Magnetic field-assisted hydrothermal growth of chain-like nanostructure of magnetite

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Received 7 June 2004; in final form 16 November 2004
Available online 15 December 2004

Abstract

Chain-like nanostructures consisted of more than 10 magnetite nanoparticles with an average size of 80 nm were hydrothermally prepared at 200 °C under a 0.18 T external magnetic field. Magnetic measurement results revealed that the chain-like structure showed higher saturation magnetization $M_s$, remnant magnetization $M_r$, coercivity $H_c$ and reduced magnetization $M_r/M_s$, compared with those of randomly distributed magnetite nanoparticles prepared without the induction of external magnetic field. Possible reasons responsible for the changes of the above magnetic parameters were tentatively discussed.

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1. Introduction

One-dimensional nanostructured materials including nanotube [1], nanorods [2] and nanowire [3] are currently one of the focuses of material science due to their special properties and potential applications in molecular-based electronic devices [4,5]. In the last decades, various approaches including anodic aluminum oxide (AAO) hard template process [6,7], lecithin soft template [8,9] and redox methods [10,11] have been developed for the preparation of one-dimensional magnetic materials, such as magnetic metals, alloys and metal oxides. Magnetic chain-like nanostructured materials, also, a member of the families of one-dimensional nanostructured materials, however, receives much less attention [12,13]. In many applications, such as those involving electrical transport and magnetic switching, the ordering of nanoparticles plays a critical role.

Interestingly, the migratory and homing animals as well as bacteria seem to possess a built-in compass to respond to earth’s magnetic field for navigation [14–16], which was assumed to be a magnetic chain resulting from the dipolar-interaction-directed self-assembly process. In fact, the system of chain-like magnetite nanostructure is an ideal model to investigate the dipolar interaction. Recently, magnetic field assisted growth of one-dimensional magnetic nanostructured materials has been the subject of fruitful research in our group. Polycrystalline Co and Ni microwires were formed by the self-assembly of Co and Ni nanocrystallites under a 0.25T external magnetic field [17,18]. Single crystalline Fe$_3$O$_4$ nanowires could be formed under the induction of an applied external field [19]. It had been indeed found that magnetic field could significantly influence the movement of magnetic particles [20,21]. In this Letter, we further report the chain-like self-assembly behavior of magnetite nanoparticles under an external magnetic field and its effect on the magnetic properties.
2. Experimental

The chemical reagents used in the work were ferrous chloride (FeCl₂·4H₂O), and sodium hydroxide (NaOH). All the chemicals were of analytical grade. Distilled water, degassed with N₂ gas for half an hour, was used for the preparation of an aqueous solution of Fe²⁺ (0.1 mol/l). 80 ml Fe²⁺ solution was put into a conical flask, and then sodium hydroxide solution (1 mol/l) was dropwise added to the Fe²⁺ solution to make the final pH value of the system to be about 7.5. During the experiment, N₂ was kept passing through the solution to prevent the oxidation of Fe²⁺ in the system. After being vigorously stirred for 10 min, the mixed solution with green precipitates was transferred into two Teflon-lined stainless steel autoclaves with 60 ml capacity, respectively (one without external magnetic field, the other with two permanent rare earth NdFeB magnet under and on the Teflon vessel, respectively. The magnetic field strength on the inner surface of the Teflon vessel was 0.25 T at room temperature, 0.18 T at reaction temperature of 200 °C). Both of the autoclaves were closed tightly to perform hydrothermal processes at 200 °C for 1 h. After the reaction was completed, the resulting black solid powder was separated easily by using a magnet, washed with alcohol and distilled water three times, respectively, then the product was dried in air at 60 °C. The same reaction was also carried out at 200 °C for 5 h. The samples obtained were labelled as S1, S1m, S5 and S5m, with 1, 5 indicating the reaction time and m indicating the case of using external magnetic field, respectively. Samples S1, S1m, S5 and S5m were characterized by X-ray powder diffraction (XRD) using an 18 KW advanced X-ray diffractometer with Cu Kα radiation (λ = 1.54056 Å), and transmission electron microscope (TEM) (Hitachi H-800) using an accelerating voltage of 200 KV. It is notable that before TEM observation, ultrasonic dispersion was performed only for 5–7 min for S1m and S5m. Magnetic hysteresis loops were measured on a vibrating sample magnetometer (VSM, BHV-55) at room temperature.

3. Results and discussion

The XRD patterns of the products S1, S1m, S5 and S5m are shown in Fig. 1. All the peaks indexed for the face-centered cubic magnetite. The rough estimates of the size of S1, S1m and S5 by using the Scherrer’s equation is about 100 nm, in agreement with that of TEM observation for the chain-like nanostructures. For S1m, the reaction time was so short that not too many chain-like products formed, while for S5m, many chain-like products with much better crystallinity were formed, evidenced by the TEM observation. It was also found that the relative intensity ratio of reflection [220] to [400] increased for S1m and S5m, which might originate from the chain structure of magnetite particle under an applied external magnetic field.

In the presence of magnetic field \(H\), the magnetic particle energy with uniaxial magnetic anisotropy is given by Eq. (1)

\[ U = KV\sin^2 \theta - \mu H \cos \alpha, \]  

where \(\theta\) is the angle between the magnetic moment and the easy magnetic axis and \(\alpha\) is the angle between the magnetic moment and the applied field. For the nucleated magnetite (<100 nm) under an external field up to 0.18T magnetic field, the Zeeman energy (\(H\)) is in the same order of magnitude as the thermal energy \(K_B T (10^{-13} \text{erg})\). This indicates that the magnetic moment of the particle can be aligned along the magnetic field direction.

Fig. 2 shows the difference in morphology between S1 and S1m, which clearly reveals the effect of magnetic field on the growth process of Fe₃O₄. Without magnetic field, square nanoparticles dominate the product of S1, with few rod-like \(\alpha\)-FeOOH existing in the S1, which is believed to be the precursor of the reaction system [22] (Fig. 2a). Interestingly, with an applied external magnetic field, some chain-like magnetite nanostructures formed with square nanoparticles still dominating the sample S1m. A typical chain-like structure is shown in Fig. 2b. Single crystalline magnetite nanowires with diameters of 35–100 nm could be formed under an applied 0.25T field in a hydrothermal system using ferrous
chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), diamine hydrate and sodium hydroxide ($\text{NaOH}$) [19]. The role played by diamine hydrate, which slowly oxidized $\text{Fe}^{2+}$ into $\text{Fe}^{3+}$ in alkalescent medium and much reduced the whole reaction rate, might be responsible for the difference of product morphology between chain-like and wire. During the preparation of S1m, the nucleus of magnetite will occur much faster than that of S5, which could be only attributed to the induction of the applied magnetic field (explained later in this Letter). Fig. 3d is a low magnetization image of sample S5m, which shows many low-quality chain-like nanostructures made of hundreds of magnetite nanoparticles. These nanoparticles were assembled along the direction of lines of magnetic force. Considering the magnetic static interaction between two particles, we could easily understand the phenomenon that nearby the nanoparticles of the chain-like nanostructure, there were located some other magnetite nanoparticles. In fact, the perfect chain-like nanostructures (shown in Fig. 3b and c) was only gotten on a limited scale. What’s more, if the ultrasonic dispersion was performed for over 15 min, chain-like nanostructures will greatly decrease. The competition between magnetic static interaction induced by the applied magnetic field together with the interparticles and the disruption induced by the vigorous ultrasonic dispersion roughly determines the number of chain-like nanostructures.

Fig. 4 shows $M$–$H$ hysteresis loops of S1, S1m, S5 and S5m at room temperature. Table 1 shows the main magnetic parameters including saturation magnetization $M_s$, coercive field $H_c$ and remnant magnetization $M_r$ reduced magnetization $M_r/M_s$. Two behaviors can be distinguished:

1: Growth for 5 h greatly enhanced all the magnetic parameters especially the saturation magnetization $M_s$ and remnant magnetization $M_r$. The elongation of growth time from 1 to 5 h could eliminate the precursor of $\alpha$-$\text{FeOOH}$, and improved the crystallinity with the size of particles remaining almost unchanged. Strong correlation between the crystallinity and the magnetic properties has been reported in barium ferrite powder [23,24]. For example, the improved crystallinity of the magnetic materials, not the increase of particle size, is the main
contributing factor to the observed increase of $M_s$ and $H_c$ in BaFe$_{12}$O$_{19}$[23]. The well-crystallized particles have a thinner surface layer, narrower cation distribution of Fe(II)-octahedral and Fe(III)-octahedral and the stronger superexchange interaction between ferric ions, all of which should be responsible for the enhanced saturation magnetization $M_s$ and remnant magnetization $M_r$.

Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>$M_s$ (emu/g)</th>
<th>$M_r$ (emu/g)</th>
<th>$M_r/M_s$</th>
<th>$H_c$ (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>33.33</td>
<td>7.39</td>
<td>0.22</td>
<td>181.2</td>
</tr>
<tr>
<td>S1m</td>
<td>42.18</td>
<td>10.05</td>
<td>0.24</td>
<td>189.3</td>
</tr>
<tr>
<td>S5</td>
<td>84.35</td>
<td>22.44</td>
<td>0.27</td>
<td>206.5</td>
</tr>
<tr>
<td>S5m</td>
<td>89.50</td>
<td>33.48</td>
<td>0.37</td>
<td>232.6</td>
</tr>
</tbody>
</table>

Fig. 3. TEM images for the samples of S5 and S5m. (a) S5. (b)-(d) S5m.

Fig. 4. The magnetization hysteresis loops for S1, S1m, S5, S5m measured at room temperature.

Fig. 4. The magnetization hysteresis loops for S1, S1m, S5, S5m measured at room temperature.
The induction of magnetic field also resulted in the increase of these four magnetic parameters by a little margin. The long range self-assembly of magnetic nanoparticles is a complex process that involves numerous competing effects including the coupling of each nucleated particle’s dipole moment to the applied field, magnetic dipole–dipole interactions, electronic polarization interactions, thermal kinetics, and other ambient condition factors. Presently, there is no rigorous theory that can completely solve all of the effects of magnetic filed induction. Recently, the lower magnetization was obtained with the increase of applied external magnetic field strength for unit mass magnetite nanowires for the fact that the high shape anisotropy of nanowires prevented them from magnetizing in directions other than along their easy magnetic axes [19]. Polycrystalline Co and Ni wires grown by the magnetic field-assisted growth showed a much higher saturation magnetization and Ni 2+ compared with that without the induction of an external magnetic field [17,18].

As is well known to us, for a rod-like magnetic medium, the demagnetization factor can be expressed as Eq. (2)

\[ N_D = 1 - \left( \frac{l}{d} \right) \left[ 1 + \left( \frac{l}{d} \right)^2 \right]^{-1/2}, \]

where \( N_D \) is the demagnetization factor; \( l \) the length of the rod, and \( d \) the diameter of the rod. For an indefinite long rod, \( l = \infty, N_D = 0 \), and for an indefinite thin plate, \( l \approx 0, N_D = 1 \). The chain-like structure, assembled by the regular square magnetite nanoparticles, could be regarded as a definite quasi-rod-like magnetic medium.

Under the external magnetic field, the chain-like structure would show a much smaller \( N_D \), compared with that of square magnetite nanoparticles. The reduced demagnetization should definitely contribute to the increase in the magnetization.

Recently, some researchers reported that an applied magnetic field could quicken the diffusion of paramagnetic ions including OH\(^-\), Fe\(^{3+}\), Fe\(^{2+}\) and paramagnetic gases, such as O\(_2\) in the water phase [25,26]. These reports were further confirmed by our experiment that external magnetic field could quicken the oxidation process for the magnetite when exposed to ambient air [27]. As far as the chain-like magnetite nanostructures are concerned, it is believed that the faster diffusion of paramagnetic ions including OH\(^-\), Fe\(^{3+}\), and Fe\(^{2+}\) will increase the reaction probability for these Fe\(^{3+}\), Fe\(^{2+}\) and O\(_2\), and makes the formation of magnetite easier when compared with that without the induction of an external magnetic field. This will lead to decrease of oxygen vacancies, stronger Fe–O–Fe exchange, better crystallinity and hence much smoother surface of S5m than that of S5 evidenced by Fig. 3. Stronger Fe–O–Fe exchange will also mean larger saturated magnetization \( M_s \).

Based on the results of the reduced demagnetization factor \( N_D \), the enhanced crystallinity, and the oriented growth in ref [17,18], we can understand the little increase of \( M_s \) in the S1m and S5m. As far as the increase of \( H_c \) and reduced remanence \( M_r/M_s \), Sahoo [28] reported that \( H_c \) and reduced remanence \( M_r/M_s \) of aligned magnetite nanoparticles showed a higher value when measured parallel to the magnetic field and the increase was attributed to the predominant alignment of the nanoparticles. Hutlova [29] pointed out that the large coercive field reflects the ‘intrinsic anisotropy’ of the particles enhanced by the interparticle dipolar fields for the case of cobalt ferrite in silica matrix. Based on the above results, the nanoparticles in the chain-like structure are expected to show large interparticle dipole field and hence larger coercive field for our S1m and S5m when compared with S1, and S5. That is to say, the magnetic parameters, such as \( M_s, M_r, H_c \), and \( M_r/M_s \) could be tuned by the use of external magnetic field.

4. Conclusions

In summary, chain-like nanostructures consisted of magnetite particles with an average size of 80 nm were formed at 200 °C under the induction of a 0.18 T external magnetic field through a convenient hydrothermal process. With the elongation of growth time, more chain-like nanostructures with better crystallinity could be obtained. Magnetic measurement indicated that when compared with those counterpart samples without the induction of external field, the chain-like structure displays improved magnetic properties, including saturation magnetization and coercivity, which were tentatively attributed to the aligned assembly behavior, reduced demagnetizing factor, better crystallinity under the induction of an external magnetic field and the interparticles dipole interaction. The induction of an external magnetic field on magnetic nanoparticles is suggested to be a promising method for the preparation of novel nanostructures and modulation of magnetic properties.

Acknowledgement

This work is supported by the National Natural Science Foundation of China (NSFC) under Grant Nos. 20125103 and 90206034.

References


