Preparation of Magnetite Nanoparticles Coated with Silica via a Sol-gel Approach

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Silica-coated magnetite nanoparticles were synthesized via sol-gel process, which comprises the hydrolysis and condensation of TEOS in ethanol/water solution with NH_3 aq. as catalyst. Transmission electron microscope and vibrating sample magnetometer was applied to characterize the nanocomposite particles. Results reveal that the reaction parameters including volume ratio of alcohol/water, the concentrations of NH_3 aq and TEOS play important roles of the formation of silica shell. The thickness of silica shell increased with TEOS concentration. The nanocomposite particles remained favorable superparamagnetism. The formation of silica shell mainly came from the aggregative growth of silica primary particles on the surface of magnetite nanoparticles.

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1. Introduction

Magnetite nanoparticles, due to their remarkable properties such as superparamagnetism and high saturation magnetization, have received growing interest for their potential application in various fields, especially in biomedicine and bioengineering, such as targeted drug delivery, cell separation, magnetic resonance imaging, immunoassay and separation of biochemical products.^{1)–3)} Most of these applications require the magnetic nanoparticles to be chemically stable, biocompatible and well dispersed in liquid media. However, as a result of anisotropic dipolar attraction, the unmodified magnetite nanoparticles tend to aggregate into large clusters, and thus lose the special magnetic properties associated with single-domain.

Surfactants are often used to create an electrostatic double layer to avoid the aggregation, however, the combination of surfactants with magnetite may not be firm enough and they may severely interfere with biomedical application. Usually, coating magnetite with an inert silica shell could help screen the magnetic dipolar attraction, which prevent the aggregation in liquid and improve their chemical stability. Meanwhile, abundant silanol groups are existed on the silica surface, allowing the easily attachment of functional groups by reacting with various coupling agents.

There are two major methods for the generation of silica shell on magnetic particles. The first method, known as reverse microemulsion synthesis,⁴⁾ relies on the use of large amount of surfactants to confine and control the coating of silica. Much effort is required to remove the surfactants. The second method is based on a sol-gel process, which comprises the hydrolysis and condensation of silicon alkoxides in a basic ethanol/water solution. This method has been applied to coat magnetic particles,^{5)–7)} however, few works have been directed to study the effects of the reactants on formation of well-defined silica-coated magnetic particles and the formation mechanism of silica shell. In this paper, we demonstrated the preparation of ultra-stable colloidal magnetite nanoparticles, and systematically studied the effects of the volume ratio of ethanol/water, NH_3 aq. and TEOS concentrations on silica shell. Finally, a formation mechanism of silica shell was proposed.

2. Experimental

2.1 Preparation of colloidal magnetite nanoparticles

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were purchased from China

Medicine (Group) Shanghai Chemical Reagent Corporation. NH_3 aq. (25 mass% aqueous solution), ethanol and tetraethyl orthosilicate (TEOS) were obtained from Sinopharm Chemical Reagent Co., Ltd.

Magnetite nanoparticles were prepared using the method already described based on the chemical coprecipitation of Fe^{2+} and Fe^{3+} by adding a concentrated NH_3 aq. (25 mass%).⁸⁾ 0.5 g magnetite nanoparticles were dispersed in 100 cm³ citric acid solution (0.05 M) under magnetic stirring, and the pH was adjusted to 5.5 by NH_3 aq. (25 mass%). After 4 h the magnetite nanoparticles were precipitated by acetone and washed with acetone by magnetic decantation to remove the redundant citric acid. Subsequently, 100 cm³ water was added to redisperse the ultrafine magnetic particles.

2.2 Silica coating to magnetite nanoparticles

Magnetite nanoparticles were coated with silica at room temperature in a basic ethanol/water solution by a sol-gel approach which was also known as the Stöber method. First, 2 cm³ of the magnetite solution was diluted with 80 cm³ ethanol, appropriate amount of water and appropriate amount of NH_3 aq. (25 mass%). Then the mixture was homogenized by ultrasonic vibration. Finally, under continuous stirring, TEOS was added slowly to the solution. The reaction, involving the hydrolysis of TEOS and subsequent condensation of silica onto the surfaces of magnetite cores, was allowed to proceed for 8 h. The final core-shell nanoparticles was separated by centrifuging and washed with water 4 times.

2.3 Characterization

The produced phases were identified by a powder X-ray diffractometer with graphite-monochromatized $\text{CuK}\alpha$ radiation, operated at 40 kV and 100 mA (XRD, RIGAKU, D/max2550, JAPAN). The crystallite size was calculated by Scherrer's formula. The size and morphology of the core-shell nanoparticles were characterized by transmission electronic microscopy (TEM, HITACHI H-800, 200 kV). Magnetic properties of the samples were characterized by vibrating sample magnetometer (VSM, Nanjing University Instrument Plant LH-3).

3. Result and discussion

3.1 Effect of volume ratio of ethanol/water

The diameter of magnetite nanoparticles observed by TEM was almost the same as their crystallite size estimated by XRD using Scherrer's formula of about 12 nm. **Figure 1** shows TEM images of magnetite nanoparticles coated with silica

Fig. 1. TEM images of $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanocomposite particles prepared under different volume ratio of ethanol/water (a: 8 : 1, b: 4 : 1, c: 2 : 1).

($\text{SiO}_2/\text{Fe}_3\text{O}_4$) prepared under different volume ratio of ethanol/water ($V_{\text{E/M}}$) values while the amounts of other reagents were the same: 0.4 M NH_3 aq. and 0.02 M TEOS. $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles could be formed in a large range of $V_{\text{E/W}}$ as shown in Fig. 1(a)–(c), however, the morphology of the particles was different. A lot of irregular particles were generated at a high $V_{\text{E/M}}$ value of 8 : 1 (Fig. 1(a)), with the decrease of $V_{\text{E/M}}$ value to 4 : 1, the particles became more spherical and uniform (Fig. 1(b)), while the $V_{\text{E/M}}$ value further decreased to 2 : 1, many magnetite-free silica particles (noted by arrows) and irregular $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles with cores of larger clusters were formed.

The polarity of the reaction media, which has effect on the surface charge of colloidal particles increased upon the decrease of $V_{\text{E/M}}$ value.⁹ When at a high $V_{\text{E/M}}$ value, the low polarity of the media would result in the decrease of surface charge of colloidal magnetite and silica shell which was generated at the early stage. As a result, the electrostatic repulsion between particles would be reduced, leading to the aggregation of magnetite cores and irregular morphology of the final products. With the decrease of $V_{\text{E/M}}$ value, the colloidal particles become better dispersed, and it's more favorable for preparation of more regular core-shell particles with little clusters, as shown in Fig. 1(b). However, when the $V_{\text{E/M}}$ value decreased further, the hydrolysis and condensation of

TEOS would become over rapid as a result of large amount of water, which may lead to the formation of lots of silica primary particles in the media. These primary particles couldn't be completely captured by magnetite nanoparticles and some of them may aggregate together to form stable secondary silica spheres (noted by arrows in Fig. 1(c)) with a typical aggregative growth mechanism.¹⁰ Furthermore, the increase in water volume ratio promotes the dissociation of NH_3 aq. and brings about an increase in ionic strength, leading to the reduction in the thickness of electrostatic double layer, and then magnetite particles become unstable and tend to aggregate into clusters. As a result, some large irregular particles with cores of magnetic clusters are founded.

3.2 Effect of NH_3 aq. concentration

Figure 2 shows TEM images of $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles prepared under different NH_3 aq. concentrations while the amounts of other reagents with the same $V_{\text{E/M}}$ value of 4 : 1 and 0.02 M TEOS. No core-shell $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles or SiO_2 nanospheres formed under 0.15 M NH_3 aq. as shown in Fig. 2(a) while irregular core-shell nanoparticles with cluster cores were generated under a high NH_3 aq. concentration as shown in Fig. 2(b).

To the base-catalyzed hydrolysis and condensation of TEOS, the surface potential and ionic strength are considered as the main factors controlling the silica growth.^{11)–13)} The

Fig. 2. TEM images of $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanocomposite particles prepared under different NH_3 aq. concentrations (a: 0.15 M, b: 0.6 M).

Fig. 3. TEM images of $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanocomposite particles prepared under different TEOS concentrations (a: 0.01 M, b: 0.05 M).

stability of colloids is the coaction of van der Waals attraction and electrostatic repulsion. As increasing the ionic strength, more reverse charged ions would enter into the electrostatic double layer and decrease the colloidal surface potential, leading to reduction of electrostatic repulsion and then the particles incline to aggregate.

Silica primary particles are formed almost immediately when the TEOS was added into the basic ethanol/water solution by the condensation of $\text{Si}(\text{OC}_2\text{H}_5)_4 - n\text{O}_n^{n-}$ which is generated by the partial hydrolysis of TEOS.¹⁴⁾ When at a low NH_3 aq. concentration, the ionic strength of the media becomes low and the surface potential of particles is high, resulting in the strong electrostatic repulsion between particles. Consequently, the silica primary particles are hard to collide with magnetite and aggregate to form a shell on the surface. Meanwhile, silica primary particles also couldn't aggregate to form secondary silica nanospheres via the aggregative growth as a result of strong electrostatic repulsion. Thus, the core-shell $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles or silica nanospheres weren't formed in Fig. 2(a).

The ionic strength of the media increased with NH_3 aq. concentration, and correspondingly, the surface potential of

particles was reduced. Most of silica primary particles were captured by magnetite and the generation of secondary silica spheres was suppressed. Core-shell $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles were formed as shown in Fig. 1(b) under 0.4 M NH_3 aq..¹²⁾ However, when the NH_3 aq. concentration was further increased to 0.6 M, many irregular $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles were generated as shown in Fig. 2(b). The high ionic strength caused the dramatic decrease in surface potential of colloidal particles and subsequently, some of the magnetite particles probably aggregated into clusters before silica coating and silica shell formed at the early stage tended to aggregate into large $\text{SiO}_2/\text{Fe}_3\text{O}_4$ clusters with ill morphology.

3.3 Effect of TEOS concentration

Figure 3 shows the TEM images of $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles prepared under different TEOS concentrations while the amounts of other reagents were the same: 4 : 1 $V_{\text{E/M}}$ value and 0.4 M NH_3 aq.. Together with Fig. 1(b) and Fig. 3 reveals that the thickness of silica shell can be controlled by TEOS concentrations. With the increase of TEOS concentration, the shell thickness shown in Figs. 3(a), 1(b) and 3(b) are about 10, 20 and 36 nm respectively, furthermore, the particles become more uniform and spherical.

Fig. 4. Schematic illustration of the mechanism for the formation of silica shell on the surface of magnetite particles.

3.4 Formation mechanism of silica shell

Based on the work presented previously,^{10)–15)} we propose that the silica shell forms via two main stages:

The first stage involves the hydrolysis and condensation of TEOS. Monomeric silica, in the form of $\text{Si}(\text{OC}_2\text{H}_5)_{4-n}\text{O}_n^{n-}$, is generated by partial hydrolysis of TEOS. TEOS concentration used in this work is much higher than the approximate saturation limit of monomeric silica (0.0002 M), therefore, considerable silica primary particles are formed immediately upon the addition of TEOS by the condensation of monomeric silica.¹⁴⁾ According to the work of Nooney and co-workers, the primary particles might be mainly in the form of D4R (double four-ring) and nD4R.¹⁴⁾

The second stage, growth of silica on the magnetite surface, may proceed via two routes: (1) the aggregative growth of silica primary particles on the magnetite seeds; (2) deposition of monomeric silica on the seeds. It's conceivable that the growth of silica shell can proceed via route (2) because of the high reactivity of monomeric silica. However, considerable silica primary particles exist in this basic ethanol/water solution, and thus the growth most probably proceeds via route (1). Silica primary particles colloid and aggregate with magnetite, then the primary particles consecutively aggregate on the seeds surface to form the shell. The schematic illustration of the mechanism for the formation of silica shell on the surface of magnetite particles is shown in Fig. 4.

3.5 The magnetic properties

The hysteresis loops of magnetite and $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles with different thickness of silica shell were measured at room temperature using a vibrating sample magnetometer. As could be seen in Fig. 5, the magnetite nanoparticles show favorable superparamagnetic behaviors and saturation magnetization (M_s) of $64.5 \text{ A} \cdot \text{m}^2/\text{kg}$. Similar with the magnetite, $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles show superparamagnetic property, indicating that the silica shell almost has no effect on the coercive force. In addition, the M_s of $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles decrease correspondingly upon the increase of the thickness of silica shell, which is resulted from the decrease of mass proportion of magnetite.

Fig. 5. Hysteresis loops of Fe_3O_4 (a) and $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles with 10 (b), 20 (c) and 36 nm shell (d).

4. Conclusion

The formation of silica shell on magnetite nanoparticles via a sol-gel approach was systematically studied. The results showed that $V_{\text{E/M}}$, concentrations of NH_3 aq. and TEOS had effects on the formation of silica shell. At high $V_{\text{E/M}}$, irregular $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles were obtained while many secondary silica nanospheres were produced at low $V_{\text{E/M}}$. NH_3 aq. concentration played an important role on the formation of silica shell. As increasing TEOS concentration, the silica shell increased, $\text{SiO}_2/\text{Fe}_3\text{O}_4$ nanoparticles became more regular and spherical, and the M_s decreased correspondingly. In addition, all the particles exhibited superparamagnetic properties. The formation of silica shell can probably explained by the aggregative growth of silica primary particles on the seeds surface.

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