Research Article

Fabrication of Magnetite/Silica/Titania Core-Shell Nanoparticles

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1. Introduction

Over the past decades, titanium dioxide (TiO_2) nanoparticles have gained much attention as a photocatalyst and catalyst support [1, 2]. TiO_2 nanoparticles have many advantages as compared to other photocatalysts, which include excellent high stability against chemical and photonic corrosion and high photocatalytic activity [3]. TiO_2 nanoparticles of small mean particle sizes possess high surface area and photocatalytic activity. However, TiO_2 nanoparticles of high surface area are thermally unstable and lose their surface area readily [3]. Therefore, much effort has been focused on coating of TiO_2 on high surface area supports such as silica or alumina in order to stabilize TiO_2 nanoparticles.

TiO_2 nanoparticles could be difficult to recover and lost readily upon being dispersed into wastewater. One of the ways to overcome this problem is to coat TiO_2 onto magnetite (Fe_3O_4) cores and the resulting Fe_3O_4/TiO_2 core-shell nanoparticles can be recovered easily through manipulation by external magnetic field. Li et al. synthesized Fe_3O_4/TiO_2 composite photocatalyst using a sol-gel method [3]. However, it was difficult to achieve complete coating of Fe_3O_4 nanoparticles with TiO_2 at nanometer scale using the sol-gel method. Besides, TiO_2 would oxidize Fe_3O_4 nanoparticles and lead to a reduction of magnetic moment. Some researchers had attempted to coat a thin layer of SiO_2 between Fe_3O_4 nanoparticles and TiO_2 shell. The presence of a SiO_2 layer between TiO_2 shell and Fe_3O_4 nanoparticles could increase the lifetime of photogenerated holes which in turn, resulted in increased photoreactivity [3, 4]. This is attributed to the SiO_2 layer which serves as an insulating layer between Fe_3O_4 nanoparticles (hole-electron trap center) and the TiO_2 shell.

However, there are currently very few literature which report on the synthesis of Fe_3O_4/SiO_2/TiO_2 core-shell nanoparticles and their photocatalytic properties. Besides, the reported synthesis methods for Fe_3O_4/SiO_2 nanoparticles were generally complicated and time consuming. Besides, the coating of Fe_3O_4 with SiO_2 using TEOS was a very slow process which required 12 to 48 hours of mechanical stirring at room temperature [5]. Santra et al. used the microemulsion method for the preparation of Fe_3O_4/SiO_2/TiO_2 core-shell nanoparticles which was a lengthy process and involved the use of several types of surfactants [6]. Gad-Allah et al. and Watson et al. reported the preparation of Fe_3O_4/SiO_2/TiO_2 nanocomposites [4, 7]. However, Fe_3O_4/SiO_2/TiO_2 core-shell nanoparticles prepared by them were in the form of patches and not discrete nanoparticles. As such, these core-shell nanoparticles exhibited in reduction on their surface area and photocatalytic properties. Song and Gao reported the use of the sol-gel process to synthesize Fe_3O_4/SiO_2/TiO_2 nanoparticles but the particles synthesized were very big size of about 500 nm [8].

Herein, we have reported a facile and efficient synthesis approach for the fabrication of Fe_3O_4/SiO_2/TiO_2 discrete core-shell nanoparticles by the sol-gel method with the aid
of sonication. Fe₃O₄ nanoparticles were being encapsulated inside discrete SiO₂ nanospheres within 90 minutes, and a TiO₂ layer was then coated directly onto each SiO₂ nanosphere via the sol-gel method. The photocatalyst properties of as-synthesized Fe₃O₄/SiO₂/TiO₂ core-shell nanoparticles were evaluated by the photodegradation of methylene blue (MB) with or without UV light irradiation.

2. Materials and Methods

2.1. Materials. Iron (II) chloride tetrahydrate, FeCl₂·4H₂O (Merck); Iron (III) chloride 6-hydrate, FeCl₃·6H₂O (AnalaR); tetraorthosilicate, TEOS (99.3%, J.T. Baker); absolute ethanol, EtOH (99.0%, HmbG Chemicals); hydrochloric acid, HCl (37%, HmbG Chemicals); ammonia solution, NH₄OH (28%, R&M Chemicals); titanium (IV) isopropoxide, TIPP (97%, Aldrich); and Milli-Q water (18.2 MΩ cm⁻¹) were used throughout the experiment. All chemicals were used as received without further purification.

2.2. Preparation of Fe₃O₄ Nanoparticles. Fe₃O₄ nanoparticles were prepared using a simple chemical coprecipitation method [8]. Typically, 0.15 mol of FeCl₂·4H₂O and 0.30 mol of FeCl₃·6H₂O were freshly prepared in aqueous HCl (2 M), respectively. Both FeCl₂·4H₂O and FeCl₃·6H₂O aqueous solution were then added rapidly to 20 mL of deaerated Milli-Q water under nitrogen flow at 80°C with the mixture being continuously stirred under nitrogen. Upon adding an aqueous NH₄OH solution (28%, 4 mL), a distinctive black precipitate of Fe₃O₄ nanoparticles was formed immediately. Fe₃O₄ nanoparticles were isolated and purified by centrifugation and then washed with Milli-Q water three to four times to remove excess NH₄OH solution.

2.3. Preparation of Magnetite/Silica (Fe₃O₄/SiO₂) Core-Shell Nanoparticles. A modified Stöber method was used to coat Fe₃O₄ nanoparticles with SiO₂ shell [9]. About 30 mg of freshly prepared Fe₃O₄ nanoparticles were dispersed in a mixture of 30 mL of ethanol and 6 mL water as seeds. The dispersion was homogenized by sonication for about 10 minutes. 3.3 mmol of TEOS was then added into the mixture and sonicated for another 20 minutes. Finally, 30 mmol of aqueous ammonia was added and the mixture was sonicated for 60 minutes. Fe₃O₄/SiO₂ core-shell nanoparticles were isolated by magnetically separation and then washed with ultrapure water.

2.4. Preparation of Fe₃O₄/SiO₂/TiO₂ Core-Shell Nanoparticles. A layer of TiO₂ shell was coated directly onto Fe₃O₄/SiO₂ nanoparticles via the hydrolysis and condensation of TIPP in the presence of Fe₃O₄/SiO₂ nanoparticles as seeds. 0.36 mL of TIPP was added into Fe₃O₄/SiO₂ suspension and stirred continuously for 18 hours at room temperature. The resulting Fe₃O₄/SiO₂/TiO₂ core-shell nanoparticles were dried in an oven and finally calcined at 450°C for 3 hours to convert the TiO₂ outer shell from amorphous phase to photocatalytically active crystalline anatase phase [10].

2.5. Photocatalytic Activity Evaluation. The photocatalytic activity of Fe₃O₄/SiO₂/TiO₂ core-shell nanoparticles was investigated by measuring the photodegradation rate of an aqueous solution of MB in the presence of Fe₃O₄/SiO₂/TiO₂ core-shell nanoparticles and under UV irradiation. 0.02 mmol MB solution (25 mL) and a measured amount of Fe₃O₄/SiO₂/TiO₂ core-shell nanoparticles were placed inside a glass vial. A 6 W UV tube with a wavelength of 254 nm was used as the irradiation light source. During the photocatalytic reaction, the core-shell nanoparticles were being well dispersed by stirring the suspension continuously. At predetermined intervals of UV irradiation, a subsample of the suspension was collected and analyzed by UV-Vis spectrophotometer at its characteristics absorption wavelength (λmax = 642 nm) of MB.

2.6. Morphological Characterization. The morphologies of all samples were examined using a scanning electron microscopy (SEM) (JEOL Model JSM-5300LV) and a transmission electron microscopy (TEM) (JEOL JSM-6710F). The elemental composition of the core-shell nanoparticles were analysed by SEM associated energy-dispersed X-ray microanalysis (EDX) operated with the beam energy of 20 kV. The BET surface area analysis was conducted using the nitrogen adsorption-desorption method at 77.30 K (Micromeritics ASAP 2010). The phase of the Fe₃O₄/SiO₂/TiO₂ core-shell nanoparticles was identified using an X-ray diffractometer (XRD) (RIGAKU, Getgerflex D/MAX-1C).

3. Results and Discussion

3.1. Preparation of Fe₃O₄/SiO₂ Nanoparticles. In this study, Fe₃O₄ nanoparticles with mean diameter of approximately 10 nm (Figure 1) were prepared by a chemical coprecipitation method [11]. These Fe₃O₄ nanoparticles were subsequently used as seeds for coating of SiO₂ shell.

Fe₃O₄ nanoparticles were being encapsulated within the SiO₂ shells upon the hydrolysis and condensation of TEOS as new bonds of Fe–O–Si were formed between the interface of Fe₃O₄ and TEOS. Ultrasonication was used...
Figure 2: TEM micrographs of (a) Fe$_3$O$_4$/SiO$_2$ nanoparticles prepared by sonication; inset shows an individual Fe$_3$O$_4$/SiO$_2$ nanoparticles and (b) Fe$_3$O$_4$/SiO$_2$ nanoparticles prepared by the stirring method.

Figure 4 shows the XRD pattern of Fe$_2$O$_3$/SiO$_2$/TiO$_2$ core-shell nanoparticles after calcination at 450°C in air. The broad peaks were characteristic of the SiO$_2$ matrix [15]. The XRD patterns also demonstrated that the apparently amorphous nature of TiO$_2$ coated on the surface of Fe$_2$O$_3$/SiO$_2$ nanoparticles. In this case, the anatase phase of TiO$_2$ could have been formed after heat treatment at 450°C for 3 hours [3, 8]. The BET specific surface area of Fe$_3$O$_4$/SiO$_2$/TiO$_2$ core-shell nanoparticles prepared in this study was 138 m$^2$/g, and this value was substantially
higher than that of Fe₃O₄/SiO₂/TiO₂ core-shell nanoparticles reported by Gad-Allah et al. at 21–54 m²/g [4].

Figure 5 presents a photograph of the Fe₃O₄/SiO₂/TiO₂ aqueous dispersion before and after a magnet was being attached to the outside of the sample vial. Fe₃O₄/SiO₂/TiO₂ core-shell nanoparticles were observed to be attracted to the magnet being attached outside of the sample vial. The result indicated that even after coating of both SiO₂ and TiO₂ layers unto Fe₃O₄ nanoparticles, their magnetic property had remained intact. As such, these Fe₃O₄/SiO₂/TiO₂ core-shell nanoparticles could be easily recovered after their application in the aqueous medium.

3.3. Photocatalytic Properties of Fe₃O₄/SiO₂/TiO₂ Core-Shell Nanoparticles. Figure 6 shows the degradation of MB dye with and without Fe₃O₄/SiO₂/TiO₂ core-shell nanoparticles added at various duration with and without UV irradiation. It was observed that without UV irradiation, the
Figure 5: Photographs of a vial containing (a) Fe₃O₄/SiO₂/TiO₂ core-shell aqueous dispersion and (b) when a magnet was attached to the outside of the sample vial.

Figure 6: Changes in concentration of MB dye (a) alone, no UV irradiation, (b) alone, UV irradiation, (c) with Fe₃O₄/SiO₂/TiO₂ core-shell nanoparticles, no UV Irradiation, and (d) with Fe₃O₄/SiO₂/TiO₂ core-shell nanoparticles, UV irradiation.

Figure 7: Absorption of MB dye solution (10⁻⁵ M, 20 mL), (a) alone, no UV irradiation, (b) alone, UV irradiation, (c) with Fe₃O₄/SiO₂/TiO₂ core-shell nanoparticles (5 mg) added, no UV irradiation, (d) Fe₃O₄/SiO₂/TiO₂ core-shell nanoparticles (30 mg) added, no UV irradiation, (e) with Fe₃O₄/SiO₂/TiO₂ core-shell nanoparticles (5 mg) added, UV irradiation, and (f) with Fe₃O₄/SiO₂/TiO₂ core-shell nanoparticles (30 mg) added, UV irradiation.

The concentration of MB dye alone remained almost constant after 24 hours. However, its concentration decreased by about 20% with UV irradiation. The degradation of MB dye was substantially enhanced by the addition of Fe₃O₄/SiO₂/TiO₂ core-shell nanoparticles with its concentration being degraded by up to 70% with UV irradiation (Figure 6(d)). We can therefore conclude that the degradation of MB dye was attributed to the photocatalytic activities of the TiO₂ layer on the core-shell nanoparticles.

The photocatalytic decomposition of MB dye catalyzed by Fe₃O₄/SiO₂/TiO₂ core-shell nanoparticles was further evidenced in Figure 7, which shows UV spectra of photocatalytic decomposition of MB dye with and without addition of Fe₃O₄/SiO₂/TiO₂ core-shell nanoparticles, as well as with and without UV irradiation. The intensity of absorption at around 650 nm (λmax) was observed to decrease gradually over the one-hour duration of UV irradiation in the presence of Fe₃O₄/SiO₂/TiO₂ core-shell nanoparticles. The intensity of absorption of MB dye had remained the same without UV irradiation.

4. Conclusion

In this study, a simple and facile synthesis approach was developed for the preparation of a magnetically separable photocatalyst consisting of an Fe₃O₄ core, an SiO₂ intermediate layer, and a photocatalytically active TiO₂ shell. This synthesis method was rapid and did not require the addition of any surfactant to direct the formation of SiO₂ or TiO₂ shells. The photocatalytic activity of TiO₂ surface shell was not affected by the intermediate SiO₂ layer and Fe₃O₄ core. The Fe₃O₄/SiO₂/TiO₂ core-shell nanoparticles possessed high specific surface area of 138 m²/g and exhibited a good photocatalytic activity for the photodegradation of MB dye in aqueous solution.

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References


