Poly(amidoamine) modified graphene oxide as an efficient adsorbent for heavy metal ions

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Poly(amidoamine) modified graphene oxide was prepared *via* a grafting-from method and characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and atomic force microscopy (AFM). Evaluation of its adsorption capacity for heavy metal ions demonstrated that the poly(amidoamine) modified graphene oxide had superior adsorption ability towards heavy metal ions such as Cu^{2+}, Zn^{2+}, Fe^{3+}, Pb^{2+} and Cr^{3+}.

1 Introduction

Heavy metal ions such as Pb^{2+}, Zn^{2+} and Cu^{2+} in wastewater or process water have caused serious environmental problems and received wide attention. Even trace amounts of these heavy metal ions in water can produce toxicity. In addition, stricter laws and regulations mean that more people are engaged in finding an efficient way to remove or recover heavy metal ions.[1–5] Therefore recycling, detection and removal of heavy metal ions from a wide variety of sources have both environmental and economical significance, especially for some precious and toxic metal ions. Currently, a variety of technologies for separating heavy metal ions, such as ion-exchange, precipitation, evaporation, electrochemical removal and membrane separation have been developed to recover the heavy metal ions.[6] However, there are some limits in the application of these methods, such as poor selectivity, relatively low loading capacity, production of solid residues and outflows of toxic compounds. Despite some failures, adsorption has been proven to be efficient and economical when compared with other methods,[5,7] and its efficacy and utility are related to the affinity between adsorbents and target contaminants.

Recently, graphene oxide (GO) has shown strong adsorption abilities arising from its large surface area and abundant oxidized functional groups.[8–13] It has been proven to be a good adsorbent for heavy metal ions such as Cu^{2+}, Pb^{2+} and Cr^{3+}.[14] Therefore, increased attention has been paid to the functionalization of graphene or graphene oxide.[15–18] In this study, we synthesized poly(amidoamine) modified graphene oxide (GO-PAMAM 2.0) and demonstrated its superior performance in heavy metal ion adsorption.

2 Experimental

2.1 Preparation of GO-PAMAM 2.0

The graphite power was purchased from Heowns Company. Ethylenediamine (EDA) and methyl acrylate were purchased from Aladdin-reagent and used as received. Water used in the experiment was ultrapure water.

GO synthesis from graphite powder was carried out based on the modified Hummers method.[19–21] After dialysis and centrifugation, a GO aqueous solution with a concentration of 2 mg mL^{-1} was prepared.

Synthesis of GO-PAMAM 2.0 included the following steps: (a) reaction between carboxyl groups of GO with EDA to produce GO-PAMAM 0.0; (b) Michael addition of a suitable amine with methyl acrylate (to produce GO-PAMAM 0.5); (c) amidation of the resulting esters with large excesses of EDA (to produce GO-PAMAM 1.0); (d) repeat steps b and c to produce GO-PAMAM 2.0.

Specifically, 200 mL GO aqueous solution (2 mg mL^{-1}) was added to a 500 mL flask. Under vigorous magnetic stirring in an ice bath, oxygen was removed by ventilating nitrogen as a protective gas. After 30 minutes, excess EDA and buffer solution (a mixture of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC), 2-morpholinoethanesulfonic acid (MES) and N-hydroxysuccinimide (NHS)) was added to the system and incubated at 30 °C for 4 hours to obtain GO-PAMAM 0.0. Before the Michael addition, the product was washed with methanol and kept at the same concentration. After oxygen removal, the mixture of GO-PAMAM 0.0 and excess methyl acrylate was stirred at 30 °C for 24 hours to produce GO-PAMAM 0.5. Repetition of the steps above resulted in GO-PAMAM 2.0, and the methanol solvent was replaced by water after dialysis.

2.2 Characterization

The samples were characterized by Fourier transform infrared spectroscopy (FT-IR) (Thermo-Nicolet 380), X-ray photoelectron spectroscopy (XPS) (Perkin-Elmer, PHI 1600 spectrometer),

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scanning electron microscopy (SEM) (Hitachi S-4800) and atomic force microscopy (AFM) (CSPM 5000).

2.3 Adsorption experiments

GO-PAMAM 2.0, GO and active carbon (AC) were evaluated for their adsorption capacities in heavy metal ion removal. Cu^{2+}, Zn^{2+}, Fe^{3+}, Pb^{2+} and Cr^{3+} were chosen as the test ions. The adsorption experiments were simultaneously carried out in 30 mL glass bottles. 1 mL homogenous dispersions of AC (1 mg mL^{-1}), GO-PAMAM 2.0 (1 mg mL^{-1}) or GO (1 mg mL^{-1}) were added to the 15 mL heavy metal ion solutions (10^{-4} mol L^{-1}). Solutions were kept at room temperature for 24 hours and mixed by a vertical mixer at a speed of 20 r min^{-1}. After complete adsorption, the supernatant was collected by centrifugation and filtering. Concentrations of the heavy metal ions in the supernatant were determined by Inductively Coupled Plasma (ICP, Varian Company, USA, VisTA-MPX). To evaluate the potential applications of GO-PAMAM 2.0 in complex wastewater treatment, adsorption experiments with 27.5 mL mixed heavy metal ions (Fe^{3+}, Cr^{3+}, Zn^{2+}, Pb^{2+} and Cu^{2+} with equal concentrations of 2×10^{-5} mol L^{-1}) were also carried out.

2.4 Adsorption capacity (Qt) measurements

The adsorption capacity (Qt) of adsorbent was obtained according the following equation:

$$Qt = (C_0 - C_t)V/W$$

where Qt (mol g^{-1}) represents the adsorption capacity of GO-PAMAM 2.0, GO and CA towards heavy metal ions, C_0 (mol L^{-1}) is the initial concentration of metal ions, C_t (mol L^{-1}) is the concentration at a given time, V (mL) denotes the volume of solution and W (g) is the weight of the adsorbents.

3 Results and discussions

The GO-PAMAM 2.0 was prepared by a grafting-from strategy as illustrated in Scheme 1. In brief, the PAMAM was first introduced to GO by the reaction between carboxyl groups of GO and EDA, followed by consecutive Michael addition and ester amidation reactions. Fig. 1a and b show the FT-IR spectra of GO (a) and GO-PAMAM 2.0 (b), respectively. In the spectrum of GO, the absorption band at 1727.9 cm^{-1} is attributed to the C=O stretching modes of carboxyl groups on the GO surfaces.[22] The same characteristic band disappears in the spectrum of GO-PAMAM 2.0 because the carboxyl group on GO is consumed by amidation in the first step. The strong band at 1631.5 cm^{-1} could be assigned to the C=O stretching of amide groups. The new band at 1560.2 cm^{-1}, a characteristic of N–H bending vibration, provides additional evidence for the successful grafting of PAMAM.

The successful grafting of PAMAM to GO was supported by further characterization. XPS was used to determine the amount and valence states of the elements C and N. The results of full range XPS spectra in Fig. 2b show evidence for the existence of N in GO-PAMAM 2.0. According to the atom percentage of N (6.58%), the amount of amines can be calculated as about

Scheme 1 Illustration of the preparation of GO-PAMAM 2.0.

5.05 mmol g^{-1}. Compared with GO, the C1s XPS spectrum of GO-PAMAM 2.0 (Fig. 2c) shows an additional component at 285.8 eV, which can be attributed to the C–N bonds from the grafted PAMAM 2.0. The corresponding N1s XPS spectrum of GO-PAMAM 2.0 (Fig. 2d) shows peaks at 399.2, 400.2 and 401.2 eV, which can be attributed to the –NH_2, C–N and O=C–N bonds of the grafted PAMAM, respectively.

A SEM image (Fig. 3) of the obtained GO-PAMAM 2.0 shows clear two dimensional structures with similar crumpling features like GO. This feature should have potential advantages in heavy metal ion adsorption, as the ions can easily access and complex with the amine groups on both sides of the two dimensional sheets. The density and distribution of the grafted PAMAM on GO are evaluated by quantitative energy dispersive X-ray spectroscopy (EDS) mapping (Fig. 3b–d). As can be seen in Fig. 3d, rather than only loading at the edges of graphene sheets, N is found to be homogeneously distributed over the whole surface, suggesting the successful grafting of PAMAM dendrimers to the carboxyl groups at the edges and defects of the GO basal-plane.

The grafting of PAMAM dendrimers to GO was further confirmed by AFM studies. In contrast to GO, which has a smooth surface with regular edges (Fig. 4a), GO-PAMAM 2.0 possesses irregular edges (Fig. 4b) with an apparent thickness of about 2 nm. This value is much larger than that of GO (mean value is 1.0 nm) (Fig. 4a), supporting the successful grafting of PAMAM dendrimers to GO. In addition, considering the theoretical size of PAMAM 2.0 is about 0.5 nm, the increased thickness here supports the successful attachment of PAMAM
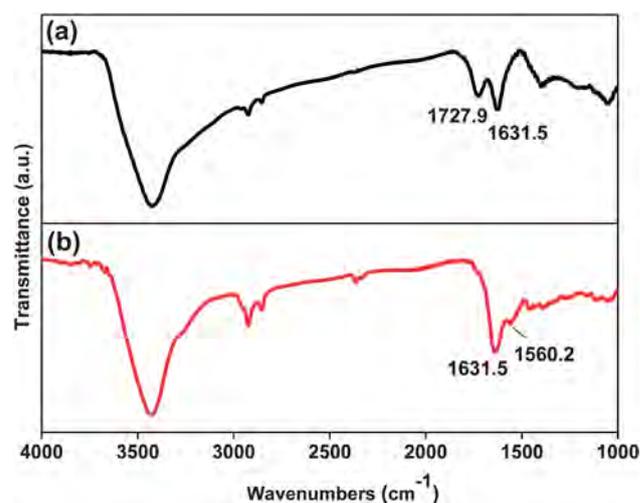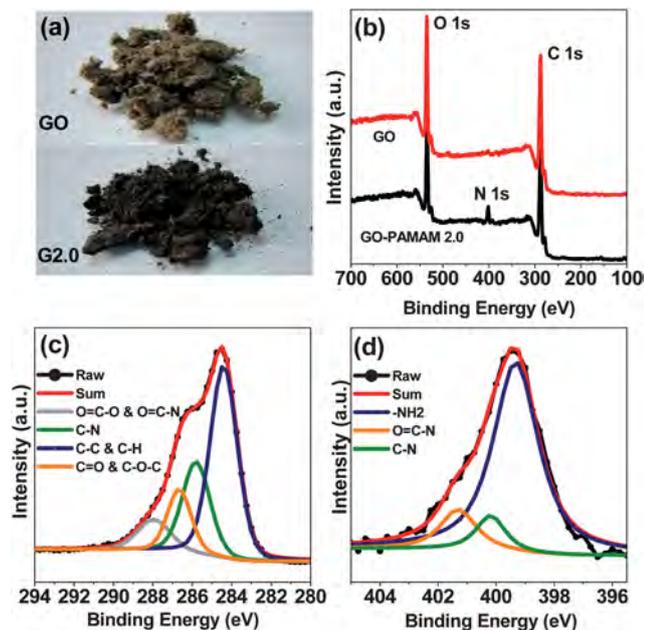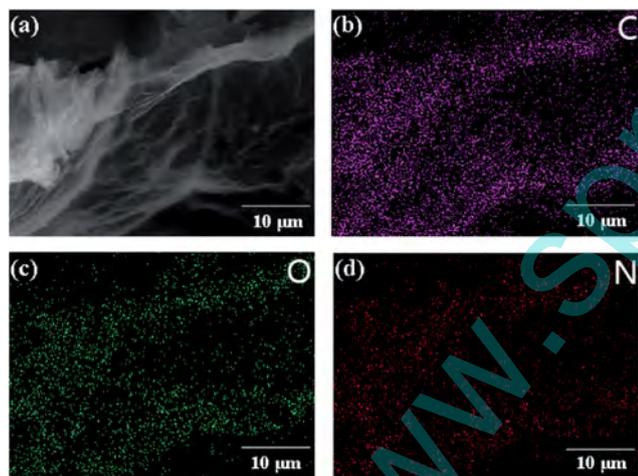

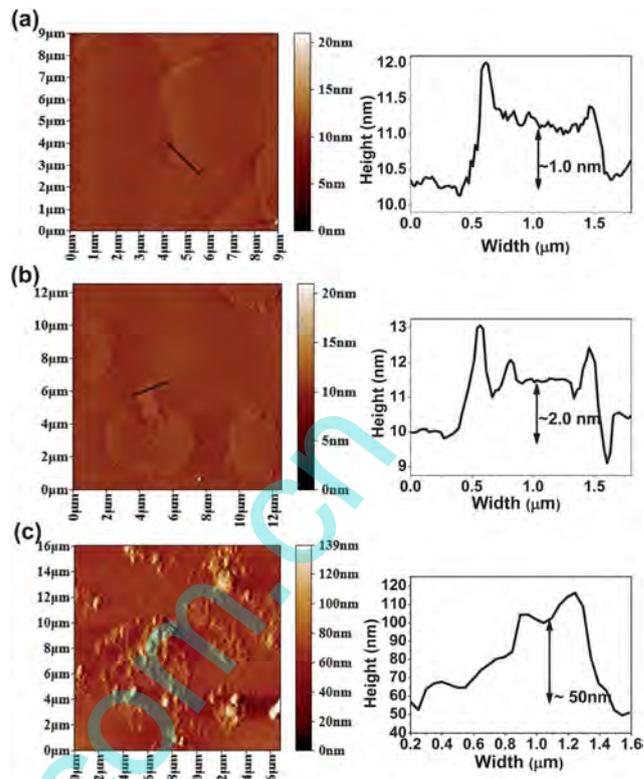**Fig. 1** FT-IR spectra of GO (a) and GO-PAMAM 2.0 (b).

Fig. 2 (a) Photos of dried GO and GO-PAMAM 2.0, (b) full range XPS spectra of GO-PAMAM 2.0 and GO, (c) C1s XPS spectrum of GO-PAMAM 2.0, and (d) N1s XPS spectrum of GO-PAMAM 2.0.
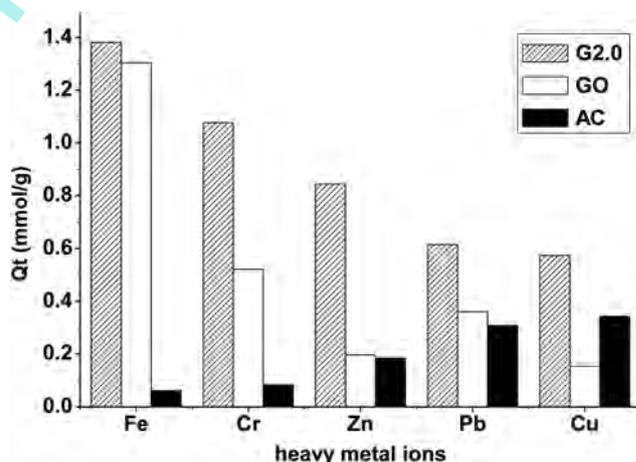

Fig. 3 SEM image of GO-PAMAM 2.0 (a) and the corresponding quantitative EDS element mapping of (b) C, (c) O, and (d) N.

Fig. 4 Typical AFM images and corresponding cross-section analysis of (a) GO, (b) GO-PAMAM 2.0 and (c) GO-PAMAM–Cu^{2+}.

Fig. 5 The adsorption capacity (Qt) of GO-PAMAM 2.0 (G 2.0), GO and AC for different heavy metal ions.

2.0 to both sides of the GO. After the adsorption experiments, however, macroscopic aggregation and obvious folding of the GO-PAMAM 2.0 sheets can be readily observed (Fig. 4c). This result is in line with the previous study on GO[23] and should be caused by the adsorbed metal ions (Cu^{2+}).

To demonstrate the potential application of the obtained GO-PAMAM 2.0 as an adsorbent for heavy metal ions, Fe^{3+}, Cr^{3+}, Zn^{2+}, Pb^{2+} and Cu^{2+} were chosen to evaluate their affinity to the GO-PAMAM 2.0, with GO and commercial active carbon (AC) as controls. As shown in Fig. 5, the adsorption capacity (Qt) value of AC increased with the order of $Fe^{3+} < Cr^{3+} < Zn^{2+} < Pb^{2+} < Cu^{2+}$. This order is in line with previous studies[24–26] and can be

explained by the microporous diffusion mechanism of AC. That is, the adsorption capacity is determined by various factors such as the pore size of AC, the size of the species to be adsorbed, the electronegativity and electronic configuration of adsorbates and Jahn–Teller effect (especially for Cu^{2+}). Surprisingly, GO-PAMAM 2.0 and GO show an almost converse trend in their adsorption capacity towards these ions in comparison with AC. This phenomenon has never been reported and should be attributed to the unique two-dimensional structure of

Table 1 Adsorption experiment with mixed heavy metal ions

	Fe^{3+}	Cr^{3+}	Zn^{2+}	Pb^{2+}	Cu^{2+}
C_0 (mmol L^{-1})	0.0193	0.0193	0.0193	0.0193	0.0193
C_t (mmol L^{-1})	0.000661	0.0165	0.0122	0.0175	0.0145
W (mg)	1	1	1	1	1
V (L)	0.0285	0.0285	0.0285	0.0285	0.0285
Qt (mmol g^{-1})	0.5312	0.0798	0.2024	0.0513	0.1368
Total (mmol g^{-1})			1.0007		

GO-PAMAM 2.0 or GO. Note that both the adsorption capacities of GO-PAMAM 2.0 and GO are obviously superior to that of AC, especially for Fe^{3+} and Cr^{3+} which are hardly adsorbed by AC. Noticeably, GO-PAMAM 2.0 has an obvious adsorption advantage over GO. For Zn^{2+}, Cu^{2+} and Pb^{2+}, the Qts of GO-PAMAM 2.0 are much larger than those of GO because of the additional complexation between amine groups and the metal ions. On the other hand, GO shows comparable adsorption ability with GO-PAMAM 2.0 for trivalent ions (Fe^{3+} in particular). This result may be explained by the fact that trivalent ions such as Fe^{3+} have a stronger electrostatic force with GO than bivalent ions, as well as the possible additional adsorption of Fe^{3+} and Cr^{3+} to the centers of hexagonal carbon rings. Therefore, the effect of additional complexation becomes less prominent.

To further evaluate the potential application of the GO-PAMAM 2.0 in complex wastewater treatment, we conducted adsorption experiments with mixed heavy metal ions to simulate real wastewater treatment. As shown in Table 1, the total adsorption capacity of these heavy metal ions can reach 1.0007 mmol g^{-1}. Interestingly, Cr^{3+} and Pb^{2+} in the mixed solution show a significant decrease in adsorption to GO-PAMAM 2.0, due to their direct competition with Fe^{3+}, Zn^{2+} and Cu^{2+}.

4 Conclusions

In summary, we successfully prepared PAMAM modified-graphene oxide (GO-PAMAM 2.0) *via* a grafting-from method and evaluated its potential applications in heavy metal ion adsorption. Comparative studies revealed that the obtained GO-PAMAM 2.0 and GO had an almost converse adsorption capacity to AC, due to their unique two-dimensional structure. Notably, GO-PAMAM 2.0 has obvious advantages over GO in heavy metal ion adsorption, especially for Zn^{2+}, Pb^{2+} and Cu^{2+}, because of the additional complexation between the amines and heavy metal ions. GO-PAMAM 2.0 should have promising applications in the recycling, detection and removal of heavy metal ions from a wide variety of sources.

Acknowledgements

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