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Preparation of graphene by exfoliation of graphite using wet ball milling

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Wet ball milling was used to exfoliate graphite platelets into graphenes in a liquid medium. Multi-layered graphite nanosheets with a thickness of 30 to 80 nm were dispersed into *N*,*N*-dimethylformamide (DMF) and exfoliated by shear-force-dominated ball milling carried out in a planetary mill. After high-speed centrifugation, irregular shaped single- and few-layer graphene sheets ($\leq$3 layers) having a thickness around 0.8–1.8 nm were found from the supernatant. The graphenes were identified and characterized using transmission and scanning electron microscopy, electron diffraction, atomic force microscopy and Raman spectroscopy. The electrical conductivity of the graphene powder was $\sim 1.2 \times 10^3$ S m^{-1} at room temperature.

Graphene, atom-thick graphite, has rapidly become the darling of materials science since its discovery in 2004.[1] Several routes have been proposed to prepare graphene, such as micromechanical cleavage of graphite using Scotch tape,[1] chemical vapor deposition (CVD) and epitaxial growth,[2,3] chemical reduction of exfoliated graphite oxide,[4] solvothermal synthesis[5] and liquid-phase exfoliation of graphite by sonication[6–8] or quenching.[9]

Of these reported approaches, the 'Scotch tape' method is original. Up to date, it creates the best graphene samples which are useful for various experimental studies. However, the unwieldy method seriously limits the graphene yields. The sonication exfoliation method aids the experimental preparation for graphene sheets remarkably. Nevertheless, it has been found that continuous sonication is helpless to give higher yield of graphenes; and excessive sonication can lead to destruction of the graphene.[6,7] Undoubtedly, to increase the supply of graphene sheets for facilitating their applications and studies, mechanical peel-off techniques still need to be extensively investigated. In this communication, ball milling, a common technique in powder production industry, was adopted in an attempt to exfoliate thick graphite flakes mechanically into graphenes in liquid media.

0.02 g of graphite nanosheets (GNs) with a thickness of 30–80 nm[10] were first dispersed homogeneously in 80 ml of anhydrous *N*,*N*-dimethylformamide (DMF) solvent (0.25 mg ml^{-1} of GNs concentration) and then milled continuously for 30 hours on a planetary mill (with zirconia balls and poly(tetrafluoroethylene) vials). To avoid any intense shock stress which will destroy the graphite in-plane crystal, the rotating tray was controlled at a low speed of 300 rpm to ensure that the shear stress is dominant. Due to the weak van der Waals-like coupling between graphite layers and strong DMF–graphene interactions, the GNs were readily exfoliated into graphene sheets under the shear forces applied by the milling impact. The obtained dark dispersion was then centrifuged at 10 000 rpm for 20 min to remove any large particles including partially exfoliated GNs and unexfoliated residual GNs, giving a dark homogeneous colloidal suspension of graphene sheets in DMF. After evaporation of the DMF from the supernatant under vacuum, graphene products in the form of powder were obtained and subjected to repeated wash with ethanol before characterization.

High-magnification scanning electron microscopy (SEM, LEO1530) observation of the resulting graphene powder (Fig. 1) shows that the graphene sheets in the product are highly transparent with folding at the edges, suggesting a very small thickness. Because of their high specific area, the graphene sheets aggregated and formed a stacked graphitic structure when their dispersion was dried.

As SEM cannot reveal the thickness of an individual sheet spatially, atomic force microscopy (AFM, NanoScope IIIa), Raman spectroscopy (Renishaw1000 at 514.5 nm), transmission electron microscopy (TEM, JEOL JEM-2010) and selected-area electron diffraction were carried out to verify that the products were the expected single- and few-layer graphene sheets rather than multi-layered graphite platelets. TEM specimens were prepared by either drop-casting graphenes from the supernatant or loading the microtomed epoxy composite slices of the as-obtained graphene powder onto standard TEM grids.

The number of layers in the graphene can be obtained visually by a high-resolution TEM analysis of the graphene edges. This can be conducted either on the folding at the rim of graphene membrane[9,11,12] or on the graphene composite slice[13] because for the both cases the sheet is locally parallel to the electron beam. High-resolution TEM image of the slice shown in Fig. 2a reveals the cross-sections of the obtained graphene sheets, in which the number of layers can be visualized directly. Individual single atomic carbon layers (corresponding to monolayer graphene sheets) dominated by one dark line with a thickness of ~0.5 nm can be readily identified, suggesting that the product truly contains a number of single-layer

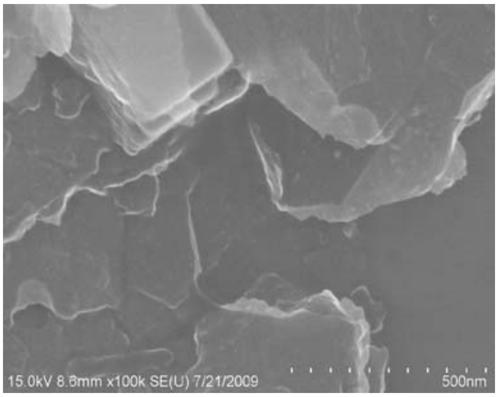

Fig. 1 SEM image of graphene products in powder form.

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graphenes. Meanwhile, the graphenes have a great tendency to restack to form graphitic structures due to the van der Waals interactions, as shown in Fig. 1. Thus, layered graphene restacking comprising several individual monolayers is also present, where the adjacent line distance seems comparable to 0.335 nm, the *d*-spacing of (002) crystal plane of bulk graphite.

The exfoliation to achieve graphene was also verified by thickness measurements of the supernatant sheets using AFM. Fig. 2b displays the typical AFM image of isolated graphene sheets evaporated from their dilute dispersion on freshly cleaved mica support. Topographic heights of the sheets estimated from the cross-sectional profile were found in the range of 0.8–1.8 nm, which are in accord with the practical thickness of individual single- and few-layer graphenes (≤3 layers).[14] In contrast to the graphene restacks seen by SEM, the typically flat graphene deposited on TEM grid shows similar lateral size (Fig. 2c). Due to the high surface area, the graphene sheets have a significant tendency to coalesce into overlapped structures and are somewhat wrinkled on the grid. The number of layers in these suspended graphene sheets can be identified unambiguously from the nano-area electron diffraction patterns, by inspecting the intensity ratio of the Bragg reflections.[12] For monolayers, studies have shown that the intensity ratio is $I_{\{1100\}}/I_{\{2100\}} > 1$.[6,15] In Fig. 2d, the electron diffraction pattern taken from the white-dot-marked fake in Fig. 2c shows the intensity ratio of $I_{\{1100\}}/I_{\{2100\}} \approx 1.4$ which is a unique feature for a monolayer sheet,[6,8,15] again confirming the presence of single-layer graphene in the products. The hexagonal pattern shows the sixfold symmetry of carbon atoms arranged in graphene plane, indicating good crystallinity of the graphene sheet.

The achievement of producing graphene sheets was further confirmed by using Raman spectroscopy. Raman measurements were conducted on several spots of the as-prepared graphene powder. Similar Raman spectra, showing a single and symmetric low frequency 2D peak at 2693 cm^{-1} (Fig. 3), were obtained, well matching the previously reported data from graphenes.[11] Whereas, as expected, the Raman spectrum of GNs displays a main 2D band with the maximum located at the high frequency side 2722 cm^{-1}, which is consistent with the multi-layer feature of bulk graphite. In addition, the D/G band intensity ratio $R = I_D/I_G$ for the graphene product is roughly 0.34, much lower than the value of the chemically derived graphene obtained by reduction of graphite oxide.[4] This again suggests that the crystal structure of graphene had been preserved satisfactorily during the mild milling treatment, although the graphenes were not of high quality. The satisfying crystalline structure of the graphene sheets was also revealed by their electrical properties. The powder conductivity of the graphenes measured by four probe method was ~1.2 × 10^3 S m^{-1}, which is only one order of magnitude lower than that of the GNs (~10^4 S m^{-1}).

Our product is a mixture of single- and few-layer graphenes with a thickness ≤3 layers. Virtually the monolayer fraction in the final product is related to many process parameters such as the diameters of milling balls, the period of milling time, the content of GNs in the DMF medium, the speed of centrifugation and the size of source graphite. Based on the current results, it is reasonable to deduce that an eventual increase of the yield of monolayer sheets can be accomplished by optimizing the milling conditions.

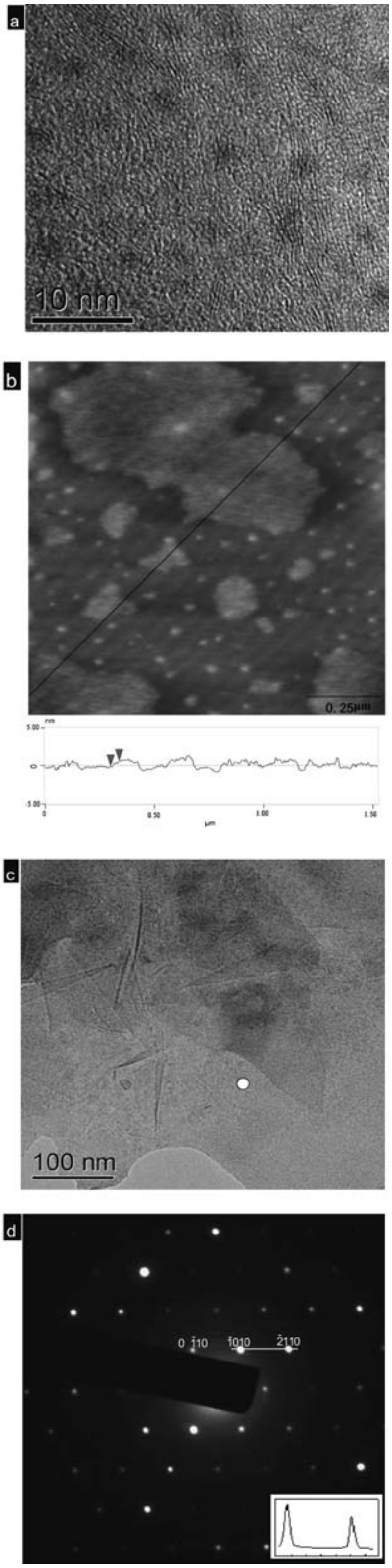

Fig. 2 (a) High-resolution TEM imaging of graphene products embedded in epoxy resin slice. (b) AFM image of the supernatant graphene sheets deposited on a mica substrate, followed with the corresponding height cross-section along the line in the image; the height difference between arrows is ~0.8 nm. (c) TEM image of graphene sheets deposited onto grid from the supernatant. (d) Electron diffraction pattern taken from the position of the white spot in (c); inset: diffraction intensity taken along the 1̄010 and 2̄110 axis.

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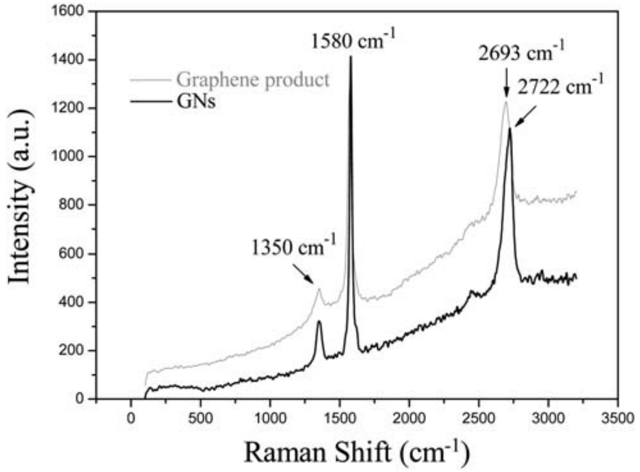

Fig. 3 Room-temperature Raman spectra of graphene sheet products and GNs.

To conclude, we have demonstrated a feasible way to produce graphene from graphite flakes using wet ball milling exfoliation. With the help of carefully selected solvent, graphene sheets with satisfying crystal structure can be produced from thick graphite flakes, such as GNs, in bulk at a low cost. The study of the optimal conditions for the ball milling exfoliation is currently under way. As a very common industrial technique, the ball milling method can be easily scaled up to mass production, offering a promising opportunity to produce graphene in volumes needed for real-life world applications.

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