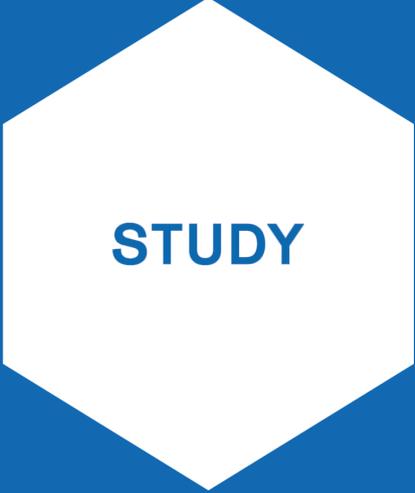


ABSTRACT BOOK

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STUDY

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Abstract Book

1. Henri Arola, 24
A novel immunoassay format for small analytes in a sensor application – HT-2 mycotoxin as an example
2. Rokhsareh Bakhtiari, Sabanci University
Fabrication of High Strength and Electrically Conducting Graphene Fibers via One-Step Wet Spinning Method
3. Antoine Bourrier, CNRS Grenoble
Bioactive brain interface with functionalized graphene nanoelectronics
4. Santiago Jose Cartamil-Bueno, TU Delft
Metrology of CVD Graphene Drumhead Sensors: Mechanical Characterization of Resonators and Self-Oscillators at Different Temperatures and Pressures
5. Alexandre Carvalho, University of Aveiro
Graphene Diamond Hybrid Films
6. André Jorge Carvalho Chaves
Anderson Localization of Light in Disordered Superlattices Containing Graphene Layers
7. Ngoc Do Quyen Chau, University of Strasbourg
Controlled covalent functionalization of graphene oxide: towards the development of an amino functionalized platform for complexation of nucleic acids
8. Alexander Epping, 2nd Institute of Physics A, RWTH Aachen University
Probing the nonlinear elasticity of 2D materials via nanoindentation experiments
9. Manfred Ersfeld, RWTH Aachen
Ultra-long electron and hole spin lifetimes in monolayer WSe₂
10. Sajjad Ghobadi, Sabanci University
Green Production of Carbon Fiber-reinforced Cellulose/Graphene/Polypyrrole Composite Papers for PEM Fuel Cell Electrode Fabrication
11. Zijun He, Monash University,
A Simplified Approach to Synthesize Elastic Graphene Aerogels
12. Dhifaf Jasim, University of Manchester
Tissue distribution and urinary excretion of intravenously administered graphene oxide: Effect on kidney structure and function
13. Pranoti Kshirsagar, NMI Natural and Medical Sciences Institute
Production of mono and bilayer graphene
14. Carlos Marquez, University of Granada
Correlation between critical parameters of laser reduced graphene oxide and its electrical properties
15. Christos Melios, National Physical Laboratory/University of Surrey
Effect of humidity on electronic properties of CVD graphene
16. Slavisa Milovanovic, University of Antwerp
Interplay between snake and quantum edge states in a graphene Hall bar with a pn-junction
17. Roman Mysyk, CIC Energigune
Thermally reduced graphene oxide for supercapacitors with high gravimetric power density
18. Marta Pedrosa, Faculdade de Engenharia, Universidade do Porto
Vacuum-assisted fabrication of graphene oxide membranes for water filtration
19. Martina Pittori, CNR National Research Council
CVD-graphene as support for lipid membranes for the fabrication of novel electrochemical biosensors
20. Thomas Saint-Paul, ONERA- SERVICE FORMATION
Ultra-sensitive detection of NO₂ by graphene gas sensors
21. Michael Schmitz, 2nd Institute of Physics 2A - RWTH AACHEN – University
High-quality monolayer and bilayer CVD graphene devices fabricated by a dry transfer method

22. Raman Singh, Monash University
Ultra-thin Graphene Coating for Remarkable Corrosion Resistance
23. Miika Soikkeli, 24
Programmable graphene biosensor
24. Chinmay Sonawane, Monash University
Functionalization of Graphene for sensing applications
25. Jens Sonntag, 2nd Institute of Physics A, RWTH Aachen University
Mechanically tunable strain fields in suspended graphene by micro electromechanical systems
26. Isabella Anna Vacchi, University of Strasbourg
Strategies for the selective chemical functionalization of graphene oxide
27. Julia F. M. Werra, Humboldt-Universität zu Berlin
Probing strained graphene through the dynamics of electric and magnetic emitters
28. Wei Yang, CNRS - LABORATOIRE PIERRE AIGRAIN
Current and Noise Saturation in Graphene Superlattice
29. Pei Yu, Monash University
Electrochemical production of graphene and its application in conductive nanocomposite for 3D printing
30. Ke Zhang, Monash University
Investigating the effect on electrolyte ions migrating process with thick densely packed graphene electrode and impact of graphene sheets directionality

A novel immunoassay format for small analytes in a sensor application – HT-2 mycotoxin as an example

Arola, H.¹, Tullila, A.¹, Campbell, K.² and Nevanen, T.¹

¹ VTT Technical Research Centre of Finland, Tietotie 2, FI-02150 Espoo, Finland

²Institute for Global Food Security, Queen's University Belfast, School of Biological Sciences, 8 Cloreen Park, Malone Road, Belfast, United Kingdom

We have developed a simple and fast one-step non-competitive immunoassay format for small analytes. The use of anti-immune complex antibodies increases both the sensitivity and selectivity of the immune complex assay when compared to the traditional competitive assays. The anti-immune complex antibodies can be applied to various immunoassays including ELISA, lateral flow assay and sensors.

There are diagnostic needs for a number of different kinds of small molecules. Those molecules include clinically relevant biomarkers e.g. hormones and metabolites, environmental toxins and pollutants, vitamins and drugs. Traditionally the fast diagnostics of these small analytes is carried out using ELISA or lateral flow immunoassays with poly- or monoclonal antibodies. These assays are based on indirect competitive detection which is sensitive to disturbances such as matrix effects.

For realizing a non-competitive immunoassay for small molecules we have developed a novel immunoassay format called immune complex assay that is based on recombinant antibody fragments. Recombinant antibodies offer advantages over the traditionally used poly- or monoclonal antibodies. Recombinant antibody fragments can be isolated *in vitro* from the antibody gene libraries and produced cost-efficiently in large scale in *E. coli* bacteria. Recombinant antibodies can also be further engineered to meet the requirements of a certain application e.g. by improving their affinity, specificity or stability. For biosensor applications, the recombinant antibody fragments offer a possibility for oriented immobilization through different tags (e.g. 6-Histidine tag, peptides) as well as a greater immobilization density due to their smaller size.

As an example, the performance of the immune complex sensor assay for HT-2 toxin is presented. The non-competitive immune complex assay was compared to the traditional competitive format using Biacore Q biosensor. The IC₅₀ values of the competition assay were 134 ng/ml for both HT-2 and T2- toxin. The corresponding EC₅₀ value of the non-competitive anti-immune complex assay was 10.5 ng/ml for HT-2 toxin making it 13-fold more sensitive than the conventional competitive assay. In addition, no detectable signal was measured for T-2 toxin showing that the new assay format is highly specific to HT-2 toxin only.

Fabrication of High Strength and Electrically Conducting Graphene Fibers via One-Step Wet Spinning Method

Rokhsareh Bakhtiari¹, Sajjad Ghobadi¹, Esmâ Nur Güllüoğlu², Elif Özden Yenigün², Selmiye Alkan Gürsel^{1,3}, Lale İşikel Şanlı³

¹ Faculty of Natural Science and Engineering, Sabanci University, 34956, Istanbul

² Istanbul Technical University, Faculty of Textile Technologies and Design, Department of Textile Engineering, 34947, Istanbul

³ Sabanci University Nanotechnology Research and Application Center (SUNUM), 34956, Sabanci University, Istanbul

Among carbon-based materials, graphene, as a 2-dimensional (2D) material with superior mechanical, thermal and electrical properties have drawn attention of numerous research groups during the past decades. Macro-scale, 3D structures produced from graphene have been proved to be promising for different applications with their significantly improved properties, among which, graphene fibers are very promising due to their ultra-high mechanical strength and electrical conductivity characteristics. Wet-spinning was reported as one of the most convenient methods for neat, and macroscopic graphene fiber preparation. During the process, different types of functionalized graphene derivative suspensions including different stabilizing agents had been used. Among the variety of suspensions, aqueous solution of graphene oxide (GO) was reported as an environment friendly material, cheap, and highly stable suspension of graphene derivatives suitable to produce graphene fiber. Based on the previous works, one of the key parameter for preparation of free standing graphene fibers, without any stabilizer or polymeric matrix assistance, through wet-spinning process is to reach a liquid crystal (LC) phase within the GO suspension. With regard to the liquid crystal fundamentals, alignment of GO particles in the suspension has led to the formation of a combination of aligned/isotropic mixture of GO nanosheets. This biphasic state is known as the nematic phase was required to obtain high-stiffness graphene fibers. Formation of such aligned LC structure was reported to occur at relatively high concentrations (> 10 mg/ml) of GO in water. Free-standing highly conductive graphene fibers were reported to be used for different applications such as renewable energy applications, e.g. fuel-cells and novel batteries, high-performance graphene reinforced nanocomposites.

In this study, GO nanosheets were prepared via a green process of oxidation inspired from modified Hummer's method, during which, production of NO_x gas bi-products were eliminated compared to conventional methods. By increasing the drying time of as-oxidized GO sheets at room temperature condition GO nanosheets with improved quality was obtained. GO aqueous LCs were then prepared by ultrasonic bath and probe dispersion of certain amounts of GO nanosheets in different solvents, e.g. *N*-dimethyl formamide (DMF), tetrahydrofuran (THF) and DI-water. Wet spinning process was conducted via trial of different coagulation bathes, as NaOH, KOH, and CaCl_2 . In order to improve mechanical and electrical properties, chemical reduction of GO fibers was conducted. Electrical conductivity, morphology, and mechanical properties of prepared fibers were studied via 4-point probe conductivity measurement, scanning electron microscopy, and universal testing machine analysis devices, respectively.

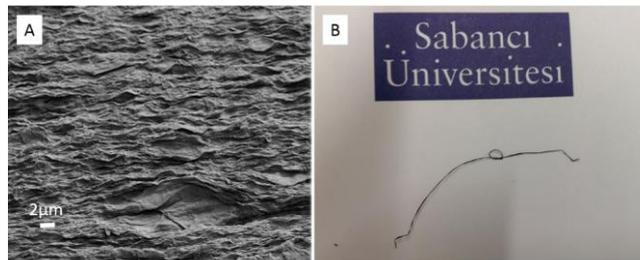


Figure 1: A) SEM image of GO fiber, B) Digital image of a tied GO fiber

Bioactive brain interface with functionalized graphene nano-electronics

A. Bourrier¹, A. Szarpak², F. Veliev¹, R. Auzely², C. Delacour¹ and V. Bouchiat¹

¹Institut Néel- CNRS, 38042 Grenoble, France

²CERMAV-CNRS, 38041 Grenoble, France

High spatial resolution sampling of brain activity using direct implants of variable nature is a key technology in brain research projects like neuro-regenerative applications. However, the current metal electrodes array based technologies present inconsistent performance in chronic signal recording [1]. The lifetime of these implants being limited both by their bio-acceptance and by the sensitivity of their electronics. This lack of reliability might be overcome thanks to a new neuronal sensing platform based on copper CVD grown monolayer graphene that is wet transferred on our future implants substrates [2]. Once RIE patterned, graphene biocompatible, soft, and chemically inert nature offers novel perspectives as biosensors [3]. The presence of readily accessible surface charges gives the unprecedented opportunity to realize a strong electrical coupling with cells. Our aim is to fabricate and test a family of implants supporting graphene neural sensors (Fig. 1a) and showing good biocompatibility, sensitivity and time stability. To this end, we functionalized our devices with a customized natural biocompatible polymer: Hyaluronic Acid (HA) (Fig. 1b). Functionalization with HA offers corrosion surface protection, decreases the graphene hydrophobicity (Fig. 1c) and improves the stability of sensors, leading to a better interaction with neurons. This opens tremendous possibilities for a new generation of bioactive graphene sensors for neural interface as much as it offers a friction protection during the surgical implantation.

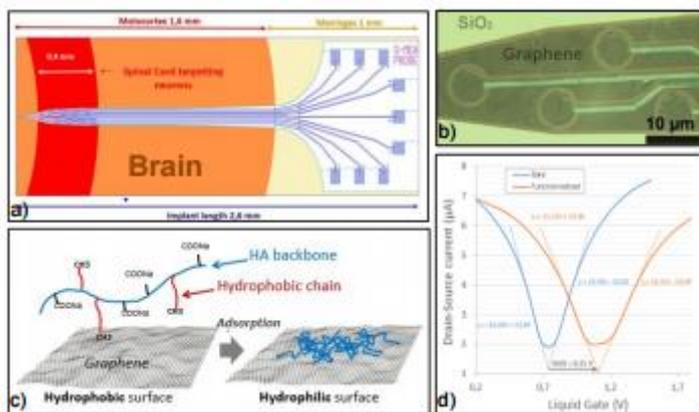


Fig. 1. a) Rat Motor cortex probe design b) Micro-fabricated probe supporting RIE patterned and gold contacted graphene sensors c) Alkylated Hyaluronic Acid (HA) graphene adsorption mechanism d) Graphene FET trans-conductance before and after HA adsorption.

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Metrology of CVD Graphene Drumhead Sensors: Mechanical Characterization of Resonators and Self-Oscillators at Different Temperatures and Pressures

Santiago J. Cartamil-Bueno¹, Alba Centeno², Dejan Davidovikj¹, Samer Houry¹, Herre S. J. van der Zant¹, Amaia Zurutuza², Peter G. Steeneken¹

¹*Kavli Institute of Nanoscience, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft (The Netherlands)*, ²*Graphenea SA, Avenida de Tolosa, 76 20018 - Donostia/San Sebastián (Spain)*

Graphene is impermeable to gas molecules and has a very low bending rigidity [1-2]. As a consequence, a small gas pressure difference across a suspended graphene membrane will cause a large deflection that is easily detectable. Graphene pressure sensors and microphones are therefore anticipated to deliver ultimate performance and sensitivity [3-4]. However, for high-volume manufacturing of sensors, these devices need to be made with a high yield and reliable properties. Determination and understanding of the material quality and fabrication processes that lead to variations in tension and Young's modulus in the devices are of utmost importance, and necessary to reduce the property deviations. However, despite the large scientific research on individual mechanical sensors [5], there are only few reports that study the yield and parameter variations on large numbers of devices [6].

Chemical vapor deposition (CVD) is the most promising route for growing large-area single-layer graphene [7]. In the Graphene Flagship (WP7&WP11), we make large arrays of CVD graphene drums for pressure sensing applications and study their properties over large numbers of devices. The devices are successfully fabricated by transfer of CVD graphene layer/s on a substrate with holes of varying sizes. We developed an automatized method to measure and analyze hundreds of devices from the same chip systematically, and we can set the devices at different temperatures and pressures. Two techniques are employed: atomic force microscopy (AFM) [5], and laser interferometry [8]. We measure the mechanical properties of each device (resonant frequency, Young's modulus, pre-tension), and analyze the statistical device parameter variations. Thus we study the impact of the fabrication process on the uniformity of the device properties and evaluate the feasibility of large scale manufacturing of graphene membrane based sensors.

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Graphene Diamond Hybrid Films

A.F. Carvalho¹, A.J.S. Fernandes¹, Júnior, G. L.², J. Borme², P. Alpuim^{2,3}, F.M. Costa¹

¹*Dept. of Physics and I3N, University of Aveiro, 3810-193 Aveiro Portugal*

³*INL-International Iberian Nanotechnology Laboratory, Braga, Portugal*

²*Dept. of Physics, University of Minho, Braga, Portugal*

The increasing interest in graphene as a material for electronics arises mainly from its outstanding transport properties. However, the lack of a non-null band-gap hinders the application of graphene as a material for logical switching electronics [1]. Theoretical reports have predicted that this problem can be addressed with the right combination of interface materials, namely other carbon allotropes [2]. In this framework, our group developed a method for the simultaneous synthesis by Microwave Plasma Chemical Vapor Deposition (MPCVD) of a hybrid structure composed by few-layer graphene and dome-like nano-crystalline diamond (NCD) clusters [3]. The material was morphologically and structurally characterized by Raman Spectroscopy, SEM and TEM. GFET's were produced using this material as the active layer, exhibiting some interesting preliminary results, with transfer curves compatible with a band-gap opening.

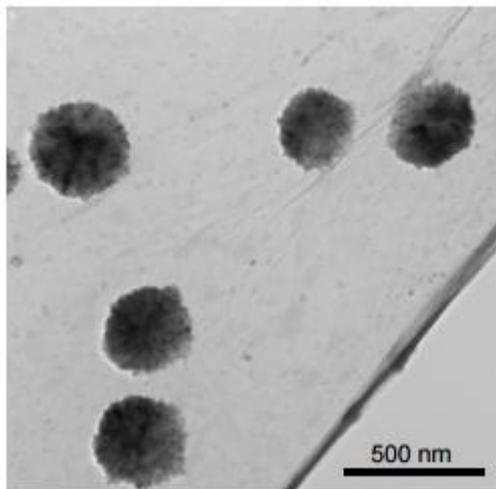


Fig. 1. NCD domes wrapped by few-layer graphene films as observed in TEM

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Anderson Localization of Light in Disordered Superlattices Containing Graphene Layers

A. J. Chaves¹, N. M. R. Peres¹ and F. A. Pinheiro ²

¹*Department of Physics and Center of Physics, University of Minho, P-4710-057, Braga, Portugal,* ²*Instituto de Física, Universidade Federal do Rio de Janeiro, Rio de Janeiro-RJ, 21941-972, Brazil.*

We theoretically investigate light propagation and Anderson localization in one-dimensional disordered superlattices composed of dielectric stacks with graphene sheets in between - [1]. Disorder is introduced either on graphene material parameters or on the widths of the dielectric stacks. We derive an analytic expression for the localization length and compare it to numerical simulations using transfer matrix (TM) technique; a very good agreement is found.

References

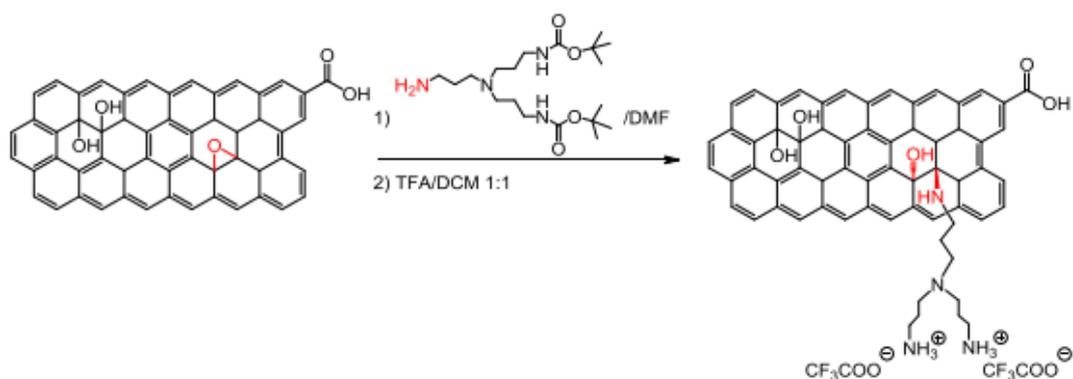
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Controlled covalent functionalization of graphene oxide: towards the development of an amino functionalized platform for complexation of nucleic acids

Ngoc Do Quyen Chau¹, Cécilia Ménard-Moyon¹, Alberto Bianco¹

¹CNRS, Institut de Biologie Moléculaire et Cellulaire, Laboratoire d'Immunopathologie et Chimie Thérapeutique, 67000 Strasbourg, France

Graphene oxide (GO), the oxidized form of graphene, has shown great potential biomedical applications, especially in drug and gene delivery. [1] Indeed, the polar oxygen-containing functional groups of GO, such as epoxide rings, carboxyl and hydroxyl groups, render it highly hydrophilic, leading to a good dispersibility in water and many other solvents. [2] The main goal of our research is to covalently functionalize GO with ammonium groups. This approach will allow to develop a novel platform complexing biologically active molecules for gene delivery study, especially for silencing specific genes using small interference RNA (siRNA). In this work, we focused on the design, synthesis and investigation of chemically functionalized GO (f-GO), following its conjugation with different dendrons bearing positive charges, to better complex siRNA. One of the first attempts was the epoxide ring opening reaction on GO to introduce different amine derivatives bearing positive charges at their termini (Scheme 1). The f-GO were characterized by complementary analytical techniques such as X-ray photoelectron spectroscopy, thermogravimetric analysis, FT-IR spectroscopy, Raman spectroscopy, zeta potential, and transmission electron microscopy. Furthermore, the ability to interact of each f-GO with siRNA was also investigated by means of agarose gel electrophoresis.



Scheme 1: GO epoxide ring opening reaction with a multiamine derivative.

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Probing the nonlinear elasticity of 2D materials via nanoindentation experiments

A. Epping^{1,2}, G. J. Verbiest^{1,2}, C. Backhaus^{1,2}, J. Sonntag^{1,2}, T. Khodkov^{1,2}, M. Goldsche^{1,2} and C. Stampfer^{1,2}

¹JARA-FIT and 2nd Institute of Physics, RWTH Aachen University, 52074 Aachen, Germany

²Peter Grünberg Institute (PGI-9), Forschungszentrum Jülich, 52425 Jülich, Germany

The Young's modulus of 2D materials, which characterizes the sensitivity to mechanical deformations, is usually determined from indentation experiments with an atomic force microscope (Fig. 1a). In these experiments, the sharp tip of a cantilever is pushed into a suspended 2D membrane while measuring the deflection of the cantilever and the indentation depth. We show by both experiments and simulations, that the generally accepted model [1] cannot fully describe these experiments, as the effective Young's modulus (E^{2D}_{eff}) is not constant during the measurement but crucially depends on the induced strain. To account for the induced strain, we perform a full non-linear simulation (Fig. 1b) and compare it with our measurements to extract E^{2D}_{eff} as a function of strain for various 2D materials and membrane thicknesses. For monolayer graphene membranes we observe an increase of E^{2D}_{eff} which is in agreement with recent theoretical [2] and experimental [3] work. In contrast, for bilayer graphene and few-layer graphene, the E^{2D}_{eff} decreases with increasing strain, which can be understood as a softening of the carbon-carbon bonds [4]. A similar behavior is seen for other 2D materials like WSe_2 or MoS_2 .

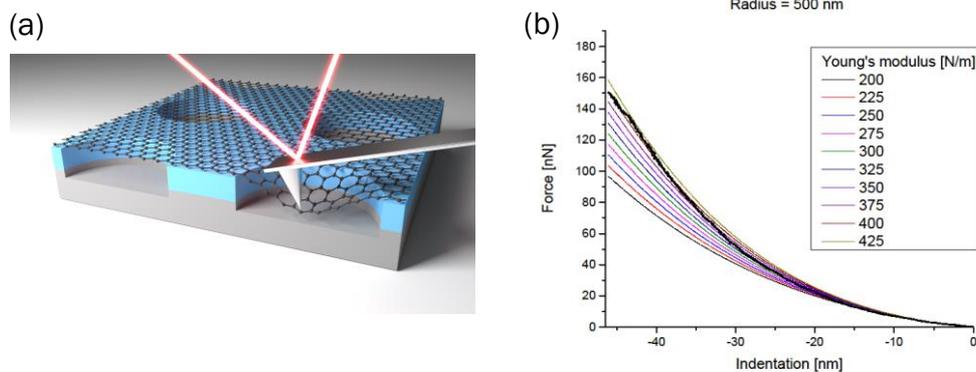


Fig. 1. (a) Illustration of the experiment. (b) Simulated force-indentation curves of a circular monolayer graphene membrane with radius $r = 0.5 \mu\text{m}$ for different Young's moduli between 200 to 425 N/m and the corresponding experimental data. With increasing indentation depth the experimental data intersects with simulations for increasing Young's modulus.

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Ultra-long electron and hole spin lifetimes in monolayer WSe₂

Sammy Pissinger¹, Christopher Franzen¹, Manfred Ersfeld¹, Sebastian Kuhlen¹, Christoph Stampfer¹ and Bernd Beschoten¹

¹2nd Institute of Physics and JARA-FIT, RWTH Aachen University, Germany

There is strong interest in optical generation and detection of valley spin polarizations in transition metal dichalcogenides. We report on time-resolved two color pump probe Kerr rotation measurements on mechanically exfoliated monolayer WSe₂ crystals. We find electron and hole spin lifetimes of up to 100 ns at low temperatures. These values are in good agreement with exciton lifetimes extracted from all-optical time-resolved reflectivity indicating that the spin lifetimes are limited by exciton recombination times in our crystals. Electron spin precession in Voigt geometry furthermore reveals inhomogeneous spin dephasing caused by a large spread in the local g factors.

Green Production of Carbon Fiber-reinforced Cellulose/Graphene/Polypyrrole Composite Papers for PEM Fuel Cell Electrode Fabrication

Sajjad Ghobadi¹, Rokhsareh Bakhtiari¹, Selmiye Alkan Gürsel^{1,2}, Lale Işikel Şanlı²

¹ Faculty of Natural Science and Engineering, Sabanci University, 34956 Istanbul

² Sabanci University Nanotechnology Research and Application Center (SUNUM), Sabanci University, 34956, Istanbul

Recently graphene-based nanocomposites have been widely used as the crucial components of green and renewable energy production systems such as batteries and fuel cells. Polymer electrolyte membrane (PEM) fuel cell is very promising due to its pollution free by products that are heat and water. PEM fuel cell electrodes consist of two main layers as gas diffusion layer (GDL) and catalyst layer (CL). GDL mainly is carbon woven cloth, felt or fiber based paper. CL which consists of platinum (Pt) electrocatalyst supported by carbon nanoparticles and Nafion® ionomer is formed onto the GDL. Today, the most used GDL layer is the carbon paper since carbon paper provides higher porosity for oxygen transport while preventing the water accumulation that results in higher lower oxygen concentration on the CL. In the tradition of the carbon paper fabrication, it is necessary to have carbonization and graphitization processes that require high temperatures (up to 2500 °C) and toxic phenolic resins as binder. Among the reported methods to overcome the mentioned issues, paper wet-laying was shown to be more eco-friendly, easy to handle, and cost effective in comparison with conventional approaches.

During this process, aqueous slurry of chopped carbon fiber (CF)/cellulose microfibers (cell) was prepared by vigorous mixing, followed by paper preparation via a commercial paper wet-laying device. Following the air-spraying of the graphene nanoplatelets (GNP) dispersion on the prepared papers to improve the electrical conductivity, the insulating cell binder was removed via phase inversion process using an ionic liquid solution, providing an electrically conducting substrate.

Finally vapor polymerization of pyrrole monomer in presence of hydrochloric acid fume in a vacuumed environment was conducted on the papers, resulting in formation of an interpenetrated network of polypyrrole (PPy) and CF/GNP papers. The effect of total mass and polymerization time on the morphological, mechanical, and electrical conductivity properties of samples was studied via scanning electron microscopy, universal testing machine, and 4-point probe conductivity analysis devices, respectively. By using this method, the preparation cost and production of hazardous byproducts were minimized and a robust conducting composite layer was formed that can be used for fuel cell applications.

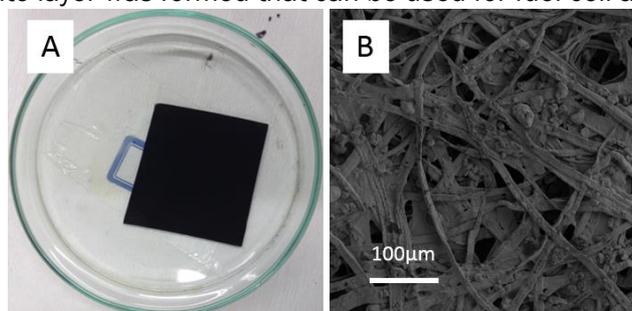


Figure 2 A) Digital image of the prepared papers, B) SEM image of the composite fibers

A Simplified Approach to Synthesize Elastic Graphene Aerogels

Zijun He¹, Ling Qiu², Dan Li¹

^{1, 2}*Department of Materials Engineering, Monash University, Clayton Campus, Clayton, Victoria 3800, Australia.*

Graphene is a wonder material with a range of amazing properties, which has attracted great attention in various application areas. Many applications proposed for graphene require multiple sheets to be assembled into a macroscopically usable structure. Nevertheless, significant restacking is inevitable when assembling two dimensional (2D) graphene sheets into one dimensional (1D) fibers or 2D papers/membranes, resulting in graphite-like structure and poor accessibility of individual graphene sheet. Three dimensional (3D) graphene aerogels/hydrogels provide possible solution for this matter. However, due to poor control of assembly behavior, in the reported 3D graphene structures are found to be dense and brittle. To realize the practical potential of graphene, synthesizing 3D graphene monolith with well-organized structure and good mechanical properties is desirable. Herein, we show that the marriage of graphene chemistry with ice physics can lead to formation of superelastic and ultralight (down to 0.5 mg cm⁻³, even lower than half of the density of air) graphene-based aerogels. Mimicking the hierarchical structure of natural cork, the resulting materials can sustain their structural integrity even under a load of over 50000 times of their own weight and can rapidly recover from >80% compression. The unique biomimetic hierarchical structure also provides this new class of elastomers with exceptionally high energy absorption capability and good electrical conductivity. The successful synthesis of such fascinating materials paves the way to explore the properties and applications of graphene in a self-supporting, structurally adaptive and 3D macroscopic form. However, large cracks or even structure failure could occur when graphene-based aerogels are subjected to multi-cycles or extremely large deformation. Thus, many potential applications for graphene-based aerogel are limited. We found that complex synthesis method is the main reason for introducing structural defects and further leads to the poor mechanical performance of graphene aerogel. Here, we have developed a simplified method to synthesize superelastic graphene aerogel with less defects and much improved mechanical properties.

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Tissue distribution and urinary excretion of intravenously administered graphene oxide: Effect on kidney structure and function

Dhifaf Jasim^{1,2}, Cécilia Ménard-Moyon³, Stephanie Murphy⁴, Rachel Lennon^{4,5}, Alberto Bianco³, Kostas Kostarelos^{1,2}

¹*Nanomedicine Laboratory AV Hill Building, Faculty of Medical and Human Sciences, University of Manchester, Manchester, UK.*

²*National Graphene Institute, University of Manchester, Manchester, UK.*

³*CNRS, Institut de Biologie Moléculaire et Cellulaire, Laboratoire d'Immunopathologie et Chimie Thérapeutique, 67000 Strasbourg, France.*

⁴*Institute of Human Development, Faculty of Medical and Human Sciences, University of Manchester, Manchester, UK.*

⁵*Department of Paediatric Nephrology, Royal Manchester Children's Hospital, Manchester, UK.*

Graphene oxide (GO) has a great potential for use in biomedicine, however, understanding how this novel 2D material interacts with biological milieu is fundamental for its development. In this study GO was administered intravenously in C57BL/6 mice. Extensive urinary excretion was one of the main biological end-fates of this material, suggesting an interaction with the kidney glomerular filtration barrier (GFB) [1]. Therefore, an immense analysis of the kidney function, histopathology and ultrastructure was carried out. Both serum and urine analyses revealed no impairment of kidney function up to one month after injection of GO at doses up to 10 mg/kg. Histological examinations suggested no damage to glomerular and tubular regions of the kidneys. Ultrastructural analysis by transition electron microscopy (TEM) showed the absence of any damage, with no change in podocyte slit, endothelial fenestra sizes or glomerular basement membrane width. This suggests that these rather large GO sheets with sizes that exceed several times the GFB cut-off (<40 nm) were excreted, by structural re-modelling of the thin and flexible GO sheets. The study provides a better understanding of how the unique 2D material (GO) interact with the kidney and shows that GO has great potential for various biomedical applications, such as diagnostic imaging and drug-delivery systems.

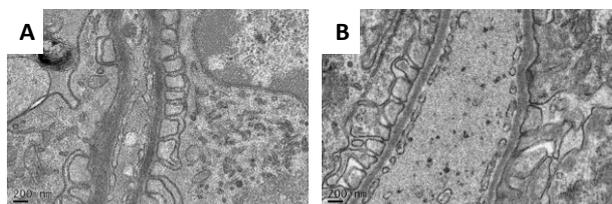


Fig. 1. Transmission electron microscopy images of kidney glomeruli. (A) Dextrose (control) and (B) Graphene oxide injected mice.

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Production of mono and bilayer graphene

Pranoti Kshirsagar, Patrick Herlinger, Jurgen Smet

*Max Planck Institute for Solid State Research, Heisenbergstraße 1, 70569
Stuttgart, Germany*

Twisted bilayer graphene is a material of great interest due to its electronic structure varying with small twist angles. Selective growth of single crystalline areas is one of the main challenges in graphene research. This contribution reports reliable growth of mono and twisted bilayered graphene structures based on chemical vapour deposition (CVD). The quality of layered graphene grown by decomposition of methane on copper can be altered by changing the flow rates of gases, degree of dilution of the precursor methane, pretreatment of catalyst surface, temperature and time of growth. Annealing conditions play an important role in providing the nucleating sites for growth of hexagonal graphene. Combination of methane flow rate and time governs the dimensions of the grown layers.

Correlation between critical parameters of laser reduced graphene oxide and its electrical properties

C. Marquez, N. Rodriguez, R.J. Ruiz, F. Gamiz

Nanoelectronic Laboratory, CITIC-UGR, University of Granada, Granada, Spain
 carlosmg@ugr.es

Abstract

Nowadays reduced Graphene Oxide (rGO) is presented as a graphene flavor with increasing interest in the field of flexible electronics [1]. This work explores the electrical characteristics and perspectives of rGO produced through laser-assisted reduction of GO (Figure 1) [2]. This method has many advantages over its counterparts, i.e. cheap, repeatable, easy to implement in mass production... but its distinctive characteristic is the possibility to produce, without any mask, large high-quality rGO patterns with micrometer resolution [2]. The precise control of the photothermal power, laser excursion speed, and the initial concentration of the GO dispersion (Figure 2) has allowed the decrease of the sheet resistivity from the typical $k\Omega/\text{sq}$ range down to $250\Omega/\text{sq}$, even breaking the values extracted from large polycrystalline CVD-graphene samples (Figure 3) [3]. A broad set of electrical results based on the standardization of non-destructive point-contact characterization methods for the bare materials will be presented. These results cover the conduction mechanisms and the correlation between electrical noise spectral density and the rGO quality. We will disclose the path for the optimization based on the selection of the critical reduction parameters, focusing the discussion on flexible conductive structures.

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Figures

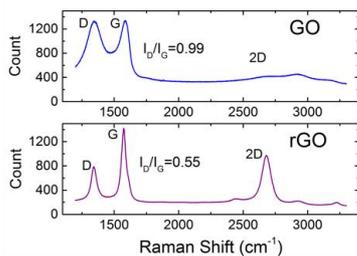


Figure 1. Raman spectra of GO (top) and reduced GO (bottom) Both Raman spectra were registered with a low power (4.7mW) 532.04nm laser line.

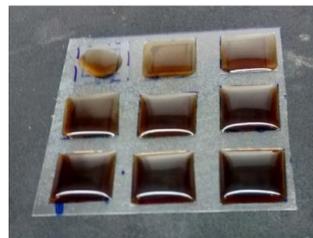


Figure 2. Sample with nine $1\text{cm}\times 1\text{cm}$ squares with increasing surface concentration of GO dispersion from $30\mu\text{L}/\text{cm}^2$ up to $180\mu\text{L}/\text{cm}^2$, before the laser reduction.

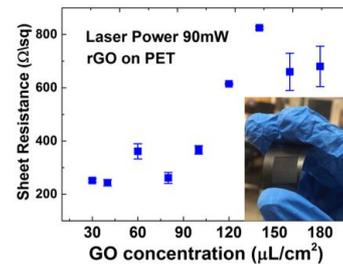


Figure 3. Sheet resistance of rGO on PET substrate extracted from four-point contact measurements as a function of the initial dispersion concentration for 80mW laser power.

Effect of humidity on electronic properties of CVD graphene

Christos Melios^{1,2}, Vishal Panchal¹, Cristina Giusca¹, Amaia Zurutuza³, Alba Centeno³, S. Ravi P. Silva² and Olga Kazakova¹

¹National Physical Laboratory, Hampton Road, Teddington, TW11 0LW, UK,

²Advanced Technology Institute, University of Surrey, Guildford, Surrey, GU2 7XH, UK

³Graphenea SA, 20018 Donostia-San Sebastián, Spain

The two-dimensional nature of graphene makes it sensitive to environmental doping. With water vapour being a significant component of the ambient air, graphene-based devices designed to operate in ambient air (e.g. sensors) will be significantly affected, as their electronic properties will change with humidity. For the successful commercialisation of graphene-based devices, the complete understanding of the water-graphene interactions is necessary. In this work, we employ local Kelvin probe force microscopy (KPFM) and global transport measurements in the van der Pauw geometry to observe the effects of water vapour on the surface potential and carrier concentration of chemical vapour deposition (CVD) grown graphene of different thicknesses transferred on SiO₂, polyethylene terephthalate (PET) and quartz. The study of the local surface potential is directly correlated to the electronic properties of graphene, such as work function (Φ) and environmental doping. We probe the local electronic properties of mono- and bilayer graphene (LG) in a series of measurements in controlled environments, starting from ambient, to vacuum, pure nitrogen and 20-60% relative humidity (R.H.), by simultaneously measuring the surface potential and carrier concentration. In ambient conditions (Fig. 1a), the CVD graphene exhibits p-type conduction (nh). One example for 1LG graphene on SiO₂ is shown in Fig. 1: $n_h = 1.05 \times 10^{13} \text{ cm}^{-2}$, $\Phi_{1LG} = 5.08 \text{ eV}$, whereas for 2LG islands $\Phi_{2LG} = 5.03 \text{ eV}$. When the environment is changed from ambient to vacuum (Fig. 1b), the hole concentration and work function decrease significantly (Fig. 1g). This is attributed to successful desorption of water and other p-dopants present in ambient air. Introduction of nitrogen and water vapour mixture with a gradual change of humidity from 20 to 60% RH results in an increase of the hole concentration (Fig. 1g), however the value saturates at ~40% and does not restore to ambient levels. This suggests that water vapour is not the most effective p-dopant in the ambient air that affects graphene. The measurements were repeated on a bi-layer graphene sample, obtained by a double transfer of two individual mono-layers. The electrical measurements exhibit similar behaviour with the 1LG. Raman measurements revealed that the bi-layer graphene sample is a nonAB stacked and electrically decoupled from the bottom layer, a finding that supports the electrical measurements. Thus, we demonstrate the influence of humidity on the electronic properties of CVD graphene, using surface potential (work function) and carrier concentration measurements on a variety of substrates.

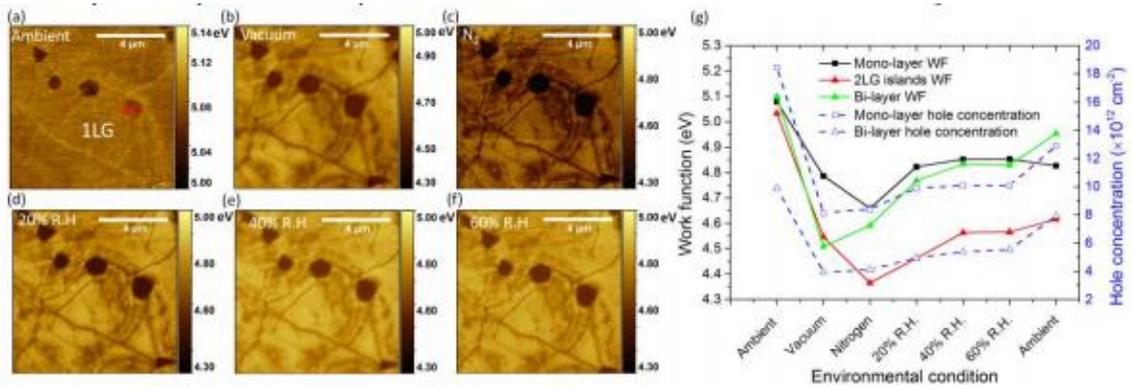


Fig. 1.: (a-f) Work function maps (scale bars are 4 μm) of the of 1LG graphene on SiO₂ showing 1LG coverage, with and 2LG nucleation islands. Each map corresponds to a specific environmental condition: ambient, vacuum, dry N₂, 20% R.H., 40% R.H., 60% R.H. (g) Environmental measurements of work function and global hole concentration mono (1LG)-/bi-layer graphene on SiO₂.

Interplay between snake and quantum edge states in a graphene Hall bar with a pn-junction

S. P. Milovanovic¹, M. R. Masir^{1,2}, and F. M. Peeters¹

¹*Department of Physics, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium*

²*Department of Physics, University of Texas at Austin, 2515 Speedway, C1600 Austin, TX 78712 - 1192*

Snake states in graphene appear in the presence of a pn-junction and a perpendicular magnetic field that were observed experimentally [1]. We investigate the influence of quantum effects on this classical phenomena. The magneto- and Hall resistance of a locally gated cross shaped graphene Hall bar was calculated in the quantum regime. The edge of the top gate is placed diagonally across the center of the Hall cross. Four-probe resistance was calculated using the Landauer-Büttiker formalism, while the transmission coefficients are obtained using the Kwant package [2]. Simulations showed that the position of the peaks in the resistance are in disagreement with the ones predicted for the snake states by classical simulations [3] (see Fig. 1(a)). We show that these peaks are a consequence of the interference between snake states that were injected from edge channels. The interplay between transport due to edge channels and snake states is further investigated. When two edge channels are occupied we predict oscillations in the Hall and the bend resistance as function of the magnetic field (see Fig. 1(b)). The effect of disorder on the oscillations observed in the resistance are also investigated. We examine cases of edge disorder as well as random vacancies.

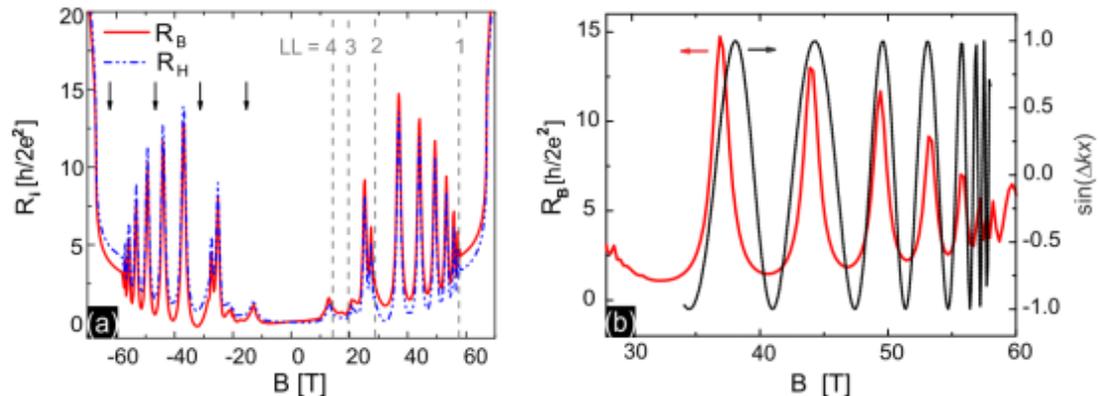


Fig. 1. (a) Resistances R_B and R_H versus the applied magnetic field. The arrows indicate the position of the resistance peaks due to the snake states as obtained from a semiclassical calculation. (b) R_B and $\sin(\Delta kx)$ for $\Delta k = k_1 - k_0$ and $x = L_{pn}$, where k_n is the wave vector of the n -th edge state and L_{pn} is the length of the pn-interface.

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Thermally reduced graphene oxide for supercapacitors with high gravimetric power density

C.Botas, D. Carriazo, N.Diez, T.Rojo, R.Mysyk
CIC Energigune, Parque Tecnológico de Álava, Miñano- Spain

State-of-the-art supercapacitors are based on microporous carbons and present inherent limitations in power delivery due to the distributed resistance of microporous networks. Alternatively, non-microporous materials do not feature high specific surface area (SSA) and cannot compete with microporous carbons in terms of deliverable energy density. This is specifically the case for reduced graphene oxides (GO), usually presenting extremely low SSA and low capacitance and energy. In this work, we fine-tuned the conditions of thermal reduction for graphene oxides so as to increase capacitance values and approach state-of-the-art materials in terms of capacitance and energy density. At the same time, reduced GO materials provide much lower resistance and are able to withstand much higher current densities than microporous carbons, thus providing the gravimetric power density of up to 75 kW/kg, significantly exceeding the typical value of 10kW/kg. Importantly, as distinct from high surface area graphene-based materials, the developed synthetic methodology does not involve harsh post-treatment conditions and can be easily implemented into mass production.

Vacuum-assisted fabrication of graphene oxide membranes for water filtration

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

Laboratory of Catalysis and Materials – Associate Laboratory LSRE-LCM, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.

Graphene oxide (GO) membranes have shown distinctive properties for gas and vapour separation [1] as well as for water treatment, particularly since the work published by Nair *et al.* in 2012 [2]. In the present work, membranes were fabricated by vacuum filtration of GO dispersions prepared by Brodie (B-GO) and Hummers (H-GO) methods (Fig. 1), using different substrates (cellulose acetate or Anodisc). Some of these membranes were speckled with an aluminium solution, as described elsewhere [3].

The characterization of the prepared materials was accomplished by thermogravimetric analysis (TG), temperature programmed desorption (TPD), attenuated total reflectance Fourier transform infrared spectroscopy (ATR - FTIR) and scanning electron microscopy (SEM), as well as contact angle, water uptake and porosity determinations. Dead-end filtration experiments were performed in continuous mode to assess the retention of ibuprofen (IBF). B-GO membrane speckled with aluminium revealed higher stability and IBF retention percentage, among the other tested membranes.

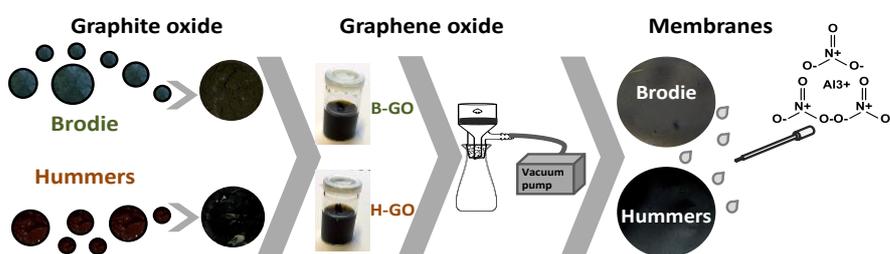


Fig. 1. Schematic representation of the fabrication of GO membranes.

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CVD-graphene as support for lipid membranes for the fabrication of novel electrochemical biosensors

M. Pittori^{1,2}, L. Ortolani¹, D. Gentili³, V. Morandi¹, R. Rizzoli¹, M. G. Santonicola²

¹*Institute for Microelectronics and Microsystems (IMM) Section of Bologna, National Research Council (CNR), Bologna, Italy*

²*Department of Chemical Materials and Environmental Engineering, Sapienza University of Rome, Rome, Italy,*

³*Institute for Nanostructured Materials (ISMN) Section of Bologna, National Research Council (CNR), Bologna, Italy*

In our work we investigate the development of a novel electrochemical biosensor using graphene as transducer and electroactive membrane proteins embedded in supported lipid membranes as biological recognition elements. Graphene is used as transducer because of its unique and intriguing properties, namely high surface area, electrical conductivity, ultra high electron mobility, wide electrochemical potential window, low charge-transfer resistance, and reduction of overvoltage [1-2]. In particular, this study is focused on the synthesis of graphene through chemical vapor deposition (CVD), on the surface treatments of graphene through a mild oxidation – to improve its biocompatibility – and on a first investigation of its interaction with liposomes, where membrane proteins are generally integrated for immobilization onto surfaces [3]. The obtained films of graphene were characterized using scanning electron microscopy (SEM) imaging, Raman spectroscopy and measuring the water contact angles (WCAs) before and after surface treatments. The graphene samples resulted to be mono- to few-layer, as can be seen in Fig. 1 (a) and (b); in addition, the values of WCAs decreased after surface treatments, in agreement with a progressive oxidation of the surface. Next, the interaction of the graphene surfaces with liposomes of 1,2-dioleoyl-sn-glicerol-3-phosphocholine lipids was investigated via electrochemical impedance spectroscopy. Results indicated the formation of a stable insulating lipid layer on the graphene surface after incubation with the liposomes.

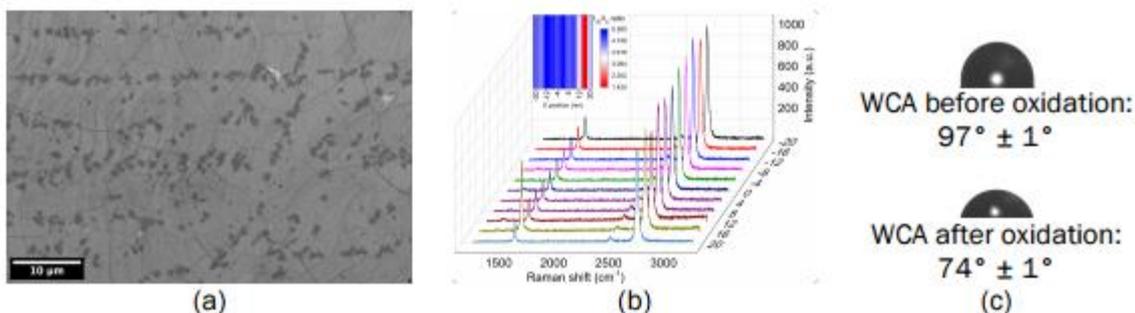


Fig. 1. (a) SEM image of transferred graphene; (b) Raman spectra and the corresponding Raman map (inset) of the ratio between the 2D and G peak intensities; (c) Mean values of the WCAs before and after surface treatments.

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Ultra-sensitive detection of NO₂ by graphene gas sensors

Thomas Saint-Paul¹, Brigitte Trétout¹, Nelly Dorval¹, Olivier Le Traon¹, Annick Loiseau², Pierre Lavenus¹

¹Physics and Instrumentation Department, ONERA – The French Aerospace Lab

²Laboratoire d'Etudes des Microstructures (LEM), UMR 104 ONERA-CNRS

Graphene is a very promising material for gas sensing applications. Indeed, it combines a two-dimensional geometry that maximizes the interaction between the carbon atoms and the gas molecules and a low noise level; those two properties could yield very low detection limits [1]. The molecules adsorbed on the graphene sheet have a doping effect [2] that modifies its conductivity and allows the detection to be performed with simple electrical measurements.

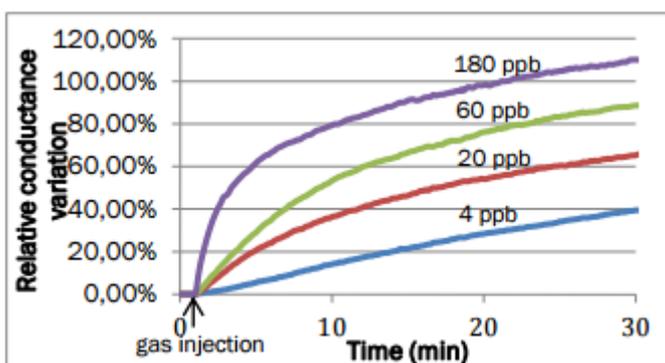


Fig. 1. Relative variation of the device conductance over time for several concentrations of nitrogen dioxide.

In this work, we investigate the properties of gas sensors fabricated from CVD-grown graphene by photolithography. The time dependence of the device conductance was measured at atmospheric pressure for NO₂ concentrations ranging from 1 ppb to 200 ppb as illustrated in Figure 1. It can be noticed that the sensor response for such low concentrations does not reach a stationary level within half an hour, meaning that the equilibrium between the graphene and the gas phase is not established within this span of time. This implies that in operating conditions the concentration cannot simply be deduced from the instantaneous conductance value by using a calibration curve. Instead, a thorough understanding of the kinetics is needed. The sensor kinetics is first analysed using a Langmuir model describing simple adsorption/desorption of the gas molecules on the graphene sheet. At low concentrations, a good agreement is found between the model and the experimental data, as confirmed by temperature-dependent measurements. However, discrepancies observed at higher concentrations indicate the presence of a more complex mechanism such as adsorption on different types of surface sites, diffusion of the molecules at the graphene/substrate interface or chemical reaction on the surface (e.g. dimerization of NO₂).

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High-quality monolayer and bilayer CVD graphene devices fabricated by a dry transfer method

M. Schmitz¹, L. Banszerus¹, S. Engels^{1,2}, K. Watanabe³, T. Taniguchi³, B. Beschoten² and C. Stampfer^{1,2}

¹ JARA-FIT and ²nd Institute of Physics, RWTH Aachen University, 52074 Aachen, Germany, ² Peter Grünberg Institute (PGI-9), Forschungszentrum Jülich, 52425 Jülich, Germany, ³National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan

We recently introduced a dry transfer method for single-layer graphene grown by chemical vapor deposition (CVD) on reusable copper foil yielding ultra-high quality graphene comparable to the best exfoliated graphene flakes [1]. Using this transfer method we were recently able to achieve ballistic transport over more than 28 μm in our graphene encapsulated in hexagonal boron nitride (hBN). This corresponds to carrier mobilities of up to around three million $\text{cm}^2/(\text{Vs})$ and was probed measuring the bend resistance in cross- and square-shaped devices [2]. Furthermore, we demonstrate that the transfer method can be extended to CVD grown bilayer graphene. Bilayer CVD graphene/hBN heterostructures can indeed be fabricated using the very same transfer method. Raman measurements reveal a high structural quality [3]. We achieve carrier mobilities of up to 45,000 $\text{cm}^2/(\text{Vs})$ at 1.8 K and up to 17,000 $\text{cm}^2/(\text{Vs})$ at room temperature outperforming all state-of-the-art CVD bilayer graphene devices. Finally we show dual-gated transport measurements to investigate band-gap opening in our CVD grown bilayer graphene.

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Ultra-thin Graphene Coating for Remarkable Corrosion Resistance

Raman Singh, Monash University

A monolayer or a few atomic layer thick graphene coatings on metals have been shown to improve their corrosion resistance by nearly orders of magnitude. Though there are very few studies reported on the topic of corrosion resistance due to graphene coating, there is still considerable variability in the degree of improvement. For example, improvement in aqueous corrosion resistance of copper due to graphene coating is reported to vary from insignificant to nearly 2 orders of magnitude [1-4], whereas the improvement for nickel can be in excess of an order of magnitude. This presentation will review the most recent research on graphene that has been claimed as 'the thinnest known corrosion-protecting coating', and potential application of such disruptive approach to corrosion resistance of common engineering alloys, such as mild steels.

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Programmable graphene biosensor

Miika Soikkeli¹, Katri Kurppa¹, Markku Kainlauri¹, Sanna Arpiainen¹, Arja Paananen¹, David Gunnarsson¹, Jussi J. Joensuu¹, Päivi Laaksonen¹, Mika Prunnila¹, Markus B. Linder^{1,2}, Jouni Ahopelto¹

¹VTT Technical Research Centre of Finland, P.O. Box 1000, FI-02044 VTT, Espoo, Finland

²Aalto University, School of Chemical Technology, P.O. Box 6100, FI-00076 AALTO, Espoo, Finland

Most of the biomolecules carry net charge detectable with a charge sensitive detector. Here we have used graphene field effect transistors (GFET) as charge detectors. The 2-dimensional nature and the non-linear characteristics near the Dirac point provide very high charge sensitivity. The main difficulty is immobilization of the receptors and achieving selectivity towards the target analyte. Hydrophobins are small proteins with a hydrophobic patch facilitating formation of well-ordered monolayers on hydrophobic surfaces and, consequently, providing means to immobilize receptors [1]. Hydrophobins can be genetically engineered to create receptor modules specific to various analytes, and the fusion proteins form a dense monolayer on the hydrophobic graphene channel [2]. The biosensor is schematically shown in Fig. 1. The programming follows from the property of the hydrophobins to form a well-oriented monolayer on graphene. The concept has been tested with several receptor-analyte pairs. In Fig. 2 is shown the response to a leucine-zipper pairs. The response is fast and the sensor can detect concentrations down to fM range.

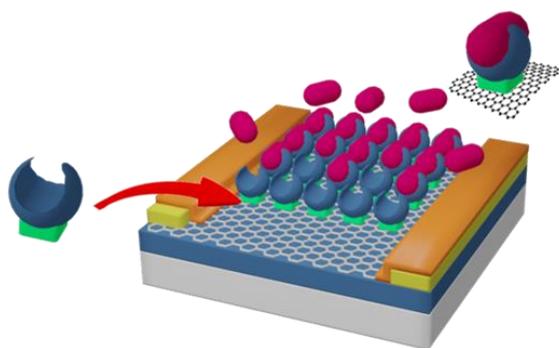


Fig. 1. Graphene bioFET shown schematically.

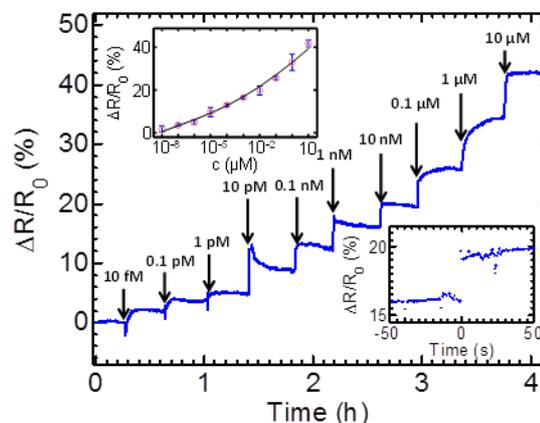


Fig. 2. Response of the sensor using a leucine-zipper Z_E - Z_R model receptor-analyte system.

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Functionalization of Graphene for sensing applications

Chinmay Sonawane¹, Raman Singh², Santosh Panjikar³

^{1,2}*Monash University, Australia*

³*Australian Synchrotron*

Graphene possesses great potential as high sensitivity sensors because it has remarkably high electronic conductivity which can be manipulated by chemical functionalization. Graphene can be suitably functionalized for specific sensing (for example, with a suitable protein) and the functionalization is to be immobilized on graphene. Research into functionalization and immobilization necessitates use of specialised and sensitive techniques, such as interrogation of proteins using synchrotron radiation.

In a research which has been initiated by the applicant, graphene oxide exfoliates will be produced by the modified Hummer's method, which will be incorporated with different functional groups and then immobilized. Functionalised graphene will be investigated using several techniques including synchrotron radiation.

Mechanically tunable strain fields in suspended graphene by micro electromechanical systems

Jens Sonntag^{1,2}, Matthias Goldsche^{1,2}, Timofiy Khodkov^{1,2}, Gerard Verbiest¹, Sven Reichardt^{1,3}, Nils von den Driesch², Dan Buca², Stefan Trellenkamp², Christoph Stampfer^{1,2}

¹ JARA-FIT and 2nd Institute of Physics, RWTH Aachen University

² Peter Grünberg Institute, Forschungszentrum Jülich

³ Physics and Materials Science Research Unit, Université du Luxembourg

As graphene is only one atom thick, it is highly susceptible to external influences, leading e.g. to a crystal lattice that is easily distorted. These distortions, or strain variations, can induce pseudomagnetic fields, which allow for pseudospin flips that, in turn, limit the mobility in high-quality graphene devices [1]. This shows the importance of understanding the electromechanical coupling of graphene. Thus, a precise control over strain fields in graphene is high up on the wish list of experimentalists.

Here, we demonstrate the realization of controllable strain fields in suspended graphene by coupling it to Si-based electrostatic micro-actuators. An actuator can theoretically apply more than 10% of strain and can operate at cryogenic temperature, allowing the investigation of quantum effects in electromechanical systems.

By means of Raman spectroscopy we characterize various strain distributions (max. 0.5% strain) in graphene. The Raman analysis confirms the accurate tuning of applied strain by the actuators independent of doping effects. This precise control over strain distributions opens up a wide field of possible experiments, ranging from strain dependent transport to strain induced pseudomagnetic fields.

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Strategies for the selective chemical functionalization of graphene oxide

Isabella Anna Vacchi¹, Jésus Raya², Cécilia Ménard-Moyon¹, Alberto Bianco¹

¹CNRS, Institut de Biologie Moléculaire et Cellulaire, Laboratoire d'Immunopathologie et Chimie Thérapeutique, 67000 Strasbourg, France,
²Membrane Biophysics and NMR, Institute of Chemistry, UMR 7177, University of Strasbourg, 67000 Strasbourg, France

The general objective of our research is the chemical investigation of graphene oxide (GO) and its reactivity via covalent functionalization reactions. GO contains different types of functional groups including hydroxyl, epoxy, carbonyl (Fig. 1).[1,2] However, the chemical composition of GO has not been fully elucidated yet and strongly depends on the synthetic procedure to obtain this type of material. Moreover, due to the complexity of GO chemical structure, much work remains to be done in developing reliable characterization methods that will aid to obtain an unambiguous structural identification as well as synthetic procedures that lead to relatively uniform products. Investigating the composition of GO is essential to control the functionalization for future applications of this material.

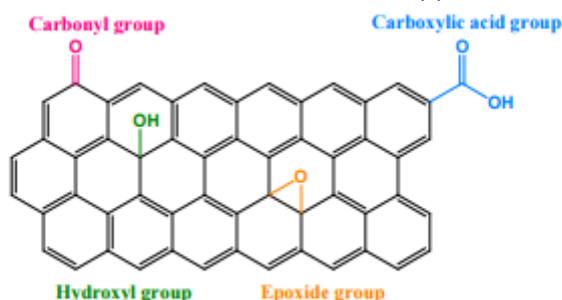


Fig. 1. Schematic and simplified representation of a graphene oxide sheet.

For this purpose we have chosen a series of selective reactions for the different GO oxygencontaining functions. We performed several reactions such as an etherification reaction (Williamson reaction) on the hydroxyl groups, the amidation and esterification reaction on the carboxylic acid groups and the ring opening of the epoxides with a primary amine derivative. Once the modified surface of GO is characterized, the intent is to develop multifunctionalization strategies. We analyzed the samples by FT-IR spectroscopy, thermogravimetric analysis, Raman spectroscopy, XPS, Kaiser test and solid state magic angle spinning (MAS) NMR spectroscopy. Due to the high reactivity of the oxygenated moieties, several derivatization reactions may occur concomitantly. For this reason a thorough investigation with control reactions was also performed.

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Probing strained graphene through the dynamics of electric and magnetic emitters

Julia F.M. Werra¹, Francesco Intravaia², Kurt Busch^{1,2}

¹*Humboldt-Universität zu Berlin, Institut für Physik, AG Theoretische Optik & Photonik, Berlin, Germany,* ²*Max Born Institute, Berlin, Germany*

Strain in graphene – as induced by a lattice constant mismatch when deposited on a substrate or by actual mechanical stress – can significantly modify the physical properties of graphene, e.g., by creating a gap in the bandstructure of an otherwise gapless system. As a consequence, graphene's optical properties are strongly affected with multiple implications in all optical and quantum-optical setups which make or will make use of this material.

If emitters such as NV-centers in nano-diamonds, quantum dots, or trapped atoms are located near graphene, the bandgap influences their dynamics. As a consequence, these emitters may be utilized as very precise sensors for investigating the electronic properties of graphene as well as other unconventional features such as the existence of TE-polarized plasmon-like resonances.

We have investigated in detail the lifetime of an emitter placed in the vicinity of a graphene sheet. By dissecting the resulting effects, we have analyzed the role played by TE-plasmons and the electronic bandgap. Our results are relevant in particular for atom-chip setups and, in general, for all quantum technologies based on hybrid atom-field condensed-matter systems.

Current and Noise Saturation in Graphene Superlattice

Wei Yang¹, Xiaobo Lu², Simon Berthou¹, Quentin Wilmart¹, Mohamed Boukhicha¹,
Christophe Voisin¹, Guangyu Zhang², & Bernard Placais¹

¹ *Laboratoire Pierre Aigrain, Ecole Normale Supérieure-PSL Research University, CNRS, Université Pierre et Marie Curie-Sorbonne Universités, Université Paris Diderot-Sorbonne Paris Cité, 24 rue Lhomond, 75231 Paris Cedex 05, France.*

² *Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China.*

Abstract: Graphene superlattice has attracted many research interests¹⁻⁴. Here we present a study of high electric field performance of graphene superlattice obtained from epitaxial approach⁴. By using microwave cavity, noise produced from graphene by joule heating is recorded up to 5GHz. Current and noise saturation are observed and investigated. Depending on Fermi energy, saturation can be attributed to intrinsic optical or remote surface polar phonon scattering at a doping far away from DP, while no saturation are found around DP. Moreover, noise saturation is identified around Fermi energy between DP and SDP, which can be attributed to the influence of van Hove singularity arising from the superlattice. Lastly, saturation due to the bias induced shift of DP, or so called Dirac fermion pinch-off, is well observed by local top gate technique.

References

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Electrochemical production of graphene and its application in conductive nanocomposite for 3D printing

Pei Yu¹

¹*Department of Materials Science and Engineering, Monash University, Clayton, VIC 3800, Australia*

Various graphene production methods have been developed since its discovery. Mechanical exfoliation, molecular assembly, CVD and SiC methods are not suitable for mass production due to relatively high cost.[1] Chemical exfoliation approaches such as modified Hummers method can produce graphene oxide in bulk scale. However, harsh oxidizing agents are required in the production process. Also, the graphene reduced from graphene oxide contains a large amount of oxygen functional groups and defects.[2] The electrochemical approach is another promising way for mass production of graphene.[3] It has many advantages: single-step, easy to operate, environmentally friendly, and operates at ambient conditions.[2] The research my group focused on is developing a proprietary electrochemical method to produce graphene in an industrial scale. The electrochemically-derived graphene oxide (EGO) has less oxygen functional groups and defects than graphene oxide (GO) derived from modified Hummers method. With the same degree of reduction, EGO also shows higher electrical conductivity than GO. With higher purity and better electrical conductivities, EGO can replace GO to be processed into conductive nanocomposites by blending with polymer. With subsequent extrusion, EGO-polymer filament is produced with concurrent thermal reduction of EGO. Then the filament can be printed into conductive microstructures through 3D printing, which may be suitable for biological applications. The process is illustrated in Fig. 1.

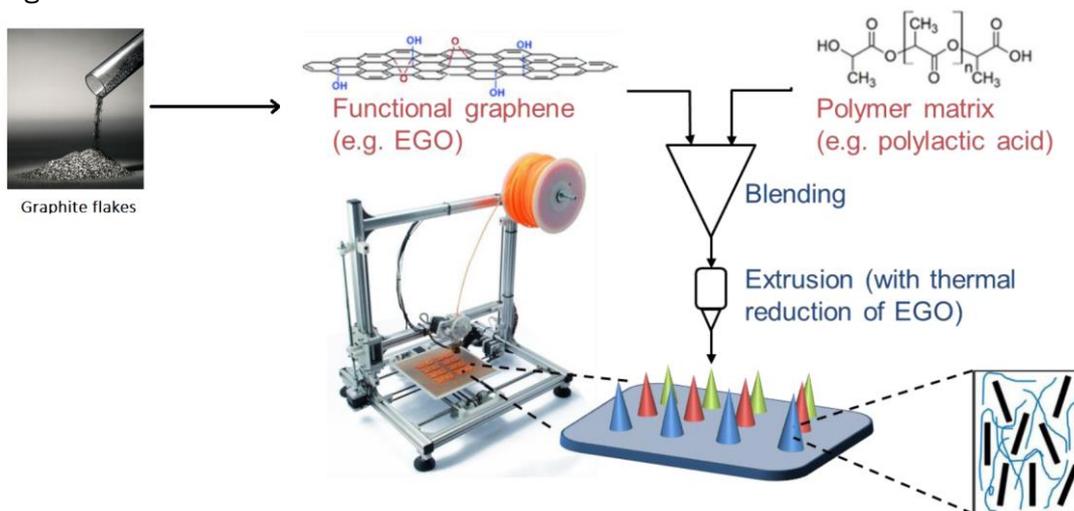


Fig. 1. Illustration of fabrication process from EGO to 3D-printed conductive microstructure.

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Investigating the effect on electrolyte ions migrating process with thick densely packed graphene electrode and impact of graphene sheets directionality

Ke Zhang^{a,b}, Dan Li^{a,b*}

^aDepartment of Materials science and Engineering, Monash University, Clayton, VIC 3800 Australia

^bMonash Centre for Atomically Thin Materials, Monash University, Clayton, VIC 3800 Australia

Abstract

Thin film graphene based supercapacitor have achieved reasonable energy storage density in recent years that benefits from its fast ions transport and high surface area. However, the device level energy storage density would be sacrificed by thin film active material when considering the weight of current collector. Moreover, improving the thickness of graphene electrode would lead to significant decay in the energy storage density of the electrode which is essentially related to ions transport ability in graphene network. To understand this contradictive process, the community requires further understanding in the ions dynamics of charging/discharging process for thick films which could be different with ions transport in thin films and molecular simulation of ultrathin films. In this work, we utilize our reduced graphene oxide (r-GO) membrane system by stacking different layer of graphene hydrogel and controlling their pore size to study the ions transport behaviour in thick films using electrochemical impedance spectroscopy (EIS). We identified the specific capacitance decays with increased thickness and decreased average pore size. With preliminary results, we suspect the decay might closely relates to the heterogeneous charging/discharging process in r-GO electrode. Also, the contribution of horizontal ions transport from the edge to the centre of the electrode might also play important role for ions transportation in addition to vertically ions transport for thick electrode. Therefore, proper edge structure of graphene electrode and directionality of graphene sheets could promote the ions transport in thick electrode.

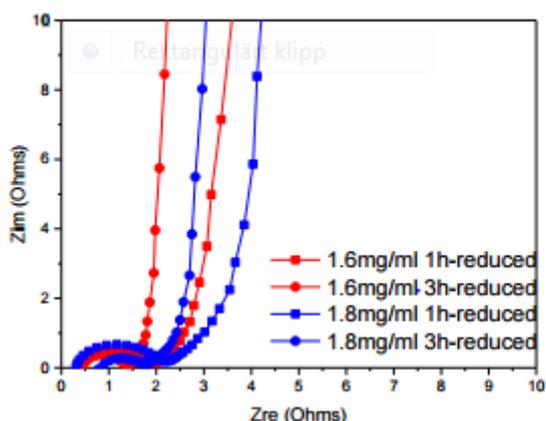


Figure 1 Nyquist plot for r-GO electrode with different reduction time and directionality

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Elena Novoselova, Head of Dissemination
elena.novoselova@chalmers.se

Helene Nilsson, Event Manager
helene@meetagain.se

Karin Weijdegard, Communication Manager
karin.weijdegard@chalmers.se

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