Surface modification of Fe$_3$O$_4$@SiO$_2$ microsphere by silane coupling agent

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Abstract

In the present study, Fe$_3$O$_4$@SiO$_2$ core–shell microspheres were prepared via two steps. First, Fe$_3$O$_4$ nanoparticles were synthesized by co-precipitation of Fe$^{3+}$ and Fe$^{2+}$ as reaction substrates and NaOH as precipitant. Second, the surface of Fe$_3$O$_4$ was coated with silica by hydrolysis of tetraethylorthosilicate as the silica source. Subsequently, in order to reduce the amount of interaction and the agglomeration of Fe$_3$O$_4$@SiO$_2$ microspheres, the silica shell of these particles was modified by vinyltriethoxysilane as the silane coupling agent. The structural properties of the samples were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and Fourier transform infrared spectroscopy analyses. The results indicated that the average sizes of Fe$_3$O$_4$ and Fe$_3$O$_4$@SiO$_2$ particles were about 50 and 500 nm, respectively. Also, the surface characterization of Fe$_3$O$_4$@SiO$_2$ microspheres showed that the silane coupling agent was covalently coupled with the silica surface.

Keywords: Agglomeration, Co-precipitation, Coupling agent, Fe$_3$O$_4$@SiO$_2$ core-shell microsphere

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Background

Magnetic microspheres and magnetic core-shell structures are highly applied in bio and environmental researches [1-3]. Magnetic microspheres, consisting of an iron oxide core and a silica shell, have attracted more attention for their unique magnetic responsivity, low cytotoxicity, good stability, and chemically modifiable surface [4-7]. The core-shell magnetic silica microspheres have shown good potential for different applications, including bioseparation, enzyme immobilization, and catalysis [8-11].

There are various ways to prepare Fe$_3$O$_4$ nanoparticles, which have been reported in several papers, such as arc discharge, mechanical grinding, laser ablation, microemulsions, high temperature decomposition of organic precursors, etc. [12]. As a simple and cheap method, chemical co-precipitation has the potential to meet the increasing demand for direct preparation of well-dispersed (water-based) Fe$_3$O$_4$ nanoparticles, and it offers a low-temperature alternative to conventional powder synthesis techniques in the production of nanoparticles. Also, through this method, the sizes of nanoparticles can be well controlled by apt surfactant [13,14].

Surface coating is one of the methods which have often been used in modifying or in improving the material’s performances [15]. There are several promising techniques for coating the surface of particles; most of them are chemical processes, such as precipitation, sol-gel, and electrochemistry methods. The heterogeneous nucleation method is usually used in surface coating because of its simple procedure, low cost, and especially, easy controlling of the thickness and composition of the coating layer [16]. The proper shell thickness is favorable to keep the coated particles stable physically and magnetically. Using this method, the surface modification of core-shell composites becomes convenient.

In the magnetic core-shell Fe$_3$O$_4$@SiO$_2$, amorphous silica shells have surfaces decorated with hydroxyl group that renders intrinsically hydrophilic. The hydrophilic surfaces easily adhere to each other through hydrogen bonding and form irregular agglomerations. In order to decrease these agglomerations of particles, the surface of the silica shell modifies with the coupling agents. The modification process is described as a hydrolysis and a condensation reaction between the coupling agents and the silica shell. Consequently, the surface modification...
removes the silanol groups on the surface of the core-shell particles and changes the hydrophilic surface into a hydrophobic one. The aim of this study is to modify the surface of Fe$_3$O$_4$@SiO$_2$ core-shell microsphere by vinyltriethoxysilane (VTES) in order to remove the silanol groups on the SiO$_2$ shell and decrease the agglomerations of this sample in its applications.

**Methods**

**Materials**

Ammonium hydroxide (25 wt% NH$_3$), ethanol (C$_2$H$_5$OH), ferric chloride hexahydrate (FeCl$_3$·6H$_2$O), hydrochloric acid (HCl), tetraethylorthosilicate (TEOS), and VTES were supplied from Sigma-Aldrich (MO, USA). Ferric sulfate heptahydrate (FeSO$_4$·7H$_2$O), sodium hydroxide (NaOH), deionized water, and cetyltrimethylammonium bromide (CTAB) were prepared from Merck & Co., Inc. (NJ, USA).

**Synthesis of Fe$_3$O$_4$ nanoparticles**

In this work, Fe$_3$O$_4$ nanoparticles were prepared by co-precipitation method. At first, 0.04 mol of FeCl$_3$·6H$_2$O and 0.02 mol of FeSO$_4$·7H$_2$O were dissolved in 50 ml of 0.5 M HCl solution. Then, 500 ml of 1.5 M NaOH was added dropwise to the solution under vigorous stirring at 80°C. The obtained Fe$_3$O$_4$ precipitant was separated with a magnet and was repeatedly washed with deionized water. Finally, the precipitant was dried at 50°C for 4 h [17]. The chemical reaction of Fe$_3$O$_4$ precipitation is expected as follows (Equation 1):

$$\text{Fe}^{3+} + 2\text{Fe}^{2+} + 8\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4\downarrow + 4\text{H}_2\text{O} \quad (1)$$

**Synthesis of Fe$_3$O$_4$@SiO$_2$ core-shell microspheres**

Fe$_3$O$_4$@SiO$_2$ core-shell microspheres were prepared through the hydrolysis of TEOS, using sol-gel process. The details were as follows: 0.50 g Fe$_3$O$_4$ nanoparticles was added in 50 ml of 0.1 M HCl aqueous solution, and the mixture was subjected to ultrasonic treatment for 10 min. Then, the precipitant was separated with a magnet and was washed with deionized water three times. The obtained precipitant was added to a mixture of 80 ml ethanol, 20 ml deionized water, 2.0 ml ammonia solution (25 wt %), and 0.2 ml TEOS. The resulting mixture was stirred for 6 h at room temperature. Then, the precipitant was separated with a magnet and was washed with deionized water three times. The obtained precipitant was dispersed in a mixture of 80 ml ethanol, 60 ml deionized water,
2.0 ml ammonia solutions (25 wt%), and 0.50 g of CTAB. The reaction mixture was stirred for 1 h; then, 1.0 ml TEOS was added. After stirring for 6 h, the resulting Fe₃O₄@SiO₂ precipitant was separated with a magnet and was washed with deionized water and ethanol. Finally, the precipitant was dried at 50°C for 12 h [18].

Surface modification of Fe₃O₄@SiO₂ core-shell microspheres
The VTES as silane coupling agent was used to covalently couple with the silica surface of the Fe₃O₄@SiO₂ microspheres. At first, 0.1 g Fe₃O₄@SiO₂ microspheres was added in a mixture of 26.6 ml ethanol and 6.6 ml deionized water; then, 1.76 ml VTES was added to this mixture. After subjecting the mixture to ultrasonic treatment for 30 min, 3 μl ammonia solution (25 wt%) was dripped into the reaction mixture, and the solution was shaken for 2 h at room temperature. The solution was heated for 1 h at 50°C. At the end, the modified Fe₃O₄@SiO₂ precipitant was separated with a magnet and was washed with ethanol three times in order to remove the excessive coupling agent. The resulting precipitant was dried at room temperature. The overall schematic is presented in Figure 1.

Results and discussion

X-ray diffraction
The X-ray diffraction (XRD) patterns of (a) Fe₃O₄ and (b) Fe₃O₄@SiO₂ are shown in Figure 2. In Figure 2 curve a, weak diffraction peaks with 2θ at 30.0°, 35.6°, 48.3°, 57.2°, and 62.5° are observed, which indicate that the Fe₃O₄ particles have an amorphous structure. From Figure 2 curve b, we can observe that the XRD pattern of the Fe₃O₄@SiO₂ microspheres is similar to the pattern of Fe₃O₄ nanoparticles because the coating of the SiO₂...
layer does not change the structure of the Fe$_3$O$_4$ nanoparticles [19].

**Scanning electron microscopy**

To determine the morphology and the average size of Fe$_3$O$_4$ particles, scanning electron microscopy (SEM) was used. In Figure 3, the SEM image of the Fe$_3$O$_4$ particles shows that these particles have an irregular morphology, and the average size is about 50 nm.

**Transmission electron microscopy**

Figure 4 shows the transmission electron microscopy (TEM) images of the Fe$_3$O$_4$@SiO$_2$ microspheres. We can clearly see that the Fe$_3$O$_4$@SiO$_2$ particles are spherical with a smooth surface. The average particle size is about 500 nm, and it was because of the agglomeration of Fe$_3$O$_4$ inside the microspheres and the surface growth of SiO$_2$ on the shell [20]. The internal structure cannot be clearly seen due to the larger particle size of the microspheres, which cannot be broken down by electron beam from transmission electron microscopy [18].

**Fourier transform infrared spectroscopy**

The Fourier transform infrared (FTIR) spectra of (a) Fe$_3$O$_4$, (b) Fe$_3$O$_4$@SiO$_2$, and (c) Fe$_3$O$_4$@SiO$_2$ modified by VTES are shown in Figure 5. In all curves in Figure 5, the bands at around 1,621 and 3,423 cm$^{-1}$ can be assigned to the H-O-H stretching modes and bending vibration of the free or adsorbed water, respectively.

In Figure 5 curve a, the band at 567 cm$^{-1}$ is related to the Fe-O bending vibration. In Figure 5 curve b, the broad high-intensity band at 1,061 cm$^{-1}$ is associated with the motion of oxygen in Si-O-Si antisymmetric stretch, due to the asymmetric stretching bonds of Si-O-Si in SiO$_2$. The band at 793 cm$^{-1}$ is assigned to the Si-O-Si symmetric stretch, while the band at 451 cm$^{-1}$ corresponds to the Si-O-Si or O-Si-O bending modes. The band at 964 cm$^{-1}$ is assigned to the Si-O symmetric stretch. The band at 570 cm$^{-1}$ is an indication of the presence of Si-O-Fe. In Figure 5 curve c, the broad band at 1,076 cm$^{-1}$ is for asymmetric stretching bonds of Si-O-Si, the band at 771 cm$^{-1}$ is for Si-O-Si symmetric stretch, the band at 454 cm$^{-1}$ is for Si-O-Si or O-Si-O bending modes, the band at 954 cm$^{-1}$ is for Si-O symmetric stretch, and the band at 578 cm$^{-1}$ is for Si-O-Fe. The C=C band cannot be seen in the Figure 5 curve c because it appears at around 1,640 cm$^{-1}$, and it overlaps with the O-H stretching vibration of H$_2$O. The absorption band at 2,971 cm$^{-1}$ is associated with the C-H of vinyl groups. These results show that the surface modification of Fe$_3$O$_4$@SiO$_2$ by VTES was successful.

**Conclusions**

The Fe$_3$O$_4$ nanoparticles were prepared by co-precipitation from Fe$^{3+}$ and Fe$^{2+}$, and silica particles were coated on the surface of Fe$_3$O$_4$ nanoparticles through the hydrolysis of TEOs in a sol-gel process. The characterization results of SEM and TEM showed that the average diameters of Fe$_3$O$_4$ and Fe$_3$O$_4$@SiO$_2$ were about 50 and 500 nm, respectively. The analysis of the XRD patterns showed that the structures of these samples were amorphous. In the FTIR spectra, we showed that the chemical bonds of Fe-O-Si happened at the surface of the Fe$_3$O$_4$ nanoparticles. Also, VTES was covalently coupled with the silica surface of the Fe$_3$O$_4$@SiO$_2$ microspheres. Consequently, it was proved that the surface modification happened. Surface chemical modification is one of the various methods to enhance the compatibility between the hydrophobic polymer and the hydrophilic fillers [21,22]. Therefore, the hydrophobic surface of Fe$_3$O$_4$@SiO$_2$-Si-CH=CH$_2$ microspheres will be advantageous to be used as the filler in polymeric materials.

**Competing interests**

The authors declare that they have no competing interests.

**Authors’ contributions**

FA prepared the samples, the characterized of the results, and prepared the manuscript. AH and SN carried out the characterization and the interpretation of the results. All authors read and approved the final manuscript.

**Authors’ information**

FA is a MSc student of Applied Chemistry. AH is an associate professor of Physical Chemistry, SN is an associate professor of Applied Chemistry.

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