Research Article

Synthesis and Characterization of Magnetic Nanosized Fe₃O₄/MnO₂ Composite Particles

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Using the prepared Fe_3O_4 particles of 10 nm–25 nm as magnetic core, we synthesized Fe_3O_4/MnO_2 composite particles with MnO_2 as the shell by homogeneous precipitation. Their structure and morphology were characterized by X-ray diffraction (XRD), X-Ray photoelectron spectroscopy (XPS), transmission electronic microscopy (TEM), Fourier transform infrared spectra (FTIR), and vibration-sample magnetometer (VSM). We show that with urea as precipitant transparent and uniform MnO_2 coating of ca.3 nm thick on Fe_3O_4 , particles can be obtained. The composite particles have better dispersivity than the starting materials, and exhibit super-paramagnetic properties and better chemical adsorption ability with saturated magnetization of 33.5 emu/g. Decoloration experiment of methyl orange solution with Fe_3O_4/MnO_2 composite suggested that the highest decoloration rate was 94.33% when the pH of methyl orange solution was 1.3 and the contact time was 50 minutes. So this kind of Fe_3O_4/MnO_2 composite particle not only has super-paramagnetic property, but also good ability of chemical adsorption.

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1. Introduction

In recent years, nanocomposite materials consisting of core and shell have been attracting great interest and attention of researchers because of their potential application in catalysis, environmental protection, and especially biomedical use. Ikram ul Haq and Egon Matijevic studied the preparation and properties of manganese compounds on hematite in 1997 [1] with three manganese compounds: manganese (II) 2, 4-pentanedionate (MP); manganese (II) methoxide (MMO); and manganese (II) sulfate/urea (MSU) solution under different experimental conditions.

In this paper, we present an approach to synthesize and characterize Fe_3O_4/MnO_2 composite particle by homogeneous precipitation with Fe_3O_4 as the magnetic core and MnO_2 as the shell, where the Fe_3O_4 nanoparticles were prepared by coprecipitation method, and the Fe_3O_4/MnO_2 composite core-shell structure was synthesized via hydrolyzation of $MnSO_4$ with precipitant. The structures and properties of the materials are discussed in some detail.

2. Materials and Methods

2.1. Preparation of Fe_3O_4 Nanoparticles. Fe_3O_4 nanoparticles were prepared by chemical coprecipitation as follows: at first, 2 mol/L NaOH solution and 5% polyethylene glycol (PEG) solution were prepared. 3.24 g of FeCl₃ and 2.39 g of FeCl₂·4H₂O were dissolved in 100 mL of distilled water, respectively. Then we mixed solutions of FeCl₃, FeCl₂·4H₂O, and 5% PEG together and dispersed them by ultrasonic stirring for 10 minutes. Then the mixture was heated to 75° C, followed by the addition of 2 mol/L NaOH solution until the pH value of the mixture reached about 11.5. The mixing and stirring lasted for 2 hours at 60° C, and then aged at 80° C for 30 minutes. The resulting particles were purified repeatedly by magnetic field separation, washed several times with distilled water or ethanol, and dried at 80° C.

2.2. Synthesis of Fe_3O_4/MnO_2 Composite by Homogeneous Precipitation. 0.5 g Fe_3O_4 particles were dispersed by ultrasonic stirring in 100 mL 5% PEG for 30 minutes, and were

mixed with 100 mL MnSO₄ solution of certain concentration, and followed by addition of $NH_3 \cdot H_2O$ or urea solution. Table 1 shows the experimental conditions. The reaction lasted for 12 hours at 60°C. At the end of the period, the solids were separated by repeated magnetic separation and washed with distilled water for three times. The products were dried at 80°C and calcined at 280°C for 3 hours.

The as-prepared magnetic Fe₃O₄ nanoparticles and Fe₃O₄/MnO₂ composite particles were characterized by D/max- γ -B X-ray diffractometer (XRD) with CuK α radiation, Thermo ESCALAB 250 X-ray photoelectron spectroscopy (XPS) with AlK α radiation, and Nicolet 200SXV Fourier transform infrared (FTIR). The morphology of the particle was studied with JEM-2100F transmission electron microscopy (TEM). Magnetic properties of Fe₃O₄ and Fe₃O₄/MnO₂ composite particles were investigated by Model-155 vibrating sample magnetometer (VSM).

2.3. Decoloration Experiment of Methyl Orange Solution with Fe_3O_4/MnO_2 Composite Particles. 20 mg/L methyl orange solution was prepared as the simulated dye wastewater. The λ_{max} of methyl orange solution was 465 nm. PH value of the methyl orange solution was regulated to the set value with NaOH and NH₃·H₂O. 50 mg Fe₃O₄/MnO₂ particles were dispersed by ultrasonic stirring in 50 mL methyl orange solution per time with different pH values for 30 minutes, and absorbance at wavelength of 465 nm was determined by UV-1700 visible spectrophotometer. By calculating the decoloration rate of methyl orange, the appropriate pH value for decoloration was found.

50 mg Fe₃O₄/MnO₂ particles were dispersed by ultrasonic stirring in 50 mL methyl orange solution per time with the appropriate pH value for a different contact time (t), and the absorbance at wavelength of 465 nm was also determined. By calculating the discoloration rate of methyl orange, the appropriate contact time value was found too.

3. Results and Discussion

3.1. Structure and Composition of the Materials. Figure 1 illustrates the X-ray diffraction patterns of the as-manufactured two samples mentioned above. While the lower pattern represents the synthesized standard Fe₃O₄ particles, differential peaks appeared at $2\theta = 27.5^{\circ}$ and $2\theta = 40.3^{\circ}$ in the upper line, which are just the evidence of the existence of MnO₂ in the Fe₃O₄/MnO₂ composite. Calculating the grain size according to Scherrer formula, we obtained 18.76 nm for the Fe₃O₄ particles.

Figure 2 shows the XPS spectrum of Mn and Fe in Fe_3O_4/MnO_2 composite particles. Binding energy of $Fe2p_{3/2}$ is 711.1 eV and binding energy of $Fe2p_{1/2}$ is 724.6 eV which correspond to the XPS spectrum of Fe_3O_4 , and that for $Mn2p_{3/2}$ and $Mn2p_{1/2}$ are, respectively, 642.2 eV and 653.8 eV. According to the Handbook of X-ray photoelectron spectroscopy [2], the Mn in the composite particles exists as Mn^{4+} . These are consistent with the XRD in Figure 1, respectively.



FIGURE 1: XRD patterns of $\rm Fe_3O_4$ and $\rm Fe_3O_4/MnO_2$ composite particles.



FIGURE 2: XPS spectrum of Mn (a) and Fe (b) in Fe_3O_4/MnO_2 composite particles.

Sample	$MnSO_4/mol \cdot L^{-1}$	V(precipitant)/mL	V(PEG)/mL	Fe ₃ O ₄ /g
(a)	0.072	15(amine)*	100	0.5
(b)	0.072	10(amine)*	100	0.5
(c)	0.036	10(amine)*	100	0.5
(d)	0.036	10(1 mol/L urea)	100	0.5

TABLE 1: Reaction condition for synthesis of Fe₃O₄/MnO₂ composite.

* Mass fraction of amine is 25%.

3.2. Morphology and Shaping Mechanism of Fe_3O_4 Nanoparticles. TEM images of the Fe_3O_4 particles are shown in Figure 3. Two different kinds of morphology can be seen some of particles are spherical with diameter of about 10 nm, and the others are square with the diameter of ca.25 nm, it is comparable to that from the XRD pattern in Figure 1.

The reason for the two different particle shapes lies in the different roles the PEG played in the reaction process. At the beginning of the reaction, the amount of PEG was relatively more than that of the Fe(OH)₃ seed formed in solution because less NaOH was added, part of PEG acted as templates. Certain surface of the Fe(OH)₃ crystal stopped to grow because of PEG absorbing on it, and in the calcine process the morphology of Fe(OH)₃ remained, and finally the square shape of the Fe₃O₄ particles was formed, this was also observed elsewhere. As more and more NaOH dropped in the solution, the nuclei of Fe(OH)₃ increased correspondingly, and the effect of dense coating of PEG dominated rather than selective absorption, stopping the Fe(OH)₃ particles to grow. Finally, small spherical Fe₃O₄ nanoparticles were released by the decomposition of Fe(OH)₃ [3, 4]. Figure 4 shows the schematic shaping mechanism of Fe₃O₄ nanoparticles.

3.3. Morphology and Shaping Mechanism of Fe_3O_4/MnO_2 Composite Particles. Figures 5(a) and 5(d) present the TEM images of Fe_3O_4/MnO_2 composite particles prepared under different conditions shown in Table 1. Figures 5(a) and 5(b) suggest that by the same concentration of MnSO₄, the volumes of NH₃·H₂O added could affect the thickness of MnO₂ coating on the Fe₃O₄ particles. Though the volume of NH₃·H₂O was reduced to 10 mL (Table 1), a lot of dissociative MnO₂ stillexisted (Figure 5(b)), so we have to reduce further the concentration of MnSO₄ solution. When the concentration of MnSO₄ solution was halved, the coating effect was much better as was expected (Figure 5(c)).

To improve the coating, we changed the precipitant from $NH_3 \cdot H_2O$ to urea (1 mol/L). As shown in Figure 5(d), the composite particles look uniformly with darker Fe_3O_4 core and transparent MnO_2 shell, and the coating thickness is ca.3 nm, a demonstration, that the conditions selected are rational.

It is very interesting to show the TEM image of large area in Figure 6, from which we may claim that the Fe_3O_4/MnO_2 core-shell nanoparticles prepared have much better dispersive behavior than the starting materials.



FIGURE 3: TEM image of Fe₃O₄ nanoparticles.



FIGURE 4: Schematic sketch of the formation of Fe_3O_4 with different morphologies.

3.4. Property for Potential Applications. Figure 7 shows the hysteresis curves of the Fe₃O₄ nanoparticles and the Fe₃O₄/MnO₂ composite particles. The two patterns resemble each other, and also the Fe₃O₄/MnO₂ composite particles have super-paramagnetic properties. With the decreasing of the magnetic field, the magnetization decreased and reached zero at H = 0, no residual magnetization remained. This prevents particles from aggregation, and the particles can be redispersed rapidly when magnetic field is removed. The saturation magnetization of Fe₃O₄ nanoparticles is 68.1 emu/g, and that for the Fe₃O₄/MnO₂ composite particles measured 33.5 emu/g.

The IR spectra of the Fe_3O_4 and the Fe_3O_4/MnO_2 composite particles are shown in Figure 8. The characteristic absorption peak of Fe_3O_4 lies in 588.13 cm⁻¹, while that in the Fe_3O_4/MnO_2 composite particles moved to 606 cm⁻¹, resulting in a blue shift of ca.18 cm⁻¹. It may be that the





FIGURE 5: TEM images of Fe₃O₄/MnO₂ composite particles prepared under different reaction conditions in Table 1.



FIGURE 6: TEM images of Fe $_3O_4/MnO_2$ composite particles in large area.

Fe₃O₄ particles in the composite were monodispersive in

relation to the starting materials. It is significant that there

appeared a new peak at 535 cm⁻¹ in the response of the

composite particles, implying that there may be some new



-■- Fe₃O₄/MnO₂
-●- Fe₃O₄

FIGURE 7: Magnetic hysteresis loop of Fe_3O_4 , Fe_3O_4/MnO_2 composite particles.

bond generated between the core and the shell. The absorption peaks near 3432 cm^{-1} are flexible vibrating peaks of hydroxy on the surface of composite; it is wider and stronger than that of Fe₃O₄. It means that the composite particles have more hydroxys than Fe₃O₄, which in turn could make MnO₂ more active. Thus, the composite particles may have better ability of chemical adsorption, which can be used for dyestuff treatment.

Then the decoloration of methyl orange with Fe_3O_4/MnO_2 was studied, and the influence of initial solution pH value and contact time on the decoloration was investigated. Figures 9(a) and 9(b) suggest that pH value is the key factor influencing decoloration efficiency. The lower pH value and adequate contact time (*t*) are favorable for the methyl orange



FIGURE 8: IR spectrum of samples Fe_3O_4 , Fe_3O_4/MnO_2 composite particles.



FIGURE 9: Effect of pH value (a) and contact time (b) on decoloration rate.

solution decoloration. With the same contact time (t = 30 minutes), the highest decoloration rate was 91.4% when the pH = 1.3, and it can reach the highest decoloration rate 94.33% when the contact time was 50 minutes. So this kind of Fe₃O₄/MnO₂ composite particle not only has superparamagnetic property, but also has good ability of chemical adsorption which may find wide applications in the field of dyestuff adsorption.

4. Conclusion

Using the prepared Fe₃O₄ particles of 10 nm-25 nm as magnetic core, we synthesized Fe₃O₄/MnO₂ composite particles with MnO₂ as the shell by homogeneous precipitation. The composite particles look uniformly with darker Fe₃O₄ core and transparent MnO₂ shell, and the coating thickness is ca.3 nm. The as-synthesized Fe₃O₄/MnO₂ composite particles exhibit super-paramagnetic properties and have better dispersivity than the starting materials. The saturation magnetization of Fe₃O₄ nanoparticles is 68.1 eum/g, and that for the Fe₃O₄/MnO₂ composite particles measured 33.5 eum/g. Decoloration experiment of methyl orange solution with Fe₃O₄/MnO₂ composite suggests that the highest decoloration rate is 94.33% when the pH value of methyl orange solution was 1.3 and the contact time was 50 minutes. So this kind of Fe₃O₄/MnO₂ composite particle not only has super-paramagnetic property but also has good ability of chemical adsorption.

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