Transparent self-assembled films of reduced graphene oxide platelets

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Transparent conducting films have been fabricated in one step, combining self-assembly and chemical reduction of graphene oxide platelets dispersed in water. The films are of centimeter scale and their thickness can be controlled by the concentration of the graphene oxide suspension. The optical transmittance values at a wavelength of 550 nm were 87% and 96% for the films made from 1.5 and 0.5 mg/ml suspensions, respectively, and have sheet resistances of 11.3 and 31.7 $k\Omega/\square$. Scanning and transmission electron microscopy, atomic force microscopy, and x-ray photoelectron spectroscopy were used to characterize the films. © *2009 American Institute of Physics*. [doi:10.1063/1.3212862]

Graphene has stimulated interest due to its unique electronic, mechanical, and thermal properties.[1] With a high transmittance of 97.7% at 550 nm for each monolayer,[2] graphene films have promise as optically transparent electrically conductive materials.[3] Graphene can be made by chemical vapor deposition on metals,[4] mechanical exfoliation of graphite,[3] epitaxial growth on SiC,[5] and by ultrasonic exfoliation of graphite in organic solvents.[6] The dispersion of graphene or reduced graphene oxide (RGO) in colloidal suspensions offers the potential of making large-area graphene films.[7] Macroscopic graphene membranes have been fabricated from organic solvents by vacuum filtration,[6,8] Langmuir–Blodgett (LB) assembly,[9] and liquid-liquid interface assembly.[10] Since a stable colloidal suspension of graphene oxide platelets can be obtained by the simple sonication of graphite oxide in water,[11] several efforts have been made to assemble graphene oxide platelets from their water suspensions to large-area films. One such method has involved the deposition of graphene oxide platelets via vacuum filtration or spin coating prior to reduction by chemical or thermal treatment.[12–14] Another approach, by Li *et al.*,[15] shows that the films composed of RGO platelets could be made directly from RGO water dispersions, by changing the *p*H to about 10 prior to reduction with hydrazine. Recently, Chen *et al.*[16] demonstrated a liquid-air interface assembly of graphite oxide membranes by evaporating a hydrosol composed of graphene oxide platelets. Reduction was then necessary to make the membranes conductive for use as electrodes. In this work, we report a method to assemble centimeter-scale membranes composed of overlapped, RGO platelets, during the chemical reduction of the aqueous suspension of graphene oxide platelets. From the RGO films prepared, a low sheet resistance of 11.3 $k\Omega/\square$ has been obtained with an optical transmittance of 87% at 550 nm.

Graphene oxide suspensions were made by sonication (VWR B2500A-MT, a bath sonicator) of graphite oxide powder produced by the modified Hummers method[17] in pure water (17.5 MΩ, Barnstead). Two concentrations, namely 0.5 and 1.5 mg/ml, were prepared for multiple trials. Chemical reduction was carried out by adding hydrazine monohydrate (1 μl/5 mg graphite oxide), followed by heating at 80 °C for 12 h while stirring at 400 rpm. After the reduction, a thin layer of material was observed on the surface of the aqueous dispersion (i.e., at the air-water interface) and also on the interior wall of the flask, while large agglomerated particles precipitated from the dispersion. The thin layer at the air-water interface was then collected onto various substrates by dip coating. Scanning electron microscopy (SEM) (FEI Quanta-600) and atomic force microscopy (AFM) (Park Systems XE-100) were used to characterize the films on Si with a 270 nm thick SiO_2 surface layer (Si/SiO_2), and on mica substrates, respectively. Samples collected on Cu grids were studied by transmission electron microscopy (TEM) (JEOL 2010F, 200kV). X-ray photoelectron spectroscopy (XPS) (Kratos AXIS Ultra DLD, Al $K\alpha$) was done on the films on Si/SiO_2. A spectroscopic ellipsometer (J. A. Woollam M2000D, beam size ~3 mm) was used to estimate the thickness of the films on Si/SiO_2 and to measure the transmittance of the samples on cover glass. The films on cover glass were masked and coated with Au electrodes in order to measure the sheet resistance (Keithley 6221 and 6514).

Figures 1(a) and 1(c) show the optical images of as-prepared RGO films on cover glass. As can be seen, this nonoptimized process has produced large-area and transparent membranes. The samples are optically uniform on a centimeter scale. The SEM image [Fig. 1(b)] of the RGO films from the 0.5 mg/ml suspension shows that the substrate is not fully covered and individual RGO platelets with size varying from a few hundred nanometers to several micrometers are connected together. Regions where there are two or three overlapped RGO platelets are also present. From the high magnification image shown in the inset of Fig. 1(b), it can be seen that most of the contacts between sheets are edge-to-edge interactions, similar with the case in the liquid-liquid interface[10] and LB assembly.[18] In contrast, a continuous and uniform film was obtained from the 1.5 mg/ml suspension [Fig. 1(d)]. Under high magnification [inset of Fig. 1(d)], it was found that the surface was "rough" and full of wrinkles.

AFM topology images and line profiles are shown in Fig. 2. In Fig. 2(a), we can see that the sample from the 0.5 mg/ml suspension has one to two layers of RGO platelets.

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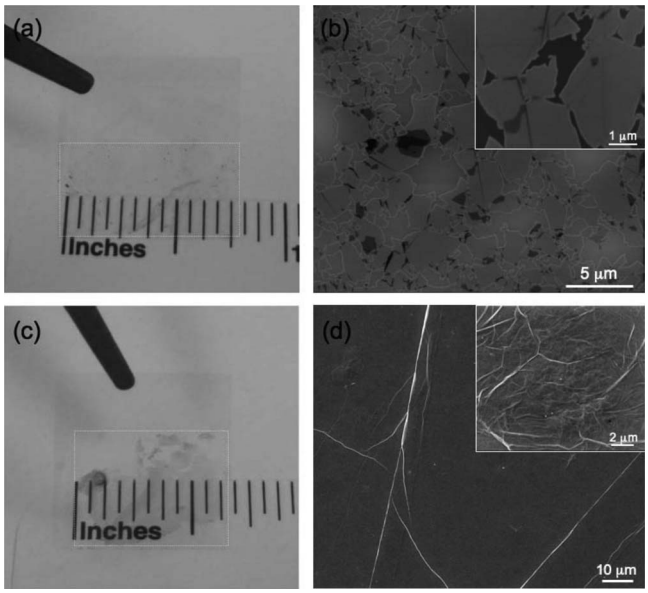

FIG. 1. Optical images of as-made RGO films on cover glass from (a) 0.5 mg/ml and (c) 1.5 mg/ml aqueous suspensions. The dotted rectangle is a guide to the eye of the area covered with the film. (b) and (d) show the corresponding SEM images with high magnification images as insets.

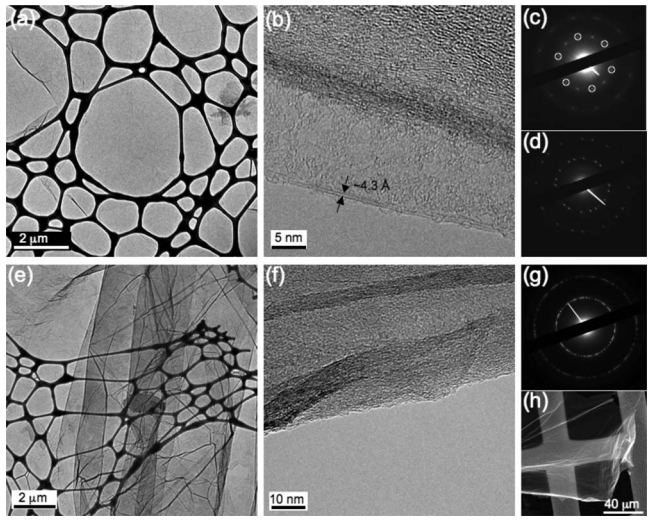

FIG. 3. (a) TEM and (b) HRTEM images for the RGO film obtained from the 0.5 mg/ml suspension. (c) and (d) show ED patterns from two random regions on the same sample. (e), (f), and (g) are TEM, HRTEM, and ED images for the film obtained from the 1.5 mg/ml suspension. (h) is a SEM image of the same sample in (e), showing a freestanding film on Cu TEM grids.

The first layer is very smooth, with a thickness of ~0.7 nm. This is slightly smaller than the ~1 nm thickness of typical graphene oxide sheets,[11,16] suggesting the removal of surface oxide groups. The layers above the first layer have wrinkles and folded regions. The density of wrinkles/folded regions as shown in Fig. 2(b) is high for the thicker films deposited from the 1.5 mg/ml suspension. The surface height difference can be as large as 8 nm along a 2 μm long scanned line. By fitting ellipsometry data, the average thicknesses for the films obtained from the 0.5 and 1.5 mg/ml suspensions were estimated as ~2.9 and ~16.2 nm, respectively.

TEM was used to investigate the microstructure of the films. As can be seen from Fig. 3(a), a film (from the 0.5 mg/ml suspension) transparent to electrons was obtained on the lacey carbon support film. Holes and boundaries between individual RGO platelets are seen, consistent with the SEM observations. Figure 3(b) shows a high resolution TEM (HRTEM) image from the same sample, indicating two to three layers of RGO platelets on the edge. The interlayer distance was measured to be about 0.43 nm, smaller than the typical interlayer distance of about 0.60–1.2 nm in graphite oxide powders.[19] The crystalline nature of the film was confirmed by electron diffraction (ED) patterns shown in Figs. 3(c) and 3(d). Two [Fig. 3(c)] and three [Fig. 3(d)] sets of ED patterns were assigned, suggesting that the film from the 0.5 mg/ml suspension consists of a few layers of overlapped RGO platelets. In contrast, the film from the 1.5 mg/ml suspension shows a large number of wrinkles and folded regions, as shown in Fig. 3(e). The HRTEM image [Fig. 3(f)] gives layer numbers of 12 and 20 on the edge. The ED pattern [Fig. 3(g)] includes many spots, which are so closely spaced as to be nearly indistinguishable from one another. It is worth noting that the macroscopic films assembled from RGO platelets are stiff enough to form a freestanding membrane, as shown in the SEM image in Fig. 3(h).

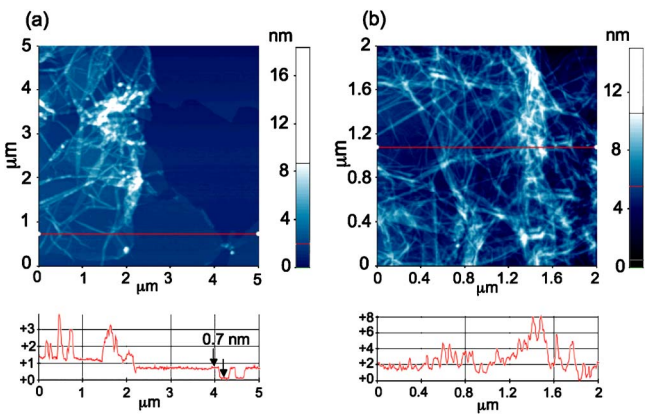

FIG. 2. (Color online) Typical topology AFM images and the line profiles of RGO films from (a) 0.5 and (b) 1.5 mg/ml suspensions.

Thus, self-assembly at interfaces, apparently assisted by the use of a magnetic stir bar spinning, yields formation of large-area films composed of RGO platelets. During the reduction of graphene oxide suspensions in water with hydrazine, the platelets near the H_2O-air interface and at the H_2O-container interface evidently have a high chance to diffuse to the interface while being reduced or shortly after reduction. "Plating out" at interfaces thus occurs. It seems that stirring the water assists the formation of a closely packed layer at the respective interfaces since such films were not obtained if the suspension was not stirred while keeping other conditions the same. The suspension with higher concentration included more platelets in the same volume of water near the interface, leading to a thicker and more densely packed film.

Figure 4(a) shows the XPS C 1*s* spectrum of the film obtained from the 1.5 mg/ml suspension with that of graphite oxide powder for comparison. From the decomposition of the spectra, it can be clearly seen that the peaks related to the oxygen containing groups were largely suppressed for the film composed of RGO platelets. The XPS results parallel those from previous studies on graphene oxide platelets exposed to hydrazine when in suspension, and then dried down,[11,20] and of films made from spin coating of aqueous suspensions of graphene oxide platelets, followed by exposure to hydrazine vapor.[13] Figure 4(b) shows the typical

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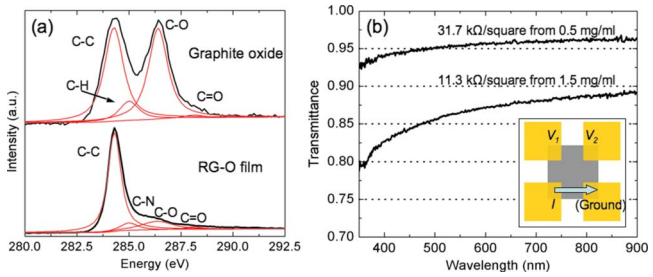

FIG. 4. (Color online) (a) XPS C 1*s* spectrum obtained from graphite oxide, and also from RGO films obtained from the 1.5 mg/ml suspension. The peaks from deconvolution fitting are shown as assigned. (b) Typical transmittance curve of the RGO films with the sheet resistance shown. Inset shows the four probe measurement configuration.

transmittance of the films as a function of wavelength. Both films feature a flat optical transmittance profile across the visible and near-infrared regions of the spectrum. At 550 nm wavelength incident light, the transmittance values were 96% and 87% for the films from the 0.5 and 1.5 mg/ml suspensions, respectively. It is worth noting that the extinction coefficient (about 0.5 at 550 nm) obtained here by fitting ellipsometry data is smaller than those of graphite (about 1.3),[21] highly ordered pyrolytic graphite (about 1.75),[22] and few-layer graphene (about 1.1),[23] but similar with that of reduced thin graphene oxide 'stacks' obtained by heating at 200 °C (~0.55).[22]

The sheet resistance of the same samples on cover glass was measured by the van der Pauw four probe method and the measurement configuration is shown in the inset of Fig. 4(b).[24] The sheet resistances of as-made films were 170.8 and 26.5 kΩ/□ for the samples from the 0.5 and 1.5 mg/ml suspensions, respectively. After annealing in argon at 200 °C for 12 h, the resistance dropped to 31.7 and 11.3 kΩ/□. This improvement in conductivity could be attributed to the removal of any remaining water that may have been adsorbed/trapped between layers and perhaps the further reduction of the RGO platelets comprising the films. With the transmittance of ~87% at 550 nm, the sheet resistance of 11.3 kΩ/□ from the 1.5 mg/ml sample is comparable to that of spin-coated graphene oxide films followed by high temperature annealing,[13] and one order or several times lower than those of films made by filtration followed by reduction and annealing,[14] or by LB assembly.[9]

In summary, we have reported a process to fabricate centimeter-area transparent conducting films composed of RGO platelets. Such a process involves assembly of graphene oxide platelets from an aqueous suspension and at the H_2O-air interface, either during their reduction by hydrazine or after they are reduced. The thickness of these films can be controlled by the concentration of the suspension of graphene oxide platelets. A transmittance of 87% at 550 nm and a sheet resistance as low as 11.3 kΩ/□ were obtained. This water-based process is likely scalable to large area, such as for fabrication of transparent conductive electrodes. The low temperature processing makes it compatible with polymer substrates.

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