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Letters to the Editor

Size-controlled synthesis of graphene oxide sheets on a large scale using chemical exfoliation

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ABSTRACT

The synthesis of graphene oxide (GO) sheets with controlled size on a large scale was developed using chemical exfoliation by simply controlling the oxidation and exfoliation procedure. The GO samples prepared under different conditions, which all have excellent water dispersion, are characterized by thermal gravimetric analysis, Ultraviolet–visible spectroscopy, X-ray diffraction and atomic force microscopy. It is found that as longer oxidation times and more oxidants are used, the mean size of the GO sheets, which has a Gaussian distribution, decreases from ~59,000 to ~550 nm².

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Graphene, with one-atom-thick two-dimensional individual sheet structure composed of sp²-hybridized carbon, has drawn a great deal of attention due to its remarkable electronic, thermal and mechanical properties [1]. Research on graphene is originally motivated by its great promise for future technological applications in many fields, such as highly conducting composite [2] and other micro to nano-scale electronic devices [3]. It is clear that the properties of graphene strongly depend on its unique structure and morphology. For example, the size of graphene plays an important role in their conductivities [4]. Accordingly, it is highly demanded to develop simple and efficient methods for the production of graphene sheets with controlled size and large quantities for their broad range of applications.

Currently, micromechanical cleavage [5], epitaxial growth on silicon carbide [6] and chemical exfoliation [2,7] have been used widely to prepare graphene sheets. Compared to the first two methods, the chemical exfoliation method is considered to be the most effective and economical way to prepare graphene sheets in large quantity from bulk graphite [8], in which a process of graphene oxide (GO) sheets is involved [2,8]. Importantly, the aromatic network and the intrinsic

properties of graphene can be most restored through the removal of the functional groups by either chemical reduction or thermal annealing for GO. Recently a simple and effective strategy to tune the number of graphene layers by selecting suitable starting graphite materials has been presented using different graphite materials [9]. However, the large scale production of high-quality graphene with controlled size still remains a significant challenge.

It is well known that the occurrence of fault lines and cracks in graphite, which leads to unzipping of graphite lattice, are directly related to the oxidation process [10]. Herein, we have studied the effect of oxidation time and the amount of oxidants on the size controlling of GO sheets by chemical exfoliation. GO sheets with different size, namely GO-1, GO-2, GO-3 and GO-4, were prepared using the modified Hummers method from flake graphite, where GO 1–4 refer to the products with progressive oxidation steps (see Supplementary material) and have statistical mean sizes of 59,000, 22,000, 3500 and 550 nm², respectively. Thus with increasing reaction time and oxidants, the mean sizes of GO sheets, which exhibit Gaussian distribution, show a regular decrease in the order from GO-1 to GO-4, and the maximum distribu-

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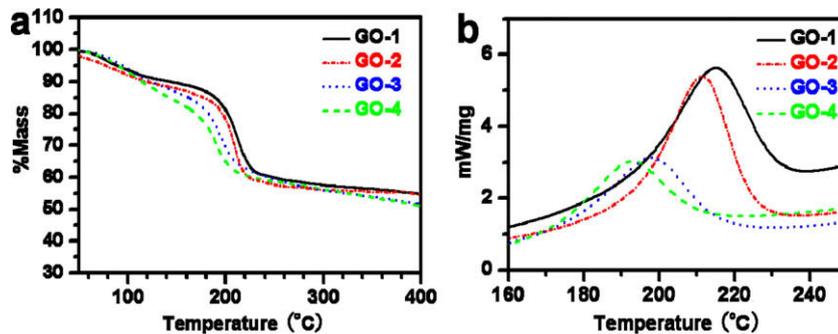


Fig. 1 – TGA (a) and DSC (b) curves of GO-1, GO-2, GO-3 and GO-4 at a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ in N_2 atmosphere.

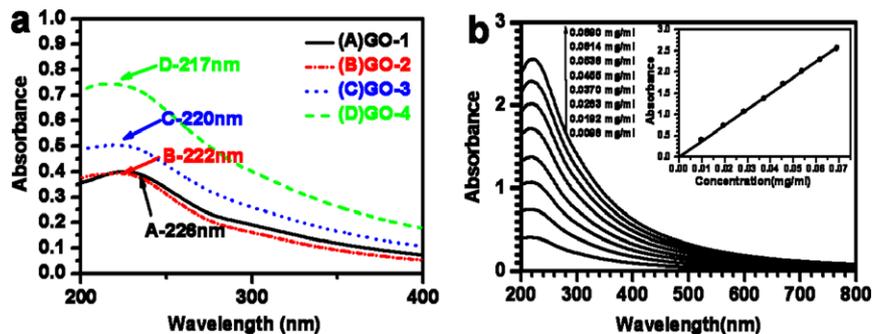


Fig. 2 – UV-vis absorption spectra of (a) GO-1, GO-2, GO-3 and GO-4 dissolved in water (concentrations are 0.019 mg ml^{-1}), (b) GO-4 dissolved in water at different concentrations ($0.0098\text{--}0.069\text{ mg ml}^{-1}$). The inset shows the linear relationship between the absorbance and the concentration of GO-4.

tion of size is 20,000, 15,000, 2400 and 550 nm^2 correspondingly.

Thermogravimetry analysis (TGA) results of all the GO samples show a major mass loss of more than 30% in the range of $110\text{--}230\text{ }^{\circ}\text{C}$ (Fig. 1a), corresponding to the removal of labile oxygen-containing groups. However, GO samples treated for longer oxidation time and more oxidants show a faster mass loss from 110 to $230\text{ }^{\circ}\text{C}$, illustrating a lower thermal stability and more functional groups. Decomposition temperature of GO-1, GO-2, GO-3 and GO-4 obtained from TGA curves are $198\text{ }^{\circ}\text{C}$, $196\text{ }^{\circ}\text{C}$, $183\text{ }^{\circ}\text{C}$ and $180\text{ }^{\circ}\text{C}$, respectively, suggesting the decrease of thermal stability from GO-1 to GO-4. Differential scanning calorimetry (DSC) curves of

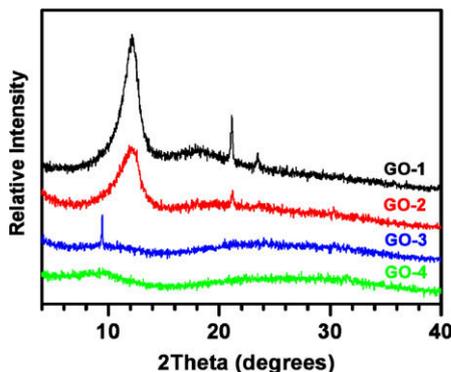


Fig. 3 – XRD patterns of GO-1, GO-2, GO-3 and GO-4.

GO-1, GO-2, GO-3 and GO-4 show the correlated degradation peaks centered $216\text{ }^{\circ}\text{C}$, $213\text{ }^{\circ}\text{C}$, $196\text{ }^{\circ}\text{C}$ and $190\text{ }^{\circ}\text{C}$, respectively (Fig. 1b). This phenomenon is principally ascribed that more oxidation and longer exfoliation introduce more defects and functional groups on the GO sheets, which reduces the size of the GO sheets with more functional groups and thus lowers decomposition temperature [8,10].

Ultraviolet-visible (UV-vis) spectroscopy measurements were employed to monitor the degree of oxidation of the GO sheets. The absorption peaks of GO-1, GO-2, GO-3 and GO-4 are 226, 222, 220 and 217 nm, respectively (Fig. 2a), indicating a hypochromatic shift of the absorption peaks which is mainly because the size of π -conjugation system gradually decreases with increasing degree of oxidation. Due to the hydrophilic nature of the oxygenated graphene layers, GO can readily be exfoliated in water and form a stable colloidal suspension of individual GO sheets [8] under a mild ultrasonic treatment. As an example for this excellent dispersion, the absorbance of GO-4 aqueous solutions was well in line with the relative concentrations (inset in Fig. 2b), obeying Beer's law, indicating that GO-4 was homogeneously dispersed in water. Similar results were observed for GO-1 to GO-3 samples.

X-ray diffraction (XRD) provides a conclusive proof for the degree of oxidation as the layer distances of starting graphite and the end products are highly different. The typical diffraction peak of native graphite was observed at about $2\theta = 26.3^{\circ}$ ($d = 0.34\text{ nm}$, Fig. S1) and the diffraction peak of GO-1 appeared at $2\theta = 12.1^{\circ}$ ($d = 0.73\text{ nm}$), with no reflection at 26.3°

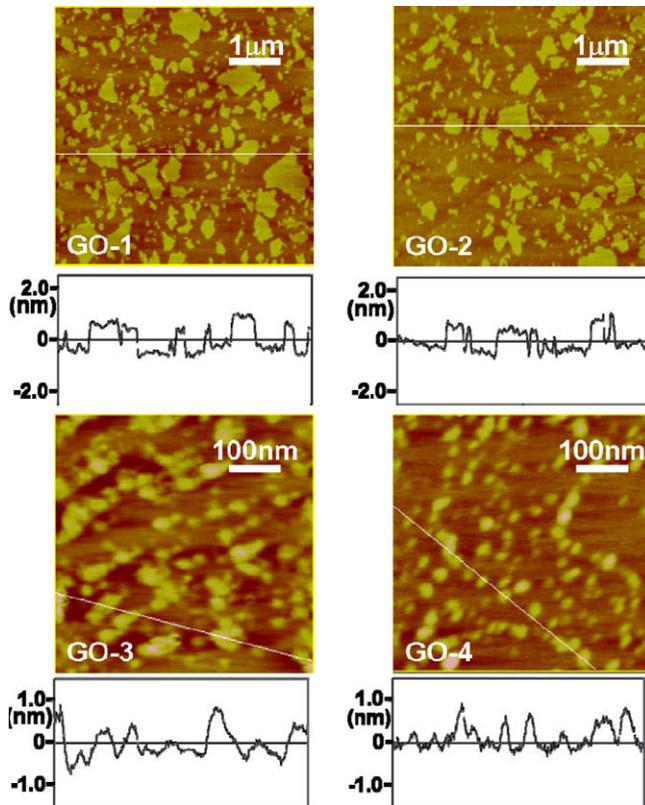


Fig. 4 – Typical tapping mode AFM images (top) and the corresponding height cross-sectional profile (bottom) of GO-1, GO-2, GO-3 and GO-4 deposited on the mica substrate. The heights of most GO sheets in four samples are in the range of 0.8–1.0 nm. The sheet size decreases pronounced from GO-1 to GO-4.

from graphite lattice, indicating that the exfoliation process increased the d-spacing by oxidation to 0.73 nm and completely eliminated the 0.34 nm graphite interlayer spacing [7]. However, as oxidation proceeds, the intensity of the diffraction peak ($\sim 12.1^\circ$) decreases gradually from GO-1 to GO-4 (Fig. 3). The diffraction around 12.1° is much weaker and broader in GO-2 than that in GO-1, presumably because of the increased functional groups and corrugated structure of the GO sheets, since the extent of folding increases with the degree of oxidation [11]. XRD patterns of GO-3 and GO-4 even feature no apparent reflection peaks, which indicate the absence of stacked layer structure due to their extremely small size and more disrupted structure of the GO sheets.

Fig. 4 displays atomic force microscopy (AFM) images of GO sheets from H₂O solution. The corresponding height cross-sectional profile from the AFM images reveal that most GO sheets of the four samples had heights in the range of 0.8–1.0 nm, which is characteristic of a fully exfoliated GO sheet [2,8]. Furthermore, based on the analysis of the AFM images for more than 1300 sheets for each sample and Gaussian fit, it is found that the size of the GO sheets decrease regularly with increasing degree of oxidation (Figs. 4 and 5). The mean size of GO-1, GO-2, GO-3 and GO-4, obtained from the AFM size statistical analysis above, are 59,000, 22,000, 3500 and 550 nm², respectively, and the average diameter are 212, 147, 62 and 24 nm, respectively. Error was estimated to be $\sim 5\%$. Moreover, the size of GO-1, GO-2, GO-3 and GO-4 sheets all exhibit a Gaussian distribution and the maximum distribution of size is 20,000, 15,000, 2400 and 550 nm² correspondingly (Fig. 5).

In conclusion, an easy and efficient approach is developed to produce GO sheets on large scale with a controlled size. The statistical analysis of large amount of AFM images indi-

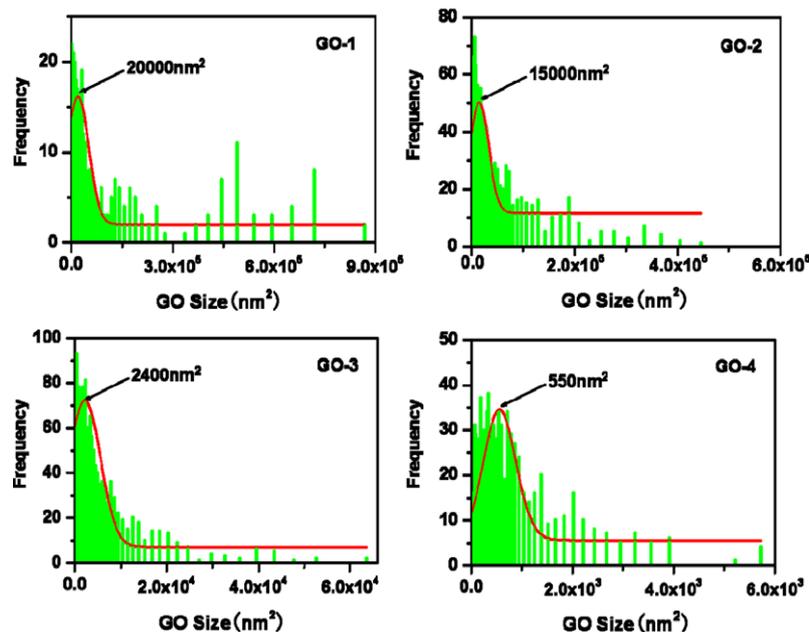


Fig. 5 – Histograms of the size distribution of GO-1, GO-2, GO-3 and GO-4 membranes, obtained from more than 1300 sheets for each sample. The red curve is the Gaussian fit and the maximum distribution of size is 20,000, 15,000, 2400 and 550 nm², correspondingly. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

cate that the average size of sheets for the chemically exfoliated GO sheets can be controlled by modifying the oxidation and exfoliation procedure. These results should enable further investigation of the physical and chemical properties of graphene with different size, and hold great promise for a broader range of technological applications in many fields.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2009.07.045.

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ZrC ablation protective coating for carbon/carbon composites

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ABSTRACT

A zirconium carbide (ZrC) protective coating was deposited on carbon/carbon (C/C) composites by atmospheric pressure chemical vapor deposition. The phase compositions, surface and cross-section microstructures, and anti-ablative properties of the coatings were investigated. Results show that the method is an effective route to prepare a dense and thick ZrC coating on C/C composites. The coating can effectively protect C/C composites from ablation for 240 s in an oxy-acetylene torch system with a mass ablation rate of 1.1×10^{-4} g/cm² s and a linear ablation rate of 0.3×10^{-3} mm/s.

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Carbon/carbon (C/C) composites are attractive materials for use in high-temperature structural components such as re-entry vehicle nose tips, rocket, and nozzles [1]. In these critical

environments in planetary entry, and other energy dissipation application, the C/C composites will be subjected to thermochemical ablation by oxidation and evaporation due to high

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