

Wednesday Afternoon, November 11, 2009

Nanometer-scale Science and Technology

Room: L - Session NS-WeA

Nanotubes - Electronics and Functionalization

Moderator: E.I. Altman, Yale University

2:00pm **NS-WeA1 Chemical and Biological Functionalization of Carbon Nanotubes**, S.S. Wong, SUNY Stony Brook and Brookhaven National Laboratory **INVITED**

In the first part of the talk, we update covalent chemical strategies commonly used for the focused functionalization of single walled carbon nanotube (SWNT) surfaces. In particular, we explore advances in the formation of nanotube derivatives that essentially maintain and even enhance their performance metrics after precise chemical modification. We especially highlight molecular insights (and corresponding correlation with properties) into the binding of functional moieties onto carbon nanotube surfaces. Controllable chemical functionalization suggests that the unique optical, electronic and mechanical properties of SWNTs can be much more readily tuned than ever before with key implications for the generation of truly functional nanoscale working devices.

In the second part of the talk, we investigate the biocompatibility, specificity, and activity of a ligand-receptor-protein system covalently bound to oxidized SWNTs as a model proof-of-concept for employing such SWNTs as biosensors. In the third part of the talk, we describe a novel SWNT-based tumor-targeted drug delivery system (DDS) which has been developed, consisting of a functionalized SWNT linked to tumor-targeting modules as well as prodrug modules. There are three key features of this nanoscale DDS: (a) use of functionalized SWNTs as a biocompatible platform for the delivery of therapeutic drugs or diagnostics, (b) conjugation of prodrug modules of an anticancer agent (taxoid with a cleavable linker) that is activated to its cytotoxic form inside the tumor cells upon internalization and *in situ* drug release, and (c) attachment of tumor-recognition modules (biotin and a spacer) to the nanotube surface.

2:40pm **NS-WeA3 Carbon Nanotube-Based Biosensor for Detection of MicroRNA**, V.Z. Poenitzsch, T. Booker, A. Clark, N. Nitin, Southwest Research Institute

Carbon nanotubes (CNT) – field effect transistor (FET) sensors are promising candidates for label-free, sensitive detection of biological molecules. In this study, we have developed a proof-of-concept biosensor for the detection of microRNA (miRNA) in which designer oligonucleotide (ODN) probes covalently attached to CNTs serve as a highly specific molecular recognition function and FET device that translate changes in CNT electric properties serves as a signal transduction function. MicroRNA-21 was selected in this study as a model miRNA molecule. Basic research has shown that over-expression of miRNA-21 is associated with development of leukemia, breast cancer and prostate cancer. CNTs were functionalized with designer oligonucleotide (ODN) probes having conformational structures and sequences that are highly specific for hybridization with target miRNA-21. Conjugation of ODN probes with CNTs was examined using zeta potential surface charge measurements, fluorescent labeling, and atomic force and scanning electron microscopies. Biological activity and hybridization of immobilized ODN probe with miRNA 21 were further monitored using quartz crystal monitor measurements and fluorescent labeling. Subsequently, CNT-ODN network films were deposited using dielectrophoretic technique. Thin and wide metal electrodes that allow for increased Schottky contact areas were fabricated by magnetron sputter deposition of metals for source and drain electrodes using a shadow mask and tilted angle. Electrical impedance spectroscopy and current-gate voltage measurements were used to study the effect of ODN attachment and hybridization event on CNT electronic properties. In this presentation, we will discuss the fabrication and characterization of the developed sensor along with challenges of meeting the required specificity and sensitivity for real-world applications such as *in vitro* medical diagnostics.

3:00pm **NS-WeA4 Effect of Carboxy-Functionalized Multiwall Carbon Nanotubes on the Conductivity Performance of Tricomponent LBL Films**, X. Gu, D.B. Knorr, University of Washington, G. Wang, Tongji University, China, R.M. Overney, University of Washington

Lithium batteries offer high energy density, a flexible, lightweight design and longer lifespan than competing battery technologies. Poly(ethylene oxide) (PEO) is a polymeric material which has extensively been adopted as an electrolyte component in solid state rechargeable lithium batteries. PEO exhibits good complexation properties and high flexibility and retains good

mechanical stability at temperatures up to its melting point. Recently, a layer-by-layer (LBL) technique was introduced to prepare battery thin films. This method offers fine control and tunability of material properties and architecture at the nanometer scale, and is a relatively simple method to implement. Films were fabricated by alternating deposition of PEO and poly(acrylic acid) (PAA) layers from aqueous solutions. However, PEO/PAA layer-by-layer (LBL) films exhibit low ionic conductivity when dry, and thus the inhibition of PEO crystallinity alone is not sufficient to improve the ionic conductivity. To achieve more enhanced conductivity in PEO films, various methods have been introduced. The exceptional electronic properties of carbon nanotubes (CNTs) have prompted intensive studies of PEO/CNTs composites. However, at present, these composites have shown only a moderate conductivity enhancement. LBL assembly has shown for other polymers to allow for excellent control of thickness and composition and diminished phase segregation compared with other methods of construction of CNT composites.

In this work, we demonstrate that fabrication of LBL films with carbon nanotubes is possible in a complex tricomponent film of PEO, PAA, and carboxy-functionalized multiwall carbon nanotubes (MWNT-COOH). Successful incorporation of carbon nanotubes layers and excellent surface coverage was observed by AFM topography images and lateral force microscopy. Our system displayed fast growth of LBL assembled films in the deposition process with film thicknesses reaching 1 mm for films composed of 10 cycles of layers. Rapid growth of the films affords fast preparation of PEO/PAA LBL films with incorporated carbon nanotubes which is essential for battery application. Impedance measurements and electrostatic force microscopy (EFM) were used to analyze the differences in ionic conductivity before and after incorporation of MWNT-COOH in to PEO/PAA assemblies. As expected, conductivity improved with the incorporation of the MWNT-COOH treatment. To this end we also employed thermomechanical characterization techniques including shear-modulation force microscopy (SM-FM) to investigate molecular mobility in the tricomponent systems.

4:00pm **NS-WeA7 Graphene Chemistry**, R.C. Haddon, University of California, Riverside **INVITED**

We have recently demonstrated the high density functionalization of epitaxial graphene wafers with nitrophenyl groups. [Bekyarova, E.; Itkis, M. E.; Ramesh, P.; Berger, C.; Sprinkle, M.; de Heer, W. A.; Haddon, R. C., Chemical Modification of Epitaxial Graphene: Spontaneous Grafting of Aryl Groups. *J. Am. Chem. Soc.* **2009**, 131, 1336-1337] The chemical formation of covalent carbon-carbon bonds involving the basal plane carbon atoms offers a versatile approach to the control of the electronic properties of graphene; the transformation of the carbon centres from sp^2 to sp^3 introduces a barrier to electron flow by saturating the carbon atoms and opening a band gap which allows the generation of insulating and semiconducting regions in graphene wafers. This prototype chemistry when applied to carbon nanotubes allowed both covalent and ionic modification of the electronic structure; covalent attachment of functional groups was shown to transform the metallic single-walled carbon nanotubes into semiconductors.

In this talk I will discuss our recent results on the electronic and magnetic properties of chemically modified graphene and its relationship to single walled carbon nanotubes.

4:40pm **NS-WeA9 Spectroscopic Study of the Electron Transport Suppression Phenomenon in Carbon Nanotubes Field-Effect Transistors**, F. Lapointe, Université de Montréal, Canada, C.M. Aguirre, École Polytechnique de Montréal, Canada, P.L. Lévesque, Université de Montréal, Canada, P. Desjardins, École Polytechnique de Montréal, Canada, R. Martel, Université de Montréal, Canada

Carbon nanotubes field-effect transistors (CNFETs) were thought to exhibit exclusive hole transport under ambient atmosphere because of the high potential barrier to electron injection at the electrode-nanotube contact interface. This hypothesis did not hold against a set of new experiments we devised, where ambipolar transport was observed under ambient atmosphere by merely changing the nature of the dielectric used as the substrate. Using controlled atmosphere experiments, we pinpointed the phenomenon responsible for the inhibition of electron transport in CNFETs, and showed it is mainly caused by an electrochemical charge transfer to the aqueous oxygen redox couple. We postulated that intermediates of the redox charge transfer are stabilised at the SiO_2 surface as charged oxygen species leaving a net negative charge at the surface and thus screening the applied gate potential. Focusing on a spectroscopic investigation, we tested the existence of these species. Thermodesorption spectroscopy experiments coupled to reflection-absorption infrared spectroscopy under high vacuum

conditions were used to probe the dielectric interface of CNFETs operated under ambient atmosphere prior to insertion into the experimental chamber.

5:00pm **NS-WeA10 Direction Control of Carbon Nanotube Growth on Corrugated Patterned SiO₂ using Casimir Force and its Application to High Current FET.** *K. Matsumoto, S. Iwasaki, T. Kamimura, K. Inoue, T. Kishimoto, Y. Ohno, K. Mehashi*, Osaka University, Japan

The direction control of the carbon nanotube(CNT) growth on the SiO₂/Si substrate was first succeeded in at our will using the attractive force of "Casimir force" which concentrates at the upper edge of the corrugated pattern. By applying the present technique for CNT FET, the drain current was enhanced more than 10 times than the conventional CNT FET because of the effective bridging of CNTs between the source and drain electrodes.

The process for the direction control of CNT growth is as follows; The SiO₂/Si substrate was processed to form the corrugated pattern using the electron beam lithography and CF₄ plasma etching. The planed width and spacing of the corrugated pattern is 100nm and its depth is 40nm. After the formation of the corrugated pattern, 0.5nm thick Co catalyst is formed at the end of the corrugated pattern by the photolithography. Then the sample was set in the thermal CVD to grow the CNT at 800C. The CNTs which started to grow from the catalyst are attracted to the upper edge of the corrugated pattern and follow the direction of the corrugated pattern. So, the direction of the CNT growth can be controlled at our will only by forming the corrugated pattern on SiO₂/Si substrate.

The direction controlled growth of CNT on the corrugated pattern was confirmed by SEM observation. The CNT grew more than 7mm straightforward along with the corrugated pattern. Furthermore, it becomes clear that the CNT follows not on the bottom edge but at the upper edge of the corrugated pattern by the SEM observation from the tilted angle. In order to clarify the reason why CNT is attracted to the upper edge of the corrugated pattern, the Casimir force, which is a kind of van der Waals force, along with the cross section of the corrugated pattern was calculated. In the calculated results, the density of the Casimir force shows the highest peaks near the upper edges of the corrugated pattern. Because of these highest peaks of the Casimir force density, it becomes clear that the carbon nanotube is attracted to the upper edge of the corrugated pattern and grow following the direction of the pattern.

By applying this technology, FET with the direction controlled CNT channel was fabricated and its electrical property was examined. From the SEM observation, it was confirmed 8 CNTs were bridged between the source and drain electrodes. The dependence of the drain current on the gate bias at room temperature was examined, and the drain current reached as high as 2.5mA at V_g = -5V, which is about ten times higher than the conventional CNT FET. This is because a number of CNTs bridged between the source and drain electrodes can work as channels of FET.

5:40pm **NS-WeA12 Field Emission Properties of Wall-Number-Selected Carbon Nanotube Arrays.** *D.H. Lee, S.O. Kim, W.J. Lee*, KAIST, Republic of Korea

The wall-number-selective growth of vertical carbon nanotube (CNT) arrays is achieved by the combination of block copolymer lithography and plasma enhanced chemical vapor deposition of CNTs, and the field emission properties were measured as a function of wall-number, length, density and doping concentration of CNT arrays. Block copolymer lithography is an attractive nanopatterning method for generating a uniform catalyst particle arrays for carbon nanotube growth. In this work, highly uniform nanopatterned iron catalyst arrays were prepared by tilted evaporation through block copolymer nanotemplates, and the sub-nanometer-scale tunability of catalyst particles enabled the excellent controllability of the wall-number and density of the CNT arrays. Moreover, the use of ammonia in the growth of CNT arrays ensured that the CNTs were nitrogen doped, and the doping concentration of nitrogen can be adjusted by controlling the flow rate of ammonia gas. Substitution of a carbon in a CNT wall with a more electron-rich nitrogen atom provided additional electrons and enhanced the conductivity of the nanotubes. With the excellent controllability of CNT arrays, we investigated the field emission properties of the grown CNT arrays. Wall-number, length, density and the doping concentration of CNT arrays were changed independently to investigate their effect on the field emission properties. Therefore, superior field emission performance of CNT arrays was acquired by controlling the physical and chemical parameters of CNT arrays.

Authors Index

Bold page numbers indicate the presenter

— **A** —

Aguirre, C.M.: NS-WeA9, 1

— **B** —

Booker, T.: NS-WeA3, 1

— **C** —

Clark, A.: NS-WeA3, 1

— **D** —

Desjardins, P.: NS-WeA9, 1

— **G** —

Gu, X.: NS-WeA4, **1**

— **H** —

Haddon, R.C.: NS-WeA7, **1**

— **I** —

Inoue, K.: NS-WeA10, 2

Iwasaki, S.: NS-WeA10, 2

— **K** —

Kamimura, T.: NS-WeA10, 2

Kim, S.O.: NS-WeA12, 2

Kishimoto, T.: NS-WeA10, 2

Knorr, D.B.: NS-WeA4, 1

— **L** —

Lapointe, F.: NS-WeA9, **1**

Lee, D.H.: NS-WeA12, **2**

Lee, W.J.: NS-WeA12, 2

Lévesque, P.L.: NS-WeA9, 1

— **M** —

Martel, R.: NS-WeA9, 1

Matsumoto, K.: NS-WeA10, **2**

Mehashi, K.: NS-WeA10, 2

— **N** —

Nitin, N.: NS-WeA3, 1

— **O** —

Ohno, Y.: NS-WeA10, 2

Overney, R.M.: NS-WeA4, 1

— **P** —

Poenitzsch, V.Z.: NS-WeA3, **1**

— **W** —

Wang, G.: NS-WeA4, 1

Wong, S.S.: NS-WeA1, **1**