

# Graphene Flagship EU-Korea Workshop Graphene and related 2D materials

Natural History Museum – Geological Museum, Copenhagen, Denmark 15-16 August 2016

# **Workshop Report**



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**Overview** 

The scope of the second EU-Korea workshop, which was held in Copenhagen during Aug 15-16, 2016, was to exchange experiences, practices and ideas related to the current and emerging topics associated with the basic chemistry approach, materials synthesis, application development and commercialisation of graphene and related 2D materials (GRM). In addition, the workshop participants discussed further opportunities for collaborative research between Europe and Korea. This workshop is a follow up of the first EU-Korea workshop held in Busan (Republic of Korea) in August 9-14 2015. The meeting was jointly prepared and co-chaired by Korean and European researchers.

Workshop chairs: Prof. Jari Kinaret (Sweden) and Prof. Hyeonsik Cheong (Republic of Korea) Program chairs: Prof. Xinliang Feng (Germany), Prof. Paolo Samori (France), Prof. Hyeon Suk Shin (Republic of Korea) and Prof. Hyun-Jong Chung (Republic of Korea)

The workshop gathered 27 participants (10 from Korea and 17 from Europe), coming from both of academic institutions and industrial companies. Speakers gave 24 talks that have shown the breadth of activities and topics covered by their respective research groups. The selection of the scientific speakers/participants was done by the two groups of organizers. All presentations stimulated questions and discussions. The programme was organised around 8 thematic sessions:

- Session 1: EU and Korea Graphene Activities
- Session 2: Chemistry and Synthesis 1
- Session 3: Chemistry and Synthesis 2
- Session 4: Chemistry and Energy related applications
- Session 5: Chemistry and Biomedical related applications
- Session 6: Optoelectronics 1
- Session 7: Optoelectronics 2
- Session 8: Production and Industrial Perspectives

The workshop was opened by Prof. Feng who set the scene and introduced the overall goals for the meeting. Prof. Kinaret presented the latest status of the Graphene Flagship and informed about the availability of mobility grants for young research involved in the Graphene flagship to support research stays overseas (including in Korea). He also mentioned that the possibility of supporting collaborative research projects between Graphene Flagship and international groups is currently being explored. Prof. Cheong, President of the Korean Graphene Society<sup>1</sup>, provided an overview of GRM research activities and funding in Korea and highlighted that the currently the interest is broadening from graphene to other 2D materials synthesis and device applications (touch panels, barrier films, EM shielding, organic LEDs, anti-corrosion coatings, etc.).

Most Graphene Flagship work-packages (WPs Enabling Materials, Polymer Composites, Sensors, Functional Foams & Coatings, Flexible Electronics, Energy Storage, Energy Generation, Health and Environment, Production, Management, Dissemination, Alignment) and leading Korean institutions active in GRM research were represented at the meeting which offered a unique opportunity for direct exchanges and development of new collaborations.

<sup>&</sup>lt;sup>1</sup> <u>http://www.koreagraphene.kr</u>

# Common challenges and opportunities for collaboration

# Open scientific questions

In the final discussion session, participants identified several topics and areas of common strength and interest that include graphene and related materials (GRM) chemistry, materials synthesis, functionalisation, processing and device engineering. The main open questions that were presented and discussed were:

# How to develop new chemical functionalization methodologies for graphene? Whether the chemistry can be better controlled or selective for the functionalization of other 2D materials?

While the functionalisation of GRM offers a wide range of opportunities in particular for the development of (biological and chemical) sensors, an open issue remains how the functionalisation of GRMs alters or even compromises graphene's properties. Systematic and controlled studies of functionalised graphene and graphene-based derivatives are therefore needed. New synthetic/functionalization strategies for graphene and 2D materials remain to be further developed. This has not been well addressed so far and offers a vast potential for exploration. An interdisciplinary approach is needed to address these questions and should involve chemists who design synthesis methods and physicists and engineers that are focused on materials properties for a specific application.

A related issue is the stability and contamination of the functionalised GRMs and the evolution of the surface depending on ambient, storage and conservation conditions. Specific and new chemical characterisation methodologies are needed since traditional techniques such as Raman and NMR do not always offer answers. In particular, electrochemical properties of ad-ons, the degree of the functionalisation, the role of impurities and adsorbates, bond formation and surface wettability (is graphene hydrophobic or hydrophilic?) should be investigated further.

Chemical functionalisation can also impact the (bio)degradability profile of GRMs. The assessment of the influence of functional groups on the stability and degradation of GRMs could orient the design of new materials and composites. These aspects are not studied yet and need some attention.

# How to use bottom-up techniques to fabricate 2D materials? Polymer science, organic chemistry and bioscience can give important contributions.

Bottom-up approaches based on (organic/polymer) chemistry synthesis seem very promising. However, the production of large-area 2d materials from solutions remains a challenge. Both liquid and solid-based fabrication techniques require control of parameters that determine the degree of order, formation of networks and self-assembly. Controlled 2D polymerisation is a challenge on solid surfaces and even more so in solution. In particular, it is very difficult to achieve layer-by-layer growth on liquid surfaces. Thus an alternative approach that has been used is to grow bulk 2D layers and then exfoliate them. This results in grain sizes of the order of  $\mu$ m, which is sufficient for some applications, but is difficult to up-scale. Other promising new approaches include the growth of sp<sup>3</sup> carbon or other novel 2D carbon nanostructures on different surfaces and CVD which has recently been demonstrated for the growth of various 2D materials.

# What are the key challenges to develop CVD growth of single-crystalline graphene, boron nitride and other 2D materials in large size? How to control grain boundaries?

The growth of large crystal size of graphene and other 2D materials for device applications remains to be addressed. While the growth of single 2D materials (such as BN) has been demonstrated, the growth of heterostructures of different materials represents a big challenge. The main issue is the in-situ nucleation and growth initiation of different layers. So far, in most cases, in-plane phase segregation is observed. Some progress has been achieved in growing lateral heterostructures. Significant efforts are still needed to find appropriate substrates and well defined growth surfaces for the growth of heterostructures.

# How can graphene and graphene oxide be produced on large-scale? What are the current challenges for graphene production?

Currently, a variety of techniques based on solution exfoliation, powder, CVD, and gas phase methods are being developed and all of them show potential and use in specific domains of application. Exfoliation still offers the advantage of being cheap but it not suitable for high-end applications. Producing pristine graphene from gas phase would represent a major breakthrough. Previous work on carbon nanotubes production from gas phase can be useful, however a major challenge is that graphene needs a structure (substrate) to grow on while CNTs are self-supported. An important issue for the production of graphene oxide is to avoid the use of strong acids. Conversely, there is need to remove chemical processing residues from the final product which requires high amounts of water and increases the overall environmental impact and costs.

# What challenges are faced for graphene and 2D materials use in energy-related applications? New energy technologies to be developed for graphene and 2D materials?

Energy applications require large-scale, uniform and stable materials. The use of graphene and 2D materials as a buffer layer is very promising since they can be spin-coated printed, functionalised and doped *in-situ*. However, stability is an important requirement. A promising route seems to be the use and optimisation of perovskites and the exploration of their growth on 2D materials or in solution. Such 2D materials for solar cells are envisioned. Graphene and 2D materials for batteries and supercapacitors remain to be further developed.

# What are the electronic device applications that have a chance to be commercialized first based on graphene or other 2D materials?

The development and commercialisation of electronic devices application is not likely to occur on a time scale shorter than 10 years.

# How to improve the low carrier transport properties in TMDCs (compared to other semiconductors like InGaAs, Si, GaAs, etc.) and in van der Walls 2D heterostructures?

Baseline measurements as well as work on heterostructured materials have been identified as two important challenges concerning transport properties and related applications. The advantages and limitations of boron nitride (BN) have been widely discussed. Passivation by BN is found to improve mobility however encapsulation should only be considered as a temporary solution since it requires complex processing steps. Research into other replacement materials as a 2D insulating layer that would substitute BN should continue. Techniques such as photoluminescence and XPS are useful to study heterostructure interfaces. It was noted that GRMs face strong competition from other, already well established (semiconductor) materials, which will be difficult to outperform.

# Do we understand enough the nature of electrical contacts to devices based on 2D materials and their hetero-interfaces?

Clearly the study of electric contacts to graphene and related materials and devices in an open issue and will require more research as it strongly influences the development of a broad range of technological applications.

# Future collaborations and next steps

Participants welcomed the availability of new mobility grants under the Graphene Flagship Core 1 which will allow young researchers from Europe to perform research stays in laboratories in Korea. Korean participants mentioned that, in principle, Korean institutions can support local costs for foreign visitors and are interested in whether a similar possibility exists in Europe. Jari Kinaret mentioned that EC Flagship funding can only be used to support European researchers travelling overseas and cover their travel and subsistence (accommodation) costs and that the possibility of having reciprocal arrangements to support local costs of visitors in Europe would depend on each institution.

In order to facilitate the contacts, Korean participants expressed interest in having a list of Flagship laboratories which could host Korean students and in providing a list of Korean laboratories which could host EU visitors supported by the mobility grants.

At the end of the meeting, there was clear interest to continue the series of workshops by organising the next workshop again in Korea, possibly in early October 2017. There was consensus that for the next workshop:

- topics to be addressed and a list of open questions should be formulated in advance and distributed to all participants prior to the workshop
- format and timing should be improved to accommodate more time for discussions. This would likely imply fewer and/or shorter presentations and more extended discussion sessions, possibly in smaller, focused break-out groups
- speakers and participants should be encouraged to focus on presenting and discussing open questions and challenges that can be addressed by collaborations



Time	15 August	16 August
8:00-8:30	Registration	Registration
8:30-8:45	Registration	Vincenzo Palermo
	Registration	Electrochemical Functionalization of
	Malassa and sussing	Graphene at the Nanoscale with Self-
8:45-9:00	Welcome and opening	Assembling Diazonium Salts
	(Xinliang Feng, Hyeon Suk Shin, Jari Kinaret)	
9:00-9:30	Jari Kinaret	Maurizio Prato
	Graphene Flagship in the global context	Functionalization of Graphene for
		Applications in Materials Science and
		Nanomedicine
9:30-10:00	Hyeonsik Cheong	Alberto Bianco
	Resonance Raman spectroscopy of 2D layered	Immune cell interaction and biodegradation
	materials	of graphene related materials
10:00-10:30	Ken Teo	Sunmin Ryu
	Towards industrial graphene production	Raman Spectroscopy for Surface Scientific
		Investigation of 2-Dimensional Crystals
10:30-11:00	Coffee break	Coffee break
11:00-11:30	Paolo Samori	Young Hee Lee
	Supramolecular approaches to 2-D materials:	What is unique in 2D layered materials?
	from complex structures to sophisticated	
	functions	
11:30-12:00	Sang Ouk Kim	Seokwoo Jeon
	Chemically Modified/Doped Graphene Based	Strong Light Emission from/with Graphene
	Nanomaterials	
12:00-12:30	Siegfried Eigler	Stephen A Hodge
	Functionalization of Graphene by Oxo-	Advanced printing and applications of 2D
	Addends	material-based inks
12:30-14:00	Lunch	Lunch
14:00-14:30	Rod Ruoff	Hyun-Jong Chung
	Diamane	Recent Progress in Graphene Barristors
14:30-15:00	Andrey Turchanin	Peter Bøggild
	2D Carbon Materials by Conversion of Organic	"Hot pick-up" batch assembly of van der
	Monolayers	Waals heterostructures
15:00-15:30	Kilwon Cho	Antti-Pekka Jauho
	Synthesis of Uniform and Defect-free	Transport properties of nanostructured
	Graphene via Control of Atomistic Dynamics	graphene
	of Carbon on Cu surface	
15:30-16:00	Coffee Break	Coffee break
16:00-16:30	Xinliang Feng	Hyeon Jin Shin
	New Generation of Graphene for Flexible	Two Dimensional Materials for Si Technology
	Energy Devices	
16:30-17:00	Hyeon Suk Shin	Julio Gomez Cordon
10.00 17.00	Growth and Application of Hexagonal Boron	Preparation bulk graphene for energy and
	Nitride	composites. Preparation of cost-effective
		ultralow percolation threshold graphene
		composites
17:00-17:30	Emmanuel Kymakis	Discussion on next steps and future
	Graphene and other 2D-based materials for	collaborations
	high efficient, stable organic and perovskite	
	solar cells	
17:30-18:00	Discussion on collaboration	1
T1.20-T0.00		
20:00-22:00	Workshop Dinner	



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Speakers and abstracts

GRAPHENE FLAGSHIP

Immune cell interaction and biodegradation of graphene related materials

# Dr. Alberto Bianco

# CNRS, UPR3572, Immunopathologie et Chimie Thérapeutique, France

### Short biography:

Alberto Bianco received his PhD in 1995 from the University of Padova (Italy). As a visiting scientist, he worked at the University of Lausanne, Tübingen (as an Alexander von Humboldt fellow) and Padova. He is currently Research Director at the CNRS in Strasbourg. His research interests focus on the design and functionalisation of carbon-based nanomaterials (carbon nanotubes, graphene and adamantane) for therapeutic, diagnostic and imaging applications. He is co-author of over 200 papers. He is also in the Advisory Board of Nanomedicine, Nanotechnology Reviews and the Journal of Peptide Science. In 2011 he has been appointed as Editor of Carbon.

### Abstract:

Despite the intense research activity, the possible impact of graphene-based materials on biological systems is still poorly studied. As for other type of nanomaterials, the intrinsic properties and characteristics of graphene and graphene oxide (GO) could have a great influence in a biological environment. In this context, we have investigated how the lateral dimensions of the GO sheets influence viability, uptake and activation of primary immune cells. Small size GO nanosheets are highly internalized by the immune cells and they affect more the cellular parameters such as cellular viability, ROS generation or cellular activation. Interestingly, our study shows a correlation between the interaction of GO with the cellular membrane (called "mask effect") and its subsequent internalization and impact on cellular parameters.

Several concerns were also raised about the biopersistence of graphene related materials in view of their future use in materials science and in biomedicine. In this context, the possible routes to degrade these materials, once administered to living species or liberated into the environment, are currently studied. Very recently, we have found that the biodegradation of GO by human myeloperoxidase is dependent on its dispersibility in the aqueous media. In addition, we have also extended the biodegradation studies to the emerging 2D analogues of graphene like MoS2 and hBN sheets. The results have revealed that the degradation profile of these 2D materials differs from GO. Overall, our biodegradation studies will offer future directions in the design of safer graphene conjugates in the context of industrial and biomedical applications.

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GRAPHENE FLAGSHIP



# Prof. Peter Bøggild DTU Nanotech, Denmark

# Short biography:

Peter Bøggild received his PhD degree in low temperature solid state physics from Copenhagen University in 1998, and has since worked at the Technical University of Denmark, on areas such as nanomanipulation, carbon nanotubes, micro four point metrology, corrosion, in-situ-TEM / NEMS and sensors but has the past five years focused his research group on 2D materials research and engineering. He was appointed a full professor at DTU Nanotech in 2013.

# Abstract:

<u>Peter Bøggild</u>, Filippo Pizzocchero, Lene Gammelgaard, Bjarke S. Jessen, Jose M. Caridad, Timothy Booth, Center for Nanostructured Graphene (CNG), DTU Nanotech, Technical University of Denmark, DK-2800, Kongens Lyngby, Denmark

James Hone, Department of Mechanical Engineering, Columbia University, New York, New York 10027, USA

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A core problem in the fabrication of van der Waals heterostructures is the formation of clean interfaces between the individual two-dimensional materials as any kind of contamination is likely to impede the device performance. We discuss here a technique for the rapid batch fabrication of van der Waals heterostructures, which uses temperature control adhesion between polymer and 2D crystals, and to expel contamination from the 2D interfaces. We present data from 22 mono-, bi- and trilayer graphene stacks encapsulated in hexagonal boron nitride with close to 100% yield. For the monolayer devices, we found room temperature mean-free paths of order 1  $\mu$ m. The presented method readily lends itself to fabrication of van der Waals heterostructures in both ambient and controlled atmospheres, while the ability to assemble and co-align multiple pre-patterned layers paves the way for complex three-dimensional architectures. The method has also been used to assemble high performance TMD devices with graphene gates, where the ability to pick up patterned graphene contacts have been used to create advanced structures with relative ease. I will also discuss practical ways to streamline the exfoliation-based fabrication procedures, for instance by automatizing the identification and analysis of flakes. If time allows, I will discuss terahertz time-domain spectroscopy as non-contact alternative to conventional transport measurement in terms of analyzing the electrical properties of graphene.



#### **Resonance Raman spectroscopy of 2D layered materials**

# Prof. Hyeonsik Cheong Sogang University, Republic of Korea

### Short biography:

Hyeonsik Cheong is the Vice President for Budget and Planning and a Professor of Physics at Sogang University in Seoul, Korea. He received his B.S. degree in physics from Seoul National University in 1986 and A.M. and Ph.D. in physics from Harvard University in 1988 and 1993, respectively. After working at Harvard as a postdoctoral fellow for 2 years, he worked at National Renewable Energy Laboratory in Golden, Colorado for 4 years. In 1999, he joined the physics faculty at Sogang University. From 2006 to 2009, he served as the Vice President of International and External Relations, and from 2010 to 2012, the Chair of the Department of Physics. He is currently serving as the President of Korean Graphene Society and also as the Chair of the Division of Applied Physics of the Korean Physical Society. He has served the KPS at several positions, including the Director of Academic Affairs. He is an Editorial Board Member of Scientific Reports and has served on the editorial boards of the Journal of the Korean Vacuum Society and the Journal of the Korean Physical Society. He has been a guest editor for Journal of Applied Physics, 2D Materials, Current Applied Physics, and Solar Energy Materials and Solar Cells. His research interest includes spectroscopic studies of graphene and 2D materials, semiconductor nanostructures, solar cell materials, electrochromic materials, and hydrogen sensors.

### Abstract:

Raman spectroscopy is playing a vital role in the 2D layered materials research as it has been in graphene research. Unlike graphene which has no band gap, many new kinds of 2-dimensional materials such as transition metal dichacogenides and black phosphorus have finite band gaps. Furthermore, reduced dielectric screening in 2-dimensional materials results in very large exciton binding energy and pronounced excitonic effects, which affects Raman scattering in significant ways. Near the resonance, several multiphonon scattering peaks are enhanced and in some cases dominate the main one-phonon peaks. Furthermore, new peaks that do not seem to depend on the number of layer appear in the low-frequency (<50 cm-1) region of the Raman spectrum. Raman spectroscopy of suspended MoS2 has been carried out and revealed that the different dielectric environment does not seem to affect the resonance as expected. Raman spectroscopy is also used to probe polytypism in MoS2 which mainly affect the low-frequency modes. In black phosphorus, a peculiar polarization behaviour that depends on the sample thickness and the excitation wavelength has been observed and is ascribed to anisotropic electron-photon interaction in this material. In this talk, a summary of recent results from resonance Raman studies of various 2-dimensional materials will be presented.



# Synthesis of Uniform and Defect-free Graphene via Control of Atomistic Dynamics of Carbon on Cu surface

# Prof. Kilwon Cho

# Department of Chemical Engineering, Pohang University of Science and Technology, Republic of Korea

### Short biography:

Kilwon Cho is a Professor of Polymer Science in the Department of Chemical Engineering and Director of the Polymer Research Institute at Pohang University of Science and Technology (POSTECH) in Korea. He is also a Director of the Global Frontier Research Centre for Advanced Soft Electronics and currently serves as President of the Polymer Society of Korea. He received his B.S. and M.S. from the Seoul National University in applied chemistry and a Ph.D. from the University of Akron in polymer science (1986). After working as a researcher at the IBM Research Centre, he joined the faculty at POSTECH in 1988. His current research interests include polymer surface and thin-film, organic electronics (organic transistors, organic photovoltaics), and graphene-based materials and electronics. He has published over 320 articles, which received over 12000 citations (h-index of 58) (http://crg.postech.ac.kr).

#### Abstract:

Despite of significant progress in chemical vapour deposition of graphene on Cu in recent years, process development and understanding in atomistic mechanism of graphene growth still require intensive investigation. In this talk, the growth mechanism of CVD graphene regarding adsorption, desorption, surface-diffusion, dissolution and assembly of carbons on Cu surfaces will be discussed.

In addition, synthetic strategies toward layer-controlled growth of CVD graphene on Cu surface and the growth mechanism will be presented. Lastly, low-temperature CVD of high-quality graphene on Cu surface using solid carbon sources will be discussed.



#### **Recent Progress in Graphene Barristors**

# Prof. Hyun-Jong Chung Konkuk University, Republic of Korea

### Short biography:

I have conducted research in graphene electronics since I joined Samsung Advanced Institute of Technology in 2006 where I initiated graphene research. I developed 6-inch wafer scale graphene-related processes to fabricate graphene RF transistors, as presented in IEDM, and later, low noise amplifiers using the transistors. Based on this research, I co-authored a review article in Nature with the president of my company, Samsung Advanced Institute of Technology.

It is well known that conventional graphene field-effect transistors are not ideal due to their poor switching characteristics *i.e.* they cannot be turned off ( $I_{ON}/I_{OFF} < 100$ ) due to the lack of an intrinsic band gap. To solve this problem, I invented a new electronic device, modulating the graphene-Si Schottky-barrier height, published in Science. I named the device "barristor", meaning barrier transistor, since the current can be modulated by modulating the Schottky-barrier. With this, I proved that graphene electronic devices can be turned off, allowing them to be used for logic electronics, without generating a graphene bandgap. The Si can be replaced with other semiconductors; in this way, I participated in research on a new barristor using InGaZnO [J7]. Note that the barristor concept has now been adopted for many device-related research activities using either organic or inorganic semiconductor-graphene junction devices.

After I moved to Konkuk University, I conducted research to determine the barristor's potential and limitations. I implemented semiconductor-less solid-state electronic devices whose  $I_{ON}/I_{OFF} \sim 10^6$  using graphene's workfunction modulation. Also I published how to engineer the properties of 2D semiconductors by controlling their thickness: bandgap and optical constants could be controllably modulated. Moreover, the WS<sub>2</sub>–Cr/Au Schottky barrier could be modulated by 0.2 eV, and thus lowered to 0.18 eV by controlling the WS<sub>2</sub> thickness. The thickness also modulated the device characteristics of graphene-WS<sub>2</sub> barristors. I conducted device research for industrial applications using 2D materials based on their unique materials properties: work function modulation of graphene, and materials and device property engineering of 2D semiconductors through film thickness control.

### Abstract:

Graphene has been considered as one of the potential post Si-materials due to its high mobility [1]. However, since graphene has no band gap, it is difficult to achieve high  $I_{on}/I_{off}$ , one of the most important requirements for commercial devices. There have been many attempts to open its band gap for high  $I_{on}/I_{off}$ , but most of them end up lowering the mobility [2]. Thus, I proposed a new device structure for graphene electronic devices and demonstrated high  $I_{on}/I_{off}$  based on its unique property of graphene: workfunction modulation [3]. In this talk, reviewed will be graphene electronic devices, graphene barristor, vertical tunnelling transistors, and graphene transistors and suggested will be the new opportunities on 2D materials devices exploiting their unique properties [3].

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#### **Functionalization of Graphene by Oxo-Addends**

# Prof. Siegfried Eigler Chalmers University of Technology, Sweden

# Short biography:

Siegfried Eigler received his PhD in organic chemistry from the Friedrich-Alexander-Universität Erlangen-Nürnberg in 2006 under the guidance of apl. Prof. Dr. Norbert Jux. The focus of the PhD thesis was on the synthesis of a water-soluble cytochrome P450 model system and in general porphyrin synthesis. Subsequently he conducted industrial research at DIC-Berlin GmbH, part of DIC Corporation, Japan. The research concentrated on electrically conductive polymers and the development of novel semiconducting monomers. In 2009 he started working on the synthesis and application of graphene oxide. Two years later he became a lecturer and research associate at the Friedrich-Alexander-Universität, Erlangen-Nürnberg. There, he conducted deep research on the synthesis of graphene oxide and he realized that defects in the carbon lattice could be avoided by controlling the synthesis. With this discovery he could investigate the controlled chemistry of graphene oxide and synthesized several new graphene derivatives and composites. Currently, his research focuses on advancing the controlled chemistry of graphene. This development led to 27 papers in the field of carbon research and one applied patent related to the wet-chemical synthesis of graphene that allows the control of the defect density. He accepted an offer from Chalmers University of Technology, Gothenburg, Sweden, as Associate Professor in 2016 and finalized habilitation at Friedrich-Alexander-Universität, Erlangen-Nürnberg the same year.

### Abstract:

Graphene derivatives are expected to be crucial for finding new properties beyond pure graphene. Selectively sensing of molecules or macromolecules is one exciting example. However, the chemical toolbox giving control over the type and degree of functionalization of graphene, on the single layer level, is far from being developed and understood. Functionalization of graphene by oxo-addends is one possibility to provide soluble graphene. With that oxo-functionalized graphene, post-functionalization reactions can be studied without affecting the reactivity by defect sites, as it is the case for graphene oxide. We demonstrate in selective examples controlled chemistry of oxo-functionalized graphene, with respect to the degree of functionalization, the ability to form graphene with very little defects and the performance in devices. We demonstrate the chemical synthesis and characterization of a composite material suitable for reversible writing, reading and erasing information at 3V. The composite formation is based on the electrostatic interaction of alkylammonium ions and sulfatesters bound on the surface of the graphene material.

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#### New Generation of Graphene for Flexible Energy Devices

# Prof. Xinliang Feng Technical University Dresden, Germany

### Short biography:

Xinliang Feng is a full professor at Technical University of Dresden. He received his Bachelor's degree in analytic chemistry in 2001 and Master's degree in organic chemistry in 2004. Then he joined Prof. Klaus Müllen's group at the Max Planck Institute for Polymer Research for PhD thesis, where he obtained his PhD degree in April 2008. Since December 2007, he was appointed as a group leader at the Max-Planck Institute for Polymer Research, and since 2012, he became a distinguished group leader at the Max-Planck Institute for Polymer Research. Since 2011, he was appointed as an adjunct distinguished professor at the Shanghai Jiao Tong University and as the director for the Institute of Advanced Organic Materials.

His current scientific interests include graphene, synthetic two-dimensional materials, organic conjugated materials, and carbon-rich molecules and materials for electronic and energy-related applications. He has published about 300 research articles which have attracted more than 16000 citations with H-index of 64. He has been awarded several prestigious prizes such as IUPAC Prize for Young Chemists (2009), Finalist of 3rd European Young Chemist Award, European Research Council (ERC) Starting Grant Award (2012), Journal of Materials Chemistry Lectureship Award (2013), ChemComm Emerging Investigator Lectureship (2014), Highly Cited Researcher (Thomson Reuters, 2014, 2015), Fellow of the Royal Society of Chemistry (FRSC, 2014). He is an Advisory Board Member for Advanced Materials, Journal of Materials Chemistry A, Chemistry -An Asian Journal, Energy Storage Materials, etc. He is also one of the Working Package Leaders for European commission's pilot project Graphene Flagship.

#### Abstract:

Energy storage devices, such as supercapacitors and batteries, have caught more and more attention due to the rapid development of portable devices and increasing individual requirements. Among these energy storage devices, supercapaciters, also named as electrochemical capacitor and ultracapacitors, which possess rapid charge and discharge feature, render them high powder delivery for multiple applications. Micro-supercapcitors, especially on-chip micro-supercapacitors, is one kind of rising stars in supercapacitors due to their possible silicon-compatible character, thin-film flexibility, as well as high specific areal capacitance. Towards the future development and practical utilization of electrochemical energy storage and conversion devices, graphene is considered as one of the key materials, which however yet suffers from up-scalable preparation with controlled quality. In this lecture, we will firstly discuss the recent developments of electrochemical exfoliation of graphite towards high quality graphene. This strategy delivers not only large scale exfoliated graphene (EG) in a short time, but also provides highly dispersible graphene in various solvents. The combination of EG with other electrochemical active components, such as conducting polymers and carbon nanoparticles, render the preparation of functional inks. In the next part, we will demonstrate the fabrication of ultrathin printable supercapacitors with AC line-filtering performance based on graphene-conducting polymer hybrid films. Such devices exhibit an unprecedented volumetric capacitance of 348 F cm-3, excellent cycling stability with no capacitance loss after 50 000 cycles, and can be operated at an ultrahigh rate of up to 2000 V s-1. Moreover, highperformance, thin-film, flexible microsupercapacitors will be demonstrated utilizing solution processable EG combined with conducting polymers or porous carbons. Not limited to the energy storage devices, asdeveloped graphene can also be used as key component for the preparation of electrocatalysts for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) in basic media.

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# Preparation bulk graphene for energy and composites. Preparation of cost-effective ultralow percolation threshold graphene composites

# Dr. Julio Gomez Cordon

Avanzare Innovacion Tecnologica S.L., Spain

# Short biography:

Julio Gomez is the Founder of AVANZARE, company producer of graphene and other 2D materials and its composites. He received his B.S. degree in Chemistry from Universidad Complutense de Madrid (1995), receiving the and a Ph.D. in Chemistry (2000) from University of La Rioja where he studied the preparation and electrical and optical properties of nanosize metallic clusters, and a postdoctoral researcher position in the Laboratoire de Synthèse Organique, University of Nantes-CNRS After finishing his Ph.D., he spent 3 years as assistant Professor in Universidad de La Rioja and 2 years as an Area Manager in the research centre CIDETEC studying electrochemical systems before joining AVANZARE at the end of 2004. His awards include among others the best B.S. degree in Chemistry in 1995 award in the University Complutense de Madrid, the best PhD degree in Science and Technology award in the University of La Rioja from the years 1999-2000, National award Entrepreneur of the year 2008 in Spain, best product NANOAWARDS 2008 (USA), F&S best practices in innovation 2013 (UK). Author of 45 papers H-index 22, 7 books and 12 invention patents.

# Abstract:

The graphene material market, bulk graphene, graphene nanoplatelets and graphene films, will grow to  $350 \in \text{million in } 2025$ . Its applications in composites will be the largest segment, followed by energy storage applications.[1] Several reviews analysed the applications of the different graphene and related products in energy [4, 1b] and in composites applications.[5, 1b]

Different synthetic methods can be used for the production of graphene and graphene related materials. In this presentation, 3 different methods for the production of bulk graphene or reduce graphene oxide: liquid exfoliation, reduced graphene oxides and high expansion were compared with other production methods and products in the market.

The complete characterization of graphene and highly reduce graphene oxide using TEM, SEM, AFM, XPS, DRX, Laser diffraction, surface area and pore size analysis, etc. will be presented.

Different types of graphene materials with variation in lateral size, defects and defects concentration, thickness, etc., have been used to obtain graphene-thermoplastic and thermoset composites studying the electrical, thermal conductivity and fire retardant properties of the composites. Related to electrical properties, some of these composites show ultralow percolation threshold limits, lower than the previously reported values, also obtaining very high electrical conductivity, opening a new range of applications and markets. We have also obtained high thermal conductive composites align with the best published result for graphene composites. Other factors as processing technique have been analysed due to their extremely high importance in the final results.

The use of different graphene materials and decorated graphene materials in energy applications, from anodes and cathodes of batteries to supercapacitors with ultrahigh energy density, will be also presented. 1. a) Zh Ma, R. Kozarsky, M. Holman., GRAPHENE MARKET UPDATE. LUX RESEARCH (2014). b) Ferrari A C et al Nanoscale 7 (2015) 4598–810, c) M. Peplow, Nature 522, (2015), 268

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# Advanced printing and applications of 2d material-based inks

# Dr. Stephen A Hodge Cambridge Graphene Centre, United Kingdom

# Short biography:

Dr Stephen Hodge is a Research Associate in the Nanomaterials and Spectroscopy Group at the Cambridge Graphene Centre in the Electrical Engineering Division of the Engineering Department. He has particular interests in the chemistry and physics of nanomaterials including fullerenes, carbon nanotubes, graphene and the many other two-dimensional analogues. His PhD at Imperial College London under the supervision of Prof. Milo Shaffer focussed on the electrochemical processing of these materials; within the University of Cambridge, the current focus is on the scalable production of these enabling materials for mechanical, optical and electronic applications. Stephen currently holds a fellowship position at Murray Edwards College.

# Abstract:

Functional inks and pastes is a large market sector with a huge growth potential for the next decade [1]. Conductive inks, for example, are currently dominated by silver materials due to its high conductivity [2], however, for mass produced flexible electronic devices, silver inks are not an ideal choice since they impart high device cost [3] and can have negative environmental impact if not disposed properly [4]. Graphene and related material (GRM) based inks are a promising solution to these issues; providing multiple functions including mixed electronic (conducting, insulating, semi-conducting), mechanical and thermal properties.

Specific applications requiring highly tuned properties including print resolution, film thickness, conductivity and mechanical performance, for example, have led us to develop an array of GRM inks (graphene, hBN and MoS2) produced using a high shear turbulent flow microfluidic processor and formulated using various polymeric rheology modifiers. Ink viscosity is tuned over the range of 1 – 1800 cP, so that printing methods from inkjet printing and spray coating to roll-to-roll flexographic and screen printing can be achieved.

Printing is typically performed on cheap, flexible paper or plastic (PET, PEN) substrates, paving the way for a huge range of commercial applications. In the current context, I will discuss realistic pathways to commercialization of GRM inks and demonstrate prototypes such as electrodes, strain sensors, gas sensors, photodetectors, biofilms or catalyst supports in (bio)fuel cells using single GRM inks, or multiple inks as a route towards fully printed heterostructures.

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# Transport properties of nanostructured graphene

# Prof. Antti-Pekka Jauho CNG, DTU Nanotech, Technical University of Denmark, Denmark

# Short biography:

Antti-Pekka Jauho is the leader of the Center-of-Excellence CNG (Center for Nanostructured Graphene), and Professor of Theoretical Nanotechnology at Technical University of Denmark. He has worked extensively on various aspects of quantum transport in mesoscopic systems out of equilibrium, and has published more than 200 papers in this area. His book, co-authored with Prof. Hartmut Haug, 'Quantum Kinetics of Transport and Optics in Semiconductors' is the standard reference on the technique of nonequilibrium Green's functions. He has directed more than twenty PhD studies and ten of his former students or post-doctoral associates are today full professors at leading universities. He is a foreign member of the Finnish Academy of Science and Letters, and an Outstanding Referee of the American Physical Society.

### Abstract:

Despite of its many wonderful properties, pristine graphene has one major drawback: being a semimetal it does not have a band gap, which complicates its applications in electronic devices. Many routes have been suggested to overcome this difficulty, such as cutting graphene into nanoribbons, using chemical methods, or making regular nanoperforations, also known antidote lattices. All these ideas work beautifully in theory, but realizing them in the lab is very difficult because all fabrication steps induce disorder and other nonidealities, with potentially disastrous consequences for the intended device operation. In this talk I introduce these ideas and review the state-of-the -art both from the theoretical and the experimental points of view. I also introduce some new ideas, such as sublattice asymmetric doping (which Nature allows!), triangular antidotes, and nanobubbles formed in graphene. Our simulations, relying on advanced numerical techniques, show that it may be possible to generate very high quality spin- and valley polarized currents with these structures - something that has not yet been achieved in the lab. Importantly, our simulations involve millions of atoms which is necessary in order to address structures feasible in the lab.



Strong Light Emission from/with Graphene

### Prof. Seokwoo Jeon

Department of Materials Science and Engineering and Graphene Research Centre of KI for the NanoCentury, Korea Advanced Institute of Science and Technology, Republic of Korea

# Short biography:

As a faculty member at KAIST (08/2008-present), Prof. Seokwoo Jeon have devoted research efforts on the creation of new nanomaterials by developing new synthetic routes with minimal loss of their intrinsic properties and by patterning three dimensional (3D) nanostructures in bulk scale to manifest novel material properties originating not from atomic composition but from nanostructures. His research goals are exploring novel electronic, mechanical, and optical properties from those nanomaterials and employing those materials in real world applications.

### Abstract:

Graphene quantum dots (GQDs), simply making graphene typically under 10 nm, and the change of emission behaviour from known fluorescents on graphene draws huge interest for potential applications to display, lighting, and optoelectronic devices. GQD could be a new class of optical material with useful properties of tuneable luminescence, superior photo-stability, and chemical resistance. Here, we demonstrate the first GQD light-emitting diodes (GQD-LEDs) with electroluminescence that exceeds 1,000 cd/m2. The GQD-LEDs are possible due to our simple synthesis method to create high-quality GQDs with minimal, or controlled, oxidation such that high quantum yields (~4.6%) are guaranteed. The GQDs are synthesized by the solvothermal formation of graphite intercalation compounds (GICs) between graphite powder and sodium potassium tartrate. The proposed method is cost-effective, eco-friendly, and can easily be scaled up, as it allows the direct fabrication of GQDs using water without a surfactant or chemical solvent. The GQD-LEDs, in which GQDs are incorporated into polymeric host layers in a multilayer electroluminescent (EL) device, irradiate blue (~400 nm) emission. Besides the direct emission from graphene, when conjugated fluorescent materials such as porphyrin interact with the conjugated plain of graphene, interesting peak shifts and emission enhancement from the fluorescent materials are observed. The demonstration of an optical transition of PtOEP, deposited on graphene, from triplet to singlet and strong PL enhancement will show the possibility of using graphene as new platform to modulate emission behaviours from fluorescent materials.



#### **Chemically Modified/Doped Graphene Based Nanomaterials**

# Prof. Sang Ouk Kim Department of Materials Science & Engineering, KAIST, Republic of Korea

#### Short biography:

Dr. Sang Ouk Kim is the KAIST designated chair professor in the department of materials science & engineering, KAIST and the director of 'National Creative Research Initiative Centre for Multi-Dimensional Directed Nanoscale Assembly' in Korea. He received his B.S., M.S. and Ph.D. in the department of chemical engineering at KAIST. After his Ph.D. at 2000, He worked with prof. Paul Nealey in the University of Wisconsin-Madison as postdoctoral researcher and contributed to the pioneering research works for the birth of DSA. He joined the faculty member of KAIST in 2004 and have served for almost 12 years already. Prof. Kim's current research is focusing on the directed assembly of various nanoscale materials, including carbon nanotubes, graphene, 2D transition metal chalcogenides as well as block copolymers. To date, he co-authored more than 160 international journal papers and his h-index is higher than 55 (google scholar). Prof. Kim is serving on the editorial board members of several academic journals, including 'Molecular Systems Design & Engineering (RSC), ACS Applied Materials & Interfaces' and 'Particle & Particle Systems Characterization' (Wiley). He has received numerous academic awards for his research, including KAIST Grand Prize for Research, Korean Prime Minister Award and Presidential Young Scientist Award.

#### Abstract:

Graphene based materials, such as fullerene, carbon nanotubes and graphene attract enormous research attention for their outstanding material properties along with molecular scale dimension. Real-world applications of the graphene based materials for many different application fields inevitably requires the subtle controllability and optimization of their structures and properties. In this presentation, our recent research achievements associated to the nanoscale assembly and chemical modification of graphene based nanomaterials will be presented. Carbon nanotubes and graphene can be efficiently assembled into various one-, two- or three-dimensional structures via self-assembly principles and directed growth. The resultant carbon assembled structures with extremely large surface and high electro-conductivity are potentially useful for energy storage/conversion, catalysis and so on. In particular, aqueous dispersion of graphene oxide shows liquid crystalline phase, whose spontaneous molecular ordering is useful for fibre spinning, large-area uniform film preparation or nanoporous material production. In addition, substitutional doping of the graphitic carbons with B- or N- was achieved via pre- or post-synthetic treatment. The resultant chemically modified graphene based nanostructures with tuneable workfunction and remarkably enhanced surface activity could be employed for organic solar cells, highly functional nanocomposites and dopant specific unzipping process for improved functionalities and device performances.



# **Graphene Flagship in the global context**

# Prof. Jari Kinaret Chalmers University of Technology, Sweden

### Short biography:

Jari Kinaret received his M.Sc. degrees in Theoretical Physics in 1986 and in Electrical Engineering in 1987, both from the University of Oulu in Finland. In 1992 he graduated with a PhD in Physics from MIT. After graduation he has held academic positions at Nordita in Copenhagen and at Gothenburg University and Chalmers University of Technology in Gothenburg, Sweden. He is currently the head of the condensed matter theory division at Chalmers, and since 2013 he is the director of the Graphene Flagship. His research interests focus on theoretical studies of nanoscale structures, most recently on mechanical and optical properties of graphene.



# Graphene and other 2D-based materials for high efficient, stable organic and perovskite solar

<u>cells</u>

# **Prof. Emmanuel Kymakis**

Technological Educational Institute of Crete, Greece

# Short biography:

Emmanuel Kymakis (1977) is an Associate Professor at the Electrical Engineering Department of the Technological Educational Institute (T.E.I) of Crete, where he heads the Nanomaterials & Organic Electronics group of the Centre of Advanced Materials & Photonics (<u>http://nano.teicrete.gr</u>). He received the B.Eng. (First Class Honours) degree in Electrical Engineering & Electronics from Liverpool University in 1999 and the Ph.D. degree in Electrical Engineering from Cambridge University in 2003. He and Prof. Gehan Amaratunga are the inventors of the polymer-nanotube solar cell. Before joining TEI of Crete, he was a technical consultant offering engineering and consultancy services in the field of photovoltaic and solar thermal power plants for various Greek and international investors and private companies. He has recently initiated a research line on organic and perovskite solar cells. His technological interests are in the synthesis and solution processing of novel carbon nanomaterials and their incorporation into organic electronic devices. His research topics presently include investigation of the opto-electronic properties of graphene, 2D transition metal dichalcogenides and inorganic-organic hybrids for the development of low cost next generation photovoltaic devices, compatible with roll-to-roll large area manufacturing methods. He has over 80 SCI publications with over 4.000 citations on these topics, with an h-index of 31 and has given 35 invited lectures. Details of publication be found in can https://scholar.google.gr/citations?user=AWrgzokAAAAJ&hl=en. He has been selected as an honorary lecturer in the UConn, and was a recipient of an Isaac Newton and an EPSRC studentship during his PhD studies in Cambridge. Prof. Kymakis is the Greek national representative in two COST actions (MP1307: Stable Next-Generation Photovoltaics; MP1202: Rational design of hybrid organic-inorganic interfaces) and the deputy leader of the WP Energy Generation of the Graphene Flagship FET. He is also serves as an Associate Editor of RSC Advances. He was named by RSC as a ChemComm Emerging Investigator (2014) and was the recipient of an Excellence Award for young scientists by the Greek General Secretariat of Research (2015). He was recently awarded a research excellence grant by the Greek State Scholarships Foundation (2016). He is the chair of the Organic & Perovskite Solar Cells conference, which will take place in October 2016 in Heraklion, Greece.

### Abstract:

Solution processable (SP) graphene and other 2D-based materials can be utilized in various components of organic (OSCs) and perovskite solar cells (PeSCs).<sup>1,2</sup> In particular, large area patterned graphene films with controlled optoelectronic properties, using a fs laser were developed. Our efforts aimed to overcome a long-standing challenge (the trade-off between the sheet resistance and transparency), that has hindered the SP graphene based films as active components in flexible optoelectronic applications.<sup>3</sup> In addition, we demonstrated an effective utilization of work-function (WF) tuned, SP graphene-based derivatives as both hole and electron transport (HT & ET) layers in OSCs, either by using photochlorination to increase the WF<sup>4</sup> or lithium alkali metal functionalization to reduce WF<sup>5</sup>. The utilization of these graphene-based HT and ET layers, led to the highest reported power conversion efficiency (PCE) for graphene-based buffer layer OSCs of 9.14%.<sup>6</sup> With respect to the photoactive layer, we presented a photochemical route for the facile synthesis of tunable bandgap graphene-based derivatives, and their incorporation as the active layer electron acceptors.<sup>7</sup>

In addition, functionalized graphene nanoflakes with controllable lateral size, in the form of an ink and graphene-inorganic nanocrystals hybrid materials were investigated as electron cascade materials,



demonstrating a promising way towards improving the OSCs performance, via novel active layer engineering approaches.<sup>8,9,10,11</sup>

Extending the research on other promising 2D materials, an in situ laser induced anchoring of noble metal nanoparticles onto the surface area of thin 2D WS2 sheets was demonstrated, achieving a PCE enhancement of ~13% for ternary OSC configurations.<sup>12</sup> Finally, SP tungsten WSe<sub>2</sub> nanoflakes with highly controllable flake size were demonstrated as additives in OSC devices, identifying an additional energy transfer.

Most recently, GO-Li was inserted between the perovskite sensitizer and m-TiO<sub>2</sub> layer, improving the electron injection by remarkably increasing the  $J_{SC}$  (+10.5%), reducing by 50% the devices hysteresis and improving the PeSC stability.<sup>13</sup> We also presented a throughout analysis on the incorporation of reduced graphene oxide in PeSCs, elucidating its main role in improving the electron transport when mixed with the m-TiO<sub>2</sub> and establishing our graphene-based materials as necessary additives for further improving the solar cells PCEs (~ 20%) and stability.

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# What is unique in 2D layered materials?

### Prof. Young Hee Lee Institute for Basic Science, Department of Physics, Department of Energy Science, Sungkyunkwan University (SKKU), Republic of Korea

# Short biography:

Prof. Lee has been a full professor of the Physics Department at SKKU, since 2001. He received Ph. D. from Kent State University in Ohio (1986) in physics. Prior to joining SKKU in 2001, Prof. Lee was a full professor in the Physics Department at Chonbuk National University since 1986. He was a visiting scholar at Ames Laboratory, Iowa State University in 1989, IBM, Zurich in 1993, and Michigan State University in 1996. Currently, he is the Director of Center for Integrated Nanostructure Physics, Institute for Basic Science at SKKU. He serves for an Associate Editor of European Physical Journal: Appl. Phys. He was awarded the first SKKU fellow in 2004 at SKKU, Science award from Korean Physical Society in 2005, Lee Hsun Research Award, IMR, Chinese Academy of Sciences, China in 2007, and Presidential Award in Science and Education in 2008. He was also nominated as a National Scholar by Ministry of Education in 2006 and has been a fellow of Korean Academy of Science and Technology since 2007. He recently got Sudang prize.

Prof. Lee's work has focused on understanding the fundamental properties of nanostructures in 0D, 1D, 2D and their hybrid heterostructures, design and synthesis of various heterostructures to implement unique physical and chemical properties. His research covers carrier dynamics, carrier multiplication phenomena, hot carrier solar cell, thermoelectrics, quantum mechanical tunneling phenomena, and nanocarbon-based soft electronics. His pioneering woks on synthesis and engineering of electronic and atomic structures of carbon nanotubes and graphene, other 2D materials and their applications to electronic devices, and energy harvesting have led not only nanoscience but also nanotechnology industry in Korea. He has published more than 420 scientific papers in international journals and his total citation number exceeds over 23,000 times with H-index of 72 (As of Jan. 2016).

### Abstract:

Motivated by graphene which has exotic Dirac-particle like feature with extremely high mobility at room temperature but still limited by the zero bandgap feature, other types of 2D materials such as insulating hexagonal-BN monolayer and semiconducting layered transition metal dichalcoginides (LTMDs) have been intensively focused as a new class of transparent and flexible materials, which can be used as essential components of transistors for soft electronics. While large-area graphene is available in a meter-scale, synthesis of large area monolayer h-BN and LTMDs are still a long way to realize. These materials have known to exhibit exotic physical and chemical phenomena which have never been accessed so far with 3D materials. I will demonstrate some key concepts of 2D materials why they differ from 3D and show some examples of some new phenomena that emerge uniquely in 2D materials in this talk. We will also demonstrate that thin MoTe2 revealed a reversible phase transition from 2H to 1T' at around 650-9000C depending on Te-rich conditions. We will further demonstrate that the phase transition of MoTe2 can be provoked by several robust parameters such as laser irradiation and strain. The problematic Ohmic contact was realized by phase patterning of the contact area at source and drain positions with laser irradiation. We further demonstrate that even the phase transition temperature can be reduced to room temperature by applying a tensile strain of ~0.2%.

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GRAPHENE FLAGSHIP KOR

**KOREAN GRAPHENE SOCIETY** 



Prof. Vincenzo Palermo CNR, Italy

### Short biography:

Vincenzo Palermo is the leader of the research unit on Advanced Materials of the National Research Council of Italy (CNR), at the Institute for Organic Synthesis and Photoreactivity (ISOF). In his work, he uses nanotechnology and supramolecular chemistry to create new materials for structural, electronics and energy applications. He was one of the nine initiators of the GRAPHENE FLAGSHIP European initiative, and is currently the leader of the flagship work package on polymer composites.

In parallel to his scientific activity, Vincenzo Palermo is involved in science dissemination and communication, giving seminars for broad public on the interplay between Science and History. In 2015 he has published a book on the life and science of Albert Einstein.

In 2013 he has been awarded the Research Award of the Italian Society of Chemistry (SCI). This prize awarded to an emerging scientist by the SCI Division of Organic Chemistry, for brilliant results obtained in the past years. In 2012 he has been awarded the Lecturer Award for Excellence of the Federation of European Materials Societies.

### Abstract:

We describe a fast and versatile method to functionalize high-quality graphene with organic molecules by exploiting the synergistic effect of supramolecular and covalent chemistry. With this goal, we designed and synthesized molecules comprising a long aliphatic chain and an aryl diazonium salt.

Thanks to the long chain these molecules physisorb from solution onto CVD graphene or bulk graphite, selfassembling in an ordered monolayer. The sample is successively transferred into an aqueous electrolyte, to block any reorganization or desorption of the monolayer. An electrochemical impulse is used to transform the diazonium group into a radical capable of grafting covalently to the substrate and transforming the physisorption into a covalent chemisorption. During covalent grafting in water the molecules retain the ordered packing formed upon self-assembly.

Our two-step approach is characterized by the independent control over the processes of immobilization of molecules on the substrate and their covalent tethering, enabling fast (t<10 sec) covalent functionalization of graphene. This strategy is highly versatile and works with many carbon-based materials including graphene deposited on silicon, plastic and quartz, as well as highly oriented pyrolytic graphite.

ACS Nano, article ASAP. DOI: 10.1021/acsnano.6b03278

Functionalization of Graphene for Applications in Materials Science and Nanomedicine

# Prof. Maurizio Prato

Dipartimento di Scienze Chimiche e Farmaceutiche, University of Trieste, Italy and CIC BiomaGUNE, Ikerbasque, San Sebastian, Spain

# Short biography:

Maurizio Prato graduated in Padova, where he was appointed Assistant Professor in 1983. He moved to Trieste in 1992 as an Associate Professor to become Full Professor in 2000. His research focuses on the functionalization chemistry of carbon nanostructures for applications in materials science and medicinal chemistry. His scientific contributions have been recognized by many National and International awards. He was the recipient of an ERC Advanced Research Grant, European Research Council, 2008 and has become a Member of the National Academy of Sciences (Accademia Nazionale dei Lincei) in 2010.

### Abstract:

After the production and characterization of mono- and few-layer graphene have made this material available, much effort has been directed toward the chemical functionalization as a tool for tuning graphene chemical and physical properties. For example, chemical functionalization can render graphene dispersible in many solvents.

We have recently reported the functionalization of graphene layers by condensation of an  $\alpha$ -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, giving a highly functionalized material. We have also performed a non-conventional approach for functionalization of graphene layers under microwave irradiation, to avoid unstable graphene suspensions and improve reaction rate and efficiency by other cycloaddition reactions. Finally, we have transferred these chemical strategies to other graphene derivatives such as chemical vapour deposited graphene.

During this talk, we will summarize our most recent results in the chemistry and applications of graphene which include the use of functionalized graphene in electrochemical devices for the splitting of water as well as novel biological applications.

KOREAN GRAPHENE SOCIETY



# Diamane

# Prof. Rodney Ruoff

Director, Centre for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS) Centre, Republic of Korea

Distinguished Professor, Department of Chemistry and School of Materials Science, Ulsan National Institute of Science & Technology (UNIST), Republic of Korea

# Short biography:

Rodney S. Ruoff, UNIST Distinguished Professor, Department of Chemistry and the School of Materials Science and Engineering, is director of the Center for Multidimensional Carbon Materials (CMCM), an IBS Center located at the Ulsan National Institute of Science and Technology (UNIST) campus. Prior to joining UNIST he was the Cockrell Family Regents Endowed Chair Professor at the University of Texas at Austin from September, 2007. He earned his Ph.D. in Chemical Physics from the University of Illinois-Urbana in 1988, and he was a Fulbright Fellow in 1988-89 at the Max Planck Institute für Strömungsforschung in Göttingen, Germany. He was at Northwestern University from January 2000 to August 2007, where he was the John Evans Professor of Nanoengineering and director of NU's Biologically Inspired Materials Institute. He has co-authored over 440 peer-reviewed publications related to chemistry, physics, materials science, mechanics, and biomedical science, and is a Fellow of the Materials Research Society, the American Physical Society, and the American Association for the Advancement of Science. He is the recipient of the 2014 Turnbull Prize from the MRS and the 2016 SGL (Skakal) Prize of the American Carbon Society. For further background on some of his research see: http://en.wikipedia.org/wiki/Rodney\_S.\_Ruoff.

# Abstract:

'Diamane' means ultrathin (few atom thick) sp3-bonded carbon films. The conversion to diamane of 'ABstacked few layer graphene' has been calculated by density functional theory calculations to be possible through the formation of sufficient C-H (or C-F) bonds on the two free surfaces. We [1] then did DFT calculations on "nG/M", where nG represents n layers of AB-stacked graphene and M a metal substrate having an interface with the nth graphene layer, and found for configurations [up to about 8-layer graphene on Cu(111) or Ni(111) or Co(00001)] that the metal surface could stabilize the conversion to diamane if the top surface was functionalized with roughly 25-30% of the C atoms having C-H (or C-F) bonds. We undertook this set of calculations because we grow AB-stacked graphene on metal substrates by chemical vapor deposition. Calculations have also been reported for the conversion of few layer hexagonal boron nitride (hBN) in the AA' stacking configuration (the typical layer stacking of h-BN), again by the atoms in the top and bottom surfaces of the multilayer hBN bonding to H or F, to a wurtzite-type BN (in an ultrathin layer). This is (also) of interest because the cubic phase of BN is the more stable phase and bulk wurtzite cannot readily be made. These methods of converting layered graphene or layered h-BN to allotropes having tetrahedral bonding represent a new pathway for such a conversion, to be contrasted with conversion by high pressure, or synthesis by plasma-enhanced chemical vapor deposition. But can they be realized experimentally? I discussed the diamane(s) 4 years ago in a perspectives article [2], and we are now pursuing making these types of materials in the CMCM at UNIST.

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**KOREAN GRAPHENE SOCIETY** 

# Raman Spectroscopy for Surface Scientific Investigation of 2-Dimensional Crystals

#### Prof. Sunmin Ryu

# Pohang University of Science and Technology (POSTECH), Republic of Korea

#### Short biography:

Dr. Sunmin Ryu is an associate professor of chemistry at POSTECH (Pohang University of Science and Technology) in Korea. He obtained his B.S. (1998), M.Sc. (2000), and Ph.D. (2005) in Chemistry at Seoul National University. He worked as a postdoctoral researcher at Korea Research Institute of Standards and Science (KRISS) until 2006 and then at the chemistry department of Columbia University until 2009. He started teaching at the department of applied chemistry at Kyung Hee University as an assistant professor and moved to POSTECH in 2014. His research group (http://sunryu.postech.ac.kr) is currently pursuing surface scientific investigation of two dimensional materials using various optical spectroscopy and scanning probe methods.

#### Abstract:

Raman spectroscopy has proven to be a versatile analytical tool in graphene research because of the varying spectral features for different thickness, stacking, defect density, charge density (n), mechanical strain ( $\epsilon$ ), temperature, etc. Such multimodal sensitivity, however, turns into difficulty when multiple unknown variables are to be determined simultaneously. Despite the strain-sensitivity of the Raman G and 2D modes, for example, optical characterization of native strain in graphene on silica substrates has been hampered by excess charges interfering with both modes. In this talk, I will show that the effects of strain and charges in graphene can be optically separated from each other by correlation analysis of the two modes, enabling simple quantification of both. Additionally, the change in the electronic structure of graphene caused by the van der Waals interaction with hexagonal boron nitride (hBN) substrates can also be optically determined. Employing the proposed analysis, I will address our recent findings on important surface scientific issues of graphene such as structural deformation caused by substrates and thermal perturbation, interfacial charge transfer, and molecular intercalation through graphene-substrate interface.

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# Supramolecular approaches to 2-D materials: from complex structures to sophisticated functions

# Prof. Paolo Samori ISIS, University of Strasbourg & CNRS, France

# Short biography:

Paolo Samorì (Imola, Italy, 1971) is Distinguished Professor (PRCE) and director of the Institut de Science et d'Ingénierie Supramoléculaires (ISIS) of the Université de Strasbourg (UdS) where he is also head of the Nanochemistry Laboratory. He is also fellow of the Royal Society of Chemistry (FRSC), fellow of the European Academy of Sciences (EURASC), member of the Academia Europaea (MAE) and junior member of the Institut Universitaire de France (IUF). He obtained a Laurea (master's degree) in Industrial Chemistry at University of Bologna in 1995. In 2000 he received his PhD in Chemistry from the Humboldt University of Berlin (Prof. J. P. Rabe). He was permanent research scientist at Istituto per la Sintesi Organica e la Fotoreattività of the Consiglio Nazionale delle Ricerche of Bologna from 2001 til 2008, and Visiting Professor at ISIS from 2003 till 2008. He has published >230 papers on applications of scanning probe microscopies beyond imaging, hierarchical self-assembly of hybrid architectures at surfaces, supramolecular electronics, and the fabrication of organic-based nanodevices. His work has been awarded various prizes, including the Young Scientist Awards at E-MRS (1998) and MRS (2000) as well as the IUPAC Prize for Young Chemists (2001), the "Vincenzo Caglioti" Award (2006) granted by the Accademia Nazionale dei Lincei (Italy), the "Nicolò Copernico" Award (2009) for his discoveries in the field of nanoscience and nanotechnology, the "Guy Ourisson" Prize (2010) of the Cercle Gutenberg (France), the ERC Starting Grant (2010) and the CNRS Silver Medal (2012). He is member of the advisory boards of Advanced Materials, Small, ChemPhysChem and ChemPlusChem (Wiley-VCH), Chemical Society Reviews, Chemical Communications, Journal of Materials Chemistry and Nanoscale (RSC).

### Abstract:

Supramolecularly engineered hybrid materials containing graphene are key multifunctional systems for applications in (opto)electronics and energy. The tuning of their dynamic physical and chemical properties can be achieved via tailored covalent or non-covalent interactions with ad-hoc macromolecules.[1] My lecture will review our recent findings on:

(i) The harnessing of the yield of exfoliation of graphene in liquid media by mastering the supramolecular approach via the combination with suitably designed functional molecules possessing high affinity for the graphene sur-face, leading ultimately to the bottom-up formation of optically responsive graphene based nanocomposites for electronics. [2]

(ii) The tuning of the graphene properties by combining them with organic semiconductors as a strategy both to promote hole mobility in an otherwise electron transporting material and to exploit the tunable ionization energy of thermally annealed liquid phase exfoliated graphene to modulate the transport regime as well as to fabricate new memory devices.[3]

(iii) The bottom-up formation of graphene based 3D covalent frameworks with tunable intersheet distance, exhibiting large specific surface areas leading to high performance in supercapacitors.[4]

Our approaches provide a glimpse on the chemist's toolbox to generate multifunctional graphene based nanocomposites with ad-hoc properties to address societal needs in electronics and energy applications.

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# **Two Dimensional Materials for Si Technology**

# Dr. Hyeon-Jin Shin Samsung Advanced Institute of Technology, Samsung Electronics, Republic of Korea

# Short biography:

Hyeon-Jin Shin, Ph.D. is a Research Master at Samsung Advanced Institute of Technology (SAIT), Samsung Electronics. She is charge of Graphene and 2D material-based research. Her primary interests are synthesis of Graphene and 2D materials for electronic, opto electronic, and energy applications. She has published over 50 articles, which received over 3000 citations (h-index of 23). She also has been filled over 190 US patents.

She received his B.S. degree in Chemistry from Kongju National University (2000). She received M.S. degree in Chemistry from Korea University (2002). She joined SAIT (2002) where she developed ultra-low-dielectric materials for back-end of lines based on silsesquoxane polymer. Since 2007, she has been researched nano-carbon based materials such as Carbon Nano Tube and Graphene for electronic device. During working at SAIT, she received Ph.D in Sungkyunkwan Advanced Institute of Nano Technology from Sungkyunkwan University (2010). Her thesis topic was electronic structure modulations of nano-carbon based materials by chemical doping for electronic device.

### Abstract:

Two dimensional (2D) materials, such as, Graphene, h-BN, and Transition Metal Di-chalcogenides (TMD's), studied intensively due to their extraordinary properties, such as, flexibility, transparency, high carrier mobilities, high responsivity, and some of chemical inertness. Based on their properties, many potential applications in the fields of electronics, opto-electronics, energy applications, and composites were proposed and demonstrated.

We have been investigated 2D materials for Si technology, especially, as interface materials due to their unique chemical properties and atomically thin nature. For example, Graphene has been suggested as a promising material for future interconnects between devices because of its electrical and chemical properties. [1] Also, they've been considered as good candidates for interface materials between metals and Si to reduce the Schottky barrier heights and contact resistances at source and drain, which is one of the most critical issues in the scaling down of Si devices. [2]

In this talk, we will discuss the possibility of Graphene and other 2D layered materials for interconnects and contact resistance reducer in Si technology. We will also cover other potential applications based on 2D materials' unique properties. In addition, we will briefly share our views on the requirements and the current status about the commercialization of these new materials.

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# **Growth and Application of Hexagonal Boron Nitride**

# Prof. Hyeon Suk Shin Ulsan National Institute of Science and Technology, Republic of Korea

### Short biography:

Hyeon Suk Shin is an associate professor at Department of Chemistry and Department of Energy Engineering, Ulsan National Institute of Science and Technology (UNIST), Korea. He received his PhD from Department of Chemistry at POSTECH in 2002. After working as a postdoctoral fellow at University of Cambridge, UK and subsequently as a research Professor at POSTECH, he joined UNIST in 2008. He received Creative Knowledge Award (Minster Award by Ministry of Science, ICT, and Future Planning) in 2015, Outstanding Researcher Award (Materials Chemistry Division, KCS) in 2015, the Faculty of the Year award of UNIST in 2014, and the Minister award of Ministry of Knowledge Economy, Korea in 2012. His current research is focused on 2D materials, including graphene, h-BN, transition metal dichalcogenides, and their heterostructures, and their applications for electrocatalysts and (opto) electronic devices.

#### Abstract:

Large-scale growth of high-quality hexagonal boron nitride (h-BN) has been a challenge in two-dimensional (2D)-material-based electronics. In this presentation, I demonstrate wafer-scale and wrinkle-free epitaxial growth of multi-layer h-BN on a sapphire substrate by using high-temperature and low-pressure chemical vapour deposition. Microscopic and spectroscopic investigations and theoretical calculations reveal that synthesized h-BN has a single rotational orientation with Bernal stacking order. A facile method for transferring h-BN onto other target substrates were developed, which provides the opportunity for using h-BN as a substrate in practical electronic circuits. A graphene field effect transistor fabricated on our h-BN sheets shows highly improved carrier mobility, because the ultra-flatness of the h-BN surface can reduce the substrate-induced degradation of the carrier mobility of 2D materials. Moreover, I show some more applications of h-BN for a shell layer capping Au nanoparticles in surface-enhance Raman scattering and an encapsulation (or passivation) layer to protect unstable transition metal dichalcogenides (TMDs).



### **Towards industrial graphene production**

# Dr. Kenneth Teo AIXTRON Ltd, United Kingdom

# Short biography:

Dr. Ken Teo is the Director of Nanoinstruments at AIXTRON. He holds a BE (Elec) from the University of Canterbury, MBA and PhD from the University of Cambridge. In 2005, Dr. Teo founded and ran Nanoinstruments Ltd (UK), which manufactures innovative Graphene and Carbon Nanotube growth equipment for research and industry; in 2007, Nanoinstruments was acquired by AIXTRON where Dr. Teo is presently responsible for driving the Graphene and Carbon Nanotube business and technology. His previous roles include Lecturer in Electrical Engineering at University of Cambridge, Fellow/Director of Studies at Christ's College Cambridge, Royal Academy of Engineering Research Fellow, Fellow of the Institute of Nanotechnology, Project Engineer at Defence Material Organisation (Singapore) and Product Engineer at PDL Holdings (NZ). Dr. Teo has extensive experience in the area of carbon nanomaterials and is the author/co-author of 150 papers and 10 patents/applications in this area.

### Abstract:

The unique properties of graphene make it a prominent candidate for a wide range of applications. These applications can be found in different industries like microelectronics or aeronautics. To become an established material into the industrial world, graphene needs to show its technological benefits as well as be available in large quantities at a competitive cost.

In this presentation, we will discuss the strategies for industrial production and integration of thin-film and bulk graphene. We will also show some of the most promising applications of graphene.



# 2D Carbon Materials by Conversion of Organic Monolayers

# Prof. Andrey Turchanin Friedrich Schiller University Jena, Germany

# Short biography:

Andrey Turchanin studied physics and materials science at the National University of Science and Technology, Moscow (Ph.D. 1999). In 2000 he moved to the University of Karlsruhe with an Alexander von Humboldt Fellowship. 2004-2014 he joined the Faculty of Physics at the University of Bielefeld where he completed his habilitation in 2010. In 2012 Turchanin was awarded a Heisenberg Fellowship of the German Research Foundation (DFG) and in 2013 the Bernhard-Heß-Prize of the University of Regensburg for his research in the field of emerging 2D materials. In 2014 he became a professor of physical chemistry at the Friedrich Schiller University Jena, where he is leading the group of "Applied Physical Chemistry & Molecular Nanotechnology". His current research interests are focused on the materials science of 2D materials and their applications in electronics, optoelectronics and nanobiotechnology.

### Abstract:

Electron irradiation of aromatic self-assembled monolayers results in their conversion into a novel 2D carbon material – Carbon Nanomembranes (CNMs) – molecular nanosheets with a thickness of ~ 1 nm [1]. Similar to graphene or other atomically thin 2D materials (hBN, MoS2, etc.) CNMs possess mechanical integrity and therefore can be transferred from their original substrates onto new substrates, fabricated as suspended sheets or stacked into van der Waals heterostructures with the precise control over their thickness. Their physical and chemical properties can be tuned via an appropriate choice of molecular precursors or their post modification, providing a flexible platform for engineering of functional 2D materials. In this talk, some examples of these materials and their device applications will be presented. These examples include: (i) biofunctional and photoactive CNMs [2]; (ii) growth of graphene with adjusted electronic and structural properties [3-4]; (iii) chemical functionalization of graphene and MoS2 field-effect devices [5]; (iv) nanolithography of free-standing atomically thin sheets [6]; (v) novel hybrid 0D/2D layered materials [7].

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[6] C. Brand et. al, Nat. Nanotech. 10 (2015) 845-848.

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Schematic representation of the conversion of aromatic self-assembled monolayers into CNMs and graphene