8:30 AM *NM01.01.01

Addressing the Limitations on the Efficient Synthesis of Single Wall Carbon Nanotube Forests

Don Futaba; National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Over two decades have passed since the discovery and structural elucidation of the carbon nanotube (CNT), and the application of its unique set of properties have yet to reach industry. One of the primary missions of our Center is to do work to promote the development of a CNT industry. We do this through the advancement in high efficiency, high purity, low cost mass production as well as processing technologies to carry the CNT material into functional materials and forms. With this as our motivation, this presentation will provide an overview of our recent progress in the synthesis and application of single-wall carbon nanotubes (SWCNTs) highlighting various milestones and their role in understanding SWCNT synthesis and industrial development.

9:00 AM

Control Multilayer Nucleation in Asymmetric Bilayer Graphene Growth

Haozhe Wang, Wei Sun Leong, Pin-chun Shen and Jing Kong; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Bilayer graphene has attracted significant attention from researchers because it holds interesting physical properties such as tunable bandgap, von Hove singularities, etc.[1] Moreover, comparing with monolayer graphene, bilayer graphene is anticipated to have better conductivity and mechanical robustness. Therefore, enable the reliable synthesis of bilayer graphene is very important both for fundamental research and potential applications. Among many synthesis methods, chemical vapor deposition (CVD) is most promising due to its scalability and economic efficiency. In order to break self-limited growth on copper substrate (which gives only monolayer graphene), asymmetric growth is needed to supply carbon atom at graphene/copper interface.[2] Nonetheless, nucleation mechanism at graphene/copper interface is still not well understood. As a result, continuous bilayer graphene is normally grown with multilayer regions (layer number ≥3), which limited the application of this approach.

Here, we report a simple method to control multilayer graphene nucleation by oxidizing copper substrate before the CVD process. Further investigation reveals that copper surface oxygen play double roles on multilayer nucleation. Slightly increasing oxygen level from initial copper foil firstly increase multilayer nucleation density. On the other hand, abundant surface oxygen helps constricting multilayer nuclei, meanwhile, accelerating bilayer growth. After surface oxidation, pure polycrystalline bilayer graphene flake can be obtained as large as 100um in diameter. Moreover, we found surface oxygen is effective on both Bernal bilayer graphene growth and random twist graphene growth. Surprisingly, for bilayer graphene growth using Ni-Cu alloy, effect of surface oxygen is also observed by confirming a more uniform bilayer film. In addition, XPS and XRD studies implies that the decrease of nuclei density is relative to formation of Cu2O on the surface indicating there exists a limit for surface oxygen level.

In summary, we developed a novel but simple pathway to control multilayer graphene nucleating during bilayer graphene growth. This method opens a door to explore the nucleation mechanism at graphene/copper interface and, to produce high quality, low cost, large area bilayer graphene.

References:

9:15 AM

How the Microstructure of the Alumina Layer Can Lead to Full Growth Reproducibility of Millimeter-Tall Forests of Carbon Nanotubes

Gilbert D. Nessim and Eti Teblum; Bar Ilan University, Ramat Gan, Israel.

The chemical vapor deposition (CVD) synthesis of millimeter-tall carbon nanotube (CNT) forests using iron catalyst on alumina underlayer has now...
become established. Many studies have elucidated the role of precursor gases and water vapor, catalyst coarsening, and possible models for growth termination. However, it is well-known to the practitioners that the synthesis is not always fully reproducible and can be affected by tiny amounts of carbon or water vapor present in the reactor, by laboratory temperature or humidity, etc. To solve this problem, we assumed that the key issue is the interface between the catalyst and the alumina underlayer and the subsurface diffusion of iron (catalyst) into alumina (underlayer). We focused on tuning the microstructure of the alumina underlayer and studied how different microstructures would affect CNT growth, keeping all the other process and material parameters constant. We postulated that the issue was the grain size of the underlayer and thus the amount of grain boundaries. Since the iron catalyst subsurface diffusion into the alumina underlayer will strongly be affected by the amount of grain boundaries, with grain boundary diffusion being much faster compared to lattice diffusion, we decided to control the grain size of the alumina. Using electron-beam evaporation, we prepared samples where we heated the substrate at 350 °C during deposition and slowly evaporated the alumina with the goal to obtain large grains in order to minimize the amount of grain boundaries. We also prepared samples where we evaporated the alumina at a fast rate to obtain small grains and to maximize the amount of grain boundaries. We used as reference samples where the alumina was e-beam evaporated at an average rate. After synthesis, we consistently observed tall CNT carpets on the samples where the substrate was heated during deposition and the alumina was evaporated at a low rate. However, the CNT carpets obtained on the other samples were significantly shorter and their height distribution was very wide. We will show statistical distributions of the CNT height obtained from multiple samples. To prove the mechanisms involved in this finding we analyzed the catalyst morphology after annealing of the different samples using atomic force microscopy (AFM) and high-resolution scanning electron microscopy (HRSEM). Using a focused ion beam (FIB), we prepared a lamella for each type of sample and analyzed the alumina nanostructure, iron subsurface diffusion, and overall composition using HRTEM. This study shows how critical it is to consider the microstructure of the alumina underlayer and how by appropriately tuning the deposition conditions, we can obtain samples that will consistently grow millimeter-tall forests of CNTs.

9:30 AM BREAK

10:00 AM *NM01.01.04 Growth of Single-Walled Carbon Nanotubes with Controlled Structure Jin Zhang: Center for Nanochemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing, China.

Carbon nanotubes (CNT) had received broad attention in the past decades due to its dramatic physical and chemical performance of individual tubes and became a powerful candidate of future star materials. As synthesis determined the future, in this talk, I will focus on the controlled growth of SWNTs arrays with ultra-high density, high ratio semiconductor properties and special chiral angles. For the SWNTs arrays with ultra-high density, Trojan catalysts (released from substrate) was developed and the density can be as high as 150 tubes/µm. For the SWNTs arrays with semiconducting properties, oxides catalysts with oxygen vacancy, bimetal catalysts and uniform MoC catalyst were used to grow semiconducting SWNTs arrays and ratio of semiconductor tubes can be higher than 95%. For the SWNTs arrays with special chiral angles, it is based on a consideration of nanotube/catalyst interfacial thermodynamics determined by symmetry, and the kinetic growth rates set by the number of kinks. Using these strategies, horizontally aligned metallic ((12, 6), abundance >90%) and semiconducting (8, 4, abundance >80%) SWNT arrays with an average density higher than 20 tubes/µm and 10 tubes/µm, respectively, were successfully obtained on uniform solid catalysts.

References:
Jin Zhang et. al., Nat. Commun. 6 (2015), 6099.

10:30 AM *NM01.01.05 Near-Monochiral Carbon Nanotubes in a Single Step Dawid Janas1, Edyta Turek1, Tomohiro Shiraki2, Tomonari Shiraishi2, Tamehito Shiga3 and Tsuyohiko Fujigaya4,1,2,5,6 Silesian University of Technology, Gliwice, Poland; 2Kyushu University of Technology, Fukuoka, Japan.

Although carbon nanotubes have shown a wide range of promising properties [1-3], the inability to fully control their chirality still remains a major impediment factor for their implementation. A few years ago, the community has realized that post-synthesis sorting of carbon nanotubes could be the solution, and so an arsenal of techniques has been developed to reach this goal [4]. Unfortunately, despite their merits, to obtain carbon nanotubes of certain chirality tedious multistep processing must be carried out each time. In this presentation, we would like to show how we have adapted and modified the method of aqueous two-phase extraction [5] to aim for separation of selected carbon nanotube type in a single step [6]. We were able to separate minor chiral species from the CNT mixture with up to 99.7% optical purity without any unnecessary iterations. What is more, we observed emergence of new optical features under certain circumstances.

References:

10:45 AM *NM01.01.06 Locally Controlled Growth of Single Lambda-Shaped Carbon Nanofibers Christian Lutz, Tobias Loritz, Julia Syurik, Sharali Malik, C.N. Shyam Kumar, Christian Kübel, Michael Bruns, Christian Greiner, Michael Hirtz and Hendrik Hoelscher; Karlsruhe Institute of Technology, Karlsruhe, Germany.

Since first studies of branched carbon nanotubes (CNTs) with L-, Y- and T-shapes were published in the mid of the 1990 various approaches were presented to grow such structures. Branched carbon nanotubes are of high interest due to their unique electrical properties making them a promising material for advanced nano-electrical devices. However, SWCNTs are not easy to grow in a defined way. Therefore, Y-shaped MWCNTs or CNFs are also examined in order to understand the growth mechanism of branched nanotubes. Beside their potential use as nano-electrical devices, branched CNFs or CNTs are also of interest as a material mimicking hierarchical nanostructures found in nature.
In general, the growth of branched or non-branched CNFs or CNTs is conducted with an elaborate infrastructure relying on a certain amount of process gases and considerable energy input. We present an approach to grow inverted V-shaped or Y-shaped CNFs in an open ethanol flame. Due to their resemblance to the Greek letter lambda we named them Λ- or λ-shaped CNFs depending on their actuals shape. Λ-shaped CNFs consist of two CNFs attached to the substrate with one end and connected to each other with the other end resulting in a free standing lambda-shape. An additional CNF can be grown from the connecting point of the first two CNFs with increasing growth time resulting in λ-shaped CNFs. Our experiments suggest that the connecting point of the lambda-CNFs is the nickel catalyst and that the third CNF growth from that center. The exact growth position of the overall structure on the substrate can be determined through microchannel cantilever spotting (μCS) or dip-pen nanolithography (DPN) via the locally controlled deposition of nickel catalysts. Down-scaling to a spot size that results solely in one single lambda-shaped CNF is demonstrated.

11:00 AM NM01.01.07
Influence of Crystallinity and Oxidation of Alumina Buffer Layers on Catalyst Behavior in Single-Walled Carbon Nanotube Growth Takahiro Maruyama1, Akishimita Kiribayashi1, Takahiro Sada1, Shigeya Nartitsuka1, Toru Asaka1, Takaniko Hihara2 and Sumio Iijima1; 1Meijo University, Nagoya, Japan; 2Nagoya Institute of Technology, Nagoya, Japan.

Single-walled carbon nanotubes (SWCNTs) are one-dimensional materials exhibiting unique properties, so they have been anticipated for various electronic devices in future. Presently, catalyst-assisted chemical vapor deposition (CVD) are widely used to obtain high-yield SWCNTs, where alumina buffer layers are used to enhance the catalyst activity. However, the enhancement mechanism of catalyst activity by the alumina buffer layers remains poorly understood. In this study, we preformed SWCNT growth at 600°C by alcohol catalytic CVD using Rh catalysts on different types of alumina buffer layers prepared using different processes, and the effects of oxidation and crystallinity of alumina buffer layers on catalysts activity were investigated. Five kinds of alumina buffer layers were used to support Rh catalysts; native oxidation of Al layer deposited by electron beam (EB); thermal oxidation of Al layer deposited by EB; EB deposition of Al₂O₃ powder; native oxidation of Al layer deposited by rf-sputtering; thermal oxidation of Al layer deposited by rf-sputtering. After deposition of Rh catalysts (nominal thickness ~0.2 nm) on them, we carried out SWCNT growth by alcohol catalytic CVD [1]. The grown SWCNTs were characterized by Raman measurements, FESEM and TEM. The alumina support layers were analyzed by XPS, XANES, AFM, TEM and ellipsometry. Rh particle sizes and subsurface diffusion were characterized by TEM and depth profile using XPS. Although Rh nanoparticles were formed on all alumina layers, SWCNTs were not grown on the alumina buffer layer in which metallic Al was contained. Depth profile showed that the large inward diffusion of Rh catalysts occurred on the “metallic” alumina buffer layer, resulting in the reduction of SWCNT yield. For the alumina buffer layers prepared by thermal oxidation, diaspore-type alumina polycristals were formed and that Ostwald ripening of Rh catalysts was enhanced on them, leading to small SWCNT yields. Conversely, on the amorphous alumina layers, Ostwald ripening was suppressed and Rh particles suitable for SWCNT growth were formed. Additionally, the inward diffusion of Rh catalysts was suppressed on the diaspore-type amorphous layers with higher densities. Our results demonstrated that amorphous alumina support layers with high densities are suitable for suppressing both Ostwald ripening and inward diffusion of catalysts, making them favorable for high-density SWCNT growth.


11:15 AM NM01.01.08
Hyperspectral Raman Spectroscopy—A Powerful Method to Investigate Plasma Treatments of Graphene Films Pierre Vincenot1, Germain Robert-Bigras1, Xavier Glad1, Charlotte Allard2, Richard Martel2 and Luc Stafford1; 1Physique, Université de Montréal, Montréal, Quebec, Canada; 2Chimie, Université de Montréal, Montréal, Québec, Canada.

Raman spectroscopy is a versatile non-destructive tool offering distinctive features for pristine, damaged and even doped graphene. Typical Raman methods are however limited by their intrinsic microscopic nature, only being able to probe the area exposed to the laser beam (~1 μm). Hence, Raman mapping is often used to assess a broader region of graphene samples. Nonetheless, especially when graphene is grown on a polycrystalline substrate, strong discrepancies may appear on a scale larger than the available mapping area (> tens or hundreds of μm). Moreover, in the case of plasma irradiation of graphene, it is essential to understand the impact of the small heterogeneities in pristine graphene (local defects, grain boundaries, etc.) on the resulting graphene structure after treatment. In this context, recent advances in laser technology combined with increased efficiencies of Charge-Coupled Devices (CCD) and the development of efficient Bragg filters opened the road to new Raman imaging methods with reasonable integration time. In particular, hyperspectral Raman Spectroscopy or RIMA (Raman Imaging) is a very powerful method to obtain qualitative as well as quantitative Raman data on a macroscopic scale [1].

In this work, RIMA was used to examine plasma-induced modification of CVD-grown graphene films. Experiments were realized in a low-pressure inductively-coupled plasma. This method is a commonly used post-processing technique to alter materials properties and thus, is a good candidate to tune graphene structure. It is however difficult to decouple doping and damage mechanisms. In damage studies of graphene, ions beams are operated at energy above a few tens of eV [2] while ions energy in our plasma conditions is below the energy threshold for atom displacement (Td = 15-20 eV). Yet, defects generation by such plasmas are reported in few studies [3] but are not clearly understood.

Graphene films were exposed to an argon plasma and RIMA measurements were performed on different areas to study the sample homogeneity. These results reveal how the initial state of graphene films is a key factor to understand plasma irradiation effects. In addition, the very large number of Raman data (>10⁶) was used to establish links between doping, strain and damage types in both as-grown and plasma-processed graphene films. To further understand plasma-graphene interactions, plasma conditions were adjusted as to vary ion energy and fluence of plasma-generated species. In addition, the very large number of Raman data (>10⁶) was used to establish links between doping, strain and damage types in both as-grown and plasma-processed graphene films. To further understand plasma-graphene interactions, plasma conditions were adjusted as to vary ion energy and fluence of plasma-generated species.


11:30 AM NM01.01.09
Chirality Distributions of SWNTs—Experimental Evaluation versus Thermodynamic Modeling Amnick Loiseau1, Frédéric Fossard1, Yann Magnin1, Hakim Amaur1, François Ducastellé1, Esko Kauppinen1, Christophe Bichara2,1; 1LEM, CNRS-ONERA, Chatillon, France; 2Multiscale Material Science for Energy and Environment, Massachusetts Institute of Technology, Boston, Massachusetts, United States; 3CNRS-Université Aix Marseille, CINAM, Marseille, France; 4Department of Applied Physics, Aalto University School of Science, Aalto, Finland.

Although significant progress has been made since 25 years, one major obstacle to realization of Single-walled carbon nanotubes (SWNTs)-based nanotechnology has been the lack of control for designing selective synthesis conditions. This is partly due to the incomplete understanding of the physical and chemical effects driving the kind of tubes able to nucleate and grow under given experimental conditions [1]. A way to address this basic question is to consider SWNT growth from a thermodynamic point of view. To that aim, we have developed a statistical thermodynamics model, valid in the case of a perpendicular growth [2], which has been experimentally proven to yield a near-armchair selectivity [3]. This model relates the stable (n,m) tube structures to the tube/catalyst interfacial energies for zigzag and armchair edges and the temperature [4]. Taking the
Two dimensional layered materials (2DLMs) are important candidates of flexible electronics applications, used for health monitors, displays, batteries, and sensors. Despite the significant progress being made in synthesis technologies and in the prototyping of 2DLM flexible electronics, the work in the scalable integration of 2DLMs with flexible polymer substrates has proven, thus far, to be minimal and limited to several specific 2DLMs and polymer substrates. In this work, we demonstrated directly assemble wafer-scale 2DLM film on a polymer substrate through a dynamic energy driven assembly (DEDA) method seamlessly integrating a liquid exfoliation and a new assembly strategy. The DEDA method includes three steps: exfoliation of 2DLM in a designated solvent using sonication, and submerge polymer substrate to process the assembly, and take out the assembled substrate to dry. The principal innovation of DEDA is to control the relative interfacial energy among solvent, 2DLM and polymer substrate such that a relative low-energy 2DLM-polymer interface and a relative high-energy solvent-polymer interface will enable effective assembly of 2DLM on the polymer. Unlike the traditional assembly strategies, which start with a stabilized solution and emphasize good wetting among all components, DEDA theory suggests poor-wetting solvent is the key that determines the assembly quality. As a proof-of-concept, we have successfully used DI water, a non-toxic but poor wetting solvent for PDMS, to exfoliate and then assemble different 2DLMs (graphene, h-BN, and MoS2) on a PDMS substrate. A uniform film can be formed as short as 10 seconds after immersing PDMS substrate in the solution and by adjusting the solution concentration and assembly time, the thickness of the assembled film can be easily tuned from several nanometers to hundreds of micrometers. It is also interesting to notes, adding 2-propanol into water decreases the driving force of assembly. In summary, the unique features of this DEDA method are (1) a new interfacial energy driven assembly strategy diminish the driving force of assembly. This results matching the prediction from DEDA theory where improved wetting between the solution and PDMS can be easily tuned from several nanometers to hundreds of micrometers. It is also interesting to notes, adding 2-propanol into water decreases the assembly efficiency dramatically. This results matching the prediction from DEDA theory where improved wetting between the solution and PDMS diminish the driving force of assembly. In summary, the unique features of this DEDA method are (1) a new interfacial energy driven assembly strategy that has the potential to be generalized broadly to arbitrary 2DLMs and polymers, (2) the usage of the non-equilibrium 2DLMs solution for rapid assembly, and (3) high controllability of the assembly through simple concentration and assembly time controls. This study not only creates a new assembly method for the scalable and hierarchical fabrication of 2DLM flexible electronics but also advances knowledge in nanomaterials assembly and will promote the field of nanomanufacturing.
A gaseous product mixture from Fischer-Tropsch synthesis (FTS-GP) has been utilized as an efficient feedstock for growth of high-quality, well-aligned, single-wall carbon nanotube (SWCNT) carpets of millimeter-scale heights on Fe and (sub) millimeter-scale heights on Co catalysts via chemical vapor deposition (CVD). Growth conducted at optimal temperatures for Co and Fe catalysts yielded predominantly SWCNTs that are largely free of carbon impurities. Growth on Fe is characterized by a growth rate of ≈50 μm/min and catalyst lifetime that is longer than 90 min, with the catalyst showing no decay of activity. In contrast, growth on a Co catalyst shows a lifetime of ≈60 min, with a slower growth rate of ≈7 μm/min. Resulting area densities of SWCNT carpets grown on Fe and Co catalysts, determined by the weight-gain method, were 1.0 × 10^{12} and 6.0 × 10^{12} cm^{-2}, respectively. The catalyst lifetime and area densities of SWCNTs are among the highest achieved on standard catalysts. Unlike SWCNT carpet growth involving conventional feedstocks (such as C_{2}H_{2}, C_{2}H_{4}, and CO), growth rate and density of SWCNTs on Fe are less sensitive to the FTS-GP fraction and thus allow for relatively easy optimization and scale-up.

2:15 PM NM01.02.03

Defect-Free Graphene Growth at Low Temperatures via Plasma Enhanced Chemical Vapor Deposition

Bilge Bekdüz, Yannick Beckmann, Jan Mischke, Jonas Twellmann, Wolfganp Mertin and Gerd Bacher, University of Duisburg-Essen and CENIDE, Duisburg, Germany.

Growth on other non-catalytic substrates. Although few groups showed nearly defect-free PE-CVD grown graphene at low temperatures, a detailed understanding of the growth mechanism is still missing [1].

In order to study the growth mechanism in PE-CVD we used a commercially available 4" cold wall reactor to fabricate graphene on electrochemically polished high-quality copper foils [2]. A cost-effective DC plasma is applied to dissociate the precursor methane. To suppress unintended vertical graphene growth and ion acceleration to the substrate we introduced a sacrificial Cu foil into the growth chamber. The growth temperature was systematically varied from 1020°C down to 600°C. By varying the growth time at different temperatures two types of samples were prepared: graphene flakes and graphene films. By analyzing the flake area the growth rate could be determined in dependence of growth time and growth temperature. A almost defect-free graphene with negligible \( \langle \rho \rangle / \langle \varepsilon \rangle < 0.1 \) contributions of the D peak in Raman spectroscopy could be prepared even at 600°C. Compared to thermal CVD we found that the activation energy for the growth rate decreases from 4 eV down to 1.8 eV in PE-CVD, indicating efficient precursor dissociation in the plasma. From our studies we conclude that the carbon attachment step is the limiting factor for the PE-CVD growth. During the early stage of growth, we observed crystalline graphene grains surrounded by amorphous carbon in Raman spectroscopy. With increasing growth time graphene flakes grow at the expense of amorphous carbon and eventually merge into an almost defect-free graphene film with a sheet resistance down to 470 Ω/sq.

References


2:30 PM NM01.02.04

Layer Number Determination of Graphene on Nickel Substrate Using EELS Spectra with Scanning Auger Electron Spectroscopy

Masahide Shima, Hiroki Kato, Kota Shihommatsu and Yoshikazu Homma, 1JEOL Ltd., Tokyo, Japan; 2Tokyo University of Science, Tokyo, Japan.

Graphene is one of the atomic layered materials which has interesting physical properties such as mechanical strength, optical transparency, electron and thermal conductivity. The identification of a layer number is necessary for graphene based technology, because these properties strongly depend on a number of layers. Optical microscopy, Raman spectroscopy, scanning electron microscopy and other microscopic techniques are used to image a map of graphene layer. SEM has superior character amongst these various techniques for its high spatial resolution and large field of view. In order to observe graphene using scanning electron microscopy, it is necessary to detect electrons emitted by the interaction between electron beam, graphene and substrate.

When the graphene on substrate are observed with SEM using secondary electrons emitted from not only graphene but also the substrate. In the present study, the effect of graphene layers on the secondary electrons including elastic and energy loss peaks were investigated using Auger electron microscopy. A carbon-doped poly crystalline nickel foil was heated (up to 900 degree or more) by electrical current supply and cooled rapidly. Through the thermal process, graphene having different number of layers was precipitated on the nickel surface by segregation. SEM observation and reflection electron energy loss spectroscopy (REELS) measurement was performed using a scanning Auger electron microscope (JAMP-9510F, JEOL Ltd.). The accelerating voltage was 1.5 kV. The full width at half maximum of the back scattered electron peak was about 0.9 eV. The angle between the SEM column and analyzer was 60 degree. The sample tilting axis of the sample stage was perpendicular to the plane made by SEM beam axis and analyzer collection direction, so called sagittal plane. Therefore, the sample could be set in specular geometry such as the incident and outgoing angle of electrons were the same, by tilting 30 degree. All experiments in this report were performed in the specular condition to get highest intensity for zero-loss and energy loss spectra. At the first, the sample was observed with SEM using out-lens secondary electron detector. The SEM image showed that various layer graphene segregated from the nickel foil. There was the bare nickel region near at the center of the foil ribbon because the center was highly heated by the DC current feed through. The SEM image shows that the layer number of graphene increased along with the ribbon. The result of REELS measurement is that the intensity of zero-loss peak monotonically decreased depending on the layer number of graphene and the shape of energy loss spectra has specific feature of each layer number of graphene on any kind of substrate can be determined by using the elastic peak and energy loss spectra.

2:45 PM NM01.02.05

Scalable CVD Manufacture and Heterostructure Integration of Graphene and h-BN with Domains Size, Alignment and Layer Control

Ruizhi Wang, Robert Weatherup, \textsuperscript{1,2} Stephan Hofmann\textsuperscript{1} and Oliver Burton\textsuperscript{1}, 1University of Cambridge, Cambridge, United Kingdom; 2University of Manchester, Manchester, United Kingdom.

Chemical vapour deposition (CVD) has emerged as the most promising method for scalable growth of two-dimensional materials (2DM), such as graphene and hexagonal boron nitride (h-BN). To improve growth, the focus has mainly been on fine-tuning the deposition process using a copper (Cu) catalyst. Notable progress has been made regarding the quality of the as-grown 2DM. However, the high vapour pressure of Cu is a source of reactor contamination and its low melting point sets a challenging limit for any process optimization. Furthermore, 2DM are prone to contamination by trace Cu, which is a constraint for CMOS integration.\textsuperscript{[1]} Here we present a holistic approach for CVD of 2DM starting with the choice of the catalyst. Based on considerations including accessible CVD parameter space, ease of CMOS integration, feasibility of growth and strategies for transfer, we have determined platinum (Pt) as the optimal catalyst for growth of graphene and h-BN.
The growth of graphene on Pt is critically dependent on the supply and removal of carbon from the catalyst surface by bulk diffusion. By tuning this kinetic process, it is possible to grow graphene epitaxially, by precipitation or through both mechanisms. By careful tuning of the growth conditions, we can achieve continuous single-layer graphene with large domains (>0.1mm), isolated bi-layer graphene domains (>0.05mm) and continuous bilayer graphene. While high-quality graphene alone is sufficient for certain applications, most require a van der Waals (vdW) heterostructure, where graphene is embedded within layers of h-BN. Currently, h-BN is mainly obtained through exfoliation of bulk crystals due to lack of clean methods of transferring CVD grown h-BN. Here, we present an approach to grow high quality h-BN on Pt, with domain sizes exceeding 0.5mm, and to transfer these layers using a delamination-based process, which avoids the contamination associated with traditional transfer methods. These layers can then be used to sequentially pick up additional layers of h-BN or graphene for scalable fabrication of vDW heterostructures. To demonstrate the feasibility of our approach, we have fabricated devices that outperform existing devices relying on CVD 2DMs.

Based on the in-depth understanding of the CVD growth mechanism and the subsequent integration pathway, we present a new approach to scalable fabrication of 2DM. Instead of additional process optimization, we show how by choosing the optimal catalyst, it is possible to offer solutions to some of the challenging problems for the scalable manufacturing of 2DM. We demonstrate the growth of both graphene and h-BN, with control over layer number, domain size and alignment, and show how these layers can then be cleanly assembled to form vDW heterostructures.

References
[2] R. Weatherup & R. Wang et al., In Submission
[3] R. Wang et al., In Submission

3:00 PM BREAK

SESSION NM01.03: Structure and Properties I
Session Chairs: Don Futaba and Naoyuki Matsumoto
Monday Afternoon, November 26, 2018
Sheraton, 2nd Floor, Republic AB

3:30 PM *NM01.03.01
Optical and Electrophysical Properties of Filled Single-Wall Carbon Nanotubes Assembled into Thin Films Elena D. Obraztsova1,2, Alexander A. Tonkikh1,2, Victor I. Tsebro3, Dmitrii V. Rybkovskiy4, Petr Obraztsov5, Timofei V. Eremin6, Esko Kauppinen7 and Andrey Chuvilin1; 1A.M. Prokhorov General Physics Institute, RAS, Moscow, Russian Federation; 2Moscow Institute of Physics and Technology, Dolgoprudny, Russia; 3Dolgoprudny, Russian Federation; 4Department of Applied Physics, Aalto University, School of Science, Aalto, Finland; 5CIC nanoGUNE Consolider, San Sebastian, Spain; 6P.N. Lebedev Physics Institute of Russian Academy of Sciences, Moscow, Russian Federation.

In the last few years, a great interest has arisen for thin (with a thickness of less than 100 nm) single-walled carbon nanotube (SWNT) films filled with electron-acceptor molecules [1-4]. They are a macroscopic object and have a transparency of about 90% and a surface resistance of 50 Ω/square [3]. These parameters make them a real candidate for replacing the most popular material for transparent electrodes today - ITO (indium tin oxide). The filling of nanotubes results in their p-type doping, confirmed by the shift of the position of the tangential mode (1592 cm-1) in the Raman spectra and suppression of the E11 and E22 transitions in the optical absorption spectra. The shift of the Fermi level to the valence band was estimated as 1 eV. After doping, the electrical resistance of the tubes decreases by almost an order of magnitude, and the optical transmission increases by 3-5% [2,3]. The effect is more pronounced in the fractions of the tubes, separated by the type of conductivity. The optical properties of hole-doped SWNTs also are also interesting. In photoluminescence (PL) spectra (in contrast to the case of pristine nanotubes), new peaks have been observed. They were assigned to trions, quasiparticles consisting of two holes and one electron. The redistribution of PL intensity between the exciton and trion peaks is demonstrated with an increase in the degree of doping. Pump-probe experiments have revealed the ways of energy transfer in doped SWNTs. The authors are grateful for the financial support in frames of RFBR projects (16-02-00979 and 17-302-50008). P.A.O. thanks RSC project 17-72-10303.

References

4:00 PM NM01.03.02
Elastocaloric Effect in Carbon Nanotubes Tiago E. Cantuário and Alexandre F. Fonseca; State University of Campinas, Campinas SP, Brazil.

When natural rubber is quickly stretched, it gets warm. Conversely, when quickly stretch released, it gets cooled. This effect, called elastocaloric effect (ECE), was discovered in the beginning of 19th century and further observed to occur with several materials. This caloric effect was also observed to happen under the application of other types of stimulus as magnetic or electric fields. Research on ECE and other types of caloric effect has been growing fast because of the interest in the development of new, hazardous chemicals or ozone depletion-free, cooling devices. Recently, the ECE was predicted to be significant in carbon nanotubes (CNTs). Lisienkov and collaborators [Nano Letters 16, 7008–7012 (2016)], showed by means of classical molecular dynamics (MD) simulations, that it is possible to obtain as large as 30 K of variation of temperature when CNTs are subjected to external moderate forces. This finding is, now, motivating the research towards the development of cooling nanodevices. Here, also using tools of MD simulations but differently from the above study, we estimated the ECE performance of CNTs during a complete thermodynamic cycle, similar in the temperature-entropy (TS) diagram to the Otto-cycle but not based on gas compression/expansion, composed by: (1) adiabatic stretch followed by; (2) isobaric thermal equilibration at room temperature; then (3) adiabatic stretch release; and (4) final isobaric thermal equilibration at room temperature. Instead of fixing a load, we fixed the strain rate and stretched the CNT up to 10% of strain. We have obtained temperature variations due to the ECE in CNTs as high as 37 K. We discuss these results and the efficiency of a cooler machine based on the CNTs ECE.

4:15 PM NM01.03.03
Entropy Driven Stability of Chiral Single-Walled Carbon Nanotubes Yann Magrin2, Hakim Amara1, François Ducastelle1, Annick Loiseau3 and Christophe Bichara1; 1CINaM – CNRS & Aix-Marseille University, Marseille, France; 2CEE, CNRS and MIT, Cambridge, Massachusetts, United States; 3LEM, ONERA and CNRS, Chatillon, France.
Since 25 years, significant progress has been achieved in the controlled synthesis of Single Walled Carbon Nanotubes (SWNTs), but we are still facing difficult issues concerning the yield and selectivity of their synthesis by Catalytic Chemical Vapor Deposition. The choice of a catalyst is critical, and hitherto made by trial and error. In fact, we don’t know what are the required properties of a “good” catalyst for a selective SWNT growth, partly because currently available models [1,2] did not directly address this issue.

Here, we answer this question by developing a statistical thermodynamics model, that in the case of a perpendicular growth[3,4], relates the stable (n,m) tube structures, to the tube/catalyst interfacial energies for zigzag and armchair edges and the temperature. This model shows that, at low temperature, only zigzag or armchair tubes are stable. Chiral tubes become stable at higher temperature because of the configurational entropy of the tube edge in contact with the catalyst, that is a key element of the model. This enables us to produce chiral stability maps and phase diagrams that relate the catalyst interfacial properties and the temperature with the resulting equilibrium chiral distribution. It explains under which conditions, a near armchair distribution can be obtained, and accounts for the temperature evolution of the chiral distributions reported in a number of experiments. The technical aspects of the model [3] and possible further developments will be discussed.


4:30 PM NM01.03.04
Measurements of van der Waals Interaction Strength of Single and Multilayer Graphene

4:45 PM NM01.03.05
Tailoring Atomic-Scale Structures in Graphene with Electron Beams

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the BNNTs into a felt-like material. Only a very limited number of reports investigating the actual formation of BNNTs are available. In order to produce BNNTs in large quantities, the fundamental science particularly the nucleation and growth of BNNTs must be first understood.

Herein, we report in situ short time reaction studies revealing the formation mechanism of BNNTs and show the nucleation and embryonic stage of BNNTs formation. At the early stages of production large amounts of nanospheres were formed possessing tail-like structures and these were found to be the seed structured of the BNNTs that formed later. 3 Magnesium, a component of the precursor, was found to play a vital role that served to generate the intermediate species and medium for the diffusion of BN species essential for the formation of BNNTs. Our findings led us to design an experimental set-up that allows the control of three important factors for the formation control; namely (a) B species, (b) N species, and (c) the catalyst. Different morphologies were obtained by controlling the dimension of the catalyst particles. Our theoretical calculations suggested which of the generated species are stable at synthesis conditions, showed the geometrical structure they form, and followed the nucleation process through molecular dynamics simulations. The combined approach of in situ experimental work and theoretical studies paves the way to design efficient production lines for the up-scaling of BNNTs and therefore provides a practical route to the efficient exploitation of BNNTs.

Reference:

NM01.04.02
Use of Refractory-Metal Diffusion Inhibitors to Slow Ostwald Ripening of Catalytic Metal Particles—A Route to Ultra-Long Carbon Nanotubes (CNTs) Michael J. Bronikowski and Melissa J. King; University of Tampa, Tampa, Florida, United States.

Growth of Carbon Nanotubes (CNTs) to lengths useful in many materials applications is currently limited by a number of factors, the most important of these being Ostwald ripening and subsequent deactivation of the metal catalyst particles from which the CNTs nucleate and grow. Here is proposed and demonstrated a novel method for overcoming this limitation. It is shown that inclusion of refractory, high-melting-point metals in the metallic catalyst used for CNT growth can substantially enhance the lifetimes of the particles of catalytic metals, enabling growth of CNTs to much greater lengths than possible using the pure catalytic metals. This lifetime enhancement occurs because the refractory metal inhibits the surface diffusion of the catalyst metals, slowing the Ostwald ripening of the catalytic particles and allowing them to grow CNTs for greater times, resulting in longer CNTs. This effect has been demonstrated for several catalyst/diffusion-inhibitor systems, and results are presented and discussed here.

NM01.04.04
Computational Study on Optimization of Sheet Conductance of Carbon Nanotube Transparent Films Masaaki Tsukuda and Takahiro Yamamoto; Department of Electrical Engineering, Tokyo University of Science, Katsushika, Japan.

Although Carbon nanotube (CNT) thin films are expected as flexible transparent conductive films, the physical origin of their high electric performance remains to be clarified yet due to complexity of nanotube network. This is because that individual variations in nanotube length and chirality are involved in nanotube network and its electrical conductivity also depends on geometrical network structure such as nanotube density and alignment. Therefore, understanding various properties of CNT thin film has been the subject of controversy over the last few years. In order to understand various properties of CNT thin film, it is essential to understand relation between the network structure with the nanotube densities, alignment, length and diameter, and their electrical transport property. We thus theoretically explored how nanotube alignment affects electrical transport properties of CNT thin films, using a numerical stick-percolation-based model.

In the present study, we investigate electric properties of a CNT films consisted of metallic CNTs. First, we generated two-dimensional random networks in a film. Nanotubes are distributed in a film with the fixed values of the film length of $L=5 \mu m$, the film width $W=5 \mu m$, nanotube length $l_{CNT}=0.5 \mu m$ and the chirality of a nanotube as $(10,10)$ and the angle between the axis of nanotube and x-axis as $\Theta$. The value of $\Theta$ takes a uniformly random value in the range $\Theta_{max}<\Theta<\Theta_{max}$, where $\Theta_{max} < 90^\circ$ (we define $\Theta_{max}$ as nanotube alignment). CNT network is transformed into effective resistor network composed of the resistance $R_{CNT}$ along an individual CNT and the junction resistance $R_j$ between CNT pairs, using ref [1]-[2]. Then, we apply a nodal analysis method to calculate a current value flowing in a film and calculate the sheet conductance in the film by changing the value of alignment angle $\Theta_{max}$ for several different nanotube area densities $\sigma$. Our simulation reveals two characteristic of CNT thin films. First, when exceeds the percolation threshold, the sheet conductance increases, depending on the increase of when $\Theta_{max}>90^\circ$. Sheet conductance at $\sigma=200$ tubes/$\mu m^2$ is $37.6 \ \Omega/sq$, which is in good agreement with the previous experimental work (40.0 $\Omega/sq$)[3]. Second, when, the sheet conductance exhibits a maximum at a certain nanotube alignment angle while there is a drop of the sheet conductance caused by the function of junction resistance of the (10,10) - (10,10) CNT. This is because of the competition between the decrease in the number of junctions and lengths of the electrical conducting paths. These results would be helpful for understanding electric transport properties of complicated nanotube network structure.


NM01.04.05
Behavior of Graphite and Graphene Under Mechanochemical Activation with Hematite and Magnetite Nanoparticles Monica Sorescu and Mark Allwes; Duquesne University, Pittsburgh, Pennsylvania, United States.

Graphite-doped hematite and magnetite nanoparticles systems (~50 nm) were prepared by mechanochemical activation for milling times ranging from 2 to 12 hours. Their structural and magnetic properties were studied by 57Fe Mossbauer spectroscopy. The spectra corresponding to hematite milled samples were analyzed by considering two sextets, corresponding to the incorporation of the carbon atoms into the iron oxide structure. For ball milling time of 12 hours a quadrupole split doublet has been added, representing the contribution of ultrafine particles. The Mossbauer spectra of graphite-doped magnetite were resolved considering a sextet and a magnetic hyperfine field distribution, corresponding to the tetrahedral and octahedral sublattices of magnetite, respectively. A quadrupole split doublet was incorporated in the fitting of the 12-hour milled sample. The recoilless fraction of all samples was determined using our previously developed dual absorber method. It was found that the recoilless fraction of graphite-doped hematite nanoparticles decreases as function of ball milling time. The T factor of graphite-containing magnetite nanoparticles for the tetrahedral sites stays constant, while that of the octahedral sublattice decreases as function of ball milling. These findings reinforce the idea that carbon adsorb on exhibit preference for the octahedral sites of magnetite.

Graphene-hematite and graphene magnetite nanoparticles systems were synthesized using mechanochemical activation for time intervals of 2-12 hours. Their structural and magnetic properties were analyzed by Mossbauer spectroscopy. For ball milling times of 2-12 hours, the least-squares fitting revealed the presence of a sextet for hematite (50.84 T), a sextet for carbon-substituted hematite (46.57 T), a broad sextet for iron carbides (29.34 T) and a quadrupole split doublet for iron-containing carbon nanoclusters (0.73 mm/s). Similarly, the Mossbauer spectra of ball-milled graphene and magnetite were
consistent with the occurrence of two sextets for the tetrahedral and octahedral positions of magnetite (49.26 and 46.12 T) and the formation of iron carbides (29.5 T) at long milling times (8 and 12 hours). Also, the appearance of the sextet representing the iron-containing carbon nanoclusters (0.73 mm/s) was manifest at the longest milling times employed. The recoilless fraction was determined from the Mossbauer spectra using our dual absorber method and it could be observed that the recoilless fraction exhibits maxima for the occurrence of additional phases at long milling times. If we relate the present results with the previous ones regarding milling graphite and iron oxide nanoparticles, we should note the additional appearance of the iron carbide phases and the occurrence of carbon nanoclusters. This means that graphene is not merely a source of carbon, but exhibits its own reactive properties during mechanochemical activation.

NM01.04.06 Laser Scribed Graphene Carbon “Grass” Establishing a Highly Selective, Sensitive and Low Detection-Limit, Point-of-Care Dopamine Sensor Guangyuan Xu1, 2, Jadranka Travas-Sejdic1, 2 and Paul Kilmartin1; 1Polymer Electronics Research Centre, School of Chemical Sciences, University of Auckland, Auckland, New Zealand; 2MacDiarmid Institute for Advanced Materials and Nanotechnology, Wellington, New Zealand.

A range of novel carbon nanomaterials, including 0D fullerene, 1D carbon nanotubes, 1D carbon nanofibers, 2D graphene and graphene oxide, and 3D carbon aerogels, has attracted considerable interest and investments from across the scientific society. Due to their excellent performance, the carbon nanomaterials have contributed significantly towards the development of miniaturized integrated point-of-care biological and chemical sensors. Graphene, as a sensing and signal transducing material is well established, and the recently developed method of “laser scribing” has already been demonstrated as a facile approach for manufacturing graphene electronics for highly selective, sensitive biological sensing devices [1, 2]. Inspired by the different morphologies and derivatives of the carbon nanomaterials that have been fabricated, including carbon nanowalls, graphene nanoribbons, vertically aligned CNTs and laser induced graphene fibers, we first fabricated laser scribed graphene (LSG carbon grass) with a novel 3D vertical aligned tree-like morphology. We have then used the LSG carbon grass in the application of dopamine detection by means of cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The electrochemical anodic peaks of dopamine (DA), ascorbic acid (AA) and uric acid (UA) using LSG carbon grass electrode were investigated, where UA and AA were considered as common interferences. The sensitivity of LSG carbon grass for DA sensing was highly improved compared to normal LSG. The fabricated LSG carbon grass sensor exhibits a sensitivity of 0.299 µA/µM and detection limit of 1 µM. The outstanding performance for dopamine detection using LSG carbon grass is a reflection of the promising future of carbon nanomaterials with interesting high surface area morphologies.

References

NM01.04.07 Electrochemical Tunneling through Atomically-Flat Hexagonal Boron Nitride Nitrite Matei Velick1, 2, 3, Sheng Hu1, Andre K. Geim2 and Robert A. Dryfe1; 1Chemistry and Chemical Biology, Cornell University, Ithaca, New York, United States; 2School of Physics and Astronomy, University of Manchester, Manchester, United Kingdom; 3School of Chemistry, University of Manchester, Manchester, United Kingdom.

Two-dimensional (2D) materials hold promise for a range of electrochemistry-related applications, including energy storage/conversion and sensing. The tunability of the electronic structure of these materials by their thickness or external stimuli such as electric field or strain suggests a range of opportunities in optoelectronics, electrochemical switching, and photocatalysis [1].

Here, we demonstrate electrochemical tunneling across monolayer and few-layer hexagonal boron nitride (hBN), a wide-gap insulator that has gained interest in device encapsulation and solid-state tunnel field-effect transistors [2]. The electrochemical behavior of tunneling devices based on ~5 µm diameter ultramicroelectrodes is studied using reversible redox mediator systems. Optical microscopy, Raman spectroscopy, and atomic force microscopy, are used to characterize the devices. We show that the tunneling current, electron transfer kinetics, and the breakdown voltage depend on the number of hBN layers between monolayer and bulk. We compare our results to other well-studied tunneling systems, such as alkylthiol chain monolayer or thin-layers of solid-state dielectrics.

Our findings show that varying the thickness of the hBN yields a tunable electrochemical response, which provides fundamental insight into the electrochemical tunneling behavior across atomically-flat insulating materials and could be exploited in applications such as electrochemical switching or surface passivation.


NM01.04.08 Electrochemical Supercapacitors from Hybrid Porous Graphene-Based 3D Structures Decorated Carbon Nanotubes-Nanoparticles Nefali L. Carrero, Jose H. Alano, Bruno Noremberg, Ricardo Marques Silva, Guilherme Maron and Lucas Rodrigues; University Federal-Pelotas, Pelotas - RS, Brazil.

The search for new supercapacitors materials is extreme importance for the development of the future of the energy sector. This is due to the fact that the technology evolution, which demands increasingly alternative devices, fast load, high power and great storage. Thus energy storage devices are currently the focus of several studies, both in the academic and industrial sector, the energy sector depends strongly on the development of the new materials. At the forefront of the materials used for electronic devices, the carbon-based materials such as graphene hybrid system with oxide (GO), carbon nanotubes (CNT) could be significant modified by chemical methods and morphology. These materials are widely used due to low density, high surface area and high load holding capacity. Thus, the objective of this work is to obtain a composite on porous graphene-based 3D structures (like sponge) decorated with nanoparticles like chalcogenides (ZnS, MoS2), transition metal (Ag, Fe, Ni), nickel cobaltite (NiCo2O4), metal oxides (In2O3, SnO2, ZnO), each nanoparticle system were previously grew homogeneously and well dispersed on the multiwalled carbon nanotubes (MWCNTs), under microwave-assisted hydrothermal synthesis (MHS). These hybrid composite display interesting morphology and appropriate electrochemical properties to be applied as electrodes for supercapacitors.

NM01.04.09 Temperature Dependence of Photoluminescence Spectra from a Suspended Single-Walled Carbon Nanotube with Water Adsorption Layer Yashiro Tanaka1, Yuta Saito1, Kazuki Yoshino1, Akiko Oza1, Shohei Chiashi1 and Yoshikazu Homma1; 1Tokyo University of Science, Shinjuku, Japan; 2The University of Tokyo, Bunkyo, Japan.
Thermal property of the single-walled carbon nanotube (SWCNT) has been intensively studied because the SWCNT is expected to be an excellent heat transport material. Many measurement methods of thermal conductivity of SWCNTs have been proposed and photoluminescence imaging spectroscopy is one of the powerful methods [1]. In this method, a suspended SWCNT is irradiated by laser, and the spatial distribution of the PL emission energy (E11) along the SWCNT axis is measured by a near-IR 2D camera, which is converted to the temperature distribution. The thermal conductivity is obtained from the temperature distribution. Thus, the accurate conversion of E11 emission energy to temperature is crucial in this method. The temperature dependence of E11 is simply expressed by Varshni’s equation independent of SWCNT chirality (n,m) when SWCNTs are in vacuum. On the other hand, when SWCNTs are located in the ambient air, water molecules adsorb on the outer surface of SWCNTs and they affect the energy of E11 [2]. Elucidation of the temperature dependence of E11 of SWCNTs with water adsorption layer is necessary to measure the thermal conductivity of SWCNTs in the ambient air. In this study, we measured the temperature dependence of the E11 in suspended SWCNTs with water adsorption. Suspended SWCNT was synthesized by chemical vapor deposition method on a quartz pattern substrate. PL spectra were measured from suspended SWCNTs with different chirality under controlling temperature (220 to 300 K). SWCNTs were exposed to water vapor at 300 K and the water adsorption layer was formed. It was found that the energy shifts of E11 exhibited a complicated temperature dependence depending on chirality in the case of SWCNTs with the adsorption layer. The energy shift was understood as the summation of intrinsic temperature dependence of the band-gap, the strain effect and the change of the dielectric constant of the adsorption layer. When the temperature decreased, axial strain due to the adsorption layer occurred in SWCNT. The strain changed E11 and the change clearly exhibited type-dependence [3]. The dielectric constant of the adsorption layer simply increased with decreasing temperature. Although the interaction between SWCNT and the water adsorption layer is weak, the adsorption layer drastically affected the optical properties of SWCNTs. By taking those effects into account, we could accurately determine the temperature along the tube axis.


NM01.04.10

In a relatively short time, 3D technology has become a new method for manufacturing prototypes and is occupying a first place in terms of research in multiple universities across the world, as well as the searching of new materials with advanced properties suitable for the development of prototypes with 3D printing. In this sense, layered graphene represents one of the most impressive materials for this purpose, due to the combination of its properties like high electrical and thermal conductivity or high mechanical strength. The main objective of the present research work is to study the impact that graphene has over the properties of the selected polymer when they are integrated in a unique compound forming a nanocomposite. In order to facilitate the integration of both components, graphene and polymer, chemical and structural modification of the layered graphene has been necessary. These modifications of the graphene lead to an improvement in the dispersion of both components, which has shown to be a critical parameter for the stress transfer from the nanoparticles to the matrix. In this way, modified graphene has been synthesized through different chemical processes, what first includes the synthesis of graphene oxide (GO) from graphite and its subsequent chemical reduction with different chemical reducing agents to obtain the reduced graphene oxide (rGO), which has similar properties to graphene. Lyophilization of the resulting graphene samples has been also carried out in order to increase the distance between graphene layers and improve the dispersion. Two different strategies have been employed during the synthesis of the nanocomposites: direct integration of the reduced graphene oxide (rGO) into the matrix of the polymer through solution in proper solvents (DMF and THF), and reduction in situ of the graphene oxide already integrated into the polymer structure. In both cases it is necessary the complete elimination of the solvent to ensure that the electrical and mechanical properties of the nanocomposite are not affected by the presence of traces of solvent. Polymers most commonly used in 3D printing have been used in this work, including ABS, PCL and PLA filaments. Nanocomposites were prepared with several loads of graphene between 3% and 15%, in order to compare the mechanical and electrical properties before being used in 3D printing. Graphene loading is also an important factor to take into account since too much loading could hinder the printing process due to the formation of graphene agglomerates. Characterization techniques employed to evaluate the samples have shown that the mechanical reinforcement of the polymeric structures is possible by addition of both GO and rGO. It also been stablish that a well dispersed rGO into the matrix not only improves properties in relation to strength and fracture toughness, but also electrical conductivity of the nanocomposite, which is not possible to get by adding only GO.

NM01.04.12

Individual carbon nanotubes (CNTs) are one of the strongest materials in nature. Networks of pristine CNTs, however, do not show similar superior mechanical properties due to weak load transfer between individual CNTs via van-der Waals interaction. Shear load transfer between CNTs can be improved by introducing covalent cross-links between nanotubes by means of ion or electron beam irradiation or chemical functionalization. The goal of this work is to quantify the effect of cross-links on quasi-static and dynamic mechanical properties of CNT network materials like CNT films, fibers, and aerogels in large-scale mesoscopic simulations. In our mesoscopic computational model, every nanotube is represented by a chain of stretchable cylinders. Mesoscopic force field accounts for stretching, bending and buckling of individual nanotubes, van-der Walls interactions, and cross-links between nanotubes. In order to account for the effect of individual cross-links on the load transfer between CNTs, we developed a novel effective bond model. This model is parameterized based on results of atomistic simulations of pulling out of a central CNT from a seven-tube bundle performed in a range of CNT diameters and cross-link linear densities. The developed model is first applied to study the shear load transfer in long CNT bundles. The simulations reveal extremely strong shear lag effect, which sets limits on the ability of cross-links to reinforce nanotube bundles. Next, we perform simulation of quasi-static and dynamic wave loading of CNT films, aerogels, and fibers. The equilibrium networks structures in these materials are obtained in preliminary mesoscopic simulations as a result of self-assembly of dispersed nanotubes into networks of entangled bundles. The cross-links are distributed inside these in-silico generated CNT material samples in order to simulate the process of irradiation or chemical functionalization of pre-existing networks of nanotubes. The simulations show that the dominant mechanisms of non-reversible structural changes in CNT networks under an applied mechanical load strongly depend on the deformation rate. The elastic and inelastic properties of CNT materials, as well as the acoustic speed, are found for materials with various degrees of anisotropy, density, CNT length, and density of cross-links. This work is supported by the NSF CAREER award CMMI-1554589 and NASA Early Stage Innovations program (project NNX16AD99G).

NM01.04.13
The Interaction of Carbon and Boron Nitride Nanotubes with Metals Christoph Roehmann1,2,3, Zwolak Michael1 and Searles Debra1; 1Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, Maryland, United States; 2The Institute for Research in Electronics and Applied Physics, University of Maryland, College Park, Maryland, United States; 3Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, Queensland, Australia.
The interaction of carbon and boron nitride nanotubes with metals is significant for a wide variety of applications. For example, the binding of tubes to transition metal nanoparticles plays a role in their catalytic growth, as well as in their nucleation. Similarly, the strength of nanotube-metal composites crucially depends on the interaction strength between the tube and the metal matrix. We performed quantum chemical calculations to investigate the binding strength and geometry of a variety of metals with carbon and boron nitride nanotubes. We examined both, binding by individual metal atoms and the binding with metallic surfaces to identify possible candidates for the creation of novel metal matrix composites.

NM01.04.14
Graphene Based Nanostructures for Matrix-Free Laser Desorption/Ionization Mass Spectrometry Detection of Ricin from Complex Media Ioana S. Hosu1, Robert Bogdanowicz2 and Yannick Coffinier1; 1Univ Lille, CNRS Centrale Lille, ISEN, Univ Valenciennes, Lille, France; 2Faculty of Electronics, Telecommunication and Informatics, Gdansk University of Technology, Gdansk, Poland.

Ricin (Mw~64 KDa) is one of the most toxic proteins, with LD50 varying from 10 µg to 20 mg/kg depending on the uptake pathway. Being soluble in water, it’s quite easy to extract from castor bean seeds. Ricin belongs to Ribosomal inhibiting protein (RIP) family and was classified by CDC (Centre of disease and control and prevention) as a category B bioterrorism agent. Detection of Ricin before or even after being assimated may be critical to survival, as there is no efficient counter-measure against its poisoning. Ricin is composed by two chains, one bearing the enzymatic activity (chain A, RNA glycosidase) and the other one acting as a recognition/transportation moiety (chain B, galactose-binding lectin). Current methods for its detection are essentially based on SPR, ELISA, colorimetric and Raman (SERS) techniques.1

SALDI-MS (surface assisted laser desorption ionization mass spectrometry) concerns the use of nanostructured materials (mainly carbon and semiconductive ones) that will absorb energy from UV laser helping the desorption/ionization of the analytes (with no use of organic matrix in the contrary to MALDI) followed by their subsequent detection by MS. Among their known properties, they should be anti-reflective, have low photoluminescence and low thermal conductivity. They have been shown to be very salt tolerant and highly sensitive to small compounds.

Recently, we have demonstrated that vertically aligned boron doped graphene sheets (known as carbon nanowalls, CNWs) are suitable nanomaterials for SALDI-MS detection of various small compounds including carbohydrates, lipids, peptides etc. However, detecting larger compounds by SALDI-MS such as proteins is still challenging. Indeed, only few examples of protein detection by SALDI-MS have been reported so far.4 Here, we propose, for the first time, to use CNWs for the SALDI-MS detection of the Ricin B chain (32 KDa) from buffered solutions and blood serum. A systematic study was conducted to optimize our interface by varying the dimensions of the nanowalls and the boron doping level. Other important parameters such as thermal conductivity, electrical resistivity, morphology, internal energy deposition, optical properties were also studied and discussed in correlation with the protein detection performances. Finally, the detection of Ricin was achieved and a limit of detection (LoD) found to be 8 ng/0.5 µL, meaning that for an average person weighing 70 kg, the lowest ricin’s LD50 can still be detected. The ability of our CNWs to detect proteins via SALDI-MS paved the way and opened new opportunities to matrix-free LDI-MS, still limited to small compounds detection so far.

References :

NM01.04.15
Micro-Fabricated Individual CNT Point Cathode Field Emission Electron Source for Focused Electron Beam Applications Xiuyuan Shao, Amit Banerjee and Anjam Khursheed; Department of Electrical and Computer Engineering, National University of Singapore, Singapore, Singapore.

There is remarkable interest and potential for field emission technology for the development of cold field emission sources for ultra-high-resolution scanning electron microscopes, lithography and other applications. However, some inherent problems have prevented the widespread practical usability of these sources, e.g. inherent ultrahigh vacuum condition requirement (10^-10 torr), relatively poor current stability and rapid emission decay. The current report presents a cold field emission electron source which overcomes these problems based upon using a resist-assisted patterning process fabricated carbon nanotube (CNT) electron emitters. The CNT emitter was grown on a silicon (Si) substrate by direct current plasma-enhanced chemical vapor deposition (DC-PECVD), using nickel (Ni) catalytic layer patterned by a conventional photolithography process, which provided several micron-scale CNT seeds and photoresist required for CNT growth. The patterned sample was formed at 600°C over 30 min under ambient argon (Ar) in DC-PECVD. The resulting CNT emitter featured unique structural properties and the geometry is determined by the temperature, total pressure, gas ratio, and in optimized process conditions for one individual CNT emitter growth. Preliminary experiments on one free-standing CNT emitter electron beam properties with tip radii ranging from 5 nm to 60 nm demonstrate to be promising in terms of current stability, high brightness, coherence, low energy spread, and small virtual source sizes, comparable to state-of-the-art conventional cold field emission sources. The freestanding CNT emitter cold-cathode electron sources have promising application possibilities to a variety of electron microscope or lithography devices, fabrication of compact glass-sealed x-ray tubes and cold cathodes for high-resolution imaging.

NM01.04.16
Towards Pure and Large-Scale Hexagonal Boron Nitride 2D Layers—A Unique Combination of PDCs Route with SPS Process Yanadi Li1,2, Catherine Journet-Gautier1, Bérangère Touyr1, Vincent Garnier1 and Philippe Steyer1; 1MATEIS, INSA Lyon, Villeurbanne, France; 2LMI, Université Lyon, Villeurbanne, France.

Since graphene's properties are strongly linked to the substrate on which it is deposited, it is clear that the promising future development of practical graphene devices will necessarily go through the development of insulating substrates on which graphene can be deposited without changing its intrinsic properties. As one of the most suitable substrates, hexagonal boron nitride nanosheets (BNNSs) are promising 2D materials for their exceptional chemical and thermal stabilities together with electrical insulating properties. These capabilities make it interesting as support for graphene in devices and also as clean, flat insulating environment for materials of heterostructure. However, in order to make h-BN relevant for real world applications, scalable synthesis routes are needed. As a consequence, the development of a novel source for highly crystallized h-BN crystals, suitable for further exfoliation, is a prime scientific issue. We have developed a promising approach to synthesize pure and highly-crystallized h-BN crystals, which can be further exfoliated into high quality, ultrathin, uniform BNNSs. This new accessible production process represents a relevant alternative source of supply in response to the increasing need of high quality BNNSs. The synthesis strategy is based on a unique combination of Polymer Derived Ceramics (PDCs) route with Spark Plasma Sintering (SPS) process. Through a multi-scale chemical and structural investigation, it is clearly shown that obtained layers are large, defect-free and well-crystallized, which are key-characteristics for a subsequent exfoliation into relevant BNNSs.

NM01.04.17
Ultralow Platinum Carbon Electrodes by Cathodic Polarization Treatment for Efficient Hydrogen Peroxide Sensing Muhammad Adil Riaz and
Hydrogen peroxide ($\text{H}_2\text{O}_2$) is a widely used oxidizer, bleaching agent, and disinfectant in many fields, such as food processing, medicine, and environment. Thus, detecting the trace amount of $\text{H}_2\text{O}_2$ is essential for many industrial and biological applications. Electrochemical $\text{H}_2\text{O}_2$ sensors, especially nonenzymatic ones, have attracted significant interests because of their relatively simple operation, low cost and fast response. Platinum (Pt) based Electrochemical $\text{H}_2\text{O}_2$ sensors demonstrate superior sensitivity performances, i.e., higher sensitivity, wider detection concentration range and lower detection limit. However, the high mass loading and cost of Pt limits their practical applications. Here, we develop a cathodic polarization treatment method to deposit ultralow mass loading of Pt nanoparticles on a high surface area (385 m$^2$/g) porous carbon substrate comprised of reduced graphene oxide (rGO) and carbon nanotubes (CNTs). Using multiple cyclic voltammetry (CV) cycles at the specific potential window (-0.8-0 V vs. standard carbon electrode) in 0.5 M $\text{H}_2\text{SO}_4$ electrolyte without Pt precursors, about 3.89 wt.% of Pt nanoparticles were anchored on the rGO-CNT composites with a narrow size distribution around 1–2 nm at a Pt mesh anode. Furthermore, different Pt mass loadings on rGO-CNT composites were obtained by varying the CV cycles and their morphological and physicochemical properties were characterized by SEM/EDS, TEM, and XPS along with $\text{H}_2\text{O}_2$-sensing performance to understand the synthesis-structure-property relationships. The optimized Pt/rGO-CNT composite obtained at 3000 CV cycles shows superior $\text{H}_2\text{O}_2$ sensing performances with a detection limit of 10 µM, a wide linear range up to 15 mM, and the sensitivity of 207 µA/MM.cm$^2$, which are one of the best among recently reported Pt-carbon composites and commercial 20 wt.% Pt/C catalysts. Further, the Pt/rGO-CNT sensor can also detect trace amount of $\text{H}_2\text{O}_2$ in milk and juice samples, demonstrating their excellent practical application potentials.

NM01.04.18 Selenium-Functionalized Graphene Oxide that Can Modulate the Balance of Reactive Oxygen Species Jiaha Xia and Huaping Xu; Department of Chemistry, Tsinghua University, Beijing, China.

Graphene oxide (GO) is an important two-dimensional material since it is water soluble and can be functionalized to adapt to different applications. Diselenide bond is a dynamic covalent bond and can respond to both redox condition and visible light irradiation in a sensitive manner. In this work, by combining the stimuli response of diselenide bond and the oxidative/radical attackable nature of GO, we achieved the in situ covalent functionalization of GO simply by stirring GO with diselenide-containing molecules in aqueous solution. The covalent functionalization was proven by FT-IR, Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), Atomic Force Microscopy (AFM), etc. And the functionalization mechanism was deduced to involve both redox reaction and radical addition reaction according to the XPS, Atomic Emission Spectroscopy (AES), etc. Moreover, we found the selenium-functionalized GO could modulate the balance of reactive oxygen species (ROS). Specifically, GOSe could decrease ROS level by accelerating the redox reaction and radical addition reaction according to the XPS, Atomic Emission Spectroscopy (AES), etc. Moreover, we found the selenium-functionalized GO could modulate the balance of reactive oxygen species (ROS). Specifically, GOSe could decrease ROS level by accelerating the reduction of peroxides when the ROS concentration is high while boosting the ROS level by in situ generating ROS when its concentration is relatively low.

NM01.04.19 High Aspect Ratio Nanomaterials in Corrosion Protection Composite Coatings David W. Johnson1, Alex Borak1, Carmen Espajo2, Simon Gibbon3, Steven Gourlay1, David James4, Jennifer MacKay5, and Jonathan Moghal2; 1Centre for Process Innovation, Sedgefield, United Kingdom; 2Crown Technology, Wantage, United Kingdom; 3AkzoNovel, Northallerton, United Kingdom; 4AkzoNovel, Birmingham, United Kingdom; 5Thomas Swan, Consett, United Kingdom.

Anti-corrosion coatings are ubiquitous with an expected market value of $20 billion by 2025. Current innovation is being driven by both demand and regulatory restrictions. (Global Market Insights 2016) A promising option is the incorporation of high aspect ratio nanomaterials (HARNs), such as graphene and boron nitride, as polymer composite coatings. (Liu, et al. 2016)

It has previously been shown that platelet like materials can improve the performance of anti-corrosion coatings. This is typically thought to be due to the creation of a “tortuous path” in which corrosive media (typically water, electrolytes and oxygen) must follow a long path through a network of impermeable filler to reach the metal substrate. (Zheng, et al. 2017) This effect is maximised when the platelets are high aspect ratio and aligned parallel to the metal substrate.

While the concept of such a system is simple there are several complex factors to consider in the production of a working coating. In producing HARNs it is challenging to control morphology and achieve both the large lateral dimensions and the thin sheet sizes desired. Dispersing HARNs in resin also presents challenges as aggregates reduce the effective aspect ratio and risks creating porous structures through which electrolytes can penetrate. Once dispersed the nanomaterial must remain wetted by the resin throughout the cure process to avoid generating voids and an associated decrease in performance. Finally, the coating must remain adhered to the substrate and not delaminate.

In this work we present data on the effect of HARN morphology and surface energy on the barrier performance of a protective coating. Consideration is given to how these variables may affect nanomaterial dispersion quality, porosity and interaction with the metal substrate. Initial results indicate that dispersion quality and HARN surface chemistry both influence performance.


NM01.04.20 Heterogeneous Metal Oxide-Graphene Porous Single Fiber Derived from Engineered Graphene-Tunicate for Sensitive Chemiresistor Ji-Soo Jang and Il Doo Kim; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Graphene oxide liquid crystal (GOLC) behavior is very intriguing and powerful phenomenon, especially for simply achieving graphene-based fibers, which have ordered graphene alignments in fiber. Taking advantages of graphene based fiber such as high mechanical strength, electrical conductivity, and supercapacitive behavior, various applications such as energy storage, photovoltaic cell, and chemical sensing have been explosively exploited. Although graphene based fiber have opened up great opportunities for various researches, high graphene density in graphene based fiber is disadvantageous to develop the porous fiber with high meso (2–50 nm) porosity; High porosity is essential for increased surface area and fast gas diffusion and penetration,
leading to enhanced detection of toxic chemicals using graphene based fiber. Unfortunately, graphene based fiber is still challenging to detect the ppm level of toxic gas molecules such as nitrogen dioxide (NO₂) because of their poor porosity and low gas reactivity. Therefore, the suggestion of novel platform for the creation of pores on graphene based fiber is significantly desired.

In this work, we propose a facile synthetic route for providing high density of pores in graphene based fiber by employing tunicate cellulose nanofiber (TCNF) engineering. For the first time, by using the liquid crystal (LC) behavior of graphene oxide (GO)-TCNF composite, we successfully develop the ultra-porous GO fibers due to the random distribution of TCNF in GO fiber. Furthermore, by using the super-hydrophilicity of TCNF, TCNF in GO fibers is also used as seed layer for growth of WO₃ nanorods (NRRs), leading to formation of porous WO₃ NRRs-GO thorn-bush like composite single fiber. Due to its high porosity and heterogeneous junction effect (WO₃, NRRs-GO), porous WO₃ NRRs-GO showed reversible NO₂ detection capability even at 1 ppm level of NO₂ chemicals.

**NM01.04.21**

**Design of Microwave Absorption Structures Based on Magnetite Multi-Granule Nanocluster—Multiwall Carbon Nanotube Composite Materials**

Boo Hyun An¹, Bum Chul Park², Sahith R. Madara³, Hamad Al Yassi⁴, Jung-Rae Park⁵, Jong E. Ryu⁶, Mihai Sanduleanu⁷, Young Keun Kim⁸ and Daniel S. Cha¹; ¹ Khalifa University of Science and Technology, Abu Dhabi, United Arab Emirates; ² Korea University, Seoul, Korea (the Republic of); ³ Amity University, Dubai, United Arab Emirates; ⁴ Minotech, Charlton, Massachusetts, United States; ⁵ North Carolina State University, Raleigh, Indiana, United States.

Recently, reduction and cancellation technology has been widely studied in military and civil areas for various applications such as radar absorption, electromagnetic interference (EMI) shielding, reduction of electromagnetic wave pollution, and wireless communication fields. Research on microwave absorption materials is widely conducted by adopting dielectric and magnetic powder material to conductive matrix, because the conductivity, dielectric constant and permeability of the materials are contributing to the microwave absorption efficiency of the materials. [1-3] Carbon nanotubes (CNT) are good candidates for materials for the conductive matrix of microwave absorption composite structures due to their high electrical conductivity, light weight, and easiness to form thin layers. Ferrite nanocostructures are generally used for microwave absorbing materials due to their magnetic and dielectric property. The magnetic properties of ferrites are different depending on microstructural and physical properties of the ferrites such as chemical composition, crystal structure, crystallite size, particle size. Such properties can be controlled by synthesis techniques and our novel synthesis method of multi-granule nanocluster (MGNCl) of magnetite (Fe₃O₄) by controlling the cluster and granule size with the modified hydrothermal polyol process was previously reported [4]. In this study, we fabricated Fe₃O₄ MGNCl – multiwall CNT (MWCNT) composites by using the surface-engineered tape-casting (SETC) method with various granule and particle size of MGNCs. The microstructural and microwave absorption properties in X-band (8.2 GHz – 12.4 GHz) with different granule size of the nanoclusters are investigated. Design and three-dimensional (3D) printing of the 3D metamaterials based on the nanocomposite materials made up of MGNc and MWSNT are also in progress.

**Reference**


**NM01.04.22**

**Evolution of Graphene Oxide from Graphite Oxide—Study of Ultra-sonication Time on the Morphological and Structural Properties**

Venkata Krishna Kasthik Tangirala, Daniel S. Campos and Ventura R. Lugo; Universidad Autonoma de Estado Hidalgo, Hidalgo, Mexico.

In the present work, graphite oxide (GO) and graphene oxide (GO) were synthesized utilizing Modified-Hummers method and the effect of ultra-sonication time (2, 4, 6 and 8 h) on their physical properties were studied. SEM and AFM analysis confirm the formation of GO sheets with lamellar morphology (width ~2 µm and thickness ~0.7 nm) and the increase in the ultra-sonication time resulted in exfoliation of GO sheets demonstrating the evolution of GO from gO. A left shift of (001) plane from 11.3 (2 h) to 10.7 (8 h) in the diffraction patterns confirms the oxidation and formation of gO and GO. Also, FTIR affirms that all samples possess similar functional groups whereas an increase in the ultra-sonication time widens the O-H band and increases C-H band intensity indicating the reduction of GO. Additionally, Raman analysis shows that the increase in ultra-sonication time increased the ID/IG ratio and decreased the in-plane crystallite size (from 18 to 12 nm) which is due to the defects occurred from additional oxidation and conversion of sp² to sp³ hybridization. Finally, in this work the principal structural and morphological differences between the gO and GO were demonstrated.

**NM01.04.23**

**Graphene Oxide Quantum Dots Synthesized from Biomass Wastes—White Light Emitting Nanomaterials in the Solid State**

Philippe Pierrat¹, Pierre Maget₁, Jean J. Gauin², Wu Luo³, Liqiang Mai⁴, Pascal Franchetti⁵, Stéphane Dalmasso⁶, Hafida Bouklah⁷, Sébastien Diliberto⁸ and Jaafar Ghanbaja⁹; ¹ Jean Barriol Institute, University of Lorraine, Metz, France; ² Wuhan University of Technology, Wuhan, China; ³ University of Skikda, Skikda, Algeria; ⁴ Jean Lamour Institute, University of Lorraine, Nancy, France.

Graphene oxide quantum dots (GOQDs) are part of a fascinating class of recently discovered nanocarbons that have both graphene oxide and quantum dots properties. Like carbon quantum dots (CQDs), GOQDs electronic and luminescent properties (e.g. wavelength-tunable emission, excellent photostability and a potential high quantum yield potential) are advantageously combined with chemical stability, water solubility and biocompatibility [1]. Microwave heating is becoming a popular method for fast, efficient and reliable preparation of CQDs, which is usually done in 2 steps (i.e. carbonization, and passivation). Current research is focusing on more sustainable and economical syntheses, greener chemistry and more diversified starting materials. This is why much efforts has been devoted to developing new means of synthesizing CQDs from raw materials such as citrus fruit peels, ground coffee, orange juice, overcooked meat [2-4]. In this context, we report herein the synthesis of GOQDs from various biomass waste materials with the use of a monomode microwave reactor. Various source materials, such as orange peels, date stones and oak acorns were first dried at 60°C for 24 h, then crushed and grounded. The prepared samples were then poured into vials and inserted in the microwave reactor with the required reactants. The accurate verification of temperature, time, pressure and power helps to provide reproducible batches of GOQDs with particles of controlled size. After purification and separation, the prepared GOQDs were then systematically characterized in terms of chemical structure (elemental analysis, TGA and XPS), size (DLS and TEM) and photophysical properties (absorbance and luminescence spectroscopies). Surprisingly, very small GOQDs (~1.2 nm) with identical...
morphological and photophysical features were elaborated regardless of their biomass waste source. The water soluble particles show excitation-dependent photoluminescence ranging from blue to orange emission wavelength in solution. Interestingly, thin films display white light emission under UV excitation, while aggregation-induced quenching is usually observed in the solid state. This latter observation opens the way to applications in OLED devices that are currently under investigation in our laboratory. In conclusion, we have been able to set up a fast, reproducible and green microwave-assisted synthetic method to prepare GOQDs. This will undoubtedly lead to new means of upgrading biomass waste as potential photosensitive materials for various applications (optoelectronic devices, energy, biosensors…).

References

NM01.04.24
Designing a Catalyst for Carbon Nanotube Growth by Ab Initio Molecular Dynamics with Respect to the Carbon Source Molecule Dissociation Process Satoru Fukuhara1, Masaaki Misawa2, Fuyuki Shimjo2 and Yasushi Shibuta1; 1Department of Materials Engineering, The University of Tokyo, Tokyo, Japan; 2Department of Physics, Kumamoto University, Kumamoto, Japan.

For the application of carbon nanotubes (CNTs), a synthesis method which can control its property (e.g. length, diameter and chirality) is required. Catalytic chemical vapor deposition (CCVD) method is the standard way to produce CNTs. In this method, the quality and quantity of CNTs largely depends on the combination of the catalyst and the carbon source. For example when using ethanol as the carbon source, which C-O bond or C=C bond dissociates have effect on CNT growth. In order to develop a better catalyst, it is required to know the mechanism of the dissociation process. In this research, we clarify the difference of ethanol dissociation reaction mechanism by catalyst element from the atomistic viewpoint, using the ab initio molecular dynamics method (AIMD method) and clarify the advantages of using the alloy catalyst and give guidance to new catalyst design. The dissociation process of ethanol and carbon monoxide on Fe, Co, FeCo catalyst is investigated by AIMD. 30 ethanol molecules and 30 carbon monoxide molecules are placed around the Fe2, Co2, FeCo6 clusters, respectively. The dissociation process of 5 ps for ethanol molecules and 2 ps for carbon monoxide molecules is analyzed at 1500 K. C=C bond and C-O bond of ethanol have been observed to dissociate on each catalysts, but C-C bond dissociation is only observed on Fe2Co16 catalyst. Regarding the calculation of carbon monoxide, C-O bond dissociation is only observed on Fe catalyst. We have clarified that bond formation of oxygen and metal atoms is important in dissociation reaction mechanism. Specifically, strong bonds with oxygen as seen with Fe atoms are disadvantageous in C-C bond dissociation but are necessary for C-O bond dissociation in ethanol and CO molecules. From these results, it is possible to design a catalyst that dissociates both C-C bonds and C=O bonds by alloying elements that form strong bonds with oxygen.

NM01.04.25
The Effect of Heat Treatment on the Structural Development and Mechanical Properties of Carbon Fibers Jeong-Fun Lee, Sojeong Hao, Kyeonghun Choi, Sang-Ha Hwang, Youngho Eom and Han Gi Chae; Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of).

Carbon fibers have been of great interest in many industrial applications due to their high mechanical properties. The tensile strength of the polyacrylonitrile (PAN)-based commercial carbon fiber is as high as 7 GPa, and the highest tensile modulus is about 600 GPa although the theoretical properties of carbon-carbon bonds are known to be 150 GPa and 1060 GPa, respectively. The property discrepancy is attributed to the defective structures including voids and structural heterogeneity. In addition, carbon fibers are often subjected to extreme environment such as high stress and high temperature, which may change their microstructure and properties. In this study, we have heat-treated commercial carbon fibers as high as 2400 °C without applying external stress, and traced the changes in microstructure using Raman spectroscopy, wide-angle X-ray diffraction, and X-ray photoelectron spectroscopy. The tensile testing and nano-indentation experiment were also conducted to examine the correlation between the microstructural variation and corresponding mechanical properties. The structure-property relationship of carbon fibers upon high temperature heat treatment will be presented.

NM01.04.26
Using Cell Membrane Models to Investigate the Toxicity of Carbon-Based Nanomaterials Juliana Cancino1, 2 and Valtelen Zacullo1, 2; 1University of Sao Paulo, Sao Carlos, Brazil; 2Nanomedicine and Nanotoxicology Group, University of Sao Paulo, Sao Carlos, Brazil.

Single-wall carbon nanotubes (SWCNTs) and polyamidoamine dendrimers (PAMAM) have been proposed for a variety of biomedical applications due to their unique physico-chemical properties. However, toxicological studies have shown that these nanomaterials may exhibit high toxicity in biological environments. In this study we used C2C12 murine cells and membrane model systems to understand the interactions occurring at the bio-nano interface, as well as the possible toxicity exhibited by SWCNT-PAMAM conjugates against to mammalian cells. The results showed that SWCNT-PAMAM and PAMAM inhibited the proliferation and caused DNA damage in C2C12 cells. Flow cytometry analyses revealed a less toxicity in C2C12 cells exposed to SWCNT compared to the other nanomaterials. The toxicity of SWCNT, SWCNT-PAMAM, and PAMAM in C2C12 cells are strongly correlated with the charge of the nanomaterials. The membrane model studies revealed a pronounced incorporation of SWCNT-PAMAM through dipalmitoylphosphatidylcholine (DPPC) monolayers even at high surface pressure values, ~30 mN/m. Therefore, the results confirm that the presence of the nanomaterial affects the packing of the synthetic membrane monolayers. The methodology introduced here may be of great importance for further nanotoxicity studies.

NM01.04.27
Detection of Acute Kidney Injury Biomarker Using Reduced Oxide Graphene Transistors Fabricio Santos1, 4, 5, Nirtzin C. Vieira1, Naiara Zambianco1 and Valtelen Zacullo1, 2; 1University of Sao Paulo, Sao Carlos, Brazil; 4Institute of Science and Technology, Federal University of São Paulo, São Jose dos Campos, Brazil; 2Nanomedicine and Nanotoxicology Group, University of Sao Paulo, Sao Carlos, Brazil.

The early detection of biomarkers of renal damage is important because the glomerular filtration rate is reduced before the onset of the signs of renal failure. Cystatin C is a protein that has been identified as the most promising biomarker to acute kidney injury diagnosis in early stages. Here, we introduce a papain-modified graphene oxide field-effect transistor (rGOFTET) for the detection of Cystatin C with enhanced sensitivity. The rGOFTETs were fabricated using the layer-by-layer (LbL) technique, employing oppositely charged rGO onto interdigitated gold electrodes. Detection of Cystatin C occurred via electrical measurements upon monitoring output and/or transfer curves of rGOFTETs. The detection mechanism is based on changes of the charge balance at the electrode surface after the formation of papain/cystatin C complex. Cystatin C could be detected at a concentration range from 5 ng.mL-1 to 100 ng.mL-1 with 0.13 mV/ngmL-1 sensitivity, suggesting that the system may useful for clinical purposes.

NM01.04.29
Enhanced Conductivity and Thermal Stability of Carbon Nanotube Yarns via Densification and Chemical Doping Karen Soule1, 2, Colleen C.
Carbon nanotube (CNT) based conductors are candidate light-weight and robust alternatives to conventional metal conductors for a variety of space, defense, and power transmission applications. Although the conductivity of bulk CNT materials is still an order of magnitude less than copper conductors, these demanding applications can benefit from the reduction in weight, increased flexure tolerance, and corrosion resistance provided by CNT conductors. Previously, CNT conductors have been produced from commercially available CNT sheet material, which is rolled into wires of varying diameter. Radial densification and chemical doping with aqueous KAuBr₄ has been used to increase the conductivity of these rolled conductors by an order of magnitude. These works demonstrated the possibilities of CNT conductors along with the effects of densification and chemical doping, but these techniques are limited in scalability due to the batch nature of CNT sheet production. Recently, continuous processes have allowed for the production of CNT yarns available in kilometer lengths, a breakthrough needed for the practical implementation of CNT conductors. With the synthesis of scaled CNT conductors, the operational stability of these materials along with the accompanying chemical doping procedures needs to be explored.

In the present work, densification and chemical doping with KAuBr₄ is shown to improve the conductivity of commercially scaled CNT yarns by 6x, while increasing the current density at failure by 67% to 35 MA/m². A current cycling procedure involving increasing current densities with intermittent rest steps and I-V sweeps is applied to as-received, H₂O densified, and KAuBr₄ doped and densified CNT yarn samples. Analysis of the data allows for changes in resistance, during operation and at low current, as a result of previous current exposure to be determined. The KAuBr₄ doped and densified samples experience no permanent change in resistance at current densities up to ~25 MA/m², exceeding the as-received materials by greater than 3x. Thermogravimetric analysis shows that ~10% of the mass of KAuBr₄ doped and densified CNT yarns oxidizes or desorbs at temperatures lower than 400°C. A series of samples were prepared with varying thermal oxidation and chemical doping treatments to understand how the desorbed or oxidized components affect the electrical properties of the CNT yarns. Analysis on how the thermal stability of KAuBr₄ results in greater electrical stability will be discussed.

NM01.04.30 Polyacrylamide Covalent Grafted on Graphene Oxide (GO) Surface for Extraction of Chromium(VI) Pei P. Yang¹, ², Ruimin Li¹ ² and Jun Wang¹ ²,¹ College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin, China; ²Key Laboratory of Superlight Material and Surface Technology, Ministry of Education, Harbin Engineering University, Harbin, China.

With the rapid growth of industrialization, water pollution caused by heavy metals has become one of the most serious environmental problems, and attracted considerable attention. Heavy metals are non-degradable and can accumulate in living tissues, so they must be removed from wastewater. Extraction of heavy metals from wastewater embraces reverse osmosis, chemical precipitation, electrodialysis, organic−inorganic ion exchange, and adsorption. Among these methods, adsorption stand out from the aforementioned methods due to its simple operation and cost-effectiveness. Thus far, the most efficient adsorbent for adsorption heavy metal has high adsorption capacity and removal rate. However, in recent years, the adsorbents designed for the capture of heavy metal have not been suitable for application at wastewater pH. Currently, the design of a suitable wastewater adsorbent shows more promise for the extraction of heavy metals. In this report, we report a facile approach to construct a suitable wastewater pH and large surface area material that polycacrylamide (PAM) covalent grafted onto the surface of GO nanosheets. In the progress, transmission electron microscope (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) were used to determine the effectiveness of the synthesis of GO-PAM composites. Meanwhile, the GO-PAM composites were investigated for adsorption of Cr(VI) from aqueous solution. It is clear that the GO-PAM composites have a high adsorption capacity (qₑ= 398.2 mg g⁻¹, T=298.15 K) at a suitable wastewater pH with a high removal rate (>90%). Based on the FTIR spectroscopy, Zeta potential, and X-ray photoelectron spectroscopy (XPS), a possible adsorption mechanism of Cr(VI) onto GO-PAM composites is revealed. Finally, the result also exhibited outstanding adsorption efficiency and adsorption capacity under the operating conditions for the adsorption-desorption of Cr(VI) from aqueous solution, which indicated a promising potential in the application of the absorbent in wastewater. (This paper is funded by the International Exchange Program of Harbin Engineering University for Innovation-oriented Talents Cultivation.)
Carbon nanotubes (NTCs) and graphene-based nanocomposites have been reported to enhance the X-ray shielding effects, for photons with energy below 17 keV [1,2]. The mechanism behind this anomalous behavior cannot be interpreted by the already-established beam attenuation theory. In this work, we report additional evidences of the improvement of X-ray attenuation efficiency by the addition of a very small amount of reduced graphene oxide (4.0 wt%) in nanocomposites made of poly(vinylidene fluoride) (PVDF) homopolymer and barium sulfate (BaSO₄) nanoparticles. The investigation was performed by using polyenergetic spectra produced by an X-ray tube energized with 20, 30, 40, 60, 80 and 100 kV. For the lowest voltage (20 kV), the beam attenuation for pure PVDF/BaSO₄ nanocomposite (50/50) and the one with the addition of 4.0 wt% of GO was found to be 9.14% and 24.56%, respectively. The respective linear attenuation coefficients (μ) were 39.9 cm⁻¹ and 54.4 cm⁻¹, respectively. The X-ray attenuation gradually decreases until 6.71% and 17.62%, respectively, for the highest energy spectrum (100 kV). Fourier transform infrared data revealed that, due to the lack of the bending vibration modes of CF₂ molecule at 656 cm⁻¹, 688 cm⁻¹, 723 cm⁻¹, 776 cm⁻¹ and 796 cm⁻¹, characteristics of the γ-crystalline phase of PVDF the nanocomposites casted from solution are mostly in the β-ferroelectric phase of PVDF, besides the γ-paraelectric phase. SEM micrographs were used to evaluate the dispersion state of graphene sheets and the BaSO₄ nanoparticles into the polymeric matrix. UV-Vis spectrometry and Differential Scanning Calorimetry were also performed in order to complement the structural analysis. The results confirm that the addition of graphene sheets in PVDF polymer-based nanocomposites enhances the X-ray shielding features. The phenomenon is discussed in terms of the reported anomalous negative thermal expansion coefficient of graphene sheets [3].

References


NM101.04.34
The Stability of Humidity Sensor Response in Graphene by Low Damage Plasma Chun-Hsuan Lin Lin1, Mingshiu Tsai1, Weitong Chen1, Chihsien Huang1, Weiyen Woon1 and Chiting Lin1, 1 Graduate Institute of Electronics Engineering, National Taiwan University, Taipei, Taiwan; 2 Materials Engineering, Ming Chi University of Technology, New Taipei, Taiwan; 3 Physics, National Central University, Jungli, Taiwan.

Graphene has been recognized as a promising material for sensing applications, such as gas detection and biomolecular sensor. Although it has been demonstrated to have good sensing characteristics, some essential aspects such as stability need to be improved for further applications. To conquer these obstacles, different kinds of surface functionalization, for example particle doping, chemical modification, and UV irradiation are used to demonstrate improvements of repeatability and stability with the cost of sensitivity degradation. Following surface functionalization idea, in this work, we used a low-damage oxygen plasma to functionalize a bilayer graphene sheet without high-energy ion bombardment and UV irradiation damage on the graphene structure. This leads to an improved performance of the developed bilayer graphene humidity sensor. Based on the experimental observation of Raman spectroscopy, the D/G ratio showed the result of the low-damage plasma functionalization and the integrity of graphene structure. Utilizing XPS spectra, at the same time, we found the fact that the compositional ratio of C-OH is increased with modified time. Similar observations can also be indicated by wettability enhancement by contact angle measurement. According to these experimental characterizations, one possible scenario is that the upper layer of the bilayer graphene is the one of the functionalization and the lower layer of the bilayer graphene keeps its original 2D structure. Then the developed low-damage bilayer graphene can be experimentally demonstrated as a humidity sensing material. Compared with traditional graphene humidity sensors, the developed low-damage bilayer graphene humidity sensor has less drifting. The drifting response is resulted from the π electron adsorption, which can easily adsorb molecules, including the water molecule and the other air molecules. These adsorbed molecules are difficult to be desorbed from the surface and cause sensor degradations. In our low-damage bilayer graphene, there are high surface ratio of O-H bond introduced by the low-damage oxygen plasma. As a result, the surface with less π-electrons helps water molecule to be desorbed from the surface. This results in a stable sensing response to humidity. This work raises a method which potentially helps to functionalize graphene-based sensing materials.

NM101.04.35

In this work, a partially reduced graphene oxide (GO) biosensor is presented. Mild thermal treatment is used to reduce GO drop-casted on a SiO₂ substrate, after hydrophilization and functionalization. As a result of the reduction, the graphene sp² lattice of GO is gradually restored and its electrical conductivity is enhanced. At the same time, the GO retains functional groups during the course of the reduction, thus facilitating the immobilization of proteins on its surface. To confirm this hypothesis, Biotinylated Bovine Serum Albumin (b-BSA) was used as a model molecule in protein immobilization experiments. The immobilization of b-BSA was confirmed by inspection of the GO drops under a fluorescence microscope after reaction with the fluorescently labeled streptavidin. Reduced GO biosensors were then constructed by first drop-casting GO on APTES functionalized SiO₂ substrates followed by a mild thermal treatment (heating for 1 h at 80°C) in order to achieve both protein immobilization and a conductive state. Silver paint conductive adhesive was then used to contact the GO drops. To test the sensor in the detection of b-BSA immobilization, a plastic frame was placed around the GO drops in order to contain the reaction fluids and prevent short-circuiting while resistance measurements were taken using the following procedure: a) inserting buffer solution in the frame and over the GO, b) adding different concentrations of b-BSA and monitor its immobilization, c) adding BSA blocking, and d) adding streptavidin at various concentrations. Using this procedure the sensor was capable to detect b-BSA concentrations down to 260 pM. Based on these initial results the sensor was then used in a medically relevant application which involves the detection of BRCA1 gene. For this experiment the characteristic gene sequence of BRCA1 is amplified and tagged during amplification with a biotin molecule at its end using Recombinase Polymerase Amplification (RPA) at 37°C for 30min. RPA was chosen as it possesses many advantages over other amplification methods in terms of speed, portability, accessibility, sensitivity and specificity. Next, the GO sensor was prepared by drop-casting and immobilizing streptavidin over the reduced GO sheet non-covalent bindings through the π electrons and O-H bonds. Upon insertion, then, of the amplified DNA the biotin end interacts with the immobilized streptavidin. Using this scheme DNA concentrations down to 200pM was detected.

These findings thus demonstrate the ability of the proposed sensor to detect on the one hand the immobilization of biotin on the sensor as well as its usefulness in a real-world application. Further work will focus on further optimizing the sensor by introducing DNA probes for label free detection.

Ethier boron or nitrogen doping was carried out while growing of graphene on a copper foil. For the boron doping, mixture of methane and the dopant vapor of phenylboronic acid, which was generated by heating between 393 and 433 K, was introduced to the furnace kept at 1273 K where the Cu foil was placed. For the nitrogen doping, we used the vapor of melamine generated at 473 K. Prior to grow of the doped graphene on Cu, the Cu foil was annealed at 1273 K for 8 hours under flowing of 20 sccm H2 at 3 kPa in order to improve the flatness of surface. Growth of the doped graphene was carried out for 2 hours at 1173-1273 K at the pressure of 3 kPa with a total flow of 100 sccm of the mixture of PR gas (10% CH4 in Ar) and Ar gas for carrying phenylboronic acid or melamine vapor by adding 2 sccm H2. After growing the doped graphene, gas flow was switched to the mixture of 5 sccm H2 and 50 sccm Ar at 3 kPa, then cooled. Cooling rate was ca. 40 K/min by 1073 K.

It was found that low pressure annealing of Cu foil was drastically improved the flatness of the surface, which would be a great benefit for growing graphene. From the Raman scattering, the number of the layers of the doped graphene was found to be excess of 5 layers which was evaluated by the intensity ratio of G'/G. Doping amount was evaluated by XPS, which was taken by an Al-Kα excitation, and was found to be in the range of a few at% for both B and N. In addition, rate of substitutional doping of B for C was increased when low level of phenylboronic acid vapor was mixed with methane by decreasing a vaporizing temperature of the dopant by 393 K. For the nitrogen doping, substitutional doping of N for C (quaternary N) was enhanced as decreasing growth temperature of graphene by 1173 K. In case of high temperature doping at 1273 K, pyridine-like (or pyrrole-like) N accompanying with atomic defect at the next of N became a major component for N-doped graphene. Electric conducting feature of B-doped and N-doped multilayered graphene will be opened as the results of sample characterization.

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9:15 AM NM01.05.03
new 2D crystals have been predicted to exhibit unique electronic structures beyond graphene, such as large band gap (graphane) and ferromagnetism. Here, in a combined investigation of scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), low-energy electron diffraction (LEED), Raman spectroscopy, and density-functional theory (DFT) calculations, we present the formation and anisotropic electronic properties of the single-crystal, millimeter-scale, one third hydrogenated graphene (OTHG) on Ru(0001) substrates. Monolayer graphene (MLG) was firstly synthesized on Ru(0001) and subsequently annealed to ~1200 K for 20 minutes and subsequently annealed to ~1200 K for 20 minutes. After four cycles of hydrogen exposure and subsequent annealing, the sample was characterized by STM and LEED. STM images show that the sample exhibits a moiré pattern with a periodicity of ~2.64 Å. Based on atomic-resolution STM images and LEED pattern, a double-sided Vs±3Vs/R30° hydrogen-adsorbed structure was proposed. Simulated STM images show excellent agreements with experimental observed STM images validating the atomic model. The size and uniformity of the fabricated OTHG were checked by taking LEED patterns and STM images on different locations of the sample. We demonstrate that the single-crystal OTHG sample has areas up to 16 mm² (the size of the Ru substrate). Raman spectra and STS measurement indicate that the interaction between the fabricated OTHG and Ru substrate is weak. DFT calculations using a high-level hybrid functional show that for the new 2D material, OTHG, there are Dirac cones at Fermi level only along one high-symmetry (Γ-M) direction. Energy gaps (~0.6 eV) are opened along other two Γ-M directions due to the hydrogenation, leading to an anisotropic electronic structure. Considering the significant anisotropic electronic structure, novel anisotropic physical properties, such as anisotropic Fermi velocity and directional conductance are expected in OTHG[1].

References:

9:30 AM BREAK

10:00 AM **NM01.05.04**

Structural and Environmental Factors for Tuning Photoluminescence Properties of Carbon Nanotube sp2 Defects S. Doern¹, Avishek Saha¹, Xiaowei He¹, Brendan Gifford¹,², Geyou Ao¹, Ming Zheng¹, Kirill Velizhanin¹, Sergei Tretiak¹,³ and Han Hoon¹; ¹Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, New Mexico, United States; ²Center for Nonlinear Studies, Los Alamos National Laboratory, Los Alamos, New Mexico, United States; ³Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

Photoluminescent defect states introduced by low-level covalent functionalization of single wall carbon nanotubes (SWCNTs) are of growing interest as routes to enhanced photoluminescence (PL) quantum yields and new functionality. In particular, exciton localization in deep traps at the defect sites gives rise to single photon emission at room temperature that is tunable to telecom wavelengths. Control over defect-state emission wavelengths and dynamics is essential for advancing potential applications of these unique emission MITes. We present results exploring the role of nanotube structure in determining the range of binding configuration that can occur for functionalizing agents. We show that functionalization occurs at ortho-only binding configurations and that nanotube structural symmetry can lead to a 3-fold decrease in emission wavelength bandwidth for zigzag structural types. Strategies for tailoring the SWCNT environment to extend defect-state PL lifetimes (to nanoseconds) and optimize linewidths will also be presented. Environmental impacts on dephasing times will also be discussed, along with temperature dependent effects on relaxation dynamics.


10:30 AM **NM01.05.05**

Concentric Dopant Segregation in CVD-Grown Nitrogen-Doped Graphene Single Crystals Jinning Lin¹, Roland Yingjie Tay¹, Hongli Li¹, Lin Jing¹, Shun Hon Tsang², Asaf Bolker², Cecile Sagué³ and Edwin Hang Tong Teo¹; ¹Nanyang Technological University, Singapore, Singapore; ²Solid State Institute, Haifa, Israel; ³Space Environment Department, Sorreq NRC, Yavne, Israel.

Heteroatom doping in graphene leads to bandgap opening and tunable electronic, magnetic and optical properties, which are important for graphene-based electronics applications. In recent years, scalable growth of nitrogen-doped graphene (NG) by chemical vapor deposition (CVD) has been extensively studied because of its potential for practical applications. A phenomenon that occurs exclusively for CVD-grown NG films is the segregation of doping concentration. However, most studies to date are conducted using highly polycrystalline MgO films comprising small grain sizes. It is still unknown whether dopant segregation occurs in single crystalline NG domains. Here, we used hexamethylenetetramine ((CH2)6N4) as a single-source solid precursor to grow hexagonal-shaped monolayer NG single crystals ~20 μm on Cu substrates. The NG single crystals exhibit discrete concentric hexagonal rings comprising N-depleted regions as determined by Raman spectroscopy. Supported by scanning tunneling microscopy experiments, we propose that the segregation of N dopants is caused by a competing N attachment mechanism to either zigzag or Klein edges during growth; where the former should result in higher N concentration and the latter with lower N concentration. This work provides critical insights into the growth mechanism of CVD-grown NG and enables new opportunities to engineer the properties of graphene by fabrication of lateral heterostructures.

10:45 AM **NM01.05.06**

Symmetry Breaking in the Plastic Deformation of Coiled Carbon Nanotubes Under Torsional Stress/Strain Socrates O. Dantas¹,², Cristiano F. Woelflner³, Alexandre F. Fonseca² and Douglas S. Galvão⁴; ¹Universidade Federal de Juiz de Fora, Juiz de Fora, Brazil; ²Applied Physics Department, State University of Campinas, Campinas, Brazil; ³Department of Physica, Universidade Federal do Paraná, Curitiba, Brazil.

Since the discovery of carbon nanotubes (CNTs) [1], other carbon allotropes and/or morphologies were obtained. One of these morphologies is coiled carbon nanotubes (CCNTs) [2]. It has been a continuous evolution in the study of the structures as well as properties (electrical, mechanical or thermal) of addition of nanostructured carbon materials (NMCs) to polymers and other host materials, forming all sort of composites. However, the molecular scale
mechanisms by which the NCMs interact with the hosts are still not fully understood. Previous studies [3-5] used theoretical simulations to address the interaction of NCMs with polymers, and a recent review also illustrated the use of simulations on the study of graphene and hexagonal boron nitride polymer nanocomposites [6]. Inspired by these studies, we investigated the mechanical properties of pristine CCNTs as well as composites formed with CCNTs and paraffins (C₆H₁₃). The methodology involves the use of fully atomistic reactive molecular dynamics simulations using the ReaxFF force field within charge optimized many-body potential included in the LAMMPS open source simulation package. Besides standard tensile and compression strain analyses, we also considered torsional deformations (clockwise and counterclockwise). For pristine systems, all the coils are left-handed: a) the stress response to tension shows a complex behavior and for some structures the stress reaches ~7-8 GPa with a strain 20-30%; b) from the compression analysis the elastic regime persist up to 4-5GPa in stress and strain range 16-18%; c) under counterclockwise torsion the systems start to exhibit failure point (symmetry breaking) within (3/8-1/2) of a turn; d) under clockwise deformation the systems evolve to a compact coiled and tube collapsed. For composite systems (CCNTs and paraffin) we observed a significant alignment of paraffin molecules with the main axis tubes. The mechanical behavior is very similar to the one for pristine systems, but as expected, at different deformation rates and/or ranges.

Controlling the structure and arrangement of single-walled carbon nanotubes (SWCNTs) directly during their growth constitutes a central bottleneck for the applications of SWCNTs in numerous fields including optics and microelectronics. Catalytic chemical vapor deposition (CCVD) is currently the most popular method for synthesizing SWCNTs because it offers more defined and versatile growth conditions, thus allowing to grow SWCNTs with a better control of their structure, orientation, surface density and purity. Although many groups reported catalyst systems and growth conditions yielding high selectivity for specific diameters or chiralities, a profound understanding of the processes impacting the structural distribution of SWCNTs is still missing. Two main reasons can explain the difficulty to experimentally correlate growth mechanism and structural features: 1) monitoring the growth of individual SWCNTs is still remain very challenging, 2) determining SWCNT structure is usually complex and requires a combination of methods. In this contribution, we will show how optical methods of spectroscopy and microscopy can help addressing this issue. First, we will present in situ and ex situ Raman measurements used to study the dynamics of the different populations of SWCNTs during their growth by CCVD [1]. Importantly, this study reveals that the nanotube diameter distribution strongly evolves during SWCNT growth but in dissimilar ways depending on the growth conditions. The origins of these evolutions will be discussed. Second, we will show how polarization-based optical methods can be used to monitor the growth of individual SWCNTs on substrates [2]. We will notably show that individual SWCNTs on substrate can be imaged during their growth with time resolution of 5-50 ms. Third, we will propose a general modeling of the polarized optical spectra of individual SWCNTs including the influence of the multi-layer substrate and of coherent and non-coherent depolarization by the optics. We will show that this model allows one to extract both the real and imaginary parts of the nanotube susceptibility and to improve the methodology of chirality assignment [3].

References

Passivation of these states can cause the complete removal of these induced local magnetic moments. Our studies provide the fundamental understanding required to design electronic 2D materials for specific applications using irradiated graphene and passivated irradiated graphene as templates.

2:15 PM NM01.06.03

Manufacture and Scaling Limits of Graphene Nano-gap Electrodes

Ghazi Sarwat Syed and Harish Bhaskaran; University of Oxford, Oxfordshire, United Kingdom.

Graphene nanogap electrodes have been of recent interest in a variety of fields, ranging from single molecule based electronics to DNA sequencing and to phase change memories. Several recent reports have highlighted that scaling graphene nanogaps to even smaller sizes is a promising route to more efficient and robust molecular and memory devices. However the reliable and large-scale device fabrication methodology remains a challenge and crucially the scaling limits are completely unknown. In this talk, I will illustrate the electroblending approach for sub-5 nm nano-gap fabrication and subsequently define the fundamental limit to scaling carbon based nano-gaps which is associated to a carbon chain filamentation process (electric field driven formation of carbon chains). Using a phase change material in the nanogap as a demonstrator device, fabricated using a self-alignment technique, I will demonstrate that for gap sizes approaching 1 nm the switching is dominated by such carbon chain formation, creating a fundamental scaling limit for potential devices. These findings have important implications, not only for fundamental science, but also in terms of potential applications.

2:30 PM NM01.06.04

Defects Enable Dark Exciton Photoluminescence in Single-Walled Carbon Nanotubes

Amanda Amori1, Jamie Rossi2, Zhentao Hou3, Brian Landi2 and Todd Krauss1; 1University of Rochester, Rochester, New York, United States; 2Rochester Institute of Technology, Rochester, New York, United States.

Single-walled carbon nanotubes (SWCNTs) are fundamentally interesting and technologically relevant materials with size-tunable absorption and emission across visible and near infrared wavelengths. However, several important aspects of SWCNT photophysical properties defy even simple physical explanation. For example, we found using variable temperature photoluminescence excitation spectroscopy that a sideband located approximately 130 meV away from the bright S1 exciton peak relating to the K-momentum dark exciton state, called Xs, decreased in intensity five-fold as the nanotubes were cooled. Direct optical excitation of this dark state is nominally forbidden, thus calling into question how the state is populated, why it is so prominent in the photoluminescence spectrum, and what causes its strong temperature dependence. Interestingly, the ratio of the integrated photoluminescence intensities of Xs to S1 scales with a Boltzmann factor completely unrelated to the photon, thus it is thought to be responsible for depopulating the K-momentum dark exciton state: an in-plane transverse optical phonon, A1. Furthermore, photoluminescence spectra from individual nanotubes show that only a small fraction exhibit the Xs feature, with varying oscillator strength, thus suggesting that intrinsic processes such as phonon scattering are not responsible for populating the dark state. Alternatively, we suggest that populating the K-momentum dark exciton state requires scattering from defects, which is consistent with the increased magnitude of the Xs feature for samples with increased sample purification and processing. Thus, the presence of an Xs peak in photoluminescence is an extremely sensitive spectroscopic indicator of defects on single-walled carbon nanotubes.

2:45 PM NM01.06.05

Thermoacoustic Generator from a Free-Standing Single Walled Carbon Nanotube Film

Stepan Romanov1,2, Ali Aliev3, Albert Nasibulin2 and Boris Fime4; 1Skolkov Institute of Science and Technology, Moscow, Russia; 2Skolkov Institute of Science and Technology, Moscow, Russian Federation; 3University of Texas at Dallas, Dallas, Texas, United States.

Recent advances in material science provoked a new wave of researches in a thermoacoustic process induced by Joule heating. Mainly due to very low heat capacity per unit area (HCPUA) of the modern materials. Here, we present the state-of-the-art performance of free-standing single walled carbon nanotubes (SWCNTs) thin films as thermoacoustic sound generators. The SWCNT films synthesized by an aerosol chemical vapor deposition (CVD) method showed record sound pressure level of 101 dB with a frequency of 100 kHz at the distance of 3 cm and the input power of 1 W. Such performance was caused by extremely low HCPUA of the films 0.35 * 10-3. The research was performed with the films of different thicknesses in the sound range from 1 kHz to 100 kHz. The importance of aerogel structure of the materials for thermoacoustic generation researched theoretically and with experiments of densification and vacuum annealing. Full theoretical model of thermoacoustic free-standing films, which included effects of diffraction and finiteness of heat capacity per unit area was derived. Theoretical model was checked numerically in 3D by solving full system of coupled Linearized Navier Stokes and Helmholtz differential equations. This work was supported by Skoltech NGP Program (Skoltech-MIT joint project).

3:00 PM BREAK

3:30 PM *NM01.06.06

Thermolectric Materials Consisting of Doped Carbon Nanotubes

Yoshiyuki Nonoguchi1,2, 1Nara Institute of Science and Technology, Nara, Japan; 2JST PRESTO, Kawaguchi, Japan.

Carbon nanotubes have recently been used as the building blocks of thermoelectric materials that enables the construction of wearable electronics and power modules. In this context, air- and thermally-stable doped, i.e. n-type materials are highly desired not only for the development of practical PN series thermoelectric modules but also for the optimal tuning of thermoelectric transport. In this presentation, I will talk about the preparation of air- and thermally-stable p- and n-type carbon nanotubes, and their application in thermoelectric transport studies [1-6]. Supramolecular (electro-) chemistry is introduced to improve, and quantify doping efficiency and stability. A recent progress on the power factor enhancement is also presented.


4:00 PM NM01.06.07

Interlayer Charge Transport in 2D Molecular Structures

Elad Koren; Materials Science and Engineering, Technion–Israel Institute of Technology, Haifa, Israel.

Weak interlayer coupling in 2-dimensional layered materials such as graphite gives rise to rich mechanical and electronic properties in particular in the case where the two atomic lattices at the interface are rotated with respect to one another. A lack of crystal symmetry leads to anti-correlations and cancellations
of the $p_z$ orbital interactions across the twisted interface, which gives rise to low friction behavior and low interlayer electrical transport. Using our recent nanomanipulation technology, based on atomic force microscopy, we studied the interlayer electrical conductivity as a function of twist angle between two misoriented graphene layers with unprecedented angular resolution of $\sim 0.1$ deg. The angular dependence indicates that the electrical transport across the interface is dominated by a phonon assisted channel which conserve the momentum of conduction band electrons, tunnelling across the twisted Dirac bands. Most intriguingly, the conduction is significantly enhanced within a narrow angular range of less than 0.5 deg at pseudo-commensurate angles of 21.8 and 38.2 degrees. This provides the first experimental evidence for the existence of a 2-dimensional interface state originating from the coherent coupling of electronic states in the twisted sheets due to commensurate superlattices. Finally, we show that combined electro-mechanical characterization techniques of mesoscopic graphite structures can be uniquely address open fundamental question related to the dielectric interlayer interactions and electronic charge transport through stacking faulted structures.

References


4:15 PM NM01.06.08
The Structure of the Electrolyte/Graphene Interface Paola Carbone, Christopher D. Williams, Jezebel Boni, Alessandro Troisi; The University of Manchester, Manchester, United Kingdom.

The physics governing the adsorption of ions onto metallic or semimetallic surfaces underpins future technological developments in many areas. Specifically for graphene-based technology new emerging applications for example in energy storage or water filtration require a precise understanding of the relative stability of ions at the graphene surface and surface wetting properties. [1] However, many questions about the atomic structure of the electrolyte/graphene interface remain unanswered. In this talk, we will show that this new model predicts that in a 1 M electrolyte solutions, cations are adsorbed onto the graphene surface with a trend (Li$^+$ < Na$^+$ < K$^+$) opposite to that predicted by the gas-phase calculations and different than from that obtained from the single-ion simulations and with an energy of adsorption now validated by microscopy and electrochemistry experiments. [5] We will discuss how these findings are relevant for the graphene exfoliation process and wetting properties of the surface.

References


4:30 PM NM01.06.09

Thin films of single-walled carbon nanotubes (SWCNT) have many attractive opto-electronic features such as tunable conductivity and visible light transmission that make them of interest for a variety of applications. We present a characterization method that employs multi-angle spectroscopic ellipsometry spanning a wide spectral range from the ultraviolet to the terahertz (210 nm – 3 mm) that is capable of simultaneously determining a variety of opto-electronic properties in a contactless manner. In particular, SWCNT films are prepared in both “de-doped” (i.e. heat treated) and heavily nitric acid doped states and measured in both ex-situ and in-situ modes. The ex-situ measurements fully leverage the wealth of spectral features present in the wide spectral range while the in-situ mode allows for tracking of changes in real time as the film properties change due to atmospheric exposure. This frequency domain spectroscopic measurement is one of the only known techniques sensitive to the optical effects arising from electrical anisotropy between the in-plane and out-of-plane directions. Comparison to direct electrical measurements sampling the in-plane electrical properties confirms accuracy. Such electrical anisotropy arises from the fact that, despite no intentional alignment of the nanotubes being made, the nanotubes tend to lie flat on the substrate surface. Nitric acid doping is shown to decrease the film resistivity by factors of ~4 and ~100 in the in-plane and out-of-plane directions, respectively. This capability of determining electrical anisotropy is particularly relevant for incorporation of SWCNT films into devices where the desired direction for conduction is a consideration. Measurement of real-time changes to the film through the in-situ measurements are of interest for SWCNT films used in sensor applications. Additionally, the influence of doping on optical features arising from metallic and semiconducting transitions is determined.

4:45 PM NM01.06.10
Gapped Graphene Nanoribbons with Spatial Symmetries as One-Dimensional Topological Insulators Kuan-sen Lin, Mei-Yin Chen; Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan.

The Berry phase is a geometrical phase that is known to provide the essential physics behind several intriguing materials properties such as the electric polarization, anomalous Hall effect, orbital magnetization, etc. It is expected that this geometrical phase also reflects the intrinsic topological properties of one-dimensional (1D) insulators, because the 1D Brillouin zone (BZ) integral forms a natural loop in the k-space. In this work, we study the system of gapped graphene nanoribbons (GNRs) with spatial symmetries (e.g., inversion) and show that a symmetry-protected Z2 topological phase exists. Although
the Berry phase turns out to be -quantized in the presence of the chiral symmetry, it does not provide the correct $Z_2$ correspondence as expected. It is found that only the origin-independent part of the Berry phase gives the correct bulk-boundary correspondence by -quantizing the $Z_2$ invariant dependent on the choice of the bulk unit cell (namely, ribbon truncation) and connected to the symmetry eigenvalues of the wave functions at the center and boundary of the BZ. Using the cove-edged GRNs as examples, we demonstrate the existence of localized states at the end of some GNR segments and at the junction between two GNRs based on topological analysis. The current results are expected to shed light on the design of electronic devices based on GNRs as well as the understanding of the topological features in 1D systems.

**Analytical TEM-EELS and Raman Spectroscopy of Nanocarbon-Al Composites Made by the Electrocharging Assisted Process**

Christopher Klingshirn1, Xiaoxiao Ge1, Karen Gaskell2, Manfred Wuttig3, Daniel Cole4, Christopher M. Shumeyko5 and Lourdes G. Salamanca-Riba6; 1Materials Science and Engineering, University of Maryland, College Park, Maryland, United States; 2Chemistry and Biochemistry, University of Maryland, College Park, Maryland, United States; 3LIG Biowise Ltd., Manchester, United Kingdom; 4U.S. Army Research Laboratory, Aberdeen, Maryland, United States.

Novel nanocarbon-metal composites called covetics have the potential to improve significantly upon the mechanical, thermal, and electrical properties of common metals and alloys, including Al. Electric current applied to the melt containing a C precursor is believed to ionize carbon atoms and cause nanoscale graphitic ribbons and chains to form within the resulting Al lattice. Despite the potential of nanocarbon incorporation to improve desirable properties of Al alloys, critical for aerospace, structural, and power transmission applications, the atomic-scale mechanism is not yet completely understood.

In this work, the effects of current density and residence time on the uniformity and extent of carbon conversion to nano-graphite are explored in order to provide further insight into the conversion process. We characterize the structural and chemical features of nanocarbon-Al covetics using Raman spectroscopy, TEM imaging, electron energy loss spectroscopy (EELS), and X-ray photoelectron spectroscopy (XPS). Raman and EEL spectra are localized to within a few μm of a selected region of interest, as guided by fiducial marks milled using a focused ion beam tool before collection of the spectrum images (SIs). The Raman and EELS SIs are subjected to nonlinear iterative fitting and hyperspectral decomposition using machine learning techniques to reveal features indicating nanocryrstalline graphite embedded within the Al lattice. The Raman G and D peak intensities and shifts are found to depend on the current parameters, with greater exposure corresponding to greater graphitic order. Evidence of $sp^2$ carbon bonding and Al-C bonding is seen by EELS and XPS. Local mechanical (nano-indentation) and electrical conductivity measurements will also be taken and related to processing conditions and local structure.

This work is based upon work supported by the U. S. Department of Energy under Award No. DE-EE0008313. Dr. David Forrest is the Project Technology Manager and Debbie Schultheis is the Project Officer/Manager.

**Light Microscopy Characterization of Graphene Oxide—A Novel Method for the Rapid and Detailed Characterization of 2D Materials**

Evangelia-Nefeli Athanasopoulou1, Sorin L. Stanescu1, Sebastien Vilain1, Valerio Galieni1, George Goh2, Fatema Rajab4, Kararzyna Karpinska2, Steve Wright1, Alex Sheppard1, Wei Guo3 and Lin Li4; 1LIG Nanowise Ltd., Manchester, United Kingdom; 2LIG Biowise Ltd., Manchester, United Kingdom; 3School of Mechanical, Aerospace and Civil Engineering, The University of Manchester, Manchester, United Kingdom; 4Laser Processing Research Centre (LPRC), School of Mechanical, Aerospace and Civil Engineering, The University of Manchester, Manchester, United Kingdom.

Graphene and graphene oxide (GO) are arguably some of the most interesting materials to have emerged in the past decade. Their unique features, such as mechanical strength, electrical, thermal, and optical properties have brought them to the forefront of technology; from basic science research, to applications in electronic devices, athletic equipment and biodevices.3Research in the field is focusing towards the development of large scale manufacturing processes, suitable for industrial production.1 One of the key prerequisites for the industrial use of graphene and GO is their rapid, reliable and cost-effective characterization and quality control via a method suitable for operation in an industrial production line. Currently, most laboratory techniques employed for the characterization of 2D materials rely on the description of their chemical, mechanical and electronic properties. Electron and scanning probe microscopy imaging offers the most direct characterization approach; however, these typically require long imaging times and oftentimes complicated sample preparation. They are, therefore, unsuitable for routine screening and quality control of a large number of samples. On the other hand, conventional optical microscopy, even though simple and time-effective, has a theoretical resolution limit too large for the characterization of 2D materials. Here we present the development of a novel imaging technique based on optical microscopy, suitable for the characterization of atomically and molecularly thin materials. Utilizing the property of negative refractive index media to enhance the normally undetectable evanescent waves,2 a microsphere objective lens was manufactured and integrated in a simple optical microscope, ultimately improving significantly the resolution limit and allowing the observation of features as small as 50 nm in the lateral direction.3 The developed technique was verified by imaging GO flakes. Bypassing any need for complicated sample preparation, it was possible to reproducibly and rapidly observe topographical features of the flakes, as well as monolayers and GO agglomerates. Using light microscopy we were able to observe topographical features of a 2D material at high lateral resolution for the first time. Our technique allows the implementation of such measurements both under well controlled laboratory conditions and alongside an industrial production line, at a high throughput rate and without requiring complicated sample preparation, enabling rapid and detailed characterization of atomically and molecularly thin materials.

**References:**

Single cell analysis is an emerging technology that can provide a mechanistic understanding of the complex biological systems and cell heterogeneity. Any disruption of its activity can be monitored through interfacial bioelectrochemistry. In this emerging technology it is necessary to have high spatial and temporal resolution over an extended period of time that has been seldom achieved in the adopted analytical measurements. This problem has been solved in the present work by using an electrochemical technique such as differential pulse voltammetry (DPV) carried out with carbon nanotube pipette electrode that is laden with graphene quantum dots (20 nm-50 nm). This modification gives rise to a sensitive electrode material for high temporal resolution through idealizing the DPV parameters. The in-vitro experiments carried out in understanding oxidative stress produced by p-aminophenol (PAP) that results in membrane disruption suggest that molecular attachment of PAP to graphene is higher than the pipette electrodes (amorphous carbon) as indicated by the signal strengths being several orders of magnitude higher than with nanotube pipette electrode. The shape and features of the current-voltage curves that are recorded can be idealized as nanotube electrode arrays acting as an ensemble in harmony. As the electric field known to influence the cells, the electric field produced during the detection of an electroactive species by this ensemble has been simulated for practical usage in in-vivo studies. The new electrode opens up an approach at observing the electroactive neurotransmitter during its functioning in chronic diseases.


Electrochemical (re)activity of graphene and graphene-based ‘hybrid’ nanomaterials is crucial for food, energy and water sustainability applications, which requires delicate control over its geometric and electronic structures. We demonstrate that precise control of the density of defects, hierarchical porosity, and topological interconnectedness, invoked in hydrothermally synthesized graphene aerogel integrated with multi-walled carbon nanotubes that can finely tune mesoporosity and enhance the electrochemical heterogeneous electron transfer rate ($k_{ET}$). We prepared range of three-dimensional solid network of graphene-based ‘hybrid’ scaffolds (i.e. aerogel) and their nitrogenated counterparts with varying graphene-carbon nanotube compositions using two schemes (approach 1 and approach 2). This study allows us to correlate quantitatively between number defect density determined (via Raman spectroscopy; RS) and heterogeneous electron transfer rate (via scanning electrochemical microscopy; SECM). RS provides nanoscale phononics characterization revealing collective atomic/molecular motions and localized vibrations. The first- and second-order phonon modes are analyzed in terms of Raman intensity, band position (intrinsic mechanical strain) and intensity ratio (structural disorder, number defect density), distinct localized π electronic states were found in photoluminescence excitation (PLE) spectra reflecting carbon atoms around oxygenated and nitrogenated species. The role of carbonyl (C=O), epoxy (C-O-C) and nitrogen (pyridinic-N and graphitic/pyrrolic-N) surface functionalities and corresponding bonding configurations besides hierarchical mesoporosity are emphasized in view of understanding the improved physicochemical properties for electrochemical energy, water desalination and sensing applications. The engineered defect density induced increase in finite electronic density of states (DOS) near Fermi level revealed using density functional theory (DFT) calculations and decrease in room temperature electrical conductivity, heled in establishing optimal defect density for moderate heterogeneous rate as a critical state such that the whole system becomes electronically activated while maintained structural integrity. Moreover, it enlarges the overlap between DOS for graphene-based aerogels and redox probe couple, which signifies the experimental correlation establishment.

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**Fabrication of Bilayer Graphene Based Films as Hygromorphic Actuators**

Omkar S. Bhatkar, Sheikh Rasel, David Smith and Reza Rizvi; Mechanical, Industrial and Manufacturing Engineering, University of Toledo, Toledo, Ohio, United States.

Extensive research is being conducted on graphene-based composite films to explore their potential in actuation mechanisms stimulated by electrical, thermal, mechanical or optical energy sources owing to its extra-ordinary electrical and mechanical properties. In this study, we report the use of all graphene based functionally graded, bilayer free-standing films as mechanical actuators triggered by adsorption of moisture at the film interface. The bilayer films were fabricated by a single-step doctor blade coating technique and dried at controlled temperature and humidity conditions. The reduction mechanism of Graphene Oxide into rGO was implemented through metal substrate-assisted reduction, which involves coating GO paste on an active metal like Aluminum that possess a high oxidation potential. The internal architecture of the films was tuned as per requirement by changing the initial process parameters like the concentration and pH of GO and the surrounding humidity and temperature. Selective reduction of Graphene Oxide into desired intricate patterns was also demonstrated, through usage of masks during film coating and deposition.

The functional grading of the films, where one side is electrically-conducting GO while the other being insulating rGO was confirmed by SEM, Raman, XRD, FTIR and XPS analyses. SEM revealed an overall understanding of the porous nature of the film throughout the cross section whereas Raman Spectroscopy showed an increase in (Id/Ig) ratio from GO to rGO face, denoting gradual restoration of sp² hybridized carbon structure. XRD, FTIR and XPS results also confirmed the functional grading throughout the thickness of the film post-reduction. The bilayer film, which is composed of Graphene Oxide and Reduced Graphene Oxide on either side, is shown to exhibit selective bending mechanism in humid environments, due to the affinity of Graphene Oxide towards polar molecules like water. Reduced Graphene Oxide being immiscible in water shows repulsive nature towards humidified surroundings, thus triggering a differential bending mechanism in the individual bilayer film. The Hygromorphic behavior, exhibited by the robust and flexible functionally graded graphene films, can intrigue a variety of applications in mechanical actuation, robotics and gas sensing systems.

**References:**

Mechanics of Triply Periodic Minimal Surfaces of Three-Dimensional Graphene Foams

GangSeob Jung and Markus Buehler; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

The mechanics of triply periodic minimal surfaces (TPMSs) with three-dimensional (3D) graphene foams are systematically studied to understand the effects of structure and size on the mechanical properties, e.g., elasticity, strength, and fracture. The design of lightweight open-shell porous solid materials with TPMSs has shown excellent and tunable load-bearing properties. However, failure mechanisms and their relations with surface topologies are largely unknown. Utilizing reactive molecular dynamics simulations, here we investigate the elastic and fracture properties of three different surface topologies with 3D graphene foams: P (primitive), D (diamond), and G (gyroid). Models with different lattice sizes are utilized to derive power laws, which can connect the properties along different sizes to shed light on the multiscale mechanics of 3D graphene with TPMSs. Our study provides a systematic understanding of the relation between TPMS topologies and their mechanical properties, including failure mechanisms of graphene foams, opening opportunities to explore designable complex structures with tailored properties.

Thermal Conductivities of Triply Periodic Minimal Surfaces of Three-Dimensional Graphene Foams

GangSeob Jung and Markus Buehler; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Graphene has excellent mechanical, thermal and electrical properties. However, there are limitations in utilizing monolayers of graphene for mechanical engineering applications due to its atomic thickness and lack of bending rigidity. Synthesizing graphene aerogels or foams is one approach to utilize graphene in three-dimensional bulk forms. The structures of graphene foams can be idealized with the triply periodic minimal surface (TPMS): P (primitive), D (diamond), and G (gyroid). Here, we investigate the thermal conductivity of three different surface topologies with 3D graphene foams by using full-atom molecular dynamics simulations. We derive a scaling law showing how the different TPMSs have different trends. Our analysis shows that the trend of the thermal conductivities can be attributed to defects and curvatures of graphene. Our study shows that three-dimensional porous graphene has potential that may be utilized in designing new lightweight structural materials with low and density-insensitive thermal properties and superior mechanical strength.

Enhancing the Thermal Conductivity of PBAT/Graphene Composites via Applying PLA as a Second Phase Reorganizer

Xianphao Zuo, Yuan Xue, Miriam Rafailovich and Yichen Guo; Stony Brook University, Stony Brook, New York, United States.

In this study, we have designed and engineered polymer blends as an improvement of the thermal diffusion structure for polymer materials. In our system, poly(lactic acid) (PLA) was used as a second phase reorganizer of the Poly (butylene adipate-co-butylene terephthalate) (PBAT)/graphene composites. Two different types of graphene, H-5 and C-750, were used in this study to guarantee the thermal conductivity of the composites. According to the contact angle measurements and the calculation of the interfacial tension between polymers and graphene, we observed that graphene will be more stable in the PBAT phase than in the PLA one. Therefore, in our blends system, PBAT was designed as the polymer matrix, while the PLA was considered as the minor phase with a comparatively lower concentration. Because the size of H-5 (average around 5 ) is larger than the PLA domain size (around 3 ), H-5 can disperse perfectly in PBAT matrix and form continuous thermal diffusion paths. With 20% of graphene H-5, the thermal conductivity of PBAT/PLA blend can achieve a 26% enhancement, as compared with the sample without PLA. Moreover, we discovered that the incorporation of C-750, unfortunately, failed in promoting the thermal conductivity of the PBAT/PLA blend. Since the PLA domain size is much larger than the size of C-750 (average around 750 nm), it can hardly help drive the dispersion of the C-750 in a preferential orientation in the PBAT matrix and makes the formation of the thermal diffusion path even harder.

Quantifying Defects in Graphene for High Performance Conductive Ink

Md Akibul Islam1, Sheikh Rasel1, Derek Keith Messer1, Wai Mak2, Reza Rizvi1, 2 and Richard B. Kaner1; 1Mechanical, Industrial and Manufacturing Engineering, University of Toledo, Toledo, Ohio, United States; 2Chemistry and Biochemistry, University of California, Berkeley, Los Angeles, California, United States.

Over the past decade, comprehensive investigations have been conducted to develop graphene based two-dimensional (2D) materials to harness their excellent and unprecedented properties such as high electrical conductivity, optical transparency, mechanical strength, and flexibility. To fully utilize these functionalities, a number of methods including chemical vapor deposition, liquid sheet exfoliation, sonication, ball milling, electrochemical exfoliation and the recently conceived compressible flow exfoliation (CFE) have been successfully studied. However, these methods can introduce significant amount of defects during exfoliation into the graphene crystal structures that have a strong influence on their properties. This study is designed to compare the defect and flake quality between CFE and bath or probe sonication process for producing high-performance conductive ink from exfoliated graphene.

In our CFE process, graphite is rapidly jetisoned through a small orifice using high-pressure gases without the need for any time-based treatment, unlike other shear-based liquid processes. Shear-induced exfoliation occurs due to the high velocities that expanding and accelerating gases can achieve in small orifices coupled with viscous friction effects resulting in a high shear rate (γ>10^5 s^-1) experienced by the graphite particles. In contrast, in the sonication methods, an ultrasonic transducer is used to induce unstable cavitation bubbles in a liquid medium, which upon their inevitable collapse emanate a shock wave. The energy of this shockwave is sufficient to fragment nearby bulk graphite powders into smaller lengths as well as thickness along the weak, secondary c-axis. But when the bulk particle is fragmented into smaller flakes, a good number of edge and basal plane defects are introduced into the flake. The defect population increases as the time for sonication rises. The occurrence of a disorder-activated D peak at 1330 cm^-1 in the Raman spectra of graphene is indicative of defects, in particular, those which disrupt the sp^2 hybridization. Such defects can be interpreted to be the creation of new edges, vacancies or substitutions, with the ratio between the peak intensities of the D to G peak (I_D/I_G) providing a qualitative indication of their population. In our study, we found the ratio of D peak to G peak is significantly less in CFE than that of bath sonicated graphene-I_D/I_G=0.66 for CFE graphene and I_D/I_G=1.1 for bath sonicated graphene. In contrast, the bulk graphite powder had I_D/I_G ratio of 0.62. The increased quantity of defects in bath sonication may be attributed to the prolonged sonication time which is well known to be responsible for reducing the flake length and hence, introducing more edges. The flake quality of exfoliated graphene was also verified using atomic force microscope (AFM) and transmission electron microscope (TEM).

3D Knitted Carbon Nanotube Fabric as Smart Textiles

Javad Foroughi; University of Wollongong, Wollongong, New South Wales, Australia.

Highly stretchable, actutable, electrically conductive knitted textiles based on Spandex (SPX)/CNT (carbon nanotube) composite yarns were prepared by an integrated knitting procedure. SPX filaments were continuously wrapped with CNT aerogel sheets and supplied directly to an interlocking circular knitting machine to form the three-dimensional electrically conductive and stretchable textiles. By adjusting the SPX/CNT feed ratio, the fabric electrical conductivities could be tailored in the range of 870 to 7092 S/m. The electrical conductivity depended on tensile strain, with a linear and largely hysterisis-free resistance change occurring on loading and unloading between 0 and 80% strain. Electrothermal heating of the stretched fabric caused large tensile contractions of up to 33%, and generated a gravimetric mechanical work capacity during contraction of up to 0.64 kJ/kg and a maximum specific power
output of 1.28 kW/kg, which far exceeds that of mammalian skeletal muscle. The knitted textile provides the combination of strain sensing and the ability to control discussions required for smart clothing that simultaneously monitors the wearer’s movements and adjusts the garment fit or exerts forces or pressures on the wearer, according to needs. The developed processing method is scalable for the fabrication of industrial quantities of strain sensing and actuating smart textiles.

NM01.07.11

Electronically Tunable SPR Biosensor with Reduced Graphene-Oxide Thin Films as Functional Layers Xiaolong Lu1, 2, Pavel Damborský3, Walid-Madhat Municic-4, Jessica Ka-Yan Law4, Vivek Pachauri1, 2, Jens-Uwe Neebohr5, Samuel Grandthyll6, Karin Jacobs7, Frank Müller1, Jaroslav Katriš4, Xiaoping Chen1 and Sven Ingebrandt1; 1Department of Electrical Engineering, RWTH Aachen University, Aachen, Germany; 2Department of Informatics and Microsystems Technology, University of Applied Sciences Kaiserslautern, Zweibruecken, Germany; 3Department of Glycoengineering, Slovak Academy of Sciences, Bratislava, Slovakia; 4RAM Group DE GmbH, Zweibruecken, Germany; 5Key Laboratory of Optoelectronic Technology & Systems, Chongqing University, Chongqing, China; 6Experimental Physics, Saarland University, Saarbruecken, Germany.

Graphene is a promising material with unique properties. However, the chemical nature of pristine graphene limits the binding of receptor biomolecules to the graphene surface. To overcome this issue, chemically exfoliated graphene oxide (rGO) has been used instead for covalent immobilization of receptor biomolecules. In this work, we investigated the sensing performances of Au/glass SPR chips with GO and rGO thin films as functional layers. As a proof-of-concept, we applied a lectin Concanavalin A (ConA) binding assay with prostate cancer-specific antigen (PSA) as receptors. The results demonstrated stronger surface plasmon resonance effects for biomolecule recognition with rGO functional layers, even though the average intensity of surface plasmons and signal-to-noise ratio was 1.7 and 3 times higher compared to the GO as a functional layer. More remarkably, taking advantage of the dipolar property of the rGO thin films, it was possible to further enhance the surface plasmon intensity by applying bias voltages to the rGO thin films.

In summary, we could successfully fabricate the locally gate controllable graphene/CNT junction transistor and analyzed the barrier height at different local gate bias of graphene. Based on the results, barrier heights were linearly changed by changing the gate voltage, which is in good agreement with our expectation due to the Fermi level movement. The barrier heights are varied from ~84.5 meV to ~69 meV for n-type and ~85.5 meV to ~71.5 meV for p-type depending on the graphene gate voltage. The values are slightly lower than that of vertically integrated graphene/TMD contact junctions, 0.01 µm. Such tunable SPR platforms based on rGO thin films lighten up a wider road for diverse surface functionalization, adjustable sensing regimes and improved sensitivity in the field of SPR biosensing.

NM01.07.12

Vertically Aligned Single-Walled Carbon Nanotube Growth from Ir Catalysts by Alcohol Gas Source Method Takuya Okada1, Takahiro Saida1, 2, Shigeyoshi Naito1 and Takahiro Maruyama1, 2; 1Applied Chemistry, Meijo University, Nagoya-shi, Japan; 2Nanomaterials Research Center, Meijo University, Nagoya-shi, Japan.

Single-wall carbon nanotubes (SWCNTs) have been anticipated for applications in a lot of future nanodevices. However, there still remain several problems for realizing the SWCNT devices, and one of the most significant issues is high-yield growth of semiconducting SWCNTs. So far, to grow SWCNTs, high-yield, Al2O3 buffer layers are widely used, because they prevent migration of catalysts on the substrate surface at growth temperature and aggregation of catalyst particles are suppressed [1]. In this study, we attempted to grow SWCNTs using Ir catalysts without Al2O3 buffer layers, which have never been used as catalysts in SWCNT growth. After deposition of Ir catalysts on SiOx/Si substrates, SWCNT growth was carried out using alcohol gas source method in a high vacuum [2]. Growth temperature and growth time were set at 800°C and 1 h, respectively. The ethanol pressure was varied between 1×10⁻³ and 1×10⁻¹ Pa. The growth SWNTs were characterized by FE-SEM, TEM and Raman spectroscopy.

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The ethanol pressure was 1×10⁻³ Pa, high-density vertically aligned SWCNTs were grown, whose lengths were about 2 µm. Raman measurement showed that SWCNT diameter were distributed between 0.83 and 1.13 nm. In addition, Raman spectra showed that semiconducting SWCNTs were dominantly grown from Ir catalysts. This study is the first report to grow SWCNTs from Ir catalysts, and our results indicated that Ir catalysts are effective to obtain high-density vertically aligned and small diameter SWCNTs using no Al2O3 buffer layers.


NM01.07.13

Band Alignment Study of Locally Gate-Controlled Graphene/Carbon Nanotube Junctions Mao Shiomori1, Takayuki Arie, Seiji Akita and Kuni Takei; Osaka Prefecture University, Sakai, Japan.

Heterojunctions of nanomaterials have attractive attention due to interesting electrical and optical characteristics. One of the interesting materials is graphene, which has Dirac-cone band structure. Utilizing this band structure and other contacting semiconductor nanomaterials, diode and transistor behaviors can be controlled by applying a global back gate voltage. However, due to vertical integration of this heterojunction, each band structure cannot be separately controlled to observe different functions. Furthermore, although the barrier height as a function of gate voltage has been studied, detail band alignment has yet to be studied due to difficulties of gate voltage separation between graphene and other nanomaterial. To address these challenges, we demonstrate a graphene-carbon nanotube (CNT) junction device laterally integrated with local gate electrodes for graphene and CNT. Furthermore, barrier height dependence is also investigated as a function of local gate voltages.

CVD-grown monolayer graphene was transferred onto a Si/SiO2 substrate with Au source and drain electrodes. After graphene was patterned by an oxygen plasma, semiconductor-enriched CNT networks were deposited by modifying the surface of graphene and SiO2 surfaces with poly-L-lysine. SiO2/Al2O3/SiO2, dielectric layers were deposited over the substrate, followed by Au gate electrode deposition. The work function of graphene, CNT, and junction of them, multi-gate stack structure was fabricated by repeating the gate dielectric and electrode deposition.

Uniform formation of graphene, CNT, and junctions were confirmed using Raman spectroscopy and AFM. Dirac point of graphene was about -3 V, and ambipolar behavior of CNT/graphene transistor was observed. When graphene voltage from -6 V to 3 V was applied, threshold voltage was modulated from 0 V to 0.28 V. These mobilities are 7.0±1.6 cm²/Vs and 1.1±0.2 cm²/Vs for p-type and n-type behaviors, respectively. After analyzing the device as a function of temperature, thermal and tunnel emission probabilities were calculated. At the transition between thermal and tunnel emission, barrier heights were extracted at different local gate bias of graphene. Based on the results, barrier heights were linearly changed by changing the gate voltage, which is in good agreement with our expectation due to the Fermi level movement. The barrier heights are varied from ~84.5 meV to ~69 meV for n-type and ~85.5 meV to ~71.5 meV for p-type depending on the graphene gate voltage. The values are slightly lower than that of vertically integrated graphene/TMD contact junctions. This may be caused by the multiple junctions with defects to the Fermi level of graphene due to solution process of CNT network formation. In summary, we could successfully fabricate the locally gate controllable graphene/CNT junction transistor and analyzed the barrier height at different local gate voltage corresponding to the Fermi level movement.

NM01.07.14

Local Structures of Polycyclic Aromatic Hydrocarbon Molecules Encapsulated in Single-Walled Carbon Nanotubes Studied by Molecular Dynamics Simulations Ryutaro Nagai, Hirofumi Ogata and Yousuke Karaoke; Hosei University, Tokyo, Japan.
Carbon nanotubes (CNTs) is one of the most promising material because of their superior electronic, thermal and mechanical properties. Single-walled carbon nanotubes (SWNTs) have a hollow space of about several nm in diameter. It is possible to encapsulate various functional molecules in hollow space and expected new functions by encapsulation. One of the polycyclic aromatic hydrocarbon (PAH) molecules, coronene has been reported to exhibit interesting fluorescent properties depending on the local structure. The unique luminescence properties of columnar stacked coronene encapsulated in SWNTs have been also reported. In this study, molecular dynamics simulation was performed to clarify the local structure and properties of various kinds of PAH molecules encapsulated in SWNTs systematically. We will report the detailed results of SWNT chirality dependence of encapsulated structures of PAH molecules.

NM01.07.15
Effect of Carboxylic and Hydroxyl Groups on the Performance of ITO-Decorated MWCNT Based Electrochemical Capacitors Neftali L. Carrero4, Matheus Kelow2 1, Guillaume Maron1, Bruno Norenberg1, Lucas Rodrigues1 and Jose H. Alano1, University Federal-Pelotas, Pelotas - RS, Brazil; 2Instituto Federal Sul-rio-grandense Câmpus Pelota-CAVG, Pelotas, Brazil.

Owing to the energy needs of the modern world, numerous studies have been performed in order to develop new materials with advanced electrical properties to be applied in energy storage devices, especially capacitors and supercapacitors. Accordingly, carbon-based materials such as carbon nanotubes (CNT) and reduced graphene oxide (rGO) are regarded as great alternatives to be used in the clean energy industry. Also, the possibility of the development of nanocomposites with carbon-based materials, metallic nanoparticles and metal oxides becomes interesting for electrochemical applications, such as energy storage devices, capacitors, gas sensors and others, and is the main focus of many researches in the last few years. A potential candidate to be used in the surface modification of CNT’s is the indium tin oxide (ITO), since it presents very interesting electrical properties and is studied for several applications. In the present work, nanocomposites of CNT/ITO have been prepared using a microwave-assisted hydrothermal synthesis (MHS), with posterior annealing of 400 °C and 600 °C, in inert atmosphere, to obtain crystalline ITO. Hydroxylated (CNTOHO) and carboxylated (CNTCOOH) multiwalled carbon nanotubes-MWCNT (30% w/w), indium nitrate and tin chloride were used as precursors. The obtained powder was investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The electrochemical properties were evaluated by cyclic voltammetry, electrochemical impedance spectroscopy e galvanostatic charge-discharge, using a two electrode cell with current collectors made of 304 stainless steel, KOH 6 mol L-1 as electrolyte and filter paper as separator. The measurements were performed in a source meter Keithley model 2651A and a potentiostat IVIUM - Compactstat. e XRD results showed that the sample annealed at 400 °C, the phase obtained was rombohedral, while at 600 °C was formed the cubic phase. Charge-discharge results showed values of 3.2 F/g and 1.4 F/g for CNTOHO/ITO-400 and CNTCOOH/ITO-400, respectively, and 5.1 F/g and 0.3 F/g for CNTCOOH/ITO-400 and CNTCOOH/ITO-600, respectively. It is possible to observe that the specific capacitance of the samples with rhombohedral ITO was higher than for cubic, which can be explained by a degradation of nanotubes structure when submitted to higher temperatures. However, these findings require further characterization, such as Raman spectroscopy and FEG-SEM images, for example.

NM01.07.16
Fabrication of Gate Tunable Graphene Lateral Tunnel Diodes Takashi Uchino1, Kanako Shiga1, Kenta Sugawara2, Hirokazu Fukidome2, Akira Satou2 and Taichi Otsuji2, 1Tohoku Institute of Technology, Sendai, Japan; 2Tohoku University, Sendai, Japan.

Two-dimensional materials have attracted attention in recent years because of their excellent electrical properties and can develop innovative devices [1-3]. In particular, single-layer graphene with the high carrier mobility and saturation velocity could push the limit of high-frequency devices [4]. In this work, we focus on fabrication and electrical characterization of gate tunable graphene lateral tunnel diodes to realize optical rectennas which receive and convert optical frequency electromagnetic radiation into DC output with high-efficiency and low-cost [5].

The gate tunable graphene lateral tunnel diodes have been fabricated using monolayer graphene grown by chemical vapor deposition (CVD) on Cu foil and later transferred on 83-nm-thick SiO2/n−Si substrates. Tunnel regions between adjacent graphene layers were defined by using electron beam lithography, and the tunnel length ranged from 60 to 150 nm. Tunnel dielectric consists of plasma Si3N4 and Al2O3. The Al2O3 layer was formed by atomic layer deposition on the native oxide of Al thin film. Metal electrodes (anode and cathode) were formed by electron beam evaporation of Ti/Pd/Au (0.5/20/100 nm) right after an oxygen plasma treatment to reduce contact resistance between graphene and electrodes. Top and back gate electrodes were formed by Ti/Au (20/80 nm) and Al (100 nm), respectively.

Typical current-voltage (I-V) characteristics of the fabricated devices showed rectifying characteristics at a low voltage below 1 V. The on-state current of the lateral diodes increased with reducing the tunnel length. The lateral diodes have p-type rectifying characteristics for positive gate voltages and n-type rectifying characteristics for negative gate voltages. This result indicated that the tunnel barrier height could be controlled by applying gate voltage. We also measure the rectifying characteristics as a function of the back gate voltage to confirm the tunneling transport. The devices exhibited steep subthreshold slope (SS) of 40 mV/decade, which was lower than the theoretical limit of MOSFETs at room temperature indicating the devices were tunnel diodes.

References

NM01.07.17
Importance of Electrical Current in Post-Synthetic Graphitization Process for Property Improvements of Single Walled Carbon Nanotubes and Graphene Sheet Naoyuki Matsumoto, Azusa Oshima, Kenji Hata and Don Futaba; National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Many papers have clarified that the healing of crystalline defects in materials improves various properties. In this study, we demonstrate a new approach for healing crystalline in single wall carbon nanotubes (SWCNTs) based on simultaneously applying electrical current and heat. In this way, we succeeded in improving the graphitization without inducing other changes to the structure, in particular diameter and wall number. To achieve this we designed and constructed a specialized treatment device capable independently applying current (~240 A cm⁻²) and heating (room temperature to 2000 °C). Our examination found that at 800 °C, 150 A cm⁻² for 1 min, we could achieve a 3.2-times increase in crystallinity as indicated by an increase in Raman G- to D-band ratio, a 3.1-times increase in electrical conductivity (from 25.2 to 78.1 S cm⁻¹), and a 3.7-times increase in thermal conductivity (from 3.5 to 12.8 W m⁻¹ K⁻¹). The simultaneous increase in electrical and thermal conductivities stems directly from defect healing, and importantly we observed no additional change in diameter or wall number. The simultaneous application of current is essential in maintaining the initial CNT structure (diameter and
Targeted tuning of the structure and properties of carbon nanotubes (CNT) using ion irradiation is very attractive for technological applications. To understand the damage formation and evolution due to ion irradiation in multiwalled (MW) CNT, we used 25 keV Ne$^{+}$ and He$^{+}$ ion irradiation with controlled fluences in the range of $10^{14}$ to $10^{15}$ ions/cm$^2$ and subsequently investigated the irradiated areas by TEM imaging and Raman spectroscopy. A new methodology involving Au TEM grids was developed to ensure compatibility across the different techniques and to preclude the Raman contribution coming from the amorphous carbon support of typical TEM grids. The experimental results indicate a significant difference in the damage evolution between He$^{+}$ and Ne$^{+}$ irradiation. Furthermore, the sample thickness was found to play an important role in determining the extent of damage. TEM imaging suggests that the thicker areas are significantly amorphized, while thin areas ($t < 10$ nm) were found to be relatively undamaged with only very minor changes in comparison to pristine samples. For He$^{+}$ and Ne$^{+}$ irradiation, damage formation evolves differently, with a change in the trend of the ratio of D to G peak in the Raman spectra being observed for He$^{+}$ but not for Ne$^{+}$. The experimental results were then compared with the Monte-Carlo (MC) simulations of ion-solid interaction by approximating the sample to a thin carbon membrane. Due to the small thickness of the MWCNTs, sputtering has been observed for the top and bottom side of the samples. Depending on thickness and ion species, the sputter yield is significantly higher for the bottom than the top side.

In this presentation, we will describe the new correlative methodology that was developed for this study and discuss the experimental results from cumulative TEM-Raman analysis of MWCNT under He$^{+}$ and Ne$^{+}$ irradiation together with insights drawn from MC simulations using SDTRIMSP.
and DLS analysis, it was found that the PNS diameter can be controlled from tens of nm to submicron by changing the pH. As a result of conducting reaction monitoring of polymer coating by ultraviolet-visible spectroscopy (UV-Vis) and fluorescence spectrophotometer (FL), it was confirmed that reaction intermediates decreased with increasing reaction time. By cross-section analysis of PNSs by field emission scanning electron microscope (FE-SEM), it was possible to confirm the polymer layer on the surface of the spherical aggregate, maintaining the spherical shape even after polymer coating, so it was thought that we succeeded in morphological transcription. Furthermore, CPNS after high temperature carbonization also maintained spherical shape with nano-sized carbon-shell. It was also possible to confirm the morphological stabilization of the superstructure before and after polymer coating under alkaline conditions. Prepared CPNSs is expected to be used in fields such as nanosensor, drug delivery, and adsorbent. In addition, this method is expected to be used as a method for preparing and functionalizing carbon nanostructures, which is convenient and versatile than ever before.

NM01.07.21
Mechanism Study of Chemical-Vapor-Deposition Graphene Adlayers Pei Zhao, Xuewei Zhang and Hongtao Wang; Zhejiang University, Hangzhou, China.

In the past few years there have been many exciting achievements in the synthesis of large-size and high-quality monolayer graphene (MLG) using the chemical vapor deposition (CVD) method on Cu substrates. During the MLG growth, accompanying adlayers occur and remain a broad interest to researchers for a deep understanding of the graphene mechanism. When methane is used as the precursors, it is believed that the adlayers are grown underneath the previous layer, whereas when ethylene or other precursors with stronger reactivity is used, adlayer growth follows a layer-by-layer regime. In this work, we studied the growth mechanism of graphene adlayers using carbon isotope labelling of the precursors and Raman spectroscopy. Results show that when methane is used, the growth of the adlayers exhibits several different modes. For most of the adlayers, they maintain their AB-stacked or twist structures with the upper layer during the growth since their nucleation, but for some of them these stacking structures can suddenly change during the growth. Moreover, we also observed that the adlayers can nucleate tens of minutes later during the growth (not together with the first layer), with an AB-stacking with the upper layer. We also compared the results with previously reported work using ethylene, whose epitaxial nucleation of the second layer is mainly due to the active CH radicals with the presence of a monolayer-graphene-covered Cu surface. We believe that this study will help clarify more growth mechanism of graphene by CVD process, and lead to many new strategies for scalable synthesis of graphene with more controllable structures and numbers of layers.

References

NM01.07.22
Extraordinary Lithium Storage Property Form Transition Metal Oxide Electrodes by Introducing Porous CNT Sponges and Massive Oxygen Vacancies Mingchu Zou; College of Engineering, Peking University, Beijing, China.

Transition metal oxides (TMOs) are regarded as alternative anode materials due to their high theoretical capacity, nontoxic and low cost. However, it is unable to take into account of high capacity and stable cycling performance which hinder their practical applications. Here, we improve both specific capacity and stability of transition metal oxides by following two aspects: 1) composing with CNTs through a hierarchical coaxial nanostructure, and 2) introducing with massive oxygen vacancies. The synergistic reaction between TMOs (shell) and CNTs (core) through a hierarchical coaxial nanostructure can effectively enhance conductivity and reduce the Li+ diffusion distance, and consequently improve the rate performance, cycling stability and specific capacity. We develop an unique three-dimensional sponge-like CNT bulk material with excellent conductivity, high porosity and stable compressibility, which can be used as an ideal current-collector. Titanium dioxide (TiO2) is directly deposited onto the CNT sponge as a coaxial structure, forming a highly porous composite sponge electrode without any redundant additives (such as conducting agent and binder). As an anode for LIBs, TiO2@CNT sponge exhibit stable charging/discharging plateau voltages, higher capacity, better stability and rate performance comparing with pure TiO2 electrodes. Moreover, due to the TMOs are directly deposited onto the CNT sponge, the morphology of electrodes are determined by the CNT sponge. We fabricate a 1D porous electrode by depositing CNT sponges on a single carbon fiber (CF) and then deposit manganese dioxide (MnO2) onto the CNT sponge and obtain a MnO2@CNT@CF fiber-shaped electrode for LIBs. Massive oxygen vacancies are introduced into TMOs to further improve the performance of LIBs. An unique electric field assistant annealing method is developed to treat TiO2@CNT sponges. After the combined function of the temperature and electric field, oxygen vacancies are rapidly formed and migrated through TiO2, forming an amorphous TiO2@CNT sponge with a large number of oxygen vacancies (~45%) uniformly distributed in the hole TiO2. As an anode for LIBs, TiO2@CNT exhibits a capacity as 604 mAh/g which is much higher than theoretical capacity of TiO2 (335 mAh/g). Even under high rate condition (10000 mA/g), the capacity is stable as 110 mAh/g. This extraordinary performance is originated from the massive uniformly distributed oxygen vacancies which significantly enhance the conductivity and Li+ diffusion ability of TiO2. Using this electric field assistant annealing method, massive oxygen vacancies can be introduced into many other TMOs (such as MnO2 and SnO2).

In conclusion, we efficiently improve the lithium storage performances of TMO electrodes by composing CNT sponge with a coaxial structure and introducing massive oxygen vacancies uniformly. Our work has a prospect in achieving advanced LIB anodes with stable and high rate capacities for many practical applications.

NM01.07.24
New Carbon Allotropes—Novamene and Protomene as Future Advanced Carbon-Based Nanomaterials Daniel Choi1, Mohamed Alfahim2, Larry Burchfield2, Rashid Alfahim2, Kim Liao1, Abdul F. Isakovic1, Boo Hyun An1, Tamodor Elboshra1, Nicola Mamin1, Khalifa University of Science and Technology, Abu Dhabi, United Arab Emirates; 2Fields, Inc, Abu Dhabi, United Arab Emirates; 3Università degli Studi di Milano, Milano, Italy.

A new classification of carbon allotropes called, Novamene is the first release in a series which fall into an entirely new class of carbon in 2016. The basis of this new classification resides on the concept of combining hexagonal diamond (sp3 bonded carbon – lonsdaleite) and ring carbon (sp2 bonded carbon – graphene), provides the basis for the new carbon allotropes, whose properties have been found to be superior to graphene than has been introduced by Nobel Laureates Andrea Geim and Konstantin Novoselov in 2010. Since hexagonal diamond acts as an insulator and sp2 bonded rings act as conductors,
these predicted materials can transform the electronic industry and have potential applications for transistors, other electronic components such as quantum computers and even energy applications. Following up the debut of Novamene, another new carbon allotrope named Protomene has been introduced as a family of Novamene recently. It turns out that Protomene exhibits surprisingly outstanding electronic/optical/thermal properties compared to Novamene. As for the comparison with diamond and other carbon allotropes, thermal properties of Protomene can be differentiated. Since thermal expansion behaviors of Protomene are associated with interplane bonding, Protomene may experience structural phase change which can lead to a more rapid change in energy band gap and thermal expansion compared with diamond and silicon. We will present our efforts of on-going development techniques for new carbon allotropes including Novamene and Protomene based on both top-down and bottom-up approaches and modeling activities by means of Density Functional Theory (DFT) simulations.

References:

NM01.07.25

Mechanical Properties of Protomene—A Molecular Dynamics Investigation
Elizer F. Oliveira¹, Pedro A. Autreto², Cristiano F. Woellner¹ and Douglas S. Galvao¹; ¹State University of Campinas, Campinas, Brazil; ²Federal University of ABC, Santo André, Brazil; ³Federal University of Paraná, Curitiba, Brazil.

Recently [1], a new class of carbon allotrope, called protomene, was proposed. This new structure is composed of sp2 and sp3 carbon-bonds. Topologically, protomene can be considered as a carbon sp3 structure (~80% of this bond type) doped by sp2 carbons. First-principles simulations have shown that protomene presents an electronic bandgap of ~3.4 eV [1]. However, up to now its mechanical properties have not been investigated. In this work, we have investigated protomene mechanical behavior under compressive/tensile strains through fully atomistic reactive molecular dynamics simulations. We used the ReaxFF force field as available in the LAMMPS code. Our results [2] show that the protomene are very stable, up to very high temperatures (> 1000 K). The obtained ultimate strength and ultimate stress show an anisotropic material; the highest ultimate strength was obtained for x direction, with a value of ~102 GPa. As for the ultimate strain, the highest one was for z direction (27% of strain) before protomene mechanical failure (fracture).

Acknowledgments:
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References:

NM01.07.26

Surface Functional Group Dependent Photoluminescence Emission and Anomalous Quenching Behavior Observed in Graphene Quantum Dots
Tamal De¹, Subhrat Mukherjeeta, Arup Ghoral¹, Soumen Das¹ and Samit K. Ray²; ¹School of Nanoscience and Technology, Indian Institute of Technology, Kharagpur, Kharagpur, India; ²Advanced Technology Development Centre, Indian Institute of Technology, Kharagpur, Kharagpur, India; ³School of Medical Science and Technology, Indian Institute of Technology, Kharagpur, Kharagpur, India; ⁴Department of Physics, Indian Institute of Technology, Kharagpur, Kharagpur, India.

Graphene quantum dots (GQDs) [1], a carbon nanomaterial, has emerged as a promising material with unique optical and electronic properties due to their quantum confinement and edge effects. They are highly fluorescent, non-toxic and can be produced in large scale, which makes them attractive candidates for optoelectronics devices, sensing and biological applications. Controlling the shapes and sizes of GQDs as well as controlling the surface functional groups can tune their optical and electronic properties which make them attractive materials for optoelectronic devices and bio-imaging. As GQDs emit primarily in UV or blue region, they are harmful for living cells.

In the current work, we have demonstrated that controlling the surface functional groups present on the surface of the GQDs by thermal treatment significantly changes the photoluminescent (PL) emission properties which are very important for optoelectronics and bio-imaging applications. Also, with increasing annealing temperature, transition from positive thermal quenching (PTQ) to negative thermal quenching (NTQ) has been observed. GQDs were prepared by oxidative cutting of graphene oxide (prepared by modified Hummer’s method [2]) and subsequent thermal reduction. Transmission electron microscopy was utilized to measure the lateral dimension of the as prepared GQDs. The as synthesized sample was drop casted on substrates and annealed at different temperatures viz. 100 °C, 200 °C and 300 °C. Evolutions of different functional groups were studied by X-ray photoelectron spectroscopy (XPS). Red shifting of the peak PL emission was observed with increasing anneal temperature. In temperature dependent PL spectroscopy, as-synthesized sample exhibited PTQ behavior while the sample annealed at 300 °C showed NTQ phenomenon with crossover at intermediate temperatures. This phenomenon has been explained using a multi-level model proposed by Shibata in 1998 [3]. The changes observed in emission properties have been correlated with evolution of surface functional groups.

References:

NM01.07.27

Electronic Modulation of Single-Walled Carbon Nanotubes by Nitrogen-Doping via Defluorination for Efficient Oxygen Reduction Catalysis
Koji Yokoyama¹, Yoshinori Sato2, Masashi Yamamoto2, Tetsuo Nishida2, Kenichi Motomiya1, Kazuyuki Tohji1 and Yoshinori Sato¹; ¹Tohoku University, Sendai, Japan; ²Stella Chemifa Corporation, Osaka, Japan; ³Shinshu University, Matsumoto, Japan.

Nitrogen-doped carbon nanomaterials are emerging as metal-free, low-cost, and high-durable catalysts for oxygen reduction reaction (ORR) at the cathode of polymer electrolyte fuel cells. According to the recent theoretical studies, the nitrogen doping alters the electronic property of carbon nanomaterials and hence provides the ORR catalytic activity. However, in experimental approaches, the role of nitrogen doping on the ORR catalytic activity has not been understood comprehensively. In addition, the relation between electronic property and ORR catalytic activity of carbon nanomaterials has not been investigated experimentally. Here, we synthesized nitrogen-doped single-walled carbon nanotubes (SWCNTs) by a combination of defluorination-assisted post-doping process and high-temperature annealing treatment, and evaluated their ORR catalytic activities in an acid electrolyte. In addition, their
Electronic properties including work function, carrier type, and conductivity were measured and correlated with their ORR catalytic activity for understanding the catalytic mechanism of the ORR on nitrogen-doped SWCNTs. Highly crystalline SWCNTs (he-SWCNTs) were prepared by the arc-discharge method. The he-SWCNTs were fluorinated at 250 °C using 20% F2 / N2 gas for 4 h. Then fluorinated SWCNTs were heated at 500 °C for 30 min in a gas flow of 1% NH3 / N2. The resulting sample (N-SWCNTs) was further annealed at 1000 °C for 3 h in a N2 flow to prepare AN-SWCNTs. The products were characterized by X-ray photoelectron spectroscopy, transmission electron microscopy, and Raman scattering spectroscopy. In addition, we evaluated the ORR catalytic activity by electrochemical measurement using the RDE technique in 0.5 M H2SO4 electrolyte. Work function measurement was conducted using ultraviolet photoelectron spectroscopy. The carrier type and conductivity of the sample films were determined and measured by thermopower measurement and four probe method, respectively.

The N-SWCNTs contained 2.4 at% nitrogen with enriched Py-N species, while the AN-SWCNTs contained 0.8 at% nitrogen with about 50% of Gr-N species to the total nitrogen species. This result indicates that the type of nitrogen species can be controlled by the annealing treatment. Judged from the onset potential, oxygen reduction current density at half-wave potential, and numbers of electrons transferred per oxygen molecule in the ORR, the AN-SWCNTs exhibited superior ORR catalytic activity to the N-SWCNTs. The work function of the AN-SWCNTs was lower than that of the N-SWCNTs, and the carrier type of the AN-SWCNT film was obviously n-type even in air. The conductivity of the AN-SWCNT film was higher than that of the N-SWCNT film. These results suggest that the low work function and high conductivity observed in the AN-SWCNTs can promote the ORR catalytic activity.

NM01.07.28
Towards Single Crystal Monolayer Films—Catalyst Engineering for High Quality CVD Graphene

Oliver Barton and Stephan Hofmann; University of Cambridge, Cambridge, United Kingdom.

Chemical Vapour Deposition (CVD) has become the dominant technique for the growth of graphene and related 2D materials, driven by the emerging industrial demand for ‘electronic-grade’ materials that are consistent over large areas. Significant progress has been made using heterogeneous catalysis[1], and among the most widely used substrates is polycrystalline copper foil. A fundamental challenge in devising a CVD process that consistently results in homogeneous single crystal graphene is the initial substrate: which has varying concentrations of different trace impurities that can affect the growth process. It has been shown that a simple oxidative pre-treatment of the Cu catalyst to remove residual carbon results in a significant reduction in nucleation density, allowing for a much larger graphene domain size to be achieved[2]. There is still a compromise between fast growth rates and reducing sources of defects such as grain boundaries. Further to this, adequate characterisation of large area monolayer graphene films has become a significant challenge on its own.

Here we report how these compromises in controlled graphene growth can be addressed by systematically studying modifications of the Cu catalyst. The effects of adding oxygen to the Cu bulk on graphene nucleation density, morphology, growth rate and quality are closely examined. The epitaxial relationship of graphene on different Cu textures is quantitatively analysed and the capability to significantly enlarge Cu grains and recrystallize the foil is demonstrated. By leveraging the epitaxial alignment seen on specific Cu facets, single crystal graphene films can be rapidly grown, paving the way for films with improved homogeneity. In addition, a novel method to characterise graphene on a large scale is introduced based on a modification of established Raman characterisation strategies.


NM01.07.29
High-Performance Magnetorheological Suspensions of Fe3O4-Deposited Carbon Nanotubes with Enhanced Stability

Hoyeon Kim, Junseok Choi and Yongseok Seo; Seoul National University, Seoul, Korea (the Republic of).

The magnetorheological (MR) performance of suspensions based on the Fe3O4-deposited carbon nanotubes (CNTs) was investigated by using a vibrating sample magnetometer (VSM) and a rotational rheometer. The Fe3O4-deposited CNTs were synthesized by the reduction process in which nano-Fe3O4 nanoparticles were generated and adsorbed on the surface of CNTs. All tested suspensions displayed excellent MR behaviors with high yield strengths. The important parameter which determined the MR performance was the surface density of Fe3O4 on the CNT surface. The morphology was observed by scanning electron microscope (SEM) and transmission electron microscope (TEM). Most Fe3O4 particles adsorbed on the surface of PS/Fe3O4 particles to make the surface topology bumpy and rough which decreased the particle sedimentation velocity. Finally, Turbiscan apparatus was used to examine the sedimentation properties of Fe3O4-deposited CNTs suspensions. The suspensions showed excellent stability against sedimentation, much better than bare Fe3O4 particle suspension due to the inherent low density of CNT and its inside pore which can reduce the density mismatch between the nanoparticles and the carrier medium as well as the surface topology change due to the adsorption of Fe3O4.

NM01.07.30
Fabrication of Nanoporous Ultrathin Membranes by Cluster Ion Irradiation

Ardak Ainabayev1, Aidyn Shaikhov2, Abat Zhuldassov2, Sean Kirkpatrick3, Michael Walsh3, Mitiitaka Terasawa2 and Zinetula Z. Insepov1, 2, 3; 1School of Nuclear Engineering, Purdue University, West Lafayette, Indiana, United States; 2Condensed Matter Physics, National Research Nuclear University MEPhI, Moscow, Russian Federation; 3Nazarbayev University, Astana, Kazakhstan; 4Laboratory of Advanced Science and Technology for Industry, Kouto, Japan; 5Exogenesis Corp., Billerica, Massachusetts, United States.

Gas Cluster Ion Beams (GCIB) is a powerful tool for surface modification of various materials and theoretically and experimentally demonstrated the ability to create defects in ultrathin graphene-like films. In this study GCIB of Ar with acceleration energy E = 30 kV (Exogenesis, MA, USA) and total fluences ranged from 1x1013 to 1x1015 ions/cm² is used to produce defects in ultrathin films such as graphene, graphene oxide, MoS2 and Si, HOPG as a reference.

GCIB irradiated ultrathin films were characterized by NEXAFS and Raman spectroscopy, scanning electron and atomic force microscopy. The Raman spectroscopy (Horiba) study of the irradiated samples was conducted by a 632 nm laser wavelengths and 100x objective with a laser spot size of ~1 μm, 2 mW power and atomic force microscopy (AIST NT) measurements were carried out in a tapping mode by SUPERSHARP SILICON™ AFM probes for high resolution. NEXAFS spectroscopy measurements were carried out at the NewSUBARU BL09A beamline of the New SUBARU SR LASTI facility at the University of Hyogo, using total-electron yield (TEY) method and without uncompleted correction of energy. Density functional theory (DFT) calculations have been performed to study the Raman spectra of pristine and graphene with vacancy defects. Large-scale parallel molecular dynamics (MD) simulations (LAMMPS) were employed for studying interactions of accelerated cluster ions with ultrathin films, such as graphene, MoS2, HOPG, and BN. The MD results showed formation of uniform holes, with the diameters of 10-20 nm, in the ultrathin films, and were used for optimization of the experimental fabrication of holes in 2D-films. The DFT and MD simulations provides fundamental understanding of the argon bombardment of ultrathin films and its influence on Raman spectra of graphene.
Single-walled carbon nanotubes (SWCNTs) are seamless cylinders of graphene that have been at the forefront of nanotechnology research for the past two decades. While mass-produced SWCNT powders are adequate for some applications, many emerging applications require stricter control over SWCNT properties and architectures, necessitating targeted growth, i.e. tailoring the physical properties of the SWCNTs (diameter, orientation/architecture, etc.). This work attempts to prove the key role of the graphene properties and the metal - catalyst interaction in the relation between catalyst size and nanotube diameter. We work on the assumption that the curvature energy is one of the most influential factors in the graphene film formation and a crucial constraint to determine the stable diameter of the nanotube during the growth. The calculation of interlayer binding energies using density functional theory (DFT) and pseudopotential functions has been valuable to find the transition diameter between fullerene and tube. Additionally, we propose a new model that links statistical mechanics theory with the possible strain energy states and allows the calculation of the expected or most probable diameter. This is just the first step to bring light to the yet undiscovered reigning principle for the nanotube’s diameter stability during nucleation.

Poly(vinylidene fluoride) (PVDF) is a well known ferroelectric polymer which can be used for various applications such as actuators, sensors and transducers. However, the piezoelectric response from PVDF is generally not as high as that of lead zirconate titanate (PZT), due to the low Curie point of the PVDF. This work presents a high performance PVDF nanocomposite for piezoelectric application, which is fabricated by sol-gel method. 1.0 wt% of ZnO nanoparticles (ZnO NPs) were mixed into PVDF matrix using sol-gel method. The PVDF/ZnO nanocomposites were synthesized by directly mixing ZnO NPs into PVDF matrix at various weight percentage. The synthesized PVDF/ZnO nanocomposites were characterized using XRD, SEM, XPS and piezoelectric measurements. The XRD results show that PVDF was successfully converted into an oriented single crystal material at room temperature and the average crystallite size increased with the addition of ZnO. SEM results shows that ZnO NPs were uniformly dispersed in the PVDF matrix. XPS results shows that ZnO NPs were chemically bonded to the PVDF matrix. The piezoelectric measurements show that the piezoelectric constant (d33) of PVDF/ZnO nanocomposites increased with the increase of ZnO content. The maximum value of d33 was 1.24 pm/V at 1.0 wt% of ZnO. This work provides a facile route to prepare high performance PVDF nanocomposites for piezoelectric application.

In this study, we use a novel conjugated polymer to exclusively disperse semiconducting SWNTs. The dispersal procedure requires a simple sonication and centrifugation, during which the metallic SWNTs sediment out. Solution purity was evaluated using UV-Vis-NIR and Raman spectroscopies. The resulting dispersions are amenable to solution processing techniques such drop casting and spin coating, allowing for the potential for fabrication treatment were all investigated to determine which parameters facilitated the production of OTFTs with high mobilities (>20 cm2V-1s-1), high large area device fabrication at room temperature. Ambipolar OTFTs were fabricated under ambient conditions using this solution and tested in both air and in nitrogen, and the results showed that the OTFTs are fully ambipolar with mobilities of >5 cm2V-1s-1. The OTFTs were used to fabricate field-effect transistors with both n- and p-type characteristics.

Printed electronics is a burgeoning field that has received intense research interest and is beginning to experience commercial successes. Single-walled carbon nanotubes (SWNTs) are a unique and promising building block for incorporation into next generation superfast electronic devices. SWNTs have very high carrier mobilities, with band gaps compatible for integration into logic circuits. Their excellent mechanical flexibility allows for potential incorporation into flexible electronics, enabling fully-printed transistors and circuits with performances that support low cost, large area fabrication. Progress in incorporating SWNTs into commercial devices has been hindered by the presence of metallic SWNTs, which are produced alongside semiconducting SWNTs during synthesis, and negatively impact device performance. Fabrication of ambipolar SWNT organic thin film transistors (OTFTs) with high carrier mobilities and high on/off ratios remains particularly challenging; many examples in the literature required high temperature, expensive and energy-demanding processes.

Since the initial discovery of conjugated polymer-assisted dispersion and purification of SWNTs in 2008, several polymer families have been successfully shown to selectively disperse semiconducting SWNTs. However, only a relatively small number of these supramolecular complexes have been incorporated into OTFTs. We used a novel conjugated polymer to exclusively disperse semiconducting SWNTs (rGO/PMAA/rPANI) with different compositions have been designed as high performance nanocomposites. Synthesis process of the rGO incorporated PMMA (rGO/PMMA) and rPANI incorporated PMMA (rGO/rPANI) and rGO/rPANI composites have been monitored by UV-Visible and FTIR spectroscopy. Performance of the synthesized segregated bilayer composites has been studied by analyzing the electrical features measured at wide range of frequencies starting from few Hz to 1MHz. Substantial enhancement in the electrical properties was observed at relatively low filler contents. Almost 15 times increase in value of dielectric constant was observed at just 0.7wt% of rGO. Impressive increase in the electrical conductivity was shown to selectively disperse semiconducting SWNTs during synthesis, and negatively impact device performance. Fabrication of ambipolar SWNT organic thin film transistors (OTFTs) with high carrier mobilities and high on/off ratios remains particularly challenging; many examples in the literature required high temperature, expensive and energy-demanding processes.

Concussions in sports and sudden other accidental cases occur very regularly. Often times concussions leads to chronic traumatic encephalopathy (CTE) and eventual death. Polydimethylsiloxane (PDMS)-based nanomaterial are gaining widespread attention in this regard. Here we report a unique bubble tunable graphene reinforced PDMS nanocomposite as a vibration dampening and possibly concussion resistant material. PDMS based nanocomposite was prepared by solvent swelling of the PDMS (Sylgard 184 from Dow Crowing Company) in chloroform/TEOS (4:1 ratio) mixture followed by ultrasonication of the graphene nanoplatelets in the solvent that swells the polymer. Various nanocomposite structures with and without bubbles were prepared. We studied the mechanical properties of PDMS-graphene nanocomposite as a function of temperature, pressure, nanoparticle size, solvent percentage, curing agent and filler concentration. The effect of different concentrations of graphene in the nanocomposite with/without bubble formation were measured and analyzed using dynamic mechanical analyzer (DMA) and impact testing. Physical interaction of PDMS adsorptions on the graphene were computed using molecular dynamic (MD) simulation. The influence of a-well controlled bubble structure on the energy absorption behavior of the nanocomposite was explored. Stiffness of the nanocomposites increased with the loading of graphene. The role of bubble and bubble-graded nanocomposites is underway.

Graphitic carbons have been considered as hydrophobic for nearly eighty years. However, recent works in our labs showed that graphitic surfaces are much more hydrophilic than previously thought. Since the water-graphitic interface is critical to many important applications including electrode,
In this presentation, we will discuss on the intrinsic water wettability of graphitic carbons and its implication on double layer capacitance. First, our recent experimental results, e.g., contact angle, XPS, ATR-FTIR and ellipsometry, will be presented showing that pristine graphene and graphite are mildly hydrophilic and airborne hydrocarbons make the surfaces appear to be hydrophobic. Second. The implication of contamination will be illustrated through comparing the electrochemical activity and double layer capacitance of pristine and contaminated graphite. Lastly, future research directions to address a few important unanswered questions will be presented.

Reference:

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Intercalation of Fullerenes Between Graphene/Cu Interfaces

Alexandre F. Fonseca1, Socrates O. Dantas2, Douglas S. Galvão1, Difan Zhang3 and Susan B. Sinnott4; 1State University of Campinas, Campinas SP, Brazil; 2Universidade Federal de Juiz de Fora, Juiz de Fora, Brazil; 3University of Florida, Gainesville, Florida, United States; 4The Pennsylvania State University, State College, Pennsylvania, United States.

Investigation of the structure and properties of the intercalated molecules between interfaces of two-dimensional layers or of a layered material and a substrate is a subject of great interest. Formation of crystalline patterns as well as induction of chemical reactions under two-dimensional covers are two of the main drivers behind this interest. One recent study by Reinke and collaborators [Nano Letters 15, 7421–7430 (2015)], showed the formation of amorphous and crystalline structures of C60 intercalated between graphene and a copper substrate. They further reported the existence of more or less strained graphene wrinkles, as well as detached graphene from substrate depending on the concentration or distance between the intercalated C60 molecules. Motivated by this work, we investigated the formation and thermal stability of graphene wrinkles as well as graphene attachment and detachment from substrate on previously distributed C60 and carbon nanotube molecules on cooper substrate. We performed fully atomistic reactive molecular dynamics (MD) simulations using the third generation of the charge optimized many-body potential as available in the LAMMPS computational package. As the timeframe of spontaneous intercalation of C60 molecules between graphene and the substrate is too high to be feasibly simulated by MD methods, we simulated the “blanketing” of graphene on different concentrations of C60 and carbon nanotubes previously laid on the substrate. We tested both fixed and non-fixed structures, i.e., we predicted the change in the height of graphene, fullerene, and substrate when the fullerenes are not fixed. We then verified that graphene attaches to the substrate when the distance between the fullerenes is at least 6 nm. Below that distance, graphene becomes locally suspended and low strain is verified. While such studies of intercalation of molecules on interfaces formed by graphene-substrate are motivated by finding out ways to control wrinkling and strain in graphene, this work reveals the role of stability and wrinkling as well as the shape and structure of intercalated molecules under the action of graphene on the final structure and its properties.

NM01.07.37
Double Charge Neutrality Point Induced by H2 Exposure in Graphene Devices

Cintia L. Pereira, Alisson R. Cadore, Natália P. Rezende, Leonardo C. Campos and Rodrigo G. Lacerda; Departamento de Física, Universidade Federal de Minas Gerais, Belo Horizonte, Brazil.

In this work, we present a study regarding the interaction between molecular hydrogen (H2) and graphene field effect transistor with different metals and contact geometries. We demonstrate that this interaction is strongly dependent on the characteristics of the graphene-metal contact interface. Three different contacts were probed: pure Au, Au/Cr and Au/Cr2O3 contacts. Interestingly, we observed that only for Au/Cr2O3 contact devices the emergence of a second charge neutrality point (CNP) in the resistance as function of gate voltage curves (“M-shape”) due the H2 exposure. This is the first time that such behavior (“M-shape”) is found due to a gas interaction with graphene devices. This effect was observed for different conditions of temperatures (25°C-200°C) and H2 concentrations (0.5%-50%) and it is totally reversible. Previous works about graphene-contact interaction, demonstrated that the difference between the Fermi level in both regions generates the two CNP [3]. Also, we believe that the thin layer of oxide formed from such regions of during the electrical measurements. In other words, our findings suggest a way of inducing the decoupling of the work function from the metallic electrodes and graphene by the use of contacts Au/Cr2O3 and hydrogen gas exposure. Additionally, we demonstrate that the high variation of the resistance generated by the emergence of the second peak and the low time of response to hydrogen provides a system that is very promising for H2 sensor applications. This work was supported by CAPES, Fapemig (Rede 2D), CNPq and INCT/Nanomaterias de Carbono. References: [1] G. Giovannetti, et al. Physical Review Letters, vol. 101, n. 026803, pp. 1-4, 2008. [2] A. R. Cadore, et al. Applied Physics Letters 109, n. 033109, pp. 1-5, 2016. [3] S. M. Song e B. J. Cho, Carbon Letters, vol. 14, n. 3, pp. 162-170, 2013.

NM01.07.38
Flexible CNT-Decorated PDMS Foams Enable Unprecedented Detection of Ultralow Strain and Pressure Coupled with Large Working Range

Rossella Iglio1, Stefano Mariani1, Valentina Robbiano1, Lucasao M. Strambini2 and Giuseppe Barillaro1; 1University of Pisa, Pisa, Italy; 2National Research Council, Pisa, Italy.

Low-cost piezoresistive strain/pressure sensors with large working range, at the same time able to reliably detect ultralow strain (<0.1%) and pressure (≤1 Pa), are one of the challenges that have still to be overcome for flexible piezoresistive materials towards personalized health-monitoring applications. Here, we report on unprecedented, simultaneous detection of ultrasmall strain (0.1%, i.e. 10 µm displacement over 10 mm) and subtle pressure (20 Pa, i.e. a force of only 2 mN over an area of 1cm2) in compression-mode, coupled with a large working range (i.e., up to 60% for strain – 6 mm in displacement - and 50 kPa for pressure) using piezoresistive, flexible three-dimensional (3D) macroporous PDMS (pPDMS) foams decorated with pristine multi-walled CNTs. pPDMS/CNTs foams with pore size up to 500 µm (i.e. twice the size of those of commonly used foams, at least) and porosity of 77%, decorated with a nanostructured surface-network of CNTs at densities ranging from 7.5 to 37 mg/cm3 are prepared using a low-cost and up-scalable process, through replica
molding of sacrificial sugar templates and subsequent drop-casting of CNT ink. A thorough characterization shows that piezoresistive properties of the foam can be finely tuned by controlling the CNT density, and reach an optimum CNT density of 25 mg/cm³, for which a maximum change of the material resistivity (e.g., ρ0/ρ50 = 4 at 50% strain) is achieved under compression. Further static and dynamic characterization of the pPDMS/CNTs foams with 25 mg/cm³ of CNTs highlights a detection limit for strain and pressure of 0.03% (3 µm displacement over 10 mm) and 6 Pa (0.6 mN over an area of 1 cm²), respectively; moreover, good stability and limited hysteresis are apparent by cycling the foams with 255 compression-release cycles over the strain range 0-60%, at different strain rates up to 10 mm/min.

Our results on piezoresistive, flexible pPDMS/CNT foams pave the way towards breakthrough applications for personalized health care, though not limited to, which were not fully addressable to date with flexible strain/sensor.


NM01.07.39
Photoluminescence Modulation of Single-Walled Carbon Nanotubes by Meta-Linked Bis-Aryldiazonium Modifiers Bodha Yu¹, Tomohiro Shiraki¹-², and Tsuyohiko Fujigaya¹-²-³, Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, Fukuoka, Japan; International Institute for Carbon Neutral Energy Research (I2CNER), Kyushu University, Fukuoka, Japan; JST-PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama, Japan.

A small amount of chemical modification of single-walled carbon nanotubes (SWNTs) has been reported to create modified sites with narrower band gaps on the tubes. The resultant locally functionalized SWNTs (lf-SWNTs) show new photoluminescence (PL) with red-shifted wavelengths and high quantum yields (Ei;*) compared to that of pristine SWNTs (Ei;[1]). We have reported largely red-shifted PL (Ei;* ≈ Ei;*) through the local functionalization using bis-aryldiazonium salts[2]. Therein, we experimentally revealed that differences in the methylene spacer lengths connecting two aryldiazonium groups induced wavelength variation of Ei;*; and the theoretical calculations indicated that the Ei;* wavelengths were also influenced by the differences in the connected position of the second aryl groups. Recently, Doom et al. reported that such secondary reacted positions related to spectral shifts of Ei;*[3]. In this study, we newly design bis-aryldiazonium salts that have two aryldiazonium groups connected by methylene spacers at the meta positions, which are different from our previous molecular design using the methylene linkage at the para positions.

The used SWNTs were (6,5) chirality-rich tubes (CoMoCAT) and they were solubilized in D2O containing sodium dodecylsulfate through sonication using bis-aryldiazonium salts.[2] Therein, we experimentally revealed that differences in the methylene spacer lengths connecting two aryldiazonium groups induced wavelength variation of Ei;*; and the theoretical calculations indicated that the Ei;* wavelengths were also influenced by the differences in the connected position of the second aryl groups. Recently, Doom et al. reported that such secondary reacted positions related to spectral shifts of Ei;*[3]. In this study, we newly design bis-aryldiazonium salts that have two aryldiazonium groups connected by methylene spacers at the meta positions, which are different from our previous molecular design using the methylene linkage at the para positions.

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References

NM01.07.40
Experimental and Theoretical Study of Aquous Dispersions of Graphene-Based Materials Shan Jiang and Karl Coleman; Department of Chemistry, Durham University, Durham, United Kingdom.

Since the first reports of its isolation in 2004, graphene has received unprecedented interest from the scientific community. This is due to its remarkable properties such as high electron mobility, thermal conductivity and mechanical strength.[1] However, in spite of this huge potential, a number of hurdles have existed which hinder graphene’s wholesale uptake by commercial applications. One of these is the need to improve the processability of graphene materials by improving their dispersibility in a range of aqueous and non-aqueous solvents.[2] A wide range of approaches have been employed to try to improve the dispersibility of graphene in many solvents such as covalent functionalization of graphene sheet, aiming to enhance dispersibility by improving interaction with the solvent.[3] The downside to all covalent modification techniques is that the presence of additional chemical functionalities disrupts the sp2 matrix of the graphene sheets by introducing defect sites which can have a significant negative effect on the properties of the material.[4] Surfactants have been used which adsorb non-covalently to the surface of the graphene sheets improving their dispersibility.[5] However, residual surfactant molecules can have a negative impact on the properties of the graphene prepared and can be difficult to remove. Herein, we have developed a method for improving the dispersibility of graphene and its related materials in commonly used, and low boiling solvents by making use of prior dispersion in good solvents (such as N-methyl-2-pyrrolidone (NMP) and dimethylformamide (DMF)). This method allows reduced graphene oxide (rGO) to be dispersed in water at concentrations of up to 20 µg ml⁻¹ which is over a six-fold improvement compared to dispersion of untreated rGO prepared under the same conditions. Precipitation of rGO in NMP can produce NMPGO which forms a stable dispersion in water, with less than 0.3% residual NMP, confirmed by the experimental characterizations. Furthermore, molecular dynamics (MD) simulations have been used to exploit how the dispersion process is facilitated by the organic solvent treatment (NMP and DMF in this study), and investigate graphene and solvent interactions, and solvent geometry and orientation with respect to the graphene sheet. Additionally, DFT calculations have been used to study the electrical properties and charge distribution upon organic solvent adsorption on the graphene surface, in order to rationalize the improved dispersibility in water and ethanol.

(4) Eigler, S. et al., Carbon 2012, 50 (10), 3666-3673.

NM01.07.41
Site-Specific Chemical Vapor Deposition from Cu(BAOC), Leading to High Conductivity Copper-Carbon Nanotube Hybrids Anthony P. Leggett¹, Kylie J. Trettin¹, Heather L. Ursino¹, Cory D. Cress¹, Stephen M. Umbocke², Dylan J. McIntryre¹, Mark Schauer¹, Eitan Zeitra¹ and Brian Landi¹; Rochester Institute of Technology, Rochester, New York, United States; ²United States Naval Research Laboratory, Washington, District of
Carbon nanotubes (CNTs) hold great theoretical promise as electrical conductors due to a combination of high conductivity, flexure tolerance, tensile strength, and a low thermal coefficient of resistivity (TCR). However, translating these nanoscale properties into bulk structures has proven difficult. The relatively weak van der Waals forces that hold bundles of CNTs together lead to issues with the alignment and packing of individual nanotubes, creating highly resistive junctions in bulk conductors. One strategy currently under investigation to alleviate these issues is to integrate CNTs with traditional metallic conductors to combine the metal’s high conductivity with the low density and TCR of CNTs.

In this study, site-selective copper nanometal seeding through chemical vapor deposition (CVD) is demonstrated as a viable method in concert with solution electrodeposition of bulk Cu to enhance the electrical conductivity of a low-density (0.12 g/cm³, ~9 mg/m) CNT roving. An electrical bias applied directly to the CNT roving causes Joule heating which provides the thermal energy necessary for the decomposition of a bis(butylacetacetoate) copper (Cu(BAOC)), precursor. Localized changes in the resistance within a bulk CNT conductor due to differences in junction density may be used to selectively deposit the precursor at thermally active sites. The deposition varies from localized Cu deposits at applied currents producing average temperatures of ~225°C to a consistent currents producing an average temperature of 50°C. Scanning electron microscopy of a cross-section of the sample reveals Cu depositions on the interior of the sample, demonstrating the penetration of the vapor into the CNT network.

The deposition mass can be controlled up to and exceeding 50% w/w of the composite mass through control of the vacuum environment and the reaction time. A commercial acid-based Cu electroplating solution was used to deposit bulk Cu onto as-prepared and CVD seeded CNT wires, followed by planar densification and H2/Ar annealing. The finished conductors with Cu loadings from ~30-95% w/w which combine CVD Cu seeding and electrodeposition result in specific conductivity 3-5X higher than Cu-CNT conductors produced by electrodeposition alone. Ultimately, a CNT hybrid conductor with 94.2% w/w Cu, achieved a specific conductivity of 5632 S·m²/kg and electrical conductivity of 28.1 MS/m; which is among the best of recent results from the literature at equivalent loadings. The measured TCR for the Cu-CNT hybrid was 3.55×10⁻³ K⁻¹ (compared to 3.9×10⁻³ K⁻¹ for bulk Cu) illustrating the benefit for high temperature applications. Overall, the present results demonstrate the potential of Joule-heating-driven-CVD towards both seeding metal prior to electroplating and as a possible method towards the enhanced nanometal interconnection of carbon conductors (NICCs).

**NM01.07.42**

**Quantum Confinement Effect in the Absorption Spectra of Graphene Quantum Dots**


Graphene quantum dots have emerged as functional material for myriad applications due to their unique properties such as deep ultraviolet and blue to green luminescence, two-photon induced fluorescence, minimal to no toxicity, chemical- photo-stability, and biocompatibility. These attractive properties of graphene quantum dots are mainly due to the bandgap opening of two-dimensional graphene quantum confinement effects, edge effects, surface functionalization, and doping. We present our results on the effect of both p- and n-doping on the absorption properties and correlate the results with the diameters to explore electronic and phonon confinement effects.

**NM01.07.43**

**Antifouling and High-Permeation Mechanisms in Reverse Osmosis Nanocomposite Membranes made of Carbon Nanotubes and Aromatic Polyamide**

Rodolfo Cruz-Silva¹⁻², Aaron Morelos-Gomez¹⁻², Josue Ortiz-Medina¹⁻², Yoshihiro Takizawa¹, Ayaka Yamakazi¹, Michio Katouda¹⁻³, Syogo Tejima¹⁻², Kenji Takenchi¹⁻², Takaya Hayashi¹⁻², Mauricio Terrones²⁻⁴ and Morinobu Endo¹⁻²; 1COI Aqua Innovation Center, Shinshu University, Nagano, Japan; 2Institute of Carbon Science and Technology, Shinsyu University, Nagano, Japan; ³Research Organization for Information Science & Technology, Tokyo, Japan; ⁴Department of Physics, Department of Materials Science and Engineering, and Department of Chemistry, The Pennsylvania State University, State College, Pennsylvania, United States.

Nanocomposite membranes made with multiwalled carbon nanotubes (MWCNTs) and aromatic polyamide (PA) have been studied do their superior performance, that combines high permeation, high salt rejection, good chlorine resistance, and low-fouling behavior. We have used a combination of experimental techniques, such as cross-flow filtration, microscopy and spectroscopy, whereas molecular dynamics studies were carried out to understand the membrane at the atomic level. MWCNT-PA nanocomposite membranes were prepared by interfacial polymerization using an aqueous phase containing MWCNTs and an organic phase. Membranes were then evaluated under cross-flow and studied by x-ray photoelectron spectroscopy, fourier transformed infrared spectroscopy, and electron microscopy. Organic nanocomposite membranes were formed using a protein (bovine serum albumin) solution, whereas scaling was produced using a mixture of calcium chloride and sodium bicarbonate that precipitates calcium carbonate. During these studies, the fouling of the membrane was followed in situ using fluorescence optical microscopy using an acrylic-made transparent cross-flow cell. The protein was labeled with fluorescein while calecin was added in the scaling study to render the calcium scales fluorescent. MWCNT-PA nanocomposite membranes showed consistently lower organic fouling and less scaling. Our findings show that the observed antiscalant and antifouling nature of the MWCNT–PA membranes is the result of several factors, among them: a smooth membrane surface morphology, a lower surface charge, an interfacial layer of water, and lower mobility of the membrane molecules. These results are important for the design and development of promising low-fouling RO membranes for water treatment. Regarding the water diffusion across the membrane, our studies shown that instead of flowing inside the MWCNTs, an oriented diffusion mechanism explains the high water permeation of these membranes. MWCNTs reduce the diffusion path of water molecules across the membranes by providing a lower energy path. The proposed water diffusion mechanism offers an alternative and most likely explanation for the high permeation phenomena observed in CNTs and PA nanocomposite membranes, and its understanding is key to improve the performance of the nanocomposite reverse osmosis desalination membranes.

**NM01.07.44**

**Coplanar Floating Gates Connected with Ionic Bridges for Remote Gating Graphene Transistors**

Hyunwoo Lee¹, Jong Ik Lee¹, Hyunseung Jung², Wonwoo Lee², Hojin Lee³ and Moon Sung Kang¹; ¹Department of Chemical Engineering, Soongsil University, Seoul, Korea (the Republic of); ²School of Electronic Engineering, Soongsil University, Seoul, Korea (the Republic of).

Exploiting an electrolyte-based gate dielectric that relies on direct migration of ions allows design of unconventional transistor architecture. For example, the current density of a transistor channel can be modulated using a gate electrode that is not located directly on top/below the channel but placed apart from the channel as long as the electrode is bridged with the channel through the electrolyte— which we refer to as the remote gating. For effective remote gating, the electric double layer at both the electrolyte/channel and the electrolyte/gate interfaces has to be formed promptly. However, the promptness of the electric double layer formation relies on the distance between the channel and the gate. This indicates that the dynamic characteristics of a remote-gated transistors degrades with this distance. Here we present new device architecture to maintain the dynamic characteristics of a graphene transistor, even if its channel is gated remotely. The new structure employs multiple coplanar floating gates bridged through short ionic dielectric layers. Unlike the dynamic characteristics of a remote-gated graphene transistor employing a single, extended electrolyte layer, the devices with multiple, short electrolyte layers could operate promptly even when they are gated from a distance; we confirmed that the effective current modulation of graphene transistor can be achieved at 1 kHz, even when the gate electrode is located 1000 µm apart from the channel, which were comparable to the dynamic characteristics of a device using a
gate located 200 μm apart. The results indicate that the distance-dependence degradation on the dynamic characteristics of the remote-gated graphene transistors can be eliminated. The new device architecture provided here shows new opportunities to exploit graphene transistors.

Reference

NM01.07.45
Hierarchically Structured Large Area Carbon-Nanossheets for Shape Deformable Electrochemical Capacitors Jong Han Jun1, Hyeonjun Song2, Changsoon Kim3, In-suk Choi, Youngjin Jeong*4 and Ji-Hoon Lee5; 1Department of Materials Science and Engineering, Seoul National University, Seoul, Korea (the Republic of); 2Department of Information Communication, Materials, and Chemistry Convergence Technology, Soongsil University, Seoul, Korea (the Republic of); 3Program in Nano Science and Technology, Graduate School of Convergence Science and Technology, Seoul National University, Seoul, Korea (the Republic of); 4Department of Organic Materials and Fiber Engineering, Soongsil University, Seoul, Korea (the Republic of); 5Advanced Functional Thin Films Department, Surface Technology Division, Korea Institute of Materials Science (KIMS), Gyeongnam, Korea (the Republic of).

The energy storage systems applied on wearable electronic devices should exhibit mechanical robustness, high cost efficiency, and high electrochemical activity in various human body motion. To solve these requirements, we introduce all-carbon-based large-area nanocomposites for freely-deformable electrochemical capacitors. Three-dimensionally incorporated all-carbon-based self-supported nanocomposites are composed of activated carbons (ACs) dispersed in carbon nanotube (CNT) sheets derived by direct spinning method without additives such as conductive agents and polymeric binders. On account of the synergetic effects from immensely porous AC particles providing large number of active sites, high electrical conductivity of CNTs, and facile ion accessibility in aqueous electrolyte solution utilized by the acid treatment, the nanocomposites show a greatly improved specific capacitance compared to that of conventional electrodes used metallic current collectors in terms of total mass of the electrodes. We also fabricated the deformable all-carbon-based electrochemical capacitors that showed excellent durability and electrochemical performances under extreme mechanical deformations of bending, folding, twisting, and stretching.

NM01.07.46
Fast Solution-Based Catalyst Preparation for Fluidized-Bed Synthesis of Submillimeter-Long Carbon Nanotubes Rita Maeda1, Toshio Osawa1, Hisashi Sugime2 and Suguru Noda1; 1Waseda University, Department of Applied Chemistry, Tokyo, Japan; 2Waseda Institute for Advanced Study, Waseda University, Tokyo, Japan.

Carbon nanotubes (CNTs) have attracted great interest for many potential applications. To realize such applications, low-cost production of high quality CNTs is highly demanded. Fluidized-bed chemical vapor deposition (CVD) is one of the candidates for the realization of mass production [1]. We previously reported fluidized-bed CVD synthesis and easy separation of submillimeter-long CNTs on/from ceramic beads with smooth surface [2]. Our previous reports revealed that the preparation of catalyst is important for CNT growth. Two methods have been examined for the preparation: ex situ sputtering and in situ CVD methods. Fe/AO, catalyst by ex situ sputtering yields single-wall CNTs [3]. On the other hand, in situ CVD method enables the fast catalyst deposition in a few minutes [2,4]. Other methods including impregnation have been introduced for the catalyst preparation [5]. However, all these methods still have limitations. For the case of sputtering and impregnation, they take long time. In situ CVD is quick but uneasy to make fine control of catalyst for single-wall CNTs. Therefore, in order to increase the productivity, it is required to find a method which realizes both the easy control of the catalyst and the short preparation time. Here we report a fast solution-based catalyst preparation on ceramic beads for CNTs. We coated catalyst on beads by gas-pressurized filtration of ethanol solution of Fe(CH3COO)2 and Al(OC3H7)3 in a vertical tube for a few minutes. We then synthesized CNTs on the beads. The beads yielded CNTs with submillimeter length but on a part of the bead surface due to the non-uniform catalyst deposition. After the separation of CNTs from the beads, the beads were reused to reduce the cost. The beads with re-coated catalyst yielded CNTs with higher coverage with increasing number of reuse, resulting in improved yield of CNTs. We will discuss the catalyst condition on the structure of the resulting CNTs.

References:
9:00 AM *NM01.08.02
Controlling the Inner Dielectric Environment of Carbon Nanotubes to Tune Their Optical Properties
Sophie Cambré1, Jochen Campo1, 2, Bea Botka1, Wouter van Werveke1, Jan Obruzet1, Wim Wenseleers1 and Jeffrey Fagan2; 1University of Antwerp, Antwerp, Belgium; 2Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

The optical properties of single-wall carbon nanotubes (SWCNTs) are extremely sensitive to their external and internal environment. For example, filling the endohedral cavity with water molecules results in characteristic shifts and broadening of both the SWCNTs’ radial breathing mode vibrational frequency and their optical (electronic) transitions, as well as a quenching of their emission.[1] Although mostly ignored in literature, solvent ingestion effects are substantial, and can also be used to passivate the nanotube interior, by controlled manipulation of the endohedral environment prior to dispersion.[2]

In this work, specific and tunable modification of the optical properties of SWCNTs is demonstrated through the direct encapsulation of guest molecules with widely varying dielectric constants. Over 30 different compounds with static dielectric constant varying from 1.8 to 109 have been encapsulated inside the SWCNTs and their spectroscopic analysis, in comparison to unfilled (empty) SWCNTs, demonstrates for the first time experimentally that the general effect of filler static dielectric on the nanotube optical properties corresponds to a monotonic energy reduction (red-shifting) of the optical transitions with increased magnitude for higher dielectric constants.

Systematic two-dimensional fitting of the fluorescence-excitation spectra enables the direct comparison of this red shifting as a function of nanotube diameter, modulus and chirality. In addition to these spectral shifts, the filling with dielectric molecules also reveals a general increase of fluorescence intensity with lower dielectric constants, with some fillers approaching the emission efficiencies of empty SWCNTs. Our investigation hence demonstrates a new degree of modulation of the SWCNTs’ optical properties by simple endohedral ingestion of various guest molecules.


9:30 AM BREAK
Establishing a 3D electrically percolating network in an insulating matrix is key to numerous engineering and functional applications including energy storage and conversion, sensing devices, and telecommunication. To this end, using hydrophobic carbon nanofillers like graphene or carbon nanotubes is tempting, but still results in suboptimal performance due to processing challenges including colloidal instabilities in aqueous media.

Here, we demonstrate how natural cellulose nanofillers (1) can be in situ transformed into graphene-like sheets connected to a 3D network, enhancing both mechanical properties and also enable the use of technologically important machining methods for electro-conductive ceramics.

In this communication we present how cellulose nanofillers are converted into FLG during spark plasma sintering within Al2O3 and yttria-stabilized ZrO2 (YSZ) matrices, respectively. The microstructure of the resulting materials was characterized by electron microscopy and spectroscopy (STEM/EELS), while the electrical and dielectrical properties were analyzed by impedance spectroscopy. The materials showed high electrical conductivity at only 2% initial CNF content, while the FLG-YSZ nanocomposites exhibited mixed ionic-electronic conduction at ≤1% CNF, which is interesting for electrode materials in solid-oxide fuel cells. Besides the transport properties, the incorporated cellulose nanofillers largely improve the mechanical properties and also enable the use of technologically important machining methods for electro-conductive ceramics.

We envisage that our results can advance the processing science and technology to provide the improved hierarchical graphene composite materials needed for advanced applications in fields like energy and telecommunications.

References
the direction of long axis of CNT. Therefore, to derive CNT properties into applications, alignment degree is one of the important structural parameters. In this study, aligned CNT sheet preforms were prepared by dry spinning from CNT forests. The aligned CNTs were mixed with epoxy or polyamide resin. A hot-melt method of the CNT sheet with the resin film enabled high CNT volume fraction up to 49%. We investigated thermal and electrical conductivity of the high CNT content composites. Spin-capable CNT array was synthesized by chloride mediated thermal chemical vapor deposition (CM-CVD).

Dimensions of CNT are 30 nm in diameter and > 1mm in length. By stacking the CNT webs, a CNT sheet was formed. Then, aligned CNT/polymer composite films were prepared by hot-pressing the CNT sheet and a polymer sheet simultaneously. We used a thermosetting polymer of B-stage epoxy and thermoplastic one of polyamide. Since polymer was impregnated in the the CNT preform, uniformly dispersed composites were obtained with a high Vf of 49 % in epoxy. With increasing Vf, thermal conductivity was increased monotonically up to 80 W/m/K. Similar increase was observed for CNT/PA. For both composites, uniform dispersion of CNTs in polymer matrix was observed. Electrical conductivity increased with increasing Vf as well as thermal conductivity, and it reached to 700 S/cm. We found that both conductivities are influenced by CNT Vf but by polymer materials.

11:45 AM NM01.09.07
Conformal Printing of Graphene Inks and Multilayered Devices onto Arbitrarily Shaped 3D Objects
Leonard Ng, Xiaoxi Zhu, Guohua Hu and Tawfiqee Hasan; University of Cambridge, Cambridge, United Kingdom.

Printing has drawn a lot of attention as a means of low per-unit-cost, high throughput and additive patterning of graphene inks for scaled-up functional thinfilm device manufacturing. However, the traditional printing processes typically require a flat surface and hence the current graphene printing methods are incapable of achieving patterning onto arbitrarily-shaped objects such as 3D printed parts and even on human skin.

Here, we present a conformal printing method to deliver conductive graphene patterns on to arbitrarily-shaped 3D objects using a sacrificial layer. We first formulate a water-insoluble conductive graphene ink and print it on to an ultrathin polyvinyl alcohol (PVA) film using conventional printing processes. The printed graphene patterns are then floated onto water, allowing the dissolution of PVA, while retaining the graphene patterns. This allows transfer of the conductive graphene patterns directly onto arbitrarily-shaped 3D objects with high resolution. I will present the formulation process and the parameters vital to achieving this and demonstrate this process onto a variety of irregularly-shaped 3D objects. Using this approach, I will also demonstrate multilayered device fabrication/transfer, including simple 2D material based electric circuits and components as well as resistive and capacitive strain sensors, without requiring post deposition processing.

1:30 PM *NM01.10.01
Structure-Defined DNA-Carbon Nanotube Hybrids and Their Applications
Mina Zheng; National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

In this talk, I will present first our current understanding of structure-defined DNA-carbon nanotube hybrids, then a description of the DNA sequence selection problem, and finally utility of DNA-carbon nanotube hybrids in molecular sensing. An artificial perception system, i.e. molecular perceptron, is proposed to take full advantage of the structure diversity of DNA-carbon nanotube hybrids.

2:00 PM NM01.10.02
Perylene-Based Functionalization of Carbon Nanotubes
Antonio Setaro, Mareen Glaeske, Katharina Huth, Mohsen Adeli, Rainer Haag and Stephanie Reich; Freie Universität Berlin, Berlin, Germany.

Functionalization aims at granting compounds with additional features. This is achieved by typically attaching novel groups to the original systems. The aftermath of such process yields complexes whose characteristics often result in more than just the mere sum of the initial products. The specific character of the functionalized structure, moreover, depends upon the way the functionalization strategy has been pursued.

We will focus on the carbon nanotube functionalization through perylene, an aromatic molecule emitting in the excitation window of most single-walled nanotubes commercially available. We have previously shown that the perylene core of custom surfactants was able to attach through pi-pi stacking interactions onto the sidewall ofCNTs while ensuring efficient excitation transfer to the tubes [1,2]. Here we will show how starting from the same elements (perylene and nanotubes) and pursuing different functionalization routines, we achieve systems with different features and functions. In particular, we will compare the characteristics of perylene-comprising polymers wrapped around the tubes [3] with the peculiarities of perylene covalently attached to the nanotubes following a novel conjugation-preserving routine we recently developed [4]. We will highlight the difference among the properties of the final products as well as the applications they would be suitable for.


2:15 PM NM01.10.03
Molecular Recognition of Carbohydrates using Alternating Phenyl Boronic Acid Co-Polymers as Carbon Nanotube Corona Phases
Minkyung Park, Jiyoung Ahn, Pingwei Liu, Daichi Kozawa, Volodymyr Koman, Song Wang, Gili Bisker, Seomyeong Kwak, Naveed A. Bakh, Michael A. Lee and Michael Strano; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

The molecular recognition of carbohydrates remains a major challenge due to their inherent structural complexity and low affinity for most substrates despite its importance in biological systems. Natural and synthetic lectins have been broadly studied and comprised the majority of molecular recognition strategies to date. However, in this work, we explore a class of specific polymers that adopt a unique 3D configuration and exhibit highly specific carbohydrate binding when adsorbed at the surface of a carbon nanotube. A compositionally diverse polymer library based on reversible addition-fragmentation chain-transfer (RAFT) polymerization of ortho-, meta-, and para-phenyl boronic acids (PBA) with acrylic, methyl acrylic, vinyl benzoic,
and maleimidopropionic monomers, forming alternating, random, and block co-polymer variations is evaluated for the ability to selectively bind various mono- or few-layer hexagonal BN seamlessly wrap around a single-walled carbon nanotube (SWCNT), and result in an atomically smooth coaxial tube consisting two different materials, SWCNT@BNNT. The structure is synthesized by chemical vapor deposition (CVD), and the length of the coaxial tubes can reach up to micrometers. As the reaction occurs on outer surface of the existing SWCNTs, we name this process conventional CVD. Various SWCNTs, e.g. vertically aligned array, horizontally aligned arrays, suspended SWCNTs, random networks and films, are employed as the starting material, and successful coating are achieved on all of them. TEM-EELS clearly demonstrated the BN-SWCNT coaxial structure in individual tube scale, while Raman, optical absorption, and cathode luminescence spectra clearly confirm the existence of this structure in large scale. After coating, the SWCNTs can be fully coated and thermal stability significantly increases. Our characterizations confirm that the outside BN coating started locally on the wall of a SWCNT and then merged into a BN nanotube on the curved surface of the SWCNT which served as a template. The thinnest inner SWCNT that can support the BN layer growth is found to be 0.6-0.7 nm. The number of walls can be tuned from 1 to few by controlling the CVD condition. The structure of inside SWCNTs are almost not affected by the conformal CVD, as evidenced by Raman and many other characterizations. The crystallization and cleanness of the starting SWCNT template are believed to be critical for the successful fabrication of outside walls. This structure is expected to have a broad interest and impact in many fields, which include but not limited in investigating the intrinsic optical properties of environment-isolated SWCNTs, fabricating BN-protected or gated SWCNT devices, and building more sophisticated 1D material systems. Part of this work was supported by JSPS KAKENHI Grant Numbers JP5107002 and JP51505760.

3:30 PM *NM01.10.04
Single-Walled Carbon Nanotubes Co-Axially Wrapped with Mono- and Few-Layer Boron Nitride Nanotubes

Rong Xiang1, Taiki Inoue1, Yongjia Zheng1, Ying Liu1, Yang Quan1, Shohei Chiashi2, Akihito Kumamoto3, Yuichi Ikahara1, Yuta Sato1, Kazutosu Suegasa1, Jia Goo1, Yan Li1, 1Department of Mechanical Engineering, The University of Tokyo, Tokyo, Japan; 2Energy NanoEngineering Lab., National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan; 3Institute of Engineering Innovation, The University of Tokyo, Tokyo, Japan.

We propose a conceptually new structure, in which mono- or few-layer hexagonal BN seamlessly wrap around a single-walled carbon nanotube (SWCNT), and result in an atomically smooth coaxial tube consisting two different materials, SWCNT@BNNT. The structure is synthesized by chemical vapor deposition (CVD), and the length of the coaxial tubes can reach up to micrometers. As the reaction occurs on outer surface of the existing SWCNTs, we name this process conventional CVD. Various SWCNTs, e.g. vertically aligned array, horizontally aligned arrays, suspended SWCNTs, random networks and films, are employed as the starting material, and successful coating are achieved on all of them. TEM-EELS clearly demonstrated the BN-SWCNT coaxial structure in individual tube scale, while Raman, optical absorption, and cathode luminescence spectra clearly confirm the existence of this structure in large scale. After coating, the SWCNTs can be fully coated and thermal stability significantly increases. Our characterizations confirm that the outside BN coating started locally on the wall of a SWCNT and then merged into a BN nanotube on the curved surface of the SWCNT which served as a template. The thinnest inner SWCNT that can support the BN layer growth is found to be 0.6-0.7 nm. The number of walls can be tuned from 1 to few by controlling the CVD condition. The structure of inside SWCNTs are almost not affected by the conformal CVD, as evidenced by Raman and many other characterizations. The crystallization and cleanness of the starting SWCNT template are believed to be critical for the successful fabrication of outside walls. This structure is expected to have a broad interest and impact in many fields, which include but not limited in investigating the intrinsic optical properties of environment-isolated SWCNTs, fabricating BN-protected or gated SWCNT devices, and building more sophisticated 1D material systems. Part of this work was supported by JSPS KAKENHI Grant Numbers JP5107002 and JP51505760.

4:00 PM NM01.10.05
Thermal Conductivity Measurement of Single-Walled Carbon Nanotubes by Photoluminescence Imaging Spectroscopy

Kazuki Yoshino1, Kazuma Nagano1, Makoto Horiguchi1, Yuichiro Tanaka1, Shohei Chiashi2 and Yoshikazu Homma1; 1Tokyo University of Science, Tokyo, Japan; 2The University of Tokyo, Tokyo, Japan.

Single-walled carbon nanotubes (SWCNTs) are expected to have high thermal conductivity along the tube axis. However, experimentally obtained values of the thermal conductivity vary widely because of the difficulties in the thermal conductivity measurements as well as the characterization of SWCNTs. We have recently developed a novel method for measuring thermal conductivity using photoluminescence (PL) imaging spectroscopy [1]. We use a long wavelength band-pass filter to remove the pumps laser light and a long integration time to enhance the signal-to-noise ratio. The temperature dependence of thermal conductivity of the thermal conductivity vary widely because of the difficulties in the thermal conductivity measurements as well as the characterization of SWCNTs.

4:15 PM NM01.10.06
Scalable Fabrication and Characterization of Vertically Aligned Carbon-Nanotube/Polymer Membranes

Richard J. Castellano1, Eric R. Meshot2, Francesco Fornasiero2, Robert Praino3 and Jerry Shan1; 1Rutgers University, Piscataway, New Jersey, United States; 2Lawrence Livermore National Laboratory, Livermore, California, United States; 3Chalmers Technologies, Canton, Massachusetts, United States.

Membranes incorporating vertically aligned carbon nanotubes (CNTs) as through-pores have been shown to transport fluids at rates orders-of-magnitude faster than predicted by theory, offering promise as highly permeable membranes for applications as diverse as breathable yet protective garments, desalination membranes, and highly efficient filters. However, there is a need for cost-effective and scalable solutions for fabricating large-area vertically aligned nanotube membranes, ideally starting from bulk nanotubes. Here, we describe a new, solution-based fabrication technique for creating polymer composite membranes using electric-field alignment and electrophoretic concentration of CNTs initially dispersed in a solvent. The solvent is then replaced with a UV-curable oligomer, which is cured to controlled thickness to form a membrane with vertically aligned carbon nanotubes. After etching to open CNT pores, the pore size and total open area are assessed with He–Ne laser fluorescence microscopy, size-exclusion tests and acentric KCl conductivity measurement. By comparing to theory, a pressure-driven gas flow enhancement factor of 200 - 300 is found for flow through the small-diameter nanotube pores, which is consistent with reports in the literature for membrane fabricated from CVD-grown aligned nanotube forests. We conclude by describing recent progress in significantly increasing nanotube number density and membrane permeability, and the remaining challenges for ultimate roll-to-roll fabrication of vertically aligned nanotube membranes.


4:30 PM NM01.10.07
Functional Graphene Oxide (GO) Templated Patterning and Anti-Microbial Properties

Rigoberto C. Advincula; Case Western Reserve University, Cleveland, Ohio, United States.

Graphene (G), Graphene Oxide (GO), and Reduced Graphene Oxide (rGO) have had an explosive growth in their applications ranging from electronic
To evaluate the influence of the synthesis temperature and the flux of the carbon precursor gas, experiments were performed between 600 and 800 °C, with hetero-atoms, like the nitrogen, in the electrical conductivity of the NC-CNTs-N is shown. In the present work a study of the influence of temperature of synthesis, the flow of the carbon precursor gas and doping was observed that doping the CNTs with nitrogen reduced the resistivity by five orders of magnitude, from 2 MΩ (NC-CNTs-650°C) to 13 Ω (NC-CNTs-N, 650°C). This phenomenon occurs because nitrogen introduces free electrons to the π conjugation system of carbon atoms.


Reduced graphene oxide (rGO) has attracted a great deal of research attention in the fields of energy storage, electronics, photonics, catalysis, environmental engineering, etc. Currently, the most popular way to prepare rGO is to reduce graphene oxide, which is obtained by modified Hummer methods using tedious treatments in a harsh environment, to rGO flakes. Industrial applications demand advanced preparation methods that can mass produce highly uniform rGO sheets on arbitrary substrates and free-standing rGO powders. Systematic spectroscopic and microscopic studies on the resulting rGO are performed. Prototypes of electronic and optoelectronic devices, such as field effect transistors (FETs), photodetectors, and humidity sensors, are fabricated and tested, demonstrating the intriguing applications of our rGO materials across a wide range of fields.
In this work, carboxyl functionalized multiwall carbon nanotubes (a-MWNTs) covalently grafted with hydroxylated functionalized poly (ether ether ketone), HPEEK, which is miscible with the pre-polymer (epoxy) through the esterification reaction. The functionalized MWNTs were systematically characterized using spectroscopic techniques. The epoxy composites containing a-MWNTs and HPEEK grafted multiwall carbon nanotubes (HPEEK-g-MWNTs) were formulated using mechanical stirring coupled with a bath sonicator to improve the dispersion property of the nanoparticles and were subsequently cured. With the addition of 0.5 wt% of HPEEK-g-MWNTs, an impressive 44% enhancement in the storage modulus, 22% increase in tensile strength and 38% increase in fracture toughness was observed with respect to neat epoxy. In addition to these mechanical properties, the epoxy composites displayed significant enhancement in the hardness without reducing thermal stability. These improved properties were attributed to the tailored interface between HPEEK-MWNTs and epoxy matrix.

NM01.11.05
An Optimization for Thermal Boundary Resistance of GaN-Diamond Devices Based on Dielectric Layer Li Chengming;
University of Science and Technology Beijing, Beijing, China.

GaN-on-diamond device cooling can be enhanced by reducing the thermal boundary resistance (TBRref, Dia/GaN) of the GaN/diamond interface. One limiting factor of TBRref, Dia/GaN is the dielectric layer type at the GaN to diamond interface. The thermal properties of this interface and the polycrystalline diamond grown onto GaN using SiN and AlN dielectric layers under same growth conditions are investigated and systematically compared for the first time. Using a combination of time-domain thermoreflectance (TDR) measurement, adhesion evaluation and microstructural analysis, the TBRref, Dia/GaN of GaN-on-diamond wafers is shown to be dominated by dielectric layer type for diamond growth seeding, with additional impacts from the diamond nucleation surface. By changing the type of dielectric layer(AIN,SiN), TBRref, Dia/GaN can be significantly reduced, and a TBRref, Dia/GaN of GaN-on-diamond wafers as low as 36–41m2K/GW is demonstrated when the dielectric layer is SiNx. This makes it possible to significantly reduce the thermal resistance of GaN/diamond transistors.

NM01.11.06
Structure and Electrical Properties of Interfaces Between a Carbon Nanocapsule and Metal Electrodes Studied by In Situ Transmission Electron Microscopy Manabu Tezura and Tokushi Kizuka; Division of Materials Science, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Japan.

Carbon nanomaterials have been promising elements for a variety of future applications in electronics. Since the contact interfaces between carbon nanomaterials and metal electrodes influence the properties of assembled structures, the extensive studies on the interfaces have been conducted. The atomic configuration and electrical properties of the interfaces have been investigated to elucidate the conduction mechanism [1]. In situ transmission electron microscopy (TEM) using nanotip operation techniques allows the simultaneous observation of the structures and electrical properties of the junction of a carbon nanocapsule (CNC) and metal electrodes [2]. In this study, we applied in situ TEM to investigate the relationship of the structure and electrical resistivity of the interfaces between a CNC and metal electrodes. CNCs were dispersed in ethanol and were dropped on the edge surfaces of a gold (Au) nanotip. This nanotip and another bare nanotip were inserted in a transmission electron microscope. Single nanoparticle junctions (SNPJs) were assembled using the CNCs and the two Au nanotips (electrodes) by piezomanipulation inside the microscope. After the preparation of SNPJs, their configuration was controlled by using piezomanipulation and was observed in situ at an atomic scale. Simultaneously, the conductance of SNPJs was measured by a two-terminal method while applying bias voltages. These process of observations and electrical measurements were performed at room temperature in a vacuum of $1 \times 10^{-5}$ Pa. The observed high-resolution TEM images and currents were analyzed.

We could observe several interfaces and measure their contact resistivity. Consequently, it was found that the contact resistivity depended on the orientational relationships of the interfaces.


NM01.11.07
Fabrication of Polyamide/Polyethersulfone Reverse Osmosis Membranes Containing Functionalized Carbon Nano-Onions Having Antibacterial Activity Soomin Lee, Eun Yeob Choi, Jeongung Nam and Chang Keun Kim; Chung-Ang University, Seoul, Korea (the Republic of).

Polyamide/polyethersulfone (PA/PES) membranes containing carbon nano-onions (NOs) were fabricated for the application in reverse osmosis (RO) membrane with enhanced antibacterial properties. The PA/PES membranes were prepared by interfacial polymerization between m-phenylenediamine (MPD) and trimesoxy chloride (TMC) on the surface of PES as support membrane. Then, the resulting PA/PES membranes were incorporated with the NOs to give antibacterial activities and use as RO membrane. The PA/PES membranes containing NOs were prepared in two variants; one contains aminated NO (NO-NH2) and another contains acyl chloride-terminated NO (NO-COCI). Each functional group in both NOs was reacted with MPD or TMC in the PA membranes, resulted in grafting NO with PA membrane. The formation of PA membranes containing NOs was confirmed by some analyses including FT-IR, XPS, FE-SEM and TGA. The PA/PES/NO-NH2 membrane exhibited better antibacterial properties compared with the PA/PES/NO-COCI composite membrane. In addition, the PA/PES/NO-NH2 membrane showed high water flux without a loss in salt rejection. Thus, the excellent permeation performances of PA/PES/NO-NH2 membrane make its potential applications as an effective RO membrane.

NM01.11.08
Fabrication of Polyamide/Polyketone Grafted Multi-Walled Carbon Nanotube Composites Using a Grignard Reagent Containing Pyrene Derivative Jeongung Nam, Eun Yeob Choi, Soomin Lee and Chang Keun Kim; Chung-Ang Univ., Seoul, Korea (the Republic of).

Aliphatic polyketone (PK) composites containing PK grafted multi-walled carbon nanotubes (PK-g-MWCNTs) were prepared and their physical properties containing interfacial adhesion between PK and multi-walled carbon nanotubes (MWCNTs) and mechanical strength of the composite were examined. To fabricate PK-g-MWCNTs, 1-pyrenylmethylmagnesium bromide (PMgBr) was absorbed on the MWCNT surface by physisorption and then reacted with PK. During this procedure, Grignard reagent in the PMgBr reacted with ketone groups in the repeat unit of PK, resulting in grafting PK with MWCNTs. The formation of PK-g-MWCNT was explored by spectroscopy, electron microscopy, and thermal analysis. The interfacial adhesion energy between PK and PK-g-MWCNT was the highest value that can be achieved with PK and modified MWCNTs. The PK/PK-g-MWCNT composite exhibited better MWCNT dispersion compared with PK-pristine MWCNT composite. As a result, the PK/PK-g-MWCNT composite showed the highest mechanical strength among the composite examined owing to the improved interfacial adhesion and MWCNT dispersion.

NM01.11.09
Covalently Connected Graphene/Carbon Nanotube Hybrid Structure and Their Application Nam Dong Kim1, Yilun Li3, Yingchao Yang2, Caitian Gao2 and James M. Tour1; 1Korea Institute of Science and Technology, Bodong-eup, Korea (the Republic of); 2Mechanical Engineering, University of Maine, Orono, Maine, United States; 3Chemistry, Rice University, Houston, Texas, United States.
Carbon materials have great potential for advanced nanotechnology. They exist in various allotropes in several dimensions, such as 0D of C60 family and graphene quantum dots, 1D of carbon nanotube (CNT), graphene nanoribbon (GNR) and carbon fiber (CF), and 2D of graphene relate materials. Each of these allotropes shows unique and interesting properties making them representative nano-materials. Recently, hybrid system of different carbon allotropes has great attentions to achieve an improved and synergistic properties. Making 3D hybrid structure gives many enhanced properties, such as high integrity, interconnectivity, porosity, conductivity and mechanical strength. New strategy to connect different carbon allotropes with covalent bonding allows us to fabricate more advanced structure which was not possible previously and to understand novel properties of materials. After first research about seamlessly connected graphene and carbon nanotube hybrid structure (G/CNT) has been reported, it has attracted great attentions due to its high surface area, excellent electrical and mechanical properties. In this presentation, several researches derived from G/CNT structure will be introduced. Such as patterning, mechanical strength at the junction and energy storage application, and its powerful possibility will be discussed.

NM01.11.10
Dielectric Analysis of Chitosan-Graphene-Lithium Perchlorate Films at Room Temperature
Swathi Somanathan1, Vinod K. Aswal2, Miriam Rafaelovich1 and Radha Perumal Ramasamy1; 1Applied Science and Technology, ACT Campus, Anna University, Chennai, India; 2Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai, India; 3Materials Science and Engineering, Stony Brook University, Stony Brook, New York, United States.

Use of environmentally friendly solid polymer electrolytes is important for battery technology. This work aims at investigating effect of lithium in chitosan-graphene films which can be useful for energy storage applications. Lithium ion are small in size. Lithium salts conduct electricity under electric field due to the mobile lithium ions which can easily migrate. Chitosan is an abundantly available biopolymer. It has good film forming ability. However chitosan films do not have good conductivity. Graphene-based functional materials have caused great interests in electronic, medical, environmental applications due to its large surface area, high electrical conductivity and high mechanical strength. H5 Graphene was purchased from XG Sciences, USA. The graphene platelets have approximate thickness of 15 nm and length of 5 micro meter. Chitosan solution was prepared by adding 1% (w/v) of chitosan powder, 1.5% (w/v) of acetic acid and 100ml of double distilled water. The solution was stirred for 30-40 minutes to form a transparent thick solution. A part of this solution was transferred to a film at room temperature. To proportionate amount of chitosan solution 33, 66 and 100% (weight with respect to chitosan) of lithium perchlorate (LiClO4) was added. To a part of the chitosan lithium solution 5% of graphene (weight with respect to chitosan) was added. The solution was stirred and heated for 30 min. This solution was poured on a plastic dish and dried at room temperature in order to obtain chitosan-graphene-lithium nanocomposites. The thickness of the nanocomposite films varied between 50-200 micro meter. Dielectric studies such as conductivity, dielectric constant, dissipation factor and impedance were measured using impedance spectrometer. The conductivity ranges from 10-4 to 10-5 S/cm for graphene-chitosan lithium system. The conductivity of chitosan was lowest. In the absence of graphene the conductivity increases with increasing LiClO4 concentration. Conductivity (at 100 Hz) for Chitosan, Chitosan 33% LiClO4, Chitosan 66% LiClO4, Chitosan 100% LiClO4 films are 6x10-5, 2x10-5, 2x10-5 and 5x10-5 S/Cm respectively. Conductivity (at 100 Hz) for Chitosan 5%H5, Chitosan 5%H5 33% LiClO4, Chitosan 5%H5 66% LiClO4 and Chitosan 5%H5 100% LiClO4 are 5x10-7, 5x10-7, 5x10-7 and 1.5x10-7 S/Cm respectively. The conductivity measurements show that incorporation of graphene decreases the conductivity for films with 66 and 100% LiClO4. This indicates that graphene induces crystallization of Lithium salts thereby reducing the conductivity. SEM image shows that graphene affects the crystallization of LiClO4. Both LiClO4 and graphene increased the dielectric constant of the nanocomposites. Dissipation factor analysis showed that the relaxation behavior is affected due to incorporation of graphene. The dissipation was also relatively low (similar to chitosan), indicating that the nanocomposites do not have much heat loss.

NM01.11.11
Ordered Fragmentation of Monolayer Graphene via Polymer Cold-Drawing
Zhixun Wang1, Ming Chen2, Zhe Wang1, Ting Zhang1 and Lei Wei1; 1School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore, Singapore; 2Center for Photovoltaic Solar Energy, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, Shenzhen, China.

Graphene, a one-atomic-thick material with honeycomb structure built from carbon atoms, which can be considered as a monolayer of graphite, is the most representative two-dimensional material. It has drawn tremendous attention due to fascinating electronic and mechanical properties. Graphene with no defect is believed to be the strongest material. Through all synthesis methods, chemical vapor deposition (CVD) is a facile approach to grow large-scale monolayer graphene, which is polycrystalline with inevitable defects and boundaries. Thus, the study on mechanics of graphene, particularly fracture behavior, is essential from both fundamental interest and technological importance. Numerous studies on fracture mechanics of graphene are emerging. The fracture toughness and crack propagation of graphene have been investigated by means of in situ methods and simulations. In these studies, fragmentation of graphene tends to initiate randomly at pre-existing defect locations, resulting in irregular morphology and is considered as a limitation in applications. However, ordered fragmentation can be utilized in nanstructuring. Here, our works proposes and demonstrate a facile method on controlling the fragmentation of graphene to fabricate ordered graphene nanoribbon arrays with sharp edges by taking the advantage of strong localized strain existing at the neck front during polymer cold-drawing process. For the thermoplastic polymer, a neck will form locally during a stretch. This necking phenomenon results from the mechanical instabilities of the polymer and will propagate along the entire length of polymer, which is called cold-drawing. The neck front moves uniaxially with strong localized strain while the deformation of after-necking areas ceases. We harness this strong localized yet moving strain to the neck front during polymer cold-drawing process. For the thermoplastic polymer, a neck will form locally during a stretch. This necking phenomenon results from the mechanical instabilities of the polymer and will propagate along the entire length of polymer, which is called cold-drawing. The neck front moves uniaxially with strong localized strain while the deformation of after-necking areas ceases. We harness this strong localized yet moving strain to

NM01.11.12
Graphene Oxide Film Strip Based Flexible Contactless Actuators Driven by Electrostatic Forces
Zhe Wang1, Yi He1, 3, Shuang Yang Ma1, Nan Zhang1, Jing Zhang1 and Lei Wei1; 1School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore, Singapore; 3National University of Singapore, Singapore, Singapore; 2School of National Defence Science & Technology, Southwest University of Science and Technology, Mianyang, China.

Recent research works have employed a wide range of materials with different structures to improve actuators’ performance and extend their application prospect. Among all the reported actuators, graphene oxide (GO) based actuators have shown superior ability in responding to various stimuli because of their lightweight, high thermal conductivity, and good mechanical properties. However, almost all the reported GO-based actuators are based on composites, whose fabrication process are quite complicated. Moreover, these reported actuators always need direct contact with strong external stimuli, which will potentially restrict their application area and reduce their service life. Additionally, noticing that most objects will bear charges because of electrification, a lightweight GO film can be easily driven by the electrostatic force to achieve contactless control. In this work, we will report a flexible contactless actuator based on GO film strip prepared by one-step solvent evaporation process. This actuator can be contactlessly controlled by electric force.
offered by a wide range of charged objects. It and shows a fast and reversible response to a weak electric force variation. In addition, a smart ‘radar’ based on GO film strip array is demonstrated for motion tracking. GO dispersion with a concentration of 0.9 mg/mL is prepared by modified Hummer’s method. 50 mL GO dispersion is transfer into a glass petri dish and then dried under 323 K for 24 h. The GO film is cut into strip (18.6mm * 2 mm) after peeled off from the dish. SEM, AFM, XRD and FTIR spectrometer are used to characterize the GO film. Results show that the GO film has a thickness of 4 micrometer and a layer distance of approximately 0.8 nm and it contains alkoxy, epoxy, and hydroxy groups. To study the behavior of the GO film strip based actuator, a PS petri dish is placed above the actuator to make it bend at a certain angle. Results show that the actuator is very sensitive to almost all the charged objects such as tweezers, gloves, human fingers, and polymer films. Also, the actuator shows fast and reversible actuation within 0.56s and good reliability over 15000 cycles. To study its working mechanism, we exclude the effect of humidity and light and put the GO film strip in uniform electric field. Results show that the actuator can be driven even under a charge amount of 1 nC. And the driving force needed is in several micro-Newton range. At last, a smart ‘radar’ consist of 3 * 3 GO film strip array is demonstrated to show its practical application in identifying the position of various objects. This study reveals its application prospect in areas such as motion tracking and small force application.

NM01.11.14 Malic Acid Carbon Dots—From Super-Resolution Live-Cell Imaging to Highly Efficient Separation Bo Zhu1, Yi Cui2, Shengyang Wang3, Ben P. Frank3, Denise Williams4, Richard P. Brown5, Eric S. Meltby6, Robert J. Hamers7, Zeev Rosenzweig8, D. H. Fairbrother9, Galya Orr7 and Christy L. Haynes10; 1Chemistry, University of Wisconsin-Madison, Madison, Wisconsin, United States; 2Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington, United States; 3Chemistry, The Johns Hopkins University, Baltimore, Maryland, United States; 4Chemistry and Biochemistry, University of Maryland, Baltimore County, Baltimore County, Maryland, United States; 5Columbia Basin College, Pasco, Washington, United States; 6Chemistry, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States.

As-synthesized malic acid carbon dots are found to possess advanced photobleaching properties compared to conventional dyes. Considering their excellent biocompatibility, malic acid carbon dots are suitable for super-resolution fluorescence localization microscopy under a variety of conditions, as we demonstrate in fixed and live trout gill epithelial cells. In addition, during imaging experiments, the so-called “excitation wavelength-dependent” emission was not observed for individual as-made malic acid carbon dots, which motivated us to develop a time-saving and high-throughput separation technique to isolate malic acid carbon dots into fractions of different particle size distributions using C18-reversed phase silica gel chromatography. This post synthesis separation allowed us to determine how particle size distribution influences the optical properties of malic acid carbon dot fractions, i.e., optical band gap energies and photoluminescence behaviors.

NM01.11.15 Electrically Probing and Tuning of Physisorption for Both Polar and Non-Polar Molecules on Graphene Wenzhe Zang1, Girish S. Kulkarni2, Karthik Reddy3, Hongbo Zhu2, Kyunghoon Lee2, Xudong Fan2 and Zhauhui Zhong1; 1Department of Electrical Engineering and Computer Science, University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States; 2Department of Biomedical Engineering, University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States.

Nanoelectronic systems are perfect testbeds to study and mimic the physicochemical nature of noncovalent interactions which, though weak in nature (~ 100s of meV), form the bedrock of most biological and cellular processes. Furthermore, the ability to electrically tune the charge density (hence the chemical potential) in nanomaterials via electrostatic gating provides another knob to control such interaction. Unfortunately, nearly all existing electronic sensing methodologies are based on charge transfer (covalent interactions) which does not fully represent the interaction between the adsorbed vapor molecules and a pristine nanosurface. Here we present results of electrical probing and tuning of the noncovalent physisorption of both polar and nonpolar molecules on graphene surface by using two different sensing techniques – heterodyne sensing and µColumnFET sensing. Temperature-dependent molecular desorptions for six different polar molecules and five non-polar species were measured in real-time to study the desorption kinetics and extract the binding affinities. Furthermore, we demonstrate electrical tuning of molecule-graphene binding kinetics via electrostatic gating of graphene. Our results not only provide insight into the non-covalent interaction dynamics between graphene and both polar and non-polar molecules, but also pave the way to electrically tailor physisorption dynamics at nanoscale interfaces.

NM01.11.16 Non-Linear Current-Voltage Behavior of Epoxy-CNT Composites Toshiyuki Sato1, Yoshitaka Kamata1, Hui Li2, Jian Song2, Howard E. Katz2 and Pawel Czuborow2; 1TNT, NAMICS, Niigata-City, Japan; 2Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland, United States; 3EM-TECH, Southborough, Massachusetts, United States.

The electronics industry is always looking for new ways of protecting devices from over-voltage, or over-current scenarios. In the present work we will introduce novel low-voltage epoxy-carbon nanotube composites with high non-linearities in resistive devices. Plots of current versus voltage can be fit to powers of voltage >3. Devices of different dimensions were made on single substrates by photolithographic patterning of interdigitated electrode pairs. These devices were tested at different speeds over different voltage ranges, and I-V relationships are compared. From the resulting data, the limiting resistances can be apportioned between injection barriers and bulk nanotube connectivity.

NM01.11.17 Effects of Graphene Oxide-Carbon Nanotube Hybrids as Nanofiller on the Interfacial Interaction in Nylon 6.6 Prepared by In Situ Interfacial Polymerization Beom-Gon Cho1, Seonghwan Lee1, Sang-Ha Hwang2, Jong Hun Han3, Han Gi Chae2 and Young-Bin Park2; 1Department of Mechanical and Aerospace Engineering, Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of); 2School of Materials Science and Engineering, Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of); 3School of Chemical Engineering, Chonnam National University, Gwangju, Korea (the Republic of).

Nylon 6,6 nanocomposites including well-dispersed graphene oxide (GO) and carbon nanotubes (CNTs) were successfully fabricated via in situ interfacial polymerization between two immiscible phases: organic phase assisted by poly(vinylpyrrolidone, PVP) surfactant containing adipoyl chloride with dispersion of GO and CNTs; aqueous phase containing hexamethylenediamine. Prior to the polymerization, GO was functionalized with thionol chloride, resulting in acyl chloride-functionalized GO (AGO). The effects of incorporation of AGO and PVP on the state of dispersion were investigated. It was observed that the addition of AGO and PVP reduced particle flocculation, leading to a well-dispersed AGO suspension as verified through dispersion stability analysis and UV-Vis spectroscopy. The interfacial interaction between the carbon nanofillers (AGO, CNTs) and nylon 6,6 chain can be induced via hydrogen and covalent bonding as confirmed using spectroscopic results. According to the analyses of thermal properties, nuclei crystallization in nylon 6,6/AGO/CNT contributes to enhanced load transfer in nanocomposites, thus enhancing the mechanical properties.
Acknowledgments

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References


NM01.11.18

Scanning Tunneling Spectroscopy of Strained Graphene—Fingerprints of a Position-Dependent Fermi Velocity

Maurice Oliva Leyva, José Eduardo Barrios Vargas and Chumin Wang, Universidad Nacional Autonoma de Mexico, Mexico City, Mexico.

Nonuniform strain fields in graphene have received much attention due to the tight relation between its morphological and electronic properties. In addition to the well–known pseudomagnetic field, another recognized effect induced by a nonuniform strain is a position-dependent Fermi velocity (PDFV) [1]. Pioneering experiments [2], through scanning tunneling spectroscopy (STS), have revealed the existence of a PDFV, but its effects on the graphene physics have been scarcely explored [3].

In this work, we present analytical and numerical studies of the local density of states (LDOS) measured by STS for graphene under a nonuniform strain, either in the absence or in the presence of a uniform magnetic field [4]. The analytical expressions of the LDOS, derived from an effective Dirac model in term of a PDFV, were verified by tight-binding numerical calculations. In consequence, such expressions can be useful to quantify appropriately nonuniform strain effects on STS experiments of strained graphene, including those of Landau level spectroscopy. Finally, our results demonstrate that PDFV effects should be considered in a full description of transport signatures of strain-induced pseudomagnetic fields in graphene.

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NM01.11.19

Structural and Electronic Characterization of the Ripples in Single-Layer Graphene on Ge by STM/STS

Cesar A. Diaz Mendoza, Marcelo Eduardo Huguenin Maia da Costa and Fernando Lazaro Freire Jr; Physics, Pontificia Universidad Católica do Rio de Janeiro, Rio de Janeiro, Brazil.

The graphene’s growth directly on germanium surface can be a good route to integrate graphene into nano-electronic-devices. Several works deal with the syntheses and characterization of the graphene on Ge [1-3]. Graphene/Ge interface interaction is not fully understood. A remarkable aspect that we found was the presence of ripples. The ripples and their characteristics can modify the electronic structure, electron/hole puddle formation and carrier transport in graphene.

The objective of this work is to identify and study how these ripples can modify the local density of states (LDOS) of the graphene growth by CVD on two different germanium crystalline orientations. The samples were characterized by the Raman Spectroscopy and Scanning tunneling microscopy and spectroscopy (STM/STS). Our experimental data shows that the graphene on Ge is strained of compressive biaxial type and such strain is related to the formation of ripples. The characterization by STM reveal the presence of ripples aligned with the Zig-Zag direction and the wavefront parallel to the Armchair direction. STS data showed no band gap in graphene due to the presence of the ripples but a shift on Fermi level.

References


NM01.11.20

Structural Changes in Carbon Nanotube Yarn Exposed to Actual Space Environment

Motoyuki Karita1, Takayuki Nakano1, Yoku Inoue1, Yasuhiro Fuchita2, Takashi Hitomi2, Yoji Ishikawa2 and Naoko Baba3; 1Department of Electronics and Materials Science, Shizuoka University, Hamamatsu, Japan; 2Obayashi Corporation, Tokyo, Japan; 3Japan Manned Space Systems Corporation, Tsukuba, Japan.

Carbon nanotubes (CNTs), which have excellent thermal and mechanical properties, are promising materials as ground or space structures. Although there have been many ground-based characterizations of the influence of radiation on CNT, no work has been performed on effect of space radiation. In this study, multi-walled CNT (MWCNT) yarns fabricated by dry spinning method were exposed to the actual space environment on the international space station (ISS) for one or two years. During the flight, ground-based comparison tests, including irradiation of atomic oxygen (AO), electron beam and ultraviolet individually, were performed. For the ground-based comparison tests, significant deterioration in tensile strength was found for AO irradiated MWCNT yarns. Transmission electron microscopy and Raman spectroscopy observations revealed that crystal structure of MWCNT was damaged with...
showing sharp open edges of graphene. For the actual space test, quite similar damages and decrease of tensile strength were observed. This study was carried collaborative research project with Obayashi Corp. and Japan Manned Space Systems Corp., which is adopted by project using Exposed Experiment Handrail Attachment Mechanism of Japan Aerospace Exploration Agency.

NM01.11.21
Gilding with Graphene—Rapid Chemical Vapor Deposition Synthesis of Graphene on Thin Metal Leaves Kaihao Zhang, Charalampos Androulidakis, Mingze Chen and Sameh Tawfick; Mechanical Science and Engineering, University of Illinois-Urbana Champaign, Urbana, Illinois, United States.

Gilding is the ancient process of coating intricate geometries with precious thin metal films. Fascinating Egyptian and Chinese sculptures, coated with < 200 nm thin metal leaves by this process, have resisted corrosion and other environmental degradations for thousands of years. Similarly, palladium (Pd) is used as gilding material for its excellent corrosion properties, mechanical performance and of course its silver color. In this work, we enrich the 150 nm thin metal leaves by doping with a single layer of graphene via low pressure chemical vapor deposition (CVD) processes. Pd leaves are made by hammer forging of micrometer thick foils. During this process, their thickness is reduced to 150 nm while the average grain size exceeds 20 μm. The Pd leaves made by high strain beating are stable at high synthesis temperature, resisting solid state dewetting owing to their extremely low grain triple junctions density (~0.017 µm⁻¹). Mathematical models of CVD synthesis kinetics on ultrathin metal catalysts guide the development of extremely rapid graphene synthesis conditions, resulting in the formation of high quality uniform graphene monolayer on Pd in less than one minute. Graphene grains growth rate is twice as fast as copper-catalyzed growth. Uniaxial strain testing with Raman spectroscopy reveals the excellent crystallinity of graphene by probing the stress-induced phonon shifts.

Using nanoindentation, we demonstrate the graphene’s ability to significantly strengthen Pd leaves by constraining dislocation motion and bridging grain boundaries and cracks in Pd leaves. The as-grown Pd-Gr composite leaves are indented by a diamond-coated atomic force microscope (AFM) probe with diameter of 100 nm. We found that the effective surface modulus of the Pd-Gr composite leaves is 223.6±23.4 GPa, which is over 2.5-fold of that of the pristine Pd leaves (83.7±14.2 GPa) by coating less than 0.05 wt % Gr. Moreover, indentation on edge-notched doubly-clamped nanostrip enables the measurement of the critical stress intensity factor in mode I fracture of ultra-thin film materials. We will describe the several systematic experiments on Pd leaves and Pd-Gr composites to reveal the strengthening and toughening mechanisms operating in this new materials. This new nanocomposite material could open exciting opportunities in utilizing high quality 2D materials to coat large structures.

NM01.11.22

Graphene Quantum Dots (GQDs) is one kind of graphene nanostructure, and it has enormous attention because of their excellent properties originated from the existence of energy bandgap. For synthesizing GQDs, the bottom-up method is required over the top-down approach on synthesis step because it has more potential to control the size and edge shape, which is directly related to their optical properties. However, preparation of GQDs using the bottom-up method requires very stringent conditions with specific organic materials after complicated reaction steps. Until now, generating uniform lateral sized GQDs at the synthesis step has not been much successful, although separation of GQDs according to the diameter size has shown marginal success such as stepwise dialysis. Synthesis of high-quality GQDs with well-controlled size, shape and surface functionalization needs to be further explored. It is still challenging to synthesize the GQDs with clear hexagonal shaped graphitic structure via solution chemistry because the conventional bottom-up processes exhibit low crystallinity and they exhibit broad photoluminescent (PL) spectrum and low quantum yield compare with the top-down method. Here, we report a novel bottom-up approach not just for the synthesizing single-crystalline graphene quantum dots (GQDs) with hexagonal shape but also discover a new phenomenon that constructing graphitic carbon structure from an understanding of nitrogen site role on graphitization and inducing the catalytic reaction intermediate. In details on selected analysis data, 5 nm lateral sized sample has ~350 pm thickness, and 70 nm lateral sized sample has ~700 pm from atomic force microscopic data and both samples consist of more than 90% carbon species from x-ray photoelectron spectroscopic data. Furthermore, we investigated the origin of luminescence via exciton decay profile through femto-second pulsed laser excitation on various size-controlled GQDs. We discuss the size effect on decay profile to elucidate the origin of luminescence on GQDs by difference core and edge-generated exciton behavior. As the application, we fabricated deep-blue emissive GQDs-light emitting diodes. It shows 2.5 V as turn-on voltage, ~450 cd/m² as max brightness and (0.16, 0.06) as CIE 1931 coordinates.

NM01.11.23
Spatial and Energetic Correlations of Workfunction for Doping Level and Hysteresis in Gate-Tunable Reduced Graphene Oxide Saimont, Suwon, Korea (the Republic of).

The graphene grown by chemical vapor deposition method (CVD) has been widely studied for device applications due to scalable growth of CVD. The reduced graphene oxide (rGO) also has attracted huge scientific and industrial interests since it can be easily synthesized in massive quantities. Even CVD-grown graphene as well as rGO show clear hysteresis in IV curves of the devices, mostly due to the inherent or inevitable defects of graphene, which originate from the CVD synthesis itself or the wet process of graphene transfer from the metal substrate to a dielectric substrate. In this work, we measured workfunction of the graphene and rGO on SiO₂ with varying the gate voltage and the distance of the probe from the source electrode. A spatial dependence mapping of workfunction in graphene and rGO layers from the source electrode (ground) showed different carrier injection with showing the hysteresis similar with that of graphene-based device. The energy shift of Dirac point and the amount of hysteresis in the graphene or rGO devices can be correlated with a crossing point (a neutral point) and the width in spatial and electric mapping of workfunction. Further details will be discussed in the presentation.

NM01.11.24
Coulomb Drag Effect in Graphene/MoS₂ Heterostructures Youngjo Jin¹, Min-Kyu Joo², Byoung Hee Moon¹, Hyun Kim³, Sanghyuh Lee¹, Hye Yun Jeong¹ and Young Hee Lee¹; ¹Center for Integrated Nanostructure Physics, Suwon, Korea (the Republic of); ²Sookmyung Women's University, Seoul, Korea (the Republic of)

Two-dimensional heterointerfaces often provide extraordinary carrier transport as exemplified by superconductivity or excitonic superfluidity. Recently, double-layer graphene separated by few-layered boron nitride demonstrated the Coulomb drag phenomenon: carriers in the active layer drag the carriers in the passive layer. Here, we propose a new switching device operating via Coulomb drag interaction at a graphene (Gr)/MoS₂ heterointerface. The ideal van der Waals distance allows strong coupling of the interlayer electron-hole pairs, whose recombination is largely suppressed by the vertical energy barrier at p-Gr/n-MoS₂ interface via dual-gate, whereas the lateral carrier transport is constructed via Coulomb drag. This device exhibits a high mobility (up to ~3,700 cm²V⁻¹s⁻¹) even at room temperature, while maintaining a high on/off current ratio (~10⁶), outperforming those of individual layers. In the electron-
Microspheres as catalysts or support materials have attracted great deal of attention over the last two decades. Here, gold nanoparticles (Au-NPs) encapsulated within the reduced graphene Oxide microsphere/ rGO microsphere were prepared by using a spray-drying method. The mass content of Au-NPs in the rGO microsphere composite reached 46.5%, and the average size of the Au-NPs was (10.5±2.5) nm, which was distributed evenly through the rGO microsphere composite. The morphologies and structural characteristics of the materials were determined by scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD) patterns. The as-prepared composite was used to catalyze the reduction of 4-nitrophenol to 4-aminophenol in the presence of excess sodium borohydride and exhibited high catalytic activity. The catalysis process was monitored by UV spectrometry, and the first rate constant of the catalytic reaction \( k = 3.05 \times 10^{-3} \text{s}^{-1} \), and the activation energy \( E_a \) was found to be 2.1±10^4 J/mol.

Thermal interface materials (TIMs) are used for enhancing heat transfer between solid surfaces by creating thermal paths. Their important characteristics are high thermal conductivity and softness for filling the air gaps. Many conventional TIMs consist of the thermal conductive fillers dispersed in polymer matrix, which has disadvantages of low thermal conductivity and poor thermal stability. Here we propose aerogel TIM replacing polymer matrix with air matrix. Air matrix is released upon pressing and conductive fillers are in direct contact with each other. A soft sponge like self-supporting film can be fabricated using carbon nanotubes (CNTs), and this structure is able to support fillers 100 times larger in weight compared with their own weight [1]. In the case of hybridization with graphite particles, the porosity of the aerogel can be controlled in the range from 20 % to 70 % by changing the amount of CNTs [1]. Moreover, the CNTs do not disturb heat conduction between fillers because CNTs have high thermal conductivity, and the CNTs have high thermal stability (500 °C in air).

We selected silver having the highest thermal conductivity among metals as conductive filler. The aerogel TIM was fabricated by hybridizing Ag particles with CNTs. The TIM was self-supporting even when the amount of fillers were 200 times larger than that of CNTs. From the result of steady-state thermal resistance measurement, the thermal resistance of 99.5 wt% Ag-0.5 wt% CNT-TIM between two Cu rods was 60 mm² K/W under 0.8 MPa. Too thick TIM had high bulk thermal conductivity and a too thin one had high contact resistance. In addition, TIM showed lower thermal resistance with lower CNT content. Optimization of the structure is now underway, and the latest results will be reported.


We have engineered a flame retardant ethylene-vinyl acetate (EVA) composite which has the similar mechanical properties as polyvinyl chloride (PVC) and therefore may prove to be an alternative material for cable sheathing. Four composites were studied, EVA with aluminum hydroxide (ATH), EVA with ATH and molybdenum disulfide (MoS2), EVA with ATH and graphene nanoplatelets (GNPs), and EVA with all three components. Tensile testing showed nearly identical results for the EVA/ATH and EVA/ATH/MoS2 compounds, while the EVA/ATH/GNPs compound had higher mechanical properties. The compound containing all three components showed further enhanced mechanical properties, indicating that a synergy was established. This was further confirmed using Scanning Electron Microscopy (SEM) where GNPs were seen to increase the dispersion of the MoS2 and ATH components within the polymer matrix. Cone calorimetry test clearly showed a large decrease in heat release rate when GNPs were added, which was further enhanced by adding GNPs and MoS2 together. Application of the UL-94 test showed that only the compound containing 36 wt% of ATH and 2 wt% each of MoS2 and GNPs can achieve the UL-94 V0 rating.

We have selected silver having the highest thermal conductivity among metals as conductive filler. The aerogel TIM was fabricated by hybridizing Ag particles with CNTs. The TIM was self-supporting even when the amount of fillers were 200 times larger than that of CNTs. From the result of steady-state thermal resistance measurement, the thermal resistance of 99.5 wt% Ag-0.5 wt% CNT-TIM between two Cu rods was 60 mm² K/W under 0.8 MPa. Too thick TIM had high bulk thermal conductivity and a too thin one had high contact resistance. In addition, TIM showed lower thermal resistance with lower CNT content. Optimization of the structure is now underway, and the latest results will be reported.


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Graphene has attracted much attention as a next-generation electronic material for its excellent properties such as ultra-high mobility. Large-size single-crystalline graphene is usually obtained on copper based catalyst with chemical vapor deposition (CVD). However, the property of the graphene is largely deteriorated by the transfer process for device fabrication. Therefore, the direct growth of graphene on the dielectric substrate is studied to overcome the problem.

C-plane sapphire is conventionally used as a substrate for the direct growth of graphene [1]. There are very few studies about the optimization of crystallographic plane of sapphire for the direct growth. In this study, we focus on the use of r-plane sapphire as a substrate, which is sometimes used for the growth of horizontally-aligned carbon nanotubes [2].

Graphene was directly grown on r-plane sapphire using low pressure CVD without metal catalyst. C-plane sapphire was also used for the comparison. Mixture gas of nitrogen (N2), hydrogen (H2), and diethylacetylene (C6H10: 3-Hexyne) was flown to a reactor for the growth of graphene. Growth temperature was systematically changed between 1090 °C and 1210 °C.

In the case of c-plane sapphire, graphene was found to grow only in the pits of sapphire, which was formed during CVD. This is very similar to the result that Saito et al. reported [3]. They reported Al-rich surface appeared inside the pits and had a catalytic effect. In our experiment, the size of pits enlarged with increasing growth temperature. Also, the growth rate of graphene increased with growth temperature and, then, decreased over 1170 °C. On the contrary, in the case of r-plane sapphire, the surface was fully covered with single-layer graphene in all samples. D/G peak intensity ratio and wrinkle density of graphene decreased with increasing growth temperature. On r-plane sapphire, the graphene was found to grow simply in 2D nucleation mode.

This is probably because the surface of r-plane sapphire has catalytic effect and enhances the decomposition of growth species. Therefore, the use of r-plane sapphire brings a faster growth rate and smoother surface than those on c-plane sapphire.

Acknowledgement: This work was supported in part by JSPS KAKENHI Grant Numbers 15H03558, 26105002.

Reference

Reinforcement of CNT Yarn by Graphitization and Cross-Linking CNTs Taichi Kira, Motoyuki Karita, Takayuki Nakano and Yoku Inoue; Shizuoka University, Hamamatsu City, Japan.

Carbon nanotube (CNT) has been reported to have high tensile strength of 150 GPa [1]. Since the discovery of dry spinning phenomenon from a CNT forest [2], a dry-spun CNT yarn has been an attractive material as the structural material. One of good things of the dry-spinning is that large-scale and highly aligned CNT structures are uniformly formed. However, since the CNTs are connected by van der Waals force, the spun yarn fails by relative sliding of CNTs, and its mechanical properties are far inferior to those of individual CNT. Moreover, even the relative sliding is suppressed by cross-linking CNTs in the yarn, tensile strength of individual CNT is not so high as expected because of crystal defects, resulting in moderate improvement of strength in the yarn. In this work, in order to reinforce the CNT yarn, CNTs were graphitized at high temperatures. Then CNTs were cross-linked by binder materials. Dry-spin capable MWCNT forests were grown by chlorine mediated CVD using FeC3 as catalyst [3]. The yarns were prepared by twisting drawn CNT webs [4]. The yarns were annealed at higher than 2500 °C in inert ambient. The highly graphitized CNT yarns were further reinforced by introducing azide-group cross-linker agent that makes covalent bonding in between CNTs. Mechanical and electrical properties of the reinforced CNT yarns will be reported.

References

The Mechanics of Reinforcement in Graphene-Based Nanocomposites Robert Young, Dimitrios Papageorgiou and Ian A. Kinloch; University of Manchester, Manchester, United Kingdom.

Although there has been a rapid growth of interest in polymer-based nanocomposites, the mechanics of reinforcement in such materials is still not yet fully understood. It has been established by the authors that stress transfer from the matrix to the reinforcement in nanocomposites reinforced by graphene nanoplatelets (GNPs) can be followed from stress-induced Raman band shifts. A detailed study has been undertaken of the mechanisms of stress transfer in a range of polymeric matrices with very different levels of Young’s modulus, Em, reinforced by graphene nanoplatelets. The matrix materials studies have been natural rubber (Em = 1 MPa), thermoplastic elastomers (Em = 10–100 MPa) and polypropylene (Em = 1000 MPa). The microstructure of the nanocomposites has been fully characterised using a range of different advanced analytical techniques that include, Raman imaging, x-ray computer tomography (CT) scans and polarized Raman spectroscopy that give an unprecedented level of information upon their microstructures.

It is found that the addition of the GNPs leads to significant increases in stiffness in each polymer showing high levels of reinforcement are obtained. For each material the effective Young’s modulus of the graphene, Em, has been determined using the rule of mixtures and it has been found that this scales with the value of Em. Additionally the stress-induced Raman band shifts show different levels of stress transfer from the polymer matrix to the GNPs which again scale with the Young modulus of the matrix. For example, shifts of the order of 1 cm−1/100% strain are found in the natural rubber matrix nanocomposites compared with ~0.1 cm−1/1% strain for the polypropylene matrix nanocomposites with a value of Em three orders of magnitude higher.

Studies of the mechanics of stress transfer in model composites consisting of single graphene flakes in polymeric matrices have also been undertaken by
using Raman spectroscopy to map the strain distribution in the individual flakes. A unifying theory has been developed to predict the stiffness of the bulk nanocomposites from the mechanisms of stress transfer from the matrix to the GNP reinforcement based upon these studies of deformation of the individual flakes. Excellent agreement has been found between the measured and predicted values of $E_{\text{eff}}$, and hence composite Young's modulus for the bulk nanocomposites. It will be shown that the theory also enables factors such as interfacial bonding, reinforcement geometry and orientation to be taken into account.

Overall it is found that it is only possible to realise the theoretical Young's modulus of graphene of 1050 GPa for discontinuous flakes as $E_o$ approaches 1 TPa; the effective modulus of the reinforcement will always be less for lower values of $E_o$. In general it is found that the highest levels of reinforcement will be obtained in nanocomposites with strong graphene-polymer interfaces and optimised reinforcement geometries and orientation.

**NM01.11.32**

**Bifunctional Electrocatalysts Based on Transition Metal Alloy Incorporated Nitrogen Doped Carbon Nanomaterials** Rajeev Kumar and Balaram Sahoo; Materials Research Centre, Indian Institute of Science, Bangalore, India.

Carbon based nanomaterials are currently in the limelight for their potential to replace expensive noble metal based electrocatalysts. Noble metal electrocatalysts (Pt, Pd, Au, Ru) suffer from monofunctionality (hydrogen evolution reaction (HER)/oxygen reduction reaction (ORR)) or oxygen evolution reaction (OER) favoured. As such, their use in electrocatalytic devices i.e. fuel cells, Zn-air batteries etc. is limited. Carbon based materials with controlled level of defects and high specific active surface area, can be tuned to serve as multifunctional materials. The overall oxygen electrochemistry towards ORR and OER is significantly lower than the noble metal group based electrocatalysts. Doping of nitrogen (or other heteroatoms) in the carbon structure also significantly improves their activity. In this context, a simple one-step pyrolysis route is used to synthesize exotic carbon based materials, especially core-shell nanostructures and nanotubes, using various transition metal precursors. It is observed that transition metal based alloy nanoparticles, in the vicinity of the carbon matrix significantly increases the cyclic stability and effective electrochemical window required for total water splitting or metal-air battery systems. Furthermore, the involvement of alloy centres and their interaction with carbon and nitrogen in the generated carbon materials is investigated, which provides useful insights into the tunability and progress in such systems.

**NM01.11.33**

**Graphene Oxide-Templated Synthesis of Crumpled Holey Metal Oxide Nanosheets via Spray Pyrolysis for Enhanced Gas Sensor** Rheebunny Kim, Ji-Su Jang, Dong-Ha Kim, Won-Tae Koo and Il Doo Kim; Material Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Two-dimensional (2D) metal oxides have widely studied in various applications due to their intriguing properties, such as super high surface-to-volume ratio, ultra-thin thickness, high meso-porosity and small grain size. However, 2D nanostructures have the tendency to restack, so they can induce the decrease of surface area and amounts of accessible mesopores. In this work, crumpled SnO$_2$ nanosheets (NSs), crumpled ZrO$_2$ NSs, and crumpled SnO$_2$-ZrO$_2$ composite NSs (C$_{\text{MO}}$ NSs, MO = SnO$_2$, ZrO$_2$ or SnO$_2$/ZrO$_2$) were successfully synthesized by using graphene oxide (GO) sheets as a sacrificial template and used as highly effective 2D oxide gas sensing layers. In detail, GO/metal ion composites were synthesized by dissolving metal precursor and GO in absolute ethanol to allow bonding between GO and the metal ion. And then, by conducting spray pyrolysis of the solution which is composed of dispersed GO/metal ion composites in DI water at 400 °C, the crumpled GO/metal oxide composites were fabricated. After calcination of them at 500 °C for 1 h, GO were thermally decomposed to form C$_{\text{MO}}$ NSs. Crumpled metal oxide NSs have high surface-to-volume ratio and high distribution of macropores as well as mesopores, which are essential for efficient surface reaction and high gas permeability. Also, ultra-small grain size affects to form complete electron depletion layer for effective modulating of resistance. Additionally, n-heteroion from C$_{\text{SnO}2/\text{ZrO}2}$ NSs can induce the energy band bending to enhance the gas sensing capability. The gas sensing performances were proceeded to VOCs (volatile organic compounds) gas species, e.g., CH$_3$COCH$_3$, NO, C$_{2}$H$_{6}$, C$_{2}$H$_{5}$OH, HCHO, H$_2$S and NO$_2$. The sensing test results demonstrated that C$_{\text{MO}}$ NSs exhibited enhanced gas sensing performance toward formaldehyde (2.5 times higher response ($R_{\text{air}}/R_{\text{gas}}$) than that of 2D metal oxide NSs) with high selectivity and fast response/recovery speed. Also, C$_{\text{SnO}2/\text{ZrO}2}$ NSs induced the improvement of gas sensing properties due to the creation of heterojunction (3 times higher response ($R_{\text{air}}/R_{\text{gas}}$) than that of C$_{\text{MO}}$ NSs). This work suggests the facile and effective synthesis method of C$_{\text{MO}}$ NSs templated by the GO for enhanced gas sensor.

**NM01.11.34**

**High Electrical Conductivity of Carbon Nanotube/Poly(Acrylonitrile) Composite Fibers Fabricated via Current-Assisted Wet Spinning** Yong-min Kim, Ho-Sung Yang and Woong-Ryeol Yu; Seoul National University, Seoul, Korea (the Republic of).

Wet spinning process is one of the most common methods of producing polymer microfibers. Wet process has been used in particular for the polymers which can decompose near their melting temperature and thus defly melt spinning process. Poly(acrylonitrile) (PAN), a representative precursor of carbon fibers, belong to this kind of polymers. On the other hand, due to high thermal conductivity and electrical conductivity, carbon nanotubes (CNTs) have been used in PAN fibers to improve the conductivity of carbon fibers. Well-aligned CNTs are known to contribute high electrical conductivity. In this study, we developed high conductive CNT/PAN composite microfibers using a new process, so called current-assisted wet spinning. The current-assisted wet spinning is different from electrospinning which utilizes the electric field to fabricate nanofibers from a charged solution. For the current-assisted spinning, the electrical current is applied to the spinning nozzle of wet spinning system, inducing the interaction of PAN and functional group of CNT and also more packing and alignment of PAN molecules via controlled diffusion between CNT/PAN and coagulation solutions. The electrical and mechanical properties of CNT/PAN fibers fabricated using current-assisted wet spinning were measured by the two-probe method and single fiber tensile test. 2D wide angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM) were used to characterize the microstructures of CNT/PAN fibers. Nuclear magnetic resonance spectroscopy(NMR) and X-ray photoelectron spectroscopy(XPS) analysis were performed to characterize the chemical bonding of CNT/PAN solutions and fibers. Finally, a mechanism behind high conductivity of CNT/PAN composite microfibers via current-assisted wet spinning was investigated and will be presented in detail at the Conference.

**NM01.11.35**

**Quasi-Freestanding Graphene on SiC by Argon Mediated Intercalation of Antimony** Susanne Wolff¹, Florian Speck¹, Martina Wanke¹, Felix Timmermann², Manfred Albrecht¹ and Thomas Seyller¹; ¹Institut für Physik, Technische Universität Chemnitz, Chemnitz, Germany; ²Institut für Physik, Universität Augsburg, Augsburg, Germany.

The intercalation of various elements under the buffer layer is an elegant method to produce so-called quasi-freestanding graphene (QFMLG) on SiC substrates. The modification of the graphene/SiC interface changes the electronic properties of QFMLG depending on the choice of the intercalant. Hence, intercalation represents a promising technique to tune graphene’s properties according to the specific application. The intercalation of various elements under the buffer layer is an elegant method to produce so-called quasi-freestanding graphene (QFMLG) on SiC substrates. The modification of the graphene/SiC interface changes the electronic properties of QFMLG depending on the choice of the intercalant. Hence, intercalation represents a promising technique to tune graphene’s properties according to the specific application. So far three methods for intercalation have been successfully demonstrated to work for different elements. Gaseous species like, e.g., hydrogen [1] or oxygen [2] can be intercalated by annealing in the respective atmosphere. Solids with low vapor pressure such as gold [3] or germanium [4] were intercalated by first depositing the material on top of the buffer layer followed by annealing at a certain temperature in ultra-high vacuum (UHV). On the
other hand, solids with high vapor pressure require a different method. Recently it was shown that implantation [5] allows the intercalation of bismuth. In this presentation, we introduce another method to intercalate solid elements with high vapor pressure. The method is based on a reduced rate of sublimation of Sb from the surface when the sample is annealed in argon (Ar) atmosphere rather than in UHV.

To that end, Sb with a thickness of approx. 50 nm was deposited by molecular beam epitaxy on top of the buffer layer and the samples were annealed in 1 bar Ar at an optimized temperature of 550°C. X-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED) confirmed the intercalation and formation of quasi-free-standing graphene. Both, elemental Sb as well as oxidized Sb were observed at the interface. The latter is caused by the transport of the Sb-covered samples in air which leads to a thin oxide layer on top of the Sb. A two-step annealing process in 1 bar Ar where (i) the oxide is removed by annealing at 400°C and (ii) the intercalation is performed at 550°C leads to the intercalation of purely elemental Sb. Angle-resolved photoelectron spectroscopy (ARPES) reveals a moderate n-type doping of the samples which were intercalated with pure metallic Sb.

Changes in impedance modulus (label-free electrochemical changes) are equivalently recorded by using an alternative and simpler voltage measurement.

### NM01.11.36

**Amine Functionalized Hierarchical 3D Network of Carbon Nanotubes Based Heart Attack Sensing Chip**

Satish Kumar, Xiaoling Lu, Vivek Pachauri and Sven Ingebrandt, Institute of Materials in Electrical Engineering, RWTH University, Aachen, Germany.

The aim of this study is to promote the ultra-fast, sensitive and real-time monitoring of different clinical cardiac Biomarkers (Myoglobin and Cardiac Troponins) for the diagnosis of the cardiac diseases like Acute Myocardial Infarction (AMI) using the 3D network of 2-ABA functionalized carbon nanotubes in a Lab-on-a-chip configuration. The development of a rapid and practical immunoassay for detecting Cardiac markers in serum samples (standard as well as spiked) is desirable due to its roles in cardiospecific diagnosis, risk stratification, and assessment. The main objective is to develop a biosensor exploiting microfluidics allowing in-situ self-functionalization. The sensitivity can be adjustable and the device can be used for detection of different cardiac biomarkers. The functionalization takes place in situ and selectively, just before the sensing, keeping the sensing area dry and inactive until the tests start, and conserving the functionality of the device. Also, the reagents and chips are stored separately and may be used before testing, without the need of overnight functionalization process or complex fabrication methods. The monitoring of the signal is performed in real-time and changes in impedance modulus (label-free electrochemical changes) are equivalently recorded by using an alternative and simpler voltage measurement. The label-free electrochemical biosensors are an attractive choice for fast, early diagnostics and monitoring of biological markers due to the direct conversion of a biological event into an electronic read-out signal.

### NM01.11.37

**Investigation of Dispersion Selectivity with Single-Walled Carbon Nanotube Sorted by Pyrene-Based Conjugated Polymer for Field-Effect Transistors**

Kyoungtae Hwang, YeonSu Choi, Yeon-Ju Kim and Dong-Yu Kim; Gwangju Institute of Science and Technology, Gwangju, Korea (the Republic of).

Since the discovery of single-walled carbon nanotube (SWNT), SWNT has attracted with great interest because of their outstanding mechanical and electrical properties. For these reasons, researches for their electronic applications such as field-effect transistors (FETs), thermoelectric devices and biological imaging have been substantially promoted. However, the co-existence of metallic (m-) and semiconducting (sc-) SWNT have disturbed the effective use for electronic applications. In the recent, conjugated polymer wrapping of SWNT has specially aroused great attention as a method for separation of SWNTs due to their advantages of high selectivity toward sc-SWNT and simple polymer sorting process. Although the m-sc interaction between conjugated polymer and wall of SWNTs is related with the selective dispersion of SWNTs, the mechanism how to separate the s-SWNTs remains as issues. In this research, we introduce the pyrene moiety as main chain of conjugated polymer to increase the π-π interaction with s-SWNTs. New pyrene-based conjugated polymers were carefully designed and synthesized via suzuki polymerization. Their dispersion selectivity and diameter of s-SWNTs enriched by pyrene-based conjugated polymers were characterized by various measurements such as UV-vis absorption spectra, Raman spectroscopy and Photoluminescence excitation/emission analysis. Finally, the sc-SWNTs were employed into FETs as an active layer.

### NM01.11.38

**Temperature Field Control of Catalyst Formation for Gas-Phase Synthesis of Single-Wall Carbon Nanotubes**

Katsuya Namiki, Toshio Osawa, Hisashi Sugime and Suguru Noda; 1Department of Applied Chemistry, Waseda University, Tokyo, Japan; 2Waseda Institute for Advanced Study, Waseda University, Tokyo, Japan; 3Waseda Research Institute for Science and Engineering, Waseda University, Tokyo, Japan.

Single-wall carbon nanotube(SWNT) is excellent material for many applications. Especially, SWCNTs with small diameter and high crystallinity are expected to have better property, however they are more difficult to synthesize which results in high cost (2-100 USD/g). One of the best synthesis methods for high quality CNT is floating catalyst chemical vapor deposition (FCCVD) [1-4]. However, the yield of CNT is still low which stems from the low efficiency of the formation of active catalyst nanoparticles. In the conventional CVD, because the gas which contain the catalyst source is heated gradually by the furnace, most of the catalyst nanoparticles aggregate and deactivate before the nucleation of the CNTs. In this report, to generate more active catalysts, we designed a new process to control the gas temperature. The catalyst sources (ferrocene and sulfur) are rapidly (i.e., ∼ 5 ms) heated to 1300 °C in the narrow flow path (Φ4 mm) to pyrolyze and vaporize efficiently. Then, the iron vapor is mixed with carbon sources (e.g., CH₄, C₂H₄, etc.) and cooled down rapidly to 1150 °C in wide flow path (Φ40 mm), which enables the formation of the catalyst nanoparticles followed by the immediate nucleation and synthesis of the CNTs. The CNT yield was 2.5 mg/mm. The TEM observation showed 90% SWCNTs with 10% double-wall CNTs with a diameter of 1.64 ± 0.40 nm. The Raman spectra (excitation wavelength: 488 nm) showed the G-band and D-band peaks at ~1590 and ~1350 cm⁻¹, respectively, with the G/D intensity ratio ranging from 40 to 100. The weight ratio of carbon to iron in the carbon products were ~10 by TGA and EDS analysis.

### References:


### NM01.11.39

**Modified Tour Method for Synthesis of Graphene for Solar Cell Applications**

Dulce K. Becerra Paniagua, Merida Sotelo Lerner and Hailin Zhao Hu; 1Instituto de Energías Renovables, Universidad Nacional Autónoma de México, Temixco, Mexico; 2Universidad de Sonora, Hermosillo, Mexico.

Single-wall carbon nanotube(SWCNT) is excellent material for many applications. Especially, SWCNTs with small diameter and high crystallinity are expected to have better property, however they are more difficult to synthesize which results in high cost (2-100 USD/g). One of the best synthesis methods for high quality CNT is floating catalyst chemical vapor deposition (FCCVD) [1-4]. However, the yield of CNT is still low which stems from the low efficiency of the formation of active catalyst nanoparticles. In the conventional CVD, because the gas which contain the catalyst source is heated gradually by the furnace, most of the catalyst nanoparticles aggregate and deactivate before the nucleation of the CNTs. In this report, to generate more active catalysts, we designed a new process to control the gas temperature. The catalyst sources (ferrocene and sulfur) are rapidly (i.e., ∼ 5 ms) heated to 1300 °C in the narrow flow path (Φ4 mm) to pyrolyze and vaporize efficiently. Then, the iron vapor is mixed with carbon sources (e.g., CH₄, C₂H₄, etc.) and cooled down rapidly to 1150 °C in wide flow path (Φ40 mm), which enables the formation of the catalyst nanoparticles followed by the immediate nucleation and synthesis of the CNTs. The CNT yield was 2.5 mg/mm. The TEM observation showed 90% SWCNTs with 10% double-wall CNTs with a diameter of 1.64 ± 0.40 nm. The Raman spectra (excitation wavelength: 488 nm) showed the G-band and D-band peaks at ~1590 and ~1350 cm⁻¹, respectively, with the G/D intensity ratio ranging from 40 to 100. The weight ratio of carbon to iron in the carbon products were ~10 by TGA and EDS analysis.

### References:

Graphene products are obtained by reduction of graphene oxide (GO). A recently chemical procedure for GO synthesis is the Tour method [1]. In this method the GO was synthesized by the oxidation of graphite powder, using KMnO₄ and a 9:1 mixture of H₂SO₄/H₃PO₄, the latter as a protective agent. In this paper a modified Tour method is designed to looking for a simple, easily controlled and an alternative approach for large scale production of GO for solar cell applications. We find that if a mixture of H₂SO₄/H₃BO₃ is used instead of H₃PO₄, then the oxidation time of graphite can be reduced under the same reaction conditions: two hours of oxidation is enough for produce the equal amount of hydrophilic oxidized graphene material as compared to Tour method that requires about seven hours. The reduced graphene oxide (rGO) was prepared by the thermal and chemistry reduction of GO by employing ascorbic acid and ammonia solution at high temperature [2]. The GO and rGO samples were characterized by UV-Visible spectroscopy, FTIR spectroscopy, Raman spectroscopy, SEM, TEM and EDS. It is found that the GO prepared by modified Tour method yields a higher fraction of well-oxidized carbon material and could have the same advantage in quality for achieving few-layers of graphene sheets for large-scale production than the original Tour method. On the other hands, the results of XRD, EDS and UV-Vis of rGO products reveal that the oxygenated groups that were present in GO products have been widely removed, this can be seen reflected in the atomic ratio C/O of rGO (3.7), it increase close to 70% with respect to the GO (1.3), so that almost 50% of the oxygenated groups were removed. Finally, thin films of GO and rGO were prepared by spin coating method with GO and rGO solutions. Optical and electrical properties of the films are analysed and their potential use as electron or hole transporting layers in perovskite solar cells are discussed. In particular, the presence of the remaining oxygenated groups in rGO reduces the electrical conductivity of the rGO films, and, consequently, the power conversion efficiency of the solar cells. The removal of a higher percentage of oxygenated groups remains as a challenge in the synthesis of graphene products.

**NM01.11.40**

**Electrical Performances of Carbon Nanotube Webs and Yarns**

Yooam Din1,2, Jean Dijon1,2 and Jérôme Faure-Vincent1,3; 1Commissariat à l’énergie atomique, Grenoble, France; 2Isère, Université Grenoble Alpes, Grenoble, France; 3Centre National de la Recherche Scientifique, Grenoble, France.

In electrical wiring, metal substitution by high conductivity materials like carbon nanotubes (CNT) is a near future challenge for high-end aeronautic and aerospace applications[1]. Several techniques exist to make CNT yarns. The most suitable, eco-friendly process for large-scale production is to directly dry spin CNTs grown by fixed- or floating-catalyst Chemical Vapor Deposition (CVD). For the last ten years, all published works on CNT yarns from CNT arrays made by fixed-catalyst CVD have faced the same resistivity limitation of around 1 mΩ.cm[2]. The basic reasons for this limitation are unclear. Is it the intrinsic CVD carbon nanotube quality or the disorganization of the CNTs inside the yarn induced by the CNT array? We recently developed a new carbon nanotube yarn production process based on a low temperature (630°C) and low pressure (1.2 mbar) hot filament CVD system. It allows us to produce small carbon nanotubes (7 nm average diameter) and yarns from our CNT arrays with state of the art resistivity (1.07 mΩ.cm). Our work answers the previous questions through extensive electrical transport studies of CNT webs and CNT yarns. Resistivity measurements from 3 K to 350 K are analyzed within the frame of known electronic transport models. The effects of the densification, the CNT lengths and the dopants on the yarn will be presented. Contrary to the typical explanation, we will show that the electrical contacts between carbon nanotubes in the yarn are good and do not limit the electrical transport at room temperature. Those contacts only hinder the yarn’s electrical transport at temperature below 70 K. We performed unique carbon nanotube web resistance measurements at room temperature. A careful scanning electron microscope image analysis of the CNT web reveals the fractal arrangement of the CNTs (fractal dimension of 1.75). Hence, we found that the average resistivity is 0.7 mΩ.cm for the CNT bundle and 0.5 mΩ.cm for the individual CNT. The CNT yarn resistivity is therefore similar to that of the CNT bundle. It appears that the 1 mΩ.cm resistivity limitation faced by yarns made from CNT arrays are mainly due to the individual CNT resistivity. Our work emphasizes that drastic enhancement of CNT yarn electrical resistivity can only be achieved by doping or by increasing the CNT quality.


**NM01.11.41**

**Preparation of Carbon-Black/Polymmer Composite Fibers**

Sang Young Yeo; Korea Institute of Industrial Technology, Ansan, Korea (the Republic of).

With the development of the wearable device industry, there is an increasing interest in conductive textiles, and research on conductive fiber manufacturing is actively being reported. Because carbon black has a high specific surface area, a composite is prepared by mixing with a polymer then a conductive network is formed in a small amount to improve electrical conductivity. In this study, carbon-black/polymer composites composed of polypropylene, polyester, and nylon matrix were prepared and their electrical properties were analyzed. The carbon-black/polymer composites were characterized by UV-visible spectroscopy, Raman spectroscopy, SEM, TEM and EDS. It is found that the GO prepared by modified Tour method yields a higher fraction of well-oxidized carbon material and could have the same advantage in quality for achieving few-layers of graphene sheets for large-scale production than the original Tour method. On the other hands, the results of XRD, EDS and UV-Vis of rGO products reveal that the oxygenated groups that were present in GO products have been widely removed, this can be seen reflected in the atomic ratio C/O of rGO (3.7), it increase close to 70% with respect to the GO (1.3), so that almost 50% of the oxygenated groups were removed. Finally, thin films of GO and rGO were prepared by spin coating method with GO and rGO solutions. Optical and electrical properties of the films are analysed and their potential use as electron or hole transporting layers in perovskite solar cells are discussed. In particular, the presence of the remaining oxygenated groups in rGO reduces the electrical conductivity of the rGO films, and, consequently, the power conversion efficiency of the solar cells. The removal of a higher percentage of oxygenated groups remains as a challenge in the synthesis of graphene products.

**SESSION NM01.12: Non-Carbon Structure and Properties**

**Session Chairs: Ranjit Pati and Yoke Khin Yap**

Thursday Morning, November 29, 2018
Sheraton, 2nd Floor, Republic AB

8:45 AM "NM01.12.01"

**Understanding Optical Absorption and Luminescence in hBN—From Bulk to the Monolayer**

Arnick Loiseau; LEM, CNRS-ONERA, Chatillon, France.

hBN layers meet a growing interest for deep UV LED [1], and has become a strategic material for the fabrication of van der Waals heterostructures. Stacked with any other 2D material it can reveal the best of their physical properties [2]. However, h-BN optoelectronic properties remain much less characterized and understood than other 2D materials.

In this talk, we review recent advances made thanks to the development of appropriate spectroscopies in the UV range - cathodoluminescence (CL) at 4K and Raman [3,4], combined with ab initio simulations [5]. Thanks to these tools, a h-BN characterization metrics has been developed on the basis of their...
original optical properties, governed, in the energy range 5.5 – 6 eV, by strong excitonic effects easily trapped at structural or chemical defects [3]. We shall discuss the interplay between structure, defects and spectroscopic properties and how these properties can be further exploited for sample benchmarking [3].

Beyond this effort, the talk will also address the recent advances made for the understanding of the high luminescence observed although bulk hBN is an indirect band gap material [1,6]. To that aim, the efficiency of radiative recombinations has been measured on a reference single crystal using temperature - dependent CL and compared to that diamond and ZnO [6]. The luminescence of hBN is confirmed to be unusually high and is found to remain constant from 10 to 300K. Enlightening analysis of this behaviour is provided by ab initio calculations of the exciton dispersion in bulk hBN. First, the lowest-energy exciton (iX) is found at 5.97eV and to be indirect, as expected for an indirect band gap, with a binding energy equal to 300 meV. This dispersion behavior accounts for an assignation of the luminescence to phonon assisted recombinations of the indirect exciton as proposed in [7] and for the assignation of the tiny peak observed in CL spectra at 5.956 eV to the zero-phonon radiative recombination of iX [6]. Further iX high binding energy is consistent with the temperature behavior of the luminescence, the high yield being the signature of a strong exciton phonon coupling. Second, calculations also confirm the direct exciton (dX) with a binding energy of 670 meV [6], an energy which turns to be only 100 meV above the indirect one. It comes out that bulk hBN displays a peculiar behavior where luminescence and optical absorption are due to different excitons. This situation totally evolves in the layer, the gap being direct and we could identify the dX line in the CL spectra recorded on very thin hBN layers [6].


9:15 AM *NM01.12.03
Boron Nitride Nanotubes vs Carbon Nanotubes — Interlayer Mechanics and Reduction Chemistry
Homin Shin, Jingwen Guan, Dennis Klug, Marek Zgierski, Keun Su Kim, Christopher Kingston and Benoit Simard; National Research Council Canada, Ottawa, Ontario, Canada.

Despite their similar crystallographic structures, boron nitride nanotubes (BNNTs) exhibit a range of physical and chemical properties distinct from carbon nanotubes (CNTs), which are mainly attributed to the partial ionic bonding character of BN. Here we present two markedly different properties between BNNTs and CNTs: interlayer mechanics [1] and reduction chemistry [2]. Firstly, we show using van der Waals (vdW) parameterized density functional theory (DFT) that the strong mechanical coupling between the buckled lattices of small-diameter BNNTs greatly elevates the threshold forces and internal friction with respect to the relative motion of BNNT walls. Unlike for CNTs, large difference between relaxed and unrelaxed energy corrugations of BNNTs could yield energy dissipation via the strain-induced anelastic relaxation of interlayer locking, resulting in the experimentally observed ultrahigh interlayer friction of BNNTs. Secondly, through DFT calculations and experimental studies of the covalent alkylation of BNNTs using 1-bromohexane, we demonstrated that the chemical reactivity of BNNTs towards radical molecules can be significantly enhanced via reducing the nanotubes (i.e., negatively charging). Our study predicts that the localization characteristics of the BNNT pi electron system lead the excess electrons to fill the empty p orbitals of boron sites, which promote covalent bond formation with an unpaired electron in radical molecules.

References:

9:30 AM *NM01.12.04
Boron and Metal Boride 2D Sheets and Nanotubes
Sohrab Ismail-Beigi; Yale University, New Haven, Connecticut, United States.

Compared to carbon, bulk and reduced dimensional forms of pure boron present more complex bonding patterns and atomic-scale geometries. An underlying reason is that boron has the same number of valence orbitals as carbon but has one fewer valence electron (i.e., is "electron deficient"). This means that standard two-center bonding motifs between neighboring atoms in familiar structures, such as hexagonal or triangular networks, are not energetically favorable. This leads to complexity and richness in the phase space of boron structures. This situation has attracted significant scientific attention over the last two decades. While the initial literature consisted of primarily of first principles theoretical studies and predictions, the last few years have witnessed experimental fabrication and characterization of 2D boron sheets which in turn has greatly enhanced interest in these materials.

This talk will provide a brief overview of the initial theoretical predictions in this field followed by a summary of some of the more salient experimental and theoretical performed recently, including some of our work on 2D and nanotubular boron and metal boride nanomaterials. In the process, we will discuss the challenges and opportunities this field may face when attempting to fabricate and use boron nanostructures.

10:30 AM *NM01.12.05
Carbon and Beyond: A Colorful Palatte of 2D Materials
Boris I. I. Yakobson; Department of Materials Science and Nanoengineering, Department of Chemistry, and the Richard E. Smalley Institute, Rice University, Houston, Texas, United States.

From our theoretical insight into evolutionary selection in synthesis of monocrystal graphene [1], into the paths of back-diffusion in growth of its bilayers [2], and into their possible conversion to monocrystal diamond films like diamond [3,4], we envisage a platform to emerge for design of the point (0D) defects in 2D-media as effective single-photon emitters (SPE) [5]. More diverse basic optics of numerous 2D materials [6] further expands possibilities for SPE realization, where theoretical assessment can guide experimental choices and tests.


11:00 AM *NM01.12.06
Harnessing the Versatility of Carbon Nanotubes for Printed Electronics Aaron D. Franklin; Duke University, Durham, North Carolina, United States.

Single-walled carbon nanotubes (CNTs) are one of the most versatile electronic materials ever discovered. Electronically, they can be semiconducting or metallic; mechanically, they are flexible yet have a tensile strength greater than steel; and physically they can be centimeters long to just a few nanometers. For nearly two decades, these diverse properties have excited and motivated researchers pursuing CNTs for electronic applications. However, thus far the versatility of CNTs has also been their greatest obstacle in terms of purification, precise positioning, and so forth. In this talk, I will discuss how the inherent versatility of CNTs can be appropriately leveraged for enabling certain applications. The tremendous progress in solution-phase processing of nanotubes has opened a path for their most suitable, near-term use as printed thin films. Recent advances will be presented in using printed thin films of CNTs for print-in-place additive electronics, sensors for harsh environments, and highly sensitive biosensors. Each of these is made possible by drawing...
from distinct properties of thin-film CNTs; properties unavailable from any other printable material. Perspectives on stability, reproducibility, and yield will also be offered, with evidence of the impact that printed silver contact morphology has on printed CNT thin-film transistor performance. The unique and reproducible behavior of printed CNT thin films suggests they be given greater consideration from the printed electronics community. In the company of organic semiconductor inks, and even that of non-printed metal-oxide semiconductors, printed films of CNTs are a standout with significant advantages and opportunities.

2:00 PM NM01.13.02
Low-voltage Operable, Highly-stretchable Carbon Nanotube Thin-Film Transistors with Novel Local Strain Control Structure Yuya Nishig1, Jun Hirotani1, Shigeru Kishimoto1 and Yutaka Ohno1-2; 1Institute of Materials and Systems for Sustainability, Nagoya University, Nagoya, Japan; 2Department of Electronics, Nagoya University, Nagoya, Japan.

Stretchable devices have intensively been studied towards a realization of wearable electronics for continuous monitoring of human activity and health condition. Recent works have demonstrated that carbon nanotube thin-film transistors (CNT TFTs) have excellent mechanical flexibility and stretching ability. [1-3] However, they still exhibited a degradation of drain current with applied strain. Another issue to be addressed is high-voltage (a few ten V) operation due to the polymer-based gate dielectric which is flexible and/or stretchable, but of low-dielectric constant. [3] Wrinkled Al2O3 gate insulator was proposed for realizing low-voltage and stretchable CNT TFTs, but the degree of tensile strain was limited up to 20%. [2] Here, we have realized low-voltage operable and highly-stretchable all-Carbon CNT TFTs by introducing a novel local strain control structure. We fabricated CNT TFTs composed of a channel of a semiconducting-CNT thin film, transparent electrodes of a CNT thin film, and a 50-nm-thick Al2O3 gate dielectric layer on a stretchable poly(dimethylsiloxane) (PDMS) film. The device may exhibit some degree of stretching ability, however, in order to fully suppress the influence of strain on the device characteristics, we formed a local strain control structure with a rather hard polymer material on top of the channel region of a CNT TFT. We also performed the numerical analysis based on the finite element method to design the strain control structure. The fabricated devices exhibited typical p-type transistor characteristics with a carrier mobility of 7.2 cm2/Vs and on/off ratio of about 103, and was operable at gate voltage of less than 5 V. By introducing the local strain control structure, only 14% of externally applied tensile strain was introduced in the channel region, whereas the CNT electrodes and the other field of the PDMS film were directly stretched. No significant degradation of drain current was observed against tensile strain up to 35%.


2:15 PM NM01.13.03
Fully-Printed Flexible Dual-Gate Carbon Nanotube Thin-Film Transistors with Tunable Ambipolar Characteristics for Complementary Logic Circuits Haochuang Wang1, Min Yu2 and Chuang Wang1; 1Electrical and Systems Engineering, Washington University in St. Louis, St Louis, Missouri, United States; 2Institute of Microelectronics, Peking University, Beijing, China.

Semiconducting single-wall carbon nanotubes (sSWCNTs) have been widely used as the channel material for high-performance printed flexible thin-film transistors (TFTs). Due to the absorption of moisture and oxygen in air, the printed sSWCNT TFTs generally exhibit p-type characteristics only. In this paper, we report fully-printed dual-gate sSWCNT TFTs that exhibit almost symmetric ambipolar characteristics. With the applied control gate voltage varying from -60 V to 60 V, a threshold voltage tuning range of 27 V is achieved, allowing the device to be effectively tuned into either predominantly p-type or predominantly n-type. The tunable ambipolar characteristics are found to be very stable over long period of time (4 months). By integrating two printed dual-gate TFTs biased with different control gate voltages, a complementary metal oxide semiconductor (CMOS) inverter with close to rail-to-rail output voltage swing is demonstrated. The use of dual-gate structure for achieving n-type printed carbon nanotube TFTs is much more controllable and repeatable compared to other methods such as chemical doping. Our work shows the feasibility of implementing more sophisticated complementary logic circuits using printed flexible carbon nanotube transistors.

2:30 PM NM01.13.04
Spectrally-Resolved Photoresponse in a Graphene-Based Gate Tunable Phototransistor Depui Zhang1, Gong Cheng1, Zhen Xu1, Che-Hung Liu1, Meiqi Guo1, Thomas Beechem1, Michael Goldflam1, François Leonard1, Steve Young1, David Peters3, Zhe Liu1, Audrey Rose Gutierrez2, Wenzhe Zang1, Theodore B. Norris1 and Zhaohui Zhong1; 1University of Michigan, Ann Arbor, Michigan, United States; 2Institute of Microelectronics, Peking University, Beijing, China.

Graphene has a unique broadband absorption from visible to microwave due to its gapless nature. Integrating graphene with microcavities, photonic crystal or surface plasmonic structures can not only increase the strength of light-matter interaction, but also achieve some degree of spectral selectivity for enhanced light absorption around the designed wavelengths. However, the above-mentioned spectral selectivity results from some forms of resonance structures; therefore once the device is fabricated, the spectral response is fixed at the resonance wavelength for such devices. In our work, we demonstrate an electrically tunable, spectrally distinguishable photoresponse in a graphene-based phototransistor. The device is composed of a 6-nm amorphous silicon tunneling barrier sandwiched by two layers of graphene, one used as the channel and the other as the gate. By applying a sweeping voltage on the graphene gate layer while recording channel layer current, we discover gate-dependent photoresponse curves for different excitation wavelengths. Importantly, this electrical tuning of photoresponse offers a new mechanism for spectrally resolved photodetection with graphene detectors. As a proof-of-concept, we build a responsivity matrix of gate voltage and excitation wavelength by measuring the gate-dependent photoresponse curves for a finite number of wavelengths. Photodetection and spectral reconstruction for mono-color lights were then successfully demonstrated. More detail will be presented at the conference. Our results open the door for on-chip spectrometers free from complex optical setups and may find its applications in technologies such as hyperspectral imaging.

2:45 PM NM01.13.05
Aligned Carbon Nanotube Sheets Integrated in Liquid Crystal Device Cells M. A. Rahman1, Hakam Agha1, Meenu Murali1, Ji Hyun Park1, Kieu Truong2, Dongseok Suh2 and Glusy Scala3; 1University of Luxembourg, Luxembourg, Luxembourg; 2Sungkyunkwan University, Suwon, Korea (the Republic of).

Sheets of unidirectionally oriented carbon nanotubes (CNTs) [1-2], among the various attractive applications, can be employed as transparent and conductive layer for switching but also, interestingly, for aligning liquid crystals (LCs) [3]. Even a single layer, tens of nanometers thick, can be used for applying electric fields strong enough to reorient LC molecules and, at the same time, for serving as an alignment layer for LCs. The successful implementation of new materials in LC cell geometries is a pre-requisite for future applications in device technology. CNT sheets as aligning electrodes are a relatively new entry that are showing very good performances for LC switching but also, present challenges to face. CNT sheets do not completely adhere to the substrate surface and methods to promote the adhesion, such as chemical treatment of the surfaces or polymer coatings, are
needed. As it will be presented, the adhesion of CNTs on different types of underlying polymer films is indeed improved by ethanol treatment but the orientational parameter of CNT sheets is affected at different extents [4]. The evaluation of the CNT sheet characteristics such as the degree of orientational order of the strands, the film thickness and its uniformity in properties like the electrical conductivity are of importance for the LC passive and active behaviour. However, there are other characteristics that we will describe here, that influence the LC behaviour, connected to the peculiar nature of the CNT sheets being formed by discrete elements, the nanotubes, even if connected in anisotropic networks. To understand the different aspects we investigate the CNT sheets using different techniques. For evaluating the morphology and the uniformity in properties we use electron and atomic force microscopy, profilometry and optical absorption. The electrical characteristics are investigated with and without LCs using DC as well as AC electric fields while monitoring the samples under a polarized optical microscope.

References:


3:00 PM BREAK

SESSION NM01.14: Structure and Properties V
Session Chairs: Ranjit Pati and Yoke Khin Yap
Thursday Afternoon, November 29, 2018
Sheraton, 2nd Floor, Republic AB

3:30 PM *NM01.14.01
Electron Microscopy Studies on Single-Walled Carbon Nanotubes
Hua Jiang1, Ying Tian1,2, Yongping Liao1, Qiang Zhang1, Nan Wei1 and Esko Kauppinen1; 1Department of Applied Physics, Aalto University School of Science, Espoo, Finland; 2Physics Department, Dalian Maritime University, Dalian, China.

With the aid of advanced electron microscopy, we have established an approach using ED as a means to evaluate the validity of Raman spectroscopy for quantification of concentrations of metallic SWNTs (M%) or of semi-conducting tubes (S-SWNT%) [1]. We have proved that the Raman RBM intensities depend largely on the resonant conditions at certain wavelengths, rather than simply on concentrations. Up to the resonance conditions, some majority nanotube species revealed by electron diffraction measurements induce relatively weak, or even missing RBMs, and vice versa. This certainly leads to an uncertainty over Raman spectroscopy for quantitative assessment of metallic tube concentrations calculating from the relative peak intensities.

Chirality distribution maps of SWNTs produced by CVD methods with Fe nanoparticles as catalysts at various synthesis conditions have been analyzed by electron diffraction technique. As a recent advance [2], we have successfully achieved direct synthesis of single-walled carbon nanotube thin films with various colors using a novel floating-catalyst-CVD process with ferrocene-based iron catalyst particles and CO as the carbon source. The color is tunable by adjusting the reaction conditions, i.e. the temperature and especially the addition of CO2. Based on unique electron diffraction analysis of individual SWCNTs in our colorful SWCNT thin films, we were able to attribute the colors of the SWCNT thin films to their narrow diameter in certain ranges which give rise to absorption peaks in the visible region. It is demonstrated that the narrow (n, m) chirality distribution also accounts for the display of certain color of a SWCNT thin film.

References


4:00 PM NM01.14.02
Energy Transport in Polymer-Free Semiconducting Single-Walled Carbon Nanotube Networks
Andrew J. Ferguson and Jeffrey Blackburn; National Renewable Energy Laboratory, Lakewood, Colorado, United States.

The chemical structure of semiconducting single-walled carbon nanotubes (SWCNTs) results in optical and electronic properties of promise for a wide variety of applications. Until quite recently the presence of metallic SWCNT impurities has hampered efforts to gain a deeper understanding of their true potential, with the additional complication that most commercially available materials contain tens of different chiral species. Significant effort has been devoted to elegant enrichment strategies aimed at extracting tailored semiconducting SWCNT species from the raw soot, from the use of subtly tunable surfactant interactions to the exploitation of specific DNA sequences. However, conjugated polymers, typically based on the fluorene moiety, appear to show the greatest promise with regards to their high selectivity and viability for scalable manufacturing approaches.

Unfortunately, the van de Waals forces between the pi-electron systems of the polymer and SWCNT that enable the selective extraction of semiconducting SWCNTs with high purity also make removal of the polymer difficult. Since these polymers typically have a wide bandgap they act as an insulating coating on the surface of the individual SWCNTs within functional networks, inhibiting the transport of energy in the form of excitons and/or charge carriers.

Here we demonstrate an approach aimed at replacing the strongly-bound polymers with variants that can be removed using simple solution-based chemical strategies, resulting in networks with vastly improved energy transport properties. We show that removal of the polymer results in a significant enhancement of the charge carrier mobility and electrical conductivity. Finally, we extend the approach to samples strongly enriched in a single chiral SWCNT species, which allows us to employ transient spectroscopic techniques to probe energy transfer and exciton transport through the SWCNT network with high spectral fidelity. We show that the efficiency of exciton transport is subtly dependent on the complex interplay between polymer removal and carbon nanotube bundling. Our studies highlight a methodology by which high-performance SWCNT thin films can be prepared that could realize their potential for electronic and optoelectronic applications.
Functional coatings have numerous properties, including anticorrosion, anti-icing, and self-cleaning leading to number of applications in future electronics, sensing, and energy. Although graphene has shown extraordinary properties that are demonstrated in past decade, scalable manufacturing and control of graphene’s structure could potentially transform the coating technology. Key to its function is the ability to tune local structure and understand its surface energy evolution. Direct pulsed laser writing (DPLW) has been shown recently an efficient technique to surface nanostructure graphene coating to tune the contact angle of graphene from hydrophobic to superhydrophobic, leading to manufacturing of multifunctional graphene surface. In this work, using molecular dynamic (MD) simulations we show that the physical orientation of graphene flakes as well as its surface chemistry in a coating influence its wettability. We show that using DPLW the contact angle of graphene coating can be tuned significantly, starting from a hydrophilic (contact angle (CA) ∼47.7°) to superhydrophobic (CA ∼157.2°) nature. Since the cohesive interactions between water molecules remain invariant for degree of graphene orientation on a surface, the wettability of the surface is driven by the net attractive energies (U_{ACO}) between water molecule and carbon atoms in graphene due to the adhesive forces that changes with the petal orientation. Furthermore, the dangling bonds on the edges of the graphene ‘petal-like’ structures affect the wettability of the sample. Molecular dynamics (MD) simulations show that the –H termination induces hydrophobicity due to hydrogen repulsion whereas –CO termination makes the substrate hydrophilic due to the polar nature of the bonds. Additionally, we model the evaporation process of water droplets on these coatings that show delays in the water evaporation. Non-equilibrium molecular dynamics (NEMD) simulations reveal that the changes in Kapitza resistance and contact area with increasing contact angle results in a slower evaporation rates in the case of superhydrophobic graphene surface.

4:30 PM NM01.14.04
Probing on the Molecular Bonding of DMSO-Dil-MWCNT—A Route to Biological MWCNT Surface Modification Examined Through Synchrotron Spectroscopies—Theory and Experiment
Wudmin Y. Rojas¹, Allen D. Winter¹, Torsten Bossing², Daniel Fischer³, Sarbjit Banerjee⁴, David Prendergast⁵ and Eva M. Campo⁶; ¹Bangor University, Bangor, United Kingdom; ²Institute of Translational & Stratified Medicine, Plymouth, United Kingdom; ³National Institute of Standards and Technology, Gaithersburg, Maryland, United States; ⁴Department of Chemistry, Texas A&M University, College Station, Texas, United States; ⁵Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California, United States; ⁶National Science Foundation—Division of Materials Research, Alexandria, Virginia, United States.

Supramolecular chemistry of carbon nanotubes (CNTs) investigates the non-covalent functionalization of CNTs to preserve their pristine physical properties typically by p-p stacking with aromatic compounds, dispersion of CNTs with surfactants and polymer wrapping surrounding the CNTs for applications such as identification coating for biological sensing based on fluorescence and the use of CNTs for drug delivery. In this context, feasibility to use polymeric spacers as dispersant agents to reduce intratubular van der Walls forces requires adequate comprehension of nature and dynamics of the CNT-polymer interaction that will pave the way to inform on pharmacological carrier ability and biocompatibility linked with specific CNTs functionalization procedures.

In this work, a physico-chemical description of non-covalently functionalized multi wall carbon nanotube (MWCNT) with DIL and dimethyl sulfoxide through high-resolution electron microscopy, Raman and Near Edge X Ray Absorption Fine Structure (NEXAFS) spectroscopy has been employed. NEXAFS is a synchrotron tool capable to reveal molecular sensitivity description at interfaces, therefore, suitable to study non-covalent interactions. Furthermore, combination of experimental and constrained density functional theory simulations of NEXAFS spectra to propose a molecular model to analyze charge exchange at CNTs-dispersants (or loaded biomolecules) interfaces has been also applied.

Our findings suggest that incorporation of fluorescent markers does not change the morphological structure on MWCNTs. CH-p bonding with nearby molecules and Hydrogen bonding with external defects and graphitic lattice has been identified as well. Theoretical modelling suggests non-covalent interaction between dimethyl sulfoxide and CNTs.

4:45 PM NM01.14.05
Microfluidic Pathways Made from Alumina Nanotubes within Hydrophobic Carbon Nanotube (CNT) Barriers
Cemile Aksu; North Carolina State University, Raleigh, North Carolina, United States.

An understanding of fluid transport within porous micro-and nanostructured materials is important for their use in microfluidic devices. In this paper we investigate the microfluidic behavior of alumina nanotube-based pathways within hydrophobic CNT barriers. These hybrid systems provide unique benefits toward the potential liquid transport control in porous structures with real-time sensing of those fluids. Specifically, we examine how the alignment of the alumina nanostructures with high internal porosity enables increasing the capillary action. Based on the Lucas and Washburn model (LW) and modified LW models, the microfluidic behavior of these systems is discussed. The predictions from the models for the time exponent for capillary transport in porous media are ≤ 0.5. The experimental results show that the average capillary rise in nanostructured media driven by capillary force followed the L(t) ~ t^{1/2} law. Integration of electronic and microfluidic functions is also presented, taking advantage of the periodic hydrophilic/electrically insulating (pure alumina part) and hydrophobic/electrically conductive (CNT part) microlayers of the structure.

SESSION NM01.15; Poster Session IV
Session Chairs: Naoyuki Matsamoto and Ranjit Pati
Thursday Afternoon, November 29, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

NM01.15.01
Plasmonic Graphene-Based 3D Nanostructures for Highly Sensitive Biosensing Platforms
Glenda Bigotto¹, Marco Fontana², Chiara Novara³, Alessandro Chiadò¹, Marco Armandi², Maria A. Zaghi², Fabrizio Giorgis² and Paola Rivolo³; ¹Department of Biochemistry and Chemical Technology, University of São Paulo State–UNESP, Araçatuba, Brazil; ²Center for Sustainable Future Technologies, Istituto Italiano di Tecnologia, Torino, Italy; ³Department of Mechanical Engineering, Iowa State University, Ames, Iowa, United States; 4National Institute of Standards and Technology, Gaithersburg, Maryland, United States; 5Department of Chemistry, Texas A&M University, College Station, Texas, United States; 6National Science Foundation—Division of Materials Research, Alexandria, Virginia, United States.
Surface-enhanced Raman scattering (SERS) spectroscopy attracted much attention for the highly sensitive label-free detection of chemical and biological species. A great research effort has been made to fabricate noble metal (Ag or Au) nanostructures incorporating as much as possible Raman hot spots yielding a huge electromagnetic (EM) field enhancement thanks to the excitation of localized surface plasmons at resonance conditions (LSPR). Moreover, taking advantage of the discovery in 2010 of the graphene-enhanced Raman scattering (GERS), graphene based structures are of great interest for Raman-enhanced (bio) sensing due to the chemical enhancement effect attributed to a charge-transfer (CT) process in synergy with the EM mechanism. The reduced Graphene Oxide (rGO) can be a suitable and low-cost graphene based-material that can be assembled in 3-D networks and allows to exploit different routes of chemical and biochemical functionalization (physiosorption or chemosorption). It can take advantage from the presence of the residual oxygen atoms or the possibility to establish p-p non-covalent bonding with the graphene layers. In this work, we report on the synthesis and characterization of a hybrid aerogel based on reduced rGO decorated with silver nanoparticles (AgNPs) exploitable for the SERS detection of biomolecules at very low concentration. Several synthesis conditions were approached by exploiting a one-pot hydrothermal process, starting from commercial GO and adding either AgNO3 as silver precursor with different additives (such as triiodium citrate) or directly a pre-synthesized Ag colloid. The resulting 3-D porous sponge-like nanoarchitecture provides both a high surface area and a homogeneous spatial distribution of AgNPs arranged in order to maximize the Raman hot spots density and thus allowing to concentrate and adsorb biomolecules from highly diluted solutions. By decorating GO with AgNPs, the synergy of the EM field and CT enhancements can be exploited. The synthesized AgNPs/rGO aerogels were characterized by means of XRD, BET, XPS, FESEM, and TEM in order to single out the best performing aerogels to be processed for biosensing applications. Promising results were obtained in terms of SERS efficiency by using, as probe molecules, Rhodamine 6G, in the 10-7 M - 10-12 M concentrations range, and 4-Mercaptobenzoic acid, in the 10-2 M- 10-7 M concentration range. Optofluidic chip were fabricated by coupling the optimized AgNPs/rGO aerogels to Polydimethylsiloxane (PDMS). Then the devices have been successfully functionalized both by thiol-ended oligos and porphyrin-ended biomolecules. These biosensor immobilization routes permit the application of the substrates as versatile SERS biorecognition bioships.

NM01.15.02 Functionalized Nano-Graphene Oxide as Multi-Modal Clinic for Effective Drug Delivery Manisha Chatterjee1, Somesh Mahapatra1 and Soumitra Satapathi2; 1Lala Lajpat Rai Memorial Medical College, Meerut, India; 2Indian Institute of Technology Roorkee, Roorkee, India.

Nano-materials based drug delivery modalities to specific organs and tissue have become one of the critical endeavors in pharmaceutical research. Recently, two dimensional graphene has elicited considerable research interest because of its potential application in drug delivery systems. Here we report, the drug delivery applications of PEGylated nano-graphene oxide (nGO-PEG), complexed with a multiphoton active and anti-cancerous diarylethanedione drug curcumin. Specifically, graphene derivatives were used as nano vectors for the delivery of the hydrophobic anticancer drug curcumin due to high surface functionalization. nGO was synthesized by modified Hummer’s method and confirmed by XRD analysis. The formation of nGO, nGO-PEG and nGO-PEG-Curcumin complex were monitored through UVvis, IR spectroscopy. MTT assay and AO/EB staining found that nGO-PEG-Curcumin complex afforded highly potent cancer cell killing in vitro with a human breast cancer cell line MCF7.

NM01.15.03 Stable, Temperature Dependent Gas Mixture Permeation and Separation Through Suspended Nanoporous Single-Layer Graphene Membranes Zhe Yuan, Jesse D. Benck, Yannick Eatmon, Daniel Blankschtein and Michael Strano; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Graphene membranes with nanometer-scale pores could exhibit extremely high permeance and selectivity for the separation of gas mixtures. However, to date, no experimental measurements of gas mixture separation through nanoporous single-layer graphene (SLG) membranes have been reported. Herein, we report the first measurements of the temperature-dependent permeance of gas mixtures in an equimolar mixture feed containing H2, He, CH4, CO2, and SF6 from 22 to 208 °C through SLG membranes containing nanopores formed spontaneously during graphene synthesis. Five membranes were fabricated by transfer of CVD graphene from catalytic Cu film onto channels framed in impermeable Ni. Two membranes exhibited gas permeances on the order of 10-6 to 10-7 mol m⁻² s⁻¹ Pa⁻¹, as well as gas mixture selectivities higher than the Knudsen effusion selectivities predicted by the gas effusion mechanism. We show that a new steric selectivity mechanism explains the permeance data and selectivities. This mechanism predicts a mean pore diameter of 3.0 nm and an areal pore density of 5.5×10¹⁴ m⁻², which is validated by experimental observations. A third membrane exhibited selectivities lower than the Knudsen effusion selectivities, suggesting a combination of effusion and viscous flow. A fourth membrane exhibited increasing permeance values as functions of temperature from 27 to 200 °C, and a CO2/SF6 selectivity of > 20 at 200 °C, suggestive of activated translocation through molecular-sized nanopores. A fifth membrane exhibited no measurable permeance of any gas above the detection limit of our technique, 2 × 10⁻⁹ mol m⁻² s⁻¹ Pa⁻¹, indicating essentially a molecularly impermeable barrier. Overall, these data demonstrate that SLG membranes can potentially provide high mixture separation selectivity for gases, with CVD synthesis alone resulting in nanometer-scale pores useful for gas separation. This work also shows that temperature-dependent permeance measurements on SLG can be used to reveal underlying permeation mechanisms.

NM01.15.04 Encapsulation of Metallic Nanoparticles Near the Surface of Graphite Ann Li-Riosales and Patricia A. Thiel; Iowa State University and Ames Laboratory, Ames, Iowa, United States.

Graphite, in the bulk, is known to form graphite intercalation compounds (GICs) with certain elemental metals, for example, rare earth and alkali metals. These metals can insert between graphene sheets and alter the magnetic or transport properties of graphite. While intercalation in the bulk of graphite has been studied, can one embed metals just beneath the graphite surface? Do the surface-intercalated metals adopt different structures compared to their bulk counterparts? What is the driving force for such surface intercalation? These are questions we seek to address.

The presentation will encompass strategies for achieving surface intercalation of metals in graphite. In short, embedding metal atoms just beneath the graphite surface requires two specific conditions: (1) ion-induced defects on the graphite surface, and (2) deposition of metals while holding the graphite substrate at elevated temperature. We find that this synthetic route works for a variety of metals, and the growth temperature is metal-specific. Results on dysprosium, copper, and ruthenium will be presented. We use scanning tunneling microscopy to probe and characterize the surface intercalation. Based on experimental results and density functional theory, we find that the intercalated metal atoms at the graphite surface adopt very different structures compared to those in bulk GICs. Furthermore, metals that are not known to form bulk GICs can be encapsulated at the graphite surface. Finally, we find that some of the metals are well protected from atmospheric oxidation by the graphene overlayer. Our synthetic strategy opens up a new avenue for metals to interact with the graphite surface, and to create novel surface nano-structures.
Highly Conductive Copper Coated Reduced Graphene Oxide Fibers for Electromagnetic Shielding Fabrics Mingxin Li and Jie Lian; Mechanical, Aerospace, and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States.

Despite no apparent evidence that the electromagnetic exposure to household mobile communication and other emitting devices poses harm to the general public, excessive electromagnetic radiation is of genuine concern for roentgenologists, radar engineers and pacemaker implanted patients. To alleviate such a concern, electromagnetic shielding clothing for these personnel made with thin steel wires are densely woven into cotton fabrics. Here, we report a new method of producing copper-reduced graphene oxide core-shell fibers for the fabrication of lightweight electromagnetic shielding fabrics. Based on a simple electroplating process, a thin layer of copper oxide is coated onto the grooved surface of reduce graphene oxide fibers. After subsequent reduction, copper-coated reduced graphene oxide fibers with high electrical conductivity and high flexibility are obtained. A fabric woven with such fibers can provide comparable electromagnetic shielding to fabrics woven with metal wires, yet is appreciably lower in density.

NM01.15.06
High-Quality Monolithic Graphene Films via Solid-Phase Coalescence and Structural Repair of Exfoliated Flakes Xinming Li1, Cheng-Te Lin2, Ying Fang1, Renzhi Ma1 and Takayoshi Sasaki3; 1International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Tsukuba, Japan; 2Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, China; 3National Center for Nanoscience and Technology, Beijing, China.

The liquid phase exfoliated graphene nanoflakes are a high-yield and low-cost synthetic method, but the quality of the graphene nanoflakes is not high due to the presence of functional groups and structural defects. Therefore, the ability to improve the crystal structure of the graphene nanoflakes with excellent electrical properties is desirable for its applications in the field of flexible and printed electronics.[1] In this talk, I will introduce a approach to structure repairing in electrochemically-exfoliated graphene flakes based on annealing with Ni thin film, accompanied by the laterally stitching of the isolated parts to form a continuous and monolithic film.[2,3] After annealing with Ni film, the graphene flakes-derived film has lower defect density, demonstrating that such a process for the crystal structure improvement is extremely effective. At the same time, the newborn-graphene in the space of the isolated flakes would stitch to form a continuous and monolithic film. After the structural repair, the electrical properties of graphene have been greatly improved, and the carrier mobility of graphene is more than 1000 cm2 V-1 S-1, nearly 10 times higher than that of the graphene via mere annealing. First-principles calculations on the adsorption of Ni and Cu atoms on different kinds of H-saturated graphene edges reveal that the binding energy depends upon the adsorption site, and the Ni case always gives a value 1.5 eV larger than that for the Cu case which is thus beneficial to the removing of edge saturates and allowing for a faster re-growth process. This approach for the graphene with structural design is promising for electronic and flexible applications. [4] (Thanks to the support of the JSPS KAKENHI Grant Number JP 17F17337.)

References

NM01.15.07
Inorganic Electroluminescence Devices with Chlorine-Functionalized Carbon Nanotubes in a Dielectric Layer So-yeon Jeon1 and SeGi Yu1,2; 1Physics, Hankuk University of Foreign Studies, Yongin, Korea (the Republic of); 2Physics, Sungkyunkwan University, Suwon, Korea (the Republic of).

We have investigated AC inorganic powder electroluminescent (EL) devices, where carbon nanotubes (CNTs) are included within the dielectric layer. Three kinds of dielectric layers were fabricated—a reference layer with BaTiO3 powder and a cyanoethyl pullulan (CEP) polymer, two CNT containing dielectric layers (one with chlorine-functionalized CNTs and the other with non-functionalized CNTs). Chlorination of CNTs were performed by adding chlorobenzene solvent to the dielectric solution for the dielectric layer. Up to 50% enhancement in the luminance was obtained for the EL device with chlorine-functionalized CNTs in the dielectric layer at the concentration of 0.01 wt%, together with a 30% reduction in the current density. This was mostly caused by a high dielectric constant of the dielectric layer, which was confirmed by fabricating a separate series of dielectric layers and measuring dielectric characteristics of the layers. Raman scattering and X-ray photoemission spectroscopy were utilized to examine how chlorination of CNTs affect the dielectric performance of the CNT-containing dielectric layers. The increment in the dielectric constant is resulted from the micro-capacitor effect by space charge polarization at the interface between the emitting and dielectric layers. It is mainly arisen from the high polarization of carbon-chlorine bonds within the dielectric layer. In addition, the critical concentration of CNTs plays an important role in the performance of the EL devices. This means that too many CNTs can produce unwanted leakage current in the dielectric layer by percolation of CNTs, here, the concentration of 0.01 wt% of CNTs is sufficiently low to escape the percolation. Therefore, chlorine functionalization of CNT within the dielectric layer could enhance the brightness of EL devices, which enables inorganic EL devices to be considered as candidates for future displays.

NM01.15.08
Crosslinking Reduced Graphene Oxide with Ethylenediamine to Stabilize Electrical Properties Against Moisture Yisian Jin and Woo Y. Lee; Stevens Institute of Technology, Hoboken, New Jersey, United States.

The electrical resistance of reduced graphene oxide (rGO) was found to increase with increasing relative humidity (RH), due to water absorption into rGO and the swelling of its interlayer spacing. This instability creates significant challenges with using rGO as an electronic material, particularly for sensing applications. In order to control its stability in humidity, the carboxyl groups of rGO were covalently crosslinked with ethylenediamine (EDA), as a means of physically limiting the swelling rGO and thus its water absorption. The crosslinked rGO limited the d-spacing increase to 0.011 nm at >95% RH and 95°C in comparison to that of 0.013 nm observed in uncrosslinked rGO. Also, after exposure to 95% RH at 37°C for 2 days, the relative resistance of crosslinked rGO increased by 52% in comparison to 208% for uncrosslinked rGO. The results suggest that crosslinking provides an effective means of stabilizing the resistance of rGO and enabling its robust use in electronic applications.

NM01.15.09
Tailored Freestanding (Reduced) Graphene Oxide Films as Advanced Separator and Electrode Materials in Lithium-Ion-Batteries Tim Ludwig and Sanjay Mathur; University of Cologne, Cologne, Germany.

Since its discovery in 2004, graphene has received enormous scientific interest due to the remarkable two-dimensional structure, making it highly promising for numerous applications. Electrodes in lithium-ion-batteries (LIBs) are one of these applications that could benefit from mechanical strength, high surface area and electrical conductivity of graphene. For the integration in commercial LIBs, it is important to develop simple, cost effective and scalable methods for the production of graphene-like structures. Due to the good dispersibility in water and other polar solvents, graphene oxide (GO)
easily forms multi- and monolayers and therefore offers advantageous properties for a green and simple wet-chemical synthesis. In this study, GO was synthesized and further processed by liquid and gas phase approaches to obtain GO films via pressure filtration with superior mechanical properties and adjustable thicknesses. These paper-like structures of regularly arranged GO flakes were mechanically stable, scalable to mass production and could be used as flexible ultrathin separators in LIBs given their high electronic insulation. Additionally, the sheet-like structure of GO is expected to suppress the polysulfide shuttle effect in lithium sulfide batteries. Moreover, films of its reduced form (rGO) could additionally be incorporated as cathode or anode material, providing several advantages over traditionally used materials. For instance, if used as anodes, these films facilitated an increased volumetric energy density due to a reduction in weight, as additional battery paste components such as current collector, carbon black and binding agent, were no longer necessary. This was supported by the low preparative effort of the freestanding electrode design. Moreover, nitrogen doping of these graphene-like structures via different approaches had been proven successful to increase the electrical conductivity and storage capacity of anodes. Further investigations focused on the influence of nitrogen-integration in the carbon structure on electrical and electrochemical properties.

Computing Modeling of the Graphene-Water Interaction and Its Applications

Jatin Kashyap1, Priyanka Solanky2 and Dibakar Datta3; 1New Jersey Institute of Technology, Newark, New Jersey, United States; 2Montville Township High School, Montville, New Jersey, United States.

Ever since its discovery in 2004, graphene has been extensively investigated for various applications such as energy storage, environmental barrier, biomedical, electronics, etc. The planar graphene sheet is hydrophobic. However, with the change in topology, i.e., defects, wrinkling, etc., we can tune its interaction with water. By performing Molecular Dynamics (MD) simulation, we discovered that water microdroplets containing graphene nanosheets spontaneously segregate into sack-cargo nanostructures upon drying. These cargo-filled nanosacks are promising for many potential applications such as current collector, carbon black and binding agent, were no longer necessary. This was supported by the low preparative effort of the freestanding electrode design. Moreover, nitrogen doping of these graphene-like structures via different approaches had been proven successful to increase the electrical conductivity and storage capacity of anodes. Further investigations focused on the influence of nitrogen-integration in the carbon structure on electrical and electrochemical properties.
In previous work\textsuperscript{1} we have calculated the growth of a graphene monolayer, two models emerged as the most favored: for Ga poor conditions a 3$sqrt$3x3$sqrt$3 graphene structure on top of a 4x4(0001) GaN surface and for Ga rich condition a 3$sqrt$2x3$sqrt$2 graphene structure on top of a 2$sqrt$3x2$sqrt$3 GaN(0001) Gallium double bilayer\textsuperscript{2} with a $-1.10\%$ and $-0.72\%$ mismatch respectively. The gallium rich model exhibit a magnetic moment of 0.19 Bohr magnetons/cell whereas the stable structure for Ga poor conditions does not presents magnetic behavior. Later we added a second graphene layer with the goal to find defect free epitaxial growth, which could serve as a basis to introduce defects or doping it with the best suited elements in such a way that we will be able to fine tuning a band gap. We also made simulations of scanning tunneling microscope (STM) that revealed a long distance buckling interaction between both layers. Our calculations were based on the plane wave periodic density functional theory and the Tersoff-Hamann formalism for simulating STM images. In this work we are analyzing what is happening when a graphene monolayer approach to the GaN surface and then when a second graphene layer comes closer to the first one, we plot the energy as a function of the interlayer separation distance and the kind of GaN surface. In this fashion we get potential energy surfaces (PES), which allow us to simulate how the graphene monolayer behaves when it is growth in a less than ideal substrate and what happens to the graphene buckling in the grain frontier. The electronic properties of these systems are studied by calculating the density of states. The calculations are performed by Density Functional Theory as implemented in the PWscf code of the Quantum ESPRESSO package.

The data are not fully analyzed yet as the work is still in progress. Acknowledgments: DGAPA project IN114817. The authors are grateful to A. Rodriguez for his technical assistance. Calculations were performed at the DGCTIC-UNAM under project LANCAD-UNAM-DGTCI-150.

References
3-D graphene or graphene foams (GFs) have received immense research attention owing to their superior electrical, mechanical, and thermal properties. Extensive applications of such 3-D GFs have been demonstrated in energy, environment, health, and biomedical research. This work presents an innovative mechanism, the Kirkendall effect, in creating 3-D microporous catalysts with tunable pore sizes for the growth of multilevel porous graphite foams (MPGFs) that offer higher crystallinity, electric conductivity, larger surface area as well as electric invariance to strains compared to conventional GFs. Based on MPGFs, another new type of ramified porous graphite foams (RPGFs) made of strategically created superstructures with covalently-attached diverging microtubes have also been synthesized. Such RPGFs exhibit even higher surface areas than MPGFs, which allows for efficient loading of active pseudocapacitive materials when applied as supercapacitor electrodes. We also integrate the RPGF-based flexible supercapacitors with a nanomotor manipulation system into a portable and self-powered device, which readily compels Au nanomotors to transport along arbitrary trajectories, e.g., tracing letters of “U” and “T”.

**NM01.15.19**

**Synthesis of Ramified Porous Graphite Foams with Diverging Microtubes with Enhanced Electrical Properties and Surface Areas**

Jianjie Guo and Donglei (Emma) Fan; The University of Texas at Austin, Austin, Texas, United States.

Biphenylene carbon (BPC), also called graphenylene, is a hypothetical porous two-dimensional (planar) allotrope carbon [1] that can be obtained from selective dehydrogenation of porous graphene [2]. The BPC molecular geometry consists of an one-atom thickness sheet with regular dodecagonal pores of diameters of 3.2 Å. Its pores resemble typical sieve cavities and/or some kind of zeolites. An open question is if the BPC natural porosity gives a selective permeability property that can lead to promising technological applications, such as gas separation. In this work, we have investigated the permeability and selectivity of natural gases such as CO2, H2, N2, CH4, and CO though BPC membrane. Fully atomistic Molecular Dynamics simulations were performed to predict the gas adsorption and the gas permeability of single components, and separation mechanism of binary gas mixtures. The simulation system is composed of single BPC sheet in contact with a gas reservoir under different thermodynamics conditions (e. g. T, P). We have systematically analyzed the permeability of each gas and the molecular arrangements on the adsorbed layers after the flux is stabilized. The selectivity is also quantified for 

**CO2/H2 (50:50), CO2/N2(15:85), CO2/CH4 (50:50), and CO2/CO (50:50) mixtures and the mechanism of gas diffusion is also discussed. The BPC porosity can be exploited to pressure tune gas selectivity. Our results show that BPC exhibits high H2 selectivity, ideally for hydrogen purification.**


**NM01.15.20**

**Gas Selective Permeability of Graphenylene Membranes**

Jesse Paulino, Daiane Damasceno Borges and Douglas S. Galvão; State University of Campinas, Campinas-SP, Brazil.

**NM01.15.21**

**Multiplexed Superbioelectronic Nose Using Olfactory Receptors Conjugated-Graphene Field-Effect Transistor for Mimicking the Human Sense of Smell**

Jung Lee and Oh Seok Kwon; KRIBB, Daejeon, Korea (the Republic of).

Human sensory-mimicking systems, such as electronic brains, tongues, skin, and ears, have been promoted for use in improving social welfare. However, no significant achievements have been made in mimicking the human nose due to the complexity of olfactory sensory neurons. Combinational coding of human olfactory receptors (hORs) is essential for odorant discrimination in mixtures, and the development of hOR-combined multiplexed systems has progressed slowly. Here, we report the first demonstration of an artificial multiplexed superbioelectronic nose (MSB-nose) that mimics the human olfactory sensory system, leading to high-performance odorant discriminatory ability in mixtures. Specifically, portable MSB-noses were constructed using highly uniform graphene micropatterns (GMs) that were conjugated with different hORs, which were employed as transducers in a liquid-ion gated field-effect transistor (FET). Field-induced signals from the MSB-nose were monitored and provided high sensitivity and selectivity toward target odorants.

graphene geometries needs to be performed in order to efficiently utilize the hybrid plasmon modes for desired optoelectronic applications. We have investigated the plasmon coupling and found that the coupled plasmonic field enhancement in these 3D geometries is strongly dependent on the 3D shape, number of 3D edges, and surface angle of inclination. The uniform coupling in graphene nanocubes gives rise to large circular areas of constant field enhancement. Moreover, if the edges of the nanocubes are spatially separated by nanometer distances, circular field interference patterns are obtained with alternate rings for constructive and destructive coupling. The circular surface enhancement modes in 3D graphene nanocubes can be leveraged for novel optoelectronic applications. In contrast, the square graphene pyramids undergo a strong point enhancement at the apex of the pyramid arising from the inclined tapering faces meeting at the apex. The strong point enhancement propagates throughout the nanoporyamid resulting in a volumetric field that is several orders of magnitude higher than in 2D graphene ribbons. Furthermore, as the number of faces and edges are increased to form pentagonal to octagonal pyramids, the point based enhancement can be transformed to uniform surface enhancement at the base of the pyramid. Thus, allowing geometrical parameters in the nanoporyamids to be utilized for designing high-sensitivity plasmonic sensors that can assess low concentration analytes in the bulk volume of targeted solution or the molecular surface binding properties at higher analyte concentrations. The graphene tube consisting of only 2 edges existing at the openings of the tube, a virtual hot spot of extremely high near-field enhancement is created due to radial plasmon coupling at the small opening of the tube. The completely sealed tube demonstrates a strong hotspot, but, the hotspot covers only 13% of the volume of the tube. However, if the nanotubes are fabricated with small slits, the strongly coupled field exists throughout the tube structure giving rise to strong volumetric field. The volumetric field in nanotubes is especially desirable due to their open-ended geometry that can be leveraged for assessing targets flowing through the 3D tube. The self-assembled 3D graphene structures can be varied geometrically to achieve diverse point, edge, surface, and volumetric enhancement modes for achieving plasmonic devices exhibiting increased sensitivity and efficiency, and a high packaging density.

NM01.15.24 Carbon Nanoscrolls Formation from Bi-Layer Graphene Nanoribbons—A Reactive Molecular Dynamics Study

Jose M. de Sousa, Vitor R. Coluci, Nicola M. Pugno, and Douglas S. Galvão; 1State University of Campinas, Campinas-SP, Brazil; 2Instituto Federal do Piauí, Jose Raimundo Nonato, Brazil; 3University of Trento, Trento, Italy.

Carbon nanoscrolls (CNSs) are families of carbon-based nanomaterials, where unlike the closed carbon nanotubes, their geometrical aspect is like graphene layers rolling up into a spiral (papyrus-like) form. They have been extensively (theory and experiments) studied [1-3]. Due to its open-end topology, where the diameter can be easily varied make them ideal for applications such as hydrogen storage, actuators, tunable water channel, etc. Most of the theoretical works have considered single layer structures; there are only few works on multi-layered scrolls [4]. In this work we have investigated, through fully atomistic reactive (ReaxFF) molecular dynamics simulations, the dynamics formation and structural stability of scrolled structures formed from bilayer graphene nanoribbons. We have also considered these structures interacting with carbon nanotubes, which has been used as a ‘trigger’ to start the scrolling process [5]. Our results show that stable (up to high temperatures ~1000 K) structures can be obtained. We did not observe the formation of covalent bonds between layers and/or carbon nanotubes for the temperature range investigated.


NM01.15.25 Properties of Bio-Inspired Low-Dimension Carbon Fiber and It’s Applications

Seongwoo Ryu1, 2; 1The University of Suwon, Hwaseong-si, Korea (the Republic of); 2Advanced Material Analysis Center, Hwaseong-si, Korea (the Republic of).

Over the past few decades, the fiber-based industry has achieved great progress in aerospace, military and many other industrial applications that require light-weight materials with high mechanical strength. As the demand for electronic devices has exponentially risen in recent years, the preparation of highly conductive fibers has become an important subject in the fiber industry. Low dimension carbon fibers such as carbon nanotube and graphene fibers may be an important material in advancing next-generation high-tech applications if their intrinsic mechanical, electrical and thermal properties can be maintained. By strategy of dopamine infiltration, oxidative polymerization and pyrolysis, we successfully fabricate low-dimension carbon composite fibers with remaining their intrinsic properties. The approach described herein presents a novel fabrication process that can enhance both the mechanical and electrical properties of low-dimension carbon based fibers.

NM01.15.26 Dielectrophoresis-Based Fabrication of Carbon Nanotube-Based Electronic Devices

Jovonte Kimbrough, Kenneth Davis, Sam Chance, Brandon Whitaker, John Elie; Roshawn Treadwell, Javita Cooper, Kaylekh Hartlage, Abram Jones, Alandria Henderson, Qunying Yuan, and Zhigang Xiao; 1Department of Biological and Environmental Science, Alabama A&M University, Normal, Alabama, United States; 2Department of Electrical Engineering and Computer Science, Alabama A&M University, Normal, Alabama, United States.

We report the dielectrophoresis (DEP)-based deposition and alignment of semiconducting carbon nanotubes and the fabrication of carbon nanotube-based electronic devices. Semiconducting carbon nanotubes, which were dispersed ultrasonically in solutions, were deposited and aligned onto a pair of gold electrodes using the electric-field-directed dielectrophoresis method. The DEP-aligned tubes were further fabricated into carbon nanotube field-effect transistors (CNTFETs) and CNTFET-based electronic devices such as CNT-based inverters and ring oscillators using the microfabrication techniques. The aligned carbon fabricated devices were imaged using the scanning electron microscope (SEM), and the electrical properties were measured from the fabricated devices using the semiconductor analyzer. The semiconducting CNTs achieved higher yield in the device fabrication, and the fabricated electronic devices demonstrated excellent electrical properties.

NM01.15.27 Multicolumn Gel Chromatography for Scalable Separation of Nanosheets Based on Size and Surface Chemistry

Dorsa Parviz and Michael Strano; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Liquid-phase exfoliation of two-dimensional nanomaterials yields nanosheet dispersions with broad size distribution and varying surface chemistry. This polydispersity in size and surface chemistry of nanosheets becomes less desirable when their properties are to be precisely controlled for different applications. Hence, scalable separation methods are highly demanded to make this class of materials industrially relevant. Here, we use multicolumn gel chromatography to separate nanosheets of graphene family based on their size (later size and thickness) and surface chemistry (density of functional groups or defects). We demonstrate that various parameters such as stabilizer type, pH, and ionic strength of the solvent alter the binding affinity of nanosheets on the gel and tune the elution time of nanosheets of different size and surface chemistry. Single particle tracking analysis was used as a powerful tool for quick and precise evaluation of nanosheets size distribution in bulk. Other spectroscopic techniques such as fluorescence and Raman spectroscopy were
applied to investigate the surface of the separated nanosheets.

**NM01.15.28**
**Graphene Oxide Polydispersity** Harish V. Kumar, Chinthani D. Liyanage and Douglas Adamson; University of Connecticut, Storrs, Connecticut, United States.

Graphene oxide (GO) finds applications in a variety of areas including, but not limited to, electronics, energy, biomedicine, and optics. Variations in oxidation of GO and its impact on various applications have not been much investigated even though these variations tend to effect the properties of GO. In order to universally understand this variation in oxidation, we have defined an oxidation dispersity number (OD) for GO samples. We divide a given GO sample in a number of differently oxidized parts. The characterization of these differently oxidized GO samples enable us quantifying the OD for a given batch and can be used to tune the density of oxygen functionalities in a GO sample. This emulsion based method is pH dependent and can also be used to sample in a number of differently oxidized parts. The characterization of these differently oxidized GO samples enable us quantifying the OD for a given number of correlated spins per single N-GQD, and number density of superparamagnetic N-GQD per gram of material were estimated. The excellent correlation between OD and magnetic behavior indicates that N-GQDs exhibit superparamagnetic behavior. The specific size, shape and zigzag edge structure of N-GQDs were considered to explain the origin of the observed magnetism. The magnetization dependence led to estimating the N-GQD material magnetic permeability which is considered to explain the origin of the observed magnetism. The magnetization dependence led to estimating the N-GQD material magnetic permeability which is considered to explain the origin of the observed magnetism. The magnetization dependence led to estimating the N-GQD material magnetic permeability which is considered to explain the origin of the observed magnetism.

**NM01.15.29**
**Wax-Enabled Graphene Transfer** Wei Sun Leong, Jin-Yong Hong, Haozhe Wang and Jing Kong; Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Charge carriers in freely suspended graphene can travel very fast (mobility ~200 000 cm²/V·s at 5K), but the reported values for large-area CVD graphene transferred on arbitrary substrate is several orders of magnitude lower, which has been attributed to the polycrystalline nature, surrounding medium, polymer residues, and wrinkles in graphene. The latter two factors were engendered by the polymer-assisted graphene transfer process. Here, we report a new wax-enabled graphene transfer technique that concurrently addresses the polymer residues and graphene wrinkles issues. Compared to poly (methyl methacrylate) (PMMA), the chemical structure of wax is much simpler and does not contain carbonyl (C=O) group, which is reactive to electrophilic or nucleophilic attack. Our density functional theory calculations further indicate that the adsorption energy of wax is 1.56 kcal/mol times lower than PMMA and wax radicals are not stable while PMMA radicals are stable enough to form covalent bonding with graphene. Remarkably, for graphene transferred with wax support layer, we observe not only much lower polymer residues, but also a substantial wrinkle reduction in graphene surface, compared to that of PMMA, through atomic force microscopy studies. Field-effect transistors fabricated on wax-assisted transferred graphene shows the Dirac voltage is closer to zero and 2-fold higher electron mobility compared to that of PMMA. In short, wax-assisted transfer process opens a new avenue for the development of graphene-based electronics by minimizing charge carrier scattering centres in graphene (i.e. polymer residues and wrinkles in graphene).

**NM01.15.30**
**Protection of Molecular Microcrystals by Encapsulation Under Single Layer graphene** Chris Bardeen, Elena Bekyarova, Wangxiang Li and Nathan Tierce; University of California-Riverside, Riverside, California, United States.

Microcrystals composed of the conjugated organic molecule perylene can be encapsulated beneath single layer graphene using mild conditions. Scanning electron and atomic force microscopy images show that the graphene exists as a conformal coating on top of the crystal. Raman spectroscopy indicates that the graphene is only slightly perturbed by the underlying crystal, probably due to strain. The graphene layer provides complete protection from a variety of solvents and prevents sublimation of the crystal at elevated temperatures. Time-resolved photoluminescence measurements do not detect any quenching of the perylene emission by the graphene layer, although nonradiative energy transfer within a few nanometers of the crystal-graphene interface cannot be ruled out. The ability to encapsulate samples on a glass surface under a graphene monolayer may provide a new way to access and interact with the organic crystal under ambient conditions.

**NM01.15.31**
**First-Principles Investigation of a H2O Molecule in a Heterogeneous Carbon/Boron Nitride (7,7) Nanotube** Gwanwoo Kim and Gunn Kim; Department of Physics and Astronomy, Sejong University, Seoul, Korea (the Republic of).

We report behavior of a H₂O molecule inside a heterogeneous carbon nanotube/boron nitride nanotube (CNT/BNNT) structure. We have investigated energetic and electronic properties of our model system using density functional theory calculations. Considering the van der Waals interaction, we used Grimme’s DFT-D2 method implemented in the VASP package. For the model structure, the (7, 7) CNT and BNNT were chosen. The equilibrium distance between a water molecule and the CNT (BNNT) wall was calculated to be 3.3 Å (3.1 Å). In the CNT (BNNT), the energy of the water molecule was 103 meV lower (122 meV lower) at the center of the tube, and was 226 meV lower (257 meV lower) at the equilibrium position in the tube than in vacuum. The potential profile along the tube axis shows a dramatic change around the heterojunction. We plotted the projected density of states (PDOS) of hydrogen and oxygen atoms in the water molecule in the tube to check whether the orbital hybridization changes between the tube wall and the H₂O molecule, depending on the location of H₂O. The PDOS shows ~1 eV downshift in the DOS peaks of O and H atoms to the deeper valence bands when the H₂O molecule is in the (7, 7) BNNT than in the (7, 7) CNT.

**NM01.15.32**
**Synthesis and Magnetic Properties of Metal-Free Nitrogen-Doped Graphene Quantum Dots** Muhammad Sajjad2, Muhammad Shehzad Sultan1, Vladimir I. Makarov1, Frank Mendoza1, Wojciech M. Jadwisienczak1, Brad R. Weiner4 and Gerardo Morell1; 1Department of Physics, University of Puerto Rico - Rio Piedras, San Juan, Puerto Rico, United States; 2Department of Physics and Astronomy, Western Kentucky University, Bowling Green, Kentucky, United States; 3School of Electrical Engineering and Computer Science, Ohio University, Athens, Ohio, United States; 4Department of Chemistry, University of Puerto Rico - Rio Piedras, San Juan, Puerto Rico, United States.

Metal-free nitrogen doped graphene quantum dots (N-GQD) were synthesized and, for the first time to our knowledge, their magnetic properties were investigated. The results indicate that N-GQDs exhibit superparamagnetic behavior. The specific size, shape and zigzag edge structure of N-GQDs were considered to explain the origin of the observed magnetism. The magnetization dependence led to estimating the N-GQD material magnetic permeability for different ambient temperatures. From the zero-field-cooled (ZFC) and field-cooled (FC) magnetization measurements, carried out at 50 Oe magnetic field strength, we estimated the blocking temperature Ƭ_B to be around 300 K. Based on the experimental data analysis, the magnetic permeability, number of correlated spins per single N-GQD, and number density of superparamagnetic N-GQD per gram of material were estimated. The excellent superparamagnetic properties together with optical properties manifested by N-GQDs have the potential to lead to high performance biomedical applications.
Two-dimensional (2D) nanosheets such as those of transition metal di-chalcogenides (TMDs) have become attractive due to the unusual properties associated with their ultrathin structure. Development of applications for these materials has been limited by the lack of a simple method to exfoliate them in single or few-layer flakes in large quantities. In this work, an exfoliation route of 2D materials such as graphitic boron nitride (hBN) using mechanical milling in solid state (cryomilling) and sonication was performed. Materials were cryomilled during 30 min and liquid sonicated. A reduction in particle size of the powders materials after cryomilling was observed and a possible disorder of layers was evident because of the decrease in the intensity of the characteristic peak of the plane (002) in DRX patterns. After sonication process, the incorporation of 2D nanosheets in previously modified polymers by physical and chemical processes changes in the optical, thermal and mechanical properties of i.e. polypropylene. The thermal diffusivity of the composite increased when the non-covalent compatibilizer was incorporated into the polymer at low level of hBN concentration.

Spintronics is the fusion field of electronics and magnets, and has attracted much attention from physical and practical viewpoints, because both electric charge and spin of electrons are utilized simultaneously. Giant magnetoresistance (GMR) and tunnel magnetoresistance (TMR) effects have been the main principles of spintronics devices such as magnetic heads and magnetic random access memories (MRAM), which use changes in the electrical resistance accompanied by switching between parallel and antiparallel magnetization alignments. These phenomena are observed in trilayered spin-valve junctions composed of top and bottom ferromagnetic layers and a nonmagnetic interlayer. Therefore, spin-valves are suitable for investigating the spin-transport potential of interlayer materials due to the simple structure. It is expected that materials composed of light elements possess long spin-transport lengths due to weak spin-orbit interactions. Thus far, we have investigated spin-valves and electrically and ultrasonically crystallized diamond (UNCD)/hydrogenated amorphous carbon (a-C:H) composite (UNCD/a-C:H) films. They comprise a large number of nano-sized diamond grains embedded in an a-C:H matrix, and have the following merits: (i) the production of p- and n-type conduction accompanied by enhanced electrical conductivities is possible by boron and nitrogen doping, respectively; (ii) they can be grown on foreign solid substrate; (iii) they can be grown at low pressure; and (iv) they have very good stability. The binding energy, HOMO-LUMO gaps and DOS were calculated to compare with the adamantane and the sila-adamantane (sila) molecules, and even BN-adamantane proposed by Fyta [1]. The Carbon atoms of the adamantane molecule have been substituted with Boron and Nitrogen atoms respecting the octet rule and considering homonuclear N-N or B-B bonds. Geometrical optimization of the nanostructures indicated that the BN-diamondoids exhibit good stability. The binding energy, HOMO-LUMO gaps and DOS were calculated to compare with the adamantane and silica-adamantane molecules. In addition, thermodynamical properties whose dependence with the temperature are discussed and indicating that all BN-isomers studied here could be synthesized, and its reaction should occur spontaneously in about 750 K. Finally, these BN-isomers have promising electronic and optical properties; in particular, the BNx-n_isomers (x = 4, 5 or 6) have an excellent optical absorption spectra in the range of ultraviolet radiation (UVA and UVB), and in particular, the 4BN-(196) isomer absorbs in the UV-Vis.

We have systematically investigated the lowest-energy structures of boron nitride (BN) diamondoids, Bnx-based nanostuctures (x = 4, 5 or 6), using the Density Functional Theory (DFT) and the Time-Dependent Density Functional Theory (TD-DFT) methods within the local density and generalized gradient approximations, LDA and GGA, respectively, were carried out to investigate the structural, electronic, thermodynamic properties and optical absorption of BN-diamondoids comparing to previous results for the adamantane (adaC) and the sila-adamantane (sila) molecules, and even BN-adamantane proposed by Fyta [1]. The Carbon atoms of the adamantane molecule have been substituted with Boron and Nitrogen atoms respecting the octet rule and considering homonuclear N-N or B-B bonds. Geometrical optimization of the nanostructures indicated that the BN-diamondoids exhibit good stability. The binding energy, HOMO-LUMO gaps and DOS were calculated to compare with the adamantane and sila-adamantane molecules. In addition, thermodynamical properties whose dependence with the temperature are discussed and indicating that all BN-isomers studied here could be synthesized, and its reaction should occur spontaneously in about 750 K. Finally, these BN-isomers have promising electronic and optical properties; in particular, the Bnx_isomers (x = 4, 5 or 6) have an excellent optical absorption spectra in the range of ultraviolet radiation (UVA and UVB), and in particular, the 4BN-(196) isomer absorbs in the UV-Vis.

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NM01.15.36
Effect of Non-Covalent Compatibilizers Agents in Mechanical and Thermal Properties of b-BN Nanosheets/Polymer Composites
Sofia Vasquez-Rodriguez1, Eder I. Santos-Alvarado1, Luis E. Roman-Quirino1, Jose L. Aceval-Davia1, Angel A. Aguilar-Morones1, Selene Sepulveda-Guzman1, Eduardo Arias2, Nora A. Garcia-Gomez1, Fernando A. Blanco-Flores1 and Rodolfo Cruz-Silva1; 1Universidad Autonoma de Nuevo Leon, San Nicolas de los Garza, N.L., Mexico; 2Centro de Investigacion en Quimica Aplicada, Saltillo, Mexico; 3Shinshu University, Nagano, Japan.

We performed low-pressure chemical vapor deposition (CVD) in an AIXTRON® Black Magic cold-wall furnace, featuring a wafer-scale, local heater stage and gas showerhead. The combination of a low flux of carbon precursors with sub-nm Fe/Mo catalyst films on alumina-coated Si wafers maintains small-diameter SWNTs. High-resolution TEM and X-ray scattering confirm that our forests contain ~99% SWNTs below 4 nm diameter (on wafers up to 4
In this work, we combined Rutherford backscattering spectroscopy and AFM to reveal that 8 at% Mo optimally preserves small, densely packed particles, templating growth of forests with high number densities up to 2.2x10^{12} cm^{-2}. Wafer-scale growth from Fe/Mo films was observed down to the micrometer scale, with the average SWNT diameter distributions with larger means and tails, which are detrimental to membrane rejection properties. While tuning the Fe thickness down does render smaller diameters, the range of densities grown from these Fe-only films is 0.2-0.6x10^{12} cm^{-2}, regardless of thicknesses studied (0.35-0.65 nm). Furthermore, we explored the catalyst-dependent growth enhancement as a function of H_{2}O vapor concentration added to the growth ambient (120-1500 ppm) and leverage this understanding to establish robust, uniform wafer-scale growth from Fe/Mo across sequential runs (up to 6).

There remains a currently inaccessible regime of the multi-dimensional parameter space that co-ordinates uniformly large-area growth of small, monodisperse, and densely long SWNTs for high-performance membranes. However, our developments in synthesis represent to our knowledge best-in-class co-optimization of small-diameter, high-density, and large-area SWNT forest growth.


NM01.15.37
High Performance Composites with Interlamellar Reinforcement from the Direct Growth of Carbon Nanotubes Richard Li, Clementine Mitchell and Brian L. Wardle; Department of Aeronautics and Astronautics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Advanced nanoeengineered composites are a promising approach towards improving the mechanical performance of filamentary composites and adding multifunctionality to lightweight structures and vehicles. In particular, the integration of carbon nanotubes into composites through the circumferential growth of radially aligned carbon nanotubes (r-CNTs) onto microfibers has already demonstrated improvements in interlamellar fracture toughness, interlamellar shear strengths, and electrical/thermal conductivities of alumina fiber composites. However, the implementation of this “fuzzy fiber” reinforced plastic (FFRP) architecture onto high performance carbon fibers (CFs) desired for demanding applications, has been met with microfiber strength loss and effectively trades off in-plane strengths for through-thickness property improvements. This work presents an approach to growing high yields of r-CNTs on carbon fibers to improve interlamellar properties while preserving the carbon fiber properties. Using a low temperature chemical vapor deposition (CVD) approach and a scalable method of catalyst deposition onto filaments, CNTs were directly grown on unidirectional (UD) carbon fibers to form UD fuzzy CFs plus. Building on previous developments of woven fuzzy carbon fiber reinforced plastic (CFRP) laminates, vacuum assisted resin infusion was used to manufacture UD fuzzy CFRP laminates that have low interlamellar spacings (<15 μm) to increase the CNT fill fraction in the weak interlamellar region, and isolate CNT reinforcement effects. Both UD baseline CFRP and UD fuzzy CFRP were manufactured using a vacuum assisted resin infusion system with interlaminar spacings and laminate quality assessed through X-ray microcomputed tomography. Transmission and scanning electron microscopies reveal conformal CNT growth around carbon filaments prior to matrix introduction. Thermogravimetric data also shows the removal of the polymeric sizing layer on carbon fibers and the thermoplastic wet (that holds the CF tows together) through CVD processing and consequently informs matrix interface changes as well as process bounds for ensuring ply handleability. Further, short-beam shear testing data of UD fuzzy CFRP are presented, showing a 4% improvement in interlamellar shear strength. Thus, this work is an important step towards realizing hierarchical carbon fiber composites with improved interlamellar properties without compromising in-plane strengths, and provides a platform for future CNT growth optimization that may result in even larger property enhancements.

NM01.15.38
Microwave-Assisted One-Pot Synthesis of Luminescent Carbon-Like Nanomaterials Nobuo Yamada, Hiroki Noguchi, Yutaka Kuwahara, Makoto Takafuji and Hirotaka Iihara; Department of Applied Chemistry and Biochemistry, Kumamoto University, Kumamoto, Japan.

The fine particles having fluorescent property is currently used as important chemical sensing. However, these materials are synthesized by complicated preparation processes or using precious metals as raw materials. In this paper, we report a simple preparation method of fluorescent nanoparticles based on self-assembling polymerization of aromatic monomers. The fluorescent polymer particles are prepared using 2,6-dihydroxyanthracene and 1,3,5-trimethylhexahydro-triazinane as monomers by microwave heating process. Solid components were obtained from the reaction solution after an appropriate heating time by centrifugal separation. The obtained particles are spherical in shape, confirmed by Transmission Electron Microscope. The size of particle can be controlled within the range of the nano to submicron scale by changing the reaction conditions. The obtained particles are well dispersed in water. The optical property of particle was evaluated by UV-vis and fluorescent spectra at pH 7. The particle has specific absorption band around 500 nm, which is not observed in monomer. And the particle shows fluorescent spectra around 600 nm, while the monomer shows around 450 nm. The storks shift of particles is about 200 nm.

NM01.15.39
Water Nanopumping via Carbon Nanotube Using SAW Abhat Zhuldassov1 and Zinetula Z. Insepov1, 2, 3; 1School of Nuclear Engineering, Purdue University, West Lafayette, Indiana, United States; 2Condensed Matter Physics, National Research Nuclear University MEPhI, Moscow, Russian Federation; 3Nazarbayev University, Astana, Kazakhstan.

One of the attractive carbon nanotube (CNT) features is its capability for water transport and purification. Many experimental and theoretical work were dedicated to studying nanofluid delivery via CNTs. However, most conventional methods seem to be inefficient and complicated. The goal of this work is to further develop a new efficient approach for fluid pumping at nanoscale level (i.e., nanopumping) using Rayleigh surface acoustic (traveling) waves propagating on the nanotube walls. In our previous studies [1-4], the nanopumping effect triggered by Rayleigh travelling waves was predicted by molecular dynamic (MD) simulation of simple gases H_{2}, H_{2}O, placed inside single layer CNTs. Propagations of surface acoustic waves (SAW) were studied at various frequencies and amplitudes on the CNT walls and interaction of CNT-walls with gas inside the tubes were demonstrated. An average axial velocity of the gas molecules reaching 20 km/s were obtained [1].

In present work, a large scale MD simulation package (LAMMPS) was used to verify that the nanopumping effect also exists in liquid water placed in CNT. Two monolayer graphene sheets with holes consistent with the CNT diameter were placed in both ends of nanotube along axial direction of the nanotube, preventing water permeation outside of the CNT. Water molecules were placed in a left chamber with a volume of 13500 Å^3 containing 1188 water molecules. A TIP3P water model was used in all simulations. The dimensions of simulation box were 44 x 44 x 160 Å^3 and the boundaries were fixed with reflecting walls in all three dimensions. In our simulation, surface acoustic wave propagation was induced by a cosine wave equation. Our results without SAW showed that water molecules were not experiencing imbibition into CNT. Application of Rayleigh surface travelling waves on CNTs, however, significantly accelerate water motion. The frequencies of SAW applied to CNT walls were varied from few of MHz to tens of THz. The results of our simulations demonstrated that water molecules passed through CNTs and exited from the other CNT side. The efficiency of the nanopumping
model was estimated. Water flow rate defined as a number of water molecules passing through CNT per time and area units, and the total flux of water were calculated depending on the SAW frequency for 100, 300, and 500 A CNTs lengths.


NM01.15.40
CNT Electromechanical Probes—Working Towards Small-Pitch, Compliant Probing Applications at Wafer Level Packaging Melmet Tas1, Mark Baker2, Jedidiah Bentz2, Keir Boxshall2 and Vlad Stolojan1; 1Advanced Technology Institute - University of Surrey, Guildford, United Kingdom; 2Department of Mechanical Engineering Sciences, University of Surrey, Guildford, United Kingdom; 3Smiths Interconnect, Kansas City, Kansas, United States.

Applications of electromechanical probing for wafer testing progressively require smaller pitches, reliable and reproducible manufacturing and lower electrical contact resistances. Current electromechanical testing probes, for instance MEMS based vertical cantilever probes, have fundamental limitations in terms of the shortest pitch that can be achieved, cost and efficiency. The exceptional mechanical and electronic properties of carbon nanotubes (CNTs) make CNTs a promising candidate material for electromechanical probing applications. We synthesise vertically-aligned CNT structures by combining photo-thermal chemical vapour deposition (PTCVD) and photolithography and assemble them into a new type of metal-CNT-Polydimethylsiloxane (PDMS) composite structure for possible probing applications at both wafer-level chip-scale packaging (WL CSP) and wafer-level packaging (WLP) testing. Up to 600 μm tall, CNT-based vertical micro-spring type probes are demonstrated. We propose a design and architecture with a scalable approach, allowing for the assembly of thousands of probes in short manufacturing times, with easy pitch control that can facilitate testing at WL CSP and WLP packaging.

NM01.15.41
Dynamic Mechanical Property of Multilayer Graphene Subjected to Supersonic Impact Wanting Xie1, 2 and Jae-Hwang Lee1; 1Department of Mechanical and Industrial Engineering, University of Massachusetts Amherst, Amherst, Massachusetts, United States; 2Department of Physics, University of Massachusetts Amherst, Amherst, Massachusetts, United States.

Graphene is considered as one of the most promising anti-ballistic materials due to its high strength, stiffness, and low density. While its low-rate behavior has been studied for years, there are few experimental investigations at the high-strain-rate regime. By the observation of micro-spheres penetrating through free-standing graphene membranes in air, Lee and his colleagues (Science 346, 1092 (2014)) directly characterized mechanical properties of multilayer graphene at very high strain rates (~107 /s). Their microscopic ballistic study demonstrated that the specific penetration energy of multilayer graphene was more than 10 times larger than that of steel for 600 m/s impact in the air. Independent numerical studies, however, predicted one order higher specific penetration energy than the experimentally measured value. A thickness effect was brought up to explain this discrepancy, as in modeling, a series of monolayer graphene with a same total mass. Moreover, aerodynamic effects of air were also suggested since the numerical simulations were carried out without introducing gases.

For more precise quantification of the high-strain-rate properties of graphene, we have performed the micro-ballistic characterization in vacuum. Since the vacuum level is approximately 1/3,000 of the atmospheric pressure, undesired effects from air, including aerodynamic friction of a projectile and a membrane specimen, become negligible. As a projectile, 3.7 μm diameter silica sphere is accelerated and a suspended graphene membrane is subjected to projectile’s impact. With an ultrafast microscopic imaging system (up to 40 million frame per second), accurate velocities of the projectile before and after penetration are obtained. The specific penetration energy are directly calculated by the ratio of kinetic energy loss of the projectile and the mass of the membrane obtained. Within the direct impact area of the projectile for different projectile’s velocities (100 – 1,000 m/s) and specimen’s thicknesses (10 – 100 nm).

Post-mortem optical micrographs and electron micrographs are taken to measure the total crack length, crack number, and penetration area to explore their relationship with the penetration energy. The fine penetration features near the impact region are mainly examined by scanning electron microscopy.

NM01.15.42
Optical Visualization and Spectral Amplification of Single-Walled Carbon Nanotubes Through the Hygroscopic Salt Micro/Nanolenses Yun-tae Kim and Chang Young Lee; Ulsan National Institute of Science and Technology (UNIST), Ulsan, Korea (the Republic of).

Micro/nanolenses of alkali metal halides are unique optical components that partially overcome the limitations of existing ones because of their hygroscopicity, solubility in water, tuneable refractive indices, excellent transmittance from UV to infrared, and high mobility of the constituent ions under an electric field. Forming such lenses and arranging them in a well-defined manner, however, remains a challenge. Here we demonstrate selective decoration of array of micro/nanolens along single-walled carbon nanotubes (SWNTs) using various salt species, which can be migrated along exterior of SWNT under an electric field. The lenses are promising for use in both the optical visualization and spectral amplification of underlying individual nanotubes. The lenses help detect molecular species located onto sidewall of a nanotube, such as amorphous carbon and diazonium that are not easily detectable using existing approaches. In addition, molecules dissolved in the solution can be captured within the lenses via exterior transport and then detected by Raman spectroscopy. Such lenses can be easily removed by a simple water rinse without degrading the properties of SWNTs. Thus, our approach will serve as a useful tool for the non-invasive visualization of nanostructures and spectral amplification of various molecular species.

NM01.15.43
The Exterior of Single-Walled Carbon Nanotubes as a Millimeter-Long Cation-Preferring Nanochannel Yun-tae Kim and Chang Young Lee; Ulsan
Interactions of Carbon Nanotubes with Magnetospirillum Magneticum via Carbon Nanotube/Polypyrrole Nanocomposite

Jake Dengelegi, Prabir Patra and Isaac Macwan; University of Bridgeport, Bridgeport, Connecticut, United States.

In this study, the exterior of single-walled carbon nanotubes is shown to preferentially migrate cations over a millimeter length scale. Applying an electric field to droplets of NaCl placed at both ends of the nanotubes causes the transport of a cation-enriched solution along the nanotubes in the direction of the electric field, while the anion-enriched solution counter-migrates along the adjacent substrate. This phenomenon is confirmed by Kelvin probe force microscopy and mass spectrometry imaging of individual nanotubes, as well as formation of bright and dark lines along the nanotubes in scanning electron microscopy (SEM). Blocking the exterior of the nanotubes prevents both the bright/dark lines in SEM and flow of current through the nanotubes, confirming the insignificance of interior ion transport and electron current. The cation-prefering transport results in the formation of positively charged salt crystals along the nanotubes (with a cation-to-anion ratio of 0.59:0.41 for KCl) followed by the subsequent shrinkage and growth of crystals in the direction of cation flux. Molecular dynamics simulations shows that cation-π interaction is responsible for such cation-preference observed during transport. The loss of cation-preference upon covalent functionalization of the nanotubes further supports this mechanism. Utilizing the short-range cation–π interaction as a transport mechanism suggests broader applications in areas where charge-specific transport is desired.

NM01.15.44

Modeling the Bipolar Switching Effect in Graphene Oxide-Based Memristors

Andres Vercik and Luci C. Vercik; University of Sao Paulo, Pirassununga, Brazil.

The memory resistor, or memristor, was theoretically predicted by Chua in 1971 as the forth fundamental circuit element needed to complete the set of six mathematical equations relating four basic electrical variables: charge, current, voltage and magnetic flux. This idea remained as a missing element until its experimental realization in 2008 as TiO2-based memories. Since then, many researchers have directed their attention and efforts not only to the fabrication of memristors, using different materials, but also to understand the physics behind the switching mechanism, in order to control the processing and structural parameters that allow overcoming some drawbacks to obtain reliable and reproducible memory devices. Two-terminal devices, with the switching material sandwiched between two electrodes, are promising structures for the next generation of non-volatile resistive random access memories, with high speed, low-power consumption and excellent scalability. The two-dimensionality of the insulating graphene oxide sheets makes this material ideal for use in low-dimensional structures in nanoscale devices.

In this work, the transport properties of graphene oxide-based Metal-Insulator-Metal (MIM) structures are addressed. The graphene oxide (GO) was synthesized using an eco-friendly modified Hummers method. The obtained GO sheets were placed between gold electrodes, and the cycling current-voltage curves were measured by applying successive forward and reverse voltage sweeps in a range between -3 and 3 V. When the absolute value of the measured current is plotted, in logarithmic scale, versus the applied voltage the typical butterfly-shaped curves are observed, which are better interpreted in terms of their first derivative, or differential conductivity, in order to understand the transport mechanism. A simple model is proposed, whose voltage dependence helps identifying the underlying physics responsible for the bipolar switching mechanism, such as bulk or electrode effects, conducting filament formation or tunneling. The analytical expressions used for the differential conductance for the low resistance state and the high resistance state (LRS and HRS respectively) leads to simple expressions for the I-V curves. The symmetry of the curves after several cycles is lost when compared to those measured on pristine devices, which might indicate the occurrence of filament forming effect, affecting the bipolar switching.

NM01.15.45

Rheological Characteristics of Chitosan - Gold - Graphene Gels

Radha Perumal Ramasamy; Department of Applied Science and Technology, ACT campus, Anna University, Chennai, India.

Gels are important class of materials and have wide applications. Gel polymer electrolytes is an interesting field and has gained much scientific attention in recent years. Controlling the rheological properties of gels can benefit its applications in fields such as batteries. In this research the effect of incorporation of graphene upon the rheological properties of chitosan-gold gels is explored. The chitosan solution was prepared by adding 1% (w/v) of chitosan powder of and 1.5% (w/v) of acetic acid to double distilled water. The solution was stirred and heated at 60° until a semitransparent thick chitosan solution was obtained. The solution was cooled to room temperature. To this solution, appropriate amounts of 1 M HAuCl4.3H2O were added to have 5 mM Au. Also graphene (grade H5 – XG Sciences) was incorporated in the gels to have 0, 10 and 20% of graphene (by weight compared to that of chitosan). The rheological and SEM measurements were made on these gels. The rheological measurements were made one day after the formation of the gels. The complex modulus for chitosan-5mM gold gels showed an increase from 100 Pa to 620 Pa as temperature increased from 25°C to 85°C. It then rapidly decreased to 36 Pa as temperature increased to 100°C. Chitosan-5mM Au-20% graphene had a peak at 95°C. Hence the viscosity has maximum values at 85, 90 and 95°C for graphene concentration of 0, 10 and 20% in chitosan-5mM Au gels. Between 25 to 70°C the viscosity of chitosan-5mM Au-10% graphene > chitosan-5mM Au > chitosan-5mM Au-20% graphene. Between 70 to 85°C the viscosity of chitosan-5mM Au > chitosan-5mM Au-10% graphene > chitosan-5mM Au-20% graphene. Phase angle measurements showed that chitosan-5mM Au, chitosan-5mM Au-10% graphene and chitosan-5mM Au-20% graphene gels had lowest values at 80, 85 and 95°C respectively. These results indicate that the rheological properties are influence by the graphene incorporated in it. Interestingly, as graphene concentration increases to 20%, chitosan-5mM Au-20% graphene remains as a gel even at 100°C (as it has high viscosity) though chitosan-5mM Au and chitosan-5mM Au-10% graphene gels collapse at 100°C (as they have low viscosity). This indicates that graphene can be incorporated in gels to increase the temperature at which it can be operated. TEM images for graphene added to 5Mm Au solution (in room temperature) showed very less presence of gold nanoparticles. TEM images for chitosan-5mM Au-10% graphene in room temperature (incubated for 10 days) showed presence of several sub-micron sized gold particles. Spherical, triangular and hexagonal shaped particles were observed. Some particles were as large as 500 nm. The particles were heterogeneous in sizes. TEM images for chitosan-5mM Au-10% graphene heated to 90°C for 60 min (until the solution turned red in color) showed that uniform gold nanoparticles formed. Also gold nanoparticles attached to graphene indicating that graphene acts as nucleation site.

NM01.15.46

Interactions of Carbon Nanotubes with Magnetospirillum Magneticon via Carbon Nanotube/Polypyrrole Nanocomposite

Jade Demergi, Prabir Patra and Isaac Macwan; University of Bridgeport, Bridgeport, Connecticut, United States.

Being able to easily manufacture uniform chirality carbon nanotubes (CNT) is a difficult problem that we face today. There are many different twists that the carbon nanotubes orient themselves in making them either more metallic or semi-conducting in nature. Being able to separate these two types is very important to the semiconductor industry because semi-conducting carbon nanotubes are better suited for electronic devices such as transistors. Magnetospirillum magneticon (AMB-1) is a bacteria that can be used through magnetotaxis for controlled assembly tasks and it has also been shown that there are favorable interactions between the surface proteins, MSP-1 and flagellin of AMB-1 with glycine along with its flanking residues interacting only with metallic but not semi-conducting CNT. It has also been shown before that graphene, pyrrole, and carbon nanotubes can form a free standing film using cyclic voltammetry (CV) owing to the fact that the process of making the films containing only CNTs is extremely challenging because they are non-polar and cannot be polymerized independently. CV electro-polymerizes the pyrrole monomer into polypyrrole (PPy) through a series of oxidation and reduction reactions along with CNT to be deposited on an electrode. In order to better study the interactions between CNT and AMB-1, this work is on the fabrication of a free standing nanocomposite CNT/PPy film using CV with a specific aim to quantify such interactions using scanning electron microscopy.
Photovoltaic Solar Cell by P3HT:PCBM Doped Graphene flakes as Photoactive Layer

NMO1.15.47
Enhancing Performance of Photovoltaic Solar Cell by P3HT:PCBM Doped Graphene flakes as Photoactive Layer

Adnan Ali and Braham Aïssa
Qatar Environment & Energy Research Institute, Hamad Bin Khalifa University, Qatar Foundation, Doha, Qatar.

Photovoltaic materials based on conjugated polymers are very promising candidates for Hybrid organic photovoltaic (OPV) cells. Conjugated polymers are inexpensive materials and therefore, their processing is very cost-effective and the ease of fabrication by solution processing techniques make them more attractive. So far, OPV with modest efficiency are obtained. The low power conversion efficiency (PCE) of OPV is one of the main reasons which has impeded large scale deployment. The low PCE of OPV solar cells is attributed to the low carrier mobility, which is closely correlated to the transport diffusion length of the charge carriers within the photovoltaic layers. 2D material like graphene which has huge carrier mobility, thermal and chemical stability and its compatibility of fabrication by solution processing techniques make it an excellent candidate for assisting charge transport improvement in the active layer of OPV cells. In this work, we report on the improvement of the optoelectronic properties and photovoltaic performance of photoactive blended layers i.e. P3HT:PCBM doped graphene flakes which was then integrated into a bulk heterojunction (BHJ) organic-photovoltaic-based device, using PEDOT:PSS on an ITO/glass substrate. Firstly, effect of graphene flakes content was studied in terms of the light absorption capacity which has shown increase with increasing concentration of graphene flakes. Besides this, quenching was observed through photoluminescence which is a clear indication of electron transfer between the graphene flakes and the polymeric matrix. P3HT:PCBM doped graphene flakes layer is incorporated into the BHJ as active layer. An increase in PV performance with respect to the reference cell was observed. The best PV performance was obtained for 3 wt% loading of graphene flakes. The solar cell showed an open-circuit voltage (VOC) of 1.24 V, a short-circuit current density (JSC) value of 6.18 mA cm−2, a fill factor of 47.12%, and a power conversion efficiency of about 3.61%. It is obvious from the organic photovoltaic solar cell efficiency that sp2-bonded carbon doping of photoactive conjugated polymer has strong role in its enhanced performance.

NMO1.15.48
Mechanism Study of Graphene Adlayers in Chemical Vapor Deposition by Isotope Labeling

Xuewei Zhang, Zhenxing Zou, Yang Wang, Yunlu Wang, Le Mei, Zilong Zhang, Zehao Wu, Pei Zhao and Hongtao Wang; Zhejiang University, Hangzhou, China.

Bilayer graphene (BLG) has attracted enormous interest due to its outstanding mechanical, chemical, electrical and thermal properties with various potential applications. By applying a ratio of H2 to CH4 in chemical vapor deposition (CVD) system, BLG can be synthesized with reversed-cake structures on polycrystalline Cu foils. Bilayer regions show distinct Raman spectra by carbon isotope labeling due to the different compositions of the graphene.

In this work, we studied the growth mechanism of BLG using carbon isotope labeling and Raman spectroscopy. Results show that the growth of BLG reveals several different modes. A new mode of "secondary" nucleation is firstly proposed in the growth of BLG, which means that graphene can be nucleated under the first layer tens of minutes later than the first layer. Moreover, during the BLG growth, the stacking structures of the two layers can suddenly change from AB-stacking to non-AB-stacking, while most of the BLG can still maintain their stacking structures during the whole CVD process. This work enables us to have a deep understanding of graphene growth mechanism as well as the layer control for large scale BLG using CVD.

NMO1.15.49
LEEM Investigations of Polymer-Assisted Sublimation Grown Graphene on SiC

Philipp Schädlich1, Florian Speck1, Georg Traeger2, Anna Sinterhauf2, Davood M. Pakdehi3, Klaus Pierz3, Martin Wenderoth2 and Thomas Seyller1; 1Institut für Physik, Technische Universität Chemnitz, Chemnitz, Germany; 2IV. Physikalisches Institut, Georg-August-Universität Göttingen, Göttingen, Germany; 3Physikalisch-Technische Bundesanstalt, Braunschweig, Germany.

Although much research has been conducted in the field of epitaxial graphene growth on silicon carbide (SiC), still new phenomena are discovered and need to be investigated in order to fully understand and control graphene synthesis and properties. Usually, during sublimation growth in argon atmosphere the substrate undergoes strong step bunching [1], which leads to relatively large step heights of multiple SiC unit cells. In contrast, the polymer-assisted sublimation growth (PASG) leads to flat and homogeneous graphene sheets on top of an SiC surface with step heights of mainly one or two SiC-bilayers [2]. This gives rise to a well-developed sequence of alternating SiC surface terminations underneath the graphene, which originate from different crystal truncations within the SiC unit cell at the surface [3].

Recently, scanning tunneling potentiometry measurements on graphene obtained by PASG revealed different values for the sheet resistance for graphene on different SiC terraces. Here, we present our results on PASG graphene investigated by low-energy electron microscopy (LEEM). The termination of the underlying SiC substrate is studied by LEEM bright field and dark field measurements as well as selected area low-energy electron diffraction (μ-LEED) and atomic force microscopy. In addition low-energy electron reflectivity (LEER) spectra reveal slightly different electronic properties of the graphene on different SiC terminations. The relationship between the termination of the SiC substrate and the electronic properties of the PASG graphene as indicated by the LEER spectra is shown. Possible explanations for the local change in sheet resistance and the influence of the substrate are discussed.


NMO1.15.50
Exceptional Multifunctional Properties of Non-Oxidized Graphene Aerogel/Epoxy Nanocomposite

Jin Kim1, Ne Myo Han2, Jungmo Kim3, Hyewon Yoon1, Minsoo Park3, Travis G. Novak4, Ashraful Azam1, Jinho Lee3, Jang-Kyo Kim1 and Seokwoo Jeon1; 1KAIST, Daejeon, Korea (the Republic of); 2MAE, HKUST; Hong Kong, Hong Kong.

Graphene aerogel, a three dimensionally interconnected porous structure, has gained significant attention due to its fascinating properties, such as high mechanical strength, electrical conductivity, thermal resistance, and ultra-light weight. Incorporation of graphene aerogel into a polymer composite is a promising route for fabrication of ultra-light multifunctional material, which is heavily demanded in various industries.
Recent studies have focused on optimization and alignment of graphene aerogel’s structure, in order to further improve the quality of the aerogel and the corresponding device. Various methods have been developed for controlling the aerogel structure such as self-assembly, direct patterning, and 3D templating of graphene flakes. Initially, graphene oxide (GO) flakes was used for fabricating graphene aerogel with aligned structure, due to its abundant surface functional groups, which facilitate both aqueous dispersion and assembly of graphene aerogel. However, those functional groups also act as defects, which severely deteriorate the property of both GO flakes and its aerogel. Therefore, it is highly desired to fabricate graphene aerogel composed of graphene flakes with minimum damage.

Here we report a fabrication method to fabricate graphene aerogel composed only with highly crystalline non-oxidized graphene flakes (NOGFs). Bi-direction freeze casting technique was utilized in order to align the pore walls in two orthogonal directions, vertically and laterally. The graphene aerogel showed low defect concentration and oxygen content of 1.4 % according to Raman and XPS analysis. Due to the synergistic effect of both high quality of NOGFs and the aligned structure, the graphene aerogel exhibited outstanding electrical conductivity of 202.9 S/m, which is the highest value ever reported among carbon nanomaterial based aerogels at similar density. Subsequently, epoxy composite was fabricated by impregnating epoxy resin within the graphene aerogel’s pores with vacuum infiltration method. The epoxy composite showed remarkable fracture resistance of 1.74 MPa m^{1/2} at 0.45 vol% and electrical conductivity of 122.6 S/m at 0.27 vol%. Both results are superior to those of epoxy composites based on GO aerogels, which demonstrate that incorporation of NOGFs is a promising approach for fabricating high quality graphene aerogel.

NM01.15.51
Fabrication of Edge-Rich MoS$_2$ Cathodes for Water Splitting via Hydrothermal Electrodeposition
Shusuke Katahira, Hiroaki Kobayashi, Yuta Nakayasu and Itaru Honma; Tohoku University, Sendai, Japan.

Water splitting is one of the carbon-free hydrogen production methods. Electric power consumption of the hydrogen evolution reaction (HER) depends on the cathode materials. Although Pt is known as the most suitable cathode for HER under acidic conditions, identified resources of platinum are limited in the world. Hence, the development of alternative HER catalysts is required. Currently, MoS$_2$ presents a promising alternative to Pt due to its low cost and high HER activity. The active sites of MoS$_2$ are located at the edges, thus it is important to develop a simple synthesis process to obtain edge-rich MoS$_2$. In previous research, edge-rich MoS$_2$ of high crystallinity was synthesized under hydrothermal conditions, but the main problem of the process was the long reaction time (24-48 h). MoS$_2$ synthesis via cathodic electrodeposition is one of the fast and facile processes because the deposited MoS$_2$ can be applied directly for application. However so far, electrochemically deposited MoS$_2$ showed low crystallinity and low purity with an amorphous structure.

In order to realize high crystallinity MoS$_2$ and short processing times, we propose a hydrothermal electrodeposition method to fabricate MoS$_2$ electrodes. This method enables to synthesize crystalline thin films and to control the composition and morphology of the products by adjusting the operating temperature, pressure, and electrochemical conditions. In this research, we attempted to electrochemically deposit MoS$_2$ on glassy carbon (GC) under hydrothermal conditions (200 °C, 10 MPa), and the MoS$_2$/GC electrodes were then applied as HER cathodes. For the hydrothermal electrodeposition, a high-pressure vessel made of Hastelloy equipped with electrodes was used as a synthesis cell, and potentiostatic measurements were carried out at voltages of –1.5 V for 1-30 min. Surface and TEM images of samples synthesized by 1 min electrolysis revealed the formation of edge-rich MoS$_2$ deposited on GC, while it seemed that the number of exposed edges of the products decreased with increasing reaction time. XRD patterns of working electrodes realized by electrodeposition for 1 min showed that crystalline MoS$_2$ was deposited on the GC. From TOF-SIMS measurements, the product was mainly identified as MoS$_2$, while compounds of molybdenum sulfides and oxides were observed in the case of the electrodes treated at ambient condition. HER catalytic activity measurements showed that products synthesized at hydrothermal condition exhibited higher HER performance than the samples synthesized at ambient conditions. Moreover, edge-rich MoS$_2$ obtained for an electrolysis time of 1 min had higher activity compared to samples realized by longer electrolysis times, the higher HER activity being attributed to the edge-rich morphology of MoS$_2$.

NM01.15.52
A Comprehensive Study on Optimizing Conversion of Waste Plastics Using Diverse Catalysts, Carrier Gases, Flow-Rates and Pre-Treatment Methods into Nano-Carbons and Fuels
Aidin Panahi, Zixiang Wei, Guangchao Song, Xiao Sun, Chuanwei Zhuo and Yiannis A. Levendis; Northeastern University, Boston, Massachusetts, United States.

As a result of China’s recent ban on the import of most plastic waste, the US and other industrialized countries that have been exporting their plastic waste to China for recycling will need to find new ways to handle the disposal of their wastes as much of it is already starting to pile up in landfills. In research conducted at Northeastern University, plastic wastes have been thermally recycled by pyrolytic gasification to nano-carbons and gaseous fuel. To achieve this conversion, a laboratory-scale pyrolysis system were used to gasify polyethylene, polypropylene, polyethylene terephthalate, polystyrene, etc., and combinations of the same in inert (N$_2$ or He or Ar or CO$_2$) atmospheres with different flow rates (0.1-2 l/min). The plastic wastes were gasified in an electrically heated reactor at 600-800 °C. Under these conditions, the polymer pyrolyzed into a gaseous mixture of hydrocarbons and hydrogen. The pyrolyzate mixture was then conducted into a separate reactor where it was used as a carbon precursor for chemical vapor deposition process to synthesize carbon nanoparticles. The second reactor was set at 800-1000 °C. Different grades of stainless steel wire cloths (SS-304, SS-316 and SS-316L) were used as catalytic substrates for the nanoparticle growth. The wire cloths were used either as-received or upon chemical etching by acid wash and/or heat-treatment in air, nitrogen or helium at 800 °C, followed by rapid air quenching. In those cases, the yields were determined, by mass relative to the mass of carbon in the feedstock and ranged from 1% to 30%. With the purpose of purification and sorting, the catalysts and the produced Nano-materials were investigated for synthesis, structure and property characterization by SEM, TEM, AFM, TEM+EDX, HAADF and TGA. Results showed that the catalyst type, composition, and pre-treatment, as well as the type of plastic waste, are all influential on the yields and physical characteristics of the synthesized CNTs.

Keywords: Carbon Nanotube, Waste Plastics, Synthesis, Pyrolysis, Purification and Sorting

NM01.15.53
Investigation of Photocatalyzed Reduction of Technetium-99 Utilizing Titanium Dioxide, Graphene Oxide and Nanocomposites Thereof
Colleen B. Gallagher, 1, 2, Sam Groveseman, 1 Michele Vittadello, 1, 3 and Lynn Francesconi 1, 2 1 PhD Program In Chemistry, The Graduate Center of The City University of New York, New York, New York, United States; 2Department of Chemistry, Hunter College, New York, New York, United States; 3Department of Chemistry, Medgar Evers College, Brooklyn, New York, United States.

Water contaminated with highly toxic long-lived radionuclides is a growing concern in the US. These contaminants are introduced into water sources from the legacy wastes of nuclear sites, and from nuclear reactors. Technetium-99 ($^{99}$Tc) is one of the major nuclear waste contributors (~6% yield) generated from thermal neutron fission of uranium-235. It is considered a long-lived radioisotope with a half-life of 2.1x10$^4$ years and emits a weak beta with a maximum energy of 0.29 MeV. $^{99}$Tc is most prevalent in its oxidized form which predominantly exists as pertechnetate (Tc(VII)O$_4^-$). This contaminant is of concern in aqueous streams because of its inert nature that allows it to spread at nearly the same rate of water flow. To remediate $^{99}$Tc, reduction of pertechnetate has been the common approach because $^{99}$Tc is more reactive and less mobile when in a reduced state. The foundation of this work involved utilizing different functionalized nanomaterials as platforms to investigate the reduction and uptake of $^{99}$Tc. Titanium dioxide is a promising candidate as it has
Graphene and their derivatives graphene oxide (GO) and reduced graphene oxides (rGO) have been of great interest in technological device applications in nanoelectronics and bio-sensors. The advantage of easy processibility of GO thin films and its compatibility with existing technology motivates using the device physics and engineering of GO-based thin films for their practical applications. The simplest structure for studying electronic properties includes sandwiching the thin film between two metal electrodes and study behaviour of charge flow. Motivated with the initial observation of bistable resistive switching behaviour in Al(GO)(200°C)/ITO structure, this work is extended to demonstrate the influence of various metal contacts in GO thin film is interpreted using X-ray photoelectron spectroscopy and the role of these electrode materials in the electrical resistance in metal(M2)/GO(T)/metal(M1) device structures [with M1 = indium tin oxide (ITO), gold (Au), or aluminium (Al), and M2 = Al or Au] have been analysed. GO is synthesised by modified Hummers method. Thin films of GO are prepared by spin coating the dispersed solution of GO (1mg/mL) on metal substrate (M1= ITO, Al, or Au) followed by annealing at different temperatures, T= 100, 200, 300, and 400 °C. The materials, optical, and electrical properties are characterized for the GO powders and GO(T)/M1 thin films [3]. The top metal electrode (M2 = Al or Au) is formed by thermal deposition technique through shadow masking. Temperature dependent current-voltage (I-V) characteristics of resulting devices M2/GO(T)/M1 are measured using Keithley-4200 Semiconductor Analyser system. The temperature dependent resistance coefficients (α) estimate values of 4.2 x 10³ and 5 x 10³ in Al/GO/ITO and Au/GO/ITO device structures, respectively. The presence of Au and Al contents in depth profile XPS spectra of GO(T)/Au or Al) films metallic behaviour in the temperature-dependent electrical resistance through M2/GO(T)/Al or Au structures with the R0 equivalent to the corresponding substrate metal, indicate migration of atoms from Al or Au electrodes through the defect sites of GO till the other electrode and connects both the top and bottom electrodes the with formation of metal filament. The electrical resistance values indicates R Al/GO/ITO ≈ R Au/GO/ITO ≈ R GO/Al ≈ R GO/Au ≈ R GO/ITO ≈ R Au/GO(T)/Al ≈ R Au/GO(T)/Au in Al/GO(T)/Au and Al/GO(T)/Al devices show more conducting compared to R Au/GO(T)/ITO due to presence of more metal contents forming the filament within the GO layer between the top and bottom contacts. The Al(GO(T)/ITO device assists only the elemental metal atoms of Al to migrate through the GO and favors the provides uniform parameters during growth process, leading to growth of near identical filament structures between the electrodes and formation of contact interfaces at Al(GO(T) and GO(T)/ITO with identical thermal and electrical behaviors for all the interconnecting filaments.

Reference:

NM01.15.54 Influence of Contact Electrode in the Electrical Resistivity through Graphene Oxide Thin Films Pooja Saini1, Manjri Singh2, Surinder P. Singh2 and Ajit K. Mahapatro2; 1University of Delhi, Delhi, India; 2CSIR, NPL, Delhi, India.

Graphene and their derivatives graphene oxide (GO) and reduced graphene oxides (rGO) have been of great interest in technological device applications in nanoelectronics and bio-sensors. The advantage of easy processibility of GO thin films and its compatibility with existing technology motivates using the device physics and engineering of GO-based thin films for their practical applications. The simplest structure for studying electrical properties includes sandwiching the thin film between two metal electrodes and study behaviour of charge flow. Motivated with the initial observation of bistable resistive switching behaviour in Al(GO)(200°C)/ITO structure, this work is extended to demonstrate the influence of various metal contacts in GO thin film is interpreted using X-ray photoelectron spectroscopy and the role of these electrode materials in the electrical resistance in metal(M2)/GO(T)/metal(M1) device structures [with M1 = indium tin oxide (ITO), gold (Au), or aluminium (Al), and M2 = Al or Au] have been analysed. GO is synthesised by modified Hummers method. Thin films of GO are prepared by spin coating the dispersed solution of GO (1mg/mL) on metal substrate (M1= ITO, Al, or Au) followed by annealing at different temperatures, T= 100, 200, 300, and 400 °C. The materials, optical, and electrical properties are characterized for the GO powders and GO(T)/M1 thin films [3]. The top metal electrode (M2 = Al or Au) is formed by thermal deposition technique through shadow masking. Temperature dependent current-voltage (I-V) characteristics of resulting devices M2/GO(T)/M1 are measured using Keithley-4200 Semiconductor Analyser system. The temperature dependent resistance coefficients (α) estimate values of 4.2 x 10³ and 5 x 10³ in Al/GO/ITO and Au/GO/ITO device structures, respectively. The presence of Au and Al contents in depth profile XPS spectra of GO(T)/Al or Au) films metallic behaviour in the temperature-dependent electrical resistance through M2/GO(T)/Al or Au structures with the R0 equivalent to the corresponding substrate metal, indicate migration of atoms from Al or Au electrodes through the defect sites of GO till the other electrode and connects both the top and bottom electrodes the with formation of metal filament. The electrical resistance values indicates R Al/GO/ITO ≈ R Au/GO/ITO ≈ R GO/Al ≈ R GO/Au ≈ R GO/ITO ≈ R Au/GO(T)/Al ≈ R Au/GO(T)/Au in Al/GO(T)/Au and Al/GO(T)/Al devices show more conducting compared to R Au/GO(T)/ITO due to presence of more metal contents forming the filament within the GO layer between the top and bottom contacts. The Al(GO(T)/ITO device assists only the elemental metal atoms of Al to migrate through the GO and favors the provides uniform parameters during growth process, leading to growth of near identical filament structures between the electrodes and formation of contact interfaces at Al(GO(T) and GO(T)/ITO with identical thermal and electrical behaviors for all the interconnecting filaments.

NM01.15.55 Mechanical Assembling and Structuring Graphene Oxide Based Materials Jing Zhong; Harbin Institute of Technology, Harbin, China.

Mechanical Assembling and Structuring Graphene Oxide Based Materials
Jing Zhonga*,b
aSchool of Civil Engineering, Harbin Institute of Technology, Harbin 150090, Peoples’ Republic of China
bInstitute for Advanced Ceramics, Harbin Institute of Technology, Harbin 150080, China.

As a building block, graphene possesses intriguing mechanical, electrical, thermal property and chemical stability. Assembling graphene into macro-structures is very appealing, if those unprecedented properties can be inherited. However, it is the physical interaction between graphene nanosheets mainly control the performance of the assembled materials. On the other hand, it should be noted that graphene is probably the most anisotropic material that has even been discovered, as manifested by the prominent contrast of bending modulus (in the order of ~2kT) and tensile modulus (~1 TPa), as well as the ballistic electron transport in-plane and tunneling between-planes. Therefore, it is extremely important to improve the alignment of graphene nanosheets in the same direction and reinforce the interaction between them. Keeping this in mind, we propose to employ mechanical strategies, namely dead-end filtration and centrifugal casting, with the advantages of high efficiency, high yield and universal, to super-align and condense-compact graphene nanosheets, both of which result to materials with outstanding performance [1-3]. Finally, we will also illustrate that the combination of proper rheology properties of graphene oxide based ink and 3D printing technique, materials beyond 2D film with much more complex structures can be obtained.

Reference:

NM01.15.56 Functionalization of Graphene Thin-Film Surface by Using 2- (dimethylamino) ethyl methacrylate by Plasma Enhanced Chemical Vapor Deposition Method Furkan Turet and Mustafa Karaman; Chemical Engineering, Konya Technical University, Konya, Turkey.

The chemical reduction of graphene oxide is a promising route towards the large-scale production of graphene for commercial applications. Graphene is an atomic-scale honeycomb lattice made of carbon atoms. Due to its extraordinary mechanical, electrical, and thermal properties, graphene has potential applications in many fields. The reason of functionalize graphene with DEAEMA by using PECVD method is to enable the matrix to be form of composite with other chemicals. In this work, graphene oxide(GO) was synthesized from graphite by using modified Hummer’s method. Modified Hummer’s method according to other methods known in the literature; it is simpler and less costly in terms of processing steps. The synthesized graphene oxide was reduced with hydrazine hydrate to obtain a graphene. The obtained graphene was functionalized with amine group 2- (dimethylamino) ethyl methacrylate (DEAEMA) monomer by using plasma enhanced chemical vapor deposition (PECVD). Unlike other chemical vapor deposition methods, the PECVD method only polymerizes with the plasma that generated on the monomer surface without using an initiator in the system. To determine coating conditions; different reactor pressures, monomer flow rates, plasma powers and coating times were tested using PECVD method. Thickness of coating on surface was found by using profilometry, to characterize compounds FTIR and to determine surface morphology AFM analyses were used. As a result, the most efficient coating speed was determined as 69 nm / min. Functionalization of graphene studies were carried out under the determined optimum coating speed.
NM01.15.57
**Elastic Properties of Bulk and Low-Dimensional Materials Using van der Waals Density Functional**

Kamal Choudhary; National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

In this work we present a high-throughput first-principles study of elastic properties of bulk and monolayer materials mainly using the vdW-DF-optB88 functional. We discuss the trends on the elastic response with respect to changes in dimensionality. We identify a relation between exfoliation energy and elastic constants for layered materials that can help to guide the search for vdW bonding in materials. We also predicted a few novel materials with auxetic behavior. The uncertainty in structural and elastic properties due to the inclusion of vdW interactions is discussed. We investigated 11 067 bulk and 257 monolayer materials. Lastly, we found that the trends in elastic constants for bulk and their monolayer counterparts can be very different. All the computational results are made publicly available at easy-to-use websites: https://www.ctcms.nist.gov/~knc6/JVASP.html and https://jarvis.nist.gov/. Our dataset can be used to identify stiff and flexible materials for industrial applications.

NM01.15.58
**Hydrogen Storage in Ti Atoms Decorated Boron-Nitrogen Doped Graphene- Effects of Electric Field on Hydrogen Adsorption and Desorption**

Santhanamoorthi Nachimuthu and Jyh-Chiang Jiang; National Taiwan University of Science & Technology, Taipei, Taiwan.

In the last two decades, the significant efforts have been made to develop alternative energy sources instead of fossil fuels because of increasing CO₂ emissions and the environmental impacts. Besides, hydrogen has been concerned to be an ideal clean energy carrier among the other renewable energy sources because of its environmental friendliness. However, some challenges have to be addressed before hydrogen will become a conventional and commonly available energy carrier. Carbon-based materials such as graphene and carbon nanotubes have been designed for hydrogen storage due to their large surface area, lightweight, and tunable properties. Recently, we proposed a new strategy in which we considered three pure transition metal (TM) atoms or/and a combination of two TM atoms and one alkali earth metal atom (AEM) with high, medium and low hydrogen adsorption energies. These different metal atoms are used to decorate the Boron doped graphene sheet (BDG) and investigated their performance towards hydrogen storage capacity through spillover mechanism using first-principles calculations. Our results indicate that that the activation energies for H atom diffusion are much smaller, indicating that a fast H diffusion on this proposed surface can be achieved. These TM and AEM atoms decorated BDG surface can have the maximum hydrogen gravimetric capacity of 6.4% for double-sided adsorptions. To further achieve higher gravimetric density, in this study, we have considered Ti atoms decorated on the Boron and Nitrogen co-doped graphene surface (BNDG) because B–N pair is isoelectronic to the C–C pair. However, controlling the binding strength of metal atoms with that of the BNDG surface is an important issue in the application of hydrogen storage. The recent studies have shown that the binding strength between the metal atom and the substrate can be controlled by means of applying an external electric field. Thus, the effects of the external electric field, as well as the effects of applying point charges on the designed medium towards its hydrogen storage capacity, will be discussed. We have also explored the stability of the decoration of metal atoms on BNDG sheet at higher temperatures using molecular dynamics simulations.

NM01.15.59
**Multifunctional Laser Induced Graphene Composite Surface**

Duy X. Luong, Kaichun Yang and James M. Tour; Rice University, Houston, Texas, United States.

Fabrication simplification and multi-functionalization are keys for universalization/popularization of current nanomaterials in many fields. Laser Induced Graphene (LIG) is one of the promising candidates in this topic by its one step production with laser ablation of commercial Polyimide (PI) Kapton film under ambient environment and many of its exploding applications [1]. However, LIG potential for realistic applications is limited by the PI substrate it attaches on and its weak robustness. Here, we present two facile methods to fabricate LIG composite (LIGC) compatible with diverse materials that are “Swiss army knife” for multi-purpose applications. The first method is the materials infiltration. Herein, we are able to engineer the morphology of several LIGCs to superhydrophobic with contact angle > 160 degree. The LIGCs retain the conductivity of the LIG and is suitable for many Joule heating applications, including de-icing and thermal therapy. Stretchable and highly conductive LIGCs is used for resistive memory device substrate and strain sensor. Additionally, LIGCs in constructional materials also show anti-biofouling property. The second step is to systematically press the LIG onto the material surface by sanding. The combination roughness induced by both sand paper and LIG result in a stable superhydrophobic composite surface. By this simple method, we have been able to produce a number of superhydrophobic surface on commercial polymer with roll-off contact angle down to less than 1 degree. The LIGCS retain the conductivity of the LIG and is suitable for many Joule heating applications, including de-icing and thermal therapy. Additionally, LIGCS in constructional materials also show anti-biofouling property.

Keywords: laser induced graphene, nanocomposite, superhydrophobic, Joule heating, de-icing, thermal therapy, memory device, anti-biofouling.


NM01.15.60
**Molecularly-Linked Gold Nanoparticle Films Across the Insulator-to-Metal Transition—From Hopping to Strong Electron Correlations**

Monique Tie and Al-Amin Dhiri; Univ of Toronto, Toronto, Ontario, Canada.

Strong electron-electron interactions are widely believed to play a key role in a range of remarkable phenomena such as high Tc superconductivity among others. Strongly correlated electrons are often described by the Hubbard model, which captures important gross features of phase diagrams of strongly correlated materials. However, open challenges include experimentally mapping correlated electron phenomena beyond those captured by the Hubbard model.

We use both film thickness and electrolyte gating to study a metal-insulator transition in a new class of strongly correlated material, namely, nanostructured materials, using 1,4-butanedithiol-linked Au nanoparticle films as an example. On the insulating side of the transition, we observe Efros-Shklovskii variable range hopping and a soft Coulomb gap, evidencing the importance of Coulomb barriers. On the metallic side of the transition, we observe signatures of strong disorder mediated electron-electron correlations. Films near the metal-insulator transition also reveal a zero-bias conductance peak, which we attribute to a resonance at the Fermi level predicted by the Hubbard and Anderson impurity models when electrons delocalize and experience strong Coulomb electron-electron interactions.

NM01.15.61
**Biogas-Slurry Derived Mesoporous Carbon for Supercapacitor Applications—Harnessing Microorganisms to Circumvent Hydrothermal Treatment for Highly Porous Electrode Materials**

Ceril Kingondo¹, Enock T. Kibona² and Cecil King’ondu¹; ¹Botswana International University of Science and Technology, Palapye, Botswana; ²Department of Physics, Mkwawa University College of Education, University of Dar es Salaam, Iringa, Tanzania, United Republic of.
Surface area, pore texture and pore distribution have been shown to have a strong influence on capacitance. Therefore, hydrothermal treatment (HT) of the most common carbon source, biomass, prior to carbonization and activation has recently received heightened interest owing to its ability to deliver high surface area carbon nanomaterials with remarkable pore texture via deconstruction of cellulose polymeric network in biomass. Nevertheless, hydrothermal strategies involve high pressure and temperature and thus expensive. This study reports on circumventing HT in preparation of the carbon materials with outstanding mesoporosity for supercapacitor electrodes by use of biogas slurry. The deconstruction of cellulose polymeric network in this case is achieved by bacteria while the carbon source is still in the biodigester for biogas generation. In the study, pore structure and surface chemistry have been modified by altering activation time, temperature and KOH/carbon mass ratio. Mesoporous carbon materials are successively developed as evidenced by type IV isotherms obtained in nitrogen sorption studies. The materials afford BET, micropore and mesopore surface area of 515, 350, and 165 m² g⁻¹, respectively as well as a narrow pore width distribution of 3-4.5 nm. X-ray photoelectron results confirms the presence of functional groups of oxygen and nitrogen in the samples which facilitates the pseudocapacitance. The materials activated at 700 °C, 3:1 KOH to carbon mass ratio, and for 120 min exhibit high specific capacitance of 289 F g⁻¹ at a scan rate of 5 mV s⁻¹. Shortening activation time to 30 and 60 min reduces specific capacitance to 163 and 182 F g⁻¹, in that order respectively. Moreover, at 3:1 KOH to carbon mass ratio and 60 min activation time, specific capacitances of 170 and 210 F g⁻¹ at 600 and 800 °C, respectively are obtained. Moreover, specific capacitance increases with increasing the KOH to carbon mass ratio from 148 F g⁻¹ for 1:1 to 163 F g⁻¹ for 3:1 at 700 °C.

Electrochemical impedance spectroscopy studies demonstrate that the materials have high conductivity. In addition; capacity retention of 96% after 20,000 cycles is attained at a scan rate of 30 mV s⁻¹. The study shows that high performance electrodes can be designed from biogas slurry thereby eliminating the need for HT to get electrode materials with high surface area and porosity from biomass.

**NM01.15.62**
Hierarchical Carbon Nanostructures for Energy-Efficient Water Purification
Yuchen Liu, Shiren Wang and Ziming Zhang; Texas A&M University, College Station, Texas, United States.

In this presentation, we demonstrate a hierarchical carbon nanostructures for energy-efficient water purification. Specifically, 2D graphene nanosheets were intercalated with zero-dimensional fullerene nanocrystals, and a fixed interlayer spacing of ~1nm was achieved for tuning water passage. The resultant hybrids were stacked via epoxy adhesive and then the cross-sectional filtration of slaty water was investigated. The as-prepared GO/C60 membrane obtains a high water flux up to 10.85 L h⁻¹ m⁻² bar⁻¹ with a salty rejection of 89.66%, which is sufficient to purify brackish water into drinkable water. The energy consumption is as low as 0.775kWh/L, more than 20-fold less than commercial desalination process. Such hierarchical GO/C60 membrane exhibits long-term stability, and thus provides a great potential for energy-efficient water desalination.

**NM01.15.63**
Molecular Detection at Ultra-Low Concentration Using Potential Gradient Traps and Interlayer Coupling of Few-Layers MoS2; Payel Sen1, Dipanjn Nandi2, Hifion Ho3 and Manisha Gupta1; Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada; Electrical and Computer Engineering, University of Alberta, Edmonton, Alberta, Canada.

Single molecule detection has played an important role in monitoring of health and environmental conditions. Health monitoring efficiency depends upon detection of an immune response to pathogen, cell mutation, etc. at its early stages or low concentration. Traditionally, solid state nanopores are fabricated by photolithography, etching and TEM drilling. Here the concentration used for detection (4E-4%) implies a 10⁴-fold sensitivity improvement when compared with detection of translocation speed for a 5nm diameter pore on 4 layers (2.6nm) MoS2 compared to 50nm thick SiNx, indicating a clear sensitivity improvement.

Translocation experiments were conducted using 4E-4% IDT-ACTB1 and 60 mM KCl with SiNx and MoS2 pores, fabricated by photolithography, etching and TEM drilling. Here the concentration used for detection (4E-4%) implies a 10⁴-fold sensitivity improvement when compared with detection demonstrated in literature (0.1-1%). MoS2 is seen to detect 102 molecules per minute whereas SiNx detects 20 molecules per minute at the ultra-low concentration without any external trapping mechanism. Moreover, the greatest dwell times obtained in literature for DNA with the Molybdenum atoms at the nanopore. The increased negative-positive charge interaction creates an additional electrophoretic pull providing platform for effective capture and detection at very low molecular concentrations, without the usage of any external trapping mechanism.

Here, we have conducted simulation and experiments to compare the detection efficiency of SiNx and MoS2; nanopores for dilute samples. We simulated translocation of nucleotide homopolymers in COMSOL Multiphysics. Our simulations show a 30-fold conductance improvement and three times lowering of translocation speed for a 5nm diameter pore on 4 layers (2.6nm) MoS2 compared to 50nm thick SiNx, indicating a clear sensitivity improvement.

REFERENCES

**NM01.64**
Complementary Dual Channel Gas Sensor Devices Based on Role-Allocated Heterostructure; Garam Hae1,2, Woosook Song1, Sung Myung3, Jongsun Lim1, Sun Sook Lee1, Chong-yun Park1 and Ki-Seok An1; Korea Research Institute of Chemical Technology, Daejeon, Korea (the Republic of); Department of Physics, Sungkyunkwan University, Suwon, Korea (the Republic of).

Intriguing electronic properties of graphene related with massless Dirac Fermions have enabled the applications in highly sensitive gas sensors. However, it is widely recognized that the poor gas desorption behavior because gas adsorption occurs defective sites of graphene only. To overcome this insurmountable hurdle, we rationally designed hybrid films including ZnO thin films and CVD-grown graphene in order to combine advantages of ZnO thin films with reliable gas adsorption/desorption property related with their gas reaction mechanism and graphene with extremely high gas sensitivity originated from its exceptional electronic structure. The complementary dual channel gas sensor based on roll-allocated graphene-ZnO heterostructures, in which ZnO acts as a gas adsorption channel and graphene plays a role of carrier conducting path, was fabricated by combining atomic layer deposition, chemical vapor deposition, and polymer-assisted wet transfer techniques. The effects of ZnO top-layer thickness on the gas sensing properties of the hybrid films were explored. As a result, NO₂ sensitivity improvement of the optimized hybrid film-based gas sensor was achieved unambiguously as ~40 times higher than that of graphene-based gas sensors. Additionally, we systematically explored the electrical interaction between thickness-controlled ZnO thin films and graphene before and after gas adsorption to explain the correlation between charge transfer and gas sensing properties.
Graphene-based materials have received tremendous attention due to their excellent mechanical and electrical properties. Among them, graphene oxide (GO), which chemically exfoliated from graphite, is possible to solution process in aqueous solutions owing to having oxygen-containing functional groups on its basal plane and edges. Moreover, they have active sites for reduction of GO and covalent functionalization of GO with small organic molecules or inorganic nanomaterials. For these reasons, GO have been researched in many applications such as polymer composites, biomedical, and energy-related materials. In particular, Reduced graphene oxide (rGO) reduced by functionalized hydrazine from GO is promising alternative material to poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) as hole transport layer (HTL) in organic solar cells because it allowed the controllability of electronic properties through versatile functionalization and can improve the long-term stability of solar cells. However, rGO is difficult to apply in inverted organic solar cells because of limited dispersibility in alcohol based solvent such as 2-propanol (IPA). The rGO is usually dispersed in dimethylformamide (DMF), which melt the organic active layer. Therefore, more research is required about controlling the dispersibility of rGO while maintaining their electrical properties in order that rGO apply to inverted organic solar cells as a HTL via solution process. In this study, we introduced trifluoromethoxy group on the rGO surface (FMrGO) for controlling the dispersibility of rGO while maintaining their electrical properties. FMrGO is well dispersed in IPA and 2-ethoxyethanol due to the flexible methoxy groups. The structural, optical, and thermal properties of FMrGO was characterized by Infrared spectroscopy, EA, XPS, UV-vis spectroscopy and TGA and their work function was estimated by UPS. Finally, we introduced the FMrGO film as a HTL on the active film through solution process and investigated the effect of FMrGO on device performance and long-term stability of inverted organic solar cells.

Perfect absorbers have many application in different fields including photovoltaic, antireflective radar absorption coatings for defence, energy harvesting and emissivity control. Here, we design and fabricate a near perfect optical broadband absorber, having absorption capacity of 99.4% from 300 to 2000 nm wavelength range. Etched Silicon wafer is used as base layer to fabricate multilayered optically graded assembly, while carbon nano tubes layer used as a top layer for impedance matching. Subsequent layers are selected as per increasing refractive index and varying micro/nano features for efficient light trapping. Less than 1% of reflectivity in entire range up to 50° beam angle has been observed. Moreover multilayered assembly shows contact angle of more than 160° with roll-off angle of less than 5° which showed that it is not only a near perfect absorber but also a self-cleaning superhydrophobic surface. Conclusively, the properties of multilayered optically graded absorption impacts attractive applications of this superabsorber in the field of photovoltaic.
Spatially Resolved Solid-State Reduction of Graphene Oxide Thin Films for Anti-Fuses

Maica Morant-Miñana1, Klaus Mullen1, Dago De Leon2 and Kamal Asad1; 1Max-Planck Institute for Polymer Research, Mainz, Germany; 2CIC energiGUNE, Miñano, Spain; 3Delft University of Technology, Delft, Netherlands.

The current paradigms at both the industrial and research level produce reduced graphene oxide (rGO), an imperfect form of graphene, only in the bulk form. For a wide range of applications, from microelectronics to water permeation, spatially resolved and controlled reduction of GO in (thin-)film is needed. Such applications require a paradigm shift in the reduction process, which should be free from intentionally used auxiliaries such as electrolytes and high temperatures.

Reestablishment of electrical conductivity in GO, is (partially) obtained by reduction through high temperature treatment in a reducing atmosphere, or using strongly reducing chemicals or electrolytic processes. The reduction methods are suited for bulk graphene oxide. Spatially resolved reduction of thin films of graphene oxide is important for wide range of applications such as in microelectronics, where an electrolyte-free, room temperature reduction process is needed. We present spatially resolved solid-state reduction of graphene oxide thin films. We show that the reduction mechanism is based on electrolysis of water that is adsorbed on the graphene oxide thin film. The rGO is obtained at room temperature with spatial resolution simply by application of voltage. The reduced graphene oxide thin-films show sheet resistance of only several kΩm, with weak temperature dependence. Graphene oxide can be produced on a large scale and processed using low-cost solution casting techniques. Spatially resolved reestablishment of conductivity in GO can be used in electrically controlled water permeation or in micro- and nanoelectronic applications for instance as an anti-fuses.

Study of the Vibrational Properties of Linear Carbon Chains Encapsulated by CNTs at Low Temperature

Nathalia L. Costa1, Wellington Q. Neves2, Paulo T. Araujo1, Alexandre R. Paschoal1 and Antonio G. Souza Filho1; 1Physical, Universidade federal do Ceará, Fortaleza, Brazil; 2Instituto Federal de Educação, Ciência e Tecnologia do Ceará - IFCE, FORTALEZA, Brazil; 3Physics, The University of Alabama, Tuscaloosa, Alabama, United States.

Linear carbon chains, also known as carbynes, are essentially one-dimensional (1D) systems that present carbon sp hybridization. The research involving linear carbon chains has been a hot topic in recent years mostly due to their unique properties and potential for technological applications. These chains are highly unstable under ambient conditions, but the internal volume of the nanotubes offers ideal conditions for stabilizing such systems. Techniques of encapsulation by DCWNTs and MWCNTs have been successful to produce long linear carbon chains with lengths reaching several hundreds of nanometers. In this work, a systematic investigation has been conducted on linear chains of carbon encapsulated by double- (Cn@DWCNT) and multi-walled carbon nanotubes (Cn@MWCNT). Temperature studies in such materials are important for considering possible applications under extreme conditions (e.g. space and nuclear reactors). Our preliminary studies using low temperature Raman spectroscopy investigations of Cn@MWCNT-Bulk (300K at 20K) showed that the band frequency of the chains (~1,800 cm⁻¹) increased when the temperature was reduced. However the results seem to indicate an anomaly in the frequency behavior for temperatures below 60K, in which a decrease of the Raman frequency takes place with decreasing the temperature. We also observed that the frequency variations are reversible in the range of temperatures from 4K to 300K. To investigate this effect in detail, these studies will be conducted at the individual level. In other words, both Cn@DWCNTs and Cn@MWCNTs will be isolated and then investigated under low temperature. Dispersion of these materials has been successfully attained and isolated species have been confirmed by Atomic Force microscopy (AFM) measurements and Raman spectral features.

References

Elucidating Surface Wettability of Graphene by Locally Probing Its Surface Free Energy

ChiaYun Lai, Mariam S. Mansouri, Abdulrahman Al-Hagri, Harry Apostoleresi, Tuza Oluken, Chunyu Lu, Ibraheem Almansouri and Matteo Chiesa; Khalifa university, Abu Dhabi, United Arab Emirates.

Graphene, a one-atom-thick sheet of carbon atoms arranged in a honeycomb-like pattern lattice, has attracted much attention owing to its potential applications in the fields of electricity, conductivity, energy generation, batteries. Intensive recent studies report the wetting transparency of graphene, suggesting that the wettability of graphene is partially governed by the underlying substrate and is more hydrophobic with increasing the number of graphene layers. This infers that its surface energy is decreased with increasing the number of graphene layers. Amongst those studies, the static contact angle measurement is a highly employed method for characterizing the graphene surface wettability; however, this technique requires large scale surface coverage of graphene to contact the milliliter size of water droplet at the solid-liquid interface. This is rather challenging since one cannot precisely control the number of graphene layers at the contact line. This challenge is often ignored despite being the origin of the uncertainty in the measurements that have led to contradictory interpretations. In order to shade light to this controversy, we combine bimodal atomic force microscopy [1] and micro-Raman spectroscopy to measure the surface energy of the graphene surface on different substrates. It is well-known that the number of graphene layers can be determined by the ratio of 2D to G peak in the Raman spectra. Therefore, the graphene sample is fabricated by using a designed two-step chemical vapor deposition method, which has large enough area of monolayer, bilayer and multilayer of graphene on the substrate, respectively. This deposition enables us to precisely measure the same area of graphene sample by using AFM and micro-Raman spectroscopy. Our experimental results show that in contradiction with graphene wettability transparency theory, the derived graphene surface energy increases with increasing the number of graphene layers. We also use density functional theory to directly predict the surface wettability of graphene on different substrate based on [2] and obtain results that qualitatively agree with our AFM experimental characterization.

Enhancing Thermal Conductivity and Mechanical Performance of PL/PAUT Blends with Boron Nitride and Graphene

Xianghao Zuo1, Yuan Xue1, Frederick Nitta2, Jinhuan Tang3, Vicki Xu1 and Miriam Rafailovich1; 1Stony Brook University, Stony Brook, New York, United States; 2Henry M. Gunn High School, Palo Alto, California, United States; 3Mater Dei High School, Santa Ana, California, United States; 4Mission San Jose High School, Fremont, California, United States.

Thermal management is critical to the continually growing electronics industry to prevent devices from overheating and losing their functionality. As low-cost, lightweight, and highly versatile materials, polymers exhibit great potential for heat exchange applications, but their low thermal conductivity is a

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Thermal management is critical to the continually growing electronics industry to prevent devices from overheating and losing their functionality. As low-cost, lightweight, and highly versatile materials, polymers exhibit great potential for heat exchange applications, but their low thermal conductivity is a
barrier to their effectiveness. Additive fillers are usually added into polymers to help enhancing the thermal conductivity.

In this study, we investigated the thermal conductivity of blends of PLA (polylactic acid) and PBAT (polybutylene adipate terephthalate) with graphene nanoplatelets (GNPs) and hexagonal boron nitride (hBN). It is hypothesized that the thermal conductivity of the PLA/PBAT nanocomposite would be elevated when adding the fillers compared to neat polymer blends.

Contact angle measurements between polymer droplets on hBN and GNP layers deposited on a silicon wafers were used to determine the polymers’ relative affinities for the fillers. The calculation of the word of adhesion between fillers and polymers indicates that both hBN and GNP exhibited more affinity for the PBAT phase than the PLA phase, which means the fillers would be interspersed in the PBAT phase. PLA/PBAT blends with various concentrations of hBN powder and GNP were blended at 180 using a twin-screw mixer at 150 rpm. The thermal conductivity of PLA/PBAT and PBAT blends with hBN alone was tested at the beginning. Slow increase in thermal conductivity with increasing weight fraction of hBN was obtained. To better enhance the thermal conductivity, considering that we have demonstrated that with the larger size of the fillers which meet the size of the domain in the polymer matrix, they will have a better arrangement, we decided to apply Graphene H-5 in the blends to make some new attempts. The results show that as the GNP content of the nanocomposite relative to the hBN content, the thermal conductivity increased significantly. Then, the samples were molded into different sizes to test the impact and tensile properties. The mechanical data indicates that although the combination of hBN and Graphene can help increasing the thermal conductivity significantly, it is difficult to maintain the mechanical properties. Therefore, to enhance the thermal conductivity of the polymer blends with relatively high mechanical performance is a new challenge. We did mechanical tests separately with PBAT/PLA/hBN and PBAT/PLA/GNPs and found that hBN can better maintain the mechanical properties. Thus, we tried different ratios of hBN and graphene and kept the total amount of the filler at 30 wt%. The results show that even 3% of hBN can help maintaining the impact toughness at 83.62 J/m, which is pretty high value that meets the demand for most of the applications.

NM01.15.73
A Novel Non-Enzymatic PEDOT:PPS/GO/MnO2 Based Biosensor for Hydrogen Peroxide Detection in Biological Samples
Vedashree Sirdeshmukha 1, Shreshtha Mishra 1, Indrayani Kadu 1 and Anup A. Kale 1; 1College of Engineering Pune, Pune, India; 2Applied Sciences, College of Engineering Pune (COEP), Pune, India.

Hydrogen Peroxide (H2O2) is a well-known reactive oxygen species produced in various biological phenomena. In various pathological and physiological conditions, higher concentrations of H2O2 can cause lipid peroxidation, DNA base modification, protein degradation etc. H2O2 present in quantities of about 20-50 μM or more can have deleterious effects as it can easily dissolve in aqueous solutions and penetrate biological membranes easily. Hence, sensitive and selective detection of H2O2 is important under physiological conditions.

In this work, we report on a non-enzymatic electrochemical method for the facile and sensitive detection of H2O2. We explored the approach of conducting polymer-nanocomposite as efficient transducer platform. We synthesized three-phase composite polymer system of PEDOT:PPS/GO/MnO2, comprising poly(3,4-ethylenedioxythiophene): poly(styrene-sulfonate) (PEDOT:PSS), graphene oxide (GO) and manganese dioxide (MnO2). On being exposed to H2O2, MnO2 undergoes a redox reaction which is responsible for the sensing ability of this material. The composite was prepared using the conventional solution mixing method and then used to modify screen printed electrodes. The physicochemical characterization was carried out Scanning Electron Microscopy, UV-Visible Spectroscopy, Raman Spectroscopy and Fourier Transform Infrared Spectroscopy. Cyclic Voltammetry results showed that the nanocomposite showed high electrochemical activity for the detection of hydrogen peroxide (H2O2) in alkaline medium. The PEDOT/GO/MnO2 based electrode exhibits high sensitivity and selectivity for electrochemical detection of H2O2 with a sensitivity of 0.5uM. The present study demonstrates that such novel nanocomposite is promising for fabrication of non-enzymatic H2O2 biosensors. This method can further be explored for Point-Of-Care detection.

SESSION NM01.16: Device and Application II
Session Chairs: Esko Kauppinen and Y Ohno
Friday Morning, November 30, 2018
Hynes, Level 2, Room 208

8:30 AM *NM01.16.01
From Energy Harvesting to Living Plants—Concepts in Biosensing and Energy Conversion Using Carbon Nanomaterials
Michael Strano; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Our lab at MIT has been interested in how the 1D and 2D electronic structures of carbon nanotubes and graphene respectively can be utilized to advance new concepts in molecular detection, as well as energy generation. By taking advantage of the exceptional electronic properties of these nano-structures, we continue to discover potential application spaces where carbon can play an important role. For example, we have pioneered a novel technique called Corona Phase Molecular Recognition, or CoPhMoRe, for discovering synthetic, heteropolymer corona phases that form molecular recognition sites at the nanoparticle interface. By screening libraries of synthetic heteropolymers chemically adsorbed onto single-walled carbon nanotubes (SWNT), we have engineered new optical biosensors that exhibit high selective recognition for bio molecules, such as riboflavin, L-thyroxine, dopamine, nitric oxide, sugar alcohols, estradiol, and fibrinogen. These results have significant potential for using SWNT-based sensors to interface to biological systems, allowing monitoring pathways at the sub-cellular, cellular, tissue, and whole-animal scale. I will also highlight our recent efforts in initiatives we call “Plant Nanobionics”. There we use techniques to deliver and transport functional nanoparticles into living plants to grant them non-native functions. Our goal is to engineer plants to go to market with a large portion of the functions now performed by electrical devices. I will introduce the nanoparticle co-localization mechanism in a plant, and highlight some of our recent nanobionic plant prototypes including a light-emitting plant. Lastly, I will briefly describe several applications of carbon nanomaterials in the polymer science that have come out of our lab. There is a pressing need to find alternatives to conventional energy generation techniques, specifically those that rely on elements in finite global supply. We introduce Asymmetric Doping Cells (ADC), which convert chemical potential to electrical energy by means of spatially selective doping along a nanostructured conduct or particle. These ADCs have applications to energy harvesting from aqueous and organic solvents, as well as electro-catalysis for chemical synthesis. An inverse length-scaling of the maximum power as L−1.03 that creates specific powers as large as 30.0 kW kg−1 highlights the potential for macroscale energy generation. We also introduce carbon materials for the first time that enable the use of the thermal storage elements with high efficiency – the product of the thermal conductivity and heat capacity to the one half power. Thermal resonators base on carbon can harvest energy indefinitely from ambient thermal fluctuations of various frequencies, opening new possibilities for remote applications.

9:00 AM NM01.16.02
Overcoming Efficiency Limits of Carbon Nanotube-Laminated Metal-Free Perovskite Solar Cells Using 3D/2D FAPbX₃ harvesters
Il Jeon 1, Jin-Wook Lee 1, Vedashree Sirdeshmukha 1, Michael Strano 1; 1The University of Tokyo, Minato-ku, Japan; 2University of California, Los
Perovskite solar cells (PSCs) have progressed remarkably through a heated power conversion efficiency (PCE) race. With a surge of research efforts, the certified PCE of the lab scale PSCs increased to 22.7% for last 5 years. Now the research efforts are being focused on enhancing the durability of the devices and reducing the production cost. PSCs typically require a metal electrode is thermally evaporated on top to serve as a counter electrode. These top metal electrodes, however, are known to substantially increase the process and material cost as expensive gold or silver layers are deposited under high vacuum. Furthermore, the metal electrodes are found to be not robust enough to render long-term stability of the PSCs as the metal ions migrate into the bulk of the device under an operational condition to react with the active materials, thus degrading the device.

As an alternative to the metal electrodes, researchers have incorporated single-walled carbon nanotubes (CNTs) into the PSC system. The CNT is a favorable electrode material, owing to its hydrophobic nature, earth-abundance, and mechanical robustness. The application of CNT realizes CNT-based PSCs with good stability and versatility. Among the reported CNT-based PSC devices, aerosol-synthesized CNT top electrode (or back electrode) replacing metals in PSCs has shown the most promising potential. The application of CNT as the top electrode substantially enhances the stability of PSCs by removing the ion migration, and drastically reduces the fabrication cost as it can be easily deposited onto devices by a simple mechanical transfer. Despite such advantages, there are three factors limiting the PCE of the CNT top electrode-based PSCs that need to be addressed: 1) the work function of the CNT does not align with the perovskite, leading to loss in potential 2) CNT top electrode is less conductive than the metal counterparts, limiting the fill factor of the devices 3) the CNT back electrode is not reflective that the devices cannot maximize the light harvesting efficiency.

In this work, we addressed those three issues by engineering CNT electrode and photo-active layer. We tuned the work function of CNT electrodes and increased their conductivity by using a vapor-assisted doping of trifluoromethanesulfonic acid (TFMS). Furthermore, by incorporation of Cs-based 2D perovskite-added low bandgap formamidinium perovskite, we enabled the harvesting of long-wavelength light, enhancing the photocurrent of the devices. By combining these technologies all into one device system, CNT electrode-based PSCs produced a PCE of 17.6% with a JSC of 24.21 mA cm⁻², Voc of 1.005 V, and FF of 0.72. The obtained PCE is the highest among the values reported from CNT top electrode-based PSCs. Moreover, the resulting CNT-based PSCs exhibited higher high-temperature operational stability than those of the devices based on metal electrodes as well as conventional CNT electrodes. Since the global energy demands are rapidly increasing, energy harvesting from the environment has received much attention. Environmental energy sources such as sunlight, wind, vibration, heat, and flow have been exploited to various extents for electricity generation. Among them, water flow exists in various forms and has potential for developing electricity generators. The interface between flowing water and graphene also shows potential of electricity generation. The energy harvesting by flowing water along the interface of graphene has been studied. The mechanisms proposed to date are still not deterministic, however, surface conditions are key factors for the understanding of the physical mechanism and maximizing the performance. The surface conditions include electrical potential at the phase interface and wettability of graphene, both of which can be tuned by heteroatom doping. In this paper, the role of the surface condition of graphene on flow-induced electricity generation is investigated by heteroatom doping.

Nitrogen-doped graphene was used to investigate the role of surface condition on electricity generation. Characterization of the nitrogen doped graphene was carried out by x-ray photoelectron spectroscopy and Raman spectroscopy. In our typical experiment condition, at least 70 % of the doped nitrogen was graphitic nitrogen. Atomic concentration of nitrogen was approximately 1 %. The electricity was studied with transferred graphene and deionized (DI) water droplets by manually dropping the droplets (0.1 ml). Pristine graphene shows approximately 80 mV and the highest voltage from nitrogen-doped graphene was approximately 380 mV, thus more than 3 times higher voltage generation was observed. The enhancement of voltage generation by nitrogen doping is explained as follows. The electronic state of the nitrogen-doped sites is considered to have an important role. Nitrogen doping of carbon in various applications acts as an electron donor by providing the unshared electron pair of nitrogen in graphene. The local charge of graphitic nitrogen is positive and that of the surrounding carbon atoms is negative. This is explained by the electron transfer from nitrogen atom. The inside of the droplet sitting on top of graphene is affected by the negative charge on the graphene surface, leading to potential formation at the interface. The induced negative charge reduces electric double layer at the interface, resulting in the formation of steep potential[1]. We have investigated the effect of graphene doping on flow-induced power generation between graphene and water interface and found that the nitrogen-doped graphene shows enhancement of power generation. The surface charge of the nitrogen-doped graphene reduces the electric double layer thickness, resulting in the formation of a steep potential, which contributes to higher power generation.


Direct Conversion of Water Energy: From fundamentals to applications
Brian Landi; Rochester Institute of Technology, Rochester, New York, United States.

Macroscopic assemblies of carbon nanotubes (CNTs) in wire format have been prepared for a variety of applications including power and data transmission for both aerospace and terrestrial scenarios. Wires fabricated from CNTs have demonstrated superior flexure tolerance, weight savings, and corrosion resistance over their traditionally used metal counterparts. Current research is focused on translating the exceptional electrical properties of individual CNTs to bulk CNT wires through fabrication technologies like extrusion and densification, chemical doping, and metal-incorporated hybrids. In this talk, a summary of CNT conductors being advanced from high-purity laser-vaporized single wall carbon nanotubes (SWCNTs) as well as commercial CNT materials will be provided. Acid dispersion and extrusion of SWCNTs into a coagulant bath has been used to fabricate wires, with the coagulation dynamics shown to govern the resulting wire structure leading to electrical conductivities of 5.1 MS/m. Alternative approaches to enhance CNT electrical conductivity have been demonstrated using IBr chemical doping whereby low-dipole moment solvent systems favor the IBr-CNT interaction over the IBr-solvent and the solvent-CNT interactions. Recent work has also utilized densification and chemical doping with KAuBr₄ to improve the conductivity of commercially scaled CNT yarns by 6x, while increasing the current density at failure by 67% to 35 MA/m² in air. The thermal stability of KAuBr₄ is proposed to provide the greater electrical stability at elevated current levels. Lastly, site-selective copper nanometal seeding through chemical vapor deposition (CVD) has demonstrated as a viable electrodeposition method in concert with solution electrodeposition of bulk Cu to enhance the electrical conductivity of a low-density CNT roving. A Cu-CNT hybrid conductor has achieved a specific conductivity of 5632 Sm²/kg and electrical conductivity of 28.1 MS/m. A summary of high-current behavior and limitations to the current carrying capacity of these wires in air due to oxidative failure will be presented. Maximum current densities for SWCNT wires in a helium environment exceed fuse-law behavior for aluminum wires of equivalent diameter. The progress and opportunities for continued advancement of carbon conductors will be highlighted.
Tailoring Electronic Structure of SWCNTs for Transparent and Conductive Film Applications Alexey Tsapenko¹, Daria Kopylova¹, Alena Aleksceva¹, Fedor Fedorov¹, Evgenia Gilshteyn¹, Vsevolod Iakovlev¹, Pranod Rajanna¹ and Albert Nasibulin¹,²; ¹Skolkovo Institute of Science and Technology, Moscow, Russian Federation; ²Aalto University, Espoo, Finland.

Single-walled carbon nanotubes (SWCNTs) are among the strongest candidates for the replacement of commonly used transparent and conductive films (TCFs) based on doped metal oxides, such as indium tin oxide (ITO). SWCNTs possess unique multifunctional nature, which is based on their outstanding combination of mechanical strength and flexibility, chemical stability, exceptional electrical conductivity, and optical properties [1]. However, to fully utilize these properties in modern transparent electrode applications, SWCNT-based TCFs have to demonstrate the optoelectronic performance at the level of high-end ITO-based TCFs. This has not been achieved for SWCNT films yet and as a result limit their practical usage.

Using gold chloride as the most effective dopant for the SWCNTs, we improve their optoelectrical characteristics by optimizing the doping solvent and conditions [2]. We examined various solvents to push the optoelectrical performance of the TFCs based on SWCNTs. As a result, we obtained the sheet resistance as low as 40 Ω/sq at the transmittance of 90% (at 550 nm) using 15 mM HAuCl₄ solution. This optoelectrical performance is better than that of ITO on PET substrates and satisfy most of the requirements for modern applications and relatively stable without additional protection over two years storing under ambient conditions.

Also, we examine the effect of ionic liquid gating and plasma treatment on the electronic structure of the SWCNTs and their optical and electrical properties. The effect of the presence of catalyst particles on the optoelectronic properties of the SWCNT films is also presented. This work was supported by the Russian Science Foundation (Project identifier: 17-19-01787).

References:

11:00 AM NM01.16.06
Carbon Nanotube Networks of Tunable Thermal Conductivity Bogumila Kumanek, Grzegorz Stando and Dawid Janas; Silesian University of Technology, Gliwice, Poland.

Carbon nanotubes are widely regarded as very promising heat conductors. Although that is certainly true for individual carbon nanotubes [1-3], the situation is not that simple for carbon nanotube networks [4,5]. The way the heat is transported through the material is highly dependent on the carbon nanotube alignment, length, purity and other parameters. In fact, the influence is so strong that the spectrum of reported thermal conductivities for carbon nanotube networks ranges from thousands or hundreds of W/mK down to values lower than unity. In this contribution, we would like to show how careful surface modification enabled us to tune the thermal conductivity of the material. Free-standing carbon nanotube films of different composition and microstructure were manufactured and their thermal properties were measured by the previously reported method [6]. The results show a big potential of carbon nanostructures for a wide range of thermal management applications.

References:

11:15 AM OPEN DISCUSSION

11:30 AM NM01.16.08
Low-Power and Highly-Uniform Carbon Nanotube Integrated Circuits with Integration Capability to Biological Surfaces Li Xiang and Youfan Hu; Peking University, Beijing, China.

Devices and integrated circuits (ICs) with bio-integration capability can significantly expand functions of electronics, which is of growing interest in clinical and biological applications. Generally, intimate and conformal biotic/abiotic interface is an essential. However, as many efforts have been demonstrated for the bio-integration purpose, ICs, the core unit of electronic systems, are still lacking with certain complexity and low power consumption for in situ biological data computation and operation. The presentation will detail carbon nanotube based devices and ICs with both high uniformity and low power consumption that can be transferred onto biological surface, such as plant leaves, person’s wrists and biological polymers, and the wafer-scale platform demonstrated operation on a curved plant leaf. The carbon nanotube transistors exhibited ultralow power consumption with off-current as low as 0.1pAμm⁻¹, a subthreshold swing of 62 mVdec⁻¹, and static power consumption of 2.5 × 10⁻¹³ W was observed in an inverter. Meanwhile, with 80mV standard deviation in threshold voltages, the transistors demonstrated high-uniformity and could be used for IC construction. The most complex carbon nanotube based ICs on flexible substrates, such as a full adder with rail-to-rail outputs and a read-only memory were present driven by a small supplied voltage of 2 V.

Reference

11:45 AM NM01.16.09

We present lightweight copper-matrix carbon nanotube (Cu/CNT) composites [1-3] with electrical performances rivalling that of Cu as promising copper-substitutes. Our Cu/CNT composites, 2/3rd as light as copper, show room-temperature electrical resistivities as low as 3.3 × 10⁶ Ωm cm (~ twice that of Cu) with temperature coefficient of resistivity (TCR) values less than Cu, our Cu/CNT electrical resistivity exhibits higher temperature-stability than...
We also realized the differential amplifiers on a flexible plastic film. Bottom-gate CNT TFTs with purified semiconducting CNTs were used as the active charge equation in weak inversion characteristics was modified. The proposed model well expresses the output characteristics. The frequency dependence photochemically sensitized tissue, or communicate to neurons. That communicate responses optically, and possibly even implantable medical devices that emit light in response to sensor input to release drugs, destroy conductors operating at high temperatures, like motor windings. Meanwhile, our microscale Cu/CNT pillars with superior current- and temperature-stability could serve as better vertical interconnects than copper in high-power electronics, aiding miniaturization with increased functionality of next-generation devices.

References

SESSION NM01.17: Device and Application III
Session Chairs: Esko Kauppinen and Y Ohno
Friday Afternoon, November 30, 2018
Hynes, Level 2, Room 208

1:30 PM *NM01.17.01
Directed Assembly of Single Walled Carbon Nanotubes via Dielectrophoresis Saiful Khondaker; Nanoscience Technology Center, University of Central Florida, Orlando, Florida, United States.

Directed assembly of single walled carbon nanotubes (SWNTs) at the selected of the circuit in a massively parallel fashion is very important for many practical applications of SWNT-based devices. Our group have been using AC dielectrophoresis technique for the directed assembly of the SWNTs. In this talk, I will discuss the assembly of individual SWNTs from aqueous solution containing mixed SWNTs and 99% pure semiconducting SWNTs. I will also discuss the assembly of SWNTs in an aligned array with tunable density. Finally, I will discuss the assembly of semiconducting SWNTs as the channel material with metallic SWNTs as electrode. Different parameters relating to the controlling of the DEP assembly will be discussed. Detailed electrical transport properties of the DEP assembled devices will also be discussed.

2:00 PM *NM01.17.02
Flexible Carbon Nanotube ICs for Wearable Electronics—Device Modeling, Circuit Design Tools and Fabrication Yutaka Ohno; Institute of Materials and Systems for Sustainability, Nagoya University, Nagoya, Japan.

Wearable sensor devices have the potential to revolutionize preventive medical care and health promotion technologies. Carbon nanotube (CNT) thin films are promising electronic materials for transistors and integrated circuits [1-3], biosensors [4,5], and other passive components to build flexible and stretchable devices with excellent wearable and performance. Recently, high-yield and reproducible fabrication of CNT TFTs have become possible by using purified semiconducting CNTs, leading extensive study on circuit applications. An integration of analog circuits with a sensor is essential for wearable sensor devices to amplify the sensing signal as preventing external noise. A differential amplifier is a fundamental analog amplification circuit used for various sensor devices. In this work, we are focusing on the analog circuit application of CNT TFTs. To design CNT-based analog circuits, circuit simulation tools have been developed with a precise device model which has been built on the basis of electrical characterizations of CNT TFTs. We have realized differential amplifiers on a flexible and transparent plastic film. Device modelling is indispensable for circuit design. We built the RC-ladder device model based on the charge based model for CNT TFTs, where a correction of pinch-off condition was taken into account, considering the contact resistances between CNTs. In order to fit the subthreshold current, the charge equation in weak inversion characteristics was modified. The proposed model well expresses the output characteristics. The frequency dependence of capacitance-voltage characteristic was also built by considering the non-quasi-static effect in the MARY model. CNT-based analog or analog/digital mixed circuits such as differential amplifiers and analog/digital converters were designed by using the circuit simulation with proposed device model. We also realized the differential amplifiers on a flexible plastic film. Bottom-gate CNT TFTs with purified semiconducting CNTs were used as the active device. A differential output was obtained with respect to a differential input. Maximum voltage gain of 16.3 (24.3 dB) was achieved for a sinusoidal wave input of 100 mVpp at 100 Hz with a power source of -12 V. Figure 2 shows the gain as a function of frequency, exhibiting -20 dB/decay. The voltage gain cut-off frequency was 210 kHz.

Acknowledgments: The semiconducting CNTs were provided by TASC. This work was partially supported by JST/CREST.
Here, we describe and demonstrate light-emitting fibers based on carbon nanotube yarns with a unique planar device concept. The light-emitting fibers are water-sensory and easy to be knitted into textiles. The water-polar-electrode-bridged mechanism, light-emitting performance and water sensory properties are discussed. This study may open up a new direction in the development of visual sensing fibers and textiles for the next-generation soft electronics.

2:45 PM NM01.17.04

Stimuli-Responsive Carbon Nanotube Membranes for Protection from Chem/Bio Threats Chiatiai Chen1, Yifan Li2, Eric R. Moshot1, Nguo Bui1, Rong Zhu2, Myles Herbert7, Sei Jin Park1, Steven F. Buchsbaum1, Kuang Jen Wu2, Timothy M. Swager6 and Francesco Fornasiero3; 1Aalto University, Espoo, Finland; 2Skolkova Institute of Science and Technology, Moscow, Russian Federation; 3School of Chemical Engineering, Peking University, Beijing, People’s Republic of China; 4Engineering and Applied Sciences, Princeton University, Princeton, New Jersey, United States; 5Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; 6Institute of Physical and Theoretical Chemistry, ETH Zurich, Zurich, Switzerland; 7Livermore National Laboratory, Livermore, California, United States; 8Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Conventional protective garments are passive protection systems that sacrifice breathability (i.e., inhibit water vapor transport) to prevent exposure to harmful agents. This trade-off can lead to overheating in extended wear of protective clothing and severely hinders the duration of their active use. For instance, the field personnel protection from chemical and biological (CB) agents, smart dynamic materials are highly desirable that exhibit a reversible, CB-triggered, rapid transition from a breathable state to a protective state. Materials of this type are expected to be particularly effective in mitigating physiological burden because a less breathable but protective state can be actuated locally and only when needed.

To achieve adaptive protection and simultaneous thermal comfort, we have developed a chemical threat responsive material based on a surface-functionalized carbon-nanotube (CNT)-membrane, in which vertically-aligned CNTs function as the only pores in a polymeric barrier film. Upon exposure to a chemical warfare agent (CWA), responsive polymers grafted at the membrane surface collapse and close the CNT pore entrance to CWA permeation, thus enabling the membrane to switch from a highly breathable state to a protective state. To demonstrate this concept, we first fabricated membranes with sub-5 nm CNT pores and quantified their breathability and rejection properties before functionalization with CWA-responsive polymers. Our results show that these membranes provide MVTR up to 11,000 gr/m²/day, thus exceeding state-of-art breathable fabrics (eVent, GoreTex, etc.) even if the moisture conductive pores are only a few nm wide. Measured water-vapor permeability in 1.9-9 nm CNT channels under a relative humidity gradient is ~100 times larger than Knudsen diffusion prediction, and this flow enhancement decreases for larger diameter tubes. Complete rejection of 3-nm charged dyes, 5-nm uncharged gold nanoparticles, and ~40-60-nm Dengue virus from aqueous solutions during filtration tests demonstrate that our CNT membranes provide a high degree of protection from bio-threats by size exclusion.1

Then, we covalently grafted actuating polymers responsive to G-agent simulants to the surface of these CNT membranes.2-3 Upon exposure to simulants, these membranes switch from a breathable state with MVTR ~ 4,000 gr/m²/day to a protective state with MVTR ~ 1,000 gr/m²/day. Permeation tests reveal that the transition is reduced by ~1-2 orders of magnitude in the protective state. Finally, we demonstrated that a simple base treatment reopens the CNT pores effectively and that regenerated membranes can be re-used for multiple cycles without performance loss.


3:00 PM BREAK

3:30 PM NM01.17.05

Pt Lean and Fee Carbon Nanotube Based Electrocatalyst for Hydrogen Evolution Taneli Rajala1, Mohammad Tavakkoli1, Albert Nasibulin2, Esko Kauppinen1, Kari Lasuonen1 and Tanja M. Kallio1; 1Aalto University, Espoo, Finland; 2Skolkova Institute of Science and Technology, Moscow, Russian Federation.

Based on the recent IEA energy outlook, both solar and wind based energy supply will increase by more than one decade by the year 2040. Such drastic increase requires development of energy storage technologies, as their availability already now is considered forming the bottleneck for further adoption of renewables. Electrochemical water splitting in a membrane electrolysis cell is a promising technology for converting excess electrical energy into chemical bond energy, namely hydrogen bond energy. Hydrogen can serve as an energy carrier and connect energy sector to chemical industry and transportation sectors. In electrolysis cells, the water splitting proceeds via two half reactions: the hydrogen evolution reaction at the cathode (HER: 2H+ + 2e- → H2) and the oxygen evolution reaction met in the anode (OER: H2O → 2H+ + 2e- + ½O2). In electrolysis cells, the water splitting proceeds via two half reactions: the hydrogen evolution reaction at the cathode (HER: 2H+ + 2e- → H2) and the oxygen evolution reaction met in the anode (OER: H2O → 2H+ + 2e- + ½O2). In acidic membrane cells, scarce platinum group metals (PGMs) are recognized the expensive and scarce PGMs cannot cover the foreseen increasing need. Hence, earth-abundant element based durable electrocatalyst for the HER are badly needed.

Carbon nanotubes (CNTs) have several beneficial properties or electrocatalyzing. In addition to high conductivity and good stability, they have appropriate properties for fabricating 3D electrodes. CNTs can function as support for ultra-low-Pt electrocatalysts, or as a scaffold for synthesizing hybrid electrocatalyst materials comprising only of earth-abundant elements. The latter include doped CNTs as well as transition metal nanoparticles encapsulated in few carbon layers on CNT supports. These materials have inherently different activities towards the HER, but their activity can be also affected by selected synthesis method and starting materials resulting in products with different morphology, surface properties or conductivity, for example. The most active hybrid materials show similar activity to the commercial Pt/C catalyst and excellent durability under the HER conditions. In this presentation, CNT based electrocatalysts promoting the HER are introduced and their properties are discussed. These materials will promote implementation of durable and high-performing electrolysers.

4:00 PM NM01.17.06

Dirac Electrons in a Dodecagonal Graphene Quasicrystal Pilkington Moon1,2,4, Mikito Koshino3 and Young-Woo Son1; 1Arts and Sciences, New York University Shanghai, Shanghai, China; 2Department of Physics, New York University, New York, New York, United States; 3Department of Physics, Osaka University, Toyonaka, Japan; 4NYU-ECNU Institute of Physics at NYU Shanghai, Shanghai, China; 5School of Computational Sciences, Korea Institute for Advanced Study, Seoul, Korea (the Republic of).

Recently, we reported that a relativistic Dirac fermion quasicrystal can be realized when the Dirac electrons in a single-layer graphene are incommensurately modulated by another single-layer graphene which is rotated by exact 30° [1]. In this structure, the effective theory for moiré superlattices (i.e., twisted bilayer graphene at angles other than 30°) [3,4] no longer works, since bilayer graphene stacked at 30° gains a 12-fold rotational symmetry which is not compatible with a translation [5].

In this talk, I will discuss the theory of Dirac electrons in a dodecagonal graphene quasicrystal. I will first explain the emergence of the infinite number of Dirac cone replicas in ARPES and the contribution of multiple scattering to the unusually strong scattering signals [1]. Then, I will report a rigorous effective model which can describe the electronic structures of the graphene quasicrystal and show that very unique features, such as the critical states and
flat bands arise in this system [6].


4:30 PM NM01.17.07
Plasma Functionalized Defected Single-Walled Carbon Nanotubes as Promising Material for Gas Sensing Application
Alena A. Alekseeva1, Fedor S. Fedorov1, Daria S. Kopylova1, Stanislav Evlashin1, Anton Anisimov2 and Albert Nasibulin1; 1Skolkovo Institute of Science and Technology, Moscow, Russian Federation; 2Canatu, Moscow, Finland.

Mobile gas sensors operating at room temperature with low power consumption, high sensitivity and selectivity are required in many industries as well as in everyday life namely for detecting explosive, combustible and toxic gases, food and air quality monitoring. The main element of the gas sensor is its sensitive material which determines sensors’ sensitivity, selectivity, response time and signal recovery, operation temperature and stability. Single-walled carbon nanotubes (SWCNTs) is a unique material for gas sensors application. Coupled with chemical, thermal and mechanical stability, SWCNTs have large specific surface area with all carbon atoms located on their surface making them exceptionally sensitive for adsorption of gases at room temperatures. In this work we propose a simple approach of SWCNTs low frequency plasma treatment, which on the one hand introduce defects into the structure of nanotubes, which increases gas adsorption and thus increase sensitivity. On the other hand, it allows to obtain different functional groups on SWCNTs surface depending on the plasma atmosphere to increase selectivity of the material. In this study we investigate SWCNTs conductivity upon adsorption of inorganic gases such like carbon monoxide, nitrogen dioxide and ammonia, and assess the optimal operation temperature and gas concentration detection limits. Particularly, we present the study of oxygen plasma treated SWCNTs with induced defects and oxygen containing groups on its surface which increase SWCNTs sensitivity to such gases as carbon monoxide (respond is 0.5%), nitrogen dioxide (respond is 15%), ammonia (respond is 1.5%), hydrogen disulfide (respond is 0.8%) at room temperature. The authors acknowledge the Russian Science Foundation (project No. 17-19-01787).

4:45 PM NM01.17.08
All Solution-Processed p-n Junction Diodes
Daisuke Yamamoto1, Takayuki Arie1, Seiji Akita1 and Kuni Takei1, 2; 1Osaka Prefecture University, Sakai, Japan; 2JST PRESTO, Chiyoda, Japan.

Solution-based device fabrications are now of great interests due to attractive applications of printed flexible and stretchable electronics, which are required to form active components on an amorphous film using deposition and/or printing methods. However, due to difficulties of both p-type and n-type semiconductor formations on a film, most of the studies reported previously are based on Schottky diodes and transistors. To address this bottleneck and challenge, we here propose a solution-based p-n junction diode using developed IZO film and CNT network film formation and integration techniques as n-type and p-type semiconductor materials, respectively. Furthermore, barrier height between IZO and CNT films are also discussed based on the experimental results. p-n junctions were formed by all solution process on Si/SiO2 substrates. First, an IZO precursor was spin-coated on the SiO2 surface with oxygen plasma treatment. After spin coating, it was cured at 300 °C in air ambient. After patterning the IZO film, semiconductor-enriched CNT solution was deposited by using van-der Waals interaction between the chemical-treated SiO2/IZO surfaces and CNTs. After cleaning the substrate, Ag electrodes were painted on IZO and CNT films. Finally, the samples were annealed at 150 °C in N2. Transistor behaviors of IZO-Vgs using Ag source-drain electrodes and a global back gate were measured. IZO and CNT transistors shows relatively good n-type and p-type behaviors, respectively, with high ON/OFF current ratio of >104. Next, CNT/IZO p-n junction diode was characterized. Based on the results, good rectified behaviors with >106 forward/backward current ratio were observed. After confirming the diode behaviors, barrier height of IZO and CNT was determined by measuring the diode characteristics as a function of temperature. From the experimental results and calculations, the barrier height of them was ~200 meV, which is in good agreement with the theoretical band alignment of CNT and IZO. In conclusion, we developed p-n junction diode and analyzed the barrier height of CNT and IZO junctions. These material systems will be applied for the flexible devices in near future.