

Forum L Advanced Carbon Materials

L01 (Invited)

Molecular Materials and Devices Shape

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Molecular materials are those constituted by weak intermolecular interactions (e.g., $\pi-\pi$ interaction, hydrogen bonding, and van der Waals force) between individual component molecules. While conventional semiconducting materials are constituted by strong intermolecular interactions (e.g., covalent bonding, metallic bonding, and ionic bonding). They possess different characteristics in condensed states, physical properties and applications. Molecular materials have a lot of advantages, such as many kinds, low cost, flexibility, solution processability, and have wide potential applications.

Molecular devices generally cover two aspects: devices at molecular scale and molecular materials applied in devices. In the later case, they consist of organic nonlinear optics, organic electroluminescence, organic/polymeric solar cells, organic field-effect transistors, and sensors. The performances of molecular devices not only depend on molecular structures but also directly on their condense state, optimization of device configuration, and interfaces of every functional layers in the devices. Similar to the role of the photolithography used in microelectronics, the solution processing techniques play an important role in the development of molecular devices.

In this presentation, I will talk about the design and synthesis of molecular materials, including π -conjugated small molecules, polymers and graphene, fabrication of high-performance devices, mainly on field-effect transistors, solution processing techniques are also involved.

L02 (Invited)

Interface Engineering of Carbon Based Electronic and Optoelectronic Materials

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In this presentation, I will describe our recent advances in preparation and characterization of high-quality organic thin films, two-dimensional (2D) layered molecular materials –namely graphene, pentacene, as well as dioctylbenzothienobenzothiophene (C_8 -BTBT), etc., and their heterostructures and hybrid combinations as well as their related electronic and optoelectronic devices.

I will introduce several approaches to realize low-voltage and high quality field-effect transistors (FETs) composed of organic thin films, organic monolayer crystals, and graphene, by fabricating high-k metal oxide dielectrics, manipulating the passive/active layer interfaces with highly ordered self-assembled monolayers (SAMs), namely octadecylphosphonic acid (ODPA) self-assembled monolayer (SAM) and octadecyltrimethoxysilane (OTMS) self-assembled monolayer (SAM) on SiO₂/Si substrates, and on atomically flat BN substrates.

Thanks to the improved interfaces, we have successfully devised the high-performance transistors by significantly reducing the electrically detrimental species in the active channels. Meanwhile, by leveraging on electromagnetic interactions via hybrid layered material/photonic waveguide and heterostructure architectures, we are able to build the high performance photodetectors from visible to the infrared spectral regions.

L03 (Invited)

Investigation on the Reliability of CVD System for Graphene Synthesis

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Graphene as one of the most promising materials has garnered tremendous attention because of its distinctive band structure and physical properties over the last decade. To date, synthesis of graphene by chemical vapor deposition (CVD) of hydrocarbons, particularly on Cu substrate, exhibits great potential as a cost-effective way to produce high-quality and large-area graphene films and various CVD methods have been explored such as hot/cold-wall CVD, low-pressure/atmosphere-pressure (LP/AP) CVD, gas/liquid/solid carbon feedstocks, etc. Most of the previous work were focused on how the processing parameters such as temperature, composition and partial pressure of the reaction gases, etc. affect graphene growth but very little on the system reliability factors such as vacuum conditions (e.g. high or low leaking rate, which indicates how much oxidants are introduced into the reaction environment) and equipment configurations (e.g. oil pump v.s. dry pump used in a LPCVD system, which determine if the reaction chamber is contaminated with the vapor of the pump oil). Here we investigated the reliability of an LPCVD system – one of the most commonly used CVD systems for graphene synthesis and how those “uncontrollable” factors affect graphene growth. Our findings are of great significance to improve the system reliability, which is essential to achieve a controllable synthesis of graphene and unambiguous understanding on graphene growth mechanism and kinetics and may provide an explanation for the discrepancies among systems from different research groups.

L04 (Invited)

Multidimensional and Multifunctional Graphenes (MMG) and Their

Industrial Applications

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Graphene oxide (GO) as a precursor was recently found to be assembled into multidimensional structure such as, quantum dots (QD), nanorolls (NR), micro-fibersthin films, aerogels, and multifunctional performance in terms of high surface areas, high thermal and electric conducting, and special magneticand optical properties.

Those multidimensional Graphene based materials such as nanorolls and one dimensional fiber can be used to fabricate next-generation energy storage materials. As an example, some resultant fibers show a specific volumetric capacity as high as 225 F/cm³, as well as a long cycle life of 2000 times. All-solid-state flexible micro-capacitors are fabricated with promising energy storage performance. The initial results indicated that these fibers could be complement or even replacement of batteries in miniaturized portable electronics systems. In addition, those multidimensional and multifunctional Graphenes (MMG) based materials could be a good candidate as electrodes for the Li- ion batteries.

The MMG also can be processed into a free-standing film form, which shows an excellent thermal conductivity for smart phone and i-pad applications. The MMG can be used as structure materials to make nanocomposite to enhance the mechanical properties and electric performance. About dozen corresponding industrial applications and some new results will be highlighted during the presentation.

L05

Incorporation of Functionalized Graphene and Analogous 2D Materials toward Efficiency Enhancement of Polymer Solar Cells

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The interfaces between electrodes/photoactive layer play a determinative role on the performance of polymer solar cells (PSCs), improving the contact between electrodes and photoactive layer via interface engineering has been demonstrated to an effective solution to enhance the performance of PSCs. Graphenes have been generally applied as hole extraction layer in PSCs to replace the commonly used poly(3,4-ethylendioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) which is acidic and might damage the ITO electrode owing to its hygroscopicity. We applied a new functionalized graphene, which is a graphene-fullerene composite (rGO-pyrene-PCBM), as electron extraction layer (EEL), leading to an efficiency enhancement of ~15% for PSCs based on P3HT:PCBM. Contrarily, the comparative devices incorporating the rGO or pyrene-PCBM component as EEL showed dramatically decreased PCE, indicating the importance of composite formation between rGO and pyrene-PCBM components for its electron extraction property. We also grafted sulfonic acid successfully onto GO via a facile noncovalent functionalization approach using pyrene as the

anchoring bridge, resulting in improved hole transport in bulk-heterojunction (BHJ) PSCs compared to that of pristine GO. Besides, we recently incorporated graphitic carbon nitride (g-C₃N₄) in the inverted BHJ-PSCs by doping solution-processable g-C₃N₄ quantum dots (C₃N₄ QDs) in the active layer, leading to a dramatic efficiency enhancement.

L06

The Study of the Preparation and Related Technology of PS

Microspheres Doped into 3D Graphene Porous Electrode Materials

Heterostructures

Guangsheng Luo

Nanchang University

Graphene is considered as an ideal electrode material for supercapacitors due to its high conductivity, large specific surface area, and chemical stability. However, it still has some problems such as low specific surface area and bad reduction efficiency when graphene was derived from the graphene oxide because of self-aggregation and restacking of graphene sheets. In this proposal, different reduction method of 3D graphene loaded on the nickel foam and preparation technology of polystyrene colloidal particles (PS) microspheres doped into graphene have been explored to prepare three-dimensional porous graphene electrode materials with a high specific capacitance, high ratio capability and good cycle stability; self-aggregation and restacking of graphene sheets have been avoided by doping PS microspheres and forming a porous structure, the reduction efficiency mechanism of graphene has been analyzed; the effect of mesoporous network structure formed by doping PS microspheres and the increase of the specific surface area and the carrier density caused by doping PS microspheres on the electrochemical properties such as the specific capacitance and cycle stability have been discussed. Our study would provide theoretical guidance and practical reference for the preparation of high performance supercapacitor electrode materials and the design of preparation of new energy storage devices with high energy density and high power density.

1. The three-dimensional porous graphene composite electrode material loaded on nickel foam was synthesized by the technology of coating solution and reduction method . In the reduction process, graphene oxide (GO) is transformed into the high conductivity of graphene network and three-dimensional continuous and interconnected microporous structure with dependent on the porous foam nickel. The microporous structure is favorable to shorten the ion diffusion path, and facilitates the efficient diffusion of electrolyte ions to the surface of graphene, the rebby effectively promote the charge transfer efficiency, and improve the utilization of active material. The results show that the specific capacitance is as high as 203 F/g, exhibited high rate capability performance, which specific capacitance still amounted to 146 F/g at 35A/g of the test current, the retention rate of the specific capacitance is 71.9% .The optimization of preparation reduction conditions: reaction temperature: 60°C ; reaction time: 5h; concentration of VC

solution:10mg/ml.

2. The porous graphene oxide (GO) gel deposited on nickel foam was prepared by using polystyrene(PS) colloidal particles as spacers for use as electrodes in high rate supercapacitors, then reduced by Vitamin C aqueous solution in ambient condition. The PS particles were surrounded by reduced graphene oxide (rGO) sheets, forming crinkles and rough textures. When PS particles were selectively removed, rGO- gel coated on the skeleton of Ni foam can form an open porous structure, which prevents self-aggregation and restacking of graphene sheets. The porous rGO-based supercapacitors exhibit excellent electrochemical performances such as a specific capacitance of 152 F/g at 1 A/g, high rate capability of 53% capacitance retention upon a current increase to 100 A/g and good cycle stability, due to effective rapid and short pathways for ionic and electronic transport provided by the sub-micrometer structure of rGO- gel and 3D interconnected network of Ni foam.

L07

Preparation and electrochemical properties of Au NPs/RGO Hybrid

Xinli Guo

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Au NPs and graphene Au nanoparticle (Au NP) has exhibited advanced catalytic properties due to its high ratio surface area and high surface activity. But its application is limited due to the aggregation problems of NPs and high price. Graphene has shown advanced conductivity and high ratio surface area, which provide a good supporter to stabilize the Au NPs and to enhance the catalytic properties by the hybrid of Au NPs and graphene. In this paper, we study the in-situ synthesis of Au nanoparticles (Au NPs) on NaBH₄-reduced reduction graphene oxide (RGO) film. And this as-prepared Au NPs /RGO hybrid material was used to catalyze the reduction of 4-nitrophenol(4-NP). Without adding additional reductant or surfactant during the in-situ synthesis process, Au NPs were prepared by the reduction of RGO to Au³⁺ and have a uniform and a controllable coverage on RGO film, which greatly weakens the hydrophobicity of RGO and turns the hybrid into a hydrophilic material, thus can disperse in the reaction system stably. In addition, there are no surfactants capped on the surface of Au NPs, which ensures the fully-contact between the surface active sites of Au NPs and reactants, which can improve the catalytic rate considerably. The results show that the Au NPs/RGO hybrid can end the reduction reaction of 4-NP in 150s with a kinetic constant as high as 1.21min⁻¹, which is much higher than adding the same molar weight of single Au NPs. This hybrid can still end the reaction in 240s after holding at ~4 °C for 40 days, which exhibits an excellent and stable catalytic activity

L08 (Invited)

Graphene Film in Flexible Electronics Devices as Transparent Electrode

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Graphene has excellent optical and electric properties, which make it a good candidate for transparent electrode. Moreover, its flexibility is very good for flexible electronics applications. Here I'd like to introduce the detailed technique of making flexible graphene touch sensor and displays, and further show its potential application in the flexible devices.

L09 (Invited)

Low-Temperature Catalyst-Free Growth of Two-Dimensional Crystals on Dielectrics for Nanodevices

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One of the largest problems, which result in little success of applying graphene in electronics industry, is the lack of a low-cost, reliable, and controllable method to produce ultra-clean high-quality graphene directly on dielectrics at low temperature, which can directly be used in electrical devices. Plasma-enhanced chemical vapor deposition (PECVD) realizes catalyst-free growth of graphene on dielectrics, however structural defects easily form on edges, which terminate the graphene growth, resulting in low-quality graphene nanoclusters or non-crystalline samples. Here, we observe a critical equilibrium state of graphene edge growth, when we introduce H₂ plasma in PECVD. Moderate H₂ plasma etching removes edge defects, keeping the edges active in the whole crystal growth. Thus, we develop a critical PECVD method, which realizes catalyst-free growth of ultra-clean high-quality graphene, with size up to μm-scale for single crystals and to cm-scale for continuous films, directly on dielectrics. Both the locations and the orientations of the graphene crystals are controlled by patterned seeds, and the growth temperature decreases to as low as 400 °C when using C₂H₄ as the carbon source in critical PECVD. STM study reveals the pivotal role of H₂ plasma and a novel catalyst-free edge growth mechanism of graphene. Electrical measurement shows a high electrical quality with mobility much higher than normal PECVD graphene, and comparable to that of Cu-CVD graphene and peel-off graphene, indicating its great potential as a general growth method for future graphene electronics.

L10

Preparation and Properties of Graphene-based Materials As Lubricating Oil Additives

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Some composites consisted of the reduced graphene oxide (rGO) nanosheets and metal oxide nanoparticles, such as rGO/zirconia (rGO/ZrO₂), rGO/ceria (rGO/CeO₂), etc., were synthesized by a one-step hydrothermal route. Moreover, the uniform distribution and moderate loading of nanoparticles on rGO surface could be controlled by regulating the volume ratios of precursors. The results demonstrated that the modification of graphene nanosheets by inorganic nanoparticles could improve the dispersion stability of graphene in the base oil; meanwhile, the introduction of a small amount of composite into the base oil could reduce extremely the coefficient of friction and wear rate. Taking the composite of rGO/ZrO₂ as an example, the average friction coefficient could be reduced from 0.26 to 0.12 while the wear rate could be decreased to 6.4% of that of base oil when the addition amount was 0.06 wt%. Meanwhile, its tribological performances were better than the commercialized additive of zinc dialkyldithiophosphate (ZDDP). The above investigation manifests that the combination of metal oxides and graphene nanosheets is an effective way to enhance the tribological performances of graphene, and it has potential application in fields of lubricating additives and lubricating coatings.

L11

Nanostructures and Properties of Biochars for LIB Anode

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Biochars have good conductivity, abundant pore structure, larger surface and excellent environment benefit that they increasingly become the research hotspots in the field of energy storage. It is found that the performance of biochars for LIB anode has a close relationship with their structures, such as the crystallinity, crystallite size, crystal cell parameters, and the surface properties of carbon particles. In this topic, according to the current research of biochars, we will mainly introduce the biochars application in lithium ion batteries, focusing on the relation between the nanostructures and electrochemical properties of biochars. We also offer an introduction of our group research in this area.

L12

Chemically Derived Graphene: from Scale-up Production to

Multifunctional Application

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Chemically derived graphene (CDG), as produced by exfoliation and reduction of graphite oxide with natural graphite as the raw material, is intrinsically decorated by abundant functionalities and lattice defects, which increased the solvent compatibility for macroscopic assembly for versatile applications. As the amphiphilic soft-matter, graphene oxide can be facially dispersed in aqueous solution to form stable hydrogel, which can be employed as the cost effective precursor for macroscopic assembly of graphene. Since Dec 2013, the kilogram scale production of graphene has been achieved in our pilot plant, the exploitation for commercial applications of which become a great challenge to the sustainable development of graphene.

As the low dimensional nano-carbons, the ultralow bulk density of CDGs (3~5 g/L) make the material inconvenient for industrial processing. This inspires us to fabricate macro-assemblies or nanocomposites as an easier form for application. For example, the flexible C/C composite films, with hierarchical structure were constructed by graphene and carbon fiber³. The material exhibit a high in-plane thermal conductivity over 1000 W/m.K with excellent tensile strength of 16 MPa, is of great potential as lateral heat spreader for electronics, PV systems and LEDs. Furthermore, the carbonization temperature at 1000 oC was found to be a crucial point for significant enhancement in thermal conductivity.

L13

Fabrication of g-C₃N₄ Microspheres without Template via Microwave

Heating Method

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Southeast University

This research reported the preparation of the graphitic carbon nitride (g-C₃N₄) microspheres without template via microwave heating method using melamine as precursor. The as-synthesized samples were characterized by powder X-ray diffraction (XRD), fourier transform infrared spectroscopy (FT-IR), field-emission scanning electron microscopy (FE-SEM). Results showed that the g-C₃N₄ microspheres were successfully synthesized. The diameters of the microspheres range from 800 nm to 1.5 μm, and the shell thickness is about 50 nm. The optical spectra covering ultraviolet-visible (UV-Vis) and photoluminescence (PL) were also measured at room temperature. UV-Vis absorption edge and PL peak of the g-C₃N₄ were shown at 457 nm and 468 nm, respectively, indicating the intrinsic semiconductor-like absorption in the blue region of the visible spectrum. This was the first attempt to prepare g-C₃N₄ microspheres without template

via microwave heating approach, which was proved to be facile and effective.

L14

Research on the Preparation of Biomass based Activated Carbon and Its Adsorption on CO₂

Mengyuan Zhu

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With the continuous development of industry and improvement of humans' living standards, the Greenhouse Effect which mainly caused by the massive emissions of CO₂ into the atmosphere has become a hot environmental issue of concern. Activated carbon, as a premium carbon adsorbent material, is widely used in industry for CO₂ adsorption and desorption. Its production and adsorption properties has drawn more and more attention. In this paper, we apply the orthogonal experimental method to study on the way for prepare the activated carbon with peanut shells, walnut shells, pecan shells as raw material, KOH as activating agent, and study the CO₂ adsorption properties of this activated carbon, then research the structure-activity relationships between activated carbon and adsorbate and make preliminary study of its adsorption mechanism. First optimize alkali carbon ratio and the preparation conditions under different activation temperature of activated carbon, therefore obtain the optimal parameters for preparing activated carbon; make comparative study the physical structure, chemical properties and adsorption behavior of activated carbon, and then combine the characteristics of CO₂, then regulate and control the surface chemical properties to increase its adsorption effect. Experimental results show that the influence of activation temperature and alkali carbon ratio on CO₂ adsorption value is greater than the biomass species, further, the former two are the main factors affecting the CO₂ adsorption effect. And the experimental results also show that the optimum value of each condition were: biomass (Pecan shell), alkali carbon ratio (2: 1) and the activation temperature (750 °C), the optimum conditions are the combination of these three optimal levels. The CO₂ adsorption value of activated carbon material, which was prepared under the optimal conditions, is 4.42mmol/g at 1 atm, 25°C.