

# Thursday Afternoon Poster Sessions

## Graphene and Related Materials Focus Topic

Room: Central Hall - Session GR-ThP

## Graphene and Related Materials Poster Session

### GR-ThP1 Using Raman Spectroscopy and X-ray Photoelectron Spectroscopy to Guide the Development of Graphene-Based Materials, *T.S. Nunney, M.H. Wall*, Thermo Fisher Scientific, UK

The potential uses of graphene are currently being explored by the materials science community. Its immediate potential as a transparent conductive electrode for the microelectronics industry is already being exploited; the unique combination of electronic, chemical and structural properties exhibited by graphene are already having a significant impact on the development of thin film transistors and touch-screen devices. Further applications for the development of graphene-based catalytic systems and molecular sensors are also underway. Good materials characterization is required at all steps in the creation of new graphene devices, from guiding the initial graphene synthesis and transfer to the desired substrate, to chemical modification and analysis of the finished device. In this presentation we will show how a multi-technique approach using both Raman spectroscopy and XPS can address the challenges posed at these steps. Raman microscopy is an analytical technique that is well suited for the characterization of graphene. It is a vibrational spectroscopy that is very sensitive to small changes in the geometric structure of a molecule and its environment. This sensitivity allows Raman to be used as a probe for a number of properties important to a specific graphene samples, such as layer thickness. X-ray photoelectron spectroscopy (XPS) is ideally suited to the determination of the surface chemistry and the way in which that chemistry changes in the surface and near-surface region. The technique provides quantitative elemental and chemical information with extremely high surface specificity and is ideal for comprehensively and quantitatively characterising the elemental composition and chemical bonding states at surfaces and interfaces. This approach will be illustrated by examples from graphene samples created by mechanical exfoliation, chemical reduction and CVD methods.

### GR-ThP2 Ionic Strength Effects on Graphene Oxide Nanosheets and Fluorescence Quenching of ssDNA Aptamers, *M.Y. Lin, Y.P. Lu*, National Applied Research Laboratories, Taiwan, Republic of China

Recently, graphene has attracted considerable attention because of its remarkable electronics, its mechanical and optical properties, and its unique single-atom thickness and two-dimensional sp<sup>2</sup> carbon networking material [1]. Graphene oxide (GO) presents excellent properties in high water dispersibility, capabilities of bridging biomolecules on the surface, and acts as a highly efficient fluorescent quencher material [2]. Single-stranded DNA (ssDNA) has been reported to bind on a graphene surface through non-covalent  $\pi$ - $\pi$  interactions, whereas double-stranded DNA (dsDNA) cannot bind on graphene surfaces. Aptamers are synthetic, single-stranded DNA or RNA molecules that fold into unique 3D structures, and bind specifically to a wide range of molecules such as chemicals, proteins, and drugs. Therefore, aptamer-based GO biosensors have been developed for detecting various targets [3-5]. Ionic strength and pH are closely related to biochemical reactions and interactions between aptamer and targets. However, less studies have been reported to the ionic strength and pH effects on GO and interaction between GO and DNA [6]. Phosphate buffer saline (PBS) was commonly used as isotonic reagent for protein solution. In this study, the fluorescence intensity of GO significantly decreasing with increasing concentration of PBS. In addition, increasing quenching effect was found in the group with PBS as solvent for GO-aptamer interaction. The reported report are of importance in further applications of GO in biosensors and biochemical reactions.

**GR-ThP3 Isotope Effect in the Graphene Deuteration Kinetics, *A. Nefedov***, Karlsruhe Institute of Technology, Germany, *A. Paris*, Interdisciplinary Laboratory for Computational Science, FBK-CMM, Italy, *N. Verbitsky*, Moscow State University, Russia, *Y. Wang*, Nagoya University, Japan, *A. Fedorov, D. Haberer*, IFW Dresden, Germany, *M. Oehzelt*, Helmholtz-Zentrum Berlin für Materialien und Energie, Germany, *L. Petaccia*, ELETTRA Synchrotron Light Laboratory, Italy, *D. Usachov*, St. Petersburg State University, Russia, *D. Vyalikh*, Technical University Dresden, Germany, *H. Sachdev*, Max-Planck-Institute for Polymer Research, Germany, *Ch. Wöll*, Karlsruhe Institute of Technology, Germany, *M. Knupfer, B. Buechner*, IFW Dresden, Germany, *L. Calliari*, Interdisciplinary Laboratory for Computational Science, FBK-CMM, Italy, *L. Yashina*, Moscow State University, Russia, *S. Irle*, Nagoya University, Japan, *A. Grueneis*, University of Vienna, Austria

Kinetic isotope effects (KIE) are important phenomena in physical chemistry and have been investigated for a long time in relation to activation and rate of chemical reactions. KIE are easily observable for the hydrogen isotopes due to the large relative mass difference and have been studied for example in hydrogen transfer in organic chemistry such as acid and base catalysis, enzyme reactions and catalytic decomposition.

Here we present results of time-dependent x-ray photoemission spectroscopy (XPS) in order to investigate the kinetics of the hydrogenation/deuteration reaction of graphene. A pristine monolayer graphene was prepared under ultrahigh vacuum conditions by chemical vapor deposition on Ni(111) thin films epitaxial grown on W(110). Then a monolayer of Au was intercalated into the interface between Ni and graphene, making the latter quasi free-standing. The graphene layer was then exposed to hydrogen or deuterium atomic gas beams, obtained by thermal cracking in a tungsten capillary at T=3000 K. The maximum surface coverage was obtained after several hydrogenation or deuteration steps of different time. After each step XPS of the C1s line was performed in order to measure H/C and D/C ratios. After reaching saturation, the electronic structure of the hydrogenated and deuterated layer was analyzed by near-edge X-ray adsorption fine structure (NEXAFS) spectroscopy at the carbon K-edge.

We have observed a strong inverse KIE for the hydrogenation/deuteration reaction leading to substantially faster adsorption and higher maximum D/C ratios as compared to H/C (D/C~35% vs. H/C~25%). These results can be understood by the fact that atomic D has a lower chemisorption barrier and a higher desorption barrier. Quantum chemical calculations and molecular dynamics simulations can reproduce the experimental trends and reveal the contribution of the constituent chemisorption, reaction and associative desorption processes of H(D) atoms onto graphene. The reported case of a strong inverse KIE is an extremely unusual case and is important for isotope specific chemical reactivity in organic molecules and functionalized graphene.

### GR-ThP4 Graphene Nanoribbons Electronic Structure Modulations, *N.B. Le, L.M. Woods*, University of South Florida

Graphene nanoribbons are studied using density functional theory methods. Various factors are considered as different ways to tailor their electronic structure properties. These include folding, types of edges, and extended defects. Of particular importance is the van der Waals interaction in the folded structures with closed edges. These are taken into account via a DFT-D2 method, which is a pragmatic approach based on a semi-empirical pairwise correction to the conventional Kohn-Sham energy. Equilibrium distances, stacking patterns, and geometry configurations upon folding are determined. The energy gaps, band structure changes, and characteristic energies are also obtained for nanoribbons with armchair and zigzag edges when folded and/or extended defects present. Our results attest to the many possible methods that can be explored to modify the properties of these graphitic nanostructures.

### GR-ThP5 Effects of an Interfacial Water Layer on Protein Adsorption to Graphene Sheets on Solid Substrates, *K. Yamazaki, T. Ogino*, Yokohama National University, Japan

Graphene is two-dimensional honeycomb lattice of carbon atoms. It is well known that the graphene sheets are strongly affected by their environment because of its extremely small thickness and large specific surface area. There are many reports about the chemical doping into graphene films induced by the support substrate and charge transfer. In this paper, we studied control of chemical doping to graphene flakes through the substrate engineering and using Raman spectroscopy. We also demonstrate the selective adsorption of biomolecules toward the unique sensors.

We used sapphire surfaces for support substrates of graphene. After the acid treatment, the sapphire surfaces are terminated with hydroxyl groups, which work as adsorption sites of water molecules. We deposited graphene flakes on sapphire (0001) and (1-102) surfaces by mechanical exfoliation method. To reveal influence of a water layer at the interface between the sapphire surface and graphene, we annealed the sapphire surfaces at 700°C for 1h just before graphene deposition and compared the G-peak and 2D-peak positions on Raman spectra.

We observed shift of G-peak and 2D-peak positions to wave numbers lower than those on the hydrophilic sapphire (0001) substrate. But, in the case of (1-102) surfaces, the G-peak and 2D-peak positions did not shift upon annealing. The peak positions are almost same among the annealed (0001), the annealed (1-102), and the on-annealed (1-102) surfaces. It is well known that formation of water layers on sapphire surfaces depends on plane directions<sup>1)</sup>. A (0001) surface has more bound water molecules than the other faces. Therefore, the peak shifts were induced by the amount of water layer that existed at the interfaces between the sapphire surfaces and the graphene flakes. We demonstrated the adsorption of protein molecules on these surfaces. We used ferritin molecules, which are negatively charged for adsorption on the graphene flakes. We observed well-correlated adsorption pattern with the G-peak and the 2D-peak positions of Raman spectra. Ferritin molecules were preferentially adsorbed to the graphene flakes that were supported by hydrophilic (0001) surfaces. Amount of adsorbed ferritin molecules to the other surfaces were dramatically small. These different adsorption behaviors directly show the effect of chemical doping from the interfacial water molecules to the graphene flakes.

In summary, we demonstrated control of protein adsorption to the graphene surfaces by using the suitable support substrates for graphene towards the biosensors without any labeling to substrates and targets.

1) T. Tsukamoto et al. *J. Phys. Chem. C* (2012) 116, 4732-4737.

**GR-ThP6 Layer Dependent Growth of Pentacene on Epitaxial Graphene.** *W. Jung, D.-H. Oh, J. Lee, B.G. Shin, C.-Y. Park, J.R. Ahn,* Sungkyunkwan University, Republic of Korea

Graphene have showed promising performance as electrodes of organic devices such as organic transistors, light-emitting diodes, and photovoltaic solar cells. In particular, among various organic materials of graphene-based organic devices, pentacene has been regarded as one of promising organic materials because of its high mobility, chemical stability, and compatibility with a low-temperature silicon processing. In the development of graphene-based organic devices, it is thus important to understand an interaction of pentacene with graphene. In this study, we focused on how the growth of pentacene depends on an interaction between graphene and a substrate. Epitaxial graphene grown on a 6H-SiC(0001) surface was used as a pristine graphene because zeroth-layer graphene, called a buffer layer, and monolayer graphene have the same graphene structure but zeroth-layer graphene, which bonds strongly to a SiC substrate, has different electronic properties from monolayer graphene. We have studied how graphene grows differently at room temperature on monolayer graphene in comparison to zeroth-layer graphene using scanning tunneling microscopy and first principles calculations. On the zeroth-layer graphene, pentacene was adsorbed on specific sites with three different orientations but did not show a long-range order. In contrast to zeroth-layer graphene, pentacene forms a two dimensional ordered structure on monolayer graphene. The orientation of pentacene in the ordered structure was determined by the zigzag direction of the edge structure of monolayer graphene. The short-range and long-range ordering on zeroth-layer and monolayer graphene, respectively, was understood by different energetics of pentacene on zeroth-layer from monolayer graphene, where a total energy of pentacene on graphene was calculated by first principles calculations.

**GR-ThP7 Optical Properties and Surface Radicals Content of Graphene Decorated with Metal Nanoparticles.** *M.A. Bratescu, T. Ueno, O. Takai, N. Saito,* Nagoya University, Japan

Recently the increased interest of carbon-based materials decorated with metal nanoparticles (NPs) for sensors and energy applications has generated a huge development of the research in this field. Unfortunately, the immediate use of graphene in sensors or fuel cells applications is not yet possible since more effort must be performed to understand how NPs decorated graphene affect the selectivity and the sensitivity of the sensor and how surface radicals content influences the fuel cell performance.

In the present research, we developed a simple synthesis method of metal NPs on graphene layer and we investigated the optical properties and the surface radicals content of this system. Graphene layer have been produced on Cu foils by CVD method and transferred on different substrates to be characterized.<sup>1</sup> The metal NPs were synthesized on the graphene layer using a well-established method used in our laboratory, based on a solution plasma process (SPP) system<sup>2,3</sup>, directly on the Cu foil covered with the graphene layer. The metal NPs were synthesized on the graphene surface

through the reduction of the metal ion from the salt to the neutral form, or by the erosion of the electrode material. The graphene layer decorated with metal NPs was transferred on glass, Si/SiO<sub>2</sub> substrate, Kapton scotch and carbon/Cu(Mo) grid surfaces to be analyzed by UV-vis spectroscopy, micro-Raman mapping spectroscopy, electron spin resonance (ESR), and transmission electron microscope (TEM) techniques, respectively. Micro-Raman mapping of 2D band at 2700 cm<sup>-1</sup> (two photon double resonance band) which has higher intensity than G band at 1583 cm<sup>-1</sup> (interlayer vibrations band of sp<sup>2</sup>-hybridized carbon) shows the quality and the uniformity of graphene layer on substrates. An enhanced Raman spectrum of graphene was detected when gold or silver NPs were adsorbed on the surface. The UV-vis spectra of graphene layer decorated with gold NPs which was transferred on a glass substrate, shows a weak absorption band of surface plasmon resonance, at 520 nm, due to the thin layer of NPs on surface. The adsorbed metal NPs on graphene layers was observed by high resolution TEM analysis. The surface radicals content will be examined using ESR through calibration with stable free radicals compounds. The dependence of the surface radicals content of the graphene decorated with NPs on the size and shape of NPs will be discussed.

1 Xuesong Li, et al., *Science* **2009**, 324, 1312.

2 Takai, O. *Pure Appl. Chem.* **2008**, 80, 2003 – 2011.

3 M.A. Bratescu, et al., *J. Phys. Chem.*, **2011**, 115, 24569.

**GR-ThP8 Electronic Structure of MoS<sub>2</sub> Monolayers on Copper.** *Q. Ma, D.Z. Sun, W.H. Lu,* University of California Riverside, *D. Le, M. Amanpour,* University of Central Florida, *J. Mann, S. Bobek,* University of California Riverside, *T. Raman,* University of Central Florida, *L. Bartels,* University of California Riverside

MoS<sub>2</sub> is a very promising material for photocatalysis and it has many current applications in catalytic hydrodesulfurization. Similar to graphene, it is a layered material. Recently, it has been shown that it transitions from an 1.6 eV indirect bandgap to a 1.9 eV direct bandgap semiconductor when reduced to a monolayer. Important for its usefulness e.g. in catalytic hydrogen splitting, is not only its bandgap but also its band alignment when deposited on different substrates. Using CVD grown MoS<sub>2</sub> on a copper surface, we use XPS to ascertain the identity of the material and the nature of its internal bonding when on this metallic substrate. Spectroscopy also shows a metal induced reduction of the bandgap to 1.5 eV and a strong signature of n-type doping through the underlayer. Density Functional Theory calculation corroborate this finding and provide a microscopic understanding of the bandgap and alignment depending on the number of MoS<sub>2</sub> layers and the presence of any substrate.

**GR-ThP9 Dry Transfer of Graphene to Organic and Inorganic Substrates.** *E.H. Lock, S. Hernandez, S.G. Walton, M. Laskoski, S.P. Mulvaney, P.E. Sheehan, W.K. Lee, T.J. Anderson, F.J. Bezares, V.D. Wheeler, F.J. Kub, J.D. Caldwell, K.D. Hobart, B.N. Feygelson, L.O. Nyakiti, R.L. Myers-Ward, C.R. Eddy, Jr., D.K. Gaskill,* Naval Research Laboratory

High quality graphene transfer is critical for preserving the extraordinary graphene properties. In this paper we report our progress on transferring graphene from different growth substrates. Our method is a dry transfer approach which exploits an azide linker molecule to establish a covalent bond to graphene. Successful transfer is observed when the adhesion between the graphene and the transfer substrate is higher than the graphene/growth substrate adhesion. Thus, this transfer technique provides a novel alternative route of graphene transfer. This work was supported by the Naval Research Laboratory Base Program.

**GR-ThP10 Controllable Assembly of Aromatic Molecules on a Surface via Diels-Alder Reaction: A Carbon Source for Graphene.** *C.L. Henderson, J. Baltazar, H. Sojoudi, J. Kowalik, S. Graham, L. Tolbert,* Georgia Institute of Technology

Graphene is of tremendous interest based on its electronic properties, such as mobilities  $\geq 200,000$  cm<sup>2</sup>/V-s, as well as a very high thermal conductivity. Furthermore, graphene is one atom thick, making it a perfect substitute for silicon in small high performance devices. Graphene formation by directed chemical synthesis, utilizing intelligently designed precursors that can be converted thermally or chemically to graphene and graphene nanostructures with interesting electronic properties are of great interest. We successfully synthesized a silyl derivative of a maleimide that allows: (1) self-assembly to produce a controllable aromatic monolayer on a CMOS compatible surface, and (2) the ability to perform a reverse Diels-Alder reaction that allows us to obtain the carbonaceous starting material of interest in the surface for further thermal or chemical consolidation. Graphene so produced was analyzed and identified by Raman spectroscopy and other methods.

**GR-ThP11 Unique Electronic Mixing between Iron Phthalocyanine and Graphene\***, *D.B. Dougherty*, *A.A. Sandin*, North Carolina State University, *A. Calzolari*, CNR-NANO, Istituto Nanoscienze, Italy, *M. Buongiorno-Nardelli*, North Carolina State University, *A. Al-Mahboob*, *J.T. Sadowski*, Brookhaven National Laboratory, *J.E. Rowe*, North Carolina State University

Graphene is an ideal material for long-range spin transport due to its very high carrier mobilities and long spin lifetimes due to minimal spin-orbit scattering effects [1]. Direct spin injection into graphene has been demonstrated, but is inefficient due to the well-known bulk conductivity mismatch between graphene and a magnetic metal electrode. The standard approach to overcome this effect is to engineer a tunneling barrier at the interface to provide an effectively large spin-dependent interface resistance. However, for insulating tunnel barrier growth on graphene, great care must be taken to avoid 3D islanding due to the typically weak interactions between the substrate and deposited species [1].

An alternate approach is to consider the use of planar organic materials as interfacial layers to enhance spin injection into graphene. Since weak intermolecular interactions can be comparable in size to molecule-substrate interactions for planar aromatics on graphene, high quality film growth is more likely. We have studied the growth of iron phthalocyanine (FePc), a chemically-robust paramagnet, on epitaxial graphene on SiC(0001) by a combination of STM, STS, LEED, UPS, and density functional theory calculations. Our calculations predict an energetically weak interaction between graphene and FePc that nevertheless leads to a unique spin-dependent electronic mixing. A non-dispersive hybrid interface state is created along with a small gap in one spin sub-band while the graphene band structure is essentially unchanged in the other sub-band. STM and LEED indicate a highly-ordered, flat-lying monolayer film of FePc on epitaxial graphene and UPS measurements compare favorably with the calculated occupied density of states. STS studies of the ordered monolayer show an unoccupied state for FePc on graphene that is *not present* for FePc on graphite. We interpret this unique state as evidence for the predicted spin-polarized interface state.

\*This work was funded by the NSF Phase I Center for Chemical Innovation: Center for Molecular Spintronics (CHE-0943975).

[1] Han et al., *J. Magn. Mag. Mat.* 324, 369 (2012).

**GR-ThP13 Raman Spectroscopy of Double Layer Graphene FETs: Mapping the Misorientation Angle**, *Z. Razavi Hesabi*, *C. Joiner*, *T. Roy*, *E.M. Vogel*, Georgia Institute of Technology

Double layer graphene, a stacked two dimensional honeycomb lattice of carbon atoms, is a very promising candidate for nanoelectronic applications. The electrical properties, such as high carrier mobility and tunable band gap, have been theoretically predicted to be highly dependent on the misorientation angle between the two layers. For industrial applications, the ability to map and control the misorientation angle between layers will be necessary to achieve the desirable electrical properties of the graphene devices. This work presents a method for systematically determining the misorientation between two layers on a wafer scale through the use of Raman spectroscopy.

# Authors Index

**Bold page numbers indicate the presenter**

## — A —

Ahn, J.R.: GR-ThP6, 2  
Al-Mahboob, A.: GR-ThP11, 3  
Amanpour, M.: GR-ThP8, 2  
Anderson, T.J.: GR-ThP9, 2

## — B —

Baltazar, J.: GR-ThP10, 2  
Bartels, L.: GR-ThP8, 2  
Bezarez, F.J.: GR-ThP9, 2  
Bobek, S.: GR-ThP8, 2  
Bratescu, M.A.: GR-ThP7, 2  
Buechner, B.: GR-ThP3, 1  
Buongiorno-Nardelli, M.: GR-ThP11, 3

## — C —

Caldwell, J.D.: GR-ThP9, 2  
Calliari, L.: GR-ThP3, 1  
Calzolari, A.: GR-ThP11, 3

## — D —

Dougherty, D.B.: GR-ThP11, 3

## — E —

Eddy, Jr., C.R.: GR-ThP9, 2

## — F —

Fedorov, A.: GR-ThP3, 1  
Feygelson, B.N.: GR-ThP9, 2

## — G —

Gaskill, D.K.: GR-ThP9, 2  
Graham, S.: GR-ThP10, 2  
Grueneis, A.: GR-ThP3, 1

## — H —

Haberer, D.: GR-ThP3, 1  
Henderson, C.L.: GR-ThP10, 2  
Hernandez, S.: GR-ThP9, 2  
Hobart, K.D.: GR-ThP9, 2

## — I —

Irle, S.: GR-ThP3, 1

## — J —

Joiner, C.: GR-ThP13, 3  
Jung, W.: GR-ThP6, 2

## — K —

Knupfer, M.: GR-ThP3, 1  
Kowalik, J.: GR-ThP10, 2  
Kub, F.J.: GR-ThP9, 2

## — L —

Laskoski, M.: GR-ThP9, 2  
Le, D.: GR-ThP8, 2  
Le, N.B.: GR-ThP4, 1  
Lee, J.: GR-ThP6, 2  
Lee, W.K.: GR-ThP9, 2  
Lin, M.Y.: GR-ThP2, 1  
Lock, E.H.: GR-ThP9, 2  
Lu, W.H.: GR-ThP8, 2  
Lu, Y.P.: GR-ThP2, 1

## — M —

Ma, Q.: GR-ThP8, 2  
Mann, J.: GR-ThP8, 2  
Mulvaney, S.P.: GR-ThP9, 2  
Myers-Ward, R.L.: GR-ThP9, 2

## — N —

Nefedov, A.: GR-ThP3, 1  
Nunney, T.S.: GR-ThP1, 1  
Nyakiti, L.O.: GR-ThP9, 2

## — O —

Oehzelt, M.: GR-ThP3, 1  
Ogino, T.: GR-ThP5, 1  
Oh, D.-H.: GR-ThP6, 2

## — P —

Paris, A.: GR-ThP3, 1  
Park, C.-Y.: GR-ThP6, 2

Petaccia, L.: GR-ThP3, 1

## — R —

Raman, T.: GR-ThP8, 2  
Razavi Hesabi, Z.: GR-ThP13, 3  
Rowe, J.E.: GR-ThP11, 3  
Roy, T.: GR-ThP13, 3

## — S —

Sachdev, H.: GR-ThP3, 1  
Sadowski, J.T.: GR-ThP11, 3  
Saito, N.: GR-ThP7, 2  
Sandin, A.A.: GR-ThP11, 3  
Sheehan, P.E.: GR-ThP9, 2  
Shin, B.G.: GR-ThP6, 2  
Sojoudi, H.: GR-ThP10, 2  
Sun, D.Z.: GR-ThP8, 2

## — T —

Takai, O.: GR-ThP7, 2  
Tolbert, L.: GR-ThP10, 2

## — U —

Ueno, T.: GR-ThP7, 2  
Usachov, D.: GR-ThP3, 1

## — V —

Verbitsky, N.: GR-ThP3, 1  
Vogel, E.M.: GR-ThP13, 3  
Vyalikh, D.: GR-ThP3, 1

## — W —

Wall, M.H.: GR-ThP1, 1  
Walton, S.G.: GR-ThP9, 2  
Wang, Y.: GR-ThP3, 1  
Wheeler, V.D.: GR-ThP9, 2  
Wöll, Ch.: GR-ThP3, 1  
Woods, L.M.: GR-ThP4, 1

## — Y —

Yamazaki, K.: GR-ThP5, 1  
Yashina, L.: GR-ThP3, 1