Size and shape tunable Fe_3O_4 nanoparticles

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Abstract. Fe_3O_4 nanoparticles with tunable size and shape were synthesized by high-temperature organic solution method. The size and shape of nanoparticles can be tuned by varying the ratio of surfactant to precursor and refluxing temperature. Large surfactant : precursor ratio resulted in cubic shape, while small ratio brought out spherical shape. As-synthesized Fe_3O_4 nanoparticles had single crystalline structure and showed ferromagnetic at room temperature. Diamond shape nanoparticles exhibited coercivity as high as 440 Oe at room temperature. Room temperature ferromagnetic Fe_3O_4 nanoparticles have many technological applications including data storage, energy conversion, and nanomedicine.

Introduction

Inverse spinel structured MFe_2O_4 nanoparticles and their dispersions have long been of scientific and technological interest[1-3]. Inverse spinel structure is specified generally as AB_2O_4, where two usually nonequivalent metal ions, A and B, are embedded in a cubically face-centered lattice of O^{2-}ions. The unit cell of this lattice is composed of 32 closely packed O^{2-}ions embracing 64 tetrahedral(A-type) and 32 octahedral (B-type) interstices. Compared to other MFe_2O_4nanoparticles, Fe_3O_4 nanoparticles have been certificated by FDA to be safe and harmless to human health and aroused considerable interest. Fe_3O_4 nanoparticles with biological safety have great applications in biomedicine, such as MRI contrast enhancement agent[4,5], targeted drug delivery[6], and magnetic hyperthermia[7-9] etc. It calls for different magnetic properties to meet various biomedical demands. For example, magnetic nanoparticle contrast agents should have high saturation magnetization, whereas, nanoparticles for hyperthermia demand maximum specific loss power under an alternative field. The magnetic properties of nanostructure are strongly dependent on their size, size distribution, and shape[1,10]. Preparation of nanostructure with controlled shape and size has been being a great challenge. Many efforts have been made to tune the size and shape of nanoparticles. Sun group attempted to tune the size and shape of MFe_2O_4 nanoparticles by changing the synthesis conditions and have made great progress[1,11]. However, MFe_2O_4 nanoparticles synthesized by Sun group were generally in size smaller than 20 nm, and cannot fully meet the biological needs. In this paper, we attempt to synthesize the Fe_3O_4 nanoparticles in size above 20 nm with controlled size and shape, which have broader applications in biomedicine.

Experiments

$Fe(acac)_3$ (1mmol), oleic acid(2-4mmol), oleylamine (2-4mmol), and 20 mL benzyl ether was mixed and magnetically stirred under a flow of nitrogen. The mixture was first heated at120Cfor 30 minutes to remove the low boiling solvent, then to 200Cat a heating rate of 2C min^{-1} for 1 hour. At a ramping rate of 3C min^{-1} the solution was further heated to reflux (~295C) and kept at 300C for 1-2 hour. The solution was cooled down to room temperature by removing the heat source. Mixtures were precipitated with ethanol, centrifuged to remove the solvent, and dispersed in hexane.

The nanoparticle size and morphology were characterized by transmission electron microscopy (TEM) using JEM-100CX microscope and by high resolution transmission electron microscopy (HRTEM) using a JEOL model 4000EX microscope. X-ray diffraction (XRD) patterns were recorded using a Bruker AXS D8-Advanced diffractometer with Cu K_α radiation(λ=1.5418 Å).The

magnetic hysteresis loops were measured using a Microsence EV9 vibrating sample magnetometer.

Results and discussion

In the thermal decomposition method, 1,2-hexadecanediol was usually used to prepare the MFe_2O_4 nanoparticles with the size smaller than 20 nm. In our modified synthesis, 1,2-hexadecanediol was removed from the mixture reaction and $Fe(acac)_3$ was decomposed in benzyl ether (BE) in the presence of oleic acid (OA) and oleylamine (OAm). Figure 1 shows the TEM images of nanoparticles synthesized using different surfactant/$Fe(acac)_3$ ratio refluxed at 295C for 1 hour. When the surfactant/$Fe(acac)_3$ ratio was no larger than 3:1, the particles were polyhedral shape. Increasing the ratio to 4:1 led to cubic-like nanoparticles. As the ratio increased from 2:1 to 3:1, the size of nanoparticles reduced obviously. Further raising the ratio to 4:1, the size of nanoparticles was roughly the same with that of 3:1, but the majority of nanoparticles varied from polyhedral shape to cubic shape.

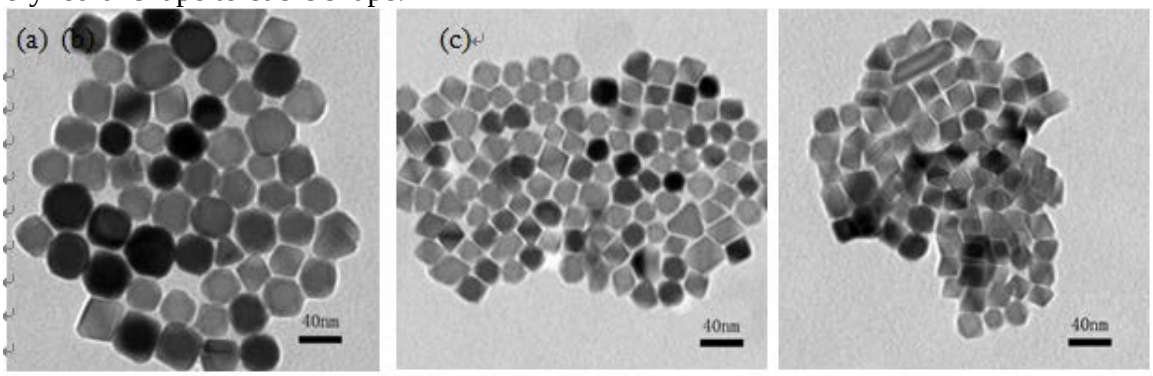

Figure 1 TEM images of nanoparticles synthesized using different surfactant/$Fe(acac)_3$ ratio refluxed at 295C for 1 hr. (a)2:1, (b) 3:1, (c) 4:1

When the refluxing time was extended to 2 hours, nanocubic demonstrated in figure 1 (c) grew a lot with diamond shape, as shown in figure 2 (a).The lattice fringes in HRTEM image shown in figure 2(b) corresponded to one group of atomic planes within the nanoparticle, which indicated that the diamond nanoparticles were single crystals. The distance between two adjacent planes is measured to be 2.45 Å, corresponding to (311) planes in the inverse spinel structured Fe_3O_4. Structure information of assembly from diamond nanoparticles was obtained by X-ray diffraction. Figure 3 is the X-ray diffraction pattern of diamond nanoparticles. The position and relative intensity of diffraction peaks all matched perfectly with Fe_3O_4 standard power diffraction data.

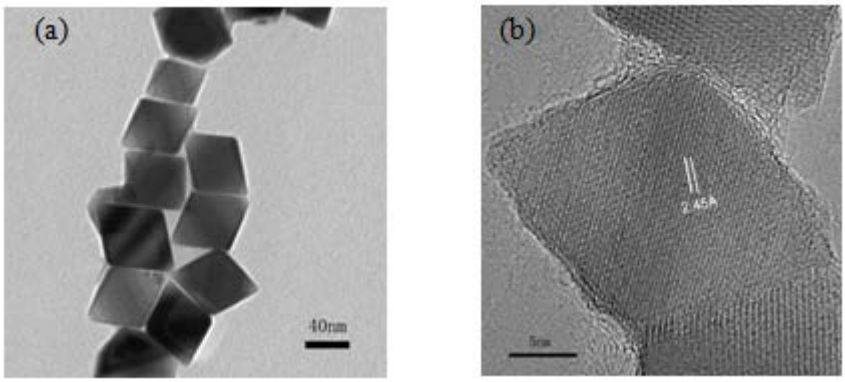

Figure 2 (a)TEM (b)HRTEM images of nanoparticles synthesized using surfactant/$Fe(acac)_3$ ratio of 4:1 refluxed at 295C for 2 hrs.

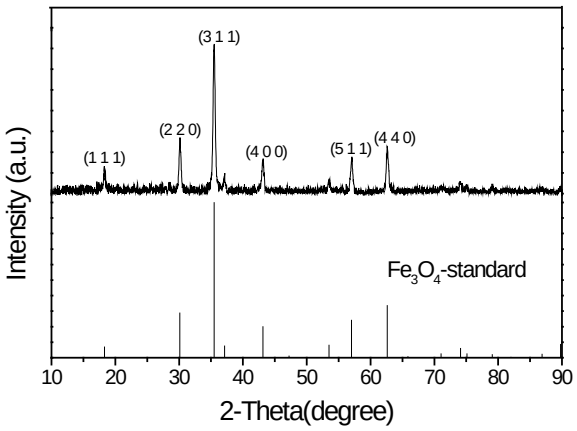

Figure 3 XRD pattern of diamond Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles synthesized by Sun et al were superparamagnetic at room temperature, and they had the size smaller than 20 nm. With increasing nanoparticles size the anisotropy energy increased. When anisotropy energy barrier of a single particle can overcome the thermal energy, nanoparticles behaved ferromagnetically at room temperature. Figure 4 demonstrated the hysteresis loops of Fe_3O_4 nanoparticles with cubic and diamond shape at room temperature. Fe_3O_4 nanoparticles with cubic and diamond shape were both ferromagnetic at room temperature. The coercivity of cubic nanoparticles is about 80 Oe at room temperature, and diamond nanoparticles showed a coercivity as high as 440 Oe.

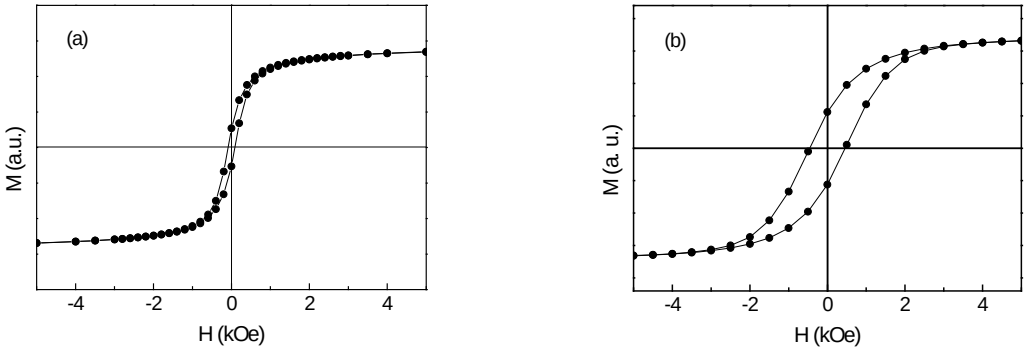

Figure 4 Hysteresis loops of nanoparticles at room temperature (a) cubic (b) diamond

Conclusion

Fe_3O_4 nanoparticles with average size larger than 20 nm were synthesized by thermal decomposition method. Removing 1,2-hexadecanediolcan in chemical synthesis yielded larger nanoparticles. By changing the ratio of surfactant to precursor, the shape of nanoparticles can be adjusted. When the surfactant/$Fe(acac)_3$ ratio was no larger than 3:1, the shape of the particles were polyhedral. Increasing the ratio to 4:1 led to cubic-like nanoparticles. Delaying refluxing temperature resulted in an obvious growth of nanoparticles. Fe_3O_4 nanoparticles have many applications in high-performance nanodevice, MRI contrast agent, and targeted drug delivery.

References

[1] Zeng H., Rice P. M., Wang S. X., Sun S. H.. Shape-controlled synthesis and shape-induced texture of MnFe2O4 nanoparticles. Journalof American Chemical Society[J], 2004,126 (37), 11458-11459.

[2] Majetich S. A., Wen T.,Booth R. A.. Functional Magnetic Nanoparticle Assemblies:

Formation, Collective Behavior, and Future Directions. Acs Nano[J], 2011,*5* (8), 6081-6084.

[3] Raj K.,Moskowitz R.. Commercial Applications of Ferrofluids. Journal of Magnetism Magnetic Materials[J], 1990,*85* (1-3), 233-245.

[4] Bruns O. T., Ittrich H., Peldschus K., Kaul M. G., Tromsdorf U. I., Lauterwasser J., Nikolic M. S., Mollwitz B., Merkell M., Bigall N. C., Sapra S., Reimer R., Hohenberg H., Weller H., Eychmuller A., Adam G., Beisiegel U., Heeren J.. Real-time magnetic resonance imaging and quantification of lipoprotein metabolism in vivo using nanocrystals. Nature Nanotechnology[J], 2009,*4* (3), 193-201.

[5] Abbasi A. Z., Gutierrez L., del Mercato L. L., Herranz F., Chubykalo-Fesenko O., Veintemillas-Verdaguer S., Parak W. J., Morales M. P., Gonzalez J. M., Hernando A., de la Presa P.. Magnetic Capsules for NMR Imaging: Effect of Magnetic Nanoparticles Spatial Distribution and Aggregation. Journal Physical Chemistry C[J], 2011,115 (14), 6257-6264.

[6] Gupta A. K., Gupta M.. Synthesis and surface engineering of iron oxide nanoparticles for biomedical applications. Biomaterials[J], 2005,26 (18), 3995-4021.

[7] Guardia P., Di Corato R., Lartigue L., Wilhelm C., Espinosa A., Garcia-Hernandez M., Gazeau F., Manna L., Pellegrino T.. Water-Soluble Iron Oxide Nanocubes with High Values of Specific Absorption Rate for Cancer Cell Hyperthermia Treatment. Acs Nano[J],2012,6 (4), 3080-3091.

[8] Martinez-Boubeta C., Simeonidis K., Makridis A., Angelakeris M., Iglesias O., Guardia P., Cabot A., Yedra L., Estrade S., PeiroF., Saghi Z., Midgley P. A., Conde-LeboranI., Serantes D.,BaldomirD.. Learning from Nature to Improve the Heat Generation of Iron-Oxide Nanoparticles for Magnetic Hyperthermia Applications. Scientific Reports[J],2013,*3*.

[9] Vallejo-Fernandez G., Whear O., Roca A. G., Hussain S., Timmis J., Patel V., O'Grady K.. Mechanisms of hyperthermia in magnetic nanoparticles. Journal of Physics D: Applied Physics[J], 2013,46 (31).

[10] Rong C. B., Li D. R., Nandwana V., Poudyal N., Ding Y., Wang Z. L., Zeng H., Liu J. P.. Size-dependent chemical and magnetic ordering in L1(0)-FePt nanoparticles. Adv Mater[J], 2006,18 (22), 2984-2987

[11] Sun S. H., Zeng H., Robinson D. B.,Raoux S., Rice P. M., Wang S. X., Li G. X.. Monodisperse MFe_2O_4 (M = Fe, Co, Mn) nanoparticles. Journal of American Chemical Society[J],2004,126 (1), 273-279.