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Letter to the editor

One-step fast electrochemical fabrication of water-dispersible graphene

ABSTRACT

Aided by Oxone, water-dispersible graphene of 2–5 atomic layers was electrochemically fabricated from graphite in one step without any extra stabilizers or additives. Oxone as a novel electrolyte and the electrochemically enhanced oxidation were responsible for the excellent aqueous dispersibility, effective exfoliation and the reasonably high yield (up to 60.1%).

Recently, electrochemical exfoliation of graphitic materials has attracted tremendous attention because of its simple, highly efficient and non-polluting characteristic to prepare the low defect graphene [1]. Under either cathodic or anodic potentials, the continuous intercalation of electrolytic ions or charged particles into graphitic layers leads to the exfoliation of graphite [2]. The typical parameters are 1–10 V, room temperature and 5–30 min, and the resulted graphene has the thickness of 1–10 layers, the lateral size of 1–5 microns, and oxygen content of <11 at. %. It should be emphasized that although electrochemical exfoliated graphene has high quality compared with graphene oxide (GO) [3], but it does not have the dispersibility in water due to the hydrophobic nature of graphene. Since aqueous dispersibility is very critical for graphene's applications, a feasible approach is to add some surfactants, such as cetyltrimethylammonium bromide [4] or 7,7,8,8-tetracyanoquinodimethane [5] into the electrolyte during the electrochemical exfoliation to facilitate the aqueous dispersibility of obtained graphene. Unfortunately, these surfactants are hard to be removed, and inevitably leave a large number of impurities, depressing the properties of graphene. An optimized electrochemical method for direct fabrication of water-dispersible graphene is highly demanded.

Our strategy is to hydrophilize the graphene surface by strengthened oxidation during the electrochemical exfoliation with the optimized electrolyte and higher anodic voltage. Oxone (potassium monopersulfate, $KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$) solution is chosen as electrolyte due to its stronger oxidizing capability than generally employed electrolytes, such as H_2SO_4, $(NH_4)_2SO_4$, NH_4NO_3 and K_2SO_4. Oxone is easy to handle, not toxic, soluble in water, above all, cheap and stable [6]. When a 50 V anodic potential is applied using a 0.05 mol L^{-1} oxone solution for 4 minutes, the graphite can be exfoliated into 2–5 layers water-dispersible graphene with a yield of ~60.1% More importantly, the obtained graphene has an oxygen content of ~16.37 at. % with excellent aqueous dispersibility. Concentration of dispersion up to 1.04 mg mL^{-1} is achieved without any additives, and it can be concentrated into viscous slurry with extremely high concentration of ~30.5 mg mL^{-1}. Graphene papers by filtrating the graphene dispersion exhibit an average conductivity of 11415.5 S m^{-1} (density = 1.44 g cm^{-3}), indicating pretty good quality. This technique enables one-step, facile and green fabrication of high-quality graphene with excellent dispersibility in water.

Oxone is rationally chosen and experimentally proven to be highly effective for exfoliation and oxidation of graphite. In a typical synthesis, as shown in Fig. 1a, a two electrodes system was employed with graphite foil as the working electrode, a platinum foil as the counter electrode, and 0.05 mol L^{-1} aqueous Oxone solution as the electrolyte. When a constant anodic potential of 50 V was loaded on two electrodes, the graphite anode expanded with numerous debris detaching from the anode and constant bubbles being generated. As shown in Fig. S1, the morphology evolution of graphite electrode after 0, 30, 90, 150 and 240 s anodization indicates the expansion and exfoliation process. The whole process lasted for about 4 minutes and the exfoliated graphene dissolved in the electrolyte, resulting in a brown suspension with obvious aggregations (Fig. 1b). However, homogeneous dispersion can be obtained from the aggregations after removal of the electrolyte and re-dispersing in water with sonication, indicating the aqueous dispersibility of the exfoliated sheets. Centrifugation at 3000 rpm was carried out to remove the thick plates and achieve a dispersion (~1.04 mg mL^{-1}) that produced no obvious sediment during 2 months standing, indicating the good stability (Fig. 1c). The water dispersibility can be further confirmed by Zeta potentials test, which is generally employed to characterize the stability of GO. A high zeta potential of −50.6 mV was detected in the aqueous graphene dispersion, which is closing to ideal value (−60–70 mV) for sterically stabilized conventional colloidal particles, and also similar to most reports about GO or other graphene dispersions.

Tyndall effect (inset of Fig. 1d) intuitively shows that the laser can clearly pass through the aqueous graphene solution (0.2 mg mL^{-1}), revealing a uniform dispersing system [7]. The UV-visible spectra of graphene dispersion show a strong absorption peak at 266 nm (Fig. S2) [8] during the initial 10 days of sedimentation, suggesting the restoration of electronic conjugation within the graphene sheets. The stability of concentration of a 0.2 mg mL^{-1} dispersion undergoes no obvious decrease, which is

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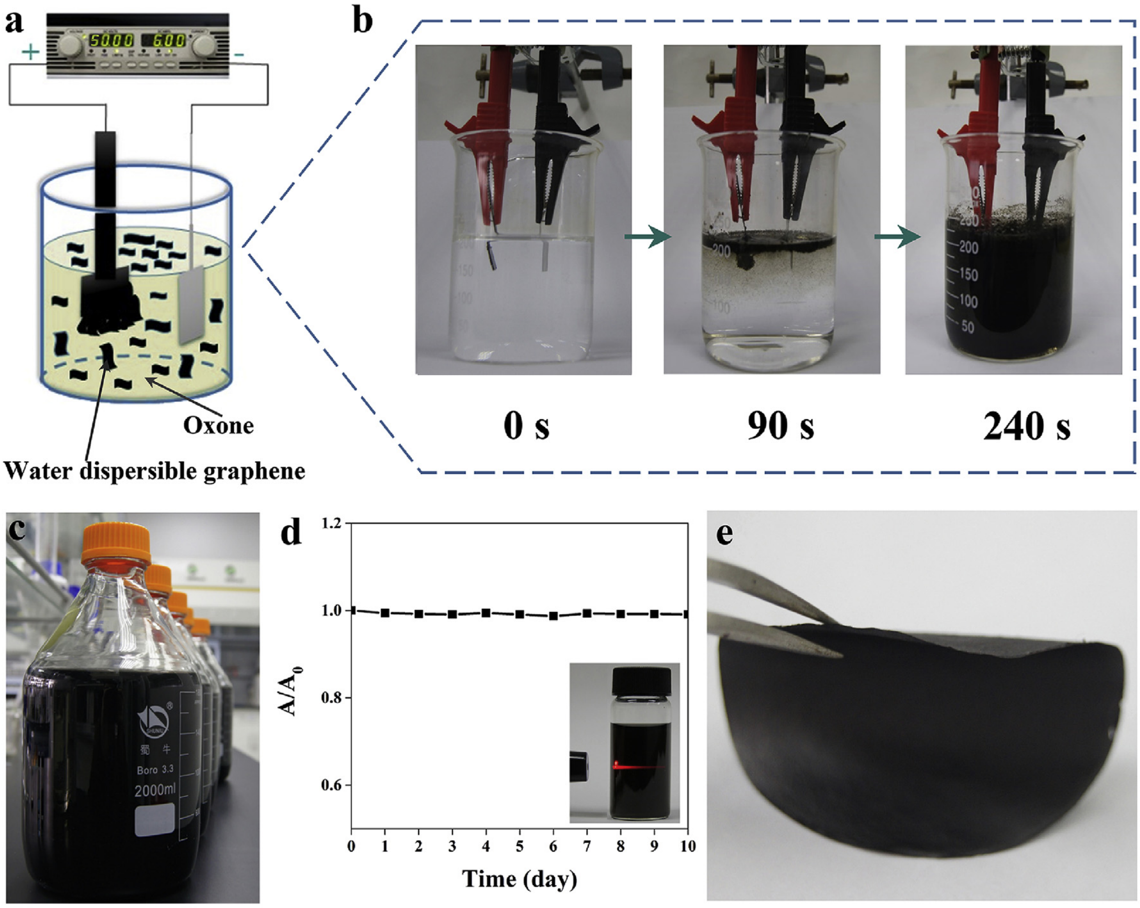

Fig. 1. (a) Schematic illustration of electrochemical exfoliation setup. (b) Electrochemical exfoliation process with increase of reacting time. (c) Photograph of 2 L aqueous graphene dispersion with a concentration of 1.04 mg mL^{-1}. (d) Intensity ratio of UV–vis absorbance peak at 266 nm of graphene dispersions in water about N days to first day with the inset showing the Tyndall effect of 0.2 mg mL^{-1} dispersion. (e) Digital photo of graphene paper prepared by filtration of aqueous dispersion. (A colour version of this figure can be viewed online.)

verified through the recorded intensity variation of UV-visible peak at 266 nm of the dispersion (Fig. 1d). It is notable that the 1.04 mg mL^{-1} graphene dispersion can be concentrated into viscous paste with ultra-high concentration of 30.5 mg mL^{-1} (Fig. S3), and the paste can be easily and quickly re-dispersed in water. Aqueous dispersibility and high quality were further confirmed by filtering the stable dispersion into a continuous, smooth, flexible graphene paper (Fig. 1e) with a high conductivity of 11,415.5 S m^{-1} at a bulk density of 1.44 g cm^{-3}. The yield of this graphene was measured to be 60.1%, which is expected to facilitate bulk fabrication.

The microstructure of obtained powder was characterized through scanning electron microscopy (SEM), atomic force microscopy (AFM), high-resolution transmission electron microscopy (HR-TEM), and Raman spectrum. The SEM image (Fig. 2a) provides distinct evidence for flexible and ultrathin morphology of as-prepared sheets. The statistical analysis of 45 sheets reveals that most of lateral size distribution is between 1 and 5 μm (Fig. 2b) and approximately 8.9% of the sheets were larger than 5 μm based on SEM image of Fig. S4. Fig. 2c shows the typical AFM image of graphene with 2.5 nm height, indicating four atomic layers. The thickness distribution in Fig. 2d, obtained through the analysis on 31 graphene sheets in AFM images of Fig. S5, displays that approximately 7.4% of the sampled graphene sheets are less than three layers (33% four layers, 33% five layers). The HR-TEM image (Fig. 2e) presents the well-defined structure of a bi-layer graphene. The thickness of the sheets ranges from 2 to 5 atomic layers, as shown in Fig. S6a and b. The selected area electron diffraction pattern in Fig. 2e exhibits a typical 6-fold symmetric diffraction with strong diffraction, indicating the conserved crystallinity of graphene. In addition, Raman spectra shows the intensity ratio of D peak to G peak ($I_D/I_G = 1.24$) in Fig. 2f. The D peak (1350 cm^{-1}) reveals the disordered or the edged carbons whereas the G peak (1580 cm^{-1}) is related to the ordered in-plane *sp*^{2} carbon structure [9]. The D and G peak mapping on a single graphene sheet was shown in Fig. S7a and b. It should be noted that the intensity of G peak is lower than that of D peak at most of points of this graphene sheet, indicating a high degree of defects and the uniform defect distribution. However, being different from GO or rGO, the Raman spectra of this graphene has an obvious 2D peak. Considering the narrower D and G peaks, and the 2D peak, the defects on our electrochemical exfoliated graphene should be different from that on GO or rGO, which needs further detailed investigations.

To further understand the defects on graphene sheets, X-ray photoelectron spectroscopy (XPS) was employed to investigate the chemical components and bonds. The survey spectra of graphene present C 1s and O 1s peaks (Fig. S8a), revealing a high oxygen content of 16.37 at. %. According to spectrum of C 1s (Fig. 3a), a strong peak located at a binding energy of 284.6 eV corresponds to the *sp*^{2} carbon (graphitic C=C species), and one peak at 286.7 eV is assigned to the *sp*^{3} carbon and hydroxyl (C–OH). The peak at