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Experimental and theoretical studies of ZnO and MgO for the rapid coagulation of graphene oxide from aqueous solutions

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ABSTRACT

The biological toxicity and negative environmental effect of graphene oxide (GO) have attracted wide public concern due to its potential risks. To assess the transport behavior and to reduce the environmental hazardous of GO in natural environment, ZnO and MgO were used as coagulant for GO removal from aqueous solutions. The results indicated that GO coagulation on ZnO and MgO were scarcely affected by ionic strength. At neutral pH, the GO removal capacities could reach 232.8 mg/g on MgO and 210.8 mg/g on ZnO. The high removal capacity and short coagulation time showed the enormous advantages for the high-efficiency removal of GO from aqueous solutions, which were important for the real application of MgO and ZnO in reality. The coagulation mechanisms of GO on ZnO and MgO could be attributed to electrostatic attraction and hydrogen bond, which were further demonstrated by DFT calculations. Considering the cost, efficiency, removal capacity and reusability, one can conclude that metal oxides can be promising materials for GO efficient removal by a simple and rapid coagulation process. The findings can provide critical information about the physicochemical behavior of GO in aquatic natural environment, which is significant to decrease the environmental toxicity of GO.

1. Introduction

Graphene oxide (GO), one of the most important derivatives of graphene, has attracted increasing concern due to its specific structures as well as excellent physiochemical properties over the past decade [1–3]. GO is a graphene sheet with hydroxyl as well as epoxide groups on its basal plane and carboxyl groups at its edges [4,5]. Because of its high surface area and oxygen-containing functional groups on the surface, GO shows tremendous potential in various fields such as biomedicine, chemistry, energy, catalysis, and environmental pollution control [6–10]. For instance, GO has demonstrated to be used as carrier for targeted drug delivery to treat cancer and other severely diseases [11]. Zhao et al. [12] reported that Cd(II) and Co(II) ions could be efficiently removed from large volumes of aqueous solutions by few-layered GO nanosheets.

With the broad application of GO products, it is inevitable that GO is released into ecosystem and may cause serious environmental pollution as a contaminant during production, transport and disposal processes [13,14]. More importantly, GO has been proved to be the most toxic graphene-based material [15,16]. Correspondingly, the biological toxicity and negative environmental effect of GO have achieved a lot of attention. In the past few years, many studies have demonstrated the toxicity of GO to bacteria, animals and humans [17–20]. For example, GO particles had been proved to reduce the viability of *Escherichia coli* and *Staphylococcus aureus* due to their sharper edges [21]. Specifically, GO could predominantly deposit in the lung, which led to significant pathological changes including inflammation cell infiltration, pulmonary edema and granuloma formation [22]. Therefore, it is necessary to research the transport of GO in natural environment to reduce its toxicity.

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In recent years, some studies have reported the removal of GO from aqueous phase. Ren et al. [23] reported the aggregation and deposition of GO on Al_2O_3 as a function of solution pH and the electrolyte concentrations. Similarly, the coagulation of GO on Mg/Al layered double hydroxide (Mg/Al-LDH) was strongly dependent on pH as well as ionic strength [24]. Comparing to the Mg/Al-LDH, the Ca/Al-LDH was more effective for GO removal from aqueous solutions [25]. Moreover, it was found that GO could be removed on quartz sand and goethite [26,27]. However, taking into consideration of the cost, efficiency and removal capacity, the efficient removal of GO on the existing material is unsatisfactory and it is urgent to search for new materials for the elimination of GO from natural environment. In the meantime, metal oxides have been studied widely for environmental pollution cleanup because of their various structures, nontoxicity and low cost [28,29]. Especially, many scholars found that ZnO and MgO had many advantages in water treatment, such as higher surface area, abundant active sites and modified by other materials. For instance, modified ZnO nanoparticles with new modifiers have been used for the removal of heavy metals such as Cu^{2+}, Cd^{2+} and Ni^{2+} [30]. These reports revealed that ZnO/MgO may be potential materials for GO removal from solution to solid particles. Nevertheless, systematic studies on the interaction mechanism between ZnO/MgO and GO in different conditions have not been reported yet.

In this work, ZnO and MgO were synthesized as the representative of metal oxides to remove GO from aqueous solutions. The main objectives were (1) to synthesize ZnO and MgO by a facile hydrothermal method and to apply for GO removal from aqueous solutions; (2) to investigate the influences of pH, ionic strength, coagulation agent concentration and coagulation time on GO coagulation onto solid particles; (3) to characterize the macroscopic and microscopic surface properties of oxides before and after GO coagulation by using transmission electron microscopy (TEM), Fourier transformed infrared spectroscopy (FT-IR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and energy-dispersive X-ray spectroscopy (EDS); (4) to research the coagulation mechanism of GO on ZnO and MgO by density functional theory (DFT) calculations at molecular level. The results would help to provide new insight into the migration and transport fate of GO in natural aqueous environment.

2. Experiments

2.1. Chemicals and materials

The chemical reagents in this study were all analytical grade, and used without any further purification. The modified Hummers' method was applied to GO preparation [12]. The detailed process and characterization of as-prepared GO were described in our previous study [25]. The GO stock suspension (350 mg/L) was used in the whole experiments.

In the typical preparation process, $Zn(NO_3)_2{\cdot}6H_2O$ (1.5 mmol), urea (7.5 mmol) and tartaric acid (0.3 mmol) were added into 30 mL Milli-Q water, then stirred for 20 min, and put at 150 °C for 6 h. After separation, the sediments were washed with Milli-Q water and ethanol. The obtained samples were dried at 70 °C for 36 h. Moreover, the samples were calcined at 400 °C for 2 h, and then cooled to room temperature. Similarly, MgO was synthesized by the same method.

2.2. Characterization

The morphologies of materials before and after GO coagulation were characterized by TEM (JEM-1011). The EDS and SEM-EDS elemental mapping were conducted by Hitachi S-4300 to check the element changes in the samples. The XRD patterns were recorded using a Rigaku D/max 2500 diffractometer ($\lambda = 1.541$ Å) to analyze the crystalline structures. The surface functional groups were detected by FT-IR (Tensor 27). Specific surface areas were determined by Quantachrome Instruments (autosorb-iQ). The XPS spectra were measured using the ESCALab220i-XL electron spectrometer.

2.3. Coagulation experiments

The experiments in this paper were performed with $C[GO]_{initial} = 25$ mg/L (except for the GO initial concentration experiment), and the system pH was adjusted by 0.1 or 0.01 M HCl and NaOH. The effects of pH, ionic strength, coagulation agent concentration, GO initial concentration and contact time on GO coagulation were investigated. The detailed description was shown in Supporting Information (SI). All the experiments were implemented in duplicate and the coagulation performances were evaluated by the average data.

The concentration of GO was detected using UV–vis spectrophotometer (UV-2600, Shimadzu) at 227 nm (Fig. S1). The GO removal percentage could be calculated from the following formula:

$$Removal\ percentage = \frac{C_0 - C_e}{C_0} \times 100\% \tag{1}$$

where C_e (mg/L) and C_0 (mg/L) are the equilibrium and initial concentrations of GO.

3. Results and discussion

3.1. Characterization of materials

The XRD technique is very useful to identify the crystal structure of material. The XRD patterns of ZnO and MgO (Fig. S2a) show the typical diffraction peaks of ZnO at 31.8° (100), 34.4° (002), 36.3° (101), 47.5° (102), 56.6° (110), 62.9° (103) and 67.9° (112) (JCPDS 05-0664), and those of MgO at 36.9° (111), 42.9° (200) and 62.3° (220) (JCPDS 43-1022). In addition, the surface functional groups of ZnO and MgO are detected by FT-IR spectra (Fig. S2b). In the XRD pattern of ZnO, the bands at 3430 and 1630 cm^{-1} are ascribed to the stretching and bending vibrations of O—H group [30,31], and the absorption peaks at 1426, 1054 and 876 cm^{-1} are caused by the asymmetric stretching vibration of CO_3^{2-} [31]. In the FT-IR spectrum of MgO, the peaks at 3429 and 1635 cm^{-1} are ascribed to the O—H stretching and bending vibrations [32], and the asymmetric stretching vibration of CO_3^{2-} results in the peak at 1446 cm^{-1} [33].

The morphologies and microstructures of MgO and ZnO before and after GO coagulation are shown in Fig. S3. It can be seen that ZnO shows the characteristic of clubbed structure more clearly (Fig. S3a). Fig. S3b reveals that GO aggregation on the surface of ZnO, which can further prove the successful coagulation of GO onto ZnO. Compared with ZnO, it is easy to observe the blocky structure of MgO in Fig. S3c, and the aggregation and deposition of GO on the surface of MgO is clearly demonstrated in Fig. S3d.

3.2. Coagulation of GO

3.2.1. Effect of pH and ionic strength

The natural sedimentation of GO at different pH values are shown in Fig. S4. It is observed that no precipitation is formed after 24 h at different pH values, suggesting the good stability of GO in aqueous solutions. The influences of pH on the coagulation of GO on ZnO and MgO are shown in Fig. 1a and 1b. From Fig. 1a, one