

Facile method to synthesize oleic acid-capped magnetite nanoparticles

Chun Yu Wang^{a,b,c}, Jian Ming Hong^d, Gong Chen^e, Yu Zhang^{a,b,*}, Ning Gu^{a,b}

^a State Key Laboratory of Bioelectronics, Southeast University, Nanjing 210096, China

^b Jiangsu Key Laboratory for Biomaterials and Devices, Southeast University, Nanjing 210096, China

^c School of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096, China

^d Center of Materials Analysis, Nanjing University, Nanjing 210096, China

^e Affiliated Hospital of Nanjing University of TCM, Nanjing 210029, China

Received 16 July 2009

Abstract

We described a simple one-step process for the synthesis of oleic acid-capped magnetite nanoparticles using the dimethyl sulfoxide (DMSO) to oxidize the precursor Fe^{2+} at 140 °C. By adjusting the alkalinity of the reaction system, magnetite nanoparticles with two sizes of 4 and 7 nm could be easily achieved. And the magnetite nanoparticles coated by oleate were well-monodispersed in organic solvent.

© 2009 Yu Zhang. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

Keywords: Magnetite nanoparticles; Monodisperse; Synthesis

Magnetite nanoparticles (NPs) have drawn much attention due to their superparamagnetism properties and potential applications in biomedical fields such as biomolecular separation [1], target-drug delivery [2], cancer hyperthermia treatment [3], DNA detection [4], and magnetic resonance imaging [5,6].

Several methods have been employed to produce monodisperse magnetite NPs smaller than 20 nm, including coprecipitation, microemulsion methods [7], thermal decomposition and/or reduction [8–11], and hydrothermal synthesis [12], etc. Among all of them, thermal decomposition of organic iron precursor is an easy and widely performed method. However, most of organometallic precursors of the reaction are toxic and expensive and the decomposition temperature is high, usually from 250 to 320 °C. In this letter, we report a facile method to synthesize oleic acid-capped magnetite NPs using $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ or $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ as the raw materials at a relatively low temperature of 140 °C.

1. Experimental

10 mL aqueous solution containing 6 mmol $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (or $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$) was first added into a 100 mL three-necked round bottom flask with nitrogen to remove oxygen, followed by the addition of 10 mL oleic acid, 10 mL

* Corresponding author at: State Key Laboratory of Bioelectronics, Southeast University, Nanjing 210096, China.

E-mail address: zhangyu@seu.edu.cn (Y. Zhang).

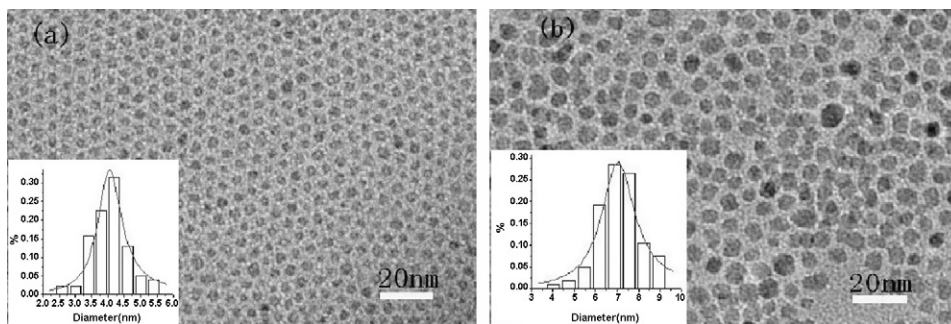


Fig. 1. TEM images of magnetite NPs: (a) S1; (b) S2.

25% (w/w) $N(CH_3)_4OH$, and 35 mL DMSO. Herein, DMSO was used as main solvent as well as oxidant of the reaction system. The mixture was stirred vigorously and refluxed at 140 °C for 1 h. Meanwhile, the solution color gradually changed from orange to black. The flask was removed from oil bath and cooled to room temperature after refluxing. The black magnetite NPs precipitates were obtained and washed immediately with excess of ethanol for three times by magnetic separation. Subsequently, the final precipitates was re-dispersed in *n*-hexane and named as S1.

The same procedure was repeated to produce larger NPs with initial 7 mL 25% (w/w) $N(CH_3)_4OH$ instead. The other precursors in the reaction system were maintained at the same quantity. The sample was named as S2.

2. Results and discussion

The particle size and the morphology of magnetite NPs were observed by transmission electron microscopy (TEM). Fig. 1 shows TEM micrographs of samples S1 and S2. These images indicate that the particles of samples S1 and S2 are not aggregated and the mean physical sizes are 4 and 7 nm, respectively. These values are obtained from the measurement of about 100 particles.

The crystalline structure of samples S1 and S2 was further determined by powder X-ray diffraction (XRD) as shown in Fig. 2. The positions and relative intensities of all diffraction peaks in Fig. 2 match well with those from the JCPDS card (19-0629) for magnetite. The average sizes of the two particles are about 4.3 and 6.8 nm calculated using Scherrer's formula, which is quite close to the result of the NPs TEM statistic measurement mentioned above.

The hysteresis loop of the as-synthesized magnetic NPs is shown in Fig. 3, which is measured at room temperature with a vibrating sample magnetometer (VSM). The synthesized magnetite NPs show a superparamagnetic behavior, as

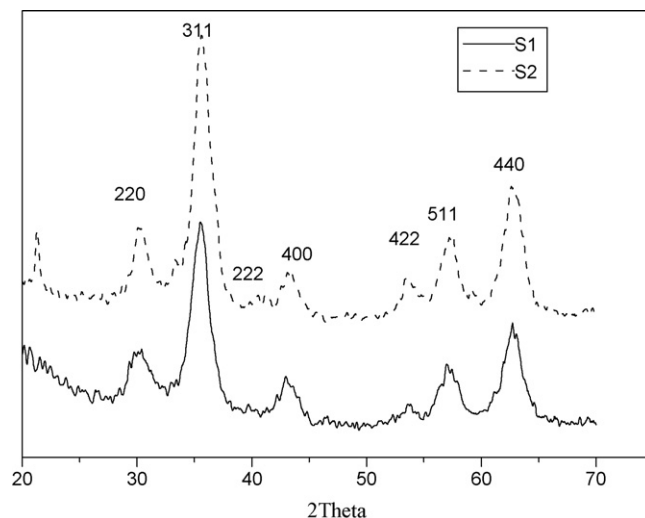


Fig. 2. X-ray diffraction pattern of samples S1 and S2.

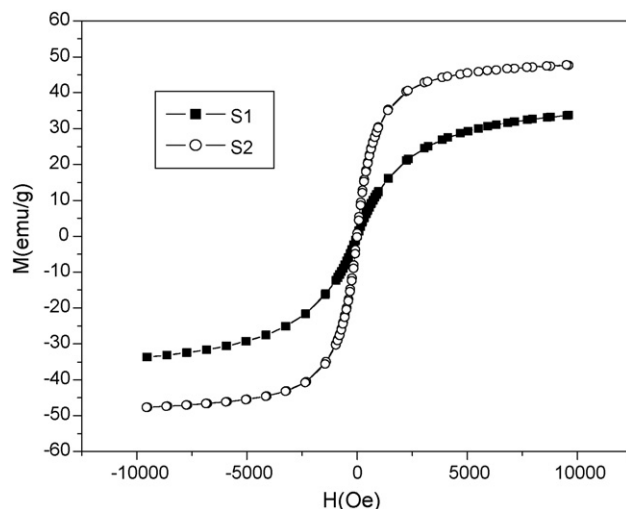


Fig. 3. Room-temperature magnetization curves of obtained magnetite NPs. Black squares: S1; hollow circles: S2.

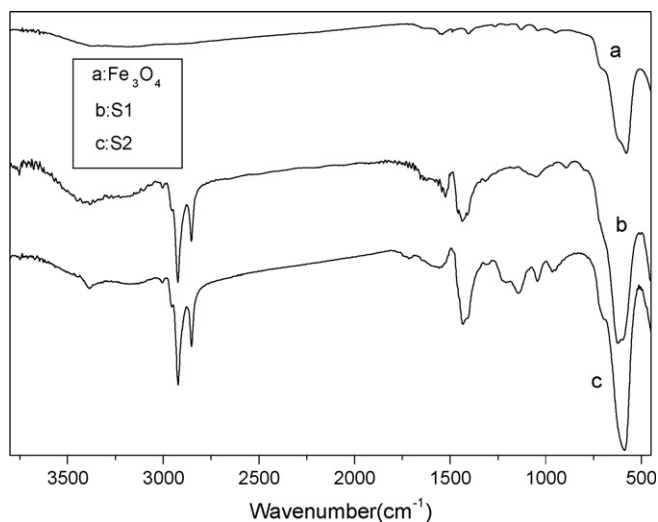


Fig. 4. FTIR spectra of (a) bare magnetite; (b) sample S1; (c) sample S2.

evidenced by zero coercivity and remanence on the magnetization loops. The saturated magnetizations of samples S1 and S2 are about 32.3 and 47.7 emu/g, much lower than the bulk value of magnetite (92 emu/g) [13]. The lower saturation magnetization can attribute to the lattice defects, which are more abundant in smaller nanocrystals. Moreover, the oleic acid that adsorbs on the surface of samples may also have a negative effect on the saturation magnetization [10].

In order to reveal the role of organic oleate in the particles, Fourier transform infrared spectrometer (FTIR) was used to detect the synthetic magnetite NPs. For comparison, the FTIR spectra of bare magnetite NPs, prepared according to our previous work [14], is also given. As shown in Fig. 4, the wide band at 3130–3630 cm^{-1} is assigned to O–H vibrations. The characteristic absorption peak of Fe–O is observed at 580 cm^{-1} for the three samples. Compared with the bare magnetite NPs, the FTIR spectra of synthetic magnetite NPs present more absorption peaks at the range of 1000–3000 cm^{-1} . The sharp bands at 2924 and 2851 cm^{-1} are attributed to asymmetric and symmetric C–H vibrations of the methylene groups. The band at 1560 and 1443 cm^{-1} can be ascribed to the asymmetric and symmetric COO^- stretches. Based on the FTIR spectra, oleic acid is believed to coat the surface of the magnetite particles [12,15].

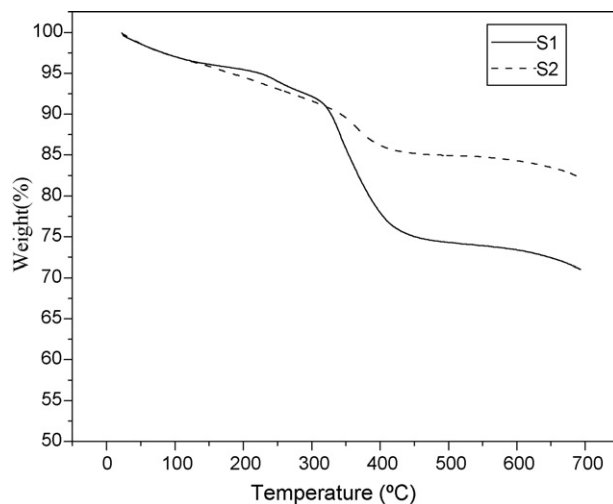


Fig. 5. TGA spectrum of samples S1 and S2.

Thermogravimetric analysis (TGA) of the particles were measured and presented in Fig. 5. The initial weight loss of magnetite NPs powder under 100 °C is likely to be caused by the contained water. From 150 to 400 °C, decomposition of the capping agents took place. The results of TGA demonstrated that oleate existed on the surface of magnetite particles of two samples and their weight ratio were about 38.9 and 17.8%, respectively.

In summary, we have developed a simple method to synthesize monodisperse iron oxide NPs. The oleic acid-capped magnetite NPs with two sizes of 4 and 7 nm can be synthesized by adjusting the base concentration of $N(CH_3)_4OH$ used in the synthetic system. These monodisperse magnetite particles have great potential in magnetic devices and biomedical engineering applications.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 30870679 and 30970787) and National Basic Research Program of China (No. 2006CB933206 and 2006CB705606).

References

- [1] J.M. Perez, F.J. Simeone, Y. Saeki, *J. Am. Chem. Soc.* 125 (2003) 10192.
- [2] T.K. Jain, M.A. Morales, S.K. Sahoo, *Mol. Pharmacol.* 2 (2005) 194.
- [3] O. Bretcanu, E. Verne, M. Coisson, *J. Magn. Magn. Mater.* 305 (2006) 529.
- [4] L. Josephson, J.M. Perez, R. Weissleder, *Angew. Chem. Int. Ed.* 40 (2001) 3204.
- [5] Y.W. Jun, Y.M. Huh, J.S. Choi, *J. Am. Chem. Soc.* 127 (2005) 5732.
- [6] Y.M. Huh, Y.W. Jun, H.T. Song, *J. Am. Chem. Soc.* 127 (2005) 12387.
- [7] D. Langevin, *Annu. Rev. Phys. Chem.* 43 (1992) 341.
- [8] S.H. Sun, H. Zeng, D.B. Robinson, *J. Am. Chem. Soc.* 126 (2004) 273.
- [9] J. Park, K.J. An, Y.S. Hwang, *Nat. Mater.* 3 (2004) 891.
- [10] W.W. Yu, J.C. Falkner, C.T. Yavuz, *Chem. Commun.* 20 (2004) 2306.
- [11] Z. Li, Q. Sun, M.Y. Gao, *Angew. Chem. Int. Ed.* 44 (2005) 123.
- [12] X. Liang, X. Wang, J. Zhuang, *Adv. Funct. Mater.* 16 (2006) 1805.
- [13] D.H. Han, J.P. Wang, H.L. Luo, *J. Magn. Mater.* 136 (1994) 176.
- [14] Y.K. Sun, M. Ma, Y. Zhang, et al. *Colloids Surf., A* 245 (2004) 15.
- [15] L. Zhang, R. He, H.C. Gu, *Appl. Surf. Sci.* 253 (2006) 2611.