

## Poster Session 4

M1

### **Designer stabilizer for preparation of pristine graphene/polysiloxane films and networks**

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A designer polysiloxane-based stabilizer for graphene was used as the polymer matrix to prepare a highly conductive polymer film. To synthesize the stabilizer, 1-ethynylpyrene was grafted to the backbone of a poly (dimethylsiloxane)-co-(methylhydrosiloxane) random copolymer by Pt-catalyzed hydrosilylation with a SiH:ethynyl ratio of 1.0:1.3. Graphene was stabilized in chloroform through the  $\pi$ - $\pi$  interactions with the pyrene groups of the resulting copolymer. A graphene/polymer film was cast from the dispersion in chloroform. SEM and TEM images confirmed the homogeneous distribution of the graphene sheets in the film. The conductivity of this film with 4 wt% loading of graphene was measured to be 220 S/m, the first case of a melt-processable, conductive graphene/polymer film reported in the literature. When the ratio of SiH:ethynyl was changed to 1.7:1.0, the copolymer self-crosslinked at 110 °C and resulted in a direct production of a conductive graphene/silicon elastomeric composite. The crosslinking reaction was observed by FT-IR spectroscopy and the network formation was confirmed by swelling and extraction of the product.

## M2

### **High-performance carbon nanotubes reinforced aluminum matrix composites fabricated by friction stir processing and rolling**

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Aluminum matrix composites with significantly enhanced mechanical and physical properties are expected by using the carbon nanotube (CNT) as the reinforcement, due to its good mechanical properties (extremely high strength ~30 GPa, modulus ~ 1 TPa) as well as good electrical and thermal conductivity. However, it is a challenging task to individually disperse CNTs into the metal matrix due to the entangling or bundling of CNTs resulting from large aspect ratio and the strong Vander force. The CNT clusters in the CNTs reinforced metal matrix (CNT/metal) composites would reduce either mechanical or physical properties of the resultant composites. Individual dispersion of CNTs, relatively long CNT length and good CNT-metal interface bonding are the keys to obtain high-performance CNT/metal matrix composites.

In this work, 1.5-4.5vol.% CNTs reinforced 2009Al (CNT/2009Al) composites were fabricated by means of friction stir processing (FSP) technique and subsequent rolling, and subjected to detailed microstructural investigation and property evaluation. Firstly, the CNT/2009Al composites were fabricated by multi-pass FSP. Microstructural observations indicated that the CNTs were uniformly and randomly dispersed in the aluminum matrix after 3-pass FSP. The CNTs were cut shorter as the FSP pass increased and it was found that the reciprocal of CNT length exhibited a linear relationship with the number of FSP passes. The grains of the matrix were significantly refined due to the effective pinning of CNTs on the growth of recrystallized grains, and the grain size tended to stable after 3-pass FSP. The maximum strength of the composites was obtained with 3-pass FSP. This is attributed to the combined effect of CNT cluster reduction, grain refinement and CNT shortening.

Secondly, in order to align CNTs in the aluminum matrix, the FSP CNT/2009Al composites with randomly arranged CNTs were subjected to hot-rolling with a reduction of 80%. Microstructural observations indicated that CNTs were directionally aligned along the rolling direction in the composites after hot-rolling. The tube structure of the CNTs was retained and the CNT-Al interface was well bonded without pores after FSP and rolling. As a result, both the strength and modulus of the composites were significantly enhanced compared to the 2009Al and increased with increasing the CNT volume fraction. In particular, 3vol.% CNT/2009Al composite exhibited an ultimate tensile strength of 600 MPa and elongation of 10%, much higher than the corresponding values for CNT/Al composites fabricated by other processes.

## M3

### **Pristine Graphene/Polymer Hydrogel and Aerogel Structures**

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Graphene-polymer hydrogels and aerogels hold interest for both fundamental studies of graphene-polymer interactions as well as the production of nano-enhanced polymeric materials. Flexible, compressible, and self-healing pristine graphene/polymer hydrogels were synthesized via in-situ polymerization of the monomer in the polymer-stabilized graphene dispersion. The graphene sheets act as physical cross-linkers and permit gelation without the presence of any chemical cross-linker. Rheological measurements indicate that these physically cross-linked gels have higher storage modulus and toughness compared to the chemically cross-linked baseline. These gels are turned into conductive aerogels (or cryogels) by critical point drying or freeze drying. The aim is to create percolating composites with ultralow filler content by utilizing aerogels or cryogels as a conductive template. This is done by backfilling and polymerizing epoxy resin into the scaffold. The infusion of the resin does not disrupt the monolithic structure or conductive network. Three different aerogel systems (inorganic, organic and polymer aerogel) are investigated with both graphene and carbon nanotubes loading, with successful percolation in each case. A percolation threshold as low as 0.012 vol. % is obtained for graphene loaded organic aerogel/epoxy composite. This is the lowest reported threshold of any graphene based nanocomposites.

## M4

### **Large Area Electrospinning of Carbon Nanotubes for Advanced Composite Materials**

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With rising fuel costs, the demand for increased efficiency has led to the need for developing further advanced materials, which can deliver increased strength and reduced weight at the same time. Due to the low-weight, high-strength properties, and having the ability to take on multi-roles, such as charge storage, composite materials are increasingly becoming the material of choice in modern applications. In order to develop composite materials to meet the modern demands for applications, electrospinning was employed to produce arrays of highly-aligned SWCNTs. These nanotube arrays were seen to increase the properties drastically in a poly(ethylene oxide) (PEO) composite material, leading to an increase of tensile strength and ductility by a factor of 3 and the Young's modulus by a factor of 4. In addition to this a large area electrospinning rig was then designed and built, producing the World's first large area sheets of aligned carbon nanotubes.

## M5

### **Preparation of Graphene wrapped LiFePO<sub>4</sub>/C nanocomposites by Mild Solution Synthesis for Lithium Ion Batteries**

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To reduce the reaction time, electrical energy consumption, and free from high reaction pressure as well as unsafe condition, we reported an easy and efficient method for synthesis of LiFePO<sub>4</sub>/C/graphene. The cathode composite material was in situ fabricated in open system using microwave-assisted solvent treatment. The carbon-coated LiFePO<sub>4</sub> nanoparticles were 20-40 nm in size, and well dispersed on the surface of graphene, which helped limit the size of nanocrystals as well as facilitate the coating process. The microstructure and morphology of LiFePO<sub>4</sub>/C/graphene were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, Raman spectroscopy, field emission scanning electron microscopy, and transmission electron microscopy. The composite material could deliver a capacity of 157 mAh g<sup>-1</sup> (theoretical specific value is 170 mAh g<sup>-1</sup>) at 0.1C discharge rate and show a decay rate no more than 1% within 15 cycles.

## M6

# **Porous Micro-spherical LiFePO<sub>4</sub>/Graphene Nanocomposites with High Tap Density for High-performance Li-Ion Battery Cathode Materials**

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Due to many appealing features, such as long cycle life, high theoretical capacity (170 mAhg<sup>-1</sup>), low cost, and environmental friendliness, LiFePO<sub>4</sub> (LFP) has been considered as a promising cathode candidate for the next generation of LIBs. Yet the intrinsically low electronic conductivity, sluggish Li<sup>+</sup> transport and low tap density degrade the rate performance and energy density of LFP, and thus limit its further applications. As reported, uniform micro-sized spherical particles exhibit higher tap density, while suffering problems of both poor ionic and electronic conductivity. To solve the problems above, we developed a simple hydrothermal method followed by a high temperature chemical lithiation process to design and synthesize porous micro-spherical LFP/graphene nanocomposites (LFP/GNs). The nanocomposites are consisted of uniform LFP microspheres (~3 μm) with most of their primary particles (~100 nm) sandwiched between layers of graphene nanosheets. Mesopores (~25 nm) are widely existed in the microspheres. These structural features promise the LiFePO<sub>4</sub>/graphene nanocomposites with high tap density (1.56 g/cm<sup>3</sup>), good electronic conductivity and fast Li-ion diffusion rate. When studied as cathode material for Li-ion batteries, the nanocomposites show excellent high rate property. At 20 °C, the nanocomposites display high capacity of 118.2 mAh/g. Since the synthetic method is simple and easily to be scaled up, it is reasonable to claim that the as-designed LiFePO<sub>4</sub>/graphene nanocomposites are promising cathode materials for the next generation Li-ion batteries.

## M7

### **Epoxy composites with aligned assemblies of carbon nanotubes and high-performance carbon nanotubes fibres**

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Amongst the different forms of carbon materials, assemblies of aligned carbon nanotubes in the form of sheets or mats, yarns and fibres are particularly fascinating and promising materials, enabling the translation of the superior axial properties of carbon nanotubes into the functionality of polymeric composites.

This report, as a part of ongoing research, will provide perspectives of the utilization of carbon nanotubes fibres, synthesized by the direct single-step spinning process, in epoxy composites using a conventional impregnation technique.

Peculiarities of carbon nanotubes mats and fibres will be linked with practical issues for nanocomposites development and their characteristics. The mechanical and thermal properties will be discussed in terms of interaction mechanisms and compared those from composites filled with conventional PAN- and pitch-based carbon fibres.

## M8

### **Preparation of Single-Walled Carbon Nanotube/Ultrathin Cross-Linked Polymer Hybrids for Biomedical Applications and their Functionalization**

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Polymer hybrids with single-walled carbon nanotubes (SWNTs) are attracting increasing attention in biological applications due to their unique thermal, physical and optical properties. We developed a novel method to prepare SWNTs/ultrathin cross-linked polymer hybrids by the polymerization in the interior of surfactant micelle encapsulating around SWNTs. Here N-isopropylacrylamide was used as a monomer. This method provides the highly stable composite materials in aqueous solution upon heating, freeze-drying and the addition of a large amount of surfactant. This method also enables further functionalization to the composite materials by the utilizing a variety of monomers in cross-linked polymer around SWNT surfaces <sup>[1]</sup>.

[1]. Y. Tsutsumi, T. Fujigaya, N. Nakashima, RSC. Adv., 2014, 4, 6318.

## M9

### **Backside fluorine-functionalized graphene for gas detection**

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Graphene is a remarkable material due to its excellent mechanical strength and ultrafast electron transport. It has the best surface to volume ratio as a fact of its 2D nature, which implies that every atom can be considered as a surface one. These features make graphene attractive for use as a sensing material. A way to enhance the sensing properties of graphene is to create reactive centers on the surface by functionalizing graphene layers. We investigate sensing properties of reduced graphene fluoride C<sub>2</sub>F revealed on ammonia exposure. The degree of the C<sub>2</sub>F surface reduction was controlled by measuring the conductivity and evaluated by XPS analysis. We demonstrate the influence of the reduction degree on the sensor response supported by calculations done within the framework of a quantum-chemical approach.

We showed a possibility of detecting certain types of molecules in a gas phase and measuring their concentrations due to different responses of individual sensors to the molecules with different chemical structures. The sensor responses to electron donor (ammonia) and acceptor (nitrogen oxide) molecules have opposite signs and different response characteristic times.

## M10

### **Large Area Graphene Ion Sensitive Field Effect Transistors with Tantalum Pentoxide Sensing Layers for pH Measurement**

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We have fabricated and characterized large area graphene ion sensitive field effect transistors (ISFETs) using different pH buffer solutions. We use resistive and capacitive measurement of graphene's Fermi level versus changes in pH. Bare graphene devices are insensitive to changes in pH due to the absence of surface sites available to participate in the protonation and deprotonation process necessary for pH sensing. Deposition of a thin layer of Ta<sub>2</sub>O<sub>5</sub> by atomic layer deposition increases the density of surface sites, enhancing the buffering capacity of the sensing surface layer, thus increasing the sensitivity of graphene based ISFETs. We have achieved a linear pH sensitivity up to 32.5 mV/pH and we interpret our results using the Bergveld ISFET model. Device response is stable over ~ two weeks. We will report our recent work towards reaching the Nernstian limit of 60 mV/pH sensitivity.

## M11

# Impedance Spectroscopy of Epoxy Matrix Nanocomposites Reinforced with Graphene Nanoplatelets

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Impedance spectroscopy measurements have been carried out to evaluate the dispersion of graphene nanoplatelets in epoxy systems, and the effect on the bulk electrical conductivity and other dielectric properties. Graphene nanoplatelets (GP), produced from natural graphite by a modified Hummers method followed by chemical reduction, have been dispersed in epoxy resin based on diglycidyl ether of bisphenol A (DGEBA), by sonication, with or without the help of a solvent (tetrahydrofuran). The nanocomposites of epoxy matrix (DGEBA) reinforced with GP have been prepared in concentrations of GP up to 2.00 wt% by in situ polymerization and molded by casting directly on disposable measurement cells. The results obtained for cured nanocomposites show an increase on the conductivity with the current frequency, consistent with dielectric materials that present dipolar relaxation. Epoxy/GP nanocomposites show a behavior of imperfect dielectric materials, with conductivity increasing with frequency. It was also observed that using a solvent to help dispersion of GP into the epoxy resin can significantly influence the electrical properties of the nanocomposites. No electric percolation has been observed for nanocomposites with less than 1 wt% of GP. The specimens containing 0.75 and 1.00 wt% of GP presented bulk conductivity in the order of  $10^{-9}$  to  $10^{-8}$  S/m, while for 2.00 wt% the conductivity goes to over  $10^{-4}$  S/m, indicating dielectrical percolation. For this nanocomposite, two different behaviors can be observed. At relatively low frequencies (102 to 105 Hz) the conductivity increases monotonically with the frequency, while at higher frequencies (over 1 MHz) the conductivity increases abruptly, indicating interfacial polarization and percolation networks. It can be concluded that the conductivities of these specimens are due to conduction currents caused by percolating paths, which are independent of the frequency, and interfacial polarization, dependent of the frequency, but with lower amplitude interference.

## **M12**

### **Preparation and characterization of epoxy/graphene nanocomposite.**

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In the Study, graphene was first chemically modified with poly(sodium-p-styrenesulfonate) (PSS) and then mixed with epoxy resin to produce epoxy/graphene nanocomposite. The morphology, mechanical, electrical and thermal properties of the graphene nanocomposite were characterized by different methods, such as SEM, XRD, TGA etc.. The results show that the PSS modified graphene can easily disperse in epoxy materials and thus leads to an enhanced mechanical properties. The tensile strength also shows an increase with the addition of PSS-Graphene content.

## M13

### **Bulk Direct Band Gap MoS<sub>2</sub> by Plasma Induced Layer Decoupling**

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We report a robust method for engineering the optical and electronic properties of few layer MoS<sub>2</sub> based on a low energy oxygen plasma treatment. Gas phase treatment of MoS<sub>2</sub> with oxygen radicals generated in an upstream N<sub>2</sub>-O<sub>2</sub> plasma is shown to enhance the photoluminescence (PL) of few layer, mechanically exfoliated MoS<sub>2</sub> flakes by up to 20 times, without reducing the layer thickness of the material. In addition to removing surface contaminants, the plasma treatment enables partial intercalation of the interlayer spaces in few layer MoS<sub>2</sub>, thereby decoupling the electronic states in the individual layers, and causing an indirect to direct band gap transition. We study the effect of this soft oxygen plasma treatment on the MoS<sub>2</sub> layer thickness using atomic force microscopy (AFM) and Raman spectroscopy. Shifts in the plasmon peak in the electron energy loss spectra (EELS) indicate that the oxygen plasma process is accompanied by an increase in the density of valence electrons in the MoS<sub>2</sub>, due to the introduction of electron donor atomic species interspersed between the individual MoS<sub>2</sub> layers. With optimized plasma treatment parameters, we observed enhanced PL signals for 32 out of 35 few layer MoS<sub>2</sub> flakes tested, indicating this method is robust and scalable.

**M14**

## **Covalent and non-covalent functionalization of graphene by dip-pen nanolithography**

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The integration and patterning of biomolecules and biomimetic membranes on graphene has significant implications in biosensing, drug delivery and toxicology. We demonstrate the assembly of biomolecules on graphene and graphene oxide using dip-pen nanolithography, a direct-write technique with sub-100 nm resolution. In the case of non-covalent assembly, self-assembled biotinylated lipid membranes can be assembled on graphene. For the covalent case, the graphene is functionalised with biotin using click-chemistry under the dip-pen tip. In either case, the biotin functional groups remains active towards streptavidin binding. The functionalization, spreading and binding is imaged using AFM in liquid and air. We also show that there is charge transfer interaction between the biomolecules and graphene, through fluorescence quenching, Raman spectroscopy and electronic transport measurements.

## Graphenylene-based nanotubes

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The electronic properties of a new type of carbon nanotube based on the graphenylene motif were investigated using density functional and tight-binding methods. The structure of a graphenylene nanotube consists of six-membered as well as four-membered rings of sp<sup>2</sup> carbon atoms, with localized pi bonds fixed around the six-membered rings. As a result, these nanotubes exhibit three distinct bond lengths between carbon atoms. They also possess unique dodecagonal pores with ~5.4 Å diameter. Analogous to conventional graphene-based carbon nanotubes, a two-dimensional graphenylene sheet can be “rolled” into a seamless cylinder in armchair, zigzag, or chiral orientations. The resulting nanotube can be described using the familiar (n,m) nomenclature. Density functional theory-based calculations predict zigzag graphenylene nanotubes to be small bandgap semiconductors, with an increasing bandgap as the diameter decreases. Similar to traditional carbon nanotubes, zigzag graphenylene nanotubes with indices mod(n-m,3)=0 exhibit a smaller bandgap than other zigzag graphenylene nanotubes with comparable diameters. Interestingly, density functional calculations predict metallic behavior for armchair graphenylene nanotubes with small diameters (< 13 Å), and semiconducting behavior with a small bandgap for armchair graphenylene nanotubes with larger diameters.

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## **Carbon Nanospheres/Silicon/Alumina Hollow Structure as Anode for Lithium-Ion Batteries**

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Silicon is regarded as one of the most promising anode materials for next generation lithium-ion batteries due to its high theoretical capacity. However, poor capacity retention induced by pulverization of silicon and high irreversible capacity resulting from unstable solid-electrolyte interphase (SEI) formation during cycling hinder its practical applications. In this report, a carbon nanospheres/silicon/alumina (CNS/Si/Al<sub>2</sub>O<sub>3</sub>) hollow structure is fabricated to overcome the above issues. CNS thin film substrate is fabricated by the electrophoretic deposition technique, and amorphous silicon and a thin layer of Al<sub>2</sub>O<sub>3</sub> are then deposited. The CNS/Si/Al<sub>2</sub>O<sub>3</sub> hollow structure not only provides a conductive CNS 3D substrate, but also accommodates large silicon volume expansion due to the existence of void space provided by CNSs. Moreover, the electrochemical performance is further improved owing to the thin and stable SEI enabled by Al<sub>2</sub>O<sub>3</sub> layer and the efficient transport of electrons and lithium ions capacitated by the surface-to-surface contact mode. The electrode exhibits high specific capacity and remarkable capacity retention simultaneously: 1560 mAh/g after 100 cycles at current density of 1 A/g with retention of 84.8% and an average decay rate of 0.16 % per cycle. The superior battery properties are confirmed by cyclic voltammetry and impedance measurement furthermore.

## **2-D Solid State Hydrogen Molecules in Layered Structure Potassium Intercalated GO**

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Due to limited fossil fuels and carbon dioxide emission, we need to research green energy fuels for automobiles. There is promising unlimited resources known as, hydrogen, has high specific energy compared with petroleum, and also the combustion of product in Hydrogen Fuel Cell Vehicle (HFCV) is water vapor. However, there is drawback storage the hydrogen in high pressure owing to latent explosion hazards. Therefore, we study hydrogen storage in layered structure potassium intercalated graphite oxide (GO) at low pressure and room temperature to meet the practical application. The storage capacity of hydrogen was determined by quadruple quartz crystal microbalance (QCM) and BET measurement. The hydrogen storage with potassium intercalated GO reached  $\sim 2$  wt % at 5 atm and 300 K from QCM. BET total surface area ( $110 \text{ m}^2 \text{ g}^{-1}$ ), micropore volume ( $0.03 \text{ mL g}^{-1}$ ), and mesopore volume ( $0.4 \text{ mL g}^{-1}$ ) were confirmed in the bulk state of material. Our potassium intercalated porous graphite oxide has possibility for promising hydrogen storage to meet the U.S Department of Energy target.

## **Chemical Route for Graphite Nanoplatelets**

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Since graphene shows promising properties, researchers have explored intensively different routes for its mass production in order to make it for application fields available. Two most feasible methods for preparation of graphene are chemical vapor deposition (CVD) and “hummer oxidation reaction”. While CVD method delivers direct graphene with large lateral size and good qualities for optical and electrical applications, the graphene oxides from the oxidation routes have to be reduced first. The non-attached graphene layers in liquid need to be stabilized by chemicals in order to prevent restacking again into non-crystalline graphite. Although the oxidation and the reduction steps both work well, the quality of the product suffers due to the aggressive reactants.

An alternative approach is the intercalation reaction of graphite with electron donors or acceptors. In case of the graphite intercalation with electron donors like alkaline metals, the alkaline metal transfers electrons into graphite. Due to the negative charge, the layer distances become larger and the separation of graphene from the stack is relieved. By this method we could obtain single graphene layers and also tiny graphene multi layers. However, in solution graphene layers are unstable and restack into multi layers or fold into crumpled graphene. By chemical stabilization, the restacking of multi layers was prevented. The results were verified by Raman and AFM measurements.

## **Carbon nanotube/polyaniline nanocomposites applied as gas sensor device for NH<sub>3</sub>**

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In this work we study the characteristics of gas sensors devices based on carbon nanotube/polyaniline (CNT/PANI) nanocomposites. The sensor device is based on an active layer film of CNT/PANI with primary doping using H<sub>2</sub>SO<sub>4</sub> and applied to detect some kind of acid vapor, and another secondary doping using camphorsulfonic acid and m-cresol, applied to organic vapor detection, by self-assembled method, deposited on a chromium/gold (Cr/Au) interdigitated electrode, achieved by common photolithography. Keeping constant the amount of CNT and varying the amount of aniline at the polymerization. A total of four ratios were synthesized, each proportion doped in three different ways. Morphological analyzes (SEM and AFM) indicated the film formation, the increase of the irregularities and roughness with the increasing amount of PANI in the composite. Electrical analyzes of devices based on these composites showed a high sensitivity (values up to 418.50±43.50%), low response times (minimum values of 75.00±15.50 s) and low recovery times (minimum values of 378.50±24.50 s) to 1,000 PPM of ammonia in air.

Acknowledgments: This work was supported by CNPq, CAPES, Fundação Araucária - PR and INCT- Nanomateriais de Carbono.

## **Near-band edge optical properties of h-BN: from bulk to nanolayers and nanotubes**

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h-BN is a wide band gap semiconductor (6.4 eV), which can be synthesized, as graphite, its carbon analog, as bulk crystallites, nanotubes and layers. These structures meet a growing interest for deep UV LED and graphene engineering. In this talk, we will review the interplay between the structure, defects and luminescence properties of different BN structures and how these properties can be further exploited for their characterization. To this aim, we carry out optical and structural characterizations by combining Photoluminescence (PL), cathodoluminescence (CL) measurements at 4K in the UV range (up to 7eV) using dedicated experimental sets-up <sup>[1, 2]</sup> and TEM analyses using HRTEM, diffraction contrast imaging, electron tomography and Energy Loss spectroscopy (EELS).

We first examined properties of high quality single crystals <sup>[3]</sup>, and have shown that their optical properties are governed, in the energy range 5.5 – 6 eV, by strong excitonic effects <sup>[1, 4]</sup>, which have been confirmed by reliable theoretical calculations <sup>[5, 6]</sup>. Near band edge luminescence consists of two series of lines called S and D <sup>[2, 4]</sup>. PLE experiments indicate that binding energy of S excitons is equal to 370 meV, whereas the gap is measured to be equal to 6.4 eV <sup>[7]</sup>. Furthermore S excitons are found to be self-trapped, due to a Jahn-Teller effect <sup>[3, 7]</sup>. Thanks to the imaging capability of the CL, emission related to D lines, is found to be localized on defects, such as grain boundaries or stacking faults. In defect free areas, D lines completely vanish and S lines only are observed. D/S ratio can therefore be used as a qualification parameter of the defect densities present in the material <sup>[1]</sup>. This procedure has been applied to understand the first luminescence studies of few layers individual BN flakes obtained by mechanical exfoliation <sup>[1]</sup> and has revealed that the luminescence is significantly perturbed by the exfoliation process.

Second, we have studied multi wall nanotubes made of typically 10 to 20 layers <sup>[8]</sup>. CL images reveal that the luminescence in the 5.5 – 6eV energy range is strongly inhomogeneous and oscillating. Thanks to a deep investigation combining different TEM techniques, we have shown that the tubes display a complex twisted faceted structure and that the twist period is correlated with the luminescence oscillations. Furthermore, we could show that excitons, responsible for the spectacular localization of the luminescence, are trapped to specific defects, twisted along with the faceting structure.

Finally, low-loss EELS providing an alternative approach to the nature of electronic excitations<sup>[9]</sup>, we will show how it is an efficient tool to investigate the local structure and optical properties with an energy resolution below 100meV of different BN layers and nanotubes.

Acknowledgements: The research leading to these results has received funding from the European Union Seventh Framework Programme under grant agreement n°604391 Graphene Flagship. D. Golberg, T. Taniguchi and K. Watanabe from NIMS, Japan, are warmly acknowledged for providing samples (Nanotubes and HPHT single crystals).

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## **2-D hybrids of graphene and single-walled carbon nanotube**

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Graphene and single-walled carbon nanotube have shown superior potential in nanoelectronics due to their excellent thermal, mechanical, electronic and optical properties. A simple method has been developed to fabricate ultra-thin graphene/single-walled carbon nanotube hybrids through chemical vapor deposition. Unlike large-area single-layer chemical vapor deposition graphene, these novel hybrids can float on the surface of water during transfer process without such polymer like PMMA as a support membrane. This 2-D material possesses good electrical conductivity and optoelectronic properties via scanning photocurrent measurement. The network in photocurrent response reflects the junction area of graphene and single-walled carbon nanotubes, which is also observed by transmission electron microscope. The introduction of single-walled carbon nanotube network into graphene plane can alter graphene morphology in 2-D, which develops promising graphene structure for future application in energy storage and optoelectronics.

## **Electrical properties and crystallization behavior of poly(ethylene terephthalate)/multiwall carbon nanotube nanocomposites**

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Nanostructuring of polymers has opened up new perspectives for multi-functional materials [1-3]. In this paper we report on the poly(ethylene terephthalate) (PET) based nanocomposites prepared with four different types of multi-walled carbon nanotubes (MWNT) through a coagulation method. The electrical conductivity study demonstrates that MWNT of 30-50 nm diameter possess the best electrical conductivity. The composites of 1 wt% MWNT in PET had a electrical resistance of 109  $\Omega$ . The morphology of nanocomposites was characterized using scanning electronic microscopy (SEM). A coating on MWNT by PET chains was observed by comparison of micrographs of raw MWNT, and this coating was considered as evidence of interfacial interaction between MWNT and PET chains. The MWNT of 8 nm diameter possess the best interfacial interaction. Crystallization behavior of PET nanocomposites was studied by differential scanning calorimetry (DSC). The very small amount of MWNT displayed a great nucleating effect on the PET crystallization. The crystallization temperature was improved for around 40 °C by using only 0.1 wt % MWNT owing to MWNT decreased chain mobility of PET. The thermal stability of PET nanocomposites was improved by adding MWNT as well.

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## **Raman Enhancement Effect on Two-dimensional Layered Materials: graphene, h-BN and MoS<sub>2</sub>**

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Realizing Raman enhancement on a flat surface has become increasingly attractive after the discovery of graphene enhanced Raman scattering (GERS). Two-dimensional (2D) layered materials, exhibiting a flat surface without dangling bonds, were thought to be strong candidates for both fundamental studies of this Raman enhancement effect and its extension to meet practical applications requirements. Here, we study the Raman enhancement effect on graphene, hexagonal boron nitride (h-BN) and molybdenum disulfide (MoS<sub>2</sub>), by using the copper phthalocyanine (CuPc) molecule as a probe. This molecule can sit on these layered materials in a face-on configuration. However, it is found that the Raman enhancement effect, which is observable on graphene, hBN and MoS<sub>2</sub>, has different enhancement factors for the different vibrational modes of CuPc, depending strongly on the surfaces. Higher frequency phonon modes of CuPc (such as those at 1342, 1452, 1531 cm<sup>-1</sup>) are enhanced more strongly on graphene than that on h-BN, while the lower frequency phonon modes of CuPc (such as those at 682, 749, 1142, 1185 cm<sup>-1</sup>) are enhanced more strongly on h-BN than that on graphene. MoS<sub>2</sub> demonstrated the weakest Raman enhancement effect as a substrate among these three 2D materials. These differences are attributed to the different enhancement mechanisms related to the different electronic properties and chemical bonds exhibited by the three substrates: (1) graphene is zero-gap semiconductor and has a non-polar C-C bond, which induces charge transfer (2) h-BN is insulating and has a strong B-N bond, while (3) MoS<sub>2</sub> is semiconducting with the sulfur atoms on the surface and has a polar covalent bond (Mo-S) with the polarity in the vertical direction to the surface. Therefore, the different Raman enhancement mechanisms differ for each material: (1) charge transfer may occur for graphene; (2) strong dipole-dipole

coupling may occur for h-BN and (3) both charge transfer and dipole-dipole coupling may occur, although weaker in magnitude, for MoS<sub>2</sub>. Consequently, this work studied the origin of the Raman enhancement (specifically, chemical enhancement), and identifies h-BN and MoS<sub>2</sub> as two different types of 2D materials with potential for use as Raman enhancement substrates.

## **Polystyrene - Poly(3-thiophene acetic acid)/MWCNT Composite Fibers by Electrospinning for Actuator Devices**

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Carbon nanostructures such as multiwalled carbon nanotubes (MWCNT) improve the electrical and mechanical performance of actuators of poly(3-thiophene acetic acid) (PTAA) composites. In this work, an electrospinning (ES) process was used to produce very thin (sub-micrometer) fibers of polystyrene (PS) on a conical-collector-system electrode, as a support. These non-woven fiber fabrics were then covered with PTAA composites by casting, and used as an electromechanical actuator, electrospun films of mixtures of PS-PTAA-MWCNT were also produced for comparison. The PTAA composites were obtained by functionalizing MWCNT with hydroxylated thiophene linker (thiophene-3-ethanol) (th-MWCNT) <sup>[1]</sup> for a better interaction with PTAA, followed by in situ polymerization of 3-thiophene acetic acid <sup>[2]</sup>. The reaction was carried out under nitrogen, with a 4:1 mole ratio of FeCl<sub>3</sub> to thiophene monomer. The response of actuators was evaluated as function of content of th-MWCNTs (~1, ~3, and ~5 wt. %) in composites. The composite fibers were characterized electrically (DC and AC measurements) to study percolation threshold of fillers and dielectric changes due to th-MWCNTs filler and conducting polymer load as function of content of PS.

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## **Effect of Different Carbon Nanostructures as Reinforcements on the Performance of Polyaniline Actuators**

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Four nanostructured carbon materials (multi-walled carbon nanotubes, MWCNT; nitrogen-doped MWCNT, CNx; helicoidal-ribbon carbon nanofibers, HR-CNF; and graphene oxide platelets, GO, from CNF) were used to reinforce polyaniline (PAni) in electromechanical bilayer bending actuators. These devices are based on the macroscopic expansion/contraction of PAni by reversible redox processes. Films of PAni-nanocarbon composite, processed with N-methylpyrrolidone (NMP), attached to a cellophane film were tested in a liquid electrolyte cell system. Experimental design was used to select type of nanocarbon filler and composite loadings that showed a good balance of electromechanical properties. Raman spectroscopy suggests good interaction between PAni and the nanocarbon fillers. Electron microscopy showed best nanofiller dispersion for graphene oxide, followed by MWCNT. CNx composites showed dispersion problems and thus poorer performance. MWCNT composite actuators had a better combination of bending angle, bending velocity and maximum working cycles (measured considering nanofiller loading and applied voltage), with GO the second best in regards to working cycles.

## **Supercompressible Porous Foam Network made of Single-Walled Carbon Nanotubes coated with Graphene**

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Lightweight, cellular solids or foams with elasticity and resilience even under large cyclic strain have been considered attractive materials for use as dampers, thermal cloaks, heat sinks, electrochemical electrodes, and sieves. Single-walled carbon nanotubes (SWCNTs) have excellent mechanical, electrical, thermal properties including high aspect ratio ( $>1,000$ ). The combination of the properties enables the nanotubes to use in building multifunctional lightweight foams. However the pristine carbon nanotube foams are physically fragile and undergo significant plastic deformation due to the weak van der Waals attractive force between the nanotubes when they are subjected to large cyclic compressive strain.

Here we will show the fabrication of SWCNT based foam networks and their mechanical improvement by coating graphene nanoplates around CNT-CNT junctions <sup>[1]</sup>. We have first produced individually dispersed SWCNTs in water using an anionic surfactant, sodium dodecyl benzene sulfonate (NaDDBS). We have then created aqueous elastic gels from these SWCNT dispersions to fabricate ultra-light-weight, electrically conducting and thermally insulating but mechanically fragile three-dimensional SWCNT foams. The introduction of the graphene layers on the nanotubes has been achieved via polyacrylonitrile (PAN) coating followed by the pyrolysis process at 1050 °C in Ar. The graphene-coated aerogel exhibits no change in mechanical properties after more than  $1 \times 10^6$  compressive cycles, and its original shape can be recovered quickly after compression release. Moreover, the graphene coating does not affect the structural integrity or the compressibility and porosity of the nanotube network. The coating also increases Young's modulus and energy storage modulus by a factor of  $\sim 6$ , and the loss modulus by a factor of  $\sim 3$ .

## **Scalable synthesis of hierarchically structured carbon nanotube-graphene fibers for capacitive energy storage**

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Micro-supercapacitors are promising energy storage devices that can complement or even replace batteries in miniaturized portable electronics and microelectromechanical systems. Their major limitation, however, is the low volumetric energy density when compared to batteries. In this work, we describe a hierarchically structured carbon microfibre made of an interconnected network of aligned single-walled carbon nanotubes with interposed nitrogen-doped reduced graphene oxide sheets. The nanomaterials form mesoporous structures of large specific surface area ( $396 \text{ m}^2 \text{ g}^{-1}$ ) and high electrical conductivity ( $102 \text{ S cm}^{-1}$ ). We develop a scalable method to continuously produce the fibres using a silica capillary column functioning as a hydrothermal microreactor. The resultant fibres show a specific volumetric capacity as high as  $305 \text{ F cm}^{-3}$  in sulphuric acid (measured at  $73.5 \text{ mA cm}^{-3}$  in a three-electrode cell) or  $300 \text{ F cm}^{-3}$  in polyvinyl alcohol (PVA)/ $\text{H}_3\text{PO}_4$  electrolyte (measured at  $26.7 \text{ mA cm}^{-3}$  in a two-electrode cell). The full micro-supercapacitor with PVA/ $\text{H}_3\text{PO}_4$  gel electrolyte, free from binder, current collector and separator, has a volumetric energy density of  $\sim 6.3 \text{ mWh cm}^{-3}$  a value comparable to that of 4V-500 Ah thin-film lithium batteries while maintaining a power density more than two-order of magnitude higher than that of batteries and a long cycle life. To demonstrate that our fibre-based, all-solid-state micro-supercapacitors can be easily integrated into miniaturized flexible devices; we used them to power a UV photo-detector and a light-emitting diode.

Reference: Nature Nanotechnology, 2014, accepted

## **Preparation of highly active nitrogen-doped few-layer graphene/carbon nanotube composite electrocatalyst for oxygen reduction reaction in alkaline media**

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We report the synthesis and electrochemical investigation of nitrogen-doped few-layer graphene/multi-walled carbon nanotube (FLG/MWCNT) composite catalyst for oxygen reduction reaction in alkaline media. In search for the best electrode material, composites were prepared from two different nitrogen precursors with addition of acid-treated MWCNTs and graphene oxide (GO) to increase conductivity and surface area. The composite materials were prepared by single step process by pyrolyzing in flowing argon atmosphere at 800 °C. The N-doped composite catalyst samples were characterized by scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy, the latter method revealed successful nitrogen doping. The oxygen reduction reaction (ORR) was studied in 0.1 M KOH on glassy carbon electrodes modified with N-doped FLG/MWCNT electrocatalysts employing the rotating disk electrode (RDE) method. The RDE results indicated that these metal-free nitrogen-doped nanocarbon catalysts possess remarkable electrocatalytic activity towards the ORR in alkaline media similar to that of commercial Pt/C catalyst. The results obtained in this work are particularly important for the development of non-Pt cathode catalysts for alkaline membrane fuel cells.

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## **Photoluminescence study of tungsten disulfide grain boundaries**

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Novel photoluminescence (PL) peak has been observed at the grain boundary of tungsten disulfide known as one of the true two dimensional (2D) semiconductor materials. Detailed atomic force microscopy and PL intensity mapping measurements show the novel peak appears only from the grain boundary region. Temperature dependent PL measurements also revealed that the novel peak can be divided into two types (type 1 and type 2) as a difference of peak energy and these can be assigned as peak of neutral excitons weakly and strongly bounded at the grain boundaries, respectively. This finding is important for the future optoelectrical applications of 2D atomic sheet with grain boundary engineering, which is one of the geometrical standpoints of 2D atomic sheet materials.

## Transition metal dichalcogenide film transistors

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Recently, TMDC monolayers, such as MoS<sub>2</sub>, MoSe<sub>2</sub> and WSe<sub>2</sub>, have attracted considerable interest because of its high carrier mobility, mechanical strength, large intrinsic bandgap and optical properties. Here, we demonstrate the fabrication of CVD-growth MoS<sub>2</sub> thin-film transistors (TFTs) using ion gel as elastic gate dielectrics <sup>[1,2]</sup>. Because these transistors revealed good performance (mobility of 12.5 cm<sup>2</sup>/Vs and On/Off ratio of 100,000), we transferred MoS<sub>2</sub> films on flexible plastic substrates and realized excellent flexibility down to a curvature radius of 0.75 mm <sup>[1,2]</sup>. We also fabricated MoS<sub>2</sub> transistors on stretchable rubber substrates and achieved high stretchability under 5% channel strain without significant degradation of the carrier mobility and on/off current ratio, which might be owing to a relaxation of ripples <sup>[1,3]</sup>. As the next step, we challenged to expand material variation and successfully fabricated high-performance CVD-growth WSe<sub>2</sub> transistors (mobility of 90 cm<sup>2</sup>/Vs and On/Off ratio of 10,000,000) and simple resistor-loaded inverters <sup>[4]</sup>.

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## **Growth and functionalization of layered transition metal dichalcogenides by controllable mild plasma treatment**

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Layered transition metal dichalcogenide (TMD) is known as a true two-dimensional (2D) material with excellent semiconducting properties. In spite of its potential, however, there are still remained lots of issues for the practical applications of TMD-based optoelectrical devices. In particular, the large area growth, defect free growth, and controllable carrier doping are regarded as crucial issues in their production stage. In this study, we have demonstrated the high quality single crystal growth of MoS<sub>2</sub> and WS<sub>2</sub>. The effects of catalysts and growth conditions on the structure of MoS<sub>2</sub> and WS<sub>2</sub> were also investigated. Furthermore, mild plasma treatment <sup>[1,2]</sup> was also carried out aiming for the controllable functionalization of these TMDs.

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## **Copper-coated Nanotubes at the Single Nanotube Scale**

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High conductivity and high ampacity are both essential specifications for next-generation solid-state electronics. Recently, Subramaniam et. al. reported remarkable increases in copper conductivity and ampacity using a bulk composite of copper and carbon nanotubes (CNTs).<sup>[1]</sup> Here, we describe similar measurements performed with a model system composed of individual single-walled or multiwalled CNTs. Cu electrodeposition on single CNTs is straightforward in bulk, but smooth challenging to control at the nanometer-scale. Cu coated single CNTs with ratios as low as 10:1 have been electrically tested as a function of film thickness and device temperature. We have not yet observed the same conductance improvement as Subramaniam et. al. reported, but we obtain similar temperature coefficients, which indicates that the CNT core plays roles in dissipation and thermal equilibration.

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## **Lysosomal membrane permeabilization induced by carbon nanohorns caused reactive oxygen species generation and apoptosis in RAW264.7 cell**

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Carbon nanomaterials have offered a wide range of potential applications including biomedicine and nanotechnology. In the meantime, public concern on their environmental and health effects is growing rapidly. Many adverse effects such as inflammatory response, oxidative stress, and thrombus induction have been reported in vitro and in vivo studies. Recent studies showed that carbon nanomaterials induced cell apoptosis, and reactive oxygen species (ROS) generation was considered as the main adverse effect, but the details are still unclear.

In this study, we investigated the cell death mechanism of macrophage (RAW264.7) induced by excess uptake of oxidized carbon nanohorns (CNH). We found that neither the mitochondria nor oxidase systems were directly involved in the CNH-related ROS production and provided another ROS generation process induced by carbon nanohorns. The overload of CNHLaox in lysosomes induced lysosomal membrane permeabilization (LMP) <sup>[1]</sup>, leading to the cathepsins (lysosomal enzyme) release, and the cathepsin caused ROS generation. Both cathepsin and ROS induced mitochondrial dysfunction, subsequently, the caspases activation and the cell apoptosis. Our studies clarified the macrophage apoptotic pathway induced by nanocarbons, provided some clues about how nanocarbons induce the ROS production and indicated LMP are the initial effectors for nanocarbon-related cell death. This work may complement the understanding of toxicology mechanism of nanocarbons.

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## **Effects of plasma on growth of suspended graphene nanoribbon from nickel nanobar under rapid heating plasma CVD**

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Graphene nanoribbons combine the unique electronic and spin properties of graphene with a transport gap that arises from quantum confinement and edge effects. This makes them an attractive candidate material for the channels of next-generation transistors. Although nanoribbons can be made in a variety of ways, the reliable site and alignment control of nanoribbons with high on/off current ratios remains a challenge. Plasma chemical vapor deposition (CVD) is known as fruitful method for the structural-controlled growth and damage-free functionalization of nano carbon materials such as carbon nanotubes <sup>[1]</sup> and graphene <sup>[2,3]</sup>. We have developed a new, simple, scalable method based on the advanced plasma CVD method for directly fabricating narrow (~23 nm) suspended graphene nanoribbon devices with a clear transport gap (58.5 meV) and a high on/off ratio (>10000) <sup>[4]</sup>. Since the establishment of our novel graphene nanoribbon fabrication method, direct conversion of a Ni nanobar to the graphene nanoribbon is now possible. The growth mechanism of graphene nanoribbon, however, is not well understood, which is important for the stable fabrication of graphene nanoribbon devices. We investigate the growth mechanism of graphene nanoribbon by comparing evaporation rate of nickel between plasma and thermal CVD. It is found that the evaporation rate of nickel is low in plasma CVD compared with that of thermal CVD. This should relate with the difference of carbon concentration in nickel. In plasma CVD, large amount of hydrocarbons can be supplied to nickel due to high rate dissociation of carbon source gas. From this result, we can give a model which reveals that the graphene nanoribbon can be grown by plasma CVD.

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## **Industrialization of Boron Nitride Nanotubes: From Synthesis to Applications**

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Boron nitride nanotubes (BNNTs) exhibit a range of properties that are as impressive as those of carbon nanotubes (CNTs), including comparable mechanical properties and thermal conductivity, but with substantially higher thermal stability and, unlike CNTs, polarizability, wide band gap, and transparency in the visible region <sup>[1]</sup>. These characteristics make BNNTs attractive for the development of high-performance light-weight engineering materials, with potential to impact a range of sectors such as aerospace and armor materials, including for reinforced transparent armor. Historically, very low production volume has prevented the science and technology of BNNTs from evolving at even a fraction of the pace of CNTs, especially in areas such as reinforced composites where substantial quantities are required even for R&D activities. The National Research Council Canada (NRC) has recently addressed this limitation through the development of an industrially scalable plasma process for BNNT production from pure hexagonal boron nitride <sup>[2,3]</sup>. The method produces few-walled, highly crystalline small-diameter, BNNTs (~5 nm diameter) at a rate of ~20 g/hr, which is 100 times previous literature reports for structurally similar BNNTs <sup>[4]</sup> (or close to 20 times rates reported for larger diameter BNNTs. E.g., <sup>[5]</sup>), and with demonstrated single-run yields approaching 200 g. A cost-effective, scalable purification protocol also has been developed and the purified material is highly stable in air to at least 900 °C. This world-leading production capacity enables, in some cases for the first time in the history of BNNTs, development of large-scale BNNT applications including for polymer, ceramic and metal composites, BNNT sheets and coatings, and BNNT fibers. A range of initial examples will be presented including non-woven BNNT sheets up to 30 cm x 100 cm showing excellent flame resistance, polymer composites based on both impregnated sheets and dispersed BNNTs, and ceramic composites. These findings represent a major advance towards the exploitation of BNNTs in real-world applications.

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## **Synthesis, Raman Spectroscopy Studies and Photoluminescence Edge Enhancement on Monolayered WS<sub>2</sub>**

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Here we describe the direct synthesis of WS<sub>2</sub> monolayers with triangular morphologies and strong room-temperature photoluminescence (PL)<sup>[1]</sup>. The Raman response as well as the luminescence as a function of the number of S–W–S layers is also reported. The PL weakens with increasing number of layers due to a transition from direct band gap in a monolayer to indirect gap in multilayers. The edges of WS<sub>2</sub> monolayers exhibit PL signals with extraordinary intensity, around 25 times stronger than that at the platelet's center. Moreover, the Raman scattering of single- and few-layered WS<sub>2</sub> is studied as a function of the number of S-W-S layers and the excitation wavelength in the visible range (488, 514 and 647 nm)<sup>[2]</sup>. For single-layer WS<sub>2</sub>, the 514.5 nm laser excitation generates a second-order Raman resonance involving the longitudinal acoustic mode (LA(M)). This resonance results from a coupling between the electronic band structure and lattice vibrations. First-principles calculations were used to determine the electronic and phonon band structures of single-layer and bulk WS<sub>2</sub>. The reduced intensity of the 2LA mode was then computed, as a function of the laser wavelength, from the fourth-order Fermi golden rule. Our observations establish an unambiguous and nondestructive Raman fingerprint for identifying single- and few-layered WS<sub>2</sub> films.

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