

Synthesis and characterization of poly acrylic acid/ graphite oxide nanocomposite^①

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Abstract: Acrylic acid-intercalated graphite oxide and poly acrylic acid (PAA)-intercalated graphite oxide were prepared and characterized by X-Ray diffraction (XRD), Fourier transform infrared spectra (FTIR) and high resolution electronic microscope (HREM). Results show that the intercalation process is not only a physical diffusion process but also mainly a chemical reaction process. The high resolution electronic microscope results also reveal that the I_c value of PAA-intercalated graphite oxide (GO) could change widely from 1.6 nm to 4.0 nm.

Key words: composites; intercalation reaction; X-ray diffraction

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1 INTRODUCTION

Organic-intercalated layered solids have been studied by scientists in different fields for many years because of their new physical and chemical properties such as electrical properties^[1], mechanical properties, thermal behavior^[2], surface and interfacial properties^[3]. Graphite oxide (GO) has been studied for many years, its structural model^[4-6], formation process and kinetics^[7, 8] have been studied in detail. It has been reported that GO possesses C-OH and epoxide functional groups^[9] which make graphite oxide easily absorb polar molecules and polar polymers to form graphite oxide intercalated or exfoliated nanocomposites^[10]. The study of GO/organic nanocomposite materials has been reported for many years. The organic materials which are intercalated into the GO include cationic surfactants^[11], alcohols^[12], polyanilines^[13], poly vinyl acetate^[14], poly ethylene oxide^[15], poly furfuryl alcohol^[16], poly acrylamide^[17], poly vinyl alcohol^[18] and poly diallyldimethylammonium chloride^[11].

In this paper, acrylic acid is chosen to synthesize nanocomposites. Acrylic acid possesses polar functional groups which enable it to intercalate into graphite oxide easily and then form poly acrylic acid by in-situ polymerization. And the preparation and structural characterization are reported.

2 EXPERIMENTAL

2.1 Preparation

GO was synthesized from natural graphite powder (less than 147 μm) using Hummers method^[19] with some modification. 10 g graphite powder was put into a 500 mL flask containing 33 ml 68% nitric acid, 200 ml 98% H_2SO_4 and stirred for 30 min in an ice-bath, then 60 g KMnO_4 was added to the solution. After 30 min, the solution temperature was raised gradually to 40 °C and maintained for 30 min, and then the products were reduced using H_2O_2 and washed several times using boiled distilled water.

When graphite powder was oxidized, washed and filtered, it became a kind of exfoliated dark thick colloid. This colloid was used to synthesize acrylic acid (AA)-intercalated GO and poly acrylic acid (PAA)-intercalated GO. AA-intercalated GO has been prepared by dispersing the AA monomer in an exfoliated GO colloid like an exfoliation/absorption process. To prepare a PAA intercalated GO, the GO colloid was dispersed in an acrylic acid (AA) monomer solution containing 0.5% (mass ratio) ammonium persulfate as an initiator, followed by in-situ polymerization at 100 °C for 2 h. The as-prepared colloid was washed and dried in a vacuum drying oven at 60 °C for 24 h, and then the PAA-intercalated GO product was obtained. The GO contents in AA/GO and in PAA/GO composites are 10% (mass fraction).

2.2 Measurements

X-Ray diffraction (XRD) experiments were performed using a Rigaku D/max-rA X-Ray diffractometer

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(30 kV, 10 mA) with Cu ($\lambda = 1.54178 \text{ \AA}$) irradiation at a scanning rate of $0.02^\circ/\text{s}$ in the 2θ ranges of $2^\circ \sim 30^\circ$. Fourier transform infrared spectra were taken using a Magna-IR 750 instrument. HREM images were obtained using a JEOL 2010 instrument with an acceleration voltage of 200 kV.

3 RESULTS AND DISCUSSION

3.1 Characterization of AA-intercalated GO and PAA-intercalated GO

Fig. 1 shows the XRD patterns of pristine GO (Fig. 1 (a)), wet thick GO colloid (Fig. 1 (b)), PAA-intercalation GO (Fig. 1 (c)), together with that of PAA (Fig. 1 (d)). Fig. 1 (a) demonstrates that the c -axis repeat distance (I_c) of pristine GO is about 0.776 nm, and Fig. 1 (b) shows that the wet thick pristine GO has been exfoliated. Clearly, when AA was polymerized in the lamellae of GO, the I_c greatly increased to 1.64 nm, and is larger than that of AA-intercalated GO, which is 1.38 nm, as shown in Fig. 2. Fig. 3 shows FTIR spectra of pristine graphite oxide (Fig. 3 (a)), PAA (Fig. 3 (b)), AA-intercalated GO (Fig. 3 (c)) and PAA-intercalated GO (Fig. 3 (d)). In Fig. 3 (a), absorption bands for the C—OH group appear at around 3404 cm^{-1} and 1109 cm^{-1} , in Fig. 3 (b) there appears carboxylic groups, while in Figs. 3 (c) and (d), carboxylic groups almost disappear, but ester groups are observed at around 1721 cm^{-1} , 1263 cm^{-1} , 1186 cm^{-1} , 1728 cm^{-1} , 1261 cm^{-1} and 1171 cm^{-1} respectively, which demonstrates that esterification has happened between the —OH of graphite oxide and —COOH of PAA.

Figs. 4 and 5 show high-resolution electron microscope (HREM) images of graphite oxide, AA-intercalated GO and PAA-intercalated GO samples, respectively. The measured I_c values of pristine GO and AA-intercalated GO are 0.8 nm (Fig. 4 (a)) and 1.4 nm (Fig. 4 (b)), respectively. Fig. 5 reveals that different I_c values of PAA-intercalated GO exist in the same sample (1.6 nm

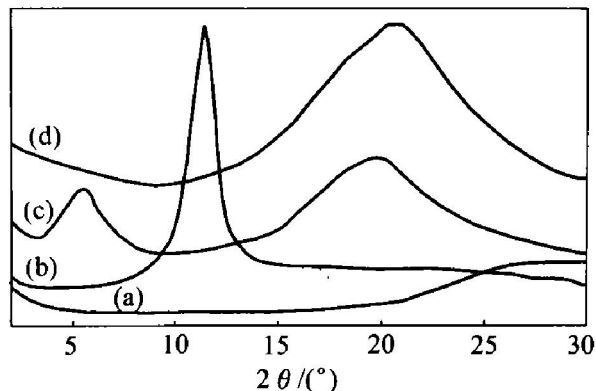


Fig. 1 XRD patterns of pristine GO (a), wet thick pristine GO colloid (b), PAA-intercalated GO (c) and PAA (d)

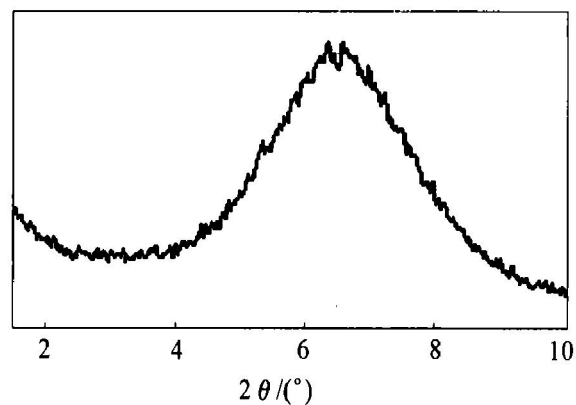


Fig. 2 XRD pattern of AA-intercalated GO

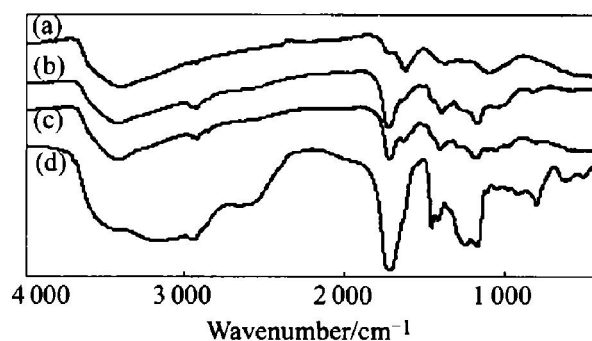


Fig. 3 FTIR spectra of pristine GO (a), PAA (b), AA-intercalated GO (c), and PAA-intercalated GO (d).

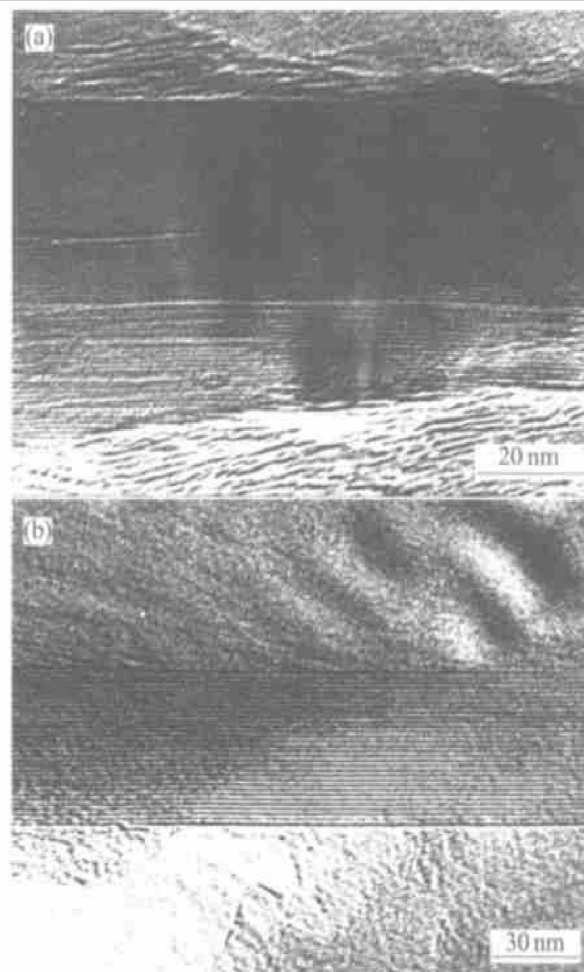


Fig. 4 High-resolution electron microscope images of pristine GO (a) and AA-intercalated GO (b).

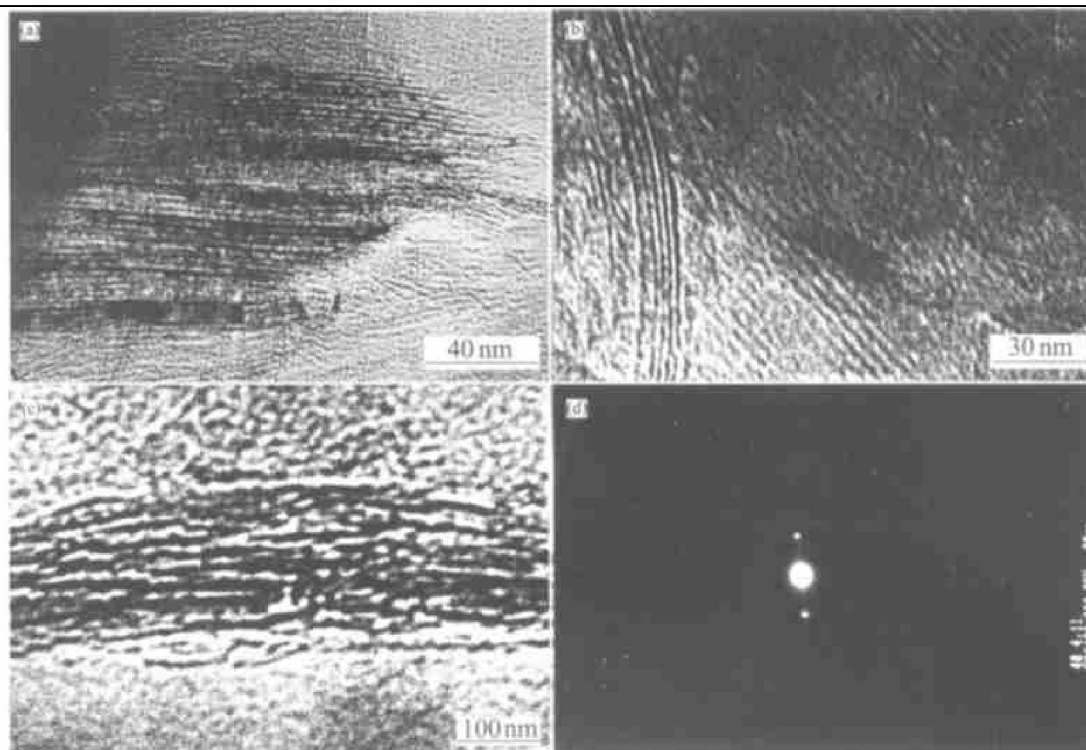


Fig. 5 HREM images ((a)–(c)) and electron diffraction pattern (d) of PAA-intercalated GO with different I_c values
(a) 1.6 nm; (b) 2.5–3.5 nm; (c) 4.0 nm

for Fig. 5(a), 2.5–3.5 nm for Fig. 5 (b), and 4.0 nm for Fig. 5 (c)). Fig. 5 suggests that I_c value of GO in PAA-intercalated GO ranges from 1.6 nm to 4.0 nm, and the bending phenomena of the GO layer in Fig. 5 (b) demonstrate that the GO layers have flexibility. From the diffraction patterns in Fig. 5, it can be seen that the crystal lattice shows deviant and has been extended to form a line. This also suggests that there exist many periods of PAA-intercalated GO and that the periods are usually very large. Usually, XRD and HREM results are consistent with each other. But sometimes, the results from these technologies are not uniform, so that the structural characterization will be more accurate if both XRD and HREM are used. XRD detects only the statistical structure and, when the contents of the reaction products are less than 1% of the total sample, the measurement results obtained by XRD are almost incorrect. Furthermore, it is difficult for XRD to detect small angle diffraction, since even a little unevenness of the sample surface can cause false results. But high-resolution electron microscopy (HREM) can remedy all these shortcomings of XRD. Specifically HREM can detect some phenomena which are hard to observe by XRD, and HREM can detect a small quantity of products, and can detect the large d -spacing phenomena of organic-intercalated GO.

3.2 Orientations of AA and PAA in intercalated GO layer

Figs. 2 and 4 show that I_c values of GO and AA-intercalated GO are about 0.8 nm and 1.4 nm respectively. Since the molecular chain length of AA is under 0.623 7 nm (for C—H, C=C, C—C, and C—O, and O—H bond lengths are 0.107 nm, 0.133 7 nm, 0.149 nm, 0.136 nm and 0.098 nm respectively^[20]), the GO gallery may hold two layers of AA.

Fig. 6 shows the orientation of the AA molecules intercalated in graphite oxide. As shown in Fig. 5, the I_c values of PAA-intercalated GO can be in the range from 1.6 nm to 4.0 nm, and this wide range suggests that PAA can take on various kinds of conformations in the layer of GO, and one GO layer may hold more than one PAA layer.

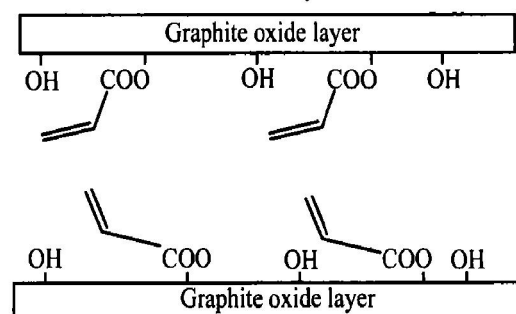


Fig. 6 Orientation of AA molecules intercalated in GO

4 CONCLUSION

AA-intercalated GO and PAA-intercalated GO have been prepared and characterized by XRD, FTIR

and HREM. The results show that chemical reaction between GO and AA (or PAA) has happened during intercalation process. I_c values of PAA-intercalated GO varied widely over the range of 1.6 - 4.0 nm. The change of I_c values over a wide range suggests that the PAA can take on various kinds of conformations in the layer of GO, and that one GO gallery may hold more than one PAA layer.

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