Combination of ultrasonic assisted liquid phase exfoliation process and oxidation-deoxidation method to prepare large-sized graphene

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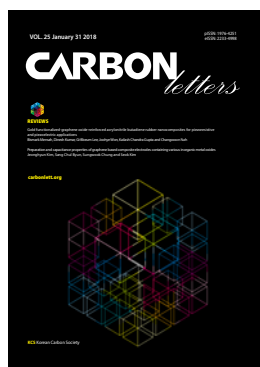
Abstract

Large-size graphene samples are successfully prepared by combining ultrosonic assisted liquid phase exfoliation process with oxidation-deoxidation method. Different from previous works, we used an ultrasound-treated expanded graphite as the raw material and prepared the graphene via a facile oxidation-reduction reaction. Results of X-ray diffraction and Raman spectroscopy confirm the crystal structure of the as-prepared graphene. Scanning electron microscopy images show that this kind of graphene has a large size (with a diameter over 100 μm), larger than the graphene from graphite powder and flake graphite prepared through single oxidation-deoxidation method. Transmission electron microscopy results also reveal the thin layers of the prepared graphene (number of layers ≤3). Furthermore, the importance of preprocessing the raw materials is also proven. Therefore, this method is an attractive way for preparing graphene with large size.

Key words: graphene, large size

1. Introduction

Graphene is a flat monolayer of hexagonal arrayed sp^2-bonded carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice and is an ideal base material for developing functional materials due to its unique chemical, electrical, mechanical, and physical properties [1]. Graphene shows a strong ambipolar electric field effect with the high charge carrier mobility of ~10 000 $cm^2 V^{-1} s^{-1}$ at room temperature [2,3]. In addition, pure graphene exhibits a mobility approaching 200 000 $cm^2 V^{-1} s^{-1}$ for the carrier density below $5 \times 10^9 cm^{-2}$ at a low temperature [4]. In addition, the white light absorbance of a ideal graphene monolayer is 2.3% (or transmittance of 97.7%) with a few negligible reflectance of 0.1% [5]. Moreover, graphene exhibits excellent thermal stability and conductivity (3000–5000 $W m^{-1} K^{-1}$) [6], high Young's modulus (≈ 1 TPa) [7], and large theoretical specific surface area (SSA, 2630 $m^2 g^{-1}$) [8]. All these outstanding properties aroused great interest, varying from the fundamental study to various applications of graphene.

Up to this day, numerous methods have been explored to obtain large-sized graphene, such as the liquid phase and thermal exfoliation, mechanical exfoliation, chemical exfoliation, chemical exfoliation via graphene oxide, chemical vapor deposition, synthesis on SiC and other growth methods [9-11]. Among them oxidation-deoxidation method is the most convenient and widespread way to prepare graphene. Unfortunately, owing to the strong hydrophobic, strong π–π stacking and van der Waals interaction, graphene made by deoxidating the graphene oxide has a strong tendency to occur irreversible agglomeration and form multilayer graphite [12-16]. It is well-known that graphene's unique properties are only associated with few layers or individual sheets of 2D hex-
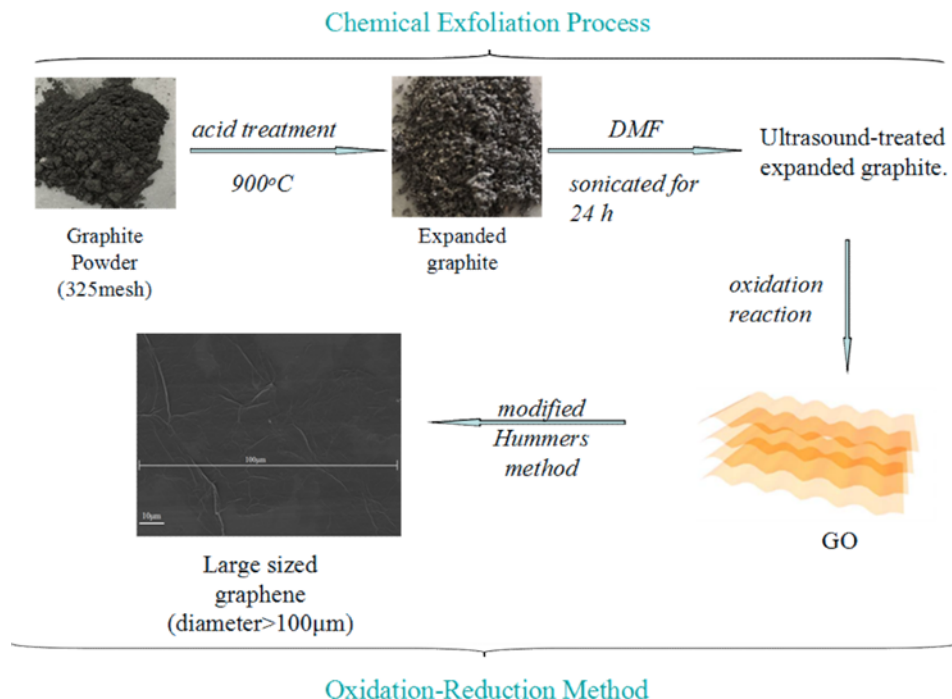
Fig. 1. A schematic illustration for preparing graphene with large size.

agonally packed carbon lattice. Therefore, the aggregation of graphene sheets pose a practical challenge that must be addressed to expand application scope of graphene in various potential fields of nanotechnology.

Herein, we reported a new way to produced graphene with large size and few layers by combining ultrosonic assisted liquid phase exfoliation process with oxidation-deoxidation. By comparing the product with other graphene prepared using graphite powder (~18 μm) or crystalline flake graphite (28 μm) as the raw materials. The produced kind of graphene has bigger slice (~100 μm) and thinner layer. Furthermore, we proved it is necessary to pretreat the raw materials before oxidation-deoxidation process and the simple synthetic method and low cost are suitable conditions for laboratory preparation.

2. Experimental

2.1. Materials

Potassium permanganate ($KMnO_4$) was brought from Dan Dong No.1 Chemical Plant. Hydrogen peroxide (H_2O_2), phosphoric acid (H_3PO_4) were purchased from China National Pharmaceutical Group. Sulfuric acid (H_2SO_4), hydrazine hydrate (HHA) and hydrochloric acid (HCl) were supplied by BaiYin LiangYou Chemical reagents Co. Ltd (Chian). Expandable graphite was gained from Aladdin Industrial Corporation Shanghai (China). Deionized water was used for preparation of all aqueous solutions. All the reagents were of analytic grade and used without further purification.

2.2. Preparation of ultrasound-treated expanded graphite

Expandable graphite (1.0 g) was placed into the muffle furnace and heated for 30 s at 900°C. The crucible was cooled to room temperature. Briefly, 0.1 g of the as prepared vermicular expansion graphite was added into 100 mL of DMF solvent and was sonicated for 24 h. The whole reaction system was subsequently maintained at room temperature. The mixture was washed with deionized water and ethanol for several times. Finally, the samples were dried at 60°C for 12 h to obtain ultrasound-treated expanded graphite.

2.3. Preparation of GO

Initially, graphite oxide (GO) was prepared by a modified Hummers. As described as follows, 1 g of ultrasound-treated expanded graphite was mixed with 5 mL of H_3PO_4 and 40 mL of concentrated H_2SO_4. The mixture was cooled to 0°C in an ice bath and stirred for 30 min. Then, 3 g of $KMnO_4$ were poured into the above solution dropwise and continuously stirred at 0°C for another 30 min. Then, the temperature of system was increased to 50°C and stirred constantly for 12 h. And the color of the mixture turned to dark brown. Then 10 mL 30% H_2O_2 and 20 mL ice were added to the diluted mixture and the solution became golden yellow. Subsequently, the mixture was washed with 10 mL of 5% HCl solution (in order to remove MnO_2) and excess water until the PH of filtrate was nearly neutral. Finally, the product was centrifuged and received GO [17].

2.4. Preparation of large-sized graphene

The as-prepared products were then added in the deionized water. After sonicating for 5 min, 1 mL of ammonia was added into the solution to ensure that the whole system is under an alkaline environment. Afterwards, 0.15 mL of HHA was quickly poured into the mixture. The whole reaction system was maintained at 80°C and stirred for 12 h. The solid products were then filtered and rinsed several times with ethanol and distilled water to remove the unreacted chemicals and other impurities. The products were then dried in a vacuum oven at 60°C for 12 h.

2.5. Characterization

The morphological features of the products were recorded on a ULTRA Plus scanning electron microscope (SEM, German Zeiss ULTRA 55) and transmission electron microscope (TEM, USA FEI Tecnai G2TF20). The crystallographic structures of samples were examined by X-ray diffraction (XRD) measurements using a D/Max-2400 powder diffractometer with Cu Kα X-ray sources (Japanese Physical Company). Raman spectroscopy was measured by SPL-RAMAN-785.

3. Results and Discussion

SEM was used to obtain direct structure and morphological information of GO and graphene. As shown in Fig. 2a, pure GO has a layered and continuous film structure with some silk-like wrinkles and folding on its surface and edge. After deoxidation, the lamella of graphene from ultrasound-treated expanded graphite remains the same continuous silk-like structure (as shown in Fig. 2b) and the agglomeration did not happen. This phenomenon occurred because of the high temperature calcination and ultrasonic process destroyed the original compact structure of graphite, so that the spacing of graphite interlayer increased, which resulted in easier exfoliation of graphene monolayer during the oxidation-deoxidation reaction. This kind of graphene can be used as ideal substrate material to synthesize some composite materials. High-resolution TEM (HRTEM, Fig. 2c) confirms the graphene is shaped by several single-deck slices (the number of graphene layers ≤3) and could be clearly observed that some fringes with inter-planar distance of 0.34 nm, which can be attributed to the (002) plane of graphene, corresponding to the XRD data. These findings are attributed to the disruption of the planar sp^2 carbon sheets caused by the introduction of sp^3-hybridized carbon upon the oxidation.

In order to confirm this method is applicable to prepare graphene. Graphite powder and crystalline flake graphite were utilized as raw materials and made graphene through oxidation-deoxidation reaction without ultrosonic assisted liquid phase exfoliation process. SEM was still employed to observe the morphologies of the products and the testing results as following. As shown in Fig. 3a, GO generated from graphite powder is thick and its edges have already began to curl. The corresponded graphene sheets (shown in Fig. 3b) accumulated serious. However, GO prepared by crystalline flake graphite also have fairly thin layers (Fig. 3c). But there is a fly in the ointment, its lamellar is narrow. Fig. 3d shows that the reduced graphene still very small
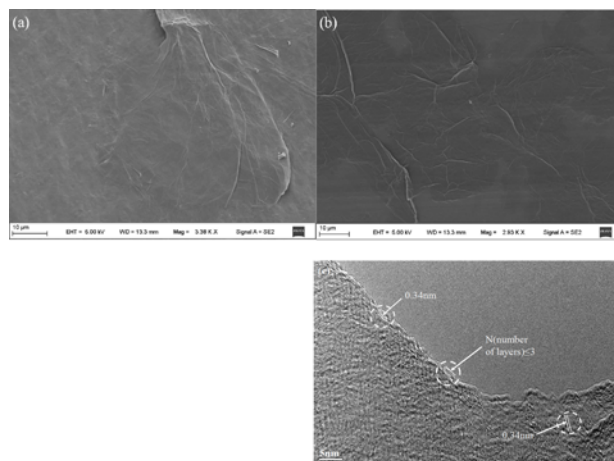

Fig. 2. SEM images of (a) GO and (b) graphene with ultrasound-treated expanded graphite as the raw material. (c) HRTEM images of graphene with large size.
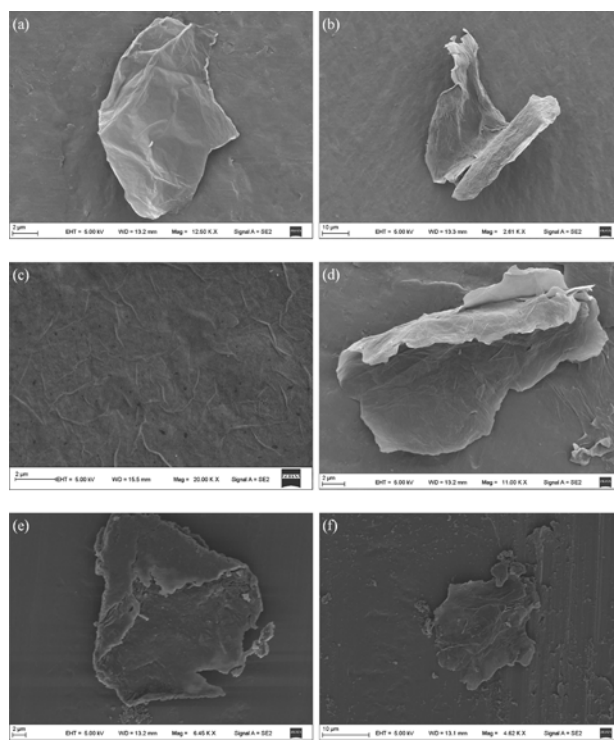

Fig. 3. SEM images of GO and graphene with (a) and (b) graphite powder as the raw material; (c) and (d) crystalline flake graphite as the raw material; (e) and (f) expandable graphite as the raw material.

and reunion phenomenon happened. Therefore, we could get information that the graphene prepared using different graphite as the raw materials have a clear distinction with their morphologies. A further investigation by using expandable graphite as raw materials to prepare graphene through only oxidation-deoxidation method was also done to validate the role that calcination and ultrasonic assisted liquid phase exfoliation process played during the course of the experiment. It can be drawn from Fig.
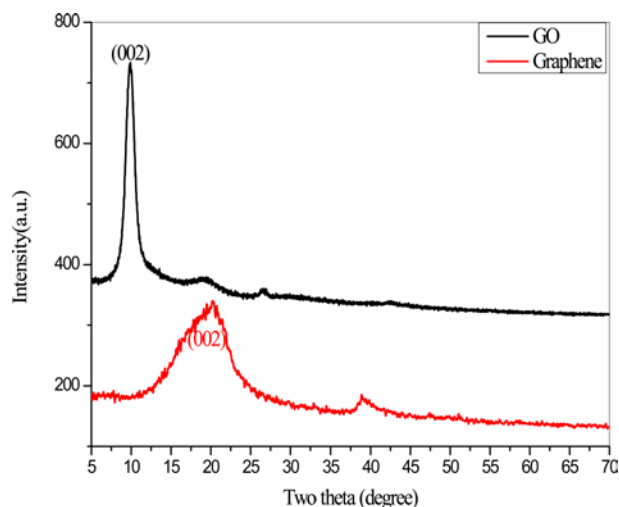
Fig. 4. XRD patterns of GO and graphene.

Fig. 5. Raman spectra of GO and graphene.

3e and f, the as prepared GO and graphene even did not form. The structure of products are much worse than graphite powder and crystalline flake graphite. According to this conclusion, we could confirm that calcination and ultrosonic assisted liquid phase exfoliation process have a major impact in graphene's preparation.

XRD analysis was used to investigate the crystalline structure of GO and graphene. As shown in Fig. 4, GO shows a strong characteristic peak at around $2\theta=10.6°$, corresponding to the (002) plane of GO [18-20]. In contrast to the d-spacing (0.337 nm) of pristine graphite, this phenomenon occurs because the oxygenated function groups were inserted into carbon sheets by the modified Hummers method and thus increased the spacing of graphite interlayer [21,22]. However, for graphene, the peak at $2\theta=10.6°$ completely disappeared due to the removal of oxygen functional groups and a typical peak appeared at $2\theta=22°$ which corresponds to the (002) diffraction peak of graphene [23,24]. These treatments eliminate part of its functional groups resulting in a drastic decrease in the interlayer spacing and emerge as evidence of the successful reduction process [25]. Moreover, a small peak appearing at around $2\theta=40°$ is ascribed to the thin monolayer graphene for the overall single-layer graphene due to the π–π stacking effect.

Raman spectroscopy is a nondestructive and rapid technological means for measuring crystalline structure, electronic energy band structures, phonon dispersion, and electron phonon coupling of materials. The Raman spectra of unreduced GO and graphenes can be seen in Fig. 5. Similar to the unreduced GO, the as prepared graphene has two prominent peaks at around 1325 cm^{-1} (caused by the disordered structure of graphene) and 1580 cm^{-1} (arised from the stretching of the C-C bonds), corresponding to the well-documented D and G bands, respectively [26-28]. The intensity ratio between D and G bands (I_D/I_G) is related with the graphitic degree of the carbon materials. Compared to the unreduced GO, the intensity ratio between D and G bands decreased, indicating that the graphene with large size graphene has lower defects than GO [29,30].
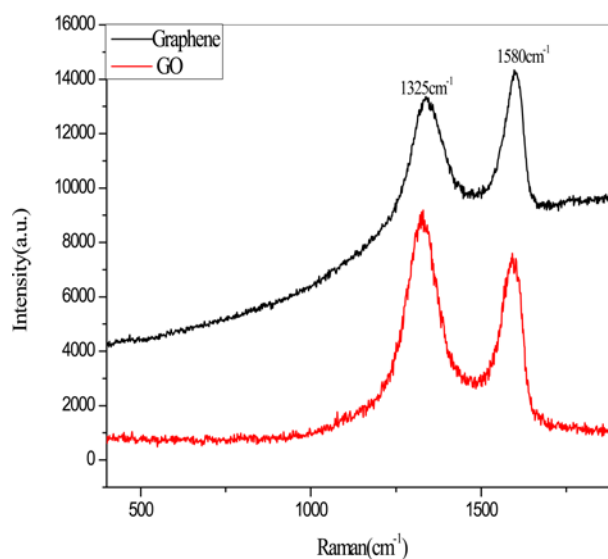
4. Conclusions

In this study, we combined chemical exfoliation with oxidation-reduction to prepare graphene with large size. Results of XRD and Raman confirmed that the as prepared product is graphene. SEM and TEM images revealed that the graphene has a large size and thin layers. Therefore, it could be confirm that pretreated raw materials before the oxidation-reduction is necessary. This method is attractive in laboratory for preparing graphene with large size.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

Acknowledgements

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