

Research Article

Preparation and Characterization of Reduced Graphene Oxide Sheets via Water-Based Exfoliation and Reduction Methods

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This research studied the synthesis of graphene oxide and graphene via a low-cost manufacturing method. The process started with the chemical oxidation of commercial graphite powder into graphite oxide by modified Hummer's method, followed by the exfoliation of graphite oxide in distilled water using the ultrasound frequency from a laboratory ultrasonic bath. Finally, the oxygen functional groups on exfoliated graphite oxide or graphene oxide were eliminated by stirring in hot distilled water at 95°C, as a replacement for highly toxic and dangerously unstable hydrazine. The results assured that stirring in hot distilled water could give the product of graphene or reduced graphene oxide. The samples were characterized by FTIR, XRD, TGA, Raman spectroscopy, SEM, and TEM methods.

1. Introduction

Graphene is a one-atom-thick planar layer of sp² hybridization carbon atoms which arrange in a hexagonal structure. It has unique and remarkable mechanical, thermal, optical, and electrical properties. In addition, the two-dimensional structure causes graphene to have a zero band gap and to act as a semimetal [1, 2]. Graphene can be synthesized by various methods such as chemical vapor deposition, mechanical exfoliation and cleavage, and annealing a single-crystal SiC under ultrahigh vacuum. These methods, however, have many disadvantages including high energy requirement, low yield, and limitation of instrument. Up to now, the chemical method has become a promising route to produce graphene sheets, although graphene derived by this method could contain a significant amount of oxygen functional groups and defects. This is because it is simple, inexpensive, and suitable for large-scale or mass production. The process involves 3 important steps: graphite oxidation, exfoliation of graphite oxide, and reduction of graphene oxide sheets.

In the first step, bulk graphite would be oxidized by chemical oxidation to become hydrophilic graphite oxide (GO). Graphite oxide is then exfoliated into monolayers or few-layered stacks of graphene oxide (XGO). This could be achieved by various thermal and mechanical methods. Sonicating or stirring in water is the most common. Finally, graphene oxide is reduced into graphene-like material. Previous works have reported the reduction by using reductants such as hydrazine. However, these chemicals might be highly toxic to human and environment [3, 4]. This has, therefore, stimulated a number of researches in recent years to develop simple methods for the reduction of graphene oxide. Liao et al. [5], for example, have reported a new simple, nontoxic and hydrazine-free method to reduce graphene oxide by stirring in hot water under acid condition.

In this paper, we first treated graphite powders with concentrated sulfuric and potassium permanganate, using modified Hummer's method, to produce graphite oxide. The process was designed to be simple and with a low risk, so that can be done in collage's laboratory. Graphite oxide was then

exfoliated and reduced into reduced graphene oxide (RGO) by ultrasonication in water and stirring in hot water. The obtained samples were studied by FTIR, XRD, TGA, Raman spectroscopy, SEM, and TEM methods. The objective of this work is to study the feasibility to simply synthesize reduced graphene oxide in a weak acid solution.

2. Materials and Methods

2.1. Materials. Graphite (fine powder extra pure) and hydrochloric acid fuming (37%) were purchased from Merck Ltd., Germany. Sulfuric acid (98%) Grade AR was purchased from Mallinckrodt Chemical Ltd. Potassium permanganate was purchased from Ajax Finechem Pty Ltd. Hydrogen peroxide (30–32%) Grade AR was purchased from QReC chemical co., Ltd. All chemicals were used as received.

2.2. Synthesis of Graphite Oxide (GO). Graphite oxide was synthesized from graphite powder by modified Hummer's method [6]. 2.0 g of graphite powder was first added into 100 mL concentrated H_2SO_4 at room temperature. Under stirring, the mixture was cooled to $5^\circ C$ using an ice bath, and the temperature of the mixture was kept to be below $5^\circ C$ for 30 min. $KMnO_4$ (8.0 g) was then added gradually under stirring and cooling, so that the temperature of the mixture was not allowed to reach $10^\circ C$. 100 mL distilled water was added into the mixture, stirred for 1 hr., and further diluted to approximately 300 mL with distilled water. After that, 20 mL of 30% H_2O_2 was added to the mixture to reduce the residual $KMnO_4$. The solid was filtered, washed with 5% HCl aqueous solution (800 mL) to remove metal ions and with distilled water until the pH was 6. The resulting graphite oxide (GO) was dried at $45^\circ C$ for 24 h.

2.3. Synthesis of Exfoliated Graphite Oxide (XGO). Aqueous colloids of XGO were prepared by dispersing 1.0 g GO into 500 mL of distilled water by ultrasonication and centrifugation for 2 hr. to remove any unexfoliated GO. The XGO was dried at $45^\circ C$ for 24 h.

2.4. Synthesis of Reduced Graphene Oxide (RGO). The RGO was prepared by dispersing 400 mg XGO into 800 mL of distilled water while stirring and heating at $95^\circ C$ for 4 days.

2.5. Characterization. Thermogravimetric analysis (TGA) was performed in a Perkin Elmer (TGA7) from 50 to $800^\circ C$ under nitrogen atmosphere (heating rate: $10^\circ C/min$). Fourier transform infrared spectroscopy (FTIR) was performed on a Bruker (Vertex 70). X-ray diffraction (XRD) patterns were recorded on a Rigaku (Miniflex II), employing a scanning rate of $0.033^\circ s^{-1}$ from 5° to 60° with $CuK\alpha$ radiation ($k = 0.154$ nm). The morphology of as-prepared samples was characterized using scanning electron microscope (SEM, Camscan: MX 200) and transmission electron microscope (TEM, JEOL: JEM-1230) operating at 80 – 120 kV. The absorbance of sample solutions was detected by UV-Vis Spectrophotometer (Shimadzu: UV-1800). Fourier transform raman spectrometer (FT-Raman, Perkin Elmer Spectrum

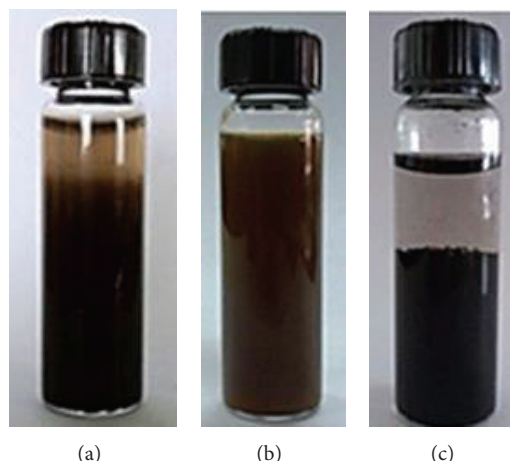


FIGURE 1: (a) Graphite oxide, (b) XGO, and (c) RGO.

GX) invariably incorporated with Nd:YAG solid state lasers operating at 1064 nm was used to characterize functional groups and structural information.

3. Results and Discussion

Figure 1 shows the obtained graphite oxide, graphene oxide, and reduced graphene oxide suspension in water. Graphite oxide prepared by a modified Hummer's method creates a brown aqueous suspension when dispersed in water as shown in Figure 1(a). The exfoliation of bulk graphite oxide in an ultrasonic bath results in a brown color and semitransparency of graphene oxide (Figure 1(b)). The negative surface charge of graphene oxide induces electrostatic repulsion among them and making it strongly hydrophilic [7]. However, when the graphene oxide was reduced in hot water, black precipitates are formed (Figure 1(c)). This is a typical hydrophobic characteristic of RGO or graphene sheets with less polar functionality on the surface of the sheets, compared to that of XGO [8].

Thermal stability of graphite, XGO and RGO was examined by TGA analysis (Figure 2). It is evident that graphite exhibits one clear step of weight loss, while XGO decomposes in three steps. The first weight loss at 50 – $120^\circ C$ relates to the loss of water molecules. The second step observed from $120^\circ C$ to $440^\circ C$ in XGO is due to the loss of oxygen-containing groups, and the third step above $440^\circ C$ relates to an unstable carbon remaining in the structure and the pyrolysis of oxygen functional groups in the main structure to yield CO and CO_2 [9–11]. The RGO shows similar characteristic but with lower amount of weight loss, compared to that of XGO. This could be explained by a smaller amount of oxygen functional groups in the structure.

The FTIR spectra of graphite and XGO are presented in Figures 3(a) and 3(b), respectively. The graphs show the stretching of hydroxyl group at 3450 cm^{-1} , the C=O carbonyl stretching at 1728 cm^{-1} , and the C–O epoxide group stretching at 1229 and 1061 cm^{-1} [12]. The high intensity of the main peaks in XGO confirms the presence of a large amount

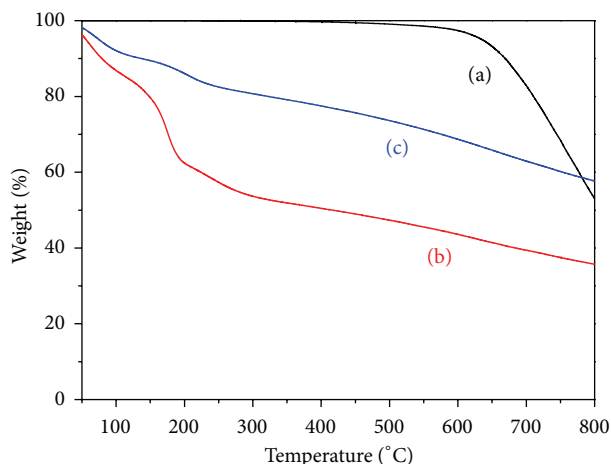


FIGURE 2: TGA of (a) graphite, (b) XGO, and (c) RGO.

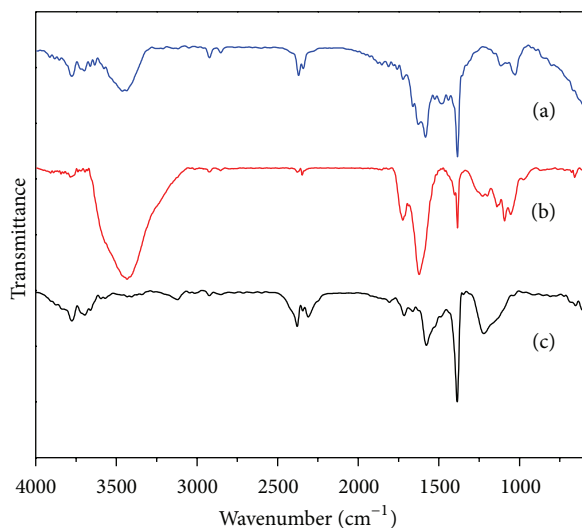


FIGURE 3: FTIR spectra of (a) graphite, (b) XGO, and (c) RGO.

of oxygen functional groups after the oxidation process. The peak at 1627 cm^{-1} is related to the vibrations of adsorbed water molecules. After the XGO was reduced, hydroxyl and alkoxy groups were significantly decreased (Figure 3(c)), and the phenol C=C ring stretching at 1585 cm^{-1} was present [10]. In order to effectively eliminate oxygen functional groups on carbon planes, however, strongly acidic environment might be required [5].

The XRD patterns of graphite, XGO, and RGO are shown in Figure 4. Pristine graphite has a strong and sharp diffraction peak at $2\theta = 26.38^\circ$, corresponding to the highly organized layer structure with an interlayer distance of 0.34 nm along the (002) orientation [12]. After the chemical oxidation and exfoliation into XGO, however, the (002) peak is shift to lower angle at $2\theta = 10.80^\circ$, indicating an increase in d-spacing from 0.34 nm to 0.82 nm. An increased interlayer distance between consecutive carbon basal planes is attributed to the intercalation of oxygen functional groups and water molecules into carbon layer structure [10, 13]. The RGO,

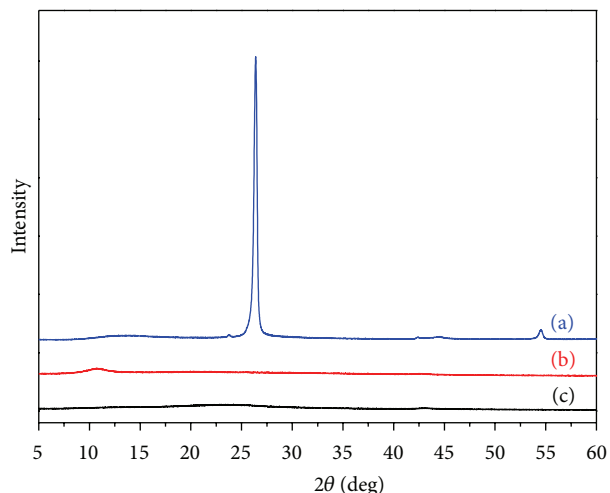


FIGURE 4: XRD patterns of (a) graphite, (b) XGO, and (c) RGO.

on the other hand, exhibits a new broad peak at $2\theta = 23.50^\circ$, corresponding to the d-spacing of 0.38 nm along the (002) orientation. This can be explained by the removal of oxygen functional groups, causing a decrease in d-spacing [14].

The UV-Visible and FT-Raman spectra of XGO and RGO are shown in Figure 5. According to the absorbance spectra, the main spectrum of XGO has an absorption peak at 230 nm, attributed to $\pi-\pi^*$ transition of the aromatic C-C ring and weak absorption at 303 nm due to $n-\pi^*$ transition of C=O bond [10, 12]. The peak of RGO is, however, shifted to 255 nm due to a decrease in oxygen functional groups and an increase in aromatic rings, causing electrons to be easily excited at a lower energy [14]. The Raman spectra of XGO and RGO reveal two prominent peaks at G band and D band. It is clearly noticed that these two bands are broader in XGO than those in RGO, corresponding to higher disorder in XGO. The sharpening of the G band and an increase in the peak intensity in RGO are due to the restoring sp^2 domains and the reestablished sp^2 network after the reduction treatment in hot water [15, 16]. After baseline correction, the I_D/I_G intensity ratio of RGO is calculated to be 1.12, which is slightly higher than that of XGO. This suggests a reduction in the average size of sp^2 domains. Nevertheless, this number is much lower than those calculated from the reduction by hydrazine in previous works ($I_D/I_G \sim 1.44-1.63$ [17, 18]). Since the D band is generally known as the disorder or defect band, the results illustrate that the current approach can produce XGO with less defect nature.

The morphology of the samples was studied using SEM and TEM. As shown in Figure 6(a), graphite particles are in the platelet-like crystalline form of carbon. After acid oxidation and ultrasonication, XGO sheets become smaller and transparent (Figure 6(b)). The sheet is so thin that electron beam can be passed through sample. Figures 6(c) and 6(d) show the SEM and TEM images of RGO. The reduced graphene oxide exhibits typical wrinkled structure that caused sheet folding [19, 20].

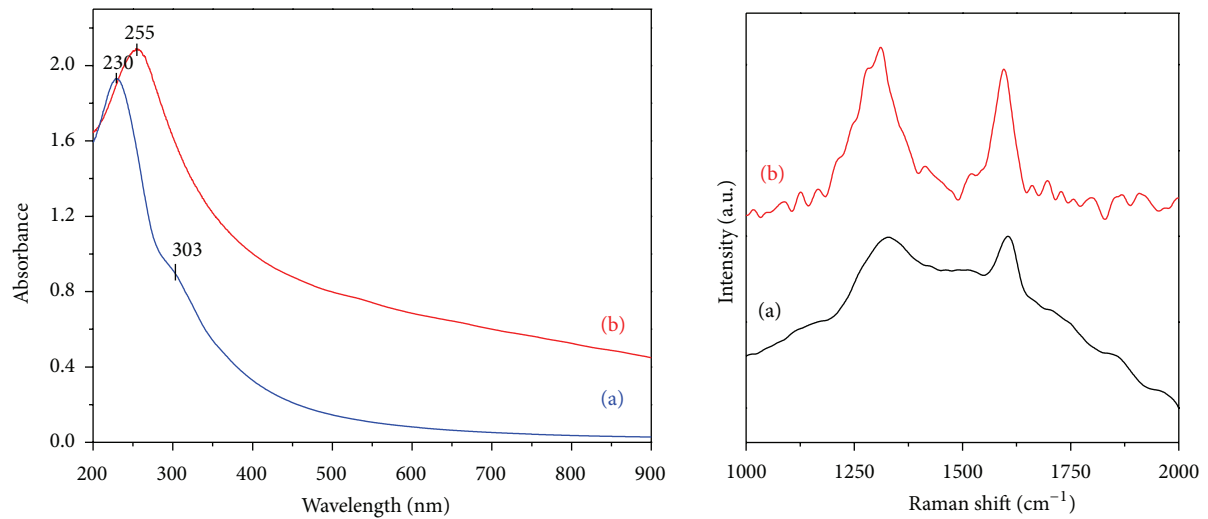


FIGURE 5: UV-Vis spectrum and FT-Raman spectra of (a) XGO and (b) RGO.

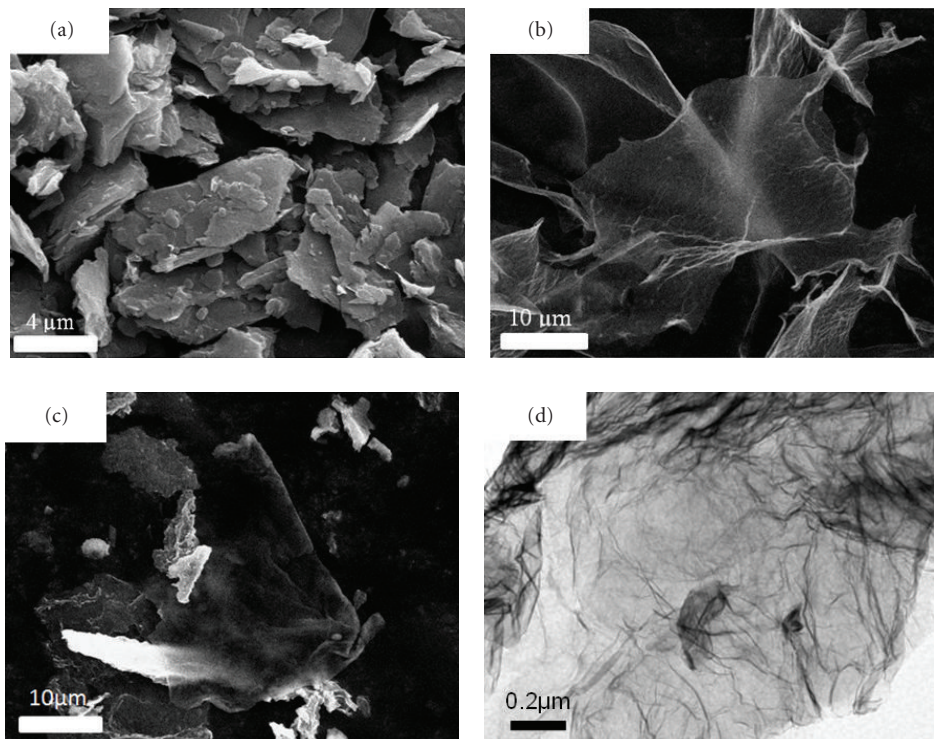


FIGURE 6: SEM (a, b, c) and TEM (d) images of graphite (a), XGO (b), and RGO (c, d).

4. Conclusions

In this study, reduced graphene oxide (RGO) can be synthesized by modified Hummer's method and reduction method by stirring in hot water. The results show that oxygen functional groups in XGO could be eliminated through stirring in hot water, as confirmed by FTIR and TGA analysis. SEM and TEM show the structures of XGO and RGO, which are very thin sheets even through there is evidence of sheet folding.

Conflict of Interests

The authors declare that there is no conflict of interests.

Acknowledgments

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