

Article

Preparation of water-soluble magnetic nanoparticles with controllable silica coating☆

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ABSTRACT

This work provides a general method for preparing monodisperse, water-soluble and paramagnetic magnetic nanoparticles which are easy to be modified. Firstly, magnetic silica with core-shell structure was prepared according to a previous work. Then, the magnetic silica was treated with alkali solution to afford magnetic nanoparticles. With the increase of calcination temperature for the preparation of magnetic silica, the crystallinity and the magnetic responsibility of magnetic silica strengthened, meanwhile, the corresponding magnetic nanoparticles kept monodisperse without any aggregation. The magnetic nanoparticles are comprised of cobalt ferrite and a silica coating. The silica coating on the cobalt ferrite facilitates the magnetic nanoparticles well-dissolved and monodisperse in water, and easily modified.

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1. Introduction

Magnetic nanoparticles have attracted a great attention in various fields due to magnetic responsibility [1,2]. For the application of magnetic nanoparticles in biomedical field or other hydrophilic system, such as forward osmosis system and food inspection, good dispersibility in water is essential [3–6]. High performance of magnetite nanoparticles is also required, including surface chemistry suitable for further functionalization, suitable size with uniform dispersion and high magnetization.

Many strategies have been explored to synthesize highly water-dispersible superparamagnetic magnetite nanoparticles. Co-precipitation is a common and simple route for synthesis of nanoparticles [7–9]. Mauricio *et al.* [10] prepared highly hydrophilic magnetic nanoparticles of Fe_3O_4 using a co-precipitation approach of Fe^{2+} and Fe^{3+} ions in a basified aqueous solution. However, serious agglomeration of pristine nanoparticles was found. Thermal-decomposition method has been widely researched for synthesis of monodisperse magnetic nanoparticles. But harsh conditions and expensive chemicals hinder the extensive application of the method [11,12].

Sol-gel method [13,14], microemulsion with oil in water micelles [15, 16] or reverse micelles [17] and hydro/solvent-thermal process [18] have been used to prepare magnetic nanoparticles. The sol-gel method enables to control the reaction rate and provides a way to control the size and surface properties of nanoparticles. Microemulsions are thermodynamically

stable colloidal dispersions in which two immiscible liquids (typically water and oil) coexist in one phase due to the presence of a monolayer of surfactant molecules with balanced hydrophilic-lipophilic properties [19–21]. Uniform nanoparticles with narrow particle size distribution could be prepared in microemulsion system. Magnetic nanoparticles prepared via a solvent-thermal process always possess complete crystallinity. In our previous work, magnetic $\text{SiO}_2/\text{CoFe}_2\text{O}_4$ (SCF) with core-shell structure had been prepared via a reverse microemulsion-mediated sol-gel method. The prepared SCF consist of silica matrix and uniformly dispersed cobalt ferrite nanoparticles [22]. It is of great interest to find that magnetic CoFe_2O_4 nanoparticles could be extracted from silica matrix with a thin silica coating left on the surface. The silica coating could be controlled and would supply magnetic nanoparticles with rich hydroxyl groups and remarkable biocompatibility [23,24]. Compared with the magnetic nanoparticles modified by post surface modification with silane agents, the obtained magnetic nanoparticles with controllable silica coating could avoid the agglomeration caused by the post modification.

In this work, CoFe_2O_4 nanoparticles (CFNPs) were prepared by alkali treatment of SCF. The crystallinity, monodispersity, magnetism and water-solubility of the CFNPs were investigated in detail. And the relationship between these performances and the surface structure of CFNPs was discussed.

2. Experimental

2.1. Materials and reagents

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, *n*-hexane, acetone, sodium hydroxide, ethanol, hydrochloric acid and tetraethoxy silicane (TEOS) were analytically pure

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and purchased from Beijing Chemical Works. Triton X-100, *n*-hexanol, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and methylamine solution were analytically pure and purchased from Sinopharm Chemical Reagent Co. Ltd. Water used in the experiments was de-ionized.

2.2. Preparation of magnetic nanoparticles

Uniform magnetic nanoparticles were prepared via alkali treatment of the magnetic silica with core-shell structure which was prepared according to the procedure reported in prior works using a reverse microemulsion-mediated sol-gel method [25,26].

Firstly, a reverse microemulsion with CoFe_2O_4 precursors was synthesized through a double-microemulsion method as illustrated in Fig. 1. Then a TEOS solution of *n*-hexane was added into the reverse microemulsion. With the diffusion of TEOS molecules from hydrophobic phase into hydrophilic phase, TEOS hydrolyzed and condensed around the CoFe_2O_4 precursors. A following solvent-thermal process was applied for promoting the further condensation of TEOS. The product was washed with ethanol, and calcined under air atmosphere to form magnetic silica.

For leaching of silica, the magnetic silica was added into an aqueous solution of NaOH, and stirred at 60 °C for some time to remove silica shell. Then, excess NaOH was neutralized with HCl aqueous solution. Finally, after multiple washing with water to remove the formed sodium salts, magnetic nanoparticles homogeneously dispersed in water were obtained.

2.3. Sample characterization

FTIR analysis was carried out on a NICOLET iS10 Fourier transform infrared spectrometer (Thermo, America) in a frequency ranged from 400 cm^{-1} to 4000 cm^{-1} using KBr as a reference. Thermal analysis was performed on a TG-DTA 6200 (SII Nano Technology Inc., Japan), with a heating rate of $10\text{ °C} \cdot \text{min}^{-1}$ from room temperature to 700 °C. XRD was collected on an Ultima IV X-ray diffractometer (Rigaku, Japan) with $\text{Cu K}\alpha$ radiation. TEM observation was performed on a JEM-2100 transmission electron microscope (JEOL, Japan). Particle size and zeta potential analysis of particles was conducted using a Beckman Coulter DelsaTM Nano C Zeta potential & particle size analyzer. Magnetism analysis was performed on a JLDJ 9600 vibrating sample magnetometer (VSM, LD, America).

3. Results and Discussion

3.1. Crystallinity and monodispersity

Calcination is indispensable for the removal of volatiles and the formation of ferrite. Thermal analysis of SCF as synthesized was carried out and the result was displayed in Fig. 2. A notable mass loss, which corresponded to a broad exothermic peak from 100 °C to 400 °C, was caused by the volatilization of water and organic solvents. The following endothermic peak accompanied with a light mass loss between 400 °C and 600 °C was caused by the formation of cobalt ferrite phase. Generally, calcination at higher temperature induced higher degree of crystallinity and stronger magnetic responsibility. Here, SCF samples calcined at 500 °C, 550 °C, 600 °C, 650 °C and 700 °C were prepared and characterized. Fig. 3 displayed the XRD patterns of these samples. As shown in the XRD patterns, the peaks at 35.44° , 43.06° , 56.97° and 62.59° were indexed to the 311, 400, 511 and 440 planes of cobalt ferrite (JCPDS PDF#22-1086), respectively. Additionally, the intensity of the characteristic peaks increased with the increase of the calcination temperature.

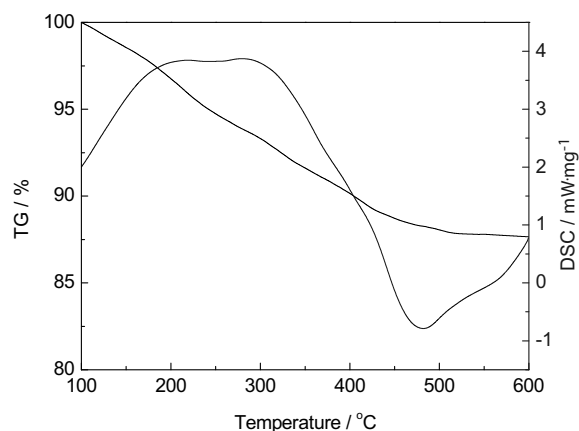


Fig. 2. TG-DSC curves of SCF as synthesized.

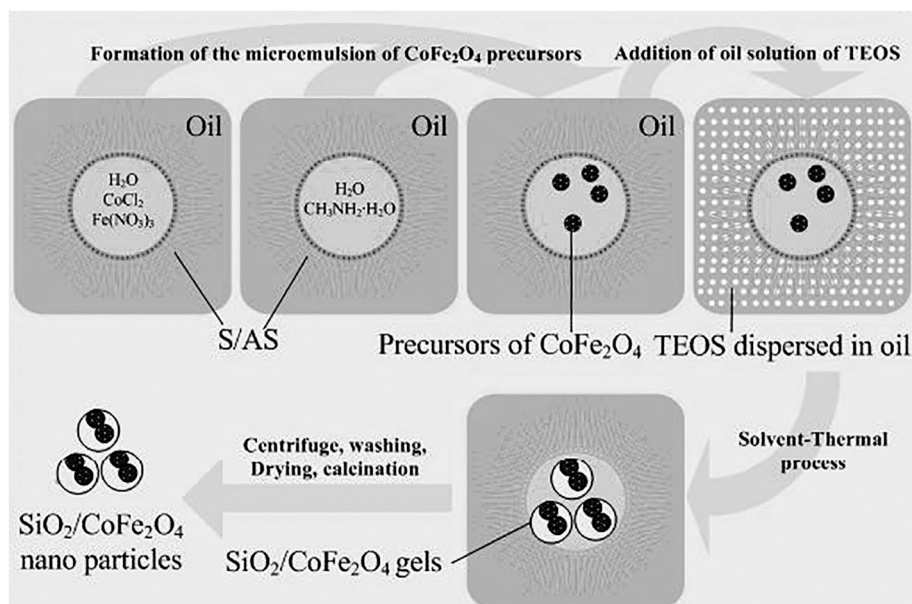


Fig. 1. Preparation process of magnetic silica.

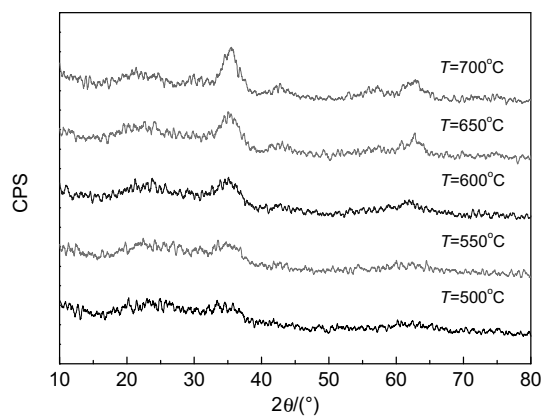


Fig. 3. XRD patterns of SCF samples calcined at different temperature.

Then, the five samples were treated with NaOH aqueous solution ($3 \text{ mol} \cdot \text{L}^{-1}$) at 60°C for 24 h to afford magnetic nanoparticles. Fig. 4 showed the TEM images and histograms of the magnetic nanoparticles. As shown in Fig. 4, the average size of the magnetic nanoparticles increased slightly from 5 nm to 8 nm as the calcination temperature increased from 500°C to 700°C . In addition, all of the five samples were monodisperse, which proved the protection effect of silica shell on the ferrite core. Particle size distribution of CFNPs measured by particle size analyzer was illustrated in Fig. 5, and the average size of the magnetic nanoparticles increased slightly from 13 nm to 15 nm with calcination temperature increase, and the monodispersity was further proved. In conclusion, high calcination temperature favored the growth of cobalt ferrite crystal, and silica matrix prevented the sintering of nanoparticles.

3.2. Magnetism and water-solubility

The five SCF samples mentioned above were characterized by VSM, and the result was listed in Table 1. It is suggested that the M_s values

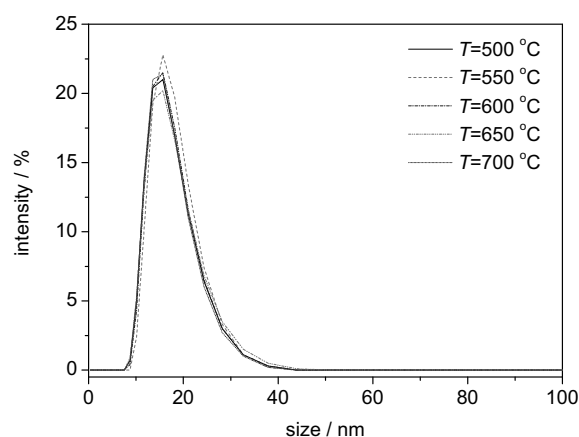


Fig. 5. Particle size distribution of CFNPs.

Table 1
Magnetic properties of SCF samples calcined at different temperature

Sample	$T/^\circ\text{C}$	$M_s/\text{emu} \cdot \text{g}^{-1}$	$M_r/\text{emu} \cdot \text{g}^{-1}$	Coercivity/G
1	500	1.314	0.027	0.000
2	550	2.651	0.030	20.000
3	600	3.988	0.047	33.000
4	650	6.040	0.057	24.000
5	700	8.296	0.067	15.000

of the SCF samples increased from $1.314 \text{ emu} \cdot \text{g}^{-1}$ to $8.296 \text{ emu} \cdot \text{g}^{-1}$ with the increase of the calcination temperature from 500°C to 700°C . Thus, the magnetic nanoparticles which were obtained from the SCF calcined at 700°C were investigated in detail. As the XRD pattern shown in Fig. 6, the peaks at 35.44° , 43.06° , 56.97° and 62.59° indexed to the 311, 400, 511 and 440 planes of cobalt ferrite phase, respectively, proved that the structure of the cobalt ferrite was not destroyed in alkali treatment process. The hysteresis loop of CFNPs shown in Fig. 7

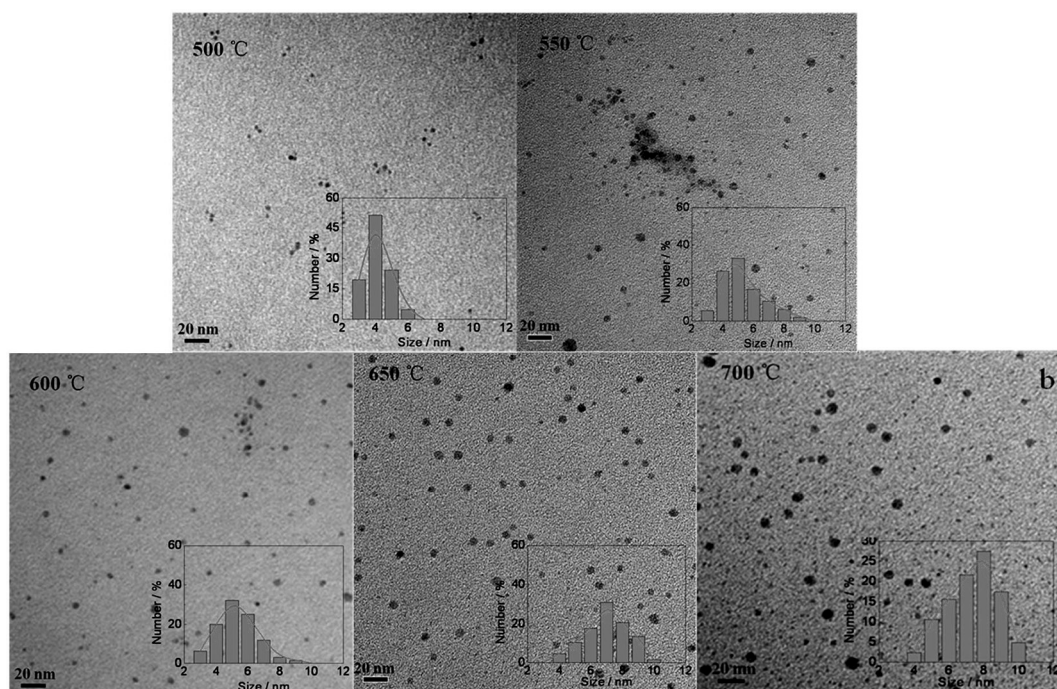


Fig. 4. TEM images and histograms of CFNPs.

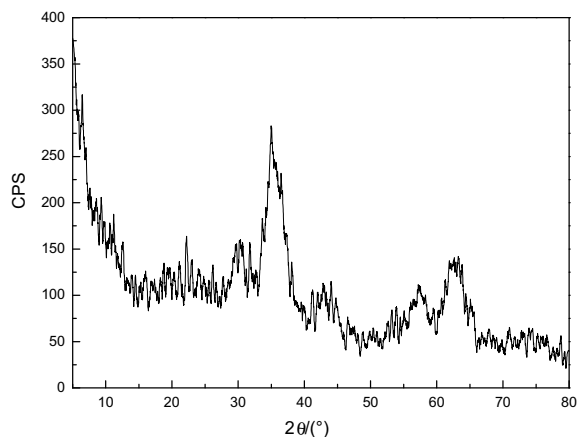


Fig. 6. XRD pattern of CFNPs.

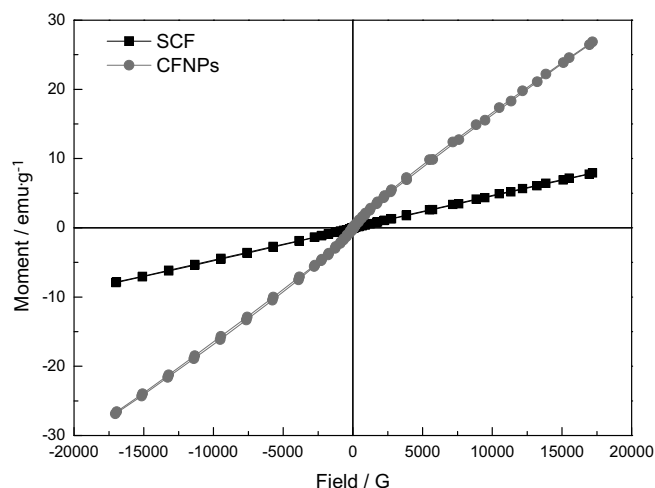


Fig. 7. Magnetic hysteresis loops of SCF and CFNPs.

indicated that CFNPs were paramagnetic, and the M_s and M_r of CFNPs were $26.8596 \text{ emu} \cdot \text{g}^{-1}$ and $0.0951 \text{ emu} \cdot \text{g}^{-1}$, respectively. It is obviously observed from Fig. 8-a that the obtained CFNPs could be easily homogeneously dispersed in water. When an extra magnetic field was applied on the right side of the bottle, CFNPs swam to the right bottle wall (Fig. 8-b). With the prolonging of time, more and more CFNPs assembled on the right bottle wall, and almost all of CFNPs were separated from water after 5 h (Fig. 8-e). In summary, the magnetic nanoparticles are paramagnetic and well-dissolved in water, and could be easily separated from water in an external magnetic field.

3.3. Surface structure of CFNPs

The water solubility and monodispersity of the magnetic nanoparticles are closely related to their surface structure. For studying their surface structure, CFNPs were characterized by FTIR and the result was shown in Fig. 9. The absorption peaks at 590 cm^{-1} and 1100 cm^{-1} were assigned to the M—O vibration ($M=\text{Fe}$ or Co) and the symmetric O—Si—O stretching vibrations, respectively [22]. It indicated that there was a silica coating on the CFNPs surface.

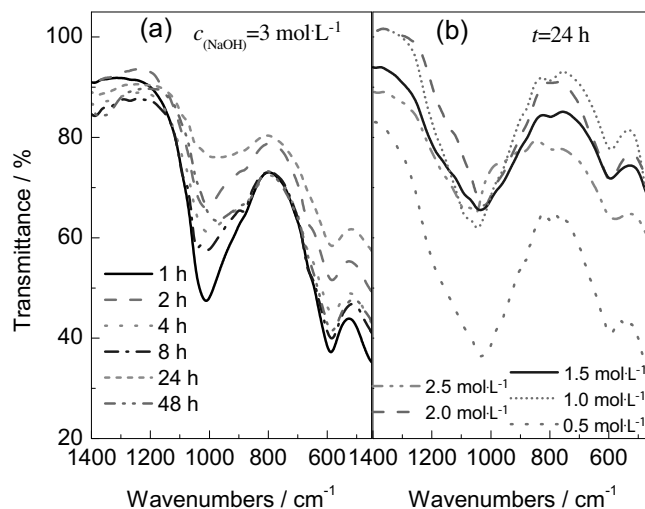


Fig. 9. FTIR of CFNPs.

Usually, nanoparticles are apt to aggregate and form bulky grain. In this work, the magnetic nanoparticles kept monodisperse in water. The silica coating on the cobalt ferrite contains abundant hydrophilic silanol groups, which attract numerous water molecules in water. The hydrophilic silanol groups and the solvation of the nanoparticles facilitate the CFNPs well-dissolved and monodisperse in water. Zeta potential of CFNPs in water was also tested and the value is $(-32 \pm 2.34) \text{ mV}$ at $\text{pH} = 7$, also indicating the stable dispersity of CFNPs in water.

In addition, the silica coating rendered easy surface-modification of the CFNPs because silanol groups could react with many organic groups, such as hydroxyl [27] and carboxyl [28].

Finally, the leftover amount of silica coating on CFNPs was further regulated by altering the alkali concentration and alkali treating time. The relative amount of leftover silica compared with cobalt ferrite was represented by the relative peak area of the two characteristic peaks at 1100 cm^{-1} and 590 cm^{-1} in FTIR spectra. The result was listed in Table 2. When the samples were treated using alkali solution with high concentration or treated for long time, the peak area ratio of 1100 cm^{-1} to 590 cm^{-1} went down, which indicated that the leftover amount of silica reduced.

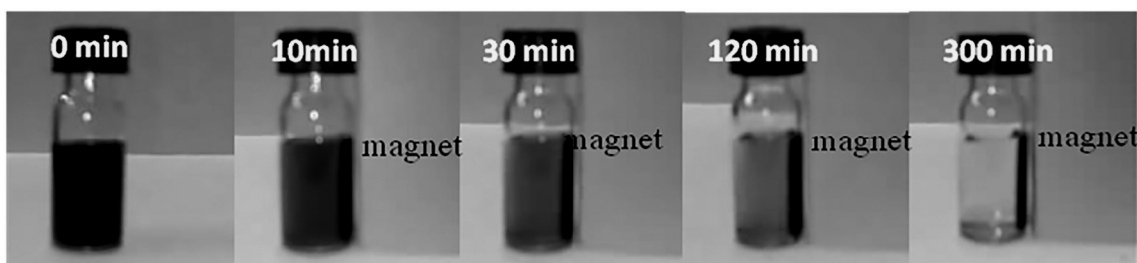


Fig. 8. Magnetic separation performance of CFNPs dispersed in water under magnetic field.

Table 2

Relative area of the two characteristic peak of CFNPs

Sample	$c(\text{NaOH})/\text{mol} \cdot \text{L}^{-1}$	Time/h	Area		A/B
			A-1100 cm^{-1}	B-590 cm^{-1}	
1	3.0	1	64.510	25.964	2.485
2	3.0	2	38.686	17.723	2.183
3	3.0	4	37.002	17.661	2.095
4	3.0	8	43.258	26.487	1.633
5	3.0	24	15.915	14.444	1.102
6	2.5	24	55.993	18.628	3.006
7	2.0	24	35.179	8.192	4.294
8	1.0	24	65.329	13.105	4.985

In summary, the magnetic nanoparticles prepared in this work were composed of cobalt ferrite and silica. The silica layer on the cobalt ferrite facilitates the CFNPs well-dissolved and monodisperse in water, and easily modified. The leftover amount of silica could be controlled by tuning the alkali treating time and the alkali concentration.

4. Conclusions

Magnetic silica with core-shell structure was prepared using a reverse microemulsion-mediated sol-gel method. Alkali treatment of the magnetic silica afforded magnetic nanoparticles which was well-dissolved and monodisperse in water. High calcination temperature for the preparation of magnetic silica favored the growth of the cobalt ferrite crystal and the enhancement of the magnetic responsibility. Silica matrix prevented the sintering of the magnetic nanoparticles, and obtained magnetic nanoparticles are monodisperse. The CFNPs were composed of cobalt ferrite and a silica layer, and the leftover amount of silica could be controlled by tuning the alkali treating time and the alkali concentration. The silica layer on the cobalt ferrite facilitates the CFNPs well-dissolved and monodisperse in water, and easily modified, due to the hydrophilicity of the silanol groups, the solvation of the nanoparticles and reactivity of silanol groups with other groups. In other words, this work supplies a general method for preparing monodisperse, water-soluble, paramagnetic, highly-magnetized and easily-modified magnetic nanoparticles.

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