

Investigation of formation of silica-coated magnetite nanoparticles via sol–gel approach

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Abstract

A systematic investigation of the formation of silica-coated magnetite particles via sol–gel approach was conducted using transmission electron microscope (TEM), X-ray diffraction (XRD) and vibrating sample magnetometer (VSM). The results show that reaction parameters including the type of alcohol, the volume ratio of alcohol to water, the amount of catalyst and the amount of precursor play important roles on the formation of silica-coated magnetite particles, and the obtained silica-coated magnetite nanoparticles possess superparamagnetic property. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

During the last decade, owing to the emergence of a new generation of high technology materials, the number of research groups involved in nanomaterials has increased exponentially [1]. Nanomaterials are implicated in several domains including electronics, sensors and biotechnology, etc. This is, to some extent, due to their novel properties of nanomaterials, which differ from both the isolated atoms and the bulk phase. Among various nanostructured materials, magnetic nanoparticles such as magnetite, maghemite, nickel and cobalt, due to their remarkable phenomena such as superparamagnetism, high field irreversibility and high saturation field, have attracted growing interest in magnetic nanostructure materials for their unique properties [2] and potential applications in various fields, especially in biomedicine and bioengineering such as magnetically assisted drug delivery [3], cell isolation [4], MRI contrast agents [5], immunoassay [6] and biomacromolecule purification [7]. However, most of these applications require magnetic nanoparticles to be embedded in a nonmagnetic

matrix to avoid aggregation and sedimentation of magnetic nanoparticles as well as to endow them with particular surface properties for specific application.

Coating magnetic nanoparticles with silica is becoming a promising and important approach in the development of magnetic nanoparticles for both fundamental study and technology application. First, silica formed on the surface of magnetic nanoparticles could screen the magnetic dipolar attraction between magnetic nanoparticles, which favors the dispersion of magnetic nanoparticles in liquid media and protects them from leaching in an acidic environment. Second, due to the existence of abundant silanol groups on the silica layer, silica-coated magnetic nanoparticles could be easily activated to provide the surface of silica-coated magnetic nanoparticles with various functional groups. Finally, the most important is that the silica layer provides a chemically inert surface for magnetic nanoparticles in biological systems. In general, there are four major methods for preparation of silica-coated magnetic nanoparticles. The first method, known as sol–gel process, relies on the use of the of silicon alkoxides as the source of silica matrix. In this method, silica phase are formed on colloidal magnetic nanoparticles in a basic alcohol/water mixture [8]. The second approach is based on either in situ formation of magnetic

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nanoparticles inside the pores of pre-synthesized silica using metal compounds (i.e. salts, complex or alkoxides) as the source of magnetic phase under certain conditions [9]. The third method is called aerosol pyrolysis, in which silica-coated magnetic nanoparticles were prepared by aerosol pyrolysis of a precursor mixture composed of silicon alkoxides and metal compound in a flame environment [10]. More recently, the fourth method, i.e. W/O microemulsion method, has been proposed for the preparation of silica-coated magnetic nanoparticles [11]. In this method, non-ionic surfactants were used to formation of inverse microemulsion for preparation or suspension of magnetic nanoparticles, and silica were formed around the magnetic nanoparticles by hydrolysis and condensation of tetraethyl orthosilicate (TEOS). Among these methods, sol–gel process has been adopted more widely for preparation of silica-coated magnetic nanoparticles for its advantages compared with the other methods, i.e. relatively mild reaction condition, low cost and surfactant-free. Ohmor and Matijevic [12] prepared spindle-type hematite particles with length of about 400 nm, and coated them directly with silica by through sol–gel process. Using surfactant stabilized magnetite nanoparticles as seeds, Philippe et al. [13] and Lu et al. [14] respectively prepared silica-coated magnetite particles through sol–gel process. Up to now, although there are many reports on preparation of magnetite-silica composite particles, most of the reported composite particles showed ill-defined structure and morphology as a result of ignoring pretreatment of magnetite before coating with silica [15–19], and few work has been directed to systemic investigation of the formation of well-defined silica-coated magnetite nanoparticles in sol–gel approach. In this paper, with an aim to give a direction for preparation of uniform silica-coated magnetite particles with core-shell structure, we study systematically the formation of silica-coated magnetite nanoparticles by utilization of transmission electron microscope (TEM), X-ray diffraction (XRD) and vibrating sample magnetometer (VSM).

2. Experimental methods and characterization

2.1. Materials

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were purchased from Fluka. Sodium hydroxide (NaOH) (Shanghai FeiDa Trade Company), trisodium citrate, tetraethyl orthosilicate (TEOS), methanol, ethanol, iso-propanol, propanol and ammonia aqueous (25 wt.%) (Shanghai Chem Reagent Co.) were all used as supplied. In this study, only distilled water was used.

2.2. Colloidal iron oxide nanoparticle synthesis

Magnetic nanoparticles were prepared using the method already described [20], based on the chemical coprecipitation of Fe^{2+} and Fe^{3+} by adding a concentrated solution of base (10 M NaOH) into the mixture of iron salts with a molar

ratio ($\text{FeCl}_2/\text{FeCl}_3$) of 1/2. The alkaline solution was stirred for 1 h at 20 °C and was then heated at 90 °C for 1 h. The iron oxide dispersion was then stirred for 30 min at 90 °C upon addition of 200 mL trisodium citrate solution (0.3 M). The ultrafine magnetic particles were precipitated with acetone, and the supernatant was decanted with the help of a magnet. Subsequently, water was added to redisperse ultrafine magnetic particles. Then, the resultant dispersion was treated by dialysis and adjusted to 2.0 wt.%. The obtained magnetite dispersion was defined as magnetic fluid (MF).

2.3. Coating iron oxide nanoparticle with silica

Followed Stöber method [21] with some modification, coating magnetite nanoparticles with silica was carried out in basic alcohol/water mixture at room temperature by using magnetic fluids as seeds. First, magnetic fluid was diluted with water, alcohol and ammonia aqueous. Then this dispersion was homogenized by ultrasonic vibration in water bath. Finally, under continuous mechanical stirring, TEOS was slowly added to this dispersion, and after stirring for 12 h, silica was formed on the surface of magnetite nanoparticles through hydrolysis and condensation of TEOS. In this paper, to study the influence of reaction parameters on the coating of magnetite with silica, four series of silica-coated magnetite nanoparticles were prepared by changing the alcohol type, volume ratio of alcohol to water ($V_{E/W}$), the feeding amount of catalyst as well as TEOS.

2.4. Transmission electron microscopy analysis

Transmission electron microscopy (TEM, Hitachi HU-11B) was used to determine the particle size of the magnetite and silica-coated magnetite particles. All sampling for size and morphology observation was done by dipping carbon-coated copper grid into sample suspension, subsequently putting them on filter paper to remove excessive solution from the grid, and taking electron micrographs of the particles retained on the film.

2.5. X-ray diffraction analysis

A crystallographic study was performed on the prepared iron oxide powder by rotating anode X-ray diffractometer (Rigaku, Japan) using $\text{Cu K}\alpha$ radiation. The distances between peaks, d , were calculated according to Bragg's law and were compared to the ASTM X-ray diffraction data in order to deduce the crystal structure.

2.6. Vibrating-sample magnetometer analysis

A vibrating-sample magnetometer (VSM, EG&G Princeton Applied Research Vibrating Sample Magnetometer, Model 155, Made in USA) was used at room temperature to study the magnetic properties of magnetite nanoparticles and silica-coated magnetite particles.

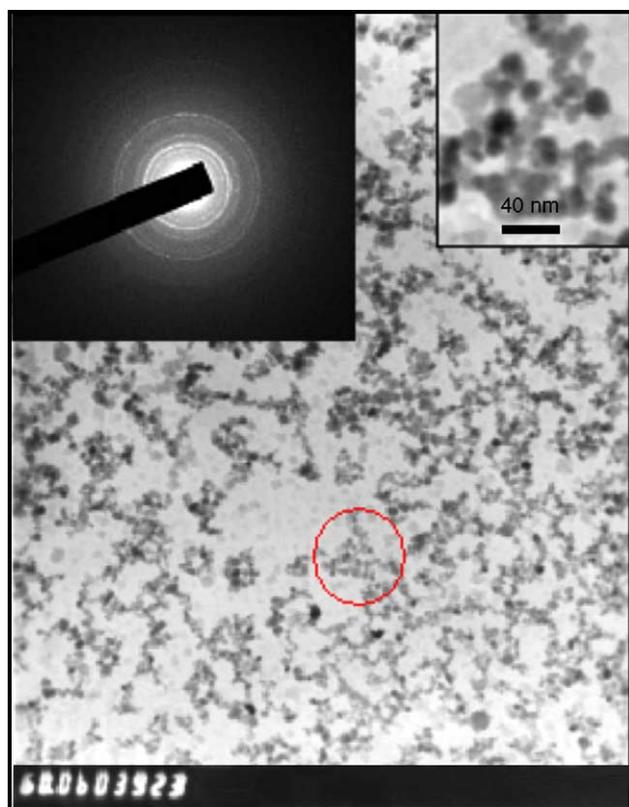


Fig. 1. TEM image and electron diffraction pattern of magnetite nanoparticles (magnification 60k).

3. Results and discussion

3.1. Synthesis of magnetite nanoparticles

Fig. 1 is TEM image and electron diffraction pattern of the synthesized magnetite nanoparticles, which shows that most of the particles are quasi-spherical with an average diameter of 15 nm. Fig. 2 shows the XRD pattern of magnetic nanoparticles. The experimental d spacing obtained from the XRD pattern and ASTM data are listed in Table 1. From Table 1, the experimental data was found similar to the ASTM data cards of the Fe_3O_4 . Based on the d spacing and the preparation method, it can be concluded that the iron oxide particles

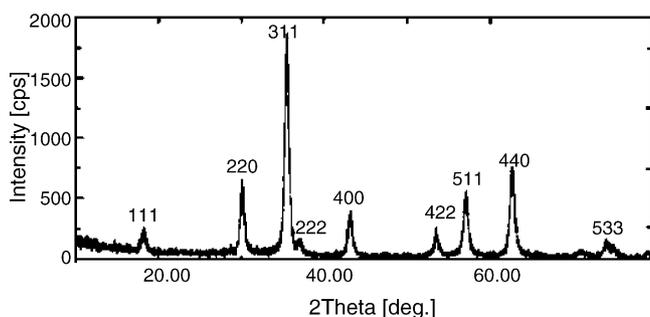


Fig. 2. X-ray diffraction spectrum of the synthesized magnetite.

Table 1

Experimental d (\AA) spacings from X-ray patterns, d (exp) and d spacings from ASTM data cards for iron oxide [Fe_3O_4] synthesized

2θ (exp)	d (exp)	d (Fe_3O_4)
18.300	4.8487	4.852
30.120	2.9668	2.967
35.480	2.5341	2.532
43.120	2.0971	2.0993
57.020	1.6151	1.6158
62.620	1.4838	1.4845

are mainly composed of the inverse cubic spinel structure of magnetite (Fe_3O_4).

3.2. Synthesis of silica-coated magnetite particles

3.2.1. Effect of alcohol type

Together with distilled water, four kinds of alcohol including methanol, ethanol, isopropanol and n -propanol were used as solvents for preparation of silica-coated magnetite particles, and the obtained products were named MS-a, MS-b, MS-c and MS-d, respectively. Except for the type of alcohol, the recipes of each reaction were the same: 2.00 g magnetic fluid, 160 mL alcohol, 40 mL distilled water 5 mL ammonia aqueous, and 1.00 g TEOS. Fig. 3a–d show the TEM images of MS-a, MS-b, MS-c and MS-d, respectively. By comparing these TEM images, it was found that the type of alcohol has great influence on the formation of silica-coated magnetite particle in both coating effect and morphology of the produced particles. With the decrease of polarity of alcohol, i.e. from methanol to ethanol to isopropanol to propanol, the morphology of the obtained silica-coated magnetite particles becomes more irregular, even large clusters of silica-coated magnetite particles were resulted. According to a previous report [15], the polarity of reaction media has effect on the zeta potential of magnetite nanoparticles. Therefore, magnetite nanoparticles with higher zeta potential would disperse more easily and stably, and it is more favorable for preparation of silica-coated magnetite particles with more regular morphology. It is worthy noting that, although silica-coated particles were formed when methanol as alcohol, a large number of small silica particles were also found in the product as shown in Fig. 3a. This is due to the relatively strong polarity of methanol which leads to formation ultrafine silica particles in sol–gel approach [15].

When ethanol was used, as could be seen in Fig. 3b, the prepared silica-coated magnetite particles have relatively uniform dispersion and show typical core-shell structure with a mean diameter of 40 nm. Therefore, to obtain uniformly silica-coated magnetite particles ethanol is seemed to be the best candidate alcohol for the process of coating magnetite nanoparticles in this study.

3.2.2. Effect of volume ratio of ethanol/water ($V_{E/W}$)

According to the report by Stöber, not only the type of alcohol, but also the amount of amount of catalyst

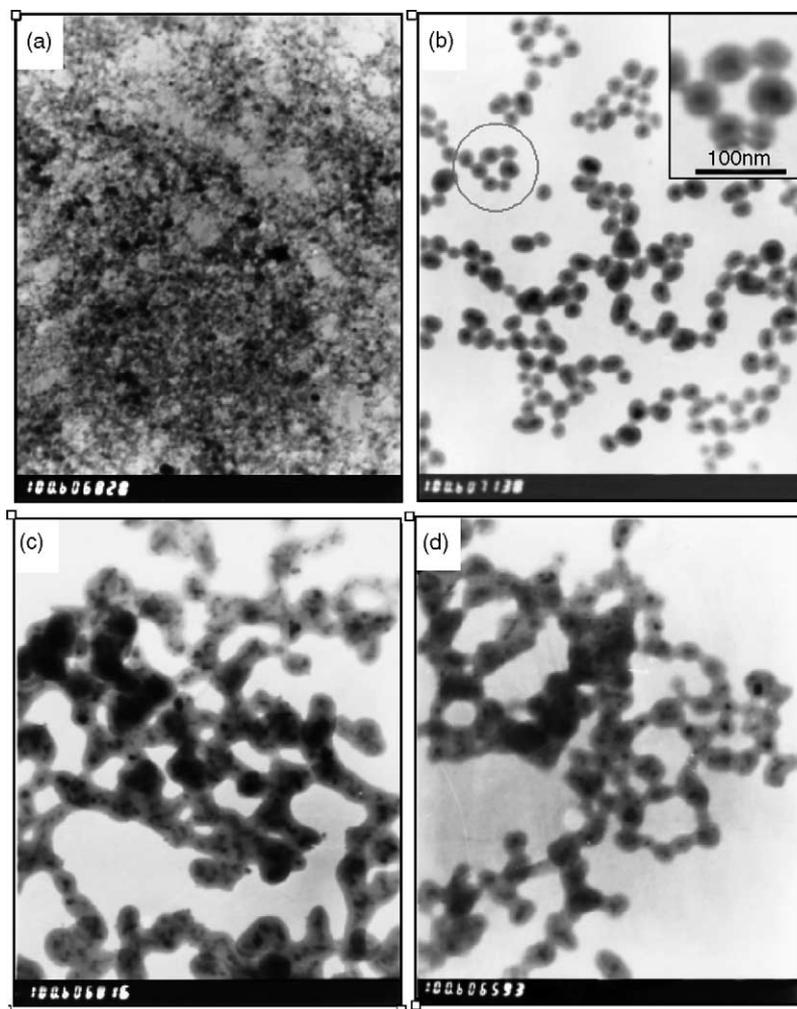


Fig. 3. TEM images of silica-coated magnetite particles (magnification 100k): (a) MS-a obtained in methanol, (b) MS-b obtained in ethanol, (c) MS-c obtained in isopropanol and (d) MS-d obtained in *n*-propanol.

(ammonia) and water play important roles on the formation silica spheres. Hereby, we study the volume ratio of ethanol/water ($V_{E/W}$) on the coating process. The amount of mixture of ethanol and water was 200 mL in total, and the $V_{E/W}$ value was alternated from 1 to 5 while the amounts of magnetic fluid, ammonia aqueous and TEOS still were 2.00 g, 5.0 mL and 1.0 mL, respectively. The obtained products were named as MS-1, MS-2, MS-3, MS-4 and MS-5, respectively. TEM observations show that silica-coated magnetite nanoparticles could form in a large $V_{E/W}$ value range (from 2 to 4), as shown in Fig. 4b–d. However, when this ratio value is lower than 2 or higher than 4, the obtained silica-coated magnetite nanoparticles show irregular morphology (Fig. 4e) and even no composite nanoparticles were obtained, i.e. phase separation happened (Fig. 4a). Although magnetite nanoparticles could disperse in reaction media more easily when larger amount of water is used (i.e. lower $V_{E/W}$ value), silica could not form surround magnetite due to too rapid hydrolysis and condensation of TEOS, resulting in phase separation between seed particle and silica. When

$V_{E/W}$ value is higher than 4, i.e. smaller amount of water was used in the reaction solvent, magnetite nanoparticles could not disperse efficiently in reaction media, leading to formation of irregular silica-coated aggregates of magnetite particles during coating process.

Furthermore, by repeating these reactions and analyzing the TEM images of the produced samples using image analysis system (DMLB/MPS-30/Q500IW, Leica), we found that reaction with a $V_{E/W}$ value of 4 could produce silica-coated magnetite particles with better dispersion and morphology. Consequently, an appropriate $V_{E/W}$ is critical for successful preparation of silica-coated magnetite particles with regular shape.

3.2.3. Effect of the amount of ammonia aqueous

To study the influence of the amount of ammonia aqueous on the formation of silica-coated magnetite nanoparticles in sol–gel process, different amounts of ammonia aqueous including 1.0, 3.0, 5.0, 7.0 and 9.0 mL were used as catalysis and the amount of other reactants were kept constant,

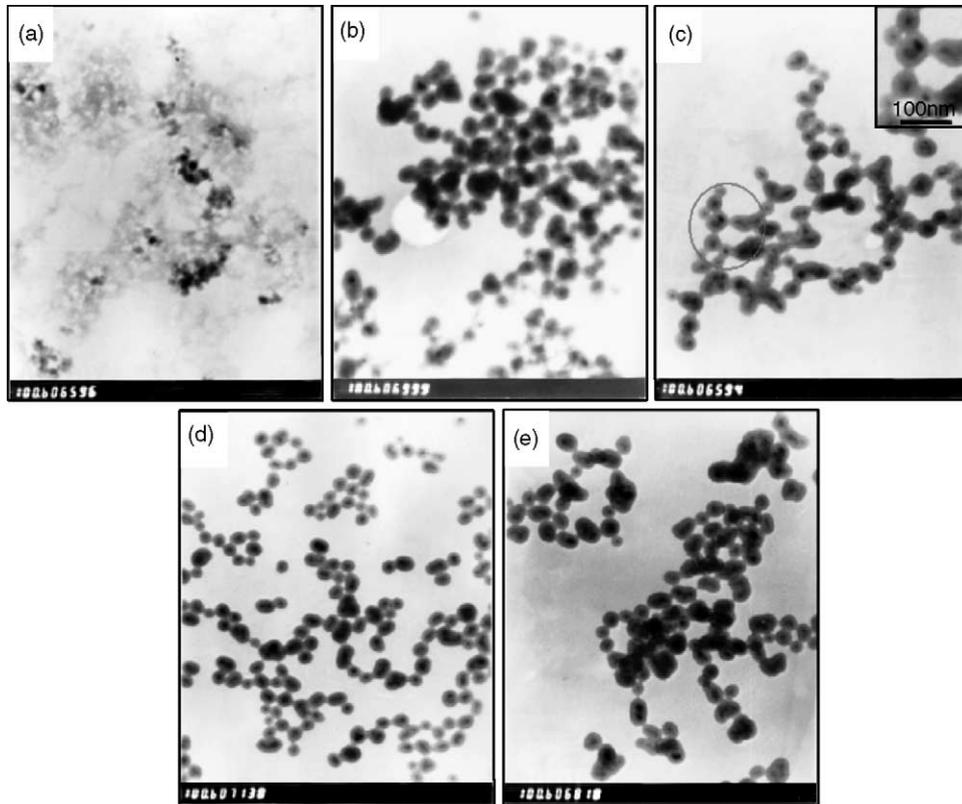


Fig. 4. TEM images of silica-coated magnetite particles (magnification 100k) using ethanol–water mixture with different volume ratio ($V_{E/W}$): (a) MS-1, $V_{E/W} = 1$, (b) MS-2, $V_{E/W} = 2$, (c) MS-3, $V_{E/W} = 3$, (d) MS-4, $V_{E/W} = 4$ and (e) MS-5, $V_{E/W} = 5$.

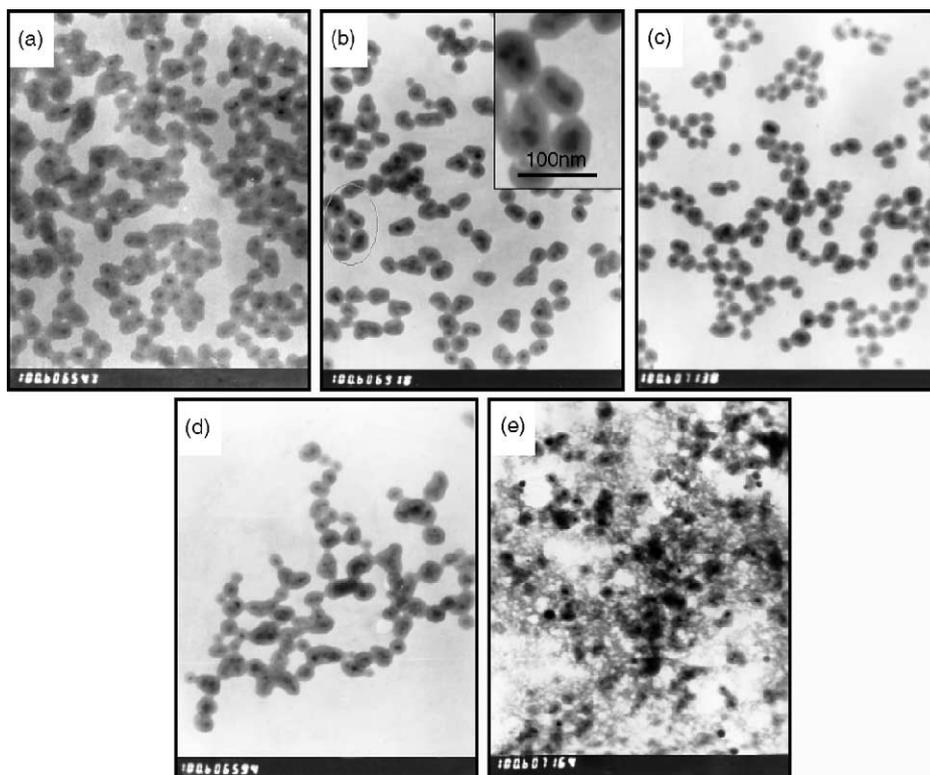


Fig. 5. TEM images of silica-coated magnetite particles (magnification 100k) using different amount of ammonia aqueous (a) MS-I, 1 mL, (b) MS-II, 3 mL, (c) MS-III, 5 mL, (d) MS-IV, 7 mL and (e) MS-V, 9 mL.

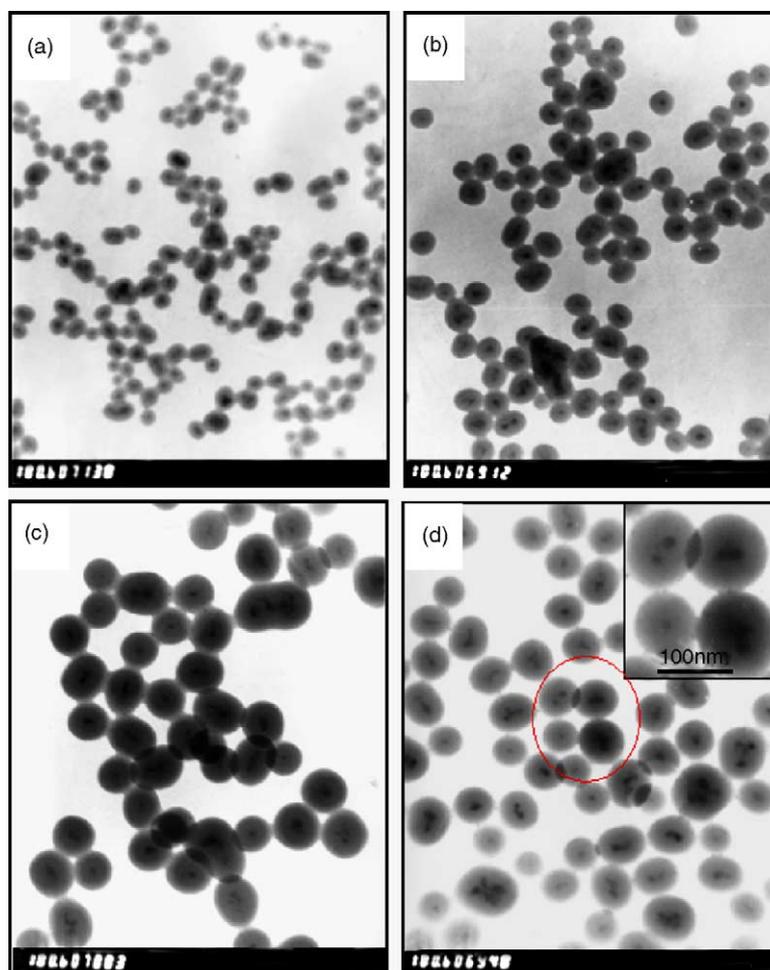


Fig. 6. TEM images of silica-coated magnetite particles (magnification 100k) using different amount of TEOS: (a) 1 mL, (b) 3 mL, (c) 5 mL and (d) 7 mL as precursor.

namely, 2.00 g magnetic fluid, 160 mL ethanol, 40 mL water and 1.0 mL TEOS. The reaction time of all the experiments was 12 h, and the products were named as MS-I, MS-II, MS-III, MS-IV and MS-V, respectively. TEM observation results show that silica-coated magnetite particles could be produced in a large range of amount of ammonia aqueous, i.e. in the range of 1.0–5.0 mL, as shown in Fig. 5a–d. Although the synthesized magnetite particles could easily disperse in the reaction media with higher concentration of ammonia aqueous (e.g. 7.0 mL was used) and silica could form on the surface of magnetite particles, however, tiny magnetite-free silica particles were simultaneously present as a result of rapid hydrolysis of TEOS during coating process as could be seen in Fig. 5e. Hence, to produce magnetic silica particles with high purity, the amount of ammonia aqueous should be controlled to avoid the formation of magnetite-free silica particles.

3.2.4. Effect of the amount of TEOS

As has been reported by Lu et al. [14], the thickness of the silica layer could be controlled by changing the amount of TEOS precursor. In the present study, to mixture con-

taining 2.00 g magnetic fluid 40 mL water, 160 mL ethanol and 5 mL ammonia aqueous different amount of TEOS were added to synthesize silica-coated magnetite particles. TEM images shown in Fig. 6 reveal that the thickness of silica coating on the surface of magnetite nanoparticles increases gradually with the increase of amount of TEOS. Furthermore, with the increase of the thickness of silica layer, silica-coated magnetite particles become more monodispersed as a result of the reduction in the relatively size distribution and global silica-coated magnetite particles were formed.

To study the magnetic properties of magnetite nanoparticles before and after silica coating, silica particles, we registered the hysteresis loops of magnetite nanoparticles and magnetic silica particles of different silica thickness at room temperature using vibrating-sample magnetometer (shown in Fig. 7). The inset of Fig. 7 is the magnetization curve of magnetite nanoparticles, showing superparamagnetic property (i.e. no remanence effect) and saturation magnetization of about 55 emu/g of magnetite nanoparticle. As could be seen from Fig. 7, similar with magnetite nanoparticles, all silica-coated magnetite nanoparticles show superparamagnetic behaviors, indicating that magnetite nanoparticles

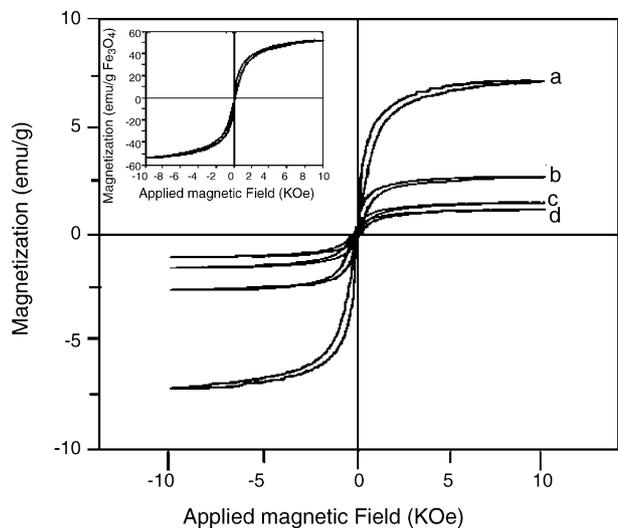


Fig. 7. Hysteresis loops of magnetite nanoparticles (inset) and magnetic silica particles of different silica thickness using different amount of TEOS: (a) 1 mL, (b) 3 mL, (c) 5 mL and (d) 7 mL as precursor.

remained in the composite particles. In addition, the saturation magnetization of the synthesized magnetic silica particles decreases dramatically upon the increase of silica layers, which is consistent with the increasing amount of TEOS for synthesis of the composite particles.

4. Conclusion

A systematic study of the formation of silica-coated magnetite particles via sol–gel approach was made. The results show that the reaction parameters including the type of alcohol, the volume ratio of alcohol/water, the amount of ammonia aqueous and TEOS on the formation of silica-coated magnetite nanoparticles. With the increase of polarity of alcohol, the shape and morphology of silica-coated magnetite particles become more irregular except that poor coating efficiency when methanol was used. Silica-coated magnetite particles with good morphology and shape could be conveniently prepared in a large $V_{E/W}$ range (from 2 to 4). The amount of catalyst (ammonia aqueous) plays important role on the formation of silica-coated magnetite

particles. By increase the amount of precursor (TEOS) larger silica-coated magnetite particles with more regular shape and monodispersed could be produced. VSM characterization shows that both magnetite nanoparticles and magnetic silica particles possess superparamagnetic properties.

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