectric response of these compounds at different temperature (from 100 K to 350 K) and in the frequency range from 10 Hz up to 1 MHz. Very interestingly, these compounds display a dielectric anomaly and we have explained the origin of the dielectric response taking into account the crystal structure of these compounds.

Keywords: Hybrid materials, organic-inorganic perovskites, functional properties, dielectric materials.

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Evaporation of aromatic hydrocarbons from mesoporous silicas: Controlled release of aromatic hydrocarbons by the complexation with mesoporous silicas

W. REANTHONGLERT[1*], K. IMWISET[2], S. BUREEKAEW[1], R. YAZAWA[3] and M. OGAWA[1,3]

[1]School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology, 555, Payupnai, Wangchan, Rayong 21210, Thailand.
[2] School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology, 555, Payupnai, Wangchan, Rayong 21210, Thailland
[3]Graduate School of Creative Science and Engineering, Waseda University, Nishiwaseda 1-6-1, Shinjuku-ku, Tokyo 169-8050, Japan

Abstract:

The desorption (or release) of molecular species from solid is a phenomenon of interests from the viewpoints of environmental protection[1] and medication as shown by the importance of slow release formulation of pesticides/herbicides[2,3] and drug delivery[4], respectively. The interactions between releasing molecules (guest) and solid support (host) have been controlled in order to achieve desired release properties.

Slow (or controlled) release of various molecular species into aqueous phase has extensively been reported.[2-4] Release into gas phase is also of interests from the viewpoints of odor management in the house and parfume release. Here, we report the incorporation of naphthalene and paradichlorobenzene into mesoporous silicas and the release of them to the air to examine the positive effect of controlled release by the confinement of the molecules into nanospaces. The prepataion of mesoporous silicas and the host guest chemistry of the mesoporous silicas have been reported so far,[5] and the controlled release for the biomedical application has been reported[4].

The incorporation of aromatic molecules were conducted by solid-state reaction, where the solid components (mesoporous silica and paradichlorobenzene or mesoporous silica and naphthalene) were mixed together with an mortar and a pestle at room temperature. The successful incorporation of the aromatic molecues into the mesopore was confirmed by the powder X-ray diffraction and optical microscope observating, where the crystals of aromatic hydrocarbons disappeared after the solid-state reaction.

The desorption behavior of the occluded aromatic molecules were monitored by the weight change of the host-guest complexes (silica-aromatic molecule adducts). If compared with the pure aromatic molecules (crystalline states), the sublimation (or the desorption) of the aromatic molecules was successfully suppressed by the complexation with silicas. The effects of the pore size on the desorption behavior was also examined.

Keywords: Controlled release, Solid-state reaction, Host-guest chemistry, Mesoporous silica, Micro-encapsulation, Herbicides, Naphthalene, Paradichlorobenzene

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Bioinspired Multifunctional Surfaces for Lab-on-Chip Applications

A.S. Moita,[1*] A.L.N. Moreira[1]

[1] IN+, Instituto Superior Técnico, Universidade de Lisboa, Lisbon, Portugal

Abstract:

Bioinspired surfaces, particularly plant-inspired, have been extensively explored for many industrial applications, from (superhydrophobic) self-cleaning surfaces, to interfaces for heat transfer enhancement. For industrial purposes, cost-effective methods must be delivered, although durability of the devised surfaces must be assured, even in demanding working conditions. Within this scope, the present work addresses the development of multifunctional superhydrophobic biocompatible surfaces, bioinspired in the Lotus leaf, in the Rose petal and in the English weed. To replicate the particular topography of the surfaces, Koch's molding technique [1] was firstly explored, as it is a highly cost-effective method. Then, laser etching (FB20-1, New Industries, China) was used as an alternative method. Afterwards, different chemical coatings were tested. The surface topography was characterized using optical and SEM/EDS microscopy. A profile meter (Dektak from Veeco) with a vertical resolution of 20nm allowed quantifying the roughness profiles. Static and dynamic wettability was also characterized from the macro to the micro angles range, combining optical tensiometry with confocal microscopy. The surface chemical composition was examined by X-ray photoelectron spectroscopy (XPS, SPECS XR50). The devised surfaces were tested as interfaces for biosamples transport in lab-on-chip devices (to check on biocompatibility) and as interfaces for cooling applications (pool boiling heat transfer enhancement). The results show that a significant part of the surface hydrophobicity is indeed achieved by the surface topography, which is also an advantage for heat transfer applications, as pool boiling heat transfer coefficients could be improved up to 22% with the optimization of the bioinspired topography. However, for sample transport, (the samples are transported in microdroplets using electrostatic actuation), surface topography often induced contact line pinning, promoting energy dissipation. A similar effect was observed due to the adsorption of biocomponents on the surface, which altered the local wettability, thus limiting the control of droplet spreading and motion. In this context, the best performing surfaces were kept smooth and coated with Glaco®, i.e. perfluoroalkyltrichlorosilane combined with perfluoropolyether carboxylic acid and a fluorinated solvent, which minimized adsorption effects, improving droplet spreading (Figure 1) and mobility. This coating withstands high temperatures (higher than 200ºC) for continuous heating periods.

Keywords: bioinspired surfaces, biocompatible, multifunctional, micro-patterning, heat transfer enhancement, lab-on-chip applications.

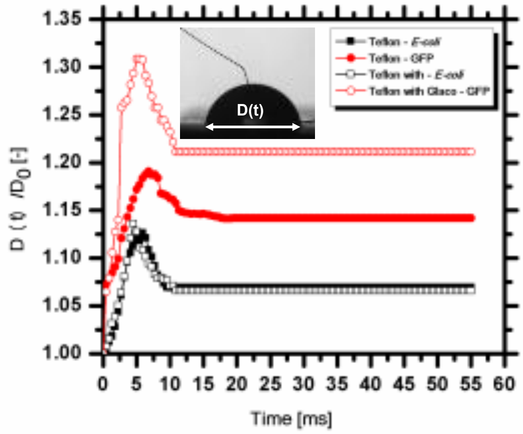

Figure 1: Effect of the chemical coating in increasing the spreading diameter during electrowetting of biosample droplets namely GFP (1.71x10^{-3}mM) and E-coli cell suspensions (1x10^9cells/mL).

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