A Simple and Practical Method for the Preparation of Magnetite Nanowires

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Single-crystalline magnetite nanowires were prepared by a facile hydrothermal process in the presence of citrate anions and PVP at 180 °C for 24 h. The magnetite nanowires have diameters of 60–180 nm and length up to several ten micrometers. The nanowires were identified to grow along the [110] direction. On the basis of the results, the formation mechanism of the magnetite nanowires was discussed.

Low-dimensional magnetic materials have attracted much attention over the past decade because of both their interesting physical properties and their potential applications in ultra-high-density data storage, magnetic sensors.[1] Fe_3O_4 is an important magnetic material for various applications in industry and technology, especially in magnetic recording applications.[2] Anisotropic magnetic nanomaterials are expected to exhibit unique magnetic properties,[3] so one-dimensional (1D) magnetite nanostructures have been the focus of considerable interests. Although considerable effort has been devoted to the design and controlled fabrication of 1D magnetite nanostructures, it is still difficult to directly prepare magnetite with 1D nanostructures owing to the complexity of its spinel structure. Up to now, only little work is related to the preparation of 1D magnetite nanostructures, among which template-assisted method,[4] hydrothermal treatment of the precursor,[5] and magnetic-field-induced growth route[6] are main. These methods are not economical and practical routes for large scale manufacturing of single-crystalline magnetite with 1D nanostructures although they have met with some success. The disadvantage of template method and hydrothermal treatment of the precursor is that additional steps are required to generate templates or the precursor, thus the two processes are complex, time-consuming and expensive. The magnetic-field-induced growth route is not appropriate for industries because external magnetic fields must be applied. Development of a simple and cost-effective method for fabricating 1D magnetite nanostructures is highly desirable. Herein, we report a low-temperature preparation route in aqueous solution for single-crystalline Fe_3O_4 nanowires in high yield in the presence of citrate anions.

In a typical hydrothermal procedure, analytically pure 0.5776 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ was dissolved in 40 mL of doubly distilled water that had been purged with high-purity N_2 gas to minimize the amount of dissolved oxygen for at least half an hour. Following this, 1.0668 g of $Na_3C_6H_5O_7 \cdot 2H_2O$ and 0.8045 g of polyvinylpyrrolidone (PVP, K-30, $M_w = 49000$) were added to the solution. After vigorous stirring for 10 min the mixed solution was transferred into a Teflon-lined stainless steel autoclave with 50-mL capacity. The autoclave was sealed and maintained at 180 °C in a reaction oven for 24 h. At the end of the experiment, the autoclave was allowed to cool to room temperature. The black fluffy precipitates were washed with distilled water and absolute ethanol in sequence and then vacuum dried at 40 °C for 4 h.

The phase of the as-prepared sample was determined by X-ray (Cu Kα) powder diffraction (XRD) with the pattern shown in Figure 1a. All the peaks can be indexed to a spinel structure with the characteristic reflections of iron oxide (γ-Fe_2O_3, JCPDS card No. 39-1346 or Fe_3O_4, JCPDS card No. 87-0244). No obvious impurities such as α-Fe_2O_3 and FeOOH were observed. Raman spectroscopy was used to distinguishing Fe_3O_4 from γ-Fe_2O_3 further. A representative Raman spectrum of as-prepared sample is presented in Figure 1b. The bands at 667 and 534 cm^{-1} were assigned to the A_{1g} and T_{2g} symmetry modes of magnetite,[7] respectively. No characteristic bands of maghemite (720, 500, and 350 cm^{-1}) and hematite (390, 280, and 220 cm^{-1}) were observed. Combining the XRD result and Raman spectrum of the sample, it can be clearly revealed that the as-prepared sample is pure Fe_3O_4.

The morphology of the product was observed by field emission scanning election microscopy (FESEM) and transmission electron microscopy (TEM). Figures 2a and 2b show the typical FESEM images of the sample, revealing that the products consist of wire-like structures with the diameter of 60–180 nm and length up to several ten micrometers.

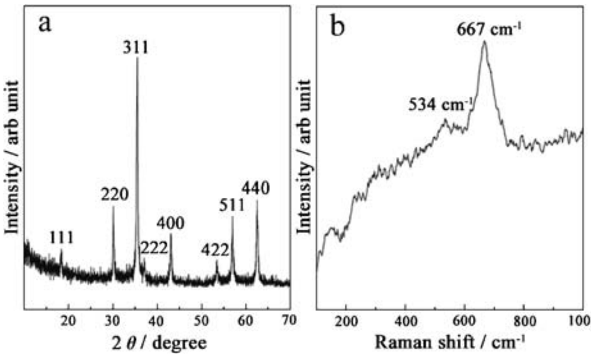

Figure 1. (a) XRD pattern and (b) Raman spectrum of as-prepared products.

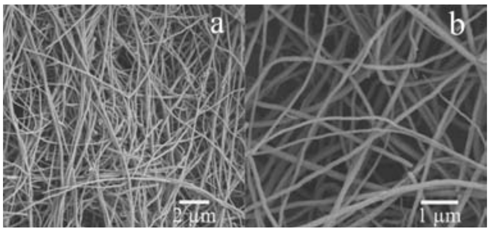

Figure 2. (a) Low-magnification and (b) high-magnification FESEM images of as-prepared products.

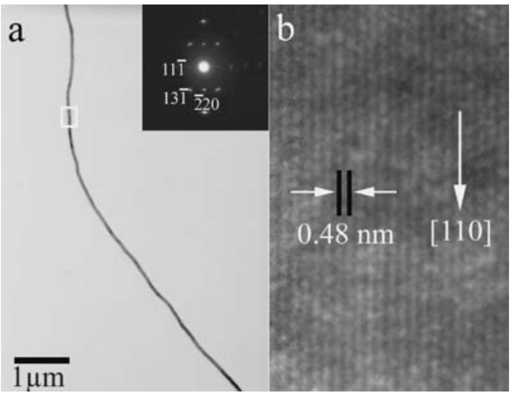

Figure 3. Representative TEM image of a typical Fe_3O_4 nanowire (a); the insert in (a) shows an ED pattern of the individual Fe_3O_4 nanowire. (b) HRTEM image of the nanowire (boxed area in (a)).

A representative TEM image of a Fe_3O_4 nanowire is shown in Figure 3a. The selected area electron diffraction (SAED) pattern (insert of Figure 3a) obtained along a typical individual nanowire reveals that the sample is single crystal. The high-resolution transmission electron microscopy (HRTEM) image in Figure 3b further confirms the single-crystalline nature of these Fe_3O_4 nanowires. The lattice fringe observed in this image is 0.48 nm, which agrees well with the separation between the (111) lattice planes. Combined with the ED results it is reasonable to suggest that the preferred growth of nanowires is along [110], one of the easy magnetic axes of Fe_3O_4.

The magnetism of the magnetite nanowires was also investigated by a vibrating sample magnetometer (VSM) at room temperature (see Figure 4). The hysteresis loop of Fe_3O_4 nanowires shows a ferromagnetic behavior with a saturation magnetization (M_s) of 69.6 emu/g and coercivity (H_c) of 97 Oe, which is lower than that of the corresponding bulk (M_s: 92 emu/g, H_c: 115–150 Oe).[8] The high shape anisotropy and small particle size of the obtained magnetite nanowires may be responsible for the relatively low magnetization and coercivity.[6,9]

Citrate ion is an important biological ligand for metal ions and forms strong complexes with metal ions such as Ag^+, Mg^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}, and Fe^{3+}.[10] Citrate ion has been used as a shape modifier for the preparation of ZnO complex structures and Ag nanowires.[11] In this preparation, the citrate ion is performing two major roles. First, it strongly complexes iron ion to form complex $[Fe(C_6H_5O_7)]^-$. Formation of this complex could sharply reduces the free Fe^{2+} concentration in solution and thus results in a relatively slow reaction rate, which is favorable for the oriented growth of magnetite nanostructures along the easy magnetic axis, namely the [110] direction. Second, citrate ion may preferentially bind to certain crystal faces of the magnetite crystals through its COO^- and OH^- functions, with the consequence that the crystal grows along only one axis. Recent works have also shown that citrate ions adsorb preferentially on the certain surface of the crystal and promote crystal growth along the unique axis,[11] which is consistent with our suggestion about the role of the citrate anions. While PVP introduced during the experiment only plays an assistant role in controlling the diameters and aspect ratios of the products. When the experiment was conducted in the absence of PVP, the magnetite nanowires with an increased mean diameter were obtained.

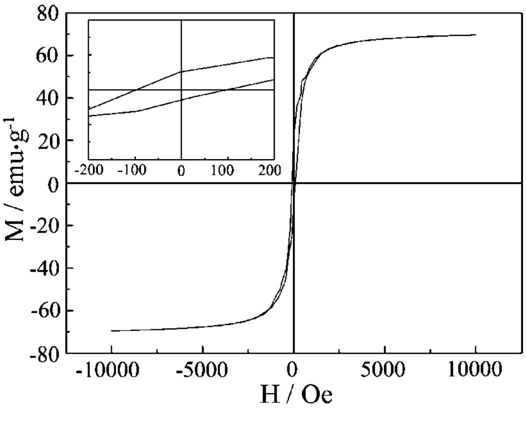

Figure 4. Magnetic hysteresis loop of as-prepared products at room temperature. The inset is an expanded low-field curve.

In summary, high yield of single-crystalline magnetite nanowires have been prepared by a simple low-temperature hydrothermal method using ferrous ammonium sulfate hexahydrate, trisodium citrate, and PVP as starting materials. The hysteresis loop of Fe_3O_4 nanowires shows a ferromagnetic behavior with saturation magnetization of 69.6 emu/g and coercivity of 97 Oe. Citrate anion is proposed to be responsible for the formation of single-crystalline magnetite nanowires. Such an approach provides a direct and cost-effective method for large-scale production of magnetite nanowires without the need of additional template, precursor or exterior magnetic field induction.

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References

1 B. Kim, S. L. Tripp, A. Wei, *J. Am. Chem. Soc.* **2001**, *123*, 7955; M. P. Pileni, *J. Phys. Chem. B* **2001**, *105*, 3358.
2 G. Bate, in *Ferromagnetic Material*, ed. by E. P. Wohlfarth, North-Holland, Amsterdam, **1980**.
3 S. J. Park, S. Kim, S. Lee, Z. G. Khim, K. Char, T. Hyeon, *J. Am. Chem. Soc.* **2000**, *122*, 8581.
4 T. A. Crowley, K. J. Ziegler, D. M. Lyons, D. Erts, H. Olin, M. A. Morris, J. D. Holmes, *Chem. Mater.* **2003**, *15*, 3518; L. Y. Zhang, D. S. Xue, X. F. Xu, A. B. Gui, C. X. Gao, *J. Phys.: Condens. Matter* **2004**, *16*, 4541.
5 S. Y. Lian, Z. H. Kang, E. B. Wang, M. Jiang, C. W. Hu, L. Xu, *Solid State Commun.* **2003**, *127*, 605; Z. M. Peng, M. Z. Wu, Y. Xiong, J. Wang, Q. W. Chen, *Chem. Lett.* **2005**, *34*, 636.
6 J. Wang, Q. W. Chen, C. Zeng, B. Y. Hou, *Adv. Mater.* **2004**, *16*, 137.
7 D. L. A. de Faria, S. V. Silva, M. T. de Oliveira, *J. Raman Spectrosc.* **1997**, *28*, 873.
8 D. H. Han, J. P. Wang, H. L. Luo, *J. Magn. Magn. Mater.* **1994**, *136*, 176; R. S. Iskhakov, S. V. Komogortsev, A. D. Balaev, A. V. Okotrub, A. G. Kudashov, V. L. Kuznetsov, Y. V. Butenko, *JETP Lett.* **2003**, *78*, 236.
9 G. F. Goya, T. S. Berquó, F. C. Fonseca, M. P. Morales, *J. Appl. Phys.* **2003**, *94*, 3520.
10 J. A. Parkinson, H. Sun, P. J. Sadler, *Chem. Commun.* **1998**, 881.
11 K. K. Caswell, C. M. Bender, C. J. Murphy, *Nano Lett.* **2003**, *3*, 667; Z. R. R. Tian, J. A. Voigt, J. Liu, B. Mckenzie, M. J. McDermott, M. A. Rodriguez, H. Konishi, H. F. Xu, *Nat. Mater.* **2003**, *2*, 821.

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