A scalable, solution-phase processing route to graphene oxide and graphene ultralarge sheets†

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High yield production of graphene oxide and graphene sheets with an ultralarge size (up to ∼200 µm) was realized using a modified solution-phase method.

Since the discovery of graphene in 2004,[1] this new material has attracted great scientific interest because of its unique, outstanding physico-chemical properties and potential applications.[2] Graphene-based applications undoubtedly require low-cost mass production of graphene with high quality. Currently, the solution-phase method[3] (*i.e.* hydrazine reduction method) shows distinct advantages, in terms of yield and cost, over other methods such as micromechanical exfoliation,[1] chemical vapor deposition[4] and epitaxial growth,[5] and hence it has been considered as the most effective way to meet the demands of large-scale applications of graphene. However, the graphene sheets in previous reports usually had lateral sizes in the range of hundreds of nanometres to a few micrometres,[6–8] with the largest ones up to 20 µm × 40 µm,[9] showing low quality in sizes. The reason is that the graphene oxide (GO) sheet precursors were prepared universally by an ultrasonication method, which could lead to severe breakage of the sheets. The development of mild delamination methods thereby is important for the preparation of large-sized sheets of GO and graphene. Furthermore, there has been a greater challenge on the preparation of homogenous colloidal suspensions of the graphene sheets, as the hydrophobic graphene sheets have a strong tendency to aggregate in aqueous solutions. To solve this problem, various strategies including non-covalent stabilization[8,10–13] and surface covalent functionalization[6,14–17] have been developed. However, the existing strategies generally bring about some demerits such as low yield, complex processes, or high cost. On all accounts, the current solution-phase route is still unable to fufill the mass preparation of large-sized GO and graphene sheets.

In this communication, we report a modified solution-phase processing route to large-sized sheets of GO and graphene. In our experiments, natural flake-like graphite of 50 mesh size (corresponding to 300 µm in mean size) was used as the starting material; the oxidation of graphite was carried out by Hummers' method;[18] the delamination of graphite oxide in water was performed by a gentle shaking treatment instead of the conventional ultrasonication; the reduction of the exfoliated GO sheets to graphene was conducted using hydrazine hydrate in the presence of a nonionic polymeric surfactant.

The delamination of the GO resulted in a stable brown suspension (see ESI, Fig. S1a†). The suspension could exhibit clear anisotropy textures after shaking, suggesting the presence of sheets with large sizes and high aspect ratios. A typical scanning electron microscopy (SEM) image of the GO sheets is shown in Fig. 1a. As can be seen, the sheets have a lateral size, dominantly, in the order of 100 µm, and some of them even possess a size as large as 200 µm. To the best of our knowledge, there have been no reports on GO sheets with such a huge size. Besides the large sheets, fragments with sizes of only a few micrometres can also be observed in a small amount. These fragments might be derived from micrometre-sized graphite flakes or by inevitable breakage during the delamination process. For better illustrating the size feature of the sheets, more SEM images are presented in the ESI (see Fig. S2†). As revealed, the sizes of major sheets are approximately comparable to those of the pristine graphite flakes.

Fig. 1b displays an atomic force microscopy (AFM) image of a GO sheet which has a size far beyond the AFM scan

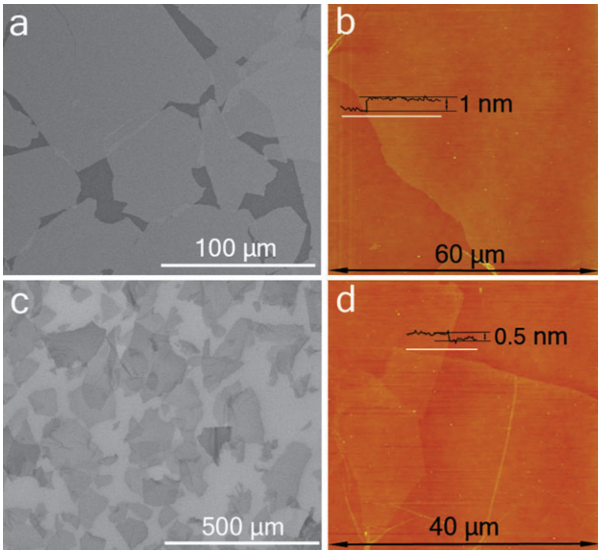

Fig. 1 (a) SEM and (b) AFM images of GO sheets that were deposited on a Si substrate by Langmuir–Blodgett assembly at a constant surface pressure of 10 mN m^{-1}. (c) SEM and (d) AFM images of graphene sheets deposited on a polyethyleneimine (PEI) pre-coated Si substrate.[19]

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† Electronic supplementary information (ESI) available: Experimental details, information of nonionic polymeric surfactants used, digital photographs of the suspensions of GO and graphene sheets, SEM images and AFM images of the GO and graphene sheets, XPS and Raman data of the GO and graphene sheets, TG curves of the freeze-dried graphene/Brij-35 foam, digital photographs and SEM images of the annealed graphene foam. See DOI: 10.1039/b914412a

range. The height profile denoted in Fig. 1b demonstrates a mean thickness of $\sim$1 nm, indicative of a unilamellar nature of the sheet. It is worth mentioning that the sizes of the exfoliated GO sheets are closely associated with those of the starting graphite flakes. For example, if the graphite flakes of 500 mesh size ($\sim$25 μm in mean size) were used, the exfoliated GO sheets had a lateral size around 15 μm, as demonstrated by SEM and AFM observations (see Fig. S3†). This result indicates that the sheet sizes can be easily controlled through the size selection of the graphite material.

From the point of view of the characterizations and applications, the availability of stable graphene suspensions containing freestanding and large-sized sheets would be very intriguing. In our case, unfortunately, the reduction of GO following the previously reported conditions[8,11] usually resulted in an aggregation of graphene sheets. The reason may be that the large sheets have a higher tendency of agglomeration. Therefore it is essential to develop a new strategy for the preparation of the stable suspensions of large sheets. Through extensively exploring the reduction conditions, we found that nonionic polymeric surfactants (such as Brij-35, Tween-80, and Triton-X100)[20] were identically effective for stabilizing graphene suspensions. As the weight ratio of polymer/GO reached about 2, the hydrazine reduction was able to result in a homogenous, black suspension (refer to Fig. S1b†). Stabilized by these nonionic polymeric surfactants, the graphene concentration could reach up to 5 mg mL^{-1},[21] and no sediments or floccules were observed upon standing for months. SEM images (Fig. 1c and Fig. S4†) demonstrate that the as-reduced graphene sheets have inherited the large size feature of the parent GO sheets. An AFM image (Fig. 1d) reveals that the sheets have an average thickness of $\sim$0.5 nm, which is close to the theoretical thickness value (0.335 nm) of single layer graphene. Evidently, the AFM characterization indicates that the polymer stabilizers can be washed off from the sheet surfaces.

The X-ray photoelectron spectroscopy (XPS) analysis (see Fig. S5†) displays that the signal intensity from oxygen bonded carbon decreases remarkably after the solution-phase reduction, implying an efficient removal of oxygenous groups during the reduction by hydrazine. Annealing treatment on the graphene samples can further remove oxygenous residues. The Raman spectrum (Fig. S6†) of graphene sheets on PEI coated Si substrates shows a strong D band centered at 1330 cm^{-1}, which suggests a large amount of defects and is coincident with the previously reported Raman data for the chemically reduced graphene.[12,22] Compared with mechanically exfoliated graphene with narrow D bands,[23] the broadened D band here provides limited information related to the layer numbers of graphene on the substrate. However, the careful AFM characterization over large amounts of sheets reveals that more than 90% are single-layered. Therefore, the mild shaking treatment proposed in this paper is an efficient exfoliation means to produce single-layer graphene, and the usage of the nonionic polymeric surfactant effectively prevents the graphene sheets from restacking.

To exploit more availability of the GO and graphene materials, we further extracted the individual sheets in solid states from their colloidal suspensions. By a freeze drying method, the suspensions were converted to solid foams (see Fig. 2a and b). SEM images (Fig. 2c and d) demonstrate that the foams possess an ultra hollow framework constructed with large sheets. Due to loose stacking between the sheets, the foams were extremely light and fragile. For the graphene foam, the coexisting polymers rendered it with a very high electric resistance. The purification of the foam could be achieved simply by annealing in an inert atmosphere. For instance of the graphene/Brij-35 foam, an almost pure graphene foam could be prepared by annealing at $\sim$400 °C, as determined by thermogravimetric analysis (TGA, refer to Fig. S7†). With the removal of the polymers, the foam became highly conductive; it also presented good elasticity and flexibility like a sponge (see Fig. S8†). An SEM image (Fig. S9†) reveals that the annealed sheets were highly cross-linked.

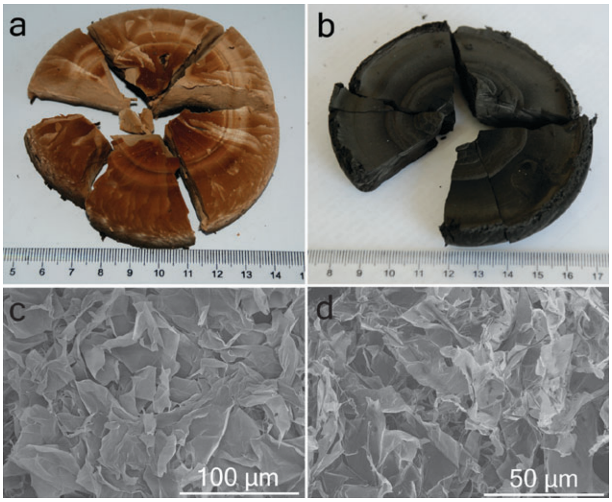

Fig. 2 Digital photographs and SEM images of the freeze-dried solid foam: (a), (c) GO sheets and (b), (d) graphene sheets.

Furthermore, the polymer-stabilized graphene suspension could also be filtered into a paper-like material. The as-filtered paper showed a very low conductivity (25 S m^{-1}), mostly due to the presence of a substantial amount of the insulating polymers. By annealing treatment of the graphene paper under Ar, the conductivity of the paper can be dramatically increased up to 10 000 S m^{-1} (annealed at 500 °C) and 40 000 S m^{-1} (annealed at 800 °C), comparable with the best result as reported earlier.[24] It is attributed to the simultaneous decomposition of insulating polymers and removal of residual oxygenous groups on graphene sheets in the paper at high temperatures. The layered structure of the paper was maintained during the annealing process as demonstrated in the SEM image (Fig. 3) of the paper cross-section.

In conclusion, we have succeeded in preparing single-layer GO and graphene sheets with lateral sizes up to 200 μm by modifying the solution-phase method. The employment of the gentle shaking in the delamination step enabled the intact preservation, to a large extent, of the large GO sheets; the use of nonionic polymeric surfactants as the stabilizers allowed the achievement of a homogeneous colloidal suspension with a high content of graphene. These modifications make the solution-phase method more reproducible and scalable, especially for the preparation of large-sized sheets.

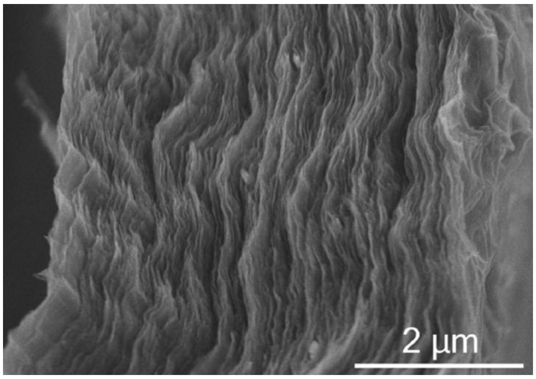

Fig. 3 SEM image of the cross-section of a fractured graphene paper annealed at 500 °C under Ar for 2 h.

The colloidal suspensions of GO and graphene sheets have been converted to solid-state foams by a freeze-drying method or to papers by a filtration method. Further removing of the polymers from the graphene foam or paper by annealing resulted in a highly conductive graphene 'sponge' or paper, which may find practical applications in Li–ion batteries, supercapacitors, catalytic carrier, and so on. In addition, the availability of the freeze-dried foams with loosely stacked sheets may offer a new route to prepare colloidal suspensions of individual sheets in various organic solvents. Further studies are under way.

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