

Synthesis of Fe_3O_4 particle-chain microwires in applied magnetic field

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Abstract

Fe_3O_4 particle-chain microwires are firstly synthesized under magnetic field by a simple coprecipitation method. The increase of magnetic field caused the lengthening of the wires, and doubled densities of starting solution lead to a halved diameter. It was supposed that the magnetic field gradient and the particular growing process of particles are the main factors of the formation of these microwires. Magnetic hysteresis curves of Fe_3O_4 microwires were also measured.

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1. Introduction

Recently, the technology called spintronics has been attracting considerable interest [1–4]. The spintronics, based on the manipulation of electronic spin, offers opportunities for a new generation of devices combining standard microelectronics with spin-dependent effects. High degree of spin polarization is the crucial property of the materials that have been investigated in this field [1], e.g., the only ferromagnetic metallic dioxide CrO_2 , various members of the mixed valence perovskites, such as $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, and the well-known magnetic oxide magnetite (Fe_3O_4). Fe_3O_4 has attracted a lot of attention not only because it has almost completely spin-polarized electron at the Fermi energy at room temperature, which has been demonstrated by both theory [5,6] and experimental measurement [7], but also for its relatively high electric conductivity ($2 \times 10^4 \Omega^{-1} \text{m}^{-1}$) and high Curie temperature (860 K) among half-metals [8]. These properties enable magnetite to be a very potential material for room temperature application. Until now, magnetite is widely investigated by researchers, various morphologies of which have been fabricated and their properties, especially MR effect, are researched, for example, junctions [9,10], polycrystal films [11,12], epitaxial films [13–15], and

nanocontacts [16,17]. But there are only few reports concerning magnetite wires [18–20], as the conventional hard-template process is convenient for fabricating metal and alloy wires but not for oxides, and the soft-template methods [21] and redox methods [22,23] tend to yield acicular particles. Previously, the author reported the successful synthesis of $\text{Mn}_{0.5}\text{Fe}_{2.5}\text{O}_4$ particle-chains [24], but the forming process of those chains is still obscure. In this article, we report the synthesis of Fe_3O_4 particle-chain microwires by the magnetic-field-induced coprecipitation method and present the presumption of their growing process. Though chains of various metallic and alloyed particles have already been prepared [25–28], this is the first time of the successful synthesis of Fe_3O_4 particle chains to the best of our knowledge.

2. Experimental section

2.1. Sample preparation

Fe_3O_4 microwires were fabricated by oxidating $\text{Fe}(\text{OH})_2$ colloid particles with KNO_3 in external magnetic field. Container was self-made cuboidal Teflon (polytetrafluoroethylene) cell with permanent magnets fixed at two opposite outer surfaces. The strengths of magnetic field on the middle of the inner surface near the magnets were 0, 0.1 and 0.3 T. The chemical reagents used were $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, KOH and KNO_3 , all of which were of analytical

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grade. Distilled water was used for the preparation of solutions. KOH solution (20 mL, 0.15 mol/L) and KNO₃ solution (5 mL, 0.6 mol/L) were boiled for 2 min to expel oxygen. Then, KOH solution was moved into the container which was kept at 80 °C in a constant temperature water-bath. The container was enclosed immediately after mixing KNO₃ solution and FeSO₄ solution (5 mL, 0.15 mol/L) into it. This mixture was kept at 80 °C for 7 h and the product was washed immediately with distilled water and absolute ethanol several times in magnetic field and dried in air at room temperature.

2.2. Sample characterization

The XRD pattern was obtained on Philips X'Pert with Cu K α radiation ($\lambda = 1.54167 \text{ \AA}$). Room temperature transmission Mössbauer spectrum was recorded using a constant acceleration spectrometer and a ⁵⁷Co(Pd) source. TEM images were taken with Hitachi H-600 transmission electron microscope using an accelerating voltage of 100 kV. SEM images were taken on Hitachi S-4800 scanning electron microscope with an accelerating voltage of 5.0 kV. Magnetic hysteresis curves were measured on Lakeshore 7304 vibrating sample magnetometer (VSM).

3. Results and discussion

XRD pattern (Fig. 1) shows the Fe₃O₄ sample formed under 0.3 T external magnetic field has cubic spinel crystal structure without impurity. Mössbauer spectrum analysis was also carried out to confirm the component. As shown in Fig. 2, the Mössbauer spectrum consists of two sextets, which are corresponding to the tetrahedral (A) and octahedral [B] lattice sites of Fe₃O₄. Hyperfine parameters obtained from the Mössbauer spectrum are listed in Table 1. Hyperfine fields of the two sites are 48.6 and 45.4 T, respectively, very close to the standard value (48.7

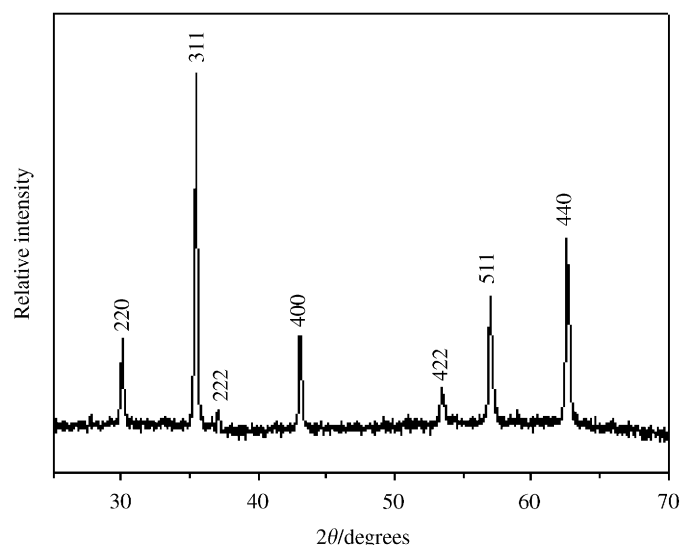


Fig. 1. XRD pattern of Fe₃O₄ wires prepared under a 0.3 T magnetic field.

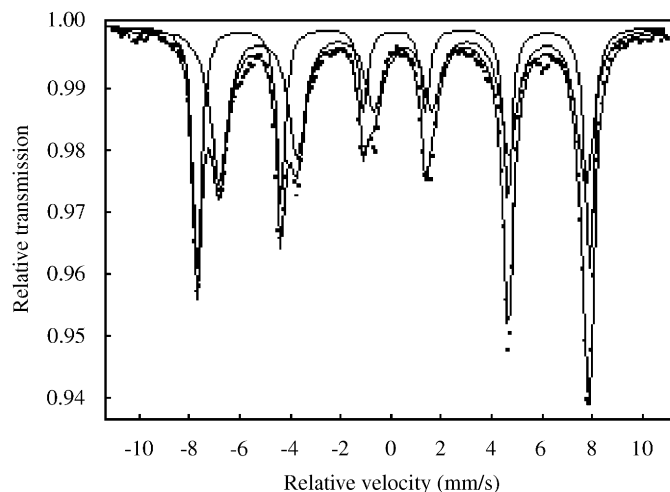


Fig. 2. Mössbauer spectrum of Fe₃O₄ microwires prepared under a 0.3 T magnetic field.

Table 1

Hyperfine parameters obtained from the Mössbauer spectrum of Fe₃O₄ microwires formed under 0.3 T external magnetic field

| Site | Area (%) | IS (mm/s) | QS (mm/s) | LW (mm/s) | H _{hr} (T) |
|------|----------|-----------|-----------|-----------|---------------------|
| A | 41 | 0.12 | -0.02 | 0.82 | 48.6 |
| B | 59 | 0.47 | -0.01 | 0.41 | 45.4 |

and 45.4 T) of Fe₃O₄ [29]. The Mössbauer spectrum demonstrates that the sample is not γ -Fe₂O but Fe₃O₄.

Fig. 3 shows the transmission electron microscopy (TEM) images of samples prepared under different external magnetic fields. As Fig. 3A shows, sample prepared without applied magnetic field is spherical magnetite particles with an average diameter of 1 μ m. But when 0.1 T external magnetic field was applied during fabrication, short microwires with an average diameter of 1 μ m and slenderness ratio more than 10 were observed in the image (Fig. 3B). Expecting to obtain longer wires, stronger magnetic field was applied to the reacting solution. TEM image (Fig. 3C) clearly demonstrates magnetite microwires with an average diameter of 1 μ m and slenderness ratio more than 30 were successfully fabricated when the applied magnetic field was improved to 0.3 T. The drastic transformation of morphology with the increase of magnetic field revealed that the external magnetic field is the critical factor in the formation of microwires.

It is noticed that the surface of these wires is not smooth. From the amplified image (Fig. 3D) we deduced the wires are chains of particles. SEM images (Fig. 4) were then taken to confirm their morphology, which demonstrate the wires are composed of polyhedral particles connecting with each other. The connection of these magnetite particles is so tight that there is no obvious gap between any two conjoint particles.

For obtaining microwires with various diameters, reacting solutions with doubled densities were utilized to

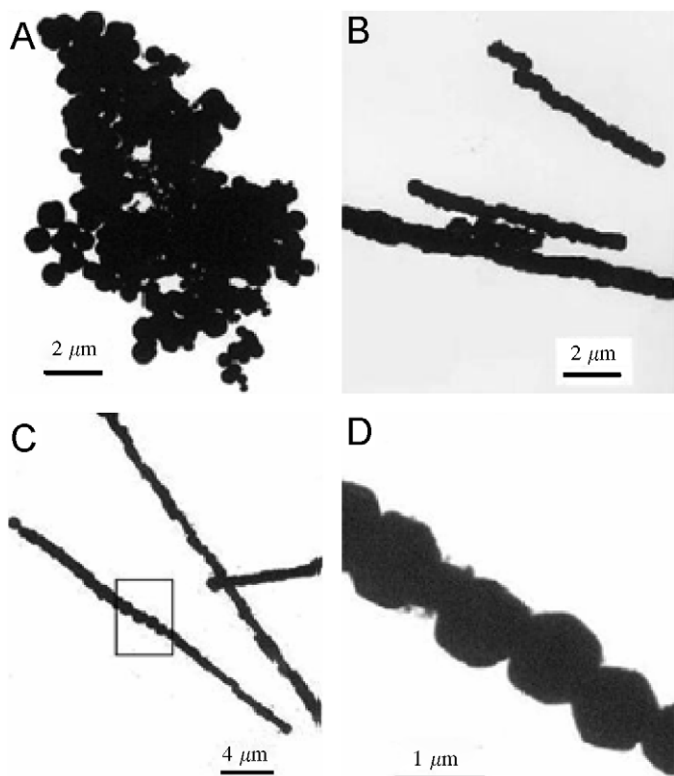


Fig. 3. TEM images of Fe_3O_4 samples fabricated under different magnetic fields. (A) $H = 0$ T, (B) $H = 0.1$ T, (C) $H = 0.3$ T, (D) amplified image of the boxed area in (C).

prepare magnetite wires. TEM images (Fig. 5) show the average diameter of this sample decreased to $0.5 \mu\text{m}$. This phenomena demonstrates it is feasible to obtain magnetite microwires with various average diameters by adjusting the density of starting solution. However, as we can see from Fig. 5, a small amount of aggregated particles also exist. That may be due to the distribution of particle size and magnetic field.

Hermanson et al., have reported the assembly of metallic microwires by dielectrophoresis from suspensions of metallic nanoparticles [24]. Though the morphology of microwires fabricated by them is not identical with magnetite microwires fabricated by us, we still believe the growing process of magnetite wires is partly similar to the process they described; the field gradient plays an important role in the assembly of particles. Due to the existence of magnetic gradient in the solution, magnetite particle will be magnetized and move towards the magnets while they are formed. During the moving process, it is very possible that one particle will meet other ones and form short rod along the magnetic curve as a result of the attraction between magnetic dipolars [30]. When they arrive at the magnets, particles and rods will attach to the tips of wires because the magnetic field gradient around those tips is relatively higher [24]. However, this presumption is not adequate to explain why the particles are not randomly agglomerated as reported in other field-induced processes [18,31], but form single-particle chain. We

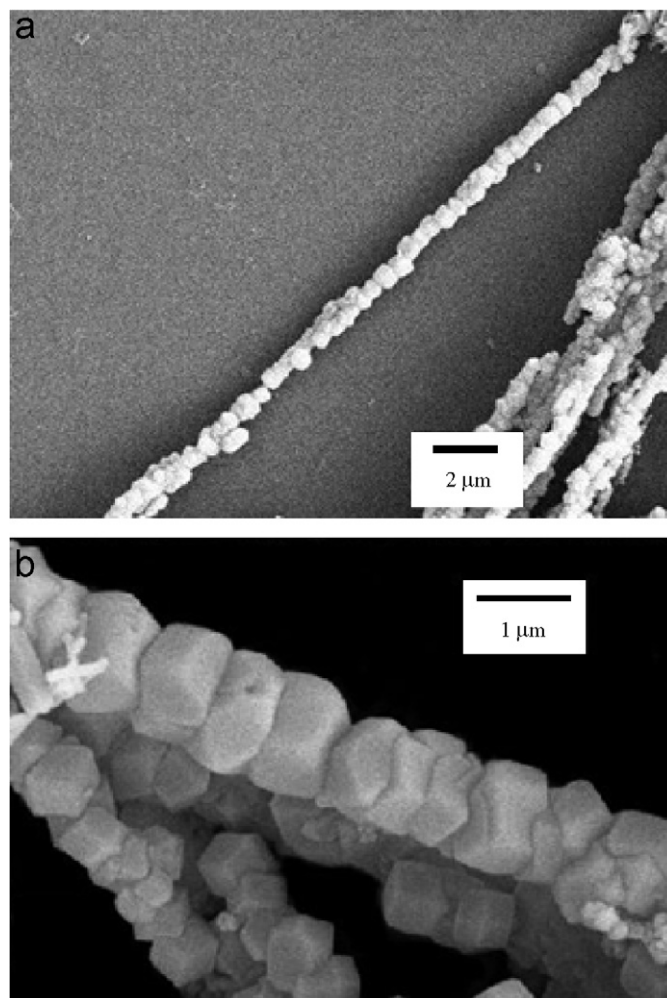


Fig. 4. SEM images of Fe_3O_4 microwires fabricated under a 0.3 T magnetic field.

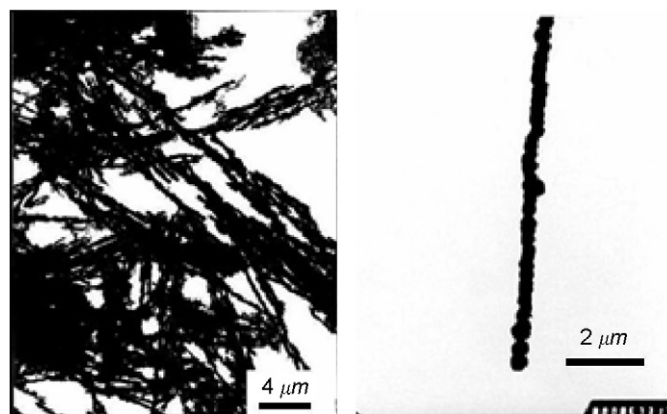


Fig. 5. TEM images of Fe_3O_4 microwires fabricated in the solution with doubled densities under a 0.3 T magnetic field.

deduced the growing mechanism of magnetite particles by this oxidation method is the crucial factor.

To demonstrate our purpose, morphologies of samples after short time reaction are observed by TEM. Other reacting conditions are as same as the fabrication of Fe_3O_4

with an average diameter of 1 μm . As Fig. 6A shows, sample reacting for 30 min consists of dispersed particles with an average diameter of about 100 nm and amorphous material which is believed to be iron hydroxide. After 1 h reaction, particles with an average diameter of 500 nm and short rods surrounded by amorphous iron hydroxide are observed in the TEM image (Fig. 6B). TEM images demonstrate these particles do not possess net magnetisation during their growing process for they are not agglomerated in magnetic field and they still have the potential of growing larger due to the existence of iron hydroxide. But the existence of short particle chain reveals that there is already a little part of particles gain net magnetization after 1 h reaction and move towards magnets. This result is coincident with L.W. Chen's report [32]: magnetite particles prepared by this oxidation of $\text{Fe}(\text{OH})_2$ method have defects in B site of crystal when they are firstly formed, which lead to the lack of net magnetization; with the carrying on of reaction, Fe^{2+} and Fe^{3+} ions enter B site gradually, so the net

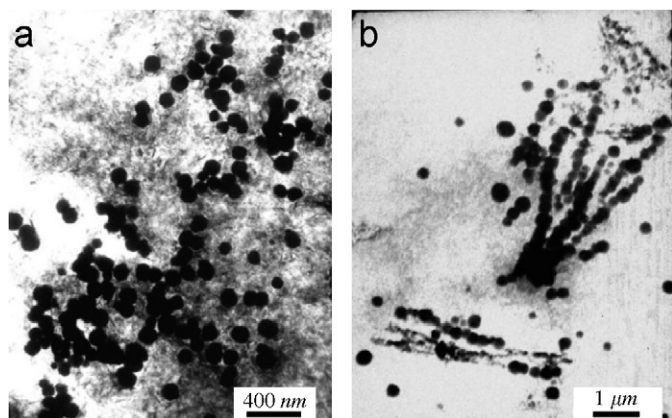


Fig. 6. TEM images of Fe_3O_4 samples after reacting for 30 min (A) and 1 h (B).

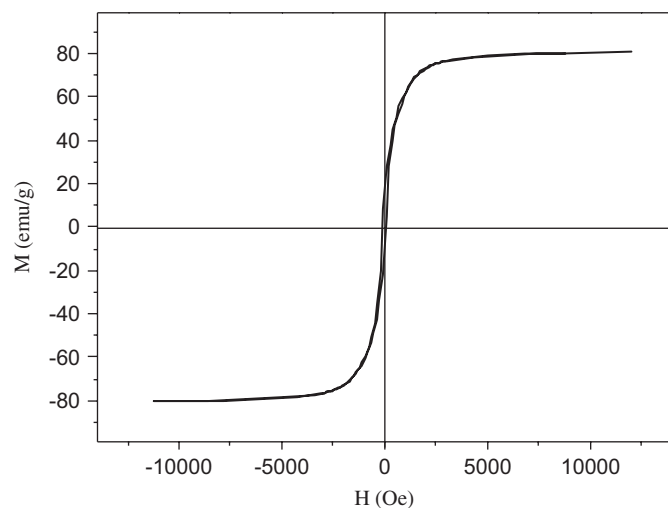


Fig. 7. Magnetic hysteresis curve of Fe_3O_4 microwires measured at room temperature.

magnetization of particles become stronger. This growing process ensures that these particles respond to the magnetic field in a long range of time, so only a little fraction of them at the same time. In this case one particle will move directly to the magnets when it obtains magnetism without the interaction with other unmagnetized particles beside it, resulting in the disappearance of agglomeration of particles.

Fig. 7 shows magnetic hysteresis curve of Fe_3O_4 microwires. The coercivity is 60 Oe and the saturation field is about 3500 Oe. Saturation magnetization of Fe_3O_4 microwires is 83 emu/g, which is a little smaller than the bulk value (92 emu/g) [33]. This result is reasonable. As we can see from Table 1, the area ratio of B-site sextet to A-site sextet (59:41) is smaller than the stoichiometric value (about 2:1), which indicates the lacking of Fe ions in the B site. Since Fe_3O_4 is ferromagnetic material, and its net magnetization comes from the difference between the magnetic moments of two sites, the lacking of Fe ions in the B site will lead to the decrease of saturation magnetization.

4. Conclusions

In summary, Fe_3O_4 microwires are successfully fabricated under external magnetic field. TEM and SEM images confirmed that the Fe_3O_4 wires are chains of polyhedral magnetite particles, and the connection of the particles is very tight. The increase of magnetic field caused the lengthening of the wires, but diameters of wires and rods are all as same as the particles fabricated without magnetic field. However, wires fabricated with doubled densities of starting solution possess a halved diameter. Further experiments demonstrate that particles are already formed but gain magnetism gradually before their assembly at the surface of the container caused by the magnetic field gradient. Though our understanding of wires' growing process is still superficial, the successful synthesis of Fe_3O_4 particle-chain microwires provides a useful approach for the preparation of magnetic micro- and nanowires.

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