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High Yield Preparation of Macroscopic Graphene Oxide Membranes

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Graphene is a single-atom thick, two-dimensional material that has attracted great attention because of its remarkable electronic, mechanical, and thermal properties.[1] This has led to renewed interest in methods to chemically functionalize and exfoliate graphite in bulk.[2−6] However, previously reported methods resulted in the production of very small (submicrometer) flakes of graphene oxide (GO) with only moderate quality electronic transport properties after chemical reduction.[2−5] The small flake size is a major obstacle that hinders fundamental studies and limits applications of this material. A practical method appropriate for large-scale production of single layer GO with large size and high quality electric properties is an important step toward the rapid and large-scale fabrication of graphene-based devices, and it will facilitate applications in the areas of electronics, molecular sensors, and composite materials.[2,7,8]

Here, we report a modification of the Hummers method that involves pre-exfoliation of the graphite by microwave heating. With this approach, we produce gram quantities of large single layer GO membranes, up to 2000 μm^2 in size, with a yield exceeding 90%. When the large membranes are deposited on an appropriate SiO_2/Si wafer and chemically reduced, they can be visualized optically, so electronic devices may be efficiently fabricated. Electronic transport measurement on such samples indicates that their conductivity is significantly higher than that of previously reported single layer GO devices.

In a typical synthesis, microwave-assisted heating is used to expand the graphite into a thinner layer structure. Specifically, a small amount of expandable graphite (Grafguard 160-50N) is sealed in a glass vial, purged with ultrahigh purity nitrogen for 2 h, and then heated in a microwave oven for less than 2 s. The high polarizabilty of graphene layers causes them to heat rapidly under microwave irradiation. The intercalated species gasify rapidly, and thus fewer point defects are generated by oxidation from intercalated compounds and robustly absorbed oxygen compared to conventional thermal expansion.[9−11] The graphite expands to ~200 times its original volume (Figure S1) and is separated into flakes whose thickness is 100 times less than that of the starting material but whose lateral dimension is effectively unchanged. Using such a pre-expanded few layer graphite as a starting material, we then prepare GO using Hummers method.[3,12] Because of the pre-expansion process, high viscosity saturated solutions are produced using only 0.5% (w/w) of microwave expanded graphite, in contrast to conventional methods,[3,12] where ~50 times more graphite is required.[3,12] The product after oxidation is centrifuged and washed with DI water extensively until the pH stabilizes at ~5.5. No ultrasonication is used.[13] During the water wash, a significant viscosity change is observed, indicating that exfoliation continues in this process. The addition of salt to the resulting solution induces aggregation of the membranes, suggesting that they are charge-stabilized. Only minute amounts (<1%) of unexfoliated graphite are observed. A single sharp peak is observed in the X-ray diffraction from a filter cake (Figure S2), corresponding to a GO layer−layer distance of ~0.94 nm, as expected for complete exfoliation.

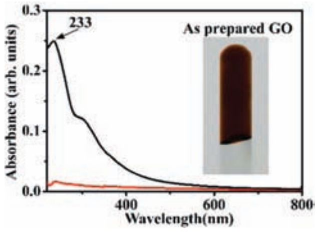

Figure 1. UV−vis absorption spectra of aqueous GO solution before and after filtration (pore size 0.45 μm). Inset: Photograph of the very viscous, 0.3% (w/w) GO solution in an inverted test tube.

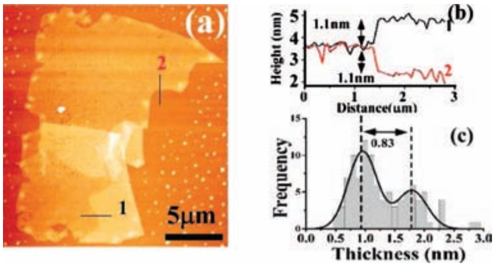

Figure 2. (a) AFM image of a graphene oxide membrane on a SiO_2/Si substrate. (b) Height profile along the lines shown in (a). (c) Histogram of sheet thickness.

Figure 1 illustrates the UV−vis absorption spectrum of a 0.003% (w/w) GO solution, compared with the absorption of the filtrate through a 0.45 μm pore size filter. Two main features are seen: (1) a peak at 233 nm, which is due to to $\pi \rightarrow \pi^*$ of C=C, and (2) a shoulder at ~290−300 nm, corresponding to $n \rightarrow \pi^*$ transition of the C=O bond.[14] The absorbance at 233 nm of the filtrate is less than 10% of that original solution, corroborating visual observation that the filtrate is clear and colorless. These data indicate that the majority of GO flakes are significantly larger than 1 μm in size, consistent with Atomic Force Microscopy (AFM; see below). The material is soluble in many solvents, e.g., acetone, methanol, ethanol, dimethylformamide, tetrahydrofuran, *N*-methyl-2-pyrrolidinone, and dimethyl sulfoxide.

Figure 2 is a typical tapping mode AFM image of a GO membrane deposited on a SiO_2/Si substrate by spin-coating. The areas of the upper and lower are ~160 and 110 μm^2, the equivalent of lateral diameters of 14 and 11 μm, respectively. The membrane height is ~1 nm (Figure 2b). A GO membrane thickness histogram compiled from multiple AFM images (Figure 2c) reveals peaks centered at 0.96 and 1.79 nm. The first peak is assigned to the average height of single layer GO on SiO_2, consistent with previous reports of 0.8−1.5 nm.[3,4,15] The peak-to-peak difference of 0.83 nm is in the range of interlayer distances of 0.68−1.0 nm inferred from X-ray diffraction measurements of GO powder[16,17] and very

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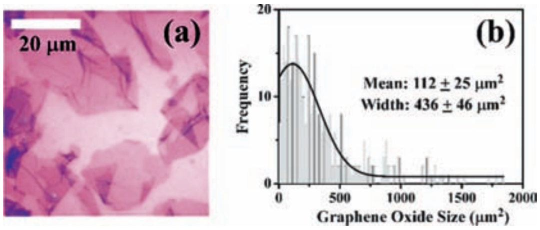

Figure 3. (a) Optical micrograph of reduced GO on SiO_2/Si. (b) Size distribution of GO membranes. Solid curve is a Gaussian fit.

close to 0.82 nm obtained from a theoretical structure model of hydroxylated graphene.[18] Residual unexfoliated graphite is insignificant in this sample, since its presence would lead to peaks separated by 0.34 nm in Figure 2c and multiple peaks in the XRD pattern, which is not seen.

Another obstacle preventing fabrication of GO nanodevices is the difficulty of locating individual flakes without using inefficient and potentially destructive methods, such as AFM or scanning electron microscopy (SEM). GO membranes reduced by exposure to hydrazine are readily imaged on the surface of 300 nm SiO_2/Si. *CAUTION: Hydrazine is extremely corrosive and should be handled with care.* The significant optical contrast and the very large membrane size make it straightforward to locate membranes and to select a region that is optimized for fabrication of GO-based devices. Figure 3b shows a size histogram of GO membranes observed using optical microscopy and SEM (Figure S3). The majority of the GO membranes are 2−3 orders of magnitude larger in area than those produced using previously reported methods.[3,4,19]

The high-yield production of macroscopic GO membranes does not derive simply from the use of large starting graphite material, since submicrometer flakes are produced by recently reported methods even when a large grain (400 μm) starting material is used.[19] Microwave-assisted pre-expansion is critical to the process; without this step, very few large GO membranes are obtained. The pre-expansion yields a fluffy material with graphite flakes that are 2−3 orders of magnitude thinner than the bulk (Figure S1). This high yield of large single sheets might be due to the fact that stronger reaction conditions usually required for graphite exfoliation (e.g., ultrasonication) are not used in our method. Microwave pre-exfoliation of graphite enables faster, more uniform functionalization under milder conditions.

Electron beam lithography and thin film evaporation were used to fabricate Au/Cr source and drain electrodes in a field effect transistor (FET) configuration, with the doped silicon substrate used as a back gate (Figure S4). Measurable drift was observed during the first few current−gate voltage ($I-V_g$) sweeps, after which the $I-V_g$ measurement stabilized. We attribute this effect to unbinding of weakly bound oxidative groups in the presence of the gate electric field. Figure 4 shows a typical, stabilized $I-V_g$ curve of a single-layer GO sample that was measured under ambient conditions (source−drain bias voltage V_{ds} = 10 mV). The "V" shape of the $I-V_g$ curve indicates that the reduced GO shows ambipolar behavior, similar to that observed for single layer graphene.[1] Taking into account the sample geometry (29 μm length, 3 μm source and drain separation, and assumed thickness of 0.83 nm), the conductivity of the GO membrane is 440 S/m (370 S/m if a layer thickness of 1 nm is assumed), significantly greater than previous reports of 5−200 S/m.[3,4] This observation is consistent with our suggestion that the microwave pre-expansion step preserves the graphite layer structure and reduces the number of defects introduced during the chemical oxidation step.

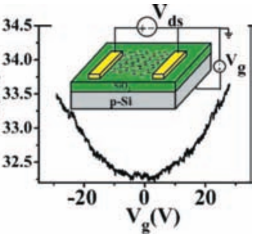

Figure 4. $I-V_g$ characteristic of a reduced, single-layer graphene oxide (GO) sample (V_{ds} = 10 mV). Inset: Schematic of GO field effect transistor.

In conclusion, we have developed a high-yield synthetic protocol for single layer GO membranes, with the size up to a few thousand square micrometeres. GO membranes reduced in hydrazine can be located optically on SiO_2/Si substrates, enabling rapid fabrication of electronic devices. Electronic transport measurements indicate that the GO conductivity is significantly higher than previously reported. The ability to create solutions of such large membranes with high yield should enhance the utility of GO for electronic applications. In addition, the accessibility of dense, aqueous solutions of structures with an unprecedentedly high diameter/thickness ratio (up to 40 000) will enable further experiments probing fundamental physics and chemistry in this unusual size regime.

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Supporting Information Available: Details of synthesis procedure; SEM and AFM images, and XRD spectrum of graphene oxides. This material is available free of charge via the Internet at http://pubs.acs.org.

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