Research Article

High Photocatalytic Activity of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ Functional Particles with Core-Shell Structure

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This paper describes a novel method of synthesizing $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ functional nanoparticles with the core-shell structure. The Fe_3O_4 cores which were mainly superparamagnetic were synthesized through a novel carbon reduction method. The Fe_3O_4 cores were then modified with SiO_2 and finally encapsulated with TiO_2 by the sol-gel method. The results of characterizations showed that the encapsulated 700 nm $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles have a relatively uniform size distribution, an anatase TiO_2 shell, and suitable magnetic properties for allowing collection in a magnetic field. These magnetic properties, large area, relative high saturation intensity, and low retentive magnetism make the particles have high dispersibility in suspension and yet enable them to be recovered well using magnetic fields. The functionality of these particles was tested by measuring the photocatalytic activity of the decolouring of methyl orange (MO) and methylene blue (MB) under ultraviolet light and sunlight. The results showed that the introduction of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ functional nanoparticles significantly increased the decoloration rate so that an MO solution at a concentration of 10 mg/L could be decoloured completely within 180 minutes. The particles were recovered after utilization, washing, and drying and the primary recovery ratio was 87.5%.

1. Introduction

Nanoparticles could find their uses in many important industrial processes [1–3]. One of these could be the treatment of chemicals [4] and biological molecules [5] in wastewater. Specifically titania can catalyse the decomposition of a wide range of chemicals such as azo dyes [6, 7], aromatic compounds [8], and endocrine disruptors [9]. The properties of titania, which is well known for the high productivity of hydroxyl free radicals when exposed to ultraviolet light, low toxicity, and low cost [10, 11] make it a popular choice in wastewater treatment.

One of the main obstacles to the application of nanoparticles in industrial applications is the concern of the release and the fate of the nanoparticles in the environment. It is hence desirable to retain and recover the nanoparticles in such applications, particularly, in wastewater treatment. One approach would be to introduce superparamagnetic

properties and hence to recover the nanoparticles using magnetic fields [6, 12, 13]. The magnetic composite photocatalyst can be magnetically agitated by an alternating magnetic field in a suspension system [14]. In this way, the superparamagnetism of nanoscale Fe_3O_4 particles makes it a suitable material.

The technical challenge here is coupling the Fe_3O_4 to SiO_2 with TiO_2 exposed as the outer surface to provide the catalytic sites and Fe_3O_4 as the core for magnetic separation and recovery [15]. This has proved to be difficult due to the fact that the photocatalytic activity of the nanoparticles shows a decline when the magnetic cores experience photodissolution [16].

In this paper, a novel approach to synthesize three-layer core-shell nanoparticles is described. Between the Fe_3O_4 core and outside surface TiO_2 layer, an SiO_2 layer is introduced to avoid the interaction between the two layers and inhibit photodissolution of the core. The inert SiO_2 acts as a barrier

for both electrons and holes and blocks any photoexcitation effects from the iron oxide, and it prevents the iron oxide from scavenging excited carriers from the titania [13, 17–19]. The resulting nanoparticles were characterized with TEM, XRD, differential light scattering, ultraviolet visible absorption spectroscopy, and VSM and the activity as a photocatalyst was tested by the decoloring of MO as an assay method. The particles showed significantly higher catalytic activity than that of the pure TiO_2 particles under visible light irradiation.

2. Materials and Methods

2.1. Synthesis of Core-Shell Structure $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$

Functional Particles

Materials. Ferric chloride, tetraethoxysilane (TEOS), tetrabutyl orthotitanate (TBOT), ethanol, hydrochloric acid, nitric acid, MO, and MB (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). P25 is a mixture of anatase (80%) and rutile (20% TiO_2) which was purchased from Evonik Degussa (Germany).

Protocols. Ferric chloride and carbon were used as reactants in a ratio of 1:3 to obtain the Fe_3O_4 superparamagnetic particles after heating at 400°C for 3 hours under 0.2 torr vacuum conditions. A tube furnace (OTF-1200X-III) from KJ Group (Hefei, China) was used to keep the reactants at this temperature. After the solid product was milled using an agate mortar 700 nm Fe_3O_4 particles were obtained. The carbon acts as a reducing agent and protector in this reaction. A part of the Fe^{3+} of ferric chloride is reduced to Fe^{2+} , and Fe_3O_4 is generated under low oxygen conditions in this way. An excessive amount of carbon produces a carbon coating around the Fe_3O_4 particles; the Fe_3O_4 particles can be protected from being oxidized to Fe_2O_3 in this way. TEOS, hydrochloric acid, ethanol, and deionized water were mixed in a ratio of 4.6:0.5:12.3:1 to obtain an SiO_2 suspension. The solution was mixed with fast stirring and the water must be added last. Deionized water of 18.25 M Ω was purified through Ultrapure (UPR) System which was purchased from Ultrapure Water Visible Ltd. The 10 g of Fe_3O_4 particles were put into the oven with the SiO_2 solution. After ultrasonication for half an hour, the SiO_2 solution was used to coat around the surface of the Fe_3O_4 particles. After further reaction for three hours at room temperature, the wet particles were calcined at 500°C for 2 hours so that the SiO_2 was encapsulated around the Fe_3O_4 particles. The $\text{Fe}_3\text{O}_4\text{-SiO}_2$ particles were obtained in this way. Then, the $\text{Fe}_3\text{O}_4\text{-SiO}_2$ particles were encapsulated with TiO_2 through the following steps: the 10 g of particles were put into a beaker with 100 mL solution whose ratio of TBOT, nitric acid, alcohol, and deionized water was 30.3:0.6:12.5:1 with continuous stirring. A multifunctional magnetic stirrer (MPL-CJ-88) was used to stir and heat the solution (Jintandadi Automation Factory, Zhejiang, China). The beaker of solution and 10 g of particles (the obtained TiO_2 solution is about 150 mL) were ultrasonicated using ultrasonic bath (KQ-2500DE) from Ultrasonic Instrument

Co., Ltd.), and then it was stirred for 30 min. The wet particles were heated at 500°C for 2 h after reacting for three hours. After milling using an agate mortar the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles were finally obtained.

Characterization. The particles of Fe_3O_4 , $\text{Fe}_3\text{O}_4\text{-SiO}_2$, and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ were characterized by XRD and TEM. The components of the particles were measured by XRD advanced X-ray diffraction system (a Bruker D8) using Cu K radiation of wavelength 1.5406 Å. The particle shapes and sizes were characterized by TEM measurements (JEOL JEM-1200EX). The working voltage is 120 kV. The particles were put into ethanol and sonicated for half an hour and several drops of the ethanol suspension were dropped onto a carbon-coated copper electron microscope grid. The particles' size distribution was measured using a Malvern Mastersizer. The ultraviolet visible absorption spectra were measured with a UV-Vis-NIR Spectrophotometer 5000 (Varian). Magnetic properties were characterized on a Lake Shore 7307 Vibrating Sample Magnetometer.

Catalytic Activity Assay. In order to check the photocatalytic effects, 10 mg/L MO or MB were mixed with 0.2 g of P25 particles or the synthesized $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles under ultraviolet and visible light, respectively. Before light irradiation, the MO or MB molecules must be absorbed by the core-shell particles completely. The MO or MB solution with the core-shell particles was put into a dark place for 48 hours before the photocatalysis. An ultraviolet light (TL-K 40W/05, Philips) is used to irradiate the reactant. After centrifuging the particle suspension, the absorbance (A) of the solution treated for some time was measured. A high-speed desktop centrifuge (TGL-16K Zhuhai Black Horse Medical Equipment Co., Ltd.) was used to centrifuge the particles and the treated solution to avoid the particles affecting the absorbance of the solution. The absorbance of the solution degenerated with time and the decoloration rate was calculated via the following equation:

$$D = \frac{A_0 - A_t}{A_0} \times 100\%, \quad (1)$$

where D is decoloration rate and A_0 and A_t represent the initial absorbance and the absorbance at particular time.

3. Results and Discussion

3.1. Characterization of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ Particles

3.1.1. Particles' Components. Figure 1 shows the XRD spectra of the Fe_3O_4 particles, $\text{Fe}_3\text{O}_4\text{-SiO}_2$ particles, and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles. The XRD spectrum of the Fe_3O_4 particle sample is shown as curve (a). The phases of Fe_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$ exist in the sample, which is illustrated by curve (a). This suggests that the Fe_3O_4 particles sample is partly oxidized. Curve (b) shows the XRD spectrum of $\text{Fe}_3\text{O}_4\text{-SiO}_2$ particles. The characteristic peaks of $\alpha\text{-Fe}_2\text{O}_3$ cannot be seen in curve (b) when comparing with curve (a). This suggests that the Fe_3O_4 particles are prevented from being oxidized by

FIGURE 1: (a) The XRD spectrum of Fe_3O_4 particles. (b) The XRD spectrum of $\text{Fe}_3\text{O}_4\text{-SiO}_2$ particles. (c) The XRD spectrum of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles.

the SiO_2 surface coating. There is a broad envelope between 20° and 30° , which is suggestive of the presence of amorphous silica in the sample.

The XRD spectrum of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles is shown as curve (c). The magnitude of the characteristic peaks suggests that the amount of the anatase phase of TiO_2 is large. Meanwhile, the crystal form of the magnetite nucleus is still Fe_3O_4 . Therefore, the particles are still probably superparamagnetic or ferromagnetic in nature. It is clear that the magnitudes of the Fe_3O_4 characteristic peaks decrease sequentially from curve (a) to curve (c). This is suggestive that the successive coatings around the Fe_3O_4 shield the cores from the X-rays and this behavior is consistent with our assumption that the $\text{Fe}_3\text{O}_4\text{-SiO}_2$ particles were encapsulated well by a TiO_2 layer.

Particle Morphology. Fe_3O_4 particles, $\text{Fe}_3\text{O}_4\text{-SiO}_2$ particles, and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles were characterized by TEM. Figure 2 shows the TEM images of these three samples.

Figure 2(a) is the TEM image of the Fe_3O_4 particles. It is shown that cubic particles of about 700 nm dimension were obtained by our procedure. There is still some evidence of carbon around the particles. The carbon can protect Fe_3O_4 particles from oxidizing to Fe_2O_3 . This result shows that cubic shaped Fe_3O_4 particles were obtained through the high temperature reduction method. Figure 2(b) is the TEM image of $\text{Fe}_3\text{O}_4\text{-SiO}_2$ particles. It can be seen that there is a very thin layer around the dark contrast Fe_3O_4 particles which can be seen clearly in Figure 2 and this is probably the SiO_2 layer. It seems that the dispersion of the $\text{Fe}_3\text{O}_4\text{-SiO}_2$ particles is better than the Fe_3O_4 particles. The TEM image of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles is shown as Figure 2(c). It is clear that the $\text{Fe}_3\text{O}_4\text{-SiO}_2$ particles were encapsulated by a TiO_2 layer which is composed of many little spherical particles. The results show that the layer-by-layer $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ functional particles have been made successfully.

3.1.2. Size Distribution and Specific Area. Figure 3 shows the size distribution spectrum of the final $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles. The results demonstrate that the average size is around 700 nm with a very big spread of sizes. The photocatalysis efficiency of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles is closely related to the specific area. The characterization result shows that the BET surface area of the composite $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles is $55 \text{ m}^2/\text{g} \pm 2\%$ while the BET surface area of the P25 is $42 \text{ m}^2/\text{g} \pm 2\%$. This suggests that, despite the large overall size, the titania formed a rough and high area surface distributed around the particles and this was confirmed in Figure 2(c). That is the reason why our particles have a relatively large specific area and this in turn is expected to lead to higher photocatalysis efficiency.

Magnetic Properties. The magnetization behavior shown in Figure 4 indicates that the saturation intensity of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles is 46.5 emu/g. The result illustrates that the saturation intensity of the particles is large when compared with the particles size. The retentive magnetism of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles is 7.7 emu/g. The result shows that the saturation intensity of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles is large enough to enable the particles to be recovered magnetically. Meanwhile, the retentive magnetism of the particles is small enough, so that the particles can be dispersed without agglomeration. These samples appear to have a mixture of ferrimagnetic and superparamagnetic properties, with only a slight indication of hysteresis.

3.1.3. Absorption Spectra. Figure 5 shows the ultraviolet visible absorption spectra of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles and P25 pure TiO_2 particles. The absorption spectrum of P25 has a strong peak between 200 and 400 nm, corresponding to the band edge absorption of light by titania. The absorption spectrum of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles has a broad absorption across the whole of the visible spectrum. Evidently the introduction of the Fe_3O_4 core makes the core-shell particles' absorption spectrum better match with the visible spectrum [13]. This is consistent with the fact that magnetite has a very small energy gap of around 0.1 eV. This result suggests that the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles obtained in this work might be suitable to have high photocatalysis efficiency in the visible part of the spectrum.

To summarize, the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles (~700 nm) with core-shell structure have a relatively uniform size distribution and have enough anatase TiO_2 shell thickness and suitable magnetic properties to be used for this project to have a recoverable particle that can be used to photocatalyse the degradation of contaminating molecules. Moreover, the novel structure that the introduction of the Fe_3O_4 core provides makes the core-shell particles' absorption spectrum match better with the visible spectrum.

3.2. Photocatalytic Activity. Figure 6 shows the relationships between irradiation time and decoloration rate of the methyl orange solution treated by P25 particles, $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles and no particles under ultraviolet light. The decoloration rates of the MO solution are 71% and 90%, respectively, for the P25 particles, and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles

FIGURE 2: (a) The TEM image of Fe_3O_4 particles. (b) The TEM image of Fe_3O_4 - SiO_2 particles. (c) The TEM image of Fe_3O_4 - SiO_2 - TiO_2 particles.

FIGURE 3: The size distribution spectrum of Fe_3O_4 - SiO_2 - TiO_2 particles.

after 180 minutes of UV light irradiation, while the decoloration rate of the MO solution without any particles is 4%. The photocatalytic activity of the Fe_3O_4 - SiO_2 - TiO_2 functional particles is a little higher than that of P25 under ultraviolet light irradiation, which is illustrated by the curves in Figure 6. The decline after 90 min in the P25 degradation curve can be seen clearly while the activity of the core-shell particles is increasing gradually. This performance suggests that the catalytic persistence of these particles is better than that of P25.

FIGURE 4: The magnetization cycle of Fe_3O_4 - SiO_2 - TiO_2 particles, showing very small hysteresis under 25°C .

The relationships between irradiation time and decoloration rate of the methyl orange solution treated by P25 particles, Fe_3O_4 - SiO_2 - TiO_2 particles, and no particles under visible light are shown in Figure 7. The decoloration rates of the MO solution are 25% and 93%, respectively, for the P25 particles and Fe_3O_4 - SiO_2 - TiO_2 particles after 180 minutes of visible light irradiation. The decoloration rates of the P25 particles under visible light irradiation are always

FIGURE 5: The ultraviolet visible absorption spectra of P25 and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles.

FIGURE 6: The relationships between irradiation time and decoloration rate of the methyl orange solution treated by P25 particles, $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles, and no particles under ultraviolet light.

about 20% in this work, which is shown as Figure 7. The results of Figures 6 and 7 are consistent with the suggestion inferred from Figure 5 that the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ functional particles should have high photocatalysis activity under the longer wavelength light. Furthermore, the pure P25 TiO_2 particles cannot easily be recovered after the experiments. Due to the magnetism of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ functional particles, at least 0.175 g particles can be recovered from the original 0.2 g that were used giving a recovery ratio of 87.5%. Comparing Figure 6 with Figure 7, the photocatalytic activity of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ functional particles under visible light irradiation is higher than that under ultraviolet light irradiation and this should have important consequences for future applications.

FIGURE 7: The relationships between irradiation time and decoloration rate of the methyl orange solution treated by P25 particles, $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles, and no particles under visible light.

From left to right, Figure 8(a) is the picture of the samples, water, and methyl orange solution, MO solution with $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles, MO solution after treatment by $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles under ultraviolet light, and MO solution after treatment by $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles under visible light. The MO solutions after treatment by the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ functional particles under ultraviolet and visible light are both almost as clear as water. Note how the sample in the middle of the picture shows how well the particles are dispersed in the MO aqueous solution. The apparent first-order kinetic equation used to fit experimental data is

$$\ln\left(\frac{A_0}{A}\right) = K_{\text{app}}t, \quad (2)$$

where K_{app} is apparent rate constant, A is the solution-phase absorbance of MO, and A_0 is the initial absorbance of the MO solution. The corresponding linear transforms in $\ln(A_0/A)$ as a function of irradiation time are given in Figure 8(b). From the figure, we can obtain the apparent rate constant for the degradation process by the particles irradiated by different light. The values are 0.0124 and 0.0120 min^{-1} for the degradation of the MO by these particles under UV light and visible light, respectively. The results show that the reaction rates are almost the same under UV light and visible light irradiation.

Under normal circumstances, the electrons of TiO_2 cannot be excited under visible light, but composite particles of visible light absorbing phenomenon are found in the experiment and this internal mechanism is described in Figure 9. Figure 9 is the diagram of the energy band of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ core-shell nanoparticles, plotted by the relative layer thickness on the horizontal axis and the relative energy band gap on the vertical axis. The TiO_2 band gap is

FIGURE 8: (a) The images of the samples of water, methyl orange solution, methyl orange solution with $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles, methyl orange solution after being treated by $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles under ultraviolet light, and methyl orange solution after being treated by $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles under visible light. (b) The kinetic curves of methyl orange disappearance for $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles.

FIGURE 9: The diagram of the energy band of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ core-shell nanoparticles.

about 3.2 eV, and SiO_2 band gap is about 8.9 eV while Fe_3O_4 band gap is only 0.1 eV. Thus, the electrons of the Fe_3O_4 can be easily excited by the visible light [20]. In order to verify the role of Fe_3O_4 , we performed the following experiment.

The ultraviolet visible absorption spectra of Fe_3O_4 and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles are shown as Figure 10(a). It is clear that the visible light activity of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles is all because of their magnetic core. The relationships between irradiation time and decoloration rate of the methylene blue solution treated by P25 particles, $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles, $\text{SiO}_2\text{-TiO}_2$ particles, and no particles under visible light are shown in Figure 10(b). The decoloration rates

of the MB solution are 5.3%, 7.9%, and 88.1%, respectively for the P25 particles, $\text{SiO}_2\text{-TiO}_2$ particles, and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles after 16 hours of visible light irradiation. The highest decoloration rate of the P25 particles under visible light irritation is 5.3% in this work, which demonstrates that the pure TiO_2 particles cannot effectively catalyse the MB under visible light irradiation. The $\text{SiO}_2\text{-TiO}_2$ particles' highest decoloration rate under visible light irritation is 8.7% in this work. These results show that the introduction of the SiO_2 is not the reason why the core-shell $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles can photocatalyse the MB under visible light irradiation.

The results of Figures 6, 7, 8, and 10 are consistent with the suggestion inferred from Figure 5 that the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ functional particles should have high photocatalytic activity under the longer wavelength light. Furthermore, the pure P25 TiO_2 particles cannot easily be recovered after the experiments. Because of the magnetic properties of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ functional particles, at least 0.35 g particles can be recovered from the original 0.4 g that were used giving a recovery ratio of 87.5%. Comparing Figure 6 with Figure 7, the photocatalytic activity of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ functional particles under visible light irradiation is almost the same as that under ultraviolet light irradiation. This phenomenon is also demonstrated by the kinetic curves in Figure 8(b). This result should have important consequences for future applications. The results of Figures 7 and 10 illustrate the high photocatalytic activity of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ functional particles in degrading dyes molecules under visible light irradiation.

The key role Fe_3O_4 cores play in the visible light photocatalysis of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles is demonstrated by Figure 10. The ultraviolet visible absorption spectra of Fe_3O_4 and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles in Figure 10(a) illustrate that

FIGURE 10: (a) The ultraviolet visible absorption spectra of Fe_3O_4 and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles. (b) The relationships between irradiation time and decoloration rate of the methylene blue solution by treated P25 particles, $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles, $\text{SiO}_2\text{-TiO}_2$ particles, and no particles under visible light.

the magnetic core makes the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ particles active under visible light irradiation. In the $\text{SiO}_2\text{-TiO}_2$ experiment, this point is confirmed. Figure 10(b) demonstrates that the composite particles without magnetic core only obtain 7.9% degradation in visible light. So Figure 10 shows that the visible light absorption is extremely based on the magnetic core.

The specific degradation mechanism is that the MB is reduced by photoexcited electrons via a series of processes. In accordance with the new understanding, the composite structure is rather special, which is formed by three different semiconductors. Visible light passes through the TiO_2 and SiO_2 layer and excites the electrons from the internal magnetite core [20]. Then the SiO_2 middle layer is formed after calcining precursor which is prepared by sol-gel method and the layer may crack somewhere or generate uneven film [21], leading to the thickness of SiO_2 layer partly reaching angstroms level. We know that the energy of incident visible light is 1.8 eV and the energy of excited electrons from Fe_3O_4 is 1.7 eV, while the barrier height of SiO_2 is 8.9 eV. When the conditions of energy and thickness are met, the electrons in Fe_3O_4 excited by the visible light can eventually tunnel through the SiO_2 layer with a large probability [22, 23]. Then the electrons drop into the conduction band of the titania and hence escape into the surrounding liquid. Further they interact with the lowest unoccupied molecular orbital (LUMO) of the MO and thus chemically reduce that molecule.

4. Conclusions

In this paper we have presented a novel method of synthesizing $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ functional nanoparticles with core-shell structure. The Fe_3O_4 cores were synthesized through a novel carbon reduction method. The recovery problem of titania-based photocatalytic particles can be solved by introducing these superparamagnetic/ferrimagnetic cores. An SiO_2 layer has been introduced successfully between the two layers, which makes the three-layer core-shell nanostructure more stable. The core-shell nanoparticles have been characterized by TEM, XRD, particle size measurement, ultraviolet visible absorption spectroscopy, and magnetic characterizations, respectively. All the results are consistent and show that the 700 nm $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ functional particles with a core-shell structure are photocatalysts and recoverable. The results for the decoloration of methyl orange show that the introduction of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ functional particles has a significant photocatalytic effect in breaking down the 10 mg/L MO by 90% and 93% under UV light and visible light over 180 minutes, while the P25 particles have very low activity under visible light irradiation. Moreover, the approximate core-shell functional particles can be recovered after use, and the primary recovery ratio is 87.5%. The mechanism of the visible light is dedicated in this paper, and the experiment results show that the magnetic core plays an irreplaceable role in the photocatalytic processes. The high photocatalytic activity of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-TiO}_2$ functional

particles under visible light makes them attractive for large scale industrial applications.

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