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Aqueous Suspension and Characterization of Chemically Modified Graphene Sheets

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Graphene-based materials are of interest because of the excellent mechanical and electrical properties that the graphene sheet has.[1−3] Individual graphene or chemically modified graphene sheets have been reported by several techniques including the scotch tape (peel off) method,[4] epitaxial growth,[5] noncovalent functionalization of reduced graphene oxide,[6] and chemical reduction of suspensions of graphene oxide,[7,8] the latter obtained by simple sonication of graphite oxide (GO) in water. Our focus here is on colloidal suspensions of reduced graphene oxide sheets that provide, for example, for versatile processing of thin films and composites. Reduction of graphene oxide has readily produced agglomeration of the hydrophobic reduced graphene oxide sheets, which have relatively high surface area by BET measurement.[9] However, Li et al. recently reported generation of homogeneous aqueous suspensions of conductive "chemically modified graphene" sheets by controlled reduction of the graphene oxide suspension by maintaining pH at about 10 and by using dialysis.[10] We report a simpler route to achieve a homogeneous aqueous suspension of chemically modified graphene that when fabricated as a paper material shows good electrical conductivity.

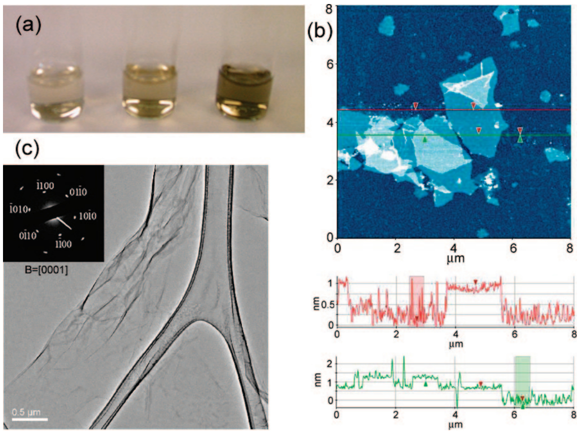

Figure 1. (a) Aqueous colloidal suspension from left: graphene oxide, K-modified graphene oxide, hKMG. (b) AFM image of hKMG sheets on a mica substrate. (c) BF TEM image of hKMG sheets; inset, selected area diffraction pattern of what were found to be two overlapping hKMG sheets.

Controlling the chemistry of graphene oxide sheets[11,12] dictates the properties of individual graphene sheets and thus of graphene-based materials such as composites and thin films. A highly conductive polystyrene/graphene composite was made by reducing chemically modified graphene oxide in the presence of polystyrene.[7] Transparent and electrically conductive ceramic/graphene thin-film composites were made by the chemical reduction of well-dispersed graphene oxide sheets in silica sol−gels, using hydrazine.[13] In addition, significant enhancement in mechanical stiffness of "graphene oxide paper" was achieved by introduction of a small amount of divalent ions;[14] alkaline earth metal ions were suggested to strongly bind to the carboxylic acid group at the edges of the layered graphene oxide sheets.

Here, we have used KOH to produce an aqueous homogeneous suspension containing conducting chemically modified graphene sheets (CMG) from a precursor dispersion of graphene oxide in water. We suggest (see below) that KOH, a strong base, can confer a large negative charge through reactions with reactive hydroxyl, epoxy, and carboxylic acid groups on the graphene oxide sheets, resulting in reduced graphene oxide sheets that remain dispersed in water for at least 4 months.

Our method involves sequential chemical reaction of graphene oxide sheets suspended in water with KOH and then with hydrazine (Figure 1a and the Supporting Information). Adding KOH to the aqueous suspension of graphene oxide sheets produced a slightly darker suspension ("KMG"). This is caused by the reaction between KOH and oxygen functional groups in the graphene oxide sheets, such as

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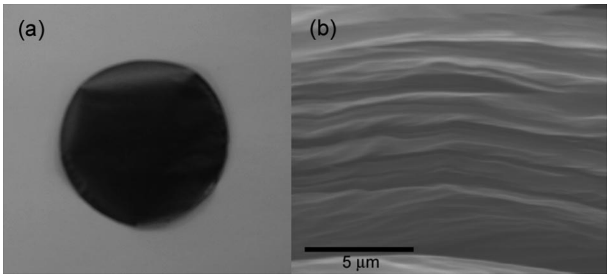

Figure 2. (a) Photo of a piece of hKMG paper 3.8 cm in diameter. (b) SEM image of a cross-section of hKMG paper made by fracturing a sample.

carboxylic acid, hydroxyl, and epoxy groups, resulting in extensive decoration of the sheets with negative charges and thus also with K^+ ions. A black and homogeneous suspension of KMG sheets was then obtained by addition of hydrazine monohydrate (hydrazine: GO = 1: 8 by weight) and stirring at 35 °C for 6 h. This aqueous "hydrazine-reduced KMG suspension (hKMG)" has been stable for more than 4 months and remains a colloidal dispersion at the time of submission of this manuscript. Although a concentration of 1 mg GO/5 mL water was used in terms of producing the "paper" material and measuring its electrical properties (see below), homogeneous hKMG suspensions with concentrations as high as 7 mg/1 mL could be obtained.

Atomic force microscopy (AFM) and bright field transmission electron microscopy (BF TEM) measurements of dried down deposits demonstrated the presence of individual hKMG sheets in the aqueous suspension (Figure 1b). The AFM image showed single hKMG sheets with an average thickness of 6 Å. On the basis of numerous AFM images, the lateral size of the hKMG sheets was in the range of several hundreds of nanometers to a few micrometers. BF TEM images acquired at 200 keV showed hKMG sheet lateral size up to several micrometers (Figure 1c). The selected area electron diffraction (SAED) pattern from the hKMG sheet in the image (inset in Figure 1c) shows a hexagonal pattern with the measured d_{1100} to be 2.135 ± 0.002 Å, close to the expected 2.131 Å. However, a small satellite peak exists next to the parent diffraction spot. This indicates that in this case, the diffraction pattern was obtained from two overlapping hKMG sheets. No amorphization of the hKMG was observed during TEM observations at 200 keV performed over 10 min on a specific hKMG sheet. Just as homogeneous suspensions of other graphene-based sheets have been used to produced paperlike materials,[6,10,15] simple filtration of the hKMG aqueous suspension gave a shiny black and compliant paper material (Figure 2a). Impurities, including unbound potassium ions, were rinsed in both hKMG and unmodified paper samples by soaking the paper in purified water 3 times, for 6 h each time. An SEM image of the cross-section of the hKMG paper sample (prepared by fracturing a sample at room temperature using tweezers) shows the layered structure of the constituent hKMG sheets (Figure 2b). The Raman spectra of both the unmodified graphene oxide and hKMG paper contain two broad peaks, a D band around 1345 cm^{-1} and a G band around 1590 cm^{-1} (see the Supporting Information).[9] The electrical conductivity of the air-dried hKMG paper as measured by the Van der Pauw method was found to be $6.87 \pm 0.07 \times 10^2$ S m^{-1}, lower than values reported for paperlike films obtained from water-dispersible reduced graphene oxide[10] and functionalized single-walled carbon nanotube paper materials,[16] and significantly higher than the essentially insulating graphene oxide paper ($0.53 \pm 0.39 \times 10^{-3}$ S m^{-1}). This shows that although the chemical reduction of the unmodified graphene oxide sheets with hydrazine produced conductive graphene sheets that are hydrophobic,[9] the hKMG graphene sheets produced in this work were conductive, but importantly, water-dispersible.

Thermogravimetric analysis (TGA) curves of both the unmodified graphene oxide and the hKMG paper samples showed a weight loss near 100 °C, evidently due to evaporation of water molecules which are held in the material, including between hKMG sheets (~17 and ~10 wt % loss for unmodified graphene oxide and hKMG paper samples respectively). The water amount in the hKMG paper was significantly smaller than that in the unmodified graphene oxide paper. The second significant weight loss was observed from 130 to 200 °C (~42 wt % loss at 200 °C) of the unmodified graphene oxide sample. This is due to loss of CO, CO_2, and steam from the sample, by water evaporation and decomposition of labile oxygen functional groups.[9,17] Interestingly, the hKMG lost a much smaller mass (~17 wt % loss at 200 °C) over this temperature span, which is very likely due to a decreased amount of oxygen functional groups in the hKMG, as would be expected from the chemical treatments used. Elemental analysis shows an increase in the C/O atomic ratio of hKMG (3.1; elemental analysis by combustion of the paperlike material) compared to unmodified graphene oxide (1.2; this value includes contributions from adsorbed H_2O) (see the Supporting Information). Notably, based on the comparison for C/O atomic ratio of the hKMG with highly reduced graphene oxide (10.3) by hydrazine,[9] hKMG contains more O atoms than the highly reduced graphene oxide, which could be due to a combination of trapped water between the hKMG sheets and O present in the oxygen functional groups on the sheets. Although the exact amount of oxygen atoms in the functional groups of the hKMG sheets is not revealed, the TGA curve and C/O value of hKMG support that the hKMG absorbs water but is less hydrophilic than the unmodified graphene oxide. Additionally, a small amount of nitrogen (~1.7 wt %) was introduced after the hydrazine reduction, probably induced by the reaction between hydrazine and oxygen functionalities.[9]

We employed X-ray photoelectron spectroscopy (XPS) to analyze paper samples of the unmodified graphene oxide and separately, of hKMG (Figure 3 and the Supporting Information). In comparison to the C1*s* spectrum of the unmodified graphene oxide paper, that of hKMG paper clearly exhibited

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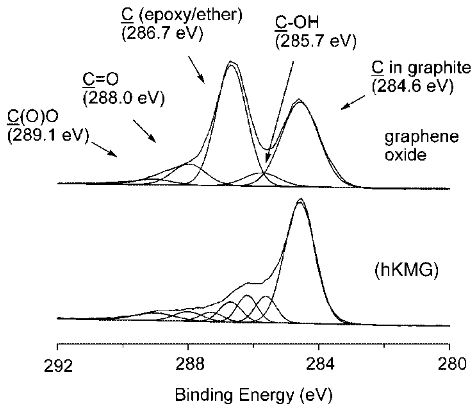

Figure 3. Deconvoluted XPS spectra in the C1s region of: top, unmodified graphene oxide paper; bottom, hKMG paper.

decreased intensity for peak(s) corresponding to the epoxy/ether group (286.7 eV).[18] However, a significant fraction of the C component of other oxygen functional groups remained. Additionally, new components at 285.6 and 286.7 eV corresponding to carbon bound to nitrogen were observed.[18] The Fourier transformed infrared spectroscopy (FT-IR) spectrum of the hKMG paper sample showed a significantly increased and broadened component at 1235 cm^{-1} corresponding to the combination of free hydroxyl group and K−O stretching/hydroxyl group,[19] supporting the reaction between potassium ions and oxygen functional groups of graphene oxide sheets (see the Supporting Information).

The successful modification of graphene oxide sheets by K^+ ions was verified by XPS and energy dispersive X-ray spectroscopy (EDS). The component for potassium in the unmodified graphene oxide paper was not observed by XPS and EDS (see the Supporting Information). After the reduction, new K2*p* peak components at 293.0 and 295.8 eV were observed in the XPS spectrum of the hKMG paper sample[18] and a significant amount (a few atomic %) of potassium in the hKMG paper was obtained by EDS (see the Supporting Information). Previously, we reported that metal ions that are unbound or weakly bound to the graphene oxide sheets can be readily removed by water rinsing.[14] On the basis of the reported results and comparison to thoroughly water-rinsed hKMG papers, we expect that the amount of unbound K^+ ions in the hKMG paper is negligible. Given the hydroxyl, epoxy, and ketone groups on the basal planes and carboxyl acid groups at the edges of graphene oxide sheets, we suggest that the interaction of K^+ ions with the carboxylic acid groups at the edges would be very strong in such basic condition (see the Supporting Information).[20] Consequently, the interaction could be stable against chemical reduction by hydrazine, and if so, one should have highly negatively charged hKMG sheets with the carboxylate anion groups decorated by K^+, forming ion pairs.

In conclusion, simple chemical modification of graphene oxide dispersed in water produced hydrazine reduced K-modified graphene (hKMG) sheets that were well-dispersed as individual sheets in water, and showed good electrical conductivity when prepared as thin, dried films. Although the reaction mechanism of the reduction step and the chemical structure of the hKMG are not at this time known, the oxygen functional groups of the precursor graphene oxide sheets are partially removed by the chemical reduction and the hKMG sheets are modified by a small amount of K^+ ions, resulting in the generation of hKMG sheets that are electrically conductive but also water-dispersible. We suggest that this simple route to achieve homogeneous suspensions of electrically conductive graphene-like sheets will afford further progress in the area of composites and thin films. Furthermore, the reactive ion pairs between K^+ ions and negatively charged oxygen functional groups of such hKMG sheets could be a good precursor for further chemical modification.

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Supporting Information Available: Experimental details; figures of Raman, FT-IR, XPS, and TGA; and table for elemental analysis (PDF). This material is available free of charge via Internet at http://pubs.acs.org.

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