

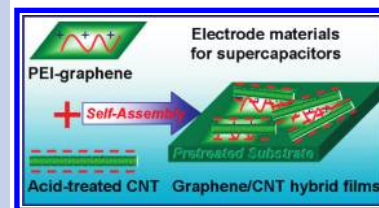
Self-Assembled Graphene/Carbon Nanotube Hybrid Films for Supercapacitors

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ABSTRACT Stable aqueous dispersions of polymer-modified graphene sheets were prepared via in situ reduction of exfoliated graphite oxides in the presence of cationic poly(ethyleneimine) (PEI). The resultant water-soluble PEI-modified graphene sheets were then used for sequential self-assembly with acid-oxidized multiwalled carbon nanotubes, forming hybrid carbon films. These hybrid films were demonstrated to possess an interconnected network of carbon structures with well-defined nanopores to be promising for supercapacitor electrodes, exhibiting a nearly rectangular cyclic voltammogram even at an exceedingly high scan rate of 1 V/s with an average specific capacitance of 120 F/g.

SECTION Nanoparticles and Nanostructures



Owing to their unique electrical and mechanical properties as well as large surface area, graphene nanosheets (GNs) with two-dimensional (2D) carbon nanostructure have emerged as a new class of promising materials attractive for potential applications in actuators, solar cells, field-emission devices, field-effect transistors, supercapacitors, and batteries.^{1–7} A particularly attractive option is to design and develop hybrid films based on graphene sheets as electrodes for energy-storage applications.^{8,9} In this context, it is critical to tailor the hybrid film properties by controlling their composition and architecture at nano/micrometer scale. Therefore, it is important to functionalize graphene sheets for controllable processing. Recent effort has led to solution-processable GNs by exfoliation of graphite into graphene oxides (GOs), followed by solution reduction and functionalization.¹⁰ The availability of solution-processable GNs allowed the formation of GN-based functional films through various solution processing methods, including filtration,¹¹ solution-casting,¹² electrophoretic deposition,¹³ and Langmuir–Blodgett deposition.¹⁴ However, most of the above-mentioned techniques suffer from a lack of the film architecture/property control, leading to the loss of the surface area for energy storage due to graphene aggregation. For energy storage applications, therefore, it is highly desirable to use one-dimensional (1D) carbon nanotubes (CNTs) to physically separate 2D GNs to preserve graphene's high surface area.

One of the most versatile fabrication techniques for hybrid thin film formation is layer-by-layer (LBL) electrostatic self-assembly through repeated, sequential immersion of a substrate into aqueous solutions of complementarily functionalized materials.¹⁵ The LBL technique has recently been used for the preparation of ultrathin electroactive multilayer films containing CNTs with carboxylic acid, amine, and other surface functional groups and polyions of opposite charges.^{16–19} However, the formation of graphene-based LBL films has

been much less discussed in the literature.^{20,21} On the other hand, some recent attempts have been made to fabricate graphene/CNT hybrid films by spin-coating homogeneously mixed solutions of the two carbon-based nanomaterials.^{12b,22}

The hybrid films thus prepared consist of aggregated graphene thick layers with poor controllability. Here, we report our recent investigation of the fabrication of large-area multi-component hybrid films by sequential self-assembly of functionalized 2D graphene sheets and 1D CNTs via electrostatic interactions onto various substrates, suitable for electrochemical measurements. The resultant hybrid films exhibit a nearly rectangular cyclic voltammogram, even at a high scan rate of 1 V/s with an average specific capacitance of 120 F/g.

In a typical experiment, we chemically reduced GO sheets with hydrazine in the presence of poly(ethyleneimine) (PEI) as a stabilizer. The introduction of the charged soluble polymer chain unit onto the graphene plane should result in a well-dispersed graphene-based material. The adsorption of the water-soluble cationic PEI chains onto graphene sheets (PEI-GNs) could not only render the GNs to be dispersible/soluble but also make it possible for controllably fabricating multi-component hybrid films by sequential self-assembly with other negatively charged nanomaterials (e.g., acid-oxidized CNTs in the present case).

Figure 1a shows a homogeneous aqueous dispersion of black PEI-GN. The dispersion was stable without precipitation, even after several week storage at ambient. This indicates that the reduced GO sheets were well-dispersed by PEI due, most probably, to the electrostatic repulsion between the GN-supported positively charged PEI chains. Atomic force microscope (AFM) image of the PEI-GN from a dilute solution shows irregularly shaped individual sheets, ranging from several

Received Date: November 25, 2009

Accepted Date: December 16, 2009

Published on Web Date: December 22, 2009

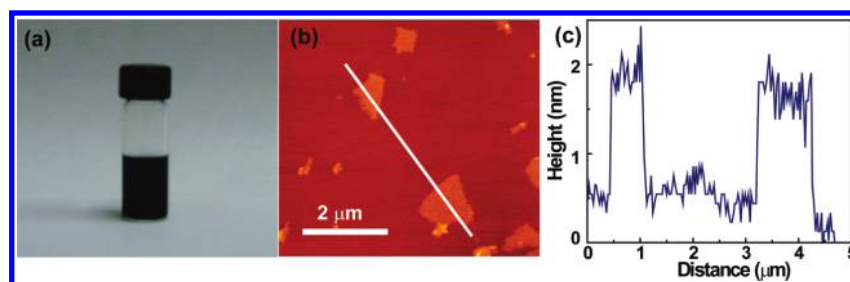


Figure 1. (a) Digital photograph showing an aqueous dispersion (0.25 mg/mL) of the reduced graphene oxide in the presence of PEI. (b) AFM image of a PEI-GN dispersion showing graphene single sheets. (c) Height profile showing that the thickness of the PEI-GN sheets is about 2–2.5 nm. Topological features observed in the AFM image are due to local roughening of the PEI molecular monolayer adsorbed on the graphene sheets.

hundreds of nanometers to several micrometers in size and 2.0–2.5 nm in height (Figure 1b,c). The observed sheet thicknesses are significantly greater than the corresponding values determined for exfoliated GO sheets (1–1.5 nm) or pristine graphene layers (0.34 nm).²³ While the adsorbed PEI chains can significantly increase the sheet thickness, the formation of a few layered graphene sheets cannot be excluded.

The as-obtained PEI modified graphene was further characterized by Raman spectroscopy (Figure S1a, Supporting Information), Fourier transform infrared spectroscopy (Figure S1b), and X-ray photoemission spectroscopy (XPS). Figure 2 shows the XPS spectra for the GO and PEI modified graphene. As shown in Figure 2a, the appearance of an N peak in the XPS survey spectrum for PEI-GN, compared to that of GO, clearly indicates the absorption of PEI chains onto the resultant GNs. As expected, the C1s spectrum of GO given in Figure 2b shows pronounced peaks at 288.1 and 286.3 eV, attributable to C=O and C–O bonds, respectively. In contrast, the C1s spectrum of PEI-GN shows significantly decreased peak intensities associated with the C–O and C=O functionalities (Figure 2c). The surface oxygen groups in GO were estimated to be 31.1 atom %, whereas the percentage of oxygen decreased to 8.9 atom % after treatment with hydrazine in the presence of PEI. These results imply that considerable deoxygenation occurred by PEI grafting and hydrazine reduction. Meanwhile, the nitrogen percentage in PEI-GN reached 8.1 atom %, indicating the attachment of PEI chains on the graphene sheets. Furthermore, the C1s and N1s XPS spectra of PEI-GN in Figure 2c,d suggest the presence of amine NH_2 (NH_3^+) (286.0 eV in C1s and 400.8 eV in N1s) and amide bonds $\text{N}=\text{C}=\text{O}$ (287.8 eV in C1s and 399.5 eV in N1s),²⁴ suggesting some of the PEI chains have been covalently linked to the graphene surface via the formation of amide bonds.

The PEI-GN surface with abundant $-\text{NH}_2$ groups could be protonated ($-\text{NH}_3^+$) over a certain pH range (pH = 2–9) after dissolving the PEI-GN into deionized (DI) water,²⁵ which was then used for sequential assembly with the negatively charged multiwalled nanotube (MWNT) prepared by acid oxidation (i.e., MWNT-COOH).²⁶ As schematically shown in Figure 3a, the fabrication of the positively charged PEI-GN and the negatively charged MWNT hybrid films on a silicon or indium tin oxide (ITO) glass substrate was carried out through a well-defined multistep sequential assembly procedure.²⁷

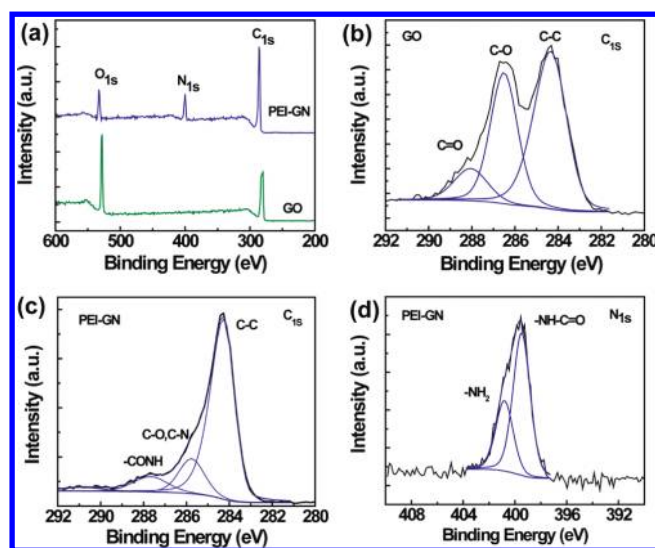


Figure 2. XPS spectra of GO and PEI-GN. (a) Wide scan survey spectra. (b) XPS C1s spectrum of GO. (c) XPS C1s spectrum of PEI-GN. (d) XPS N1s spectrum of PEI-GN.

The immobilized graphene layer on the substrate was analyzed by optical absorption measurements (Figure S2) and scanning electron microscopy (SEM, Figure 5). As can be seen from Figure 3b, graphene thin films of a broad size distribution over 0.5 to 5 μm were initially formed on the substrate with a high surface coverage, even after the first immersion of the substrate into the aqueous PEI-GN solution (0.25 mg/mL, pH = 8) (Figure 3b).²⁵ After a subsequent immersion of the substrate into the aqueous MWNT-COOH solution (0.5 mg/mL, pH = 6.5),²⁶ it can be observed that another layer of randomly oriented nanotubes with various lengths was assembled on the graphene-coated substrate (Figure 3c). These results confirm that the sequential self-assembly process has successfully led to the fabrication of a reasonably uniform film with well-interconnected carbon-based hybrid materials. By repeating the above immersion steps, thin films with a desired thickness and architecture were obtained. Thereafter, the substrate-supported self-assembled hybrid film was heated at 150 $^\circ\text{C}$ for 12 h in a vacuum oven, resulting in the formation of amide bonds between the PEI-modified graphene and carboxylic acids on the acid-oxidized MWNT surface.²⁷ The SEM images of the [PEI-GN/MWNT-COOH]_n

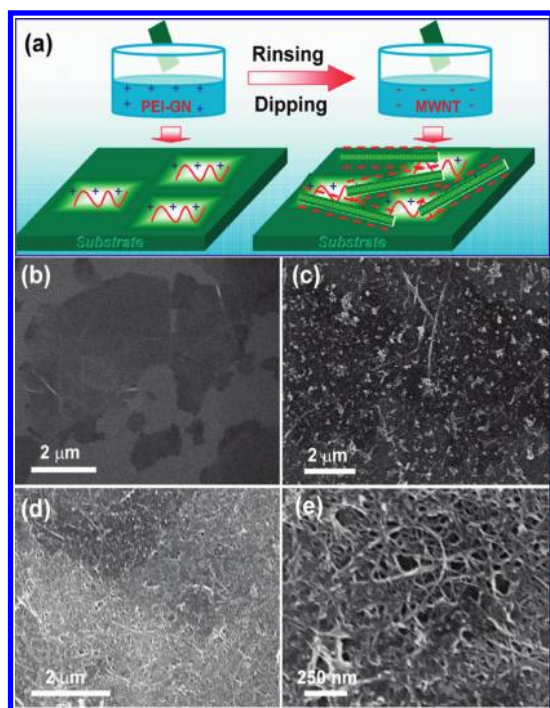


Figure 3. (a) Illustration of positively charged PEI-GN and negatively charged MWNT film deposition process on an appropriate substrate (e.g., silicon wafer, ITO glass). SEM images of (b) the first layer PEI-GN and (c) the first bilayer [PEI-GN/MWNT-COOH]₁ film deposited on a silicon substrate. (d,e) SEM images of the [PEI-GN/MWNT-COOH]₉ film after the ninth deposition cycle under different magnifications.

multilayer films after the ninth deposition cycle in Figure 3d,e reveal a relatively dense and uniform network carbon nanostructure with well-defined nanoscale pores. It is anticipated that an extended conjugated network can be formed with nanotubes bridging between graphene sheets. Since both graphene and CNTs could have intrinsically high electrical conductivity and large surface area, the observed network structures with well-defined pores could serve as fast electronic and ionic conducting channels, providing ideal electrodes for energy storage devices.

Cyclic voltammograms (CVs) of the heat-treated [PEI-GN/MWNT-COOH]₉ films on ITO glasses were obtained in 1.0 M H₂SO₄ solution at room temperature as a function of the bilayer number (Figure 4). The coated ITO glass was used as the working electrode, an Ag/AgCl (3 M KCl-filled) electrode as the reference electrode, and a platinum wire as the counter electrode. CV studies were performed within the potential range of -0.4 to 0.6 V at scan rates of 0.01–1 V/S. The measured voltammetry curves show a quite rectangular shape, attractive for capacitor applications. An average capacitance (120 F/g) was obtained, which is considerably higher than those of vertically aligned²⁸ and nonaligned CNT electrodes.^{29,30} It should be noted that the CVs are still rectangular in shape even at exceedingly high scan rates of ~0.8 and 1 V/s, indicating rapid charging and discharging with a low equivalent series resistance of the electrodes.³¹ These results indicate the exciting potential for the use of this new class of hybrid carbon films in high-performance supercapacitors.

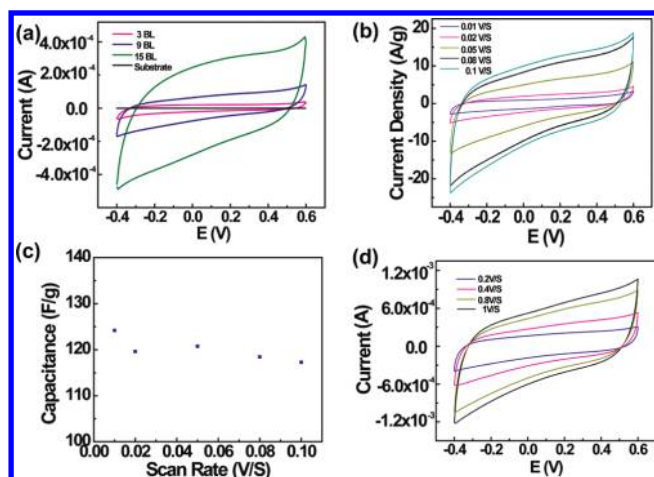


Figure 4. (a) CVs at a scan rate of 0.05 V/s in 1.0 M H₂SO₄ at room temperature obtained from heat-treated [PEI-GN/MWNT-COOH]_n films with bilayer number $n = 3, 9, 15$. (b,c) CVs and specific capacitance at scan rates of 0.01, 0.02, 0.05, 0.08, and 0.1 V/s from [PEI-GN/MWNT-COOH]₉ film in 1.0 M H₂SO₄ at room temperature (specific capacitance is derived at the potential of 0.1 V). (d) CVs from [PEI-GN/MWNT-COOH]₉ film at higher scan rates of 0.2, 0.4, 0.8, and 1 V/s in 1.0 M H₂SO₄ at room temperature.

In conclusion, stable aqueous dispersion of polymer-bound graphene sheets was produced via in situ reduction of exfoliated graphite oxide in the presence of cationic PEI. The resultant water-soluble PEI-modified graphene sheets were then used for sequential self-assembly with acid-oxidized MWNTs, forming hybrid carbon films with interconnected carbon structures of well-defined nanoscale pores. Therefore, this self-assembly method can be used to fabricate large-area multicomponent hybrid films with a well-defined architecture and tunable thickness on various substrates, suitable for electrochemical applications. The obtained hybrid films having interconnected network carbon structures with well-defined nanopores for fast ion diffusion were demonstrated to show a rectangular CV even at a high scan rate of 1 V/s with the average specific capacitance of 120 F/g, which is promising as supercapacitor electrodes.

SUPPORTING INFORMATION AVAILABLE Experimental details, Raman spectra and infrared spectra of GO and PEI-GN (Figure S1) and optical absorption spectra of the hybrid films (Figure S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ACKNOWLEDGMENT The authors acknowledge the support from AFOSR (FA9550-09-1-0331).

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