Research Article

Study of Reduced Graphene Oxide Preparation by Hummers' Method and Related Characterization

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As a novel two-dimensional carbon material, graphene has fine potential applications in the fields of electron transfer agent and supercapacitor material for its excellent electronic and optical property. However, the challenge is to synthesize graphene in a bulk quantity. In this paper, graphite oxide was prepared from natural flake graphite by Hummers' method through liquid oxidation, and the reduced graphene oxide was obtained by chemical reduction of graphene oxide using $\text{NH}_3 \cdot \text{H}_2\text{O}$ aqueous solution and hydrazine hydrate. The raw material graphite, graphite oxide, and reduced graphene oxide were characterized by X-ray diffraction (XRD), attenuated total reflectance-infrared spectroscopy (ATR-IR), and field emission scanning electron microscope (SEM). The results indicated that the distance spacing of graphite oxide was longer than that of graphite and the crystal structure of graphite was changed. The flake graphite was oxidized to graphite oxide and lots of oxygen-containing groups were found in the graphite oxide. In the morphologies of samples, fold structure was found on both the surface and the edge of reduced graphene oxide.

1. Introduction

Graphene is a novel 2-dimensional material which was first separated from graphite by mechanical stripping method in 2004 [1]. As an allotrope of element carbon, it is a planar sheet of carbon atoms arranged into hexagon [2]. The "thinnest" known material graphene can be used for biosensors [3], transparent electrodes [4], hydrogen storage, composites [5], and high energy supercapacitors [6] for its high optical and electron transparency and excellent mechanical properties [7].

There are many ways to synthesize graphene [1, 8, 9], such as exfoliation and cleavage, chemical vapor deposition (CVD), thermal decomposition, and electrochemical reduction. Among these preparation methods, solution-based reduction of graphite oxide (GO) is attractive for its easy operation in recent years. It includes three typical steps in this method. They are graphite oxidation, GO aqueous dispersion, and GO reduction. The methods invented by Brodie, Staudenmaier, and Hummers are widely used for graphite oxidation [10]. And Hummers' method is popular for the following reasons. First, KClO_3 was replaced by KMnO_4 as the oxidation agent. In this condition, the byproducts of toxic

gas were eliminated and the securities of experiments were improved. Moreover, the oxidation time was shortened, and last it was easy to exfoliate the resulted product in water. In this paper, Hummers' method was employed to prepare GO and reduced GO (rGO) was obtained with the aid of $\text{NH}_3 \cdot \text{H}_2\text{O}$ aqueous and hydrazine hydrate.

2. Experimental

2.1. Raw Materials. Flake graphite powder, 98 wt.% H_2SO_4 , KMnO_4 , NaNO_3 , deionized water, $\text{NH}_3 \cdot \text{H}_2\text{O}$ aqueous, dilute HCl aqueous, 30% H_2O_2 aqueous, and 80% hydrazine hydrate aqueous.

2.2. Graphene Preparation

2.2.1. GO Preparation. The mixture of flake graphite/ NaNO_3 was prepared in weight ratio of 2:1. The mixture was added into a beaker with a certain amount of 98 wt.% H_2SO_4 at 15°C and a suspension was obtained. Then, KMnO_4 powder which acted as an oxidation agent was gradually added into the suspension with continuous stirring. The weight of the KMnO_4 powder is 3 times as much as the one of the mixture.

FIGURE 1: Pattern of resulting suspension.

There were 3 steps for the following process. First of all, it is the low temperature reaction. The temperature of the mixture was controlled below 20°C for 2 hours; at the same time, the suspension should be stirred continuously. The second step is the mid temperature reaction. The temperature of the mixture was maintained at 35°C for 30 minutes after KMnO_4 was totally dissolved. Finally, it is the high temperature reaction. A certain amount of deionized water was added into the mixture slowly; therefore a large amount of heat was released when concentrated H_2SO_4 was diluted. 15 minutes later, certain amounts of hot water and 30% H_2O_2 aqueous were added into the mixture, respectively, with continuously stirring. As Figure 1 shows, the bright yellow resulted suspension was filtered by the qualitative filter paper when it was still hot, and the solid mixture was washed with dilute HCl aqueous and distilled water and dried in vacuum oven at 70°C for 24 h.

2.2.2. rGO Preparation. 400 mg GO was dispersed in 400 mL water by means of 30 minutes' ultrasonic treatment. As a result, a homogeneous brown GO aqueous suspension was obtained. The pH of the suspension was adjusted to 10 by dropping $\text{NH}_3\cdot\text{H}_2\text{O}$. A mount of hydrazine hydrate was added into suspension and heated at 80°C for 24 hours, and the weight ratio of hydrazine hydrate and GO was controlled at 10:7. A kind of black flocculent substance was gradually precipitated out of the solution. The product was obtained by filtered with the qualitative filter paper. Finally, the resulting black product was washed with methanol and water and dried at 80°C for 24 h.

2.3. Characterization of Materials. Crystal features of flake graphite, GO, and rGO were obtained by XRD [10] (AXS cooperation, Germany), with a scan speed of $4^{\circ}/\text{min}$ from 5 to 60° of 2θ angles. The layer spacing (d spacing) could be calculated with the aid of Bragg equation, and the change of diffraction peak could also be observed. The micromorphology of rGO was observed by SEM (JSM-6700F, Japan), with the acceleration voltage from 0.5 to 30 KV. Spectra of dried GO and rGO were obtained by Tensor 27 FTIR-ATR (Bruker

cooperation, Germany), with the resolution of 4 cm^{-1} from 3700 to 500 cm^{-1} of spectral region, and functional groups of GO and rGO can be observed.

3. Result and Discussion

3.1. X-Ray Diffraction. As shown in Figure 2(a). Flake graphite exhibits a basal diffraction peak (002) at $2\theta = 26.5^{\circ}$ (d spacing = 0.33630 nm), which is very sharp. There is also a very weak diffraction peak (004) at $2\theta = 54.8^{\circ}$ (d spacing = 0.16738 nm). The diffraction peak (004) is the second diffraction [11] of the diffraction peak (002) according to layer spatial arrangement rules of microcrystals; thus diffraction peak (004) intensity is much weaker than that of diffraction peak (002). The diffraction peak at about $2\theta = 9.8^{\circ}$ is very typical for GO; no apparent diffraction peak could be found for rGO in its XRD pattern. This result is similar to that of Tapas Kuila [2], who had already described the structure of GO and rGO by XRD. Figures 2(b) and 2(c) show the enlarged XRD patterns of GO and rGO. Diffraction peak becomes broader in the enlarged pattern of GO at $2\theta = 9.8^{\circ}$ (d spacing = 0.88160) and the significant increase in d spacing is believed due to the following reason: oxygen functional groups intercalate in the interlayer of graphite. There is a very weak diffraction peak at $2\theta = 42.3^{\circ}$, which is believed due to the incomplete oxidation. As is shown in Figure 2(c), a very weak and broad diffraction peak can be observed in the XRD pattern of rGO at $2\theta = 25\text{--}30^{\circ}$; the diffraction peak of rGO is so weak that it cannot be visible when drawn together in the XRD pattern with graphite and GO (Figure 2(a)). There is also a weak diffraction peak at $2\theta = 42.3^{\circ}$.

3.2. FTIR-ATR. FTIR-ATR spectra of GO and rGO are shown in Figures 3 and 4. Some carbon-oxygen functional groups of GO are observed in Figure 3, such as O-H, C=O, C-OH, and C-O. Characteristic peak ($\sim 3464\text{ cm}^{-1}$) [12] is believed to be attributed to O-H stretching of hydroxyl and carboxyl groups, and characteristic peaks of C=O ($\sim 1639\text{ cm}^{-1}$), C-OH ($\sim 1288\text{ cm}^{-1}$), and C-O ($\sim 1003\text{ cm}^{-1}$) are also believed to be attributed to carboxylic acid and carbonyl groups [13]. And the characteristic peak at 1493 cm^{-1} is corresponding to the C=C skeletal vibration of unoxidized graphitic domain. These oxygen functional groups indicate that the flake graphite powder has been oxidized to GO. As shown in Figure 4, no obvious peak could be observed, which means that full reduction of GO was made. While carbon-oxygen functional groups all existed, their characteristic peaks are just very weak.

3.3. Scanning Electron Microscope. Figure 5 shows SEM morphologies of rGO which was dried at 80°C for 1 day. As is shown in Figure 5, 2-dimensional material can be observed. Fold structure can be found on both the surface and the edge of rGO powder. They are the typical morphologies of few-layer rGo [14]. The thickness of rGO may be 10 nm and it is obviously that rGO layers have fairly large dimension (much larger than 100 nm), and rGO retacked together. The reason of the reagglomerate may be the long-time high temperature

FIGURE 2: X-ray diffraction patterns. (a) graphite, GO, and rGO; (b) enlarged view of GO; (c) enlarged view of rGO.

FIGURE 3: FTIR-ATR spectra of GO.

FIGURE 4: FTIR-ATR spectra of rGO.

FIGURE 5: SEM morphology of rGO.

treatment. The morphology of graphite (fold structure) can also be found in Figure 5.

Reaction mechanism of solution-based reduction of graphite oxide will be discussed, to begin with the mechanism of Hummers, though KMnO_4 is used as a kind of oxidizing agent. Dreyer et al. [15] believed that the active species was Mn_2O_7 . The following equation gives the reaction between KMnO_4 and H_2SO_4 :

In low temperature reaction, the edge of graphite was oxidized and intercalated with the aid of oxidizing agent. $-\text{OH}$ was formed during this process. In mid temperature reaction, with the increasing of temperature, the oxidation ability improves furthermore. More oxygen functional groups are formed in this process, and the oxidizing agent penetrates into the internal of graphite layer; therefore this process results in the increasing of d spacing. In the high temperature reaction, concentrated H_2SO_4 releases large amount of heat during the process of watering. Force between layers is

destroyed and finally the GO could be fully exfoliated to single layers. Secondly, the fully exfoliated GO will be reduced to rGO with the help of $\text{NH}_3 \cdot \text{H}_2\text{O}$ aqueous and hydrazine hydrate.

The mechanism of solution-based reduction of GO is quite different with that of the traditional CVD ones. The formation of graphene on bulk metal through CVD includes three steps [1, 16, 17]. First, a hydrocarbon could be dissociated through dehydrogenation; second, the carbon species diffuse and dissolve into the bulk metal at the growth temperature; the reason why transition metals could serve as an electron acceptor is because of the empty d -shell; third, carbon species precipitate out of the bulk metal onto the metal surface upon the rapid quenching, start the segregation process, and build up honeycomb lattice because the solubility decreases during the cooling process.

4. Conclusion

GO was prepared by Hummers' method and rGO was prepared with the aid of $\text{NH}_3 \cdot \text{H}_2\text{O}$ aqueous and hydrazine hydrate successfully. The characterization results indicate that

the layer spacing of graphite oxide was longer than that of graphite. The crystal structure of graphite was changed. Graphite was oxidized to GO and lots of oxygen-containing groups were found in the GO. The typical fold morphologies were found on both the surface and the edge of rGO.

Compared with the traditional CVD method, Hummers' method can synthesize GO in large scale, then rGO can be prepared with the help of reduced agent, and this process costs a little. Meanwhile, the prepared GO is dispersed easily in solution. In this case, the modification of the GO is easy and it is suitable for GO application in composites and energy storage devices.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publishing of this paper.

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