

Research Article

Effect of Ammonium Bicarbonate on Intercalation and Exfoliation of Graphite Materials

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Intercalation and exfoliation are key steps in the preparation of graphene by thermal exfoliation, and they determine the quality of the final product. Therefore, it is important to explore the influence of intercalation agents on the intercalation and exfoliation of graphite. In this article, ammonium bicarbonate is intercalated into graphite with different degrees of oxidation to form a graphite intercalation compound (GIC) by means of ultrasound and stirring. Then, they are exfoliated by being heated at high temperatures. After ammonium bicarbonate intercalation and heating treatment, XRD, TG, and BET show that the intercalation and exfoliation effect of graphite oxide (GO) is better than that of graphite (G) and expanded graphite (EG). The intercalation mechanism is that the ammonia molecule in ammonium bicarbonate solution contains a wedge-shaped structure and active point, which provides empty orbits for graphite electrons and forms edge intercalation through physical interaction at the same time.

1. Introduction

Intercalation and exfoliation can increase the graphite layer-to-layer spacing and reduce the number of layers. They are methods to change the properties of graphite materials and even prepare isomers, such as graphene. Graphene is one of the hottest materials in research, and it has many applications, such as energy-related materials, sensors, field-effect transistors, and biomedical applications [1–3]. Currently, graphene preparation methods suitable for industrial production include graphite oxide reduction, liquid-phase exfoliation of graphite, and thermal exfoliation [4–7]. Intercalation and exfoliation are the most important steps in the preparation of graphene by thermal exfoliation, which determines the quality of graphene. They are also the key to overcome the van der Waals force between the graphite layers. To destroy van der Waals forces, some researchers immersed graphite in surfactants and then sonicated them to overcome van der Waals forces through cavitation. Hernandez et al. [8] completed graphite exfoliation in N-methyl-2-pyrrolidone (NMP) and obtained raw graphene without chemical modification. Other researchers

introduced various intercalation agents between the layers, which bonded with carbon atoms between the graphite layers to form a graphite intercalation compound (GIC). The GIC thermal decomposition produces a large amount of gas (H_2O or CO_2) between layers, rapidly increasing interlayer pressure and overcoming van der Waals force through expansion. Gu et al. [9] introduced concentrated sulfuric acid and hydrogen peroxide into natural graphite, and the GIC was rapidly heated and exfoliated at $900^\circ C$. As a result, there were more than 50% of single-layer graphene in the product. Lin et al. [10] used ammonium bicarbonate as the intercalation agent and permeate it through the expanded graphite layer by ball milling and then used the microwave to quickly exfoliate the GIC to obtain graphene with fewer defects. Based on the above research, ammonium bicarbonate is a suitable intercalation agent, which can be inserted between graphite layers by a mechanical or ultrasonic means, avoiding the use of a reinforcing oxidant [9, 10]. In addition, it can be completely decomposed under the heat, with large amount of produced gas and harmless produced gas, and the whole intercalation-exfoliation process is less polluting.

Here, we introduce ammonium bicarbonate molecular groups into graphite materials with different oxidation degrees, then heat GIC to make it undergo chemical phase transition, and then research the effect of ammonium bicarbonate on the intercalation and exfoliation of graphite materials with different oxidation degrees.

2. Experiment

2.1. Materials. Natural graphite was purchased from Qingdao Tengshengda Carbon Machinery Co. (Qingdao, China). Sulfuric acid, hydrochloric acid, and potassium permanganate were supplied by Yantai Yuandong Fine Chemical Co. (Yantai, China). Nitric acid was gotten from Tianjin Damao Chemical Reagent Factory (Tianjin, China). Sodium nitrate and ammonium bicarbonate were obtained from Aladdin (Beijing, China). Hydrogen peroxide was purchased from Zhengzhou Huize Biochemical Technology Co. (Zhengzhou, China).

2.2. Preparation of EG and GO. Expanded graphite (EG) was prepared by mixing natural graphite (NG), HNO_3 , and H_2SO_4 in a 100 mL beaker at a weight ratio of 1:37.5:12.5 for 15 h [11], then washing with distilled water to neutral, drying overnight in a vacuum drying chamber at 50°C , and heating in a muffle furnace at 800°C to 900°C for 20 seconds.

Graphite oxide (GO) was prepared by the optimized Hummers method [12]. NG, sodium nitrate, and sulfuric acid were added to a 500 mL beaker at the weight ratio of 1:0.5:37 (in grams) and stirred continuously under ice bath for 5 minutes. 3 g of potassium permanganate was added slowly. The reaction mixture was stirred at 5°C for 2 h. 46 mL of deionized water was added to the suspension, and the mixture was stirred for 30 minutes. Then, deionized water (140 mL) and hydrogen peroxide (30% W/W, 5 mL) were added to complete the reaction. The prepared graphite oxide powder was washed 5 times with diluted hydrochloric acid (5%, 200 mL) solution and thermal deionized water (70°C) and then dried in an oven at 60°C for 12 h.

2.3. Preparation of an Ammonium Bicarbonate-Intercalated Compound. 1 g of NG, EG, and GO was dispersed in 100 mL saturated ammonium bicarbonate aqueous solution (22 g/100 mL), stirred for 40 min, ultrasonicated for 40 min, centrifuged and filtered to get the mixture, then dried in an oven at 50°C for 12 h, and heated in an oven at 800°C to 900°C for 20 s.

2.4. Characterization. Images from a scanning electron microscope were recorded with Hitachi SU8010 (Hitachi, Ltd., Japan). Oxidation degrees of graphite materials were monitored by Renishaw inVia Raman spectroscopy (Renishaw plc, Britain). X-ray diffraction patterns were measured with D-max 2500/PC (Rigaku Corporation, Japan). IR spectral measurements were carried out using Nicolet iS50 (Syme Fisher Technology Co. Ltd., America).

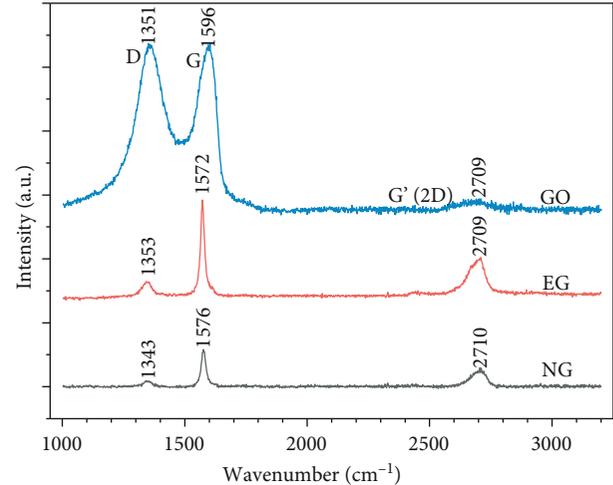


FIGURE 1: Raman spectra of three graphite materials.

TABLE 1: Raman spectral I_D/I_G ratio of three graphite materials.

Types	I_D	I_G	I_D/I_G
NG	190	1138	0.167
EG	1027	3592	0.286
GO	5235	5220	1.003

3. Results and Discussion

3.1. Oxidation Degree of Different Graphite Materials. Figure 1 shows that NG, EG, and GO have peaks at three positions: 1350 cm^{-1} , 1580 cm^{-1} , and 2700 cm^{-1} , but the ratios of the corresponding peaks are different. The graphite materials have a D peak at 1350 cm^{-1} , which is attributed to ring vibration of sp^2 hybrid carbon atoms [13]. It reflects grain size, disordered structure, and graphite defects. The G peak at 1580 cm^{-1} is caused by the stretching of the sp^2 -type C-C bond in the hexagonal ring structure of the graphite lattice [14], and the G' peak (2D peak) at 2700 cm^{-1} is attributed to the vibration of the two-photon lattice. The information in the figure shows that NG and EG have high crystallinity and few defects, while GO has a large number of defects and low crystallinity [15]. EG and GO have different degrees of interlayer oxidation, and GO has a higher degree of oxidation. In addition, the intensity ratio I_D/I_G (intensity of peak D and peak G) is usually used as an important parameter to characterize the defect density of carbon materials [16].

In Table 1, the I_D/I_G values of EG and GO are 0.286 and 1.003, both of which are greater than the intensity ratio of NG (0.167), and the I_D/I_G intensity ratio of GO is much higher than those of EG and NG. This indicates that the defect density of the three graphite materials is NG, EG, and GO from low to high [17]. According to the information in Figure 1 and Table 1, the disordered structure of graphite materials and graphite defects increase, from NG to GO.

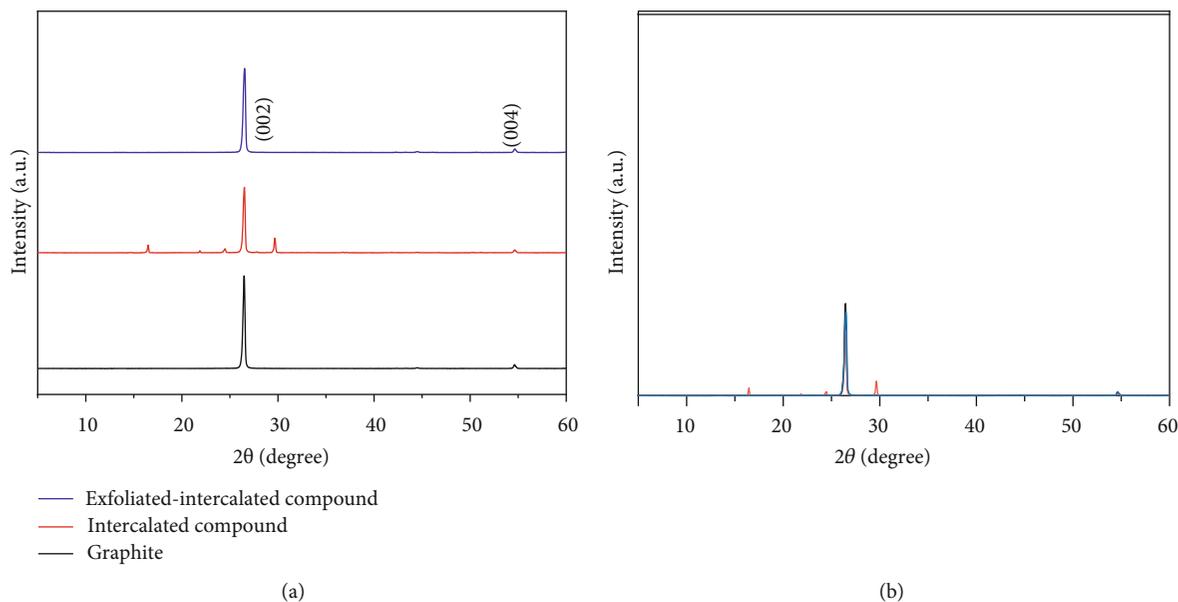


FIGURE 2: X-ray diffraction patterns of NG in three stages: (a) original XRD data in three stages; (b) locally amplified XRD data in three stages.

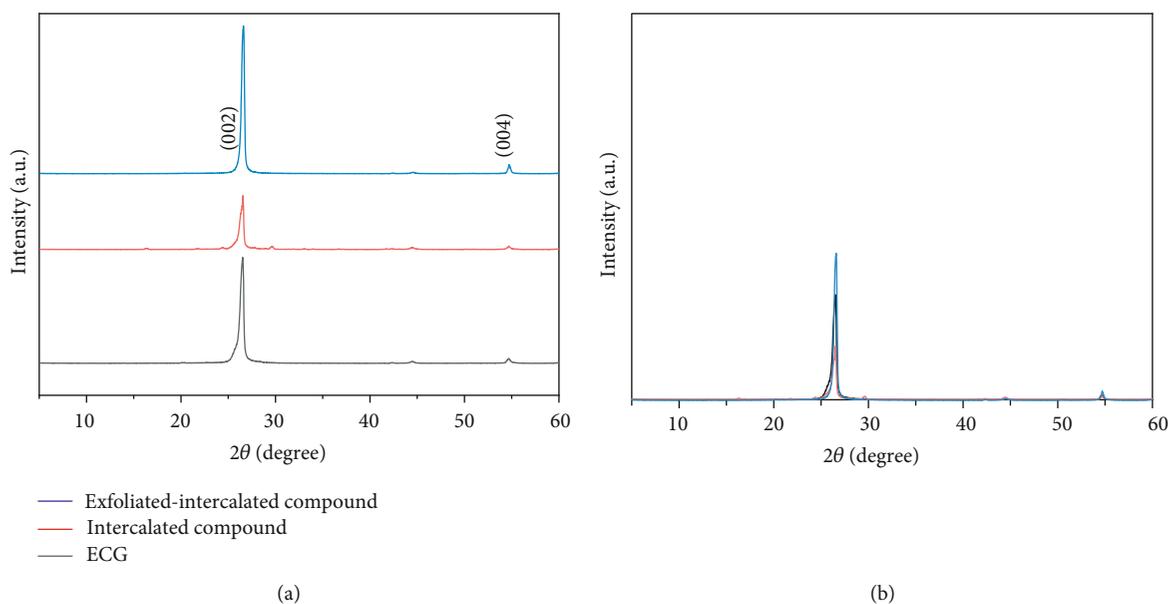


FIGURE 3: X-ray diffraction patterns of EG in three stages: (a) original XRD data in three stages; (b) locally amplified XRD data in three stages.

4. Intercalation Effect of Different Graphite Materials

In Figure 2(a), the peak corresponding to graphite-2 h can be clearly seen. The (002) peak and (004) peak are the two peaks in the XRD patterns of natural graphite, indicating the vertical direction (c -axis) with the hexagon plane of graphite. 2θ of the (002) crystal face is 26.480 , and the d value is 3.3632 . After ammonium bicarbonate intercalation, 2θ of the (002) crystal surface reduces to 26.518 and the d value increases to 3.3584 . After high-temperature exfoliation, 2θ of the (002) crystal surface turns into 26.518 and the d value

changes to 3.3584 . The three curves were shifted to the same horizontal position as that shown in Figure 2(b), in which the (002) peak has not shifted. It indicates that ammonium bicarbonate cannot enter into the graphite layers and no atoms will enter into the lattice of the original crystal.

Figure 3 shows the X-ray diffraction patterns of EG in three stages, where the peak corresponding to graphite-2 h can also be clearly seen. 2θ of the (002) crystal face is 26.161 , and the d value is 3.4035 . After ammonium bicarbonate being inserted, 2θ of the (002) crystal surface reduces to 26.009 and the d value increases to 3.4230 . This indicates that ammonium bicarbonate intrudes into the graphite layers,

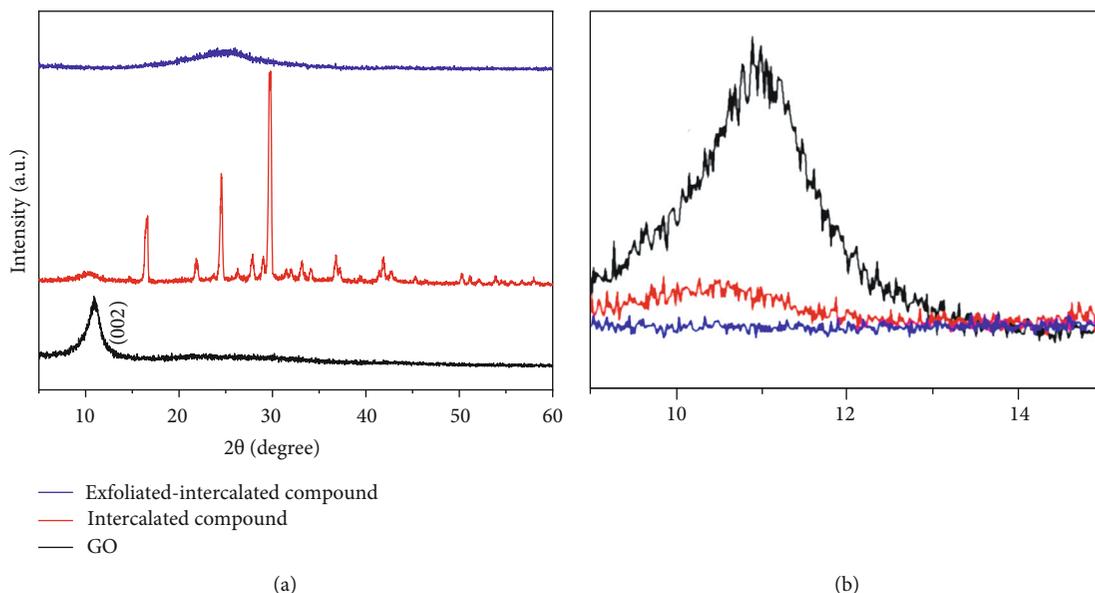


FIGURE 4: X-ray diffraction patterns of GO in three stages: (a) original XRD data in three stages; (b) locally amplified XRD data in three stages.

TABLE 2: The elemental composition of the three graphite materials before and after treatment.

		C (wt.%)	N (wt.%)	O (wt.%)	Na (wt.%)	S (wt.%)
G	Original	85.365	0	13.132	0.573	0.930
	After exfoliation	81.474	0	17.600	0.419	0.507
EG	Original	79.404	0	18.984	0.778	0.833
	After exfoliation	89.675	0	9.530	0.646	0.149
GO	Original	47.390	0	47.429	0.697	4.484
	After exfoliation	58.936	0	36.512	1.316	3.236

causing the change of its peak position. After high-temperature exfoliation, there are almost no other hybrid peaks except the peak of graphite, which indicated that high-temperature treatment could completely remove ammonium bicarbonate. XRD of the exfoliated-intercalated compound showed that the 2θ and d value are 22.798 and 3.8974, respectively, which means that the spacing of graphite layers has changed greatly, and the expansion effect is obvious after high-temperature treatment. It can be clearly seen from Figure 3(b) that the peak after high-temperature treatment has a significant deviation from the original peak.

According to Figure 4, due to the complete oxidation of graphite, the d value is 8.0085, and the interlayer spacing is much larger than that of NG. After adding ammonium bicarbonate, the peak of graphite oxide shifted significantly to the left and the d value changes from 8.0085 to 8.4680, indicating that ammonium bicarbonate is introduced into the GO layers. It can be clearly seen from Figure 4(b) that the peak after ammonium bicarbonate intercalation is significantly offset from the original peak. After high-temperature treatment, the exfoliated-intercalated compound has a very wide peak at 26° , which indicated that graphite oxide had low crystallinity after high-temperature treatment. This may be inserted into the ammonium bicarbonate high-temperature

decomposition with graphite oxide reaction and graphite oxide nitrogen doping.

In this regard, we add the content of compounds after EDS analysis. According to the data in Table 2, the content of the N element is still 0 after high-temperature treatment, which indicates that GO does not react with decomposition products of ammonium bicarbonate at high temperature. The relative content of O, Na, and S decreased significantly, which indicates that the functional groups of GO cracked and produced a high-temperature reduction phenomenon.

In order to further prove that ammonium bicarbonate is inserted into graphite layers, we conducted thermogravimetric analysis of the three graphite materials, observing whether the weight loss temperature of the three kinds of graphite materials will be different. In Figure 5, it can be observed that at the beginning, ammonium bicarbonate and water were decomposed in order to lose weight, and the weight loss proportions of the three graphite materials were different. It can be observed that the desorption temperature of graphite materials varies with the degree of oxidation. Their desorption completion temperatures were all pushed back. The desorption completion temperatures of ammonium bicarbonate in G, EG, and GO were 56°C , 79°C , and 110°C , respectively. The desorption temperatures of water in G, EG, and

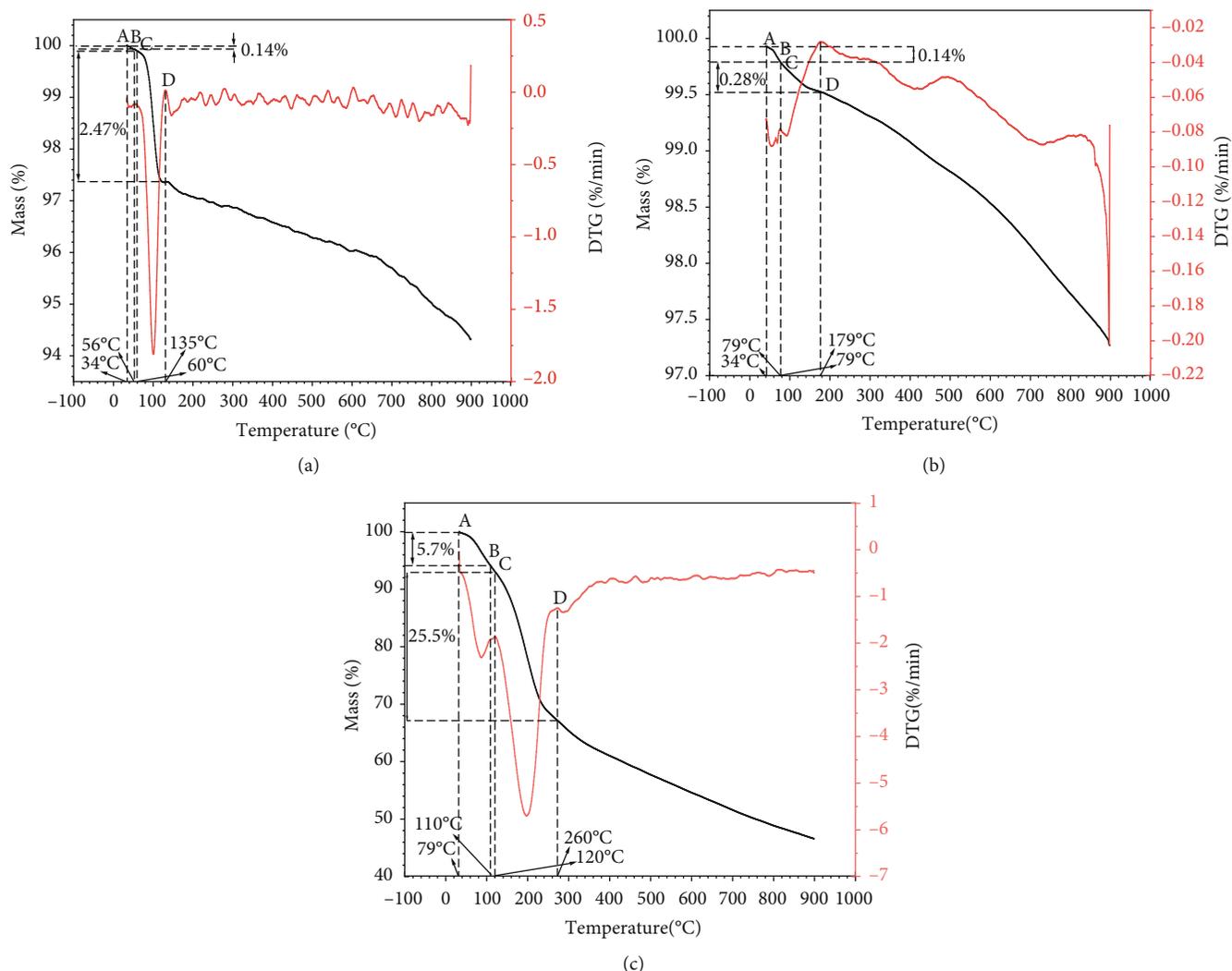


FIGURE 5: TG and DTG curve of the three graphite materials at a constant heat rate of $20 \text{ K} \cdot \text{min}^{-1}$: (a) G; (b) EG; (c) GO.

GO were 135°C , 179°C , and 260°C , respectively. This indicates that they have different binding forces with different levels of graphite oxide, which should be caused by ammonium bicarbonate and water entering between layers of the graphite oxide material.

4.1. Changes of Chemical Bonds after Intercalation of Different Graphite Materials. The peak at 1580 cm^{-1} was contributed by sp^2 hybrid $\text{C}=\text{C}$ stretching vibration in a graphite carbon hexagon ring [18], and a wide absorption region appeared near the peak at 3447 cm^{-1} , which was attributed to the antisymmetry of $-\text{OH}$ and the stretching vibration in free water. Both appear in NG, EG, and GO and throughout the whole process. The vibration appearance of 1178 cm^{-1} and 1578 cm^{-1} shows the natural characteristic vibration of ammonia belonging to stage δ_s (NH_3) and N-H [19, 20], respectively. NG, EG, and GO have these characteristic peaks at stage (B). In Figure 6, the peaks of 1178 cm^{-1} and 1578 cm^{-1} at stage (C) disappeared after heat treatment, indicating ammonium bicarbonate molecule and carboxyl group breakdown. The peak appeared at the 1634 cm^{-1} position, which

may be due to oxidation of graphite or groups on the graphite surface during thermal expansion [21].

However, the three oxidized graphite materials did not vibrate at 1500 cm^{-1} , which indicates that $\text{C}=\text{N}$ was not formed, and it also indicated that ammonium bicarbonate could not form stable chemical bonds with graphite materials. Jiang et al. [22] proposed a “wedge” model of intercalation ammonia, which is considered to be slightly larger than the layer spacing of graphite and can easily enter the graphite layer. As ammonia has an active point, it can provide empty orbitals for interlayer electrons of graphite.

4.2. Intercalation Process and Effect of Different Graphite Materials. To further investigate the whole process of intercalation and exfoliation, typical SEM secondary electron images of the three kinds of graphite materials are shown in Figure 7. The thickness of the NG layer is on the order of micrometers, and the arrangement is very tight. Some flocs appear on the graphite layer in stage (B), which is the crystal formed by ammonium bicarbonate. However, no ammonium bicarbonate crystals are observed between the graphite

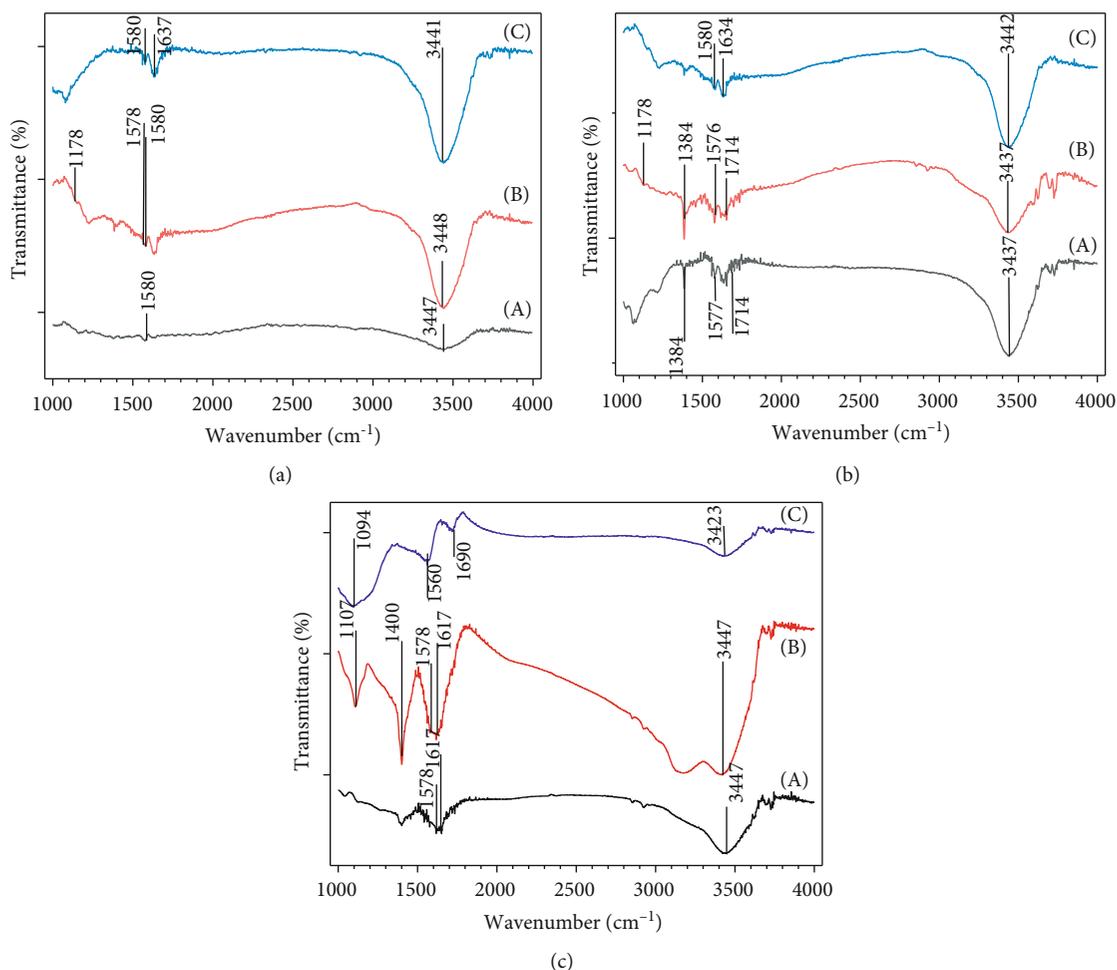


FIGURE 6: IR spectra of graphite materials in three stages: (a) NG; (b) EG; (c) GO. Stage (A): graphite materials before treatment, stage (B): ammonium bicarbonate-intercalated compound, and stage (C): exfoliated-intercalated compound.

sheets, after the high-temperature treatment, and the graphite was closely arranged after the high-temperature treatment with no obvious change of the interlayer spacing. The EG layer is wider than the NG layer, which provides favorable conditions for the intrusion of ammonium bicarbonate into the EG layer. It can be clearly observed that the EG layer spacing increases after the heat treatment and that these floccs appear between the graphite layers. It can be clearly observed that the distance between the graphite layers and the layer become large after the heat treatment, the edge portion is so transparent that the image is blurred, and the number of layers on the edge is small.

GO sheets are wrinkled and coarse, which indicates that the oxidation degree is very high. After adding ammonium bicarbonate, the addition of ammonium bicarbonate does not generate any flocculent products but caused severe shrinkage and agglomeration. The degree of shrinkage decreases after high-temperature exfoliation.

Table 3 shows the specific surface area changes of the three graphite materials. There is no significant increase in the NG-specific surface area. However, EG and GO showed an obvious increase in the specific surface area, which proved

that ammonium bicarbonate intercalation of them could produce a certain exfoliation effect after heating treatment at 800~900°C.

5. Conclusion

- (1) The oxidation degree of NG, EG, and GO, from high to low, is GO, EG, and NG. The higher the oxidation degree, the greater the layer spacing. The larger the layer spacing, the more obvious the ammonia carbonate intercalation layer. IR data show that the mechanism of ammonium bicarbonate intercalated into graphite materials is that ammonia molecules in ammonium bicarbonate solution have wedge-shaped structure and active points, which can provide vacant orbitals for electrons in the graphite layer and form edge intercalation through a physical approach. Generally speaking, within a certain range, the degree of oxidation of graphite materials increases, the location of defects increases, and ammonia can easily combine with graphite materials

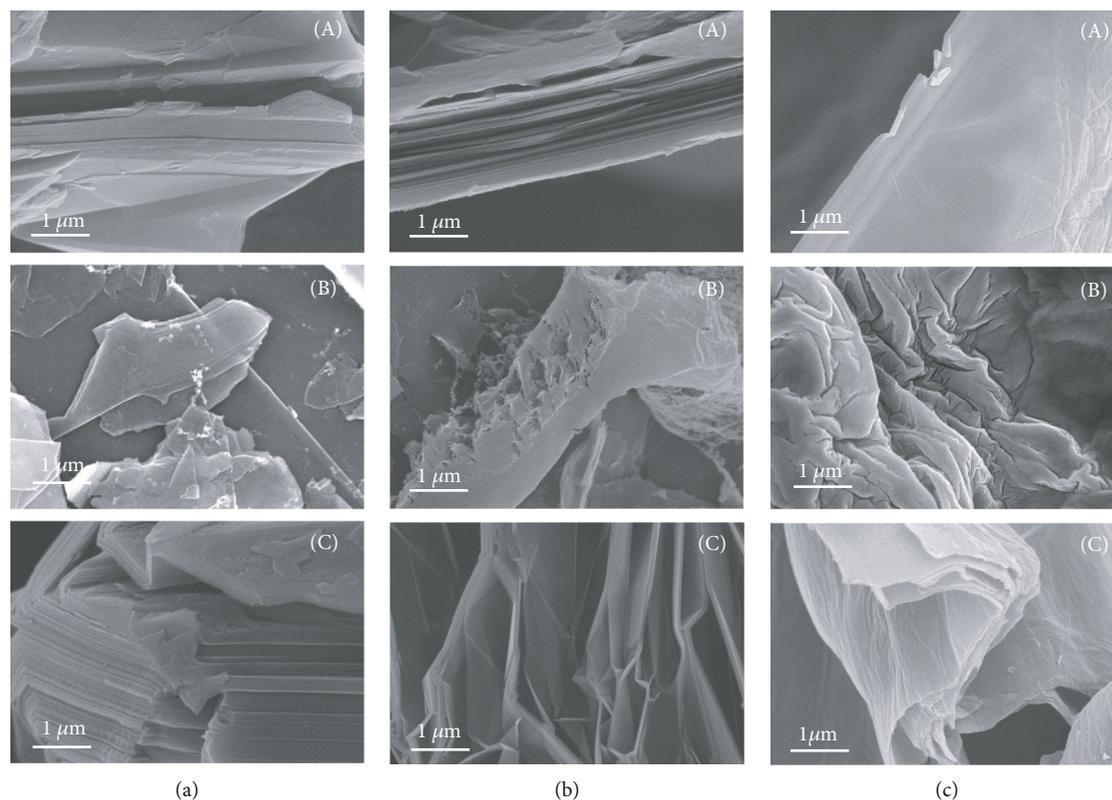


FIGURE 7: Typical SEM images of graphite materials in three stages: (a) NG; (b) EG; (c) GO. Stage (A): graphite materials before treatment, stage (B): ammonium bicarbonate-intercalated compound, and stage (C): exfoliated-intercalated compound.

TABLE 3: Specific surface area of the three graphite materials.

	Original (m^2/g)	After exfoliation (m^2/g)
NG	2.5822	2.6392
EG	3.272	4.8211
GO	125.0601	127.0308

- (2) GICs were heated at 800°C to 900°C for 20 seconds. The results showed that there is no exfoliating phenomenon in NG and the exfoliation of GO was best, but the crystallinity would be poor after high-temperature treatment. EG's exfoliating effect is good, but the graphitized structure can be maintained after high-temperature treatment, and the expansion effect is obvious

Data Availability

All data generated or analyzed during this study are included in this article.

Conflicts of Interest

The authors declare that there is no conflict of interest.

Acknowledgments

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