Formation of Magnetic Graphene Nanosheets for Rapid Enrichment and Separation of Methyl Orange from Water

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(Received November 9, 2013; Revised July 2, 2014; Accepted September 9, 2014)

ABSTRACT

Magnetic-graphene nanosheets have been synthesized via a simple effective chemical precipitation method followed by heat treatment. The composite nanosheets are super paramagnetic at room temperature and can be separated by an external magnetic field. The prepared magnetic-graphene nanosheets were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, and BET surface area analysis. The results demonstrated the successful attachment of iron oxide nanoparticles to graphene nanosheets. It was found that the attached nanoparticles were mainly Fe$_3$O$_4$. The magnetic-graphene nanosheets showed near complete methyl orange removal within 10 mintues and would be practically usable for methyl orange separation from water.

Key words : Magnetic-graphene, Methyl orange, Enrichment and separation

1. Introduction

A prefect nanosheet containing sp$^2$-hybridized carbon atoms in a honeycomb lattice, graphene has been emerging as a fascinating material due to its unique physical, chemical, electrical, and mechanical properties. Therefore, graphene or graphene-based composite materials with the combination of its excellent properties and inexpensive sources have attracted a great deal of attention as promising candidates for a wide variety of potential applications in catalyst supports. It is now well-known that many types of metals can be deposited on graphene sheets in the form of nanoparticles to impart new functionality to this increasingly popular 2D nanomaterial. The combination of ferromagnetic elements, such as Ni, Co, and Fe, with graphene could create composites with the capability of shielding against electromagnetic interference, and Au (or Pd)-graphene composites could be used to make ultrasensitive chemical sensors to detect hydrogen. The dispersion of metal nanoparticles on graphene sheets potentially provides a new way to develop catalytic, magnetic, and optoelectronic materials.

It is believed that composites of magnetic nanoparticles and graphene/graphene oxide would achieve better functionality and performance in these applications. More recently, Cong et al. synthesized magnetic graphene by decorating Fe$_3$O$_4$ nanoparticles on hydrazine-reduced graphene oxide sheets through a high-temperature decomposition method and found that the reduced Fe$_3$O$_4$-graphene oxide hybrid could be used as a magnetic resonance contrast agent. Pham et al. reported the immobilization of magnetic nanoparticles on the surface of graphene oxide sheets and their application as templates for anchoring magnetic nanoparticles. Such Fe$_3$O$_4$-graphene oxide composites not only have great potential as an effective absorbent for removing cationic dyes from water, but also could be used to prepare Fe$_3$O$_4$-graphene composites and magnetic graphene oxide films.

The structure of Fe$_3$O$_4$-graphene is to the benefit of effective immobilization of enzymes, proteins, and other bioactive substances. In this work, we synthesized a composite of graphene sheets decorated with iron oxide nanoparticles by a simple method. Furthermore, we demonstrated that our magnetic-graphene composites had great potential as an effective absorbent for the removal of methyl orange (MO) from water due to its rapid adsorption rate, high absorption capacity, and convenient magnetic separation.

2. Experimental Procedure

2.1. Preparation of magnetic–graphene nanosheets

Graphite (KS-6) was selected as the starting material. Graphene oxide (GO) was prepared from graphite according to the modified Hummers-Offeman method. Magnetic-
graphene nanosheets were formed as follows: Twenty-five milligrams of the GO powder was placed in a cup, and 200 ml de-ionized water was then added. Ten minutes of magnetic stirring at 200 rpm yielded an inhomogeneous brown suspension. The resulting suspension was further treated with a bis(cyclopentadienyl) iron solution (0.86 g bis(cyclopentadienyl). The iron was dissolved in 200 mL alcohol under ultrasonication (30 min, 1.3×10^5 J), dried at 373 K, and then heated at 973 K under an oxygen-free condition for 1 h. After being cooled to room temperature, the sample magnetic–graphene nanosheets were produced.

### 2.2. Characterization of samples

XRD measurements were performed for the magnetic–graphene nanosheets at room temperature. XRD patterns were obtained with a diffractometer (Shimata XD-D1, Japan) using Cu Kα radiation. SEM was used to observe the surface state and structure of the samples using a scanning electron microscope (JOEL, JSM-5200, Japan). Raman spectra were analyzed to detect possible structural defects in the graphene sheets. The measurements were carried out by a Horiba Jobin Yvon LabRAM using a 100×objective lens with 532 nm laser excitation. Thin films (~ 30 nm) were prepared by placing a few drops of sample solution on the graphene nanosheet support. TEM specimens were prepared by placing a few drops of sample solution on a carbon grid. Nitrogen adsorption–desorption isotherms for surface area and pore analysis were measured with an SSA-4200 (Builder Instruments) volumetric adsorption analyzer. Before measurement, the samples were degassed under vacuum at 353 K for 5 h. The clean transparent solution was analyzed using a UV/Vis spectrophotometer. The UV–vis transmittance spectra of the concentration of the MO solution evolved from photocatalysis were recorded on a Shimadzu UV-3101PC spectrophotometer. The concentration of MO in the water was calculated by using the absorbance at 460 nm of the spectra.

### 2.3. Adsorption ability

To check the adsorption ability of the fabricated sheets, 5 mg magnetic–graphene nanosheets were added to 20 mL 0.1 g L^-1 methyl orange aqueous solution. After 30 s of magnetic separation by an external magnetic field under natural lighting, the clean transparent solution was analyzed by a UV/Vis spectrophotometer, and the absorbance at the characteristic wavelength of 460 nm was determined for each methyl orange solution.

### 3. Results and Discussion

XRD is a rapid analytical technique primarily used for the phase identification of a crystalline material, and it can provide information on unit cell dimensions. Fig. 1 shows the XRD patterns of GO, graphene, and magnetic-graphene. Since GO prepared from graphite by liquid-phase oxidation is an intercalation compound, it can be found that the d-spacing of GO layers (0.42 nm) is larger than that of graphene layers (0.34 nm). XRD analysis showed that the sample of magnetic-graphene consisted of a mixture of iron oxide and graphene oxide. The d-spacing values of new significant peaks matched well with data from the JCPDS card (19-0629) for Fe₃O₄ (the diffraction angles at 2θ = 30.2°, 35.6°, 43.3°, 57.3°, and 62.8° can be assigned to (220), (311), (400), (511), and (440) of crystal planes of Fe₃O₄). The results indicated the existence of Fe₃O₄ in the composite material.

The microstructure of the magnetic-graphene composite was characterized by TEM and SEM. In the case of graphene, because of oxidation and the heat treatment process, the graphene sheets break into pieces smaller than pristine graphite as shown in Fig. 2(a). TEM images taken from the graphene and magnetic-graphene composites (Fig. 2) show a layer-by-layer assembled structure consisting of graphene nanosheets and Fe₃O₄ particles. It reveals that Fe₃O₄ particles with diameters in the range of <50 nm are attached to the surface of graphene, especially along the edges of the stacked nanosheets with thicknesses of several nanometers. The TEM image (Fig. 3) reveals that these Fe₃O₄ particles are firmly attached to the graphene nanosheets, even after ultrasonication to disperse the graphene/Fe₃O₄ composite for TEM characterization. As shown in Fig. 3(b), the Fe₃O₄ particle is wrapped by graphene nanosheets, which helps to prevent Fe₃O₄ agglomeration and enables a good dispersion of these oxide particles over the graphene nanosheet support. The short-range disordered structure observed at the interfacial region of the graphene nanosheets and Fe₃O₄ suggests the formation of interfacial bonds for the stabilization of the oxide particles on the graphene nanosheet support.

![Fig. 1. XRD patterns of (a) GO, (b) graphene, and (c) magnetic-graphene.](image-url)
Raman spectroscopy is a powerful, nondestructive tool to characterize carbonaceous materials. Fig. 4 shows the Raman spectra of graphene, and magnetic-graphene. In the spectrum of graphene, the peak at 1592.95 cm\(^{-1}\) (G band) corresponds to an \(E_{2g}\) mode of graphite and is related to the vibration of sp\(^2\)-bonded carbon atoms in a 2D hexagonal lattice. The peak at 1350.91 cm\(^{-1}\) (D band, the breathing mode of \(\kappa\)-point phonons of A\(_{1g}\) symmetry) is associated with vibrations of carbon atoms with dangling bonds in the plane terminations of disordered graphite. Compared with graphene, the G mode of magnetic-graphene became weaker and broader, suggesting a higher level of disorder of the graphene layers, and defects increased during the functionalization process. Moreover, the ratio of the intensities \((I_D/I_G)\) for the magnetic-graphene samples markedly increased, indicating the formation of some sp\(^3\) carbon by functionalization. This phenomenon can be attributed to a significant decrease in the size of the in-plane sp\(^2\) domains due to oxidation and ultrasonic exfoliation and the partially ordered graphite crystal structure of graphene nanoplatelets. The spectrum shows the D and G bands in the ratio expected for magnetic-graphene and is consistent with data previously reported. As for magnetic nanoparticles, compared with data in the literature,\(^{20,21}\) we conclude that the prepared iron oxide nanoparticles consisted of Fe\(_3\)O\(_4\). As for Fe\(_3\)O\(_4\)-graphene, the peaks of the magnetic nanoparticles blue-shifted, which can be explained by the charge doping of oxygen atoms with carbon dangling bonds during the oxidation process.\(^{22,23}\)

The porous structure characteristics and Brunauer-Emmett-Teller (BET) specific surface area of the magnetic
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The presence of heavy metal ions, dyes, and aromatic compounds in polluted water is a serious environmental problem because of their toxicity for human beings and the ecosystem. The magnetic-graphene composite combines the high adsorption capacity of graphene and the separation convenience of magnetic nanoparticles (Fig. 6), which makes it an excellent candidate for the removal of contaminants from water. In this study, we demonstrated a simple experiment to prove that the magnetic-graphene composite was very efficient to remove methyl orange from water. As shown in the Fig. 7, after dispersal of the magnetic-graphene composites in the methyl orange solution and shaking the resultant mixture by hand for only 10 minutes, the magnetic graphene nanosheets could be easily separated from the mixture by an external magnetic field and the solution became colorless.

4. Conclusion

In this work, we prepared magnetic-graphene composites via a simple and effective chemical method followed by heat treatment. Iron oxide nanoparticles were strongly attached to graphene layers or interlayers. We further found that such magnetic-graphene composites had great potential as an effective absorbent for the removal of methyl orange from water. We believe that magnetic-graphene composites are particularly attractive for the design of novel composites, and detailed studies on this application are underway.

Acknowledgment

This work was financially supported by the National Science and Technology Support Project (Grant No. 2011BAJ09B04), Natural Science Foundation of Anhui province (1408085MB33), and College Students’ Science and Technology Innovation Foundations (201310878018, AH201310878075 and AH201310878061).

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