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Research Article

Synthesis of Core-Shell Fe_3O_4@SiO_2@TiO_2 Microspheres and Their Application as Recyclable Photocatalysts

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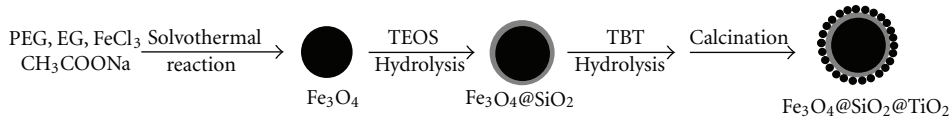
We report the fabrication of core-shell Fe_3O_4@SiO_2@TiO_2 microspheres through a wet-chemical approach. The Fe_3O_4@SiO_2@TiO_2 microspheres possess both ferromagnetic and photocatalytic properties. The TiO_2 nanoparticles on the surfaces of microspheres can degrade organic dyes under the illumination of UV light. Furthermore, the microspheres are easily separated from the solution after the photocatalytic process due to the ferromagnetic Fe_3O_4 core. The photocatalysts can be recycled for further use with slightly lower photocatalytic efficiency.

1. Introduction

In recent years, an enormous research effort has been dedicated to the study of semiconductors in the area of photocatalysis. Among the semiconductor photocatalysts, TiO_2 has attracted a lot of attention because of its high photocatalytic efficiency, high stability, and low cost [1–5]. For the application of TiO_2 in the area of wastewater purification, TiO_2 slurry reactor is the most common device because of its high specific surface area, efficient light absorption, and good dispersion [6–8]. However, the separation of TiO_2 particles from treated water, especially from a large volume of water, is an expensive and time-consuming work, which limited the application of TiO_2 slurry reactor in industrial application. To solve this problem, many methods including titania beads [9], TiO_2-based thin film [10, 11], fiberglass loaded with titania [12], and encapsulated titania within a zeolite framework [13] have been developed to immobilize TiO_2 in fixed beds. However, the photocatalytic activity of TiO_2 is considerably reduced by these immobilization techniques because the effective surface area of photocatalysts is decreased.

Recently, magnetic core-shell composites have gained a great deal of attentions. The magnetic core has good magnetic responsibility and can be easily magnetized. Therefore, the magnetic composites can be conveniently separated and collected from water by applying an external magnetic field. Many studies have been carried out on the preparation and application of TiO_2/magnetic composites [14–20]. In these studies, Fe_3O_4 and γ-Fe_2O_3 nanoparticles were applied as the core magnetic materials. However, Fe_3O_4 nanoparticles are easily oxidized, even at room temperature. The TiO_2 shell in the composites was usually prepared by sol-gel methods, where heat treatment was essential. After heat treatment, the ferromagnetic γ-Fe_2O_3 may transform to paramagnetic α-Fe_2O_3.

In this work, through the medium of SiO_2, TiO_2 nanoparticles were successfully coated on Fe_3O_4 microspheres, and Fe_3O_4@SiO_2@TiO_2 microspheres with well-defined core-shell structures were obtained. The prepared Fe_3O_4@SiO_2@TiO_2 microspheres are multifunctional. The TiO_2 nanoparticles are at the outmost of the core-shell microspheres, which can act as photocatalysts to decompose organic dyes in wastewater. The Fe_3O_4 core makes them very easy to be separated and recycled from water with the help of an external magnet. Furthermore, the Fe_3O_4 microspheres are stable at room temperature, and are unchanged after heat treatment under nitrogen atmosphere. Therefore, the Fe_3O_4@SiO_2@TiO_2 microspheres may serve as an ideal photocatalyst for the treatment of wastewater.



Scheme 1: The synthetic route to Fe_3O_4@SiO_2@TiO_2 core-shell microspheres.

2. Experimental

All the chemical reagents were of analytical grade and were used without further purification.

2.1. Synthesis of Fe_3O_4 Microspheres. The procedure for the synthesis of Fe_3O_4 microspheres was carried out according to a previous report [21], summarized as follows: 1.35 g of iron chloride (III) hexahydrate, 1.0 g of polyethylene glycol (Mw = 4000), and 3.6 g of sodium acetate trihydrate were added into 40 mL ethylene glycol under constant magnetic stirring to form a clear solution. Then the solution was transferred into a Teflon-lined stainless steel autoclave with a capacity of 50 mL and heated at 180°C for 19 h. The products were collected and fully rinsed with deionized water and absolute ethanol with the help of an external magnet, and then dried under vacuum at 60°C for 2 h for further use.

2.2. Synthesis of Fe_3O_4@SiO_2 Microspheres. The synthesis of Fe_3O_4@SiO_2 microspheres was carried out according to a previous report [22]. Typically, 0.2 g of as-prepared Fe_3O_4 microspheres was dispersed into a mixture of 20 mL ethanol and 4 mL deionized water in a glass beaker, and then, under constant mechanical stirring, 1 mL of ammonia solution (25%) and 0.8 mL of tetraethyl orthosilicate (TEOS) were consecutively added. The mixture was further stirred for 3 h. The resultant products were collected and washed, and then dried under vacuum at 60°C for 2 h for further use.

2.3. Synthesis of Fe_3O_4@SiO_2@TiO_2 Microspheres. The synthesis of Fe_3O_4@SiO_2@TiO_2 microspheres was carried out according to following procedure. Firstly, 5 mL tetrabutyltitanate was dissolved in 35 mL ethanol to form a clear solution. Then, 0.1 g of Fe_3O_4@SiO_2 microspheres as dispersed in the above solution with the aid of ultrasonication for 5 min. After that, 20 mL of a 1 : 5 (v/v) mixture of water and ethanol was added dropwise to the suspension of Fe_3O_4@SiO_2 microspheres with constant mechanical stirring over a period of approximately 15 min. The suspension was further stirred for about 1 h. The products were collected and washed with ethanol for three times, then calcined under nitrogen atmosphere at 500°C for 3 h. The whole synthesis procedure is shown in Scheme 1.

2.4. Photocatalytic Degradation of Methyl Orange. The photocatalytic degradation was conducted as the following procedure: 40 mg of Fe_3O_4@SiO_2@TiO_2 microspheres were dispersed into an aqueous solution of methyl orange (0.01 g L^{-1}, 50 mL). The pH value of the methyl orange solution was adjusted by hydrochloric acid and sodium hydroxide solution. Before photocatalytic experiments, the solution was stirred in the dark to permit the adsorption/desorption equilibrium until the concentration of methyl orange solution was constant. After that, a 300 W column-like low-pressure mercury lamp was placed over the solution with a distance of 20 cm, and the solution was irradiated with the lamp under constant mechanical stirring and fan cooling. At intervals of 10 min, 3 mL of the solution was taken out and analyzed with a UV-vis absorption spectrometer.

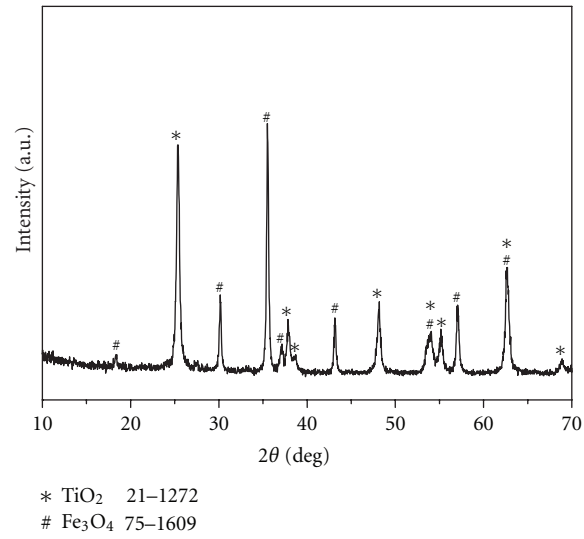


Figure 1: XRD pattern of the Fe_3O_4@SiO_2@TiO_2 microspheres.

2.5. Characterization. X-ray powder diffraction (XRD) patterns were recorded using a Shimadzu XRD-6000 X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 0.15406 nm). The field-emission scanning electron microscopy (FESEM) images were captured with a Hitachi S-4800 field-emission scanning electron microscope. Transmission electron microscopy (TEM) images were taken on a JEOL-2010 high-resolution transmission electron microscope. UV-vis absorption spectra were measured with a Shimadzu UV-3010 spectrometer.

3. Results and Discussion

The phase and composition of the as-obtained samples were examined by XRD. Figure 1 shows a typical XRD pattern of the Fe_3O_4@SiO_2@TiO_2 microspheres. All of the diffraction peaks in this pattern can be classified into two sets. The peaks that marked with "#" can be indexed to the orthorhombic phase of Fe_3O_4 (JCPDS card no. 75–1609), while the other

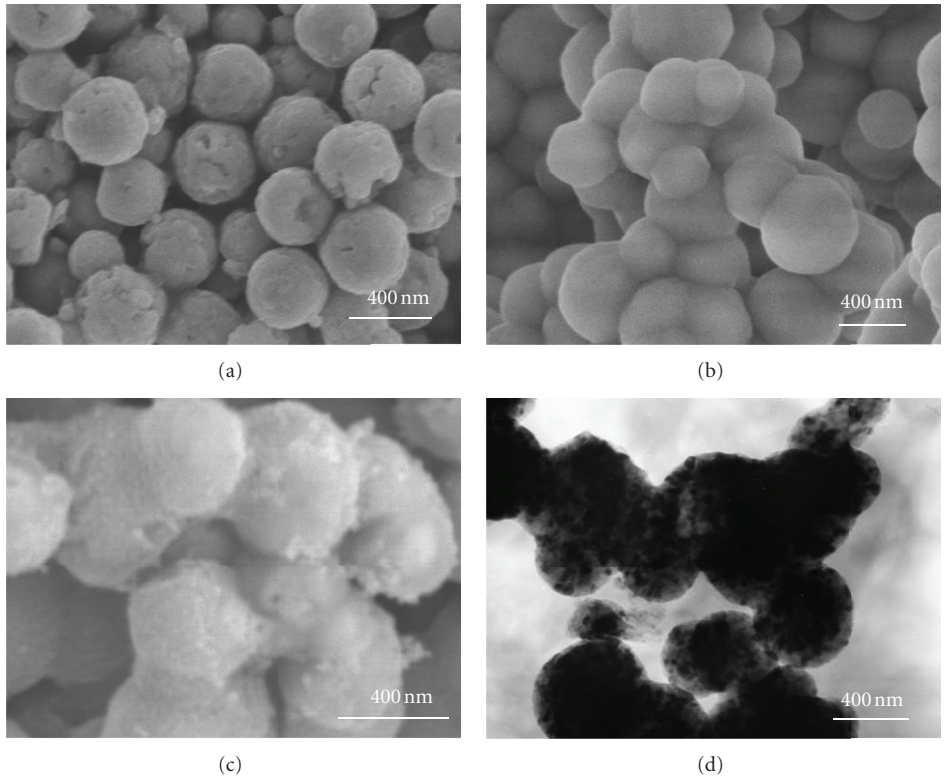


Figure 2: (a)–(c) FESEM images of the Fe_3O_4 microspheres, Fe_3O_4@SiO_2 microspheres, and Fe_3O_4@SiO_2@TiO_2 microspheres, (d) TEM image of the Fe_3O_4@SiO_2@TiO_2 microspheres.

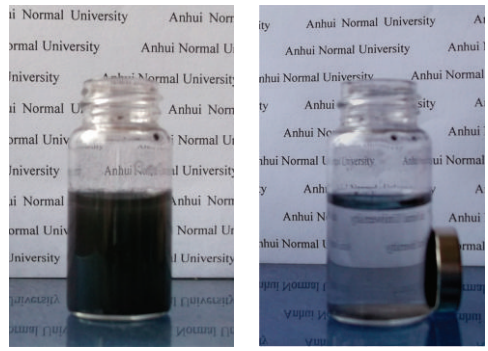
peaks that marked with "*" can be indexed to the tetragonal phase of TiO_2 (JCPDS card no. 21–1272). No diffraction peaks corresponding to SiO_2 were observed because the SiO_2 is amorphous.

The morphology and size of the as-prepared products were characterized by FESEM and TEM. Figure 2(a) displays an FESEM image of the Fe_3O_4 microspheres, in which many nearly monodisperse microspheres with diameters of about 400 nm can be seen. The surfaces of the Fe_3O_4 microspheres are rough. Figure 2(b) shows an FESEM image of the Fe_3O_4@SiO_2 microspheres. The surfaces of the Fe_3O_4@SiO_2 microspheres are smooth, which is distinctly different from the initial Fe_3O_4 microspheres that are shown in Figure 2(a). Such a difference can be attributed to the coating of SiO_2 layer on Fe_3O_4. Figure 2(c) is an FESEM image of the Fe_3O_4@SiO_2@TiO_2 microspheres, from which we can see that many tiny TiO_2 nanoparticles with diameters of 10–20 nm are adhered to the SiO_2 layer. Figure 2(d) is a TEM image of the Fe_3O_4@SiO_2@TiO_2 microspheres, which shows many nanoparticles adhered to the microspheres, consistent with the FESEM obser vations.

Figure 3(a) shows a digital photograph of the Fe_3O_4@SiO_2@TiO_2 microspheres that were dispersed in deionized water with the assistance of ultrasonication. The microspheres can be easily dispersed in water, and this suspension can be kept constant for several minutes. When a magnet was placed aside, the black microspheres can be quickly collected in several seconds, leaving a clear solution, as shown in Figure 3(b). This result shows that the Fe_3O_4@SiO_2@TiO_2 microspheres can be easily separated and collected from water with the assistance of external magnetic force.

The photocatalytic activities of the Fe_3O_4@SiO_2@TiO_2 microspheres were investigated by photodegradation of methyl orange in aqueous solution under the irradiation of UV light. Figure 4 shows the time-dependent UV-vis absorption spectra of methyl orange aqueous solution ($0.01\,g\,L^{-1}$, pH = 3) in the presence of Fe_3O_4@SiO_2@TiO_2 microspheres under exposure to UV light. The main absorption peak of methyl orange is centered at 506 nm. It is clear that the intensity of the main absorption peak of methyl orange gradually decreases with increasing time due to the concentration decreasing of methyl orange. This result shows that methyl orange is gradually degraded or changes into other structures under the irradiation of UV light in the presence of Fe_3O_4@SiO_2@TiO_2 microspheres.

As a comparison, the photodegradation of methyl orange under different conditions was measured, as shown in Figure 5. When the reaction was carried out in the dark, there is hardly any degradation of methyl orange occurred. When Fe_3O_4@SiO_2@TiO_2 microspheres were substituted by Fe_3O_4@SiO_2 or Fe_3O_4 microspheres, the degradation rate of methyl orange is dramatically decreased. This result shows that the TiO_2 nanoparticles in the Fe_3O_4@SiO_2@TiO_2 microspheres play key role in the photodegradation of methyl orange.



(a) (b)

Figure 3: (a) Digital photograph of Fe_3O_4@SiO_2@TiO_2 microspheres dispersed in water, (b) digital photograph of Fe_3O_4@SiO_2@TiO_2 microspheres collected by an external magnet.

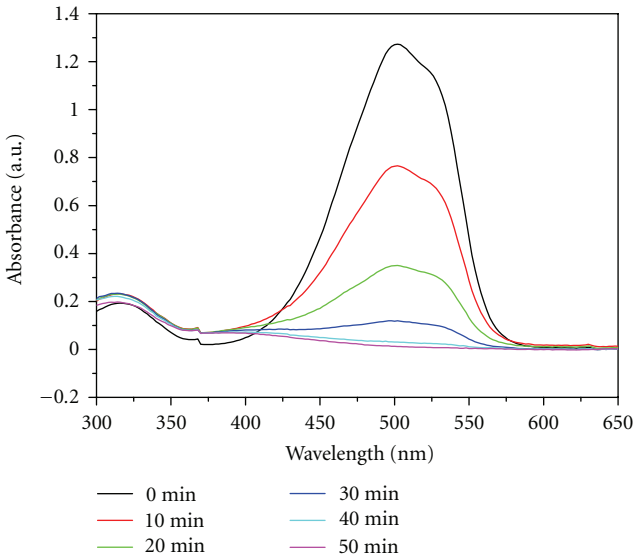


Figure 4: Time-dependent absorption spectra of a methyl orange aqueous solution (0.01 g L^{-1}, pH = 3) in the presence of Fe_3O_4@SiO_2@TiO_2 composites under exposure to UV light.

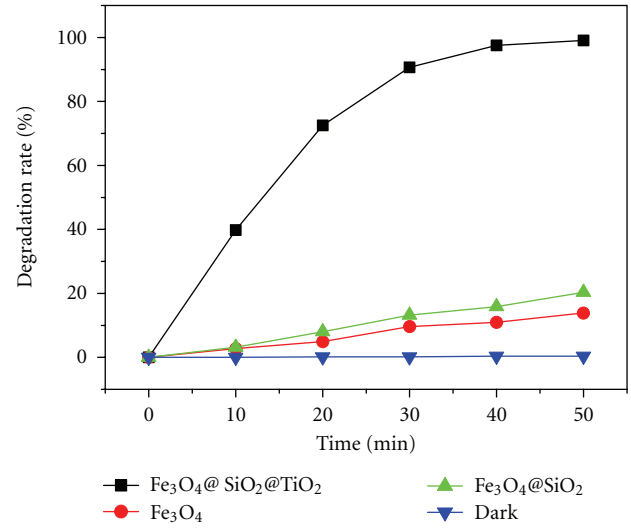


Figure 5: Degradation rate of methyl orange aqueous solution in the dark or in the presence of different photocatalyst under exposure to UV light.

The pH value of solution is an important parameter in photocatalytic degradation reactions that are taking place on the surfaces of semiconductors. It dictates the surface charge properties of the photocatalyst and therefore the adsorption behavior of pollutants [23]. Here we examined the photocatalytic activities of the Fe_3O_4@SiO_2@TiO_2 microspheres at different pH conditions. The results are shown in Figure 6. It is obvious that at acidic conditions the photocatalytic efficiency of the Fe_3O_4@SiO_2@TiO_2 microspheres is much higher, and the photocatalytic efficiency decreases with the increase of pH value. At acidic conditions, the surface of TiO_2 will be positively charged, so the negatively charged dye anion can be effectively adsorbed, and higher photocatalytic efficiency is obtained.

The Fe_3O_4@SiO_2@TiO_2 microspheres can be conveniently separated and collected from the treated water after photocatalytic reactions are completed; therefore, they can be recycled for further use. Here we studied the photocatalytic efficiency of the Fe_3O_4@SiO_2@TiO_2 microspheres for recyclable usage. Figure 7 shows the photocatalytic efficiency of the Fe_3O_4@SiO_2@TiO_2 microspheres after 6 cycles. In each cycle, the methyl orange solution (0.01 g L^{-1}, pH = 3) was irradiated under UV light for 45 min. The results show that the photocatalytic activity of the Fe_3O_4@SiO_2@TiO_2 microspheres only decreased a little after 6 cycles of the photocatalysis experiments. The reason may be that some of the TiO_2 nanoparticles are broken away from the Fe_3O_4@SiO_2@TiO_2 microspheres when they are stirred; as a result, the photocatalytic efficiency of the Fe_3O_4@SiO_2@TiO_2 microspheres decreases. However, the degradation rate of methyl orange can still reach 91% after 6 cycles of reuse. So the Fe_3O_4@SiO_2@TiO_2 microspheres can be applied as recyclable photocatalysts.

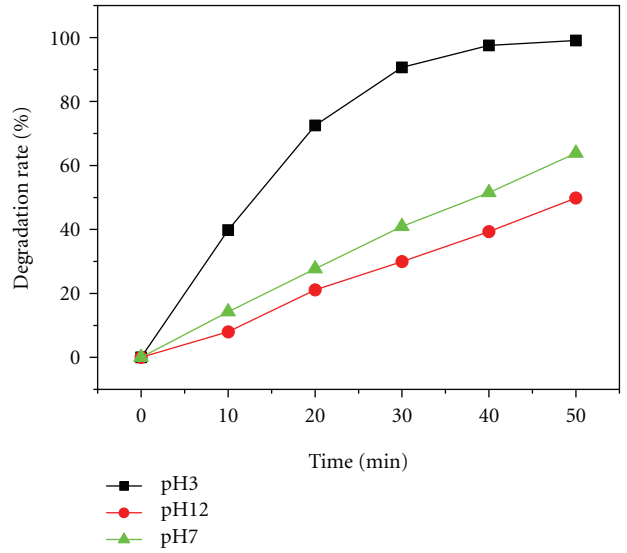


Figure 6: Degradation rate of methyl orange aqueous solution at different pH values in the presence of Fe_3O_4@SiO_2@TiO_2 composites under exposure to UV light.

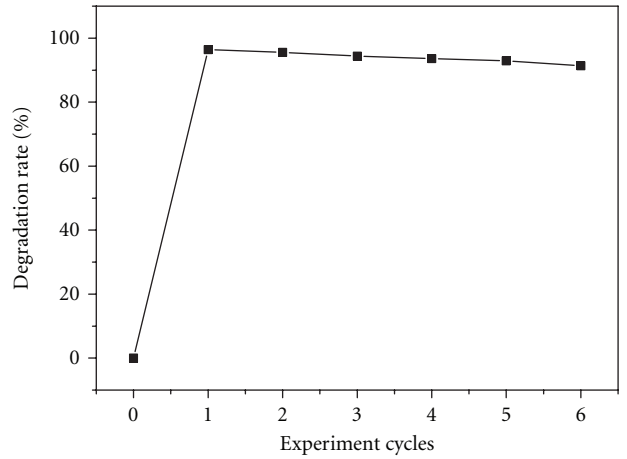


Figure 7: Relationship between the degradation efficiency of Fe_3O_4@SiO_2@TiO_2 photocatalyst and cyclic time.

4. Conclusions

In summary, we have successfully prepared Fe_3O_4@SiO_2@TiO_2 microspheres with well-defined core-shell structures through a wet-chemical method. The Fe_3O_4@SiO_2@TiO_2 microspheres are multifunctional. The magnetic core makes the microspheres very easy to be separated from solution with the help of an external magnet, and the titania nanoparticles at the outside can act as photocatalyst to decompose organic dyes in waste water. Photocatalytic experiments show that the prepared Fe_3O_4@SiO_2@TiO_2 microspheres have good photocatalytic activities under the illumination of UV light and can be applied as recyclable photocatalysts.

Acknowledgment

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