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Exfoliation of Graphite Oxide in Propylene Carbonate and Thermal Reduction of the Resulting Graphene Oxide Platelets

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ABSTRACT Graphite oxide was exfoliated and dispersed in propylene carbonate (PC) by bath sonication. Heating the graphene oxide suspensions at 150 °C significantly reduced the graphene oxide platelets; paper samples comprising such reduced graphene oxide platelets had an electrical conductivity of 5230 S/m. By adding tetraethylammonium tetrafluoroborate (TEA BF$_4$) to the reduced graphene oxide/PC slurry and making a two-cell ultracapacitor, specific capacitance values of about 120 F/g were obtained.

KEYWORDS: graphene · graphite oxide · propylene carbonate · ultracapacitor · characterization

Graphene and graphene-based materials have attracted intensive research interest due to their fascinating properties.[1,2] The exfoliation of graphite oxide (GO) followed by reduction has provided an affordable route to the large scale processing of graphene-based materials. In particular, the importance of solution-processable graphene oxide (by the exfoliation of GO) has been demonstrated by the fabrication of paperlike films,[3] transparent conductive electrodes,[4−6] and conductive polymeric[7] and ceramic composites.[8] Since a stable colloidal suspension of graphene oxide platelets is obtained by the simple sonication of GO in water,[9,10] much of the solution processing of graphene oxide reported to date has been carried out in aqueous media.[11] Li *et al.* reported aqueous dispersions of reduced graphene oxide (RG-O) nanoplatelets by changing the pH to about 10 prior to reduction with hydrazine.[12] The dispersion of RG-O in water at a pH of approximately 7 could be achieved by addition of poly(sodium 4-styrenesulfonate) to the aqueous suspension of graphene oxide platelets prior to addition of hydrazine.[13] The preparation of large-scale graphene oxide dispersions in organic solvents is also highly desirable and may further broaden the scope of applications and facilitate the practical use of graphene-based materials.[11] Paredes *et al.* stated that the full exfoliation of GO and stable dispersion of graphene oxide could be obtained in *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), and ethylene glycol (EG).[14] Recently, Park *et al.* reported achieving colloidal suspensions of highly reduced graphene oxide in various organic solvents by diluting the colloidal suspension of RG-O platelets in DMF/H$_2$O (9:1) with solvents such as DMF, NMP, ethanol, acetonitrile (AN), and dimethylsulfoxide (DMSO), among others.[15] The dispersion of graphene oxide in chloroform has been realized by transferring surfactant decorated graphene oxide from water to chloroform.[16]

Graphene oxide is electrically insulating and various reduction methods have been developed to restore the conjugated network and electrical conductivity of graphene. Reducing agents such as hydrazine or dimethylhydrazine,[9,15,17,18] hydroquinone,[19] and NaBH$_4$[20,21] have been used to reduce graphene oxide. Cote *et al.* have demonstrated a flash-assisted reduction of films composed of graphene oxide platelets and their polymer composites, where a flash beam with an energy flux of about 1 J/cm^2 was used to irradiate and heat the samples to over 100 °C to trigger thermal reduction.[22] A method involving heating graphene oxide suspensions in water under alkaline conditions has been proposed as a "green" route to suspensions of RG-O.[23] Direct thermal treatment at elevated temperatures provides another method to reduce individual graphene oxide platelets
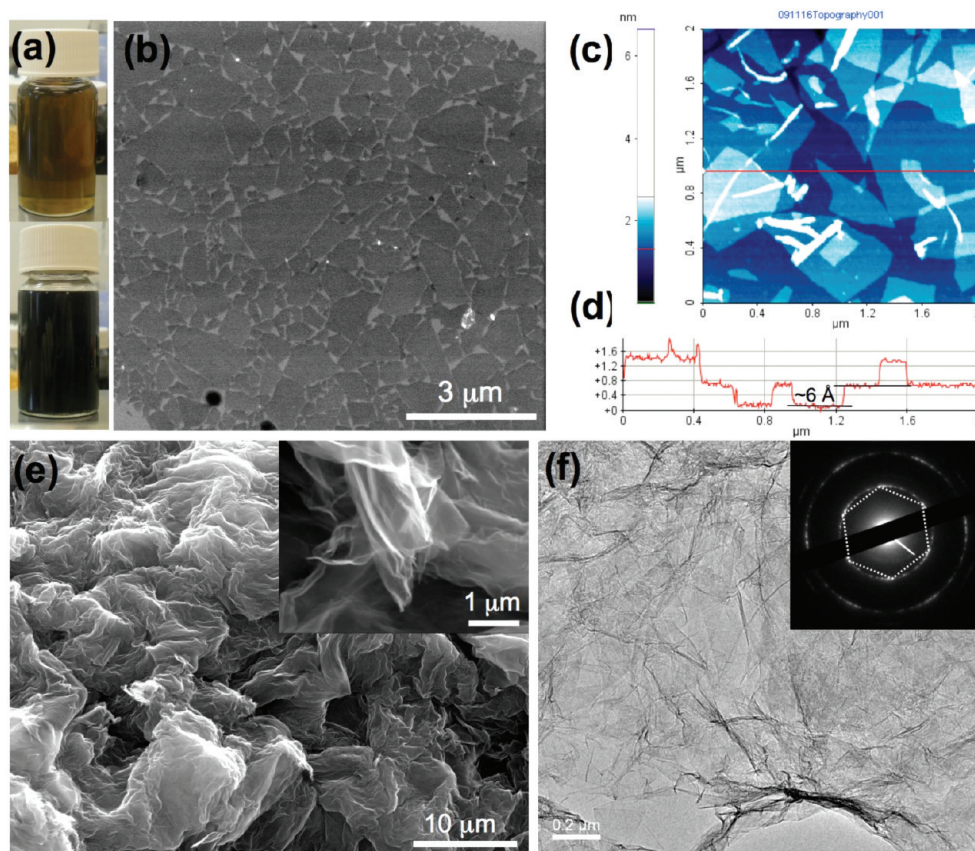
Figure 1. (a) Optical images of a graphene oxide suspension in PC (top) before and (bottom) after heating at 150 °C for 12 h. (b) SEM image of graphene oxide platelets deposited on a Si substrate. (c) AFM image of graphene oxide platelets dispersed on mica and (d) corresponding line profile. (e) SEM image of the RG-O powder obtained by heating graphene oxide in PC at 150 °C with a high magnification SEM image in the inset. (f) TEM image of the RG-O platelets from the 150 °C treatment and the corresponding SAED pattern.

adhered to a substrate, without using reducing agents.[24] "Thermal shock" of GO powders at temperatures up to ~1050 °C has been used,[25,26] and there is a long history of thermal treatment of intercalated graphite powders as presented in numerous peer-reviewed publications.[27−30] Recently, Zhou *et al.* discussed a "hydrothermal dehydration" for the reduction of graphene oxide platelets in supercritical water at 180 °C.[31]

We report here the formation of stable suspensions of graphene oxide platelets by the dispersion and exfoliation of GO in propylene carbonate (PC) *via* sonication. We found that PC is an excellent solvent for achieving exfoliated GO dispersions and to our knowledge this is the first report of this result. Furthermore, we show that thermally treating the suspension at 150 °C can remove a significant fraction of the oxygen functional groups and yield an electrically conductive film composed of such RG-O platelets with a conductivity value as high as 5230 S/m. Since PC is frequently used as a high-permittivity component of electrolytes, the RG-O platelets obtained by heating graphene oxide suspensions in PC may yield an economical processing route for such applications as electrode materials for ultracapacitors. To illustrate this potential, we have con-

structed an ultracapacitor cell, with RG-O electrodes and using an organic electrolyte commonly used in commercial ultracapacitors, that yields specific capacitance values greater than 120 F/g, thus demonstrating superb performance.

RESULTS AND DISCUSSION

Dispersion of GO in PC. Figure 1a (top image) shows that 1 h of bath sonication generated a uniform brown-colored graphene oxide suspension in PC at pH 3 with the suspension remaining stable for several months without any visible precipitation. When the pH was increased to 7 and 10, only very low concentrations of dispersed GO in PC could be achieved (Supporting Information, Figure S1). In contrast to the high zeta potential values reported for aqueous suspensions of graphene oxide platelets at pH 7 (~36 mV) and aqueous suspensions of RG-O platelets at pH of around 10 (~42 mV),[12] the value of the zeta potential from the graphene oxide suspensions in PC at pH 3 was about −10 mV for the specific batch of GO used in the experiments described here. The excellent dispersion of GO in PC thus may not be caused by electrostatic repulsion—at least not as far as the zeta potential of the suspension is an indicator of such repulsion. The high dipole moment of PC,

5.0 D,[32] could play a role in dispersing graphene oxide platelets at pH 3;[14] the Hansen, and perhaps other, solubility parameters of PC may also be factors.[15]

To evaluate the degree of exfoliation of the GO into graphene oxide platelets, a suspension with 0.05 mg/mL concentration (diluted from 1 mg/mL) was dropped onto Si substrates and mica substrates followed by drying and inspection with scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively. As seen from the SEM image in Figure 1b, a closely packed "tiling" of graphene oxide platelets with a uniform contrast was observed on the substrate. The platelets have lateral dimensions ranging from several hundred nanometers to several micrometers and are arranged in an edge-to-edge configuration. No significant folding or overlapping was observed, similar to the Langmuir–Blodgett (LB) assembly of graphene oxide platelets.[33] From a typical AFM topography image (Figure 1c), we can observe again that the contrast of the platelets is very uniform except for isolated wrinkles and protrusions. The corresponding line profile (Figure 1d) shows a thickness of ~0.6 nm for the graphene oxide platelets. It should be noted that not only is this value about half that of the typical 1–1.2 nm thickness of graphene oxide platelets exfoliated in water,[9,34] but also less than that of RG-O in water (~1 nm)[12] or in a 9:1 DMF/H_2O mixture (0.7–0.8 nm),[15] when reduced by hydrazine.

Reduction of Graphene Oxide Suspensions in PC. The relatively high boiling point (~240 °C) of PC has allowed the reduction of the as-dispersed graphene oxide by heating the suspension at moderate temperatures. After being heated in an oil bath at 150 °C for 12 h the suspension became black, as shown by the optical image in Figure 1a (bottom image). Unlike the irreversible agglomeration of RG-O reduced by hydrazine in water at pH 7,[9] the RG-O suspension in PC obtained by thermal treatment remains a homogeneous black suspension, with only minute particles visible to the eye. The RG-O suspension thus obtained could last for several hours before significant precipitation was observed.

Characterization of RG-O Samples. RG-O powders, obtained by filtration of the as-heated (reduced) graphene oxide suspension followed by vacuum drying, are composed of platelets displaying a fluffy and crumpled morphology as viewed using SEM and shown in Figure 1e. The high magnification SEM image (Figure 1e inset) demonstrates thin and wrinkled platelets transparent to electrons. Figure 1f shows a typical transmission electron microscopy (TEM) image from the RG-O sample that was thermally reduced at 150 °C in PC. As can be seen, the RG-O platelets have wrinkles and folded regions. From these RG-O platelets, the selected area electron diffraction (SAED) yields a ring-like pattern consisting of many diffraction spots for each order of diffraction, as seen in the inset of Figure 1f. These spots make regular hexagons (e.g., the one marked in the fig-

ure) with different rotational angles between such hexagons, indicating the essentially random overlay of individual RG-O platelets, or from folds that cause overlays. A high resolution TEM (HRTEM) image (Supporting Information, Figure S2) from the same sample showed that the edge of the sample is composed of a stack of RG-O platelets with the number of layers ranging from 2 to more than 10.

Freestanding paperlike RG-O materials with a thickness of about 700 nm were obtained when a small amount (e.g., 2 mL for the concentration of 1 mg/mL) of RG-O suspension in PC was deposited by vacuum filtration followed by vacuum drying at 80 °C for 2 days. The upper inset of Figure 2a is an optical image showing a shiny, 1 inch sheet of RG-O paper made from the RG-O suspension. The cross-section SEM image (bottom inset of Figure 2a) shows the RG-O paper's layered structure.

The suspension of graphene oxide platelets in PC was also heat-treated at a higher temperature of 200 °C, for 12 h. The RG-O powders and papers obtained from heating at 200 °C had a similar morphology to those obtained from heating at 150 °C. From the X-ray diffraction (XRD) spectrum shown in Figure 2b, a dominant peak was observed at $2\theta = 9.1°$ from GO powder, corresponding to an interlayer distance of 0.97 nm (at a relative humidity of approximately 35%). For the RG-O papers obtained by heating the suspension of graphene oxide in PC, this peak completely disappeared and broad peaks centered at around 25° were observed, corresponding to an interlayer spacing of about 0.36 nm. This spacing is comparable to that of RG-O papers made from RG-O platelets obtained by hydrazine treatment of graphene oxide dispersed in a 9:1 DMF/H_2O mixture (0.37 nm).[15] The broadness of the XRD peak from the RG-O samples could be due to increased disorder in the through-plane direction of the RG-O paper samples, and also perhaps due to structural defects (if any) induced by sonication and/or thermal treatment, and the smaller platelet sizes caused by the sonication. X-ray photoelectron spectroscopy (XPS) spectra in Figure 2c show that the deconvoluted peaks with binding energies higher than 284.5 eV (sp^2 carbon) were largely suppressed for the RG-O paper samples. The peaks between 286 and 289 eV are typically assigned to epoxide, hydroxyl, carboxyl groups, and so on.[23,31,35] The XPS results suggest that these oxygen-containing groups have been effectively removed by the thermal treatment. Furthermore, the C/O atomic ratio calculated from the XPS spectra is 1.7 for the GO powders but 8.3 and 6.8 for RG-O papers made from graphene oxide suspensions heated in PC at 150 and 200 °C, respectively. Fourier transformed infrared (FT-IR) spectroscopy also indicates that the oxygen functional groups in GO were significantly reduced after thermal treatment and that there was no detectable trace of PC in the RG-O paper (Supporting Information,
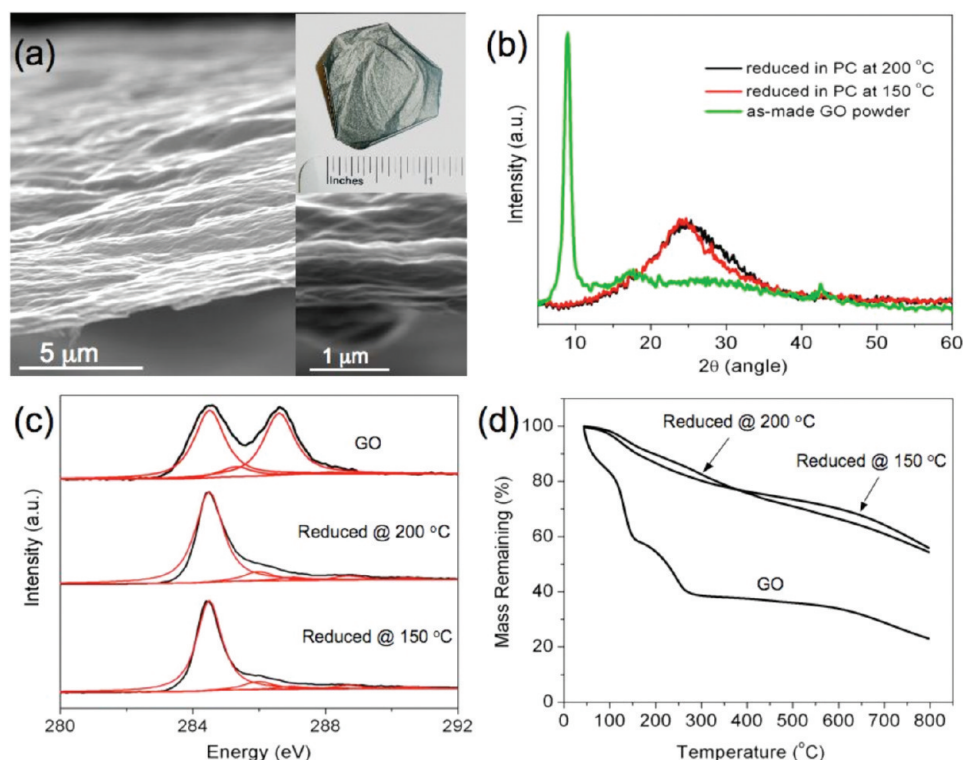
Figure 2. (a) SEM image of the RG-O paper from the 150 °C treatment. Insets show (top) an optical image and (bottom) cross section SEM image of the paper. **(b)** XRD, **(c)** XPS, and **(d)** TGA characterizations of the RG-O synthesized at 150 and 200 °C, with those of GO powder as a reference in each case.

Figure S3). The results from thermal gravimetric analysis (TGA) under nitrogen flow with a heating rate of 1 °C/min are shown in Figure 2d. Three significant weight loss events were observed for GO powders, corresponding to the evaporation of water (below 100 °C) and the loss of what is likely carbon oxide gas species (120−150 °C and 200−260 °C) from the decomposition of labile oxygen functional groups.[9,36] In contrast, the RG-O powders obtained by heating graphene oxide suspensions in PC followed by drying have less than 2% of weight loss below 100 °C. The gradual weight loss (about 20%) below 350 °C is likely due to the loss of residual functional groups on the RG-O platelets in these RG-O powders.

Conductivity of RG-O Papers. To further test whether the dispersed graphene oxide platelets were rendered conductive by thermal treatment in PC, the electrical sheet resistance of the RG-O papers was measured using the van der Pauw four-probe method.[24] The average thickness of each paper sample was measured using cross-section SEM images. The average conductivity of RG-O papers dried in vacuum at 80 °C was about 2100 and 1800 S/m for the samples from the 150 and 200 °C treatments, respectively. Further annealing the samples at 250 °C for 12 h under vacuum (~60 mTorr) in a tube furnace improved the conductivity to 5230 and 2640 S/m for the samples derived from the 150 and 200 °C treatments, respectively. The electrical conductivities of the RG-O papers derived from heating of graphene oxide suspensions in PC are comparable to those of RG-O ob-

tained by chemical reduction of graphene oxide suspensions[12,20] or from thermal shock of GO powders at 1050 °C.[26] Table S1 (in Supporting Information) includes a more extensive list of electrical properties for various GO reduction methods.

While the method for achieving dispersed RG-O platelets described in this work provides a facile method to reduce graphene oxide platelets dispersed in PC, the specific mechanisms are not yet understood in detail. McAllister *et al.*[25] and Jeong *et al.*[37,38] have suggested that temperatures greater than 200 °C are necessary for significantly removing the oxygen-containing groups in GO. Our TGA data (Figure 2d) also showed a third significant weight loss for GO powders occurring in a range of 200−260 °C. On the other hand, Jung *et al.* stated that a thermal reduction indicated by a corresponding drop in electrical resistance could begin at about 160 °C.[24] In addition, increasing the temperature of graphene oxide suspension in PC from 150 to 200 °C results in a lower C/O ratio, slightly higher weight loss at elevated temperatures (>350 °C) measured with TGA and a lower conductivity. Further study is necessary to develop an understanding of chemical changes as a function of the time−temperature exposure for given concentrations of graphene oxide platelets in PC.

Performance of RG-O Based Ultracapacitors. To evaluate one possible application for electrical energy storage, the RG-O material was used as electrodes in an ultracapacitor cell. Since commercial ultracapacitors use tetraethylammonium tetrafluoroborate (TEA BF$_4$) in PC or AN
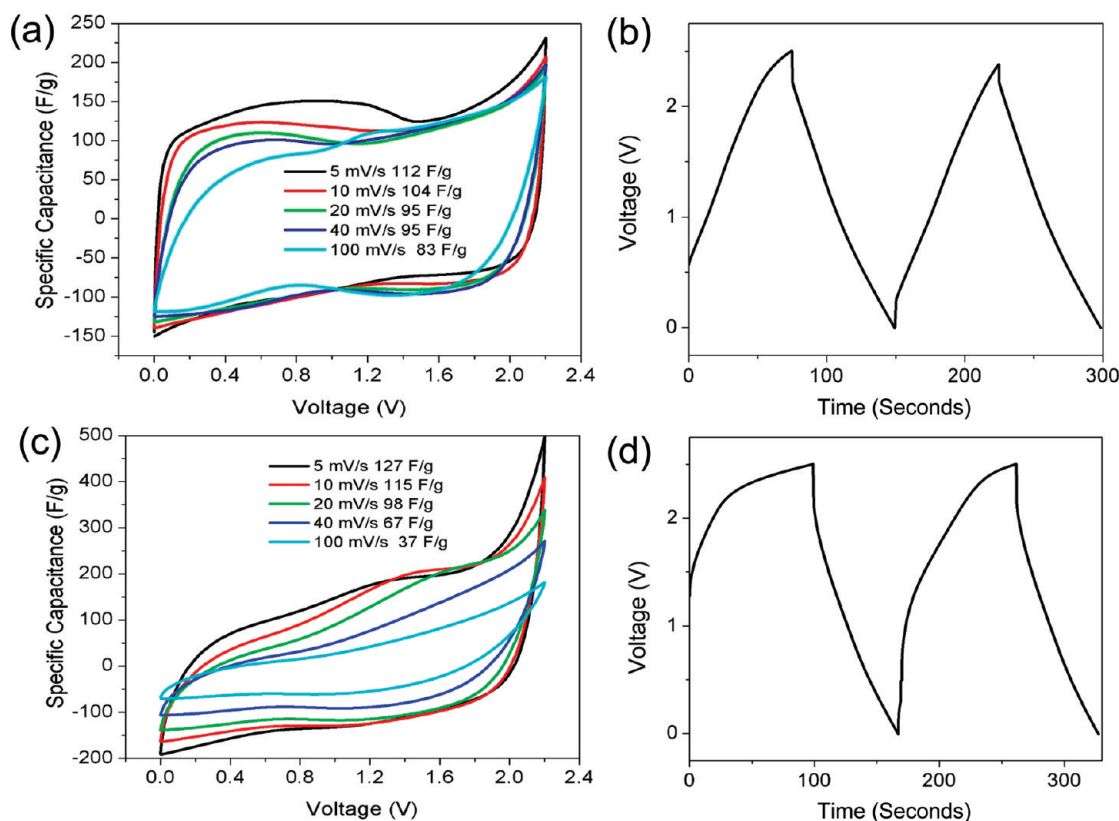
Figure 3. (a and b) Ultracapacitor performance of RG-O derived from 150 °C treatment. (a) CV curves. Different scan rates are labeled with the average specific capacitance values marked. (b) Galvanostatic charge/discharge curves at a constant current of ∼830 mA/g. (c and d) Ultracapacitor performance of RG-O derived from the 200 °C treatment. (c) CV curves. Different scan rates are labeled with the average specific capacitance values marked. (d) Galvanostatic charge/discharge curves at a constant current of ∼1000 mA/g.

for the electrolyte, TEA BF$_4$ was simply added to the PC/RG-O suspension with the resulting slurry then used for the electrodes. Figure 3a shows the cyclic voltammetry (CV) curves of the ultracapacitor made from the 150 °C reduced RG-O. With the exception of the faster scan rates, the CV curves have a rectangular shape, indicating good capacitive behavior. A specific capacitance of 112 F/g calculated from CV data was measured for a scan rate of 5 mV/s. Figure 3b shows a galvanostatic charge/discharge curve at a constant current of 5 mA (corresponding to a charge/discharge rate of 830 mA/g). From the discharge curve, a specific capacitance of about 112 F/g was calculated, consistent with the values obtained from the CV tests for the scan rate of 5 mV/s. For the sample treated at 200 °C, the CV (Figure 3c) and galvanostatic charge/discharge curves (Figure 3d) have different features from those of the 150 °C sample. Nonrectangular CV curves with a nonlinear increase in current and a rapid specific capacitance decrease with the increase in the scan rate were observed for the 200 °C sample. Moreover, the charge and discharge curves are asymmetric, suggesting irreversible faradic processes are occurring during charging. The charge/discharge curve (Figure 3d) from the 200 °C sample at 5 mA (corresponding to a charge/discharge rate of ∼1000 mA/g) gave a specific capacitance of

about 122 F/g. Compared with our previous report on ultracapacitors based on RG-O reduced with hydrazine,[39] the RG-O obtained here by heating graphene oxide suspensions in PC yields an improvement of ∼20% in terms of specific capacitance and compares favorably with the performance of other electrode materials (80−120 F/g) using PC-based electrolytes.[40]

CONCLUSIONS

We report the exfoliation and thermal reduction of suspensions of graphene oxide platelets in propylene carbonate. Thermally treating the suspensions at 150 °C effectively reduced the graphene oxide platelets. The excellent dispersion and subsequent effective reduction of graphene oxide platelets in propylene carbonate opens an exciting opportunity for the production of reduced graphene oxide on a large scale. This scalable and potentially green process may enable important commercial applications for graphene materials. As one example, we have demonstrated the use of this material for electrical energy storage. Ultracapacitor electrodes made by adding TEA BF$_4$ to the RG-O/PC slurry gave specific capacitances that rival the activated carbon materials currently used in commercial ultracapacitors.

METHOD

Preparation. GO powder was prepared by the modified Hummers method.[10] Graphene oxide suspensions were obtained by dispersing GO powder in anhydrous PC (99.7%, Sigma Aldrich) with the aid of sonication in an ultrasonic bath (VWR B2500A-MT). In a typical process, a uniform brown suspension with a concentration of 1 mg/mL was generated by 1 h of sonication. Thermal reduction of graphene oxide platelets in such suspensions was carried out by heating the suspension in an oil bath for 12 h while stirring at 400 rpm with a Teflon-coated stir bar. Two temperatures were used for the thermal treatment, 150 and 200 °C. After cooling, 80 mL of heated suspension was filtered through a 47-mm diameter alumina membrane (0.2 μm size, Whatman, Middlesex, UK) to prepare RG-O powders. When a small amount (*e.g.*, 2 mL) of heated suspension was filtered, paperlike RG-O was formed on the membrane after drying in air. Both powders and papers were subject to further drying at 80 °C in vacuum for 2 days. With these preparation and drying procedures, the mass of the RG-O is about 55% of that of the starting GO.

Characterization. The suspension of graphene oxide platelets in PC was dropped onto native oxide/silicon and mica substrates followed by vacuum drying for SEM (FEI Quanta-600) and AFM (Park Systems XE-100) studies, respectively. SEM imaging was also done on the RG-O powders and papers. Zeta-potential measurements (Zeta Plus, Brookhaven Instruments) were done on the as-dispersed graphene oxide suspension; 10 μL of as-heated suspension was dropped onto Cu grids followed by vacuum drying at 80 °C for TEM (JEOL 2010F, 200 kV) observation. TGA (TGA 4000, Perkin-Elmer) was done on the GO and RG-O powder samples. XRD (Philips X'Pert PRO, λ=1.54 Å), XPS (Kratos AXIS Ultra DLD, Al Kα), and FT-IR (Perkin-Elmer Spectrum BX) were done on the RG-O papers. The paper samples were also placed in the four-probe system (Keithley 6221 and 6514) to measure the conductivity of the RG-O.

Ultracapacitance Measurements. Typically, 10 mL of as-heated suspension (starting from 1 mg/mL graphene oxide suspension in PC) was filtered on alumina membranes (0.2 μm pore size) with the filtration lasting approximately 20 min. Then, 1 mL of TEA BF$_4$/PC solution (1 M) was dropped on the sample as electrolyte and the sample kept under filtration for another 2 min. After the filtration, a black slurry was formed on the alumina membrane. A "doctor blade" method was used to apply the RG-O/PC/TEA BF$_4$ slurry onto carbon-coated foil collectors (0.75 in. in diameter) to form electrodes. Each electrode typically consisted of ~70 mg of slurry, itself a mixture of RG-O, TEA BF$_4$, and PC. Electrodes were assembled into a two-electrode test cell; the cell and test methods are described elsewhere.[39]

Supporting Information Available: Effect of pH on the dispersion of GO powders in PC by sonication, HRTEM of RG-O, FT-IR measurement results, comparison of the conductivity obtained from RG-O papers in this work with those from references, and ultracapacitance calculation method from CV and constant current charge/discharge curves. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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