Symposium F
Graphene and Other Emerging 2D-layered Nanomaterials: Synthesis, Properties and Potential Applications

ABSTRACTS

Session F-1 - General Physical and Chemical Properties

F-1:KL **2D Materials: Standards, Science, and Technology**
A.H. CASTRO NETO, National University of Singapore, Singapore

The field of 2D materials is one of the fastest growing fields in Physics. The scientific developments in the last few months have shown that one can reach unprecedent control of the electronic properties of these materials. Nevertheless, the technological development of new applications has been stalled by the lack of clear standards for characterization and processing. I will review the evolution in this exciting field and discuss what lies ahead.

F-1:L01 **Optoelectronic Properties of Transition Metal Dichalcogenides**
L. BALICAS, **D. RHODES**, National High Magnetic Field Lab, Florida State University, Tallahassee, FL, USA

Here, we will discuss a broad range of optoelectronic properties measured from transition metal dichalcogenides, ranging from photoconductivity, photovoltaic response, a density of carriers induced metal-insulator transition, new functionalities associated with the intrinsic Schottky barrier at the level of the electrical contacts, and the electronic structure at the Fermi level of semi metallic systems. For example, photo-transistors based upon a few atomic layers of these systems can show extremely high photo-responsivities with reasonable although optimizable photo-responsive times while PN-junctions can display photovoltaic responses approaching 12 to 14 %. Through a scaling analysis of the conductivity as a function of the temperature we show that the metal insulator transition observed in these systems is ascribable to a second-order phase-transition driven by electronic correlations. We also show that in ambipolar systems a gate voltage can modulate the relative size of the Schottky barriers, which upon illumination leads to a novel type of optoelectronic switch. Finally, we show that the electronic structure at the Fermi level of semi metallic compounds cannot be captured by band structure calculations.

F-1:IL02 **Role of Edge Geometry and Chemistry in Electronic and Magnetic Structures of Nanographenes**
TOSHIAKI ENOKI, Tokyo Institute of Technology, Tokyo, Japan

The electronic structures of graphene nanostructures depend crucially on their edge geometries, in which zigzag and armchair edges are two fundamental components. In armchair-edged nanostructures, electron wave interference gives rise to the formation of a standing wave, resulting in energetically stabilizing these nanostructures. In contrast, spin-polarized nonbonding edge states are created at zigzag edges, giving the electronic, magnetic and chemical activities to zigzag-edged nanostructures. The electronic structures depend also on how edges are terminated with foreign chemical species. We have investigated the electronic structures of graphene nanostructures using STM/STS and AFM observations together with DFT calculations. Monohydrogenated and dihydrogenated linear zigzag edges were found to possess edge states well localized and less localized in the vicinity of zigzag edges, respectively. In contrast, an edge consisting of a mixture of mono- and di-hydrogenated carbon atoms has no edge state, instead it is subjected to the formation of standing wave similar to armchair-edged nanostructures. Oxygen-terminated linear zigzag edges have less localized edge state owing to charge transfer from edge carbon atoms to oxygen atoms.

F-1:IL03 **Raman Spectroscopy of Graphene-related Materials**
C. CASIRAGHI, School of Chemistry, University of Manchester, UK

Raman Spectroscopy is the most used technique to probe the properties of graphene and related materials. In this talk I will give an overview on the use of this technique to identify graphene, and to probe amount of defects, doping, strain and superlattices [1-5]. I will also show that Raman spectroscopy is able to identify ultra-narrow and atomically precise graphene nanoribbons [6-8].
1 Ferrari et al. (2006), Phys. Rev. Lett. 97, 18740; 2 Pisana et al (2007), Nature Materials, 6, 198; 3 Zabel et al (2011), Nano Letters, 12, 617; 4 Eckmann et al (2012), Nano Letters, 12, 3925; 5 Eckmann et al (2013), Nano Letters, 13, 5242; 6 Narita et al (2014), Nature Chemistry, 6, 126; 7 Narita et al (2014), ACS Nano, 8, 11622; 8 Verzhbitskiy et al, submitted

F-1:L05 **Understanding the Structural Evolution of Graphene Heated with Electrical Current in Air**
IN-SANG YANG, MINKYUNG CHOI, Ewha University, Korea; JANGYUP SON, JONGIN CHA, JONGILL HONG, Yonsei University, Korea; HEECHAE CHOI, SEUNGCHUL KIM, KWANG-RYEOL LEE, KIST, KOREA; SANG JIN KIM, BYUNG HEE HONG, Seoul National University, Korea; SANPON VANTASIN, ICHIRO TANABE, YUKIHIRO OZAKI, Kwansei Gakuin University, Japan

In various applications of graphene, understanding the mechanism of the changes of the graphene in harsh environments should precede many activities in tamed conditions. In this presentation, we report the unusual structural evolution of microbridge graphene in air near the electrical current-breakdown limit. In-situ micro-Raman study revealed expensive equipments. We, propose here Soft processing of functionalized Graphenes at ambient conditions. The Soft processing provides number of advantages which includes (a) simple reaction set up,(b) at ambient conditions, (c) simple procedure and (d)less operating costs and wastes. In the present study, we have utilized “Submerged Liquid Plasma [SLP]” and “Electrocemical Exfoliation[ECE] methods. SLP methods resulted the direct synthesis of Nitrogen functionalized Graphene Nano-sheets from Graphene suspension and/or Graphite electrode in acetonitrile liquids.[1,2] Products contains few layers (< 5) Graphene nanosheets. Unsaturated or high energy functional group (e.g. C＝C, C＝N and C≡N) have formed in the products. We could confirm those functionalized Graphenes are electrochemically active. Using pencil rods instead of Graphite rods we have also succeeded to prepare the Nano-clay/Graphene hybrids by this SLP methods [3]. Reduction and functionalization of Graphene oxides [2] and Synthesis of Graphene/Au Hybrids [4] also realized by SLP. In the ECE, graphite anode is exfoliated electrochemically by H_2O_2-NaOH[5,6] or Glycine-H_2SO_4[7] aqueous solutions under ambient temperature and pressure,for 5-30 min with +1-+5 volt, into 3-6 layers Graphene Nanosheets[GNs]. Those conditions are much milder than those reported before using other chemicals like ionic liquids and/or H_2SO_4-$KMnO_4$,etc.,because O_2^{2-} ions or ionic complex like Glycine-HSO_4^- would assist the exfoliation of graphite layers. Our products:GNs suspended in solutions can be transformed in the 2nd step in the same container using $BrCH_2CN$/dioxane into N-FG, further into Au-Hybridized N-FG by the sonification with Au nanoparticles. We have confirmed the excellent catalytic performance of those hybrids[5,6] It should be noted that Soft Processing can directly produce “Graphene Ink”;Graphenes dispersed in various liquids, under mild conditions.

*1) J. Mater Chem A,(2014) **2,** 3332; 2) Scientific Reports, **4**(2014), 04395; 3) Carbon,**78** (2014),446; 4) J. Mater Chem A, 2015, **3**,3035-30435) Sci. Rep. **4** ,4237 (2014); 6) Nanoscale (2014) **6,**12758; 7) Adv. Funct. Mater. 2015, **25,** 298-305.*

F-3:L09 **How the Nanostructure of Layered Titanates Influences the Mechanical Properties**

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Layered materials find many applications in electronics, coatings or lubrication. One example are titanium oxide nanosheets, which can be obtained through the exfoliation of protonated layered titanates with lepidocrocite-like structures (H1.07Ti1.73O4). Layered titanates are constituted by negatively charged oxide layers that can be intercalated by a wide range of cations. Here, they were functionalized with linear alkylamines. The amines are weak bases that react with the protons of the layered host. This reaction is the driving force for molecular intercalation and swelling of the layered structure. Small Angle X-ray Scattering was performed to investigate the dynamic swelling and exfoliation behavior of these layered systems in aqueous solution. The ratios of amine to layered host and the carbon chain length were varied. Layered compounds find an important application in lubrication. The mechanical tests of the new solid lubricants helped to establish a relationship between the nanostructure of the layered material and its lubricating properties. Pin-on-disc tests showed low friction coefficients (from $\mu \approx 0.05$). The results suggest that the chemical modification decreased the electrostatic interactions between the titania planes, making the layered compound easily deformable.

F-3:L11 **Lessons learned from Carbon Nanotube Growth can be applied to Graphene: 100% Reproducibility and Improved Graphene Quality by Preheating Precursor Gases using Thermal Chemical Vapor Deposition**

G.D. NESSIM, Bar Ilan University, Department of Chemistry and Center for Nanotechnology and Advanced Materials, Ramat Gan, Israel

Years ago, we showed how preheating precursor gases helped to synthesize carbon nanotubes (CNTs) at lower temperature and with increased crystallinity. We now demonstrate how by applying a similar technique, we synthesized high quality, few-layer graphene at reduced temperature with full reproducibility on nickel thin films. Raman spectroscopy showed that the graphene films synthesized using gas preheating exhibited 50% less defects compared to those obtained without gas preheating. However, the most important outcome is that all experiments performed using gas preheating were fully reproducible, while less than 15% of the experiments performed without gas preheating led to graphene of only acceptable quality. Gas chromatography/mass spectrometry (GC-MS) of the preheated gases showed an increased formation of polycyclic aromatic hydrocarbons (PAHs), as it did in our previous studies on CNTs. >From the results obtained, we postulated a new growth mechanism that fits previous density functional theory (DFT) reports of hydrocarbon stability on a nickel surface. The results presented are an important step in the direction of graphene synthesis at lower temperatures with full reproducibility. In this presentation, we will focus on the parallels between CNT and graphene synthesis.

F-3:L12 **One-pot Electrochemical Exfoliation and Functionalization of Graphene Sheets**

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Graphene can be prepared in large scale by the classical Hummers' method and subsequent chemical reduction. A major drawback of this widely used method is that it is a multi-steps process that requires aggressive chemicals. On the other hand, graphene sheets can be also prepared by electrochemical exfoliation of graphite. In this work, graphene was produced by electrochemical exfoliation of graphite in aqueous electrolyte. Acidic and neutral electrolyte were used. With this procedure, graphene sheets with low oxygen content is produced. Graphene sheets were also functionalized with specific organic molecules during the electrochemical exfoliation process by using appropriate reagants and experimental conditions. The resulting materials were characterized by several techniques such as Fourier transform infrared, X-ray photoelectron and Raman spectroscopy, thermogravimetric analysis, elemental analysis, electronic conductivity measurements and electrochemical techniques.

F-3:L14 **Selective Modification of as-grown CVD Graphene on Cu by Oxygen Plasma for Flexible Electronics Applications**

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The global market of flexible electronics is currently reaching the $4 billion mark and is estimated to become $13 billion by 2020. However, the market still has a high demand for new flexible materials. Graphene and other 2D materials offer an exciting route for the realization of flexible devices – they are light, strong, and possess high bending endurance. Electronic and optical properties of these materials can be tailored by functionalization with chemical elements such as fluorine, hydrogen, or oxygen[1]. In the present work we utilise plasma treatment[2] as a novel technique for