

Preparation of Fe (core)/SiO₂ (shell) composite particles with improved oxidation-resistance

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Abstract

The preparation of silica coated iron particles with improved oxidation-resistance was described in the paper. XRD, TEM and XPS were used to characterize the product, which indicated that a thin film of silica was coated on the surface of Fe particles through a silica–oxide–iron bond. The content of silica to iron in the sample was quantitatively determined by ICP. Magnetic measurements results of the particles almost kept constant before and after coating process. DTA and TG results showed that the coating shell of silica could effectively protect the Fe cores from oxidation.

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1. Introduction

Nanosized magnetic metals such as Fe, Co and Ni exhibit unique properties and applications in a range of fields, such as data storage technology, magnetocaloric refrigeration, contrast enhancement in magnetic resonance imaging, and magnetically guided drug delivery in biomedicine [1]. But the properties of easy oxidation and aggregation usually limited their applications [2]. A good way to conquer the limitations is encapsulating them in inorganic materials, which could effectively protect them from oxidation and reduce the dipole interaction. Furthermore, the coating could provide the nanomagnets with several other benefits such as compatibility in biological system, functionality and high suspension stability under different solution [3]. Reasons that easy control of the deposition process, controllable porosity and optical transparency, make silica an ideal, low-cost material to tailor the surface properties, while basically maintaining the physical integrity of the underlying core nanocrystals [3]. Customarily, silica coating of oxides can be easily performed, which binds to the silica through OH surface groups. However, silica deposition on pure metal particles is more complicated because of the lack of OH groups on the metal surface [4]. To overcome this difficulty, surfactant was usually added to make the surface “vitrophilic”, but this may introduce new

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impurities to the composites [5]. Currently, the coating of magnetic metal particles without any additional organic molecules is still challenging.

Iron particles have been attracting great attention for their wide applications and low cost [6]. Recently, we reported the preparation of iron nanoparticles through a simple hydrazine reduction method [7]. However, its applications were likewise much limited for ready oxidation. In this paper, we coated iron crystallites with a thin film of silica, which can effectively protected the iron cores from oxidation.

2. Experimental

All the reagents were all analytical grade and used without further purification. Iron nanoparticles were prepared by the method reported previously by our group [7]. In a typical procedure, 4.0 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 20 ml ethanol, then 10.0 g NaOH and 10.0 ml hydrazine hydrate (80%) was added. The mixture was stirred to uniformity and subsequently transferred into a stainless autoclave, sealed and maintained at 80 °C for 10 h. The obtained black powders were collected, purified with distilled water and ethanol, and then vacuum dried at 60 °C for 4 h.

The coating of silica shell is realized through the well-known stöber method. In a typical experiment, iron powder was dispersed in ethanol in an ultrasonic bath. Then the solution was refluxed at 40 °C in a three-necked round bottom flask equipped with a condenser, a stirring bar and a thermometer. After the temperature was stabilized, predetermined volumes of TEOS were added to the dispersion at a continuous stirring rate of 600 rpm. Subsequently, ammonia was injected to adjust pH of the solution at 8–9. Three samples were prepared with the molar ratio of TEOS to Fe as 1/5 (sample 1), 1/1 (sample 2) and 10/1 (sample 3), respectively. After the reaction was completed, the product was collected and vacuum dried at 50 °C for 4 h.

X-ray diffraction (XRD) patterns of the samples were conducted on a Philips X'pert diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). Transmission electron microscopy (TEM) images were recorded with a Hitachi Model H-800 transmission electron microscope. X-ray photoelectron spectroscopy (XPS) was studied on a VG ESCALAB MK apparatus with Mg (K α) X-ray (energy = 1486.6 eV). The content of the samples was determined with inductively coupled plasma atomic emission spectrometer (ICP-AES) made by Thermo Janell Ash Corporation. Their magnetic properties at room temperature were investigated using a vibrating sample magnetometer. The thermal degradation of the dried product was examined by a Perkin-Elmer TGA-7 at a heating rate of 10 °C/min under air atmosphere with a flow rate of 25 ml/min.

3. Results and discussion

XRD patterns of the three samples (1–3) were shown in Fig. 1. In all the patterns, three sharp peaks located at $2\theta = 44.6^\circ$, 61.2° and 82.4° were observed easily, which could be assigned to body-centered cubic (bcc) iron.

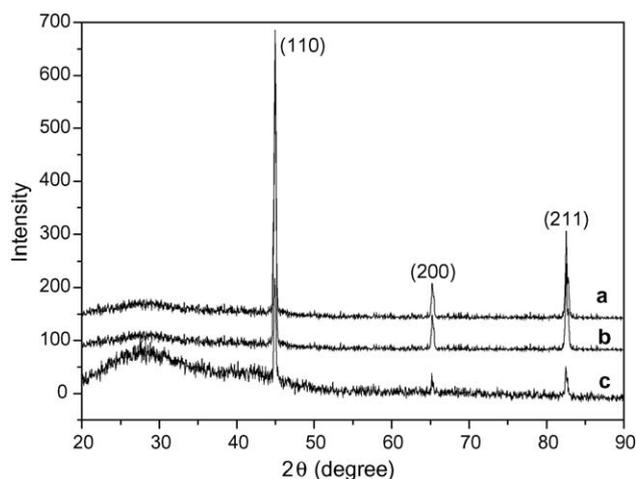


Fig. 1. XRD patterns of the samples prepared at different ratios of TEOS/Fe: (a) 1:5, (b) 1:1, (c) 10:1.

Meanwhile, a broad peak centered around 21.0° appeared, which was due to amorphous silica. From patterns 1 to 3, the relative intensity of the peak of silica to that of iron was increased, which implied an increasing content of silica from samples 1 to 3. However, only the XRD results cannot determine whether the samples were the mixture of SiO_2 and Fe powders or Fe@SiO_2 particles, and further characterizations were required.

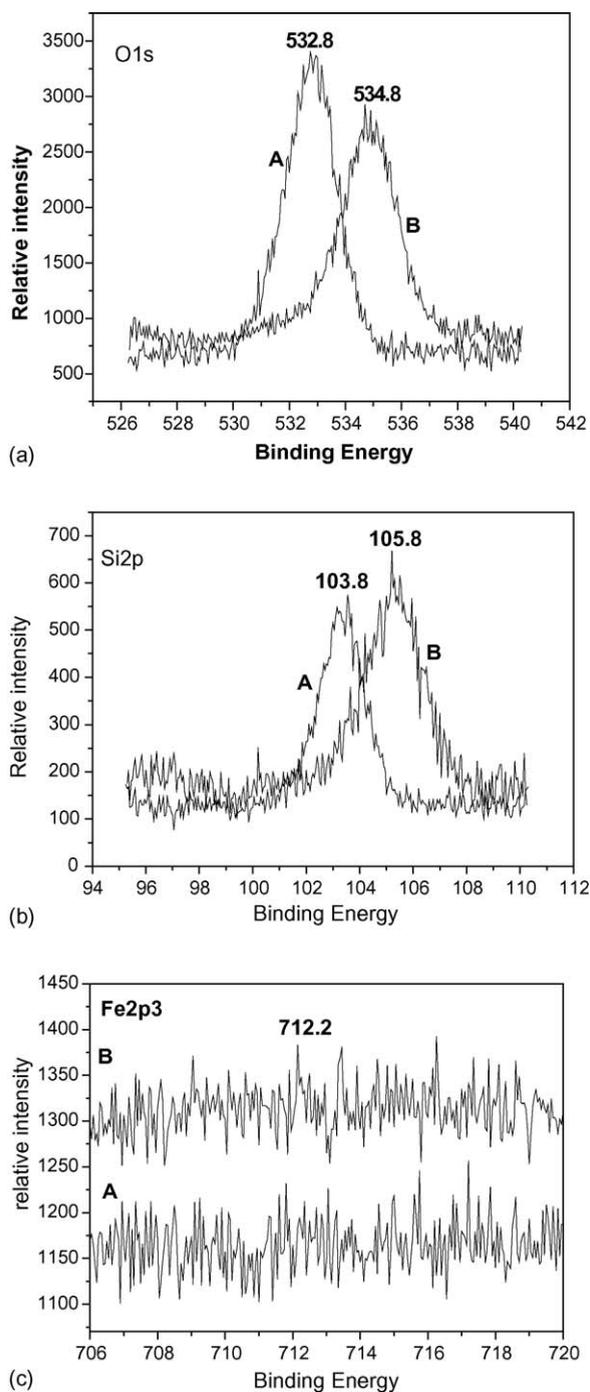


Fig. 2. (a) The O 1s region of the XPS spectrum of sample 2: (A) before Ar^+ abrasion, (B) after 7 min Ar^+ abrasion; (b) the Si 2p region of the XPS spectrum of sample 2: (A) before Ar^+ abrasion, (B) after 7 min Ar^+ abrasion; (c) the Fe 2p3 region of the XPS spectrum of sample 2: (A) before Ar^+ abrasion, (B) after 7 min Ar^+ abrasion.

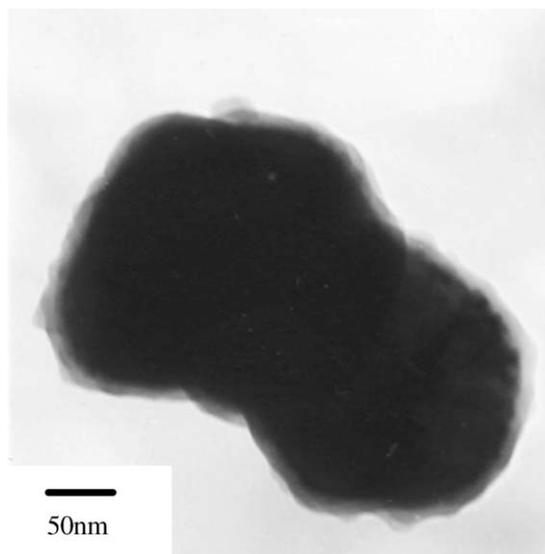


Fig. 3. A typical TEM image of sample 2.

As XPS is a powerful tool to characterize the material surface, we turned to XPS to analyze the surface elements of the samples. A typical spectrum of sample 2 was given in Fig. 2, showing peaks of Si 2p (103.4 eV) and O 1s (532.8 eV) (seen in Fig. 2(a) and (b)). No characteristic peak of iron was observed (Fig. 2(c)), indicating that the metallic iron particles had been coated by silica [8]. The corresponding TEM image visually revealed this core-shell structure, as seen in Fig. 3. XPS spectra of samples 1 and 3 were essentially the same with Fig. 2, showing that all the three samples were SiO₂-coated Fe particles, not the mixture of Fe and SiO₂ particles.

To further investigate the coated structure, Ar⁺ abrasion was taken on the sample 2 for 3 min, and the peak of iron still cannot be detected, showing a relative compact and thick coating of silica. When the Ar⁺ abrasion was prolonged to 7 min, a weak peak of core Fe 2p_{3/2} (712 eV) appeared in the spectra of coated particles (Fig. 2(c)), which could be assigned to FeO_x. This result revealed the presence of a very thin film of iron oxides on the surface of the iron powders, which may result from a slight inevitable surface oxidation during the process of cleaning and dryness. The loose layer of iron oxides could not well protect iron from further oxidation for its loose structure, however, it was essential for the successful coating in the absence of any surfactants. Generally, in the absence of any surfactants, the pure metallic iron surface was vitreophobic, which made the interaction between silica and the metallic particles difficult. However, the thin layer of surface oxides modified the particle surface into vitreophilic, which made the attachment of silica on iron much easier through the OH surface groups [4]. Compared with that of the sample before Ar⁺ abrasion, a chemical shift of 2 and 3 eV was observed for the peak position of Si 2p and O 1s, respectively. Such results indicated that some chemical bond of Si–O–Fe was formed between the silica shell and iron cores. This chemical bond was believed responsible for the compact coating of silica on iron particles [8].

The content of Fe in the samples was qualitatively determined by ICP, and the results were shown in Table 1. The increasing content of silica from samples 1 to 3 indicated an increasing thickness of silica shell. However, the ratio of silica to iron in all the three samples was found higher than that of TEOS to iron. Such a difference was possibly due to

Table 1
The element compositions of the three samples determined from ICP analysis

	Samples		
	Sample 1	Sample 2	Sample 3
Atomic ratio of Si/Fe (raw materials)	1:5	1:1	10:1
Atomic ratio of Si/Fe (ICP results)	1:9	1:5.6	1:2
SiO ₂ wt. %	7.35	11.31	26.3

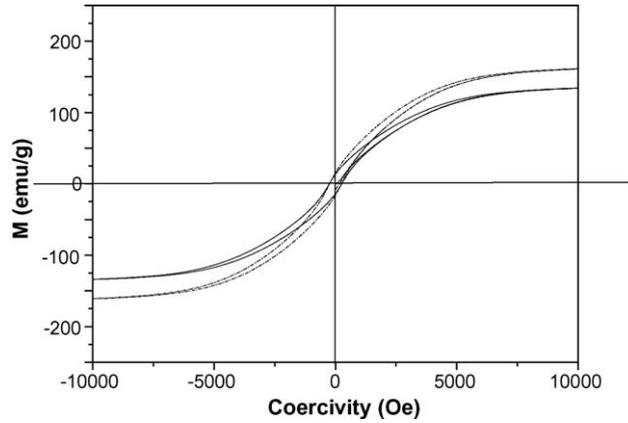
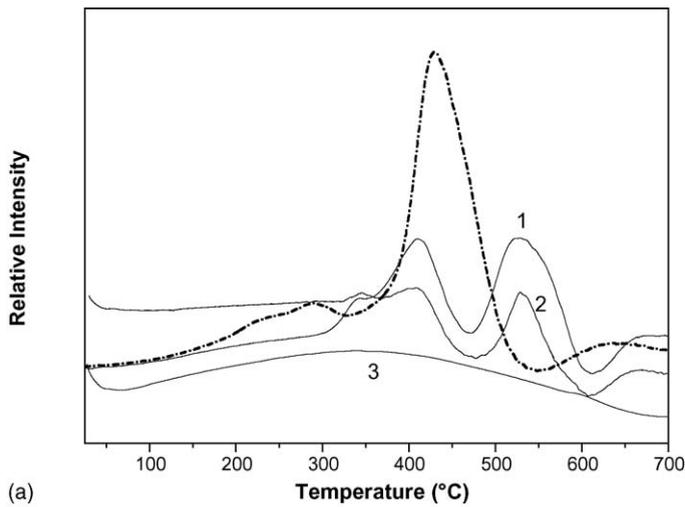
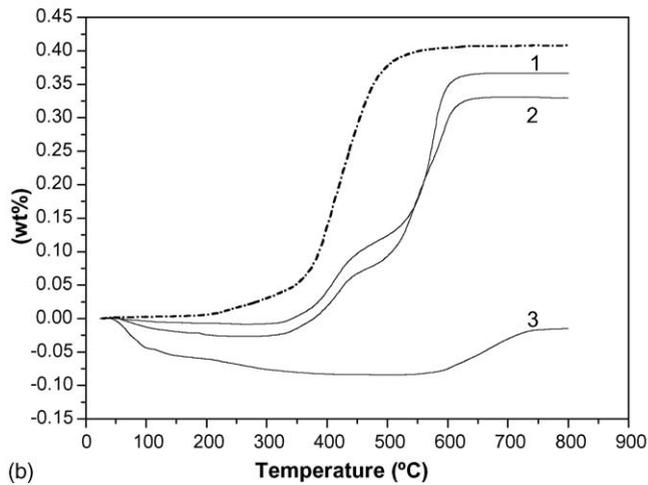


Fig. 4. Magnetic hysteresis loop of the sample 2 (solid) and the uncoated iron powder (dash dotted).



(a)



(b)

Fig. 5. (a) The DTA-TG spectra of the three samples different molar ratios of TEOS/Fe: (1) sample 1, (2) sample 2, (3) sample 3; the curve with dotted dash was that of the uncoated particles; (b) the DTA-TG spectra of the samples with different molar ratios of TEOS/Fe: (1) sample 1, (2) sample 2, (3) sample 3; the curve with dotted dash was that of the uncoated particles.

Table 2

Positions of the exothermal peaks of the three samples and the uncoated iron powder from DTA analysis

	Exothermal peaks		
	I (°C)	II (°C)	III (°C)
Uncoated iron particles	280	420	620
Sample 1	340	520	670
Sample 2	342	527	676
Sample 3	350	–	–

the loss of the core-free silica particles in the experiments. Practically, it was unavoidable for the formation of some core-free silica particles during the hydrolyzation of TEOS [9]. But, in the following rinsing procedure by magnetic decantation, these nonmagnetic particles would be rejected, eventually led into the decrease of the composition of silica in the product.

Magnetic properties of the silica coated iron particles were studied. Fig. 4 presented the magnetic hysteresis loops of sample 2 (solid) and the uncoated iron powder (dash dotted) at room temperature in an applied field of 10k Oe. Compared with that of the uncoated iron particles, coercivity of the Fe@SiO₂ composite particles nearly kept constant of about 250 Oe. However, a little reduction of saturation magnetism (Ms) was observed in the coated samples relative to pure metallic iron particles. The decreased Ms should be attributed to the interaction between the iron cores with the silica shell, which reduced the total magnetic moments. A similar reduction of Ms was also reported in the cobalt and magnetite based core-shell nanostructures [10,11].

The properties of oxidation-resistance of the samples were tested by TG-DTA. Fig. 5(a) and (b) showed the DTA-TG curves of the above three samples and the uncoated iron particles, respectively. It was shown that the three exothermal peaks of iron were all delayed 40–100 °C behind (seen in Table 2). In the sample 3, even no obvious sharp peaks appeared when the temperature ascended to 800 °C, indicating an excellent resistance to oxidation. Correspondingly, the weight increment of the coated particles decreased from 30 to 5% relative to that of the metallic iron particles. It is clear that a thicker shell of silica can protect the iron from oxidation more effectively.

4. Conclusion

In summary, amorphous silica coated iron particles with controlled thickness have been synthesized via a simple method. The thickness of the silica shell was varied with original molar ratios of TEOS to iron powder, which was determined by ICP characterizations. The chemical shift of Si 2p and O 1s peak in the coated particles revealed that the coating of SiO₂ on Fe particles was realized through some chemical bond of Si–O–Fe. Magnetic properties of the particles before and after coating process were discussed. The results showed that the coercivity of iron particles changed little after the coating process. TG and DTA curves indicated that the ability of oxidation-resistance of as-prepared composite particles increased with the promotion of the thickness of silica shell.

References

- [1] M.F. Casula, A. Corrias, G. Paschina, *J. Mater. Chem.* 12 (2002) 1505–1510.
- [2] L.M. Liz-Marzan, P. Mulvaney, *J. Phys. Chem. B* 107 (30) (2003) 7312–7326.
- [3] V.V. Hardikar, E. Matijevic, *J. Colloid Interface Sci.* 221 (2000) 133–136.
- [4] G. Liu, G. Hong, Duocian, *Sun Powder Technol.* 145 (2004) 149–153.
- [5] Q. Liu, Z. Xu, J.A. Finch, R. Egerton, *Chem. Mater.* 10 (1998) 3936–3940.
- [6] F.G. Aliev, M.A. Correa-Duarte, A. Mamedov, J.W. Ostrander, M. Giersig, L.M. Liz-Marzan, N.A. Kotov, *Adv. Mater.* 12 (1999) 1006–1009.
- [7] X. Ni, X. Su, H. Zheng, D. Zhang, D. Yang, Q. Zhao, *J. Cryst. Growth* 275 (2005) 548.
- [8] H. Cui, G. Hong, X. Wu, Y. Hong, *Mater. Res. Bull.* 37 (2002) 2155–2163.
- [9] E. Mine, A. Yamada, Y. Kobayashi, M. Konno, L.M. Liz-marzan, *J. Colloid Interface Sci.* 264 (2003) 385–390.
- [10] J.P. Chen, C.M. Sorensen, K.J. Klabunde, G.C. Hadjipanayis, *Phys. Rev. B* 51 (1995) 11527.
- [11] F.G. Aliev, M.A. Correa-Duarte, A. Manedov, J.W. Ostrander, M. Giersig, L.M. Liz-Marzán, N.A. Kotov, *Adv. Mater.* 11 (1999) 1006.