Monday Afternoon, October 18, 2010

Graphene Focus Topic
Room: Brazos - Session GR+NS-MoA

Graphene: Chemical Reactions
Moderator: T. Seyller, Universität Erlangen, Germany

2:00pm **GR+NS-MoA1 Chemical Interactions during Thermal Reduction of Multilayered Graphene Oxide**, *M. Acik*, University of Texas at Dallas, *C. Mattevi*, Imperial College London, *C. Gong, G. Lee, K.J. Cho,* University of Texas at Dallas, *M. Chhowalla,* Imperial College London, *Y.J. Chabal*, University of Texas at Dallas

2:20pm **GR+NS-MoA2 Non-bonding State formed Around Defects on HOPG**, *J. Nakamura*, *T. Kondo, J. Oh, D. Guo, Y. Honma, T. Machida*, University of Tsukuba, Japan
Understanding the interface interaction between metal nano-clusters and carbon supports composed of graphite materials is one of the most important needs in the development of carbon related-catalysts. We have studied the carbon support effects on the electrocatalysts for fuel cell as well as the interface interaction using model catalysts of Pt-deposited highly oriented pyrolytic graphite (HOPG) by IETS-STS-STM, TPD, and molecular/atomic beam technique. Here, we report the formation of non-bonding state in the vicinity of defects on the HOPG surface. We have measured STS spectra at many different points in the vicinity of the point defect. STS spectra were very different depending on the point of the measurement. In the directions perpendicular to short zigzag edges at the point defect, STS peaks appear near the Fermi level, suggesting the edge state or non-bonding state. The non-bonding state propagates 3-4 nanometers away from the defect with three-fold symmetry. No such a STS peak was observed near the point defect in the other directions. We thus constructed a STS map showing the distribution of the non-bonding state. We also observed spatial "*oscillations*" in the *dI/dV* peak position and the intensity. The oscillations have been explained as electron-electron interaction or electron-hole interaction. We currently consider that the non-bonding state is responsible for the chemical reactivity such as adsorption of atom, molecules, and clusters.

References

1. E. Yoo, J. Nakamura, et al., Nano Letters 9 (2009) 2255.

2. T. Kondo, J. Nakamura, et al., Phys. Rev. B 80 (2009) 233408.

3. J. Oh, T. Kondo, J. Nakamura, et al., J. Phys. Chem. Lett. 1 (2010) 463.

4. T. Kondo, J. Nakamura, et al.,J. Phys. Chem. C 112 (2008) 15607.

2:40pm **GR+NS-MoA3 Opto-electronic Properties of Solution Processable Chemically Derived Graphene Oxide**, *M. Chhowalla*, Rutgers University **INVITED**
A solution based method that allows uniform and controllable deposition of reduced graphene oxide thin films with thicknesses ranging from a single monolayer up to several layers over large areas will be described. Transport of carriers in reduced GO is limited by the structural disorder. However, conductivity of 10^5 S/m and mobilities of ~ 10 cm^2/V-s are sufficiently large for applications where inexpensive and moderate performance electronics are required. The oxidation treatment during synthesis of GO creates sp^3 C-O sites where oxygen atoms are bonded in the form of various functional groups. GO is therefore a two dimensional network of sp^2 and sp^3 bonded atoms, in contrast to an ideal graphene sheet which consists of 100% sp^2 carbon atoms. This unique atomic and electronic structure of GO, consisting of variable sp^2/sp^3 fraction, opens up possibilities for new functionalities. The most notable difference between GO and mechanically exfoliated graphene is the opto-electronic properties arising from the presence of finite band gap. In particular, the photoluminescence can be tuned from blue to green emission. The atomic and electronic structure along with tunable photoluminescence of graphene oxide at various degrees of reduction will be described.

3:40pm **GR+NS-MoA6 Structural Evolution during the Reduction of Chemically Derived Graphene Oxide**, *V.B. Shenoy*, Brown University / Rhode Island Hospital
The excellent electrical, optical and mechanical properties of graphene have driven the search to find methods for its

large-scale production, but established procedures (such as mechanical exfoliation or chemical vapour deposition) are not

ideal for the manufacture of processable graphene sheets. An alternative method is the reduction of graphene oxide, a

material that shares the same atomically thin structural framework as graphene, but bears oxygen-containing functional

groups. Here we use molecular dynamics simulations to study the atomistic structure of progressively reduced graphene

oxide. The chemical changes of oxygen-containing functional groups on the annealing of graphene oxide are elucidated and

the simulations reveal the formation of highly stable carbonyl and ether groups that hinder its complete reduction to

graphene. The calculations are supported by infrared and X-ray photoelectron spectroscopy measurements. Finally, more

effective reduction treatments to improve the reduction of graphene oxide are proposed [1].

[1] Akbar Bagri, Cecilia Mattevi, Muge Acik, Yves J. Chabal, Manish Chhowalla and

Vivek B. Shenoy, Nature Chemistry (in press, 2010).

4:00pm **GR+NS-MoA7 Perfluorographane: Synthesis and Properties**, *J.S. Burgess*, National Research Council, *J.A. Robinson,* Naval Research Laboratory, *M. Zalalutdinov,* SFA, inc, *K. Perkins, P.M. Campbell, E. Snow, B.H. Houston, J.W. Baldwin*, Naval Research Laboratory
Graphene was grown by CVD on a copper substrate. The as-grown samples and samples transferred to silicon on insulator (SOI) and SiO$_2$ substrates were then exposed to XeF$_2$ gas resulting in fluorination of the graphene sheets. The samples were characterized using XPS and Raman spectroscopies. XPS showed maximum fluorine content in the graphene of 20 % for the graphene on copper and 50 % on SOI. The marked difference is owed to the etching of the silicon layer on the SOI substrate, allowing exposure of the underside of the graphene sheet to the XeF$_2$ gas and fluorination of both sides of the graphene sheet. The fluorine was removed from the film using both thermal and chemical (hydrazine reduction) methods. Chemical, mechanical, and electrical properties of these materials will also be discussed.

4:20pm **GR+NS-MoA8 Stability and Activity of Pt Nanoclusters Supported on Graphene Monolayers on Ru(0001)**, *O. Alves, C. Lorenz, H.E. Hoster, R.J. Behm*, Ulm University, Germany
Being an atomically thin half-metal and exhibiting moiré-type nm-scale superstructure, graphene monolayers supported on metal single crystals [1-3] can serve as a template for the growth of ordered arrays of nanosized metallic (electro-)catalyst particles. These particles, which are fabricated by simple metal vapour deposition in ultrahigh vacuum [4-6] and comprise monodispersed Pt clusters seeded on the grahene monolayer on Ru(0001), were found to nucleate preferentially at a unique region in the Moiré unit cell and displayed heights of 1-5 atomic layers and lateral diameters within the range 1-4 nm. The size selectivity of the Pt nanoclusters, jointly with their self-assembled array, assign them as interest and promising system for (electro-)catalytic model studies.

We will report on the activity and stability either of a single graphene monolayer or of the Pt clusters. The graphene layers and the cluster arrays are prepared in ultrahigh vacuum, whilst the potential-dependent reaction studies are measured in a wall-jet type flow cell sited in an electrochemical pre-chamber attached to the main UHV system. Cluster arrays with different total Pt coverages and cluster size distributions were tested as electrodes for elementary reactions as hydrogen evolution/oxidation, CO oxidation, or O2 reduction. According to STM analyses before and after the electrochemical tests, we discuss in how far the stabilities of clusters of various sizes can be rationalized in terms of reaction conditions and applied potentials. The general electrochemical behaviour of the Pt cluster arrays will be discussed in comparison to bulk Pt. As a main (electro-)catalytic result, we find a surprisingly high activity for hydrogen evolution.

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[2] S. Marchini et al., Phys. Rev. B 76, 075429 (2007).

[3] Coraux et al., Nano Lett. 8, 565 (2008).

[4] N'Diaye et al., New J. Phys. 11, 103045 (2009).

[5] Yi Pan et al., Appl. Phys. Lett. 95, 093106 (2009).

[6] K. Donner and P. Jakob, J. Chem. Phys. 131 164701 (2009).

4:40pm GR+NS-MoA9 Writing Graphene Electronics Into Chemically Modified Graphene, *P.E. Sheehan, Z. Wei,* Naval Research Laboratory, *D. Wang,* Georgia Institute of Technology, *W.-K. Lee, M.K. Yakes,* Naval Research Laboratory, *W.P. King,* University of Illinois at Urbana-Champaign, *E. Riedo,* Georgia Institute of Technology, *A.R. Laracuente, J.A. Robinson, S.G. Walton*, Naval Research Laboratory

Graphene is the most likely carbon-based successor material for CMOS electronics. Recently, interest in chemically modified graphene (CMG) has risen for producing large-scale flexible conductors and for its potential to open an electronic gap in graphene structures. We have developed a means to tune the topographical and electrical properties of several CMGs with nanoscopic resolution by local thermal processing with an AFM tip. Heating converts the CMG back towards graphene with nanoscale resolution. Nanostructures of one CMG, graphene oxide, show an increase in conductivity up to four orders of magnitude as compared to pristine material. Variably conductive graphene nanoribbons have been produced in a single step that is clean, rapid and reliable. Critically, the "carbon skeleton" is continuous across the CMG/graphene boundary. Recent work suggests that ribbons formed this way may be superior to ribbons that were cut.

5:00pm GR+NS-MoA10 Oxygen Etching of Graphene on Ir and Ru, *E. Starodub, N.C. Bartelt, K.F. McCarty*, Sandia National Laboratories

We have used low-energy electron microscopy to investigate how graphene is removed from Ru(0001) and Ir(111) by reaction with oxygen. We find two mechanisms on Ru(0001). At short times, oxygen reacts with carbon monomers on the surrounding Ru surface, decreasing their concentration below the equilibrium value. This undersaturation causes a flux of carbon from graphene to the monomer gas. In this initial mechanism, graphene is etched at a rate that is given precisely by the same nonlinear dependence on carbon monomer concentration that governs growth. Thus, during both growth and etching, carbon attaches and detaches to graphene as clusters of several carbon atoms. At later times, etching accelerates. We present evidence that this process involves intercalated oxygen, which destabilizes graphene. On Ir, this mechanism creates observable holes. It also occurs most quickly near wrinkles in the graphene islands, depends on the orientation of the graphene with respect to the Ir substrate, and, in contrast to the first mechanism, can increase the density of carbon monomers. We also observe that both layers of bilayer graphene islands on Ir etch together, not sequentially. Work at Sandia was supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U. S. Department of Energy under Contract No. DE-AC04-94AL85000.

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