Appl Phys A (2011) 102: 559–563
DOI 10.1007/s00339-010-6072-7

Applied Physics A
Materials Science & Processing

Template-free synthesis of hollow α-Fe_2O_3 microspheres

Hao-Jie Song · Na Li · Xiang-Qian Shen

Received: 22 September 2010 / Accepted: 28 September 2010 / Published online: 20 October 2010

Abstract Nearly monodisperse hollow α-Fe_2O_3 microspheres composed of nanoparticles have been successfully synthesized through a facile template-free hydrothermal method. The products were characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. It is shown that the hollow α-Fe_2O_3 microspheres consist of well-aligned α-Fe_2O_3 nanoparticles with a mean diameter of about 15 nm. This facile reaction route presents an efficient method for mass production of monodisperse hollow magnetic nanomaterials. The final α-Fe_2O_3 microspheres exhibit special magnetic properties with a small remnant magnetization of 0.09 emu g^{-1} and a high coercivity of 1121.67 Oe at room temperature.

1 Introduction

Morphology-controlled synthesis of functional nanostructured materials has attracted increasing attention among scientists and industrialists, because of their important role in shaping future technological advances in magnetic, electronic, optoelectronic, and memory devices. Among different particle geometries, hollow metal oxide spheres have recently received much attention. This interest is primarily fueled by the ability to confine chemicals for controlled release, isolate metal nanoparticle catalysts to prevent ripening, create high-surface area materials for batteries, and create low-index-of refraction materials [1–7].

Hematite (α-Fe_2O_3), the most stable iron oxide under ambient conditions, is of scientific and technological importance, mainly due to its magnetic properties and chemical stability. Developing new routes for the preparation of α-Fe_2O_3 nanocrystals with various sizes and shapes and investigating their distinguished properties is of considerable interest. For instance, Wan group have selected $FeCl_3 \cdot 6H_2O$, urea, and tetrabutylammonium bromide as a precursor, utilizing ethylene glycol as a solvent to achieve novel 3D flowerlike iron oxide and it showed an excellent ability to remove heavy-metal ions and other pollutants in water treatment [8]. Ganguli et al. have reported a reverse micellar route to synthesize iron oxalate nanorods using cetyltrimethyl ammonium bromide as surfactant. Spherical α-Fe_2O_3 nanoparticles were obtained by decomposition of these nanorods at 500°C [9]. Recently, three-dimensional (3D) urchin-like α-Fe_2O_3 superstructures have been synthesized by Fu et al. through a template-free hydrothermal synthetic route using $FeSO_4 \cdot 7H_2O$ and $NaClO_3$ as reagents and display weak ferromagnetic behavior [10]. These studies were important for understanding the formation of complex α-Fe_2O_3 microspheres and their potential applications. Despite these advances, however, these methods mentioned above relied on relative higher temperature and special equipments or surfactants and templates. Therefore, development of a simple synthetic methodology for preparation of novel micro-nanostructured α-Fe_2O_3 superstructures is a major challenge till now. To the best of our knowledge, the studies about the microspheric self-assembly of aggregated α-Fe_2O_3 nanoparticles with hierarchically hollow structures by a simple hydrothermal method (without any catalysts or templates) are still less reported.

Herein, a facile one-step and template-free synthesis of monodisperse hollow α-Fe_2O_3 microspheres by hydrothermal method was reported. Compared with the methods men-

H.-J. Song (✉) · N. Li · X.-Q. Shen
School of Materials Science and Engineering, Jiangsu University,
Zhenjiang, Jiangsu, 212013, P.R. China
e-mail: shj6922@163.com
Fax: +86-511-88780191

tioned above, this synthetic procedure has the advantages of simplicity (without any special equipments, organic solvents or templates). Furthermore, the magnetic properties of the as-synthesized hollow α-Fe_2O_3 microspheres have been investigated.

2 Materials and methods

All reagents were analytical grade from Shanghai Chemical Reagent Ltd. and were used without further purification. In a typical experiment, 7.5 mmol $FeCl_3 \cdot 7H_2O$ and 0.75 mmol of NaH_2PO_4 were dissolved in 25 mL de-ionized water in a flask at room temperature, respectively. Then, the ferrous solution was added dropwise into the NaH_2PO_4 solution and stirred with a magnetic stirrer until a primrose yellow transparent solution was obtained. The mixed solution was transferred into a 60 mL Teflon-lined stainless steel autoclave. The autoclave was then sealed and slowly heated to 200°C. Afterwards, the autoclave was maintained at the same temperature for several hours. After being cooled to room temperature, the products were isolated by centrifugation, repeatedly washed with de-ionized water and absolute ethanol several times to remove the remaining NaCl, NaH_2PO_4 and other impurities. Finally, the products were dried in air at 60°C for 5 h.

The phase structure and phase purity of the as-synthesized powders were examined by X-ray diffraction (XRD, Holland Philips X'pert X-ray diffractometer with Cu-Kα radiation, $\lambda = 1.5406$ Å) at 40 kV, 30 mA over the 2θ range 20–70°. The surface morphology and sizes of the products were observed by field-emission scanning electron microscopy (FE-SEM, Zeiss, Germany, supra 55 microscope with an accelerating voltage of 20 kV) with energy-dispersive spectra. High-resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns were taken with a Hitachi Model H-800 transmission electron microscope operating at 20 kV. Magnetic measurements for the samples in the powder form were carried out at room temperature using a vibrating sample magnetometer (VSM) with a maximum magnetic field of 10 kOe.

3 Results and discussion

The crystal structure and phase composition of the products obtained at 200°C for 12 h were characterized by XRD and EDX analysis. As shown in Fig. 1a, according to the main diffraction peak locations, the sample could be easily indexed to a hexagonal α-Fe_2O_3. The calculated cell constants $a = 0.5038$ nm and $c = 1.377$ nm was in good agreement with the standard data (JCPDS No. 33-0664). In addition, no diffraction peaks other than those from α-Fe_2O_3 are detected, indicating high purity of α-Fe_2O_3 products. Furthermore, the EDX method was utilized to identify the chemical composition of our products. It was observed that the as-prepared sample mainly contained Fe and O elements (Fig. 1b) in addition to the Cu peaks which came from sputtering, further confirming the formation of iron oxides.

The morphology of the products obtained at 200°C for 12 h was determined by FESEM. Figure 2a is the overall morphology of the products, which indicates that the obtained product consisted of large-scale uniform microspheres. The magnified FESEM image shown in Fig. 2b clearly displays that the surfaces of these spheres with diameters of 150–200 nm are not smooth. Obviously, they are composed of small primary particles. Close observation as shown in the inset in Fig. 2b reveals that the in-

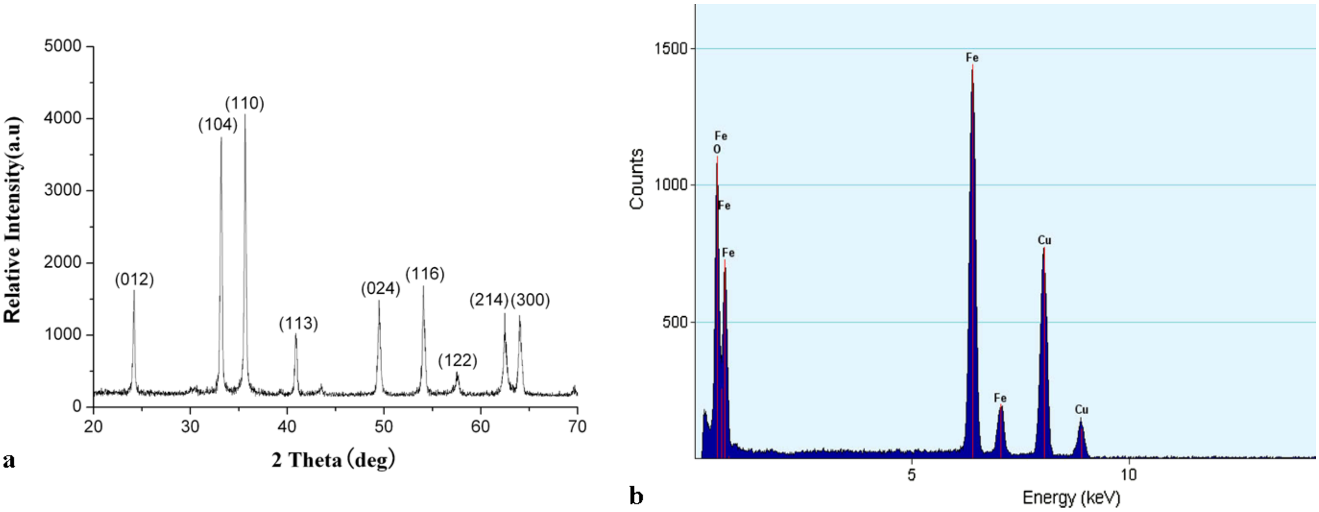

Fig. 1 (**a**) X-ray diffraction (XRD) pattern and (**b**) energy-dispersive X-ray analysis (EDX) of the samples obtained at 200°C for 12 h

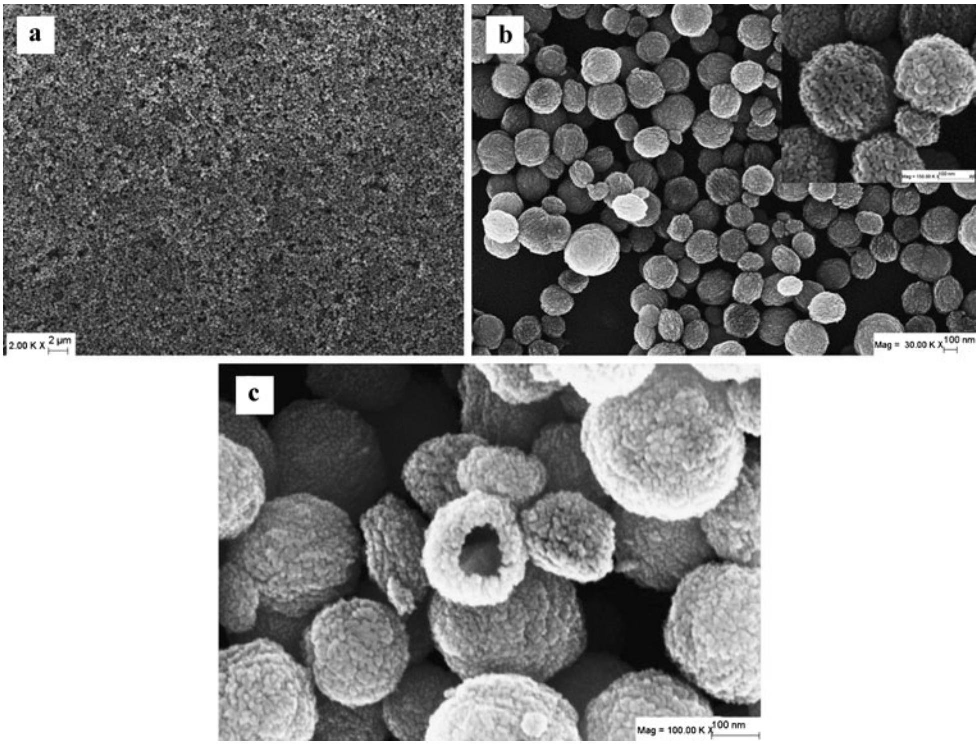

Fig. 2 SEM images of hollow α-Fe_2O_3 microspheres obtained at 200°C for 12 h: (**a**) the overall morphology; (**b**) the magnified SEM image; (**c**) close observation of (**a**)

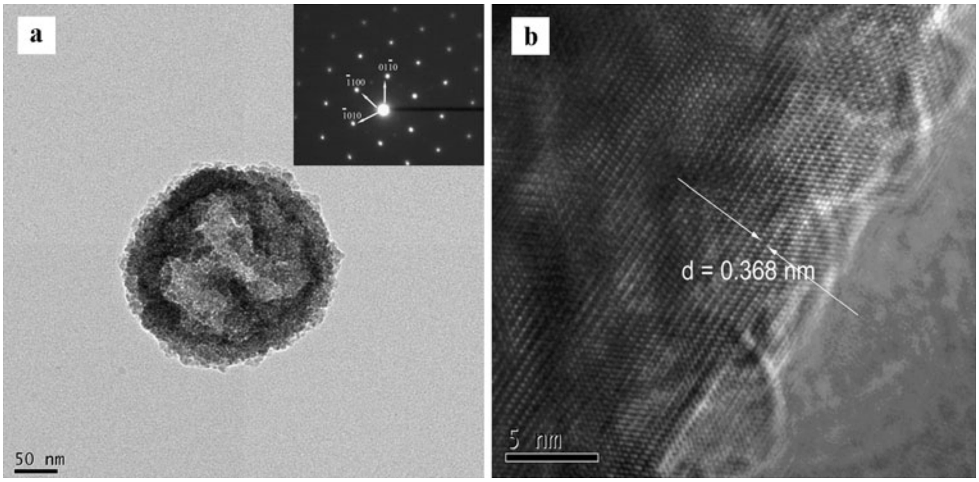

Fig. 3 TEM of hollow α-Fe_2O_3 spheres obtained at 200°C for 12 h (**a**) and high-resolution TEM image; (**b**) selected area electron diffraction (SAED)

dividual α-Fe_2O_3 nanoparticles have a mean diameter of about 10–20 nm. α-Fe_2O_3 nanoparticles get attached together and assemble into microsphere structure. The hollow structure of the microspheres can be clearly seen in Fig. 2c, where the partly broken microspheres show the hollow feature. The ordered arrangement of the nanoparticles on the edge of the broken microsphere also can be seen. The average shell thickness of the microsphere is about 10 nm. The FESEM image at high magnification further reveals that the nanoparticles have a rodlike morphology with about several tens of nanometers in diameter and 10–20 nm in length.

The products obtained at 200°C for 12 h were further characterized by HR-TEM accompanied by selected area electron diffraction (SAED). As shown in Fig. 3a, the products clearly show the hollow structure, and the strong contrast between the dark edges and the pale center confirms that almost all the spherical particles have a hollow cavity inside. The detailed observation in Fig. 3a reveals the fact that the thickness of the shell is about 10 nm. The corresponding SAED pattern (in the inset of the Fig. 3a), which is very sharp, shows that the product is highly crystalline, which is also in agreement with the XRD result. The HR-TEM image in Fig. 3b shows the lattice image obtained at the edge of

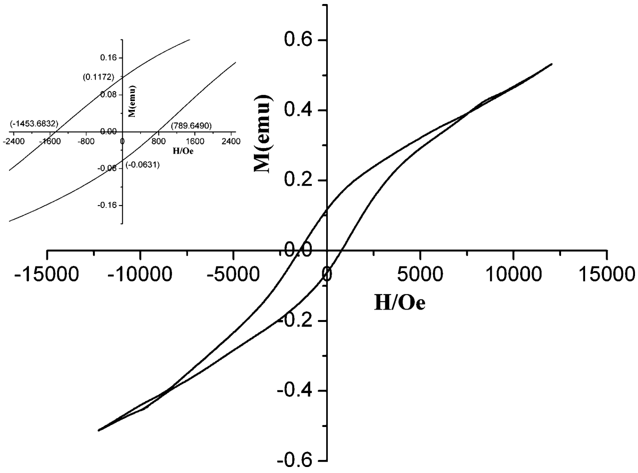

Fig. 4 The hysteresis loop of the as-synthesized products at 200°C

the particles, demonstrating clearly the lattice fringes of the walls around several small mesopores, and the continuous lattice fringes demonstrate the single-crystal nature of the particle, the lattice spacing of 0.368 correspond to (012) lattice planes, giving additional evidence that the nanoparticles are highly crystalline. The stability of these microspheres is extraordinarily good at ultrasonic conditions, though they are composed of nanoparticles. These microspheres could keep their morphology intact when the ultrasonic time was prolonged from 5 to 30 min.

It is well known that the magnetic properties of materials have been believed to be highly dependent on many factors, such as the morphology, size, and crystal structure (including impurities or substitutions) of the as-synthesized sample [11–14]. Nanoscaled α-Fe_2O_3 often exhibits unusual magnetic behaviors, which are different from those of the bulk sample, owing to the shape- and size-dependent effects [15, 16]. Therefore, the magnetic property measurements of the as-synthesized α-Fe_2O_3 microspheres were investigated. Figure 4 shows the magnetic hysteresis loops of the samples obtained at 200°C at room temperature in the applied magnetic field sweeping from -10 to 10 kOe. The hysteresis loops (M–H) do not reach saturation, even at the maximum applied magnetic field. The hysteresis loop of the products obtained at 200°C shows weak ferromagnetic behavior with a remanent magnetization of 0.09 $\mathrm{emu\,g^{-1}}$ and a coercivity of 1121.67 Oe at room temperature. The values of the remanent magnetization and coercivity of the hollow α-Fe_2O_3 microspheres are higher than those of urchin-like α-Fe_2O_3 superstructures (4.68×10^{-3} $\mathrm{emu\,g^{-1}}$ for remanent magnetization and 92.23 Oe for coercivity, respectively) [10]. The higher remanent magnetization and coercivity observed in the present study must be associated with the unique morphology and structure of the hollow α-Fe_2O_3 microspheres and nanorods. The assembled hollow α-Fe_2O_3 microspheres and nanorods in fact consisted of many primary nanoparticles with a diameter of 20 nm, which makes the number of subparticles increase, resulting in the enhancement in the values of remanent magnetization and coercivity. Therefore, it can be concluded that the remanent magnetization and coercivity value decreased as the size of the corresponding α-Fe_2O_3 nanostructures increased. The small coercivity of α-Fe_2O_3 nanocrystals suggests that they belong to semi-hard magnetic materials, which may find applications as relay, switch, semi-fixed storage, and in magnetooptical nanodevices [17, 18].

4 Conclusion

In summary, hollow α-Fe_2O_3 microspheres have been synthesized by hydrothermal method without the use of any template or organic surfactant. The hollow microspheres are composed of α-Fe_2O_3 nanoparticles. The final α-Fe_2O_3 microspheres exhibit special magnetic properties with a small remnant magnetization of 0.09 $\mathrm{emu\,g^{-1}}$ and a high coercivity of 1121.67 Oe at room temperature. This facile and environmentally friendly hydrothermal method endows large-scale synthesis of the hollow α-Fe_2O_3 microspheres and good crystal quality, which may pave the way for the potential applications of these hollow microspheres as building blocks in gas sensors, heterogeneous catalysis, optical devices, and microreactors.

Acknowledgements This work has been supported by the National Nature Science Foundation (50903040), China Postdoctoral Science Foundation (20090451169), Jiangsu Postdoctoral Science Foundation (0901078C), Jiangsu Key Lab of material tribology Foundation (kjsmcx0905), and the Senior Intellectuals Fund of Jiangsu University (09JDG003).

References

1. F. Caruso, R.A. Caruso, H.M. Lhwald, Science **282**, 1111 (1998)
2. A.D. Dinsmore, M.F. Hsu, M.G. Nikolaides, M. Marquez, A.R. Bausch, D.A. Weitz, Science **298**, 1006 (2002)
3. H.C. Zeng, J. Mater. Chem. **16**, 649 (2006)
4. H.G. Yang, H.C. Zeng, Angew. Chem. **116**, 5318 (2004)
5. J. Goldberger, R. He, Y. Zhang, S. Lee, H. Yan, H.J. Choi, P. Yang, Nature **422**, 599 (2003)
6. X. Huang, C. Guo, J. Zuo, N. Zheng, G.D. Stucky, Small **5**, 36 (2009)
7. Z.C. Wu, K. Yu, S.D. Zhang, Y. Xie, J. Phys. Chem. C **112**, 11307 (2008)
8. L.S. Zhong, J.S. Hu, H.P. Liang, A.M. Cao, W.G. Song, L. Wan, J. Adv. Mater. **18**, 2426 (2006)
9. A.K. Ganguli, T. Ahmad, J. Nanosci. Nanotechnol. **7**, 2029 (2007)
10. L.P. Zhu, H.M. Xiao, X.M. Liu, S.Y. Fu, J. Mater. Chem. **16**, 1794 (2006)
11. H.G. Yang, H.C. Zeng, Angew. Chem. **43**, 5930 (2004)
12. N.K. Chaudhari, J.S. Yu, J. Phys. Chem. C **112**, 19957 (2008)
13. T.P. Raming, A.J. A Winnubst, C.M. Van Kats, A.P. Philipse, J. Colloid Interface Sci. **249**, 346 (2002)

14. B. Tang, G.L. Wang, L.H. Zhuo, J.C. Ge, L.J. Cui, Inorg. Chem. **45**, 5196 (2006)
15. W.Y. Yin, X. Chen, M.H. Cao, C.W. Hu, B.Q. Wei, J. Phys. Chem. C **113**, 15897 (2009)
16. M. Sorescu, R.A. Brand, D.M. Tarabasanu, L. Diamandescu, J. Appl. Phys. **85**, 5546 (1999)
17. M.B. Tian (ed.), *Magnetic Materials* (Tsinghua University, Beijing, 2001)
18. R.F. Ziolo, E.P. Giannelis, B.A. Weinstein, M.P. O'Horo, B.N. Ganguly, V. Mehrotra, M.W. Russell, D.R. Huffman, Science **257**, 219 (1992)