Synthesis and Magnetic Properties of Single-Crystals of $MnFe_2O_4$ Nanorods

Jun Wang,[a] Qianwang Chen,*[a] Binyang Hou,[a] and Zhenmeng Peng[a]

Keywords: Iron / Magnetic properties / Nanorods / Nanowires / X-ray diffraction

Single-crystals of $MnFe_2O_4$ nanorods with an average diameter of 20 nm and length of 250 nm were synthesized by a hydrothermal process at 180 °C after 12 h. High-resolution transmission electron microscopy (HRTEM) and electron diffraction (ED) analysis revealed that the nanorods grow along the [110] axis, which is one of the easy magnetization axes of the material $MnFe_2O_4$. It was found that the nanorods exhibited a saturation magnetization (*Ms*) of 68.02 emu/g, which is much higher than that of quasi-spherical particles of $MnFe_2O_4$, prepared by other approaches such as solid-state reaction methods (*Ms* = 36.7 emu/g), and coprecipitation processes followed by annealing in vacuo at 400 °C (*Ms* = 24.4 emu/g). The oriented growth along the easy magnetization axis of $MnFe_2O_4$ was suggested to be responsible for the improvement of magnetic properties of $MnFe_2O_4$ nanorods.

Introduction

In the nanoscale regime, magnetic nanoparticles have been a subject of increasing interest from both fundamental and technological points of view.[1] It has been shown that the shape of magnetic particles strongly influences their magnetic properties.[2,3] Nanorods and nanowires not only exhibit unique magnetic properties but are also key components for ultrahigh-density magnetic recording media.[4] Many efforts have been made to synthesize nanorods and nanowires of magnetic materials.[5,6] For example, Chaudret et al.[7,8] prepared magnetic nanorods of cobalt by thermal decomposition. Iron nanorods were synthesized through controlled coalescence of spherical iron nanoparticles protected by trioctylphosphane oxide (TOPO).[9] Acicular iron particles were prepared by reduction of ferrous ions with sodium borohydride in tubular lecithin.[10]

The substance $MnFe_2O_4$, one of the most important magnetic materials, has been widely used in electronic applications[11,12] and contrast-enhancement agents in magnetic resonance imaging (MRI) technology,[13−16] in addition to recording media. Several techniques have been developed to synthesize $MnFe_2O_4$ nanoparticles, such as solid-phase reactions,[17] mechanical ball-milling,[18,19] thermal decomposition,[20] and coprecipitation methods.[13,14,21,22] However, the synthesis of $MnFe_2O_4$ nanorods has seldom been reported. The coprecipitation process can provide a quick and easy way to prepare $MnFe_2O_4$ nanoparticles; however, it usually yields nanoparticles with large size-distributions and less well-defined crystals. The rapid formation process is also very disadvantageous to synthesize single-crystal nanorods or nanowires as the product is formed far from equilibrium conditions. The hydrothermal process is one of the more successful ways to grow crystals of many different materials such as quartz and malachite. This technique has also been used to grow dislocation-free single-crystals; grains formed in this process could have a better crystallinity than those from other processes.

Our aim was to develop a low-temperature hydrothermal process for the preparation of $MnFe_2O_4$ nanorods that might find applications in perpendicular recording media.

Results and Discussion

X-ray diffraction (XRD) patterns for the samples obtained at different reaction conditions, which are compatible with cubic $MnFe_2O_4$ crystals (JCPDS card No. 73−1964), are shown in Figures 1 and 2. They revealed that the samples were pure $MnFe_2O_4$ crystals without impurity phases. From Figure 1, one can see that the reflection peaks become sharper and stronger on increasing the hydrothermal temperature and the time period, indicating that crystallinity tends to improve. For example, the crystallinity of the sample prepared at 180 °C (see A in Figure 1) was better after 6 h than after 3 h (see B in Figure 1). The dimensions and shapes of the particles were found to depend strongly on reaction conditions such as temperature, time, and the pH of the reaction system. Uniform $MnFe_2O_4$ nanorods were synthesized at 180 °C after 12 h. Lower temperatures and shorter time periods were favorable for the formation of quasi-spherical particles. For example, the products were dominated by quasi-spherical particles when the reaction was carried out at 140 °C (see A in Figure 3); when the

[a] Structure Research Laboratory and Department of Materials Science & Engineering, University of Science & Technology of China,
Hefei 230026, China
Fax: (internat.) + 86-551-3607292
E-mail: cqw@ustc.edu.cn

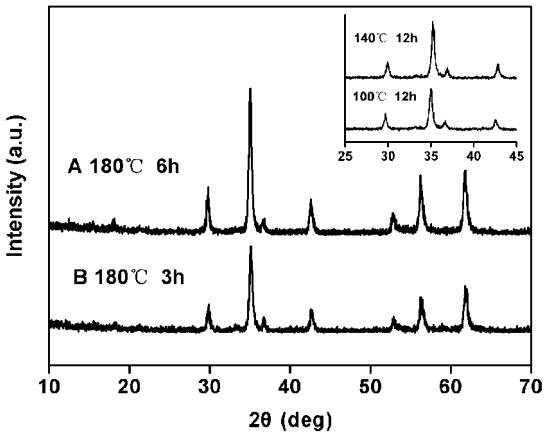

Figure 1. The XRD patterns of the samples prepared at 180 °C after 6 h (A) and 3 h (B); the inset shows XRD patterns of the samples formed at 140 °C and 100 °C after 12 h

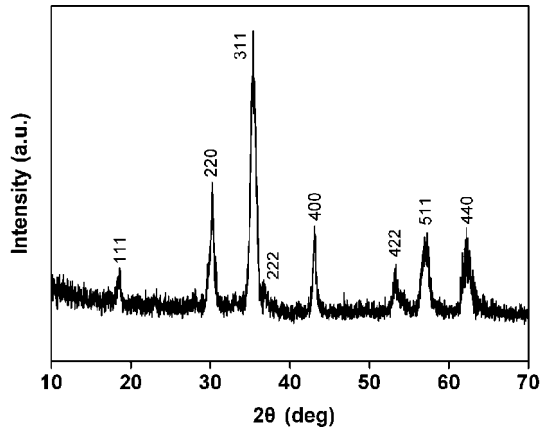

Figure 2. The XRD pattern of the sample prepared at 180 °C after 12 h

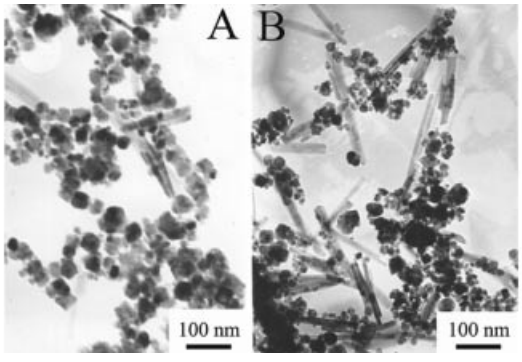

Figure 3. TEM images of the samples obtained at 140 °C after 12 h (A) and at 180 °C after 6 h (B)

temperature was increased to 180 °C, nanorods formed as the major product of the reaction (see A in Figure 4). At 180 °C, as the reaction time was reduced to 6 h, the product was also dominated by quasi-spherical particles (see B in Figure 3). It should be noted that the initial pH of the system had to be higher than 11, otherwise quasi-spherical particles were obtained.

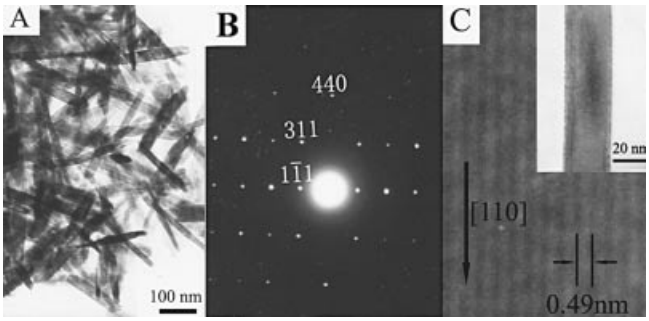

Figure 4. Representative TEM image of $MnFe_2O_4$ nanorods (A), ED pattern of a single-crystals of a nanorod (B) and HRTEM image of the nanorod in the inset (C); the inset in C is a magnified image of one individual $MnFe_2O_4$ nanorod shown in A; the sample was obtained after 12 h at 180 °C.

As shown in Figure 4 (see A), uniform nanorods with an average length of 250 nm and a width of 20 nm were produced at 180 °C after 12 h. From the XRD pattern of the sample shown in Figure 2, we found that the ratio between the intensities of the (220) and (311) diffraction peaks was higher than the conventional value (0.5 versus 0.28), indicating the oriented growth of the nanoparticles. Figure 4 (see B) shows the electron diffraction (ED) patterns obtained from one typical nanorod. The diffraction spots suggest that the nanorod was a single crystal. The high-resolution transmission electron microscopy (HRTEM) image further supports the existence of these $MnFe_2O_4$ nanorods as single crystals (see C in Figure 4). The lattice fringes (ca. 0.49 nm) observed in this image agree well with the separation between the [111] lattice planes. Combined with the result from ED, it was confirmed that the nanorods grew along the [110] plane, which is one of the easy magnetization axes of the $MnFe_2O_4$ nanorods.[23,24]

Indeed, single-crystals of nanorods and nanowires are formed because the relative growth rates of the various faces favor oriented growth along one crystal direction. The experimental conditions such as temperature, time, and pH influence the relative growth rates and can then be used to control the morphology and dimensions of the nanoparticles.

The magnetic properties of the Mn-ferrite samples obtained at 180 °C (see A in Figure 5) and 140 °C (see B in Figure 5) after 12 h were evaluated by a vibrating sample magnetometer. The hysteresis loops of the samples measured at room temperature (Figure 5) show ferromagnetic behavior with a saturation magnetization of 68.02 emu/g, which is slightly smaller than the corresponding bulk material (80 emu/g).[13,25] The reason may mainly depend on the nature of ultrafine particles: surface disorder, cation distribution, and defects etc. For example, a surface-disordered layer could serve as a nonmagnetic layer and decrease saturation magnetization. However, the saturation magnetization of the nanorods is much higher than that for $MnFe_2O_4$ quasi-spherical nanoparticles synthesized by other methods, such as solid-state reactions at 1200 °C (Ms = 36.7 emu/g),[26] coprecipitation followed by annealing in vacuo at 400 °C (Ms = 24.4 emu/g),[25] and is

also higher than that of our sample (see B in Figure 5) that was hydrothermally prepared at 140 °C after 12 h (*Ms* = 55.8 emu/g), in which quasi-spherical particles are the major products. It is, therefore, reasonable to suggest that the growth along the easy magnetic axis could improve the magnetic properties of the nanorods. During the measurement process, the $MnFe_2O_4$ nanorods tend to align along the magnetic line of force, which makes the easy magnetization axis correspond to the magnetic line of force. Magnetization makes all the net magnetic moments of the $MnFe_2O_4$ nanorods orientate themselves along the magnetic line of force. As a result, the saturation magnetization can be improved. It is, therefore, reasonable to suggest that in addition to the nonmagnetic layer on the surface of the nanoparticles, the morphology could also be an important factor determining the magnetic properties; growth of nanorods along the easy magnetization axis is a way to improve the magnetic properties of nanosized materials.

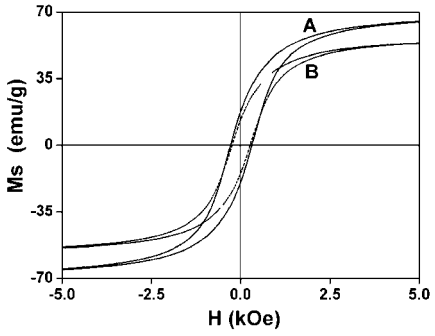

Figure 5. Magnetic hysteresis curves of $MnFe_2O_4$ samples hydrothermally obtained at 180 °C (A) and at 140 °C (B) after 12 h; the measurements were carried out at room temperature

Conclusions

Single crystals of $MnFe_2O_4$ nanorods were synthesized by a hydrothermal process at 180 °C after 12 h. The nanorods (average diameter of 20 nm and length of 250 nm) were found to grow along the easy magnetization axis [110] of the $MnFe_2O_4$ nanoparticles. The saturation magnetization of the nanorods (*Ms* = 68 emu/g) increases significantly to that of quasi-spherical particles prepared by other methods, which indicates that the controlled growth of nanorods along the easy magnetization axis of magnetic materials is a way to improve their magnetic properties. This process might be of general interest for the synthesis of nanorods and other ferrite materials in order to improve their magnetic properties.

Experimental Section

General: The chemical reagents used in this work were iron(III) chloride ($FeCl_3 \cdot 6\,H_2O$), manganese(II) chloride ($MnCl_2 \cdot 4H_2O$), and sodium hydroxide (NaOH). All chemicals were of analytical grade. The reaction is described by Equation (1):

$$MnCl_2 + 2\,FeCl_3 + 8\,NaOH \rightleftarrows MnFe_2O_4 + 4\,H_2O + 8\,NaCl \quad (1)$$

$MnCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6\,H_2O$ were dissolved in water at concentrations of 0.05 M and 0.1 M, respectively, ($[Fe^{3+}]/[Mn^{2+}]$ = 2:1. 35 mL). The metal-ion solution mixture was put into a Teflon™-lined stainless autoclave. Sodium hydroxide (0.880 g) dissolved with 5.0 mL distilled water was slowly added dropwise into the Teflon-lined stainless autoclave. A brown precipitate formed immediately. The autoclave was placed into an oven and kept at 180 °C for 12 hours, then allowed to cool to room temperature. The product was washed several times with distilled water and absolute ethanol. The products were finally dried in oven at 60 °C for 12 hours.

X-ray diffraction was performed on a Rigaku X-ray diffractometer with high-strength Cu-K_α radiation. Transmission electron microscope (TEM) images were taken with a Hitachi model H-800 with an accelerating voltage of 200 kV. High-resolution transmission electron microscopy (HRTEM) images were recorded on JEOL-2010 with an accelerating voltage of 200 kV. Their magnetic properties were evaluated on a BHV-55 vibrating sample magnetometer (VSM).

Acknowledgments

This work was supported by the National Natural Science Foundation under the contract No. 20125103 and 90206034.

[1] J. L. Dormann, D. Fiorani, *Magnetic Properties of Fine Particles*, North-Holland, Amsterdam, **1992**.
[2] M. Ozaki, H. Suzuki, K. Takahashi, E. Matijevic, *J. Colloid Interface Sci.* **1986**, *113*, 76.
[3] M. Ozaki, T. Egami, N. Sugiyama, E. Matijevic, *J. Colloid Interface Sci.* **1988**, *126*, 212.
[4] Q. F. Zhan, Z. Y. Chen, D. S. Xue, F. S. Li, *Phys. Rev. B* **2002**, *66*, 134436.
[5] [5a] Y. N. Xia, P. D. Yang, Y. G. Sun, Y. Y. Wu, B. Mayers, B. Gates, Y. D. Yin, F. Kim, H. Q. Yan, *Adv. Mater.* **2003**, *15*, 353. [5b] C. J. Murphy, N. R. Jana, *Adv. Mater.* **2002**, *14*, 80. [5c] S. Valizadeh, L. Hultman, J. M. George, P. Leisner, *Adv. Funct. Mater.* **2002**, *12*, 766. [5d] F. S. Li, L. Y. Ren, *Phys. Status Solidi A* **2002**, *193*, 196.
[6] [6a] L. Vayssieres, N. Beermann, S. E. Lindquist, A. Hagfeldt, *Chem. Mater.* **2001**, *13*, 233. [6b] L. Vayssieres, L. Rabenberg, A. Manthiram, *Nano Letters* **2002**, *2*, 1393. [6c] N. Cordente, M. Respaud, F. Senocq, M. J. Casanove, C. Amiens, B. Chaudret, *Nano Letters* **2001**, *10*, 565.
[7] F. Dumestre, B. Chaudret, C. Amiens, M. C. Fromen, M. J. Casanove, P. Renaud, P. Zurcher, *Angew. Chem. Int. Ed.* **2002**, *41*, 4286.
[8] [8a] Z. A. Peng, X. Peng, *J. Am. Chem. Soc.* **2001**, *123*, 1389. [8b] J. M. Petrovski, Z. L. Wang, *J. Phys. Chem. B* **1998**, *102*, 3316.
[9] S. J. Park, S. Kim, S. Lee, Z. G. Khim, K. Char, T. Hyeon, *J. Am. Chem. Soc.* **2000**, *122*, 8581.
[10] [10a] J. L. Cain, D. E. Nikles, *IEEE Trans. Magn.* **1997**, *33*, 3718. [10b] J. L. Cain, D. E. Nikles, *J. Appl. Phys.* **1996**, *79*, 4860.
[11] B. Gillot, *Eur. Phys. J. Appl.* **1998**, *4*, 243.
[12] M. Sugimoto, *J. Am. Ceram. Soc.* **1999**, *82*, 269.
[13] Z. X. Tang, C. M. Sorensen, K. J. Klabunde, G. C. Hadjipanayis, *Phys. Rev. Lett.* **1991**, *67*, 3602.
[14] G. U. Kulkarni, K. R. Kannan, T. Arunarkavalli, C. N. R. Rao, *Phys. Rev. B* **1994**, *49*, 724.
[15] P. J. van der Zaag, V. A. M. Brabers, M. T. Johnson, A. Noordermeer, P. E. Bongers, *Phys. Rev. B* **1995**, *51*, 12009.

[16] B. Gillot, M. Laarj, S. Kacim, *J. Mater. Chem.* **1997**, *7*, 827.
[17] M. D. Nasr-Allah, G. A. El-shobaky, *Thermochimica Acta* **2001**, *375*, 137.
[18] M. Muroi, R. Street, P. G. McCormick, J. Amighian, *Phys. Rev. B* **2001**, *63*, 184414.
[19] J. Ding, P. G. McCormick, R. Street, *J. Magn. Magn. Mater.* **1997**, *171*, 309.
[20] G. Balaji, N. S. Gajbhiye, G. Wilde, J. Weissmuller, *J. Magn. Magn. Mater.* **2002**, *242−245*, 617.
[21] Z. X. Tang, J. P. Chen, C. M. Sorensen, K. J. Klabunde, G. C. Hadjipanayis, *Phys. Rev. Lett.* **1992**, *68*, 3114.
[22] J. P. Chen, C. M. Sorensen, K. J. Klabunde, G. C. Hadjipanayis, E. Devlin, A. Kostikas, *Phys. Rev. B* **1996**, *54*, 9288.
[23] Y. L. Li, G. D. Li, *Physics of Ferrite*, Publishing House of Electronics Industry of Science, Beijing, **1978**, p. 381.
[24] D. F. Wan, X. L. Ma, *Magnetic Physics*, Publishing House of Electronics Industry, Beijing, **1999**, p. 169.
[25] M. Zheng, X. C. Wu, B. S. Zou, Y. J. Wang, *J. Magn. Magn. Mater.* **1998**, *183*, 152.
[26] J. F. Hu, H. W. Qin, Y. Z. Wang, S. G. Zhang, Z. X. Wang, *J. Mater. Sci. Lett.* **2001**, *20*, 1531.

Received August 10, 2003

