

Preparation of Fe₂O₃ microtubules and the effect of a surfactant on their properties

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Fe₂O₃ microtubules were synthesised by a sol-gel method using a cotton template. The surfactant was added in the formation process of the sol to change the morphology of the microtubules and improve their properties. The phase, morphology, particle diameter, and magnetic properties of the samples were determined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and by using a vibrating sample magnetometer (VSM), respectively. The external diameters of Fe₂O₃ microtubules ranged between 8 μm and 13 μm, and the wall thicknesses ranged between 0.5 μm and 2 μm. The type of calcination method plays a significant role in developing the Fe₂O₃ phase and the variation in the magnetic properties in the sol-gel template complexing method. γ-Fe₂O₃ was synthesized by a self-propagation method. However, α-Fe₂O₃ was synthesized after calcination at 400 °C for 2 h. The effect of different types of surfactant on the magnetic properties of the Fe₂O₃ microtubules was different. However, the coercivity decreased with the addition of a surfactant.

Key words: Fe₂O₃, microtubule, surfactant.

Introduction

Iron oxides have been widely used for a long time due to their excellent ferromagnetic properties. Among them, α-Fe₂O₃ is the most researched polymorph existing in nature as the mineral hematite. α-Fe₂O₃ (hematite) is not only a strategic industrial material, but also one of the most used metal oxides with various applications in many scientific and industrial fields. Due to the importance of the shape and texture of materials in determining their macroscopical properties [1-3], how to control the morphologies of micro- and nanoscale materials has become an important goal of modern materials chemistry. Up to now, many developments have been made and many novel morphologies such as nanoribbons [4], nanocubes, nanofibers, dendrite and star-like nanostructures [5] have been synthesized successfully. However the preparation of Fe₂O₃ microtubules has seldom been reported. Also these features correlate strongly with the preparation process [1, 2]. There has been much interest in the development of synthetic methods to prepare nanofiber α-Fe₂O₃, such as using a hydrothermal reaction [5-7], a microwave process [8], a sol-gel method [9], a micro-emulsion method [10], a forced hydrolysis method [11], solid-phase grinding [12], and high-energy ball milling.

In the study, Fe(NO₃)₃ was used as a crude material to form a sol in the solvent. Then the sol was dipped onto the surface of an absorbent cotton template. The sol formed a gel on the surface of the cotton template. Fe₂O₃ microtubules were synthesized after the process of self-propagation or calcination. A surfactant was added in the formation process

of the sol to change the morphology of the microtubules and their properties improved. The phase, morphology, particle diameter, and the magnetic property of samples were determined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and by using a vibration sample magnetometer (VSM), respectively. Further, in this study, the mechanism of formation of Fe₂O₃ microtubules and the effect of the surfactant on their properties was examined.

Experimental

10g Fe(NO₃)₃·9H₂O was dissolved in 150 ml de-ionized water. The solution was heated and agitated in a magnetic stirring apparatus until the volume was about 120 ml to form a sol. The sol was dipped onto the prepared loose and dry absorbent cotton fibers. Then, the absorbent cotton was dried for 12 h at room temperature and then dried in a drying cabinet at 70 °C. Further, the dried gel was divided to three parts. The first part was self-propagated in order to prepare sample A, the second part was calcined at 400 °C for 2 h to prepare sample B, and the third part was self-propagated first and then calcined at 400 °C for 2 h to prepare sample C. With the above heat processing, 1 g hexadecyl trimethyl ammonium bromide(CTAB) was added to the solution in the process of adding Fe(NO₃)₃·9H₂O to obtain samples D, E, F respectively, and 1 g sodium lauryl benzenesulfate (DBS) was added for the preparation of samples G, H, I respectively. The preparation processes are shown in Table 1.

The magnetic properties were measured at room temperature using a VSM with a maximum field of 15 T. The reaction products were identified by XRD using Cu-Kα radiation. The grain size and morphology were determined using SEM.

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Table 1. The preparation process of different Fe₂O₃ microtubules

Sample	Surfactant	Self-propagation	Calcination
A	Blank	Yes	No
B	Blank	No	Yes
C	Blank	Yes	Yes
D	CTAB	Yes	No
E	CTAB	No	Yes
F	CTAB	Yes	Yes
G	DBS	Yes	No
H	DBS	No	Yes
I	DBS	Yes	Yes

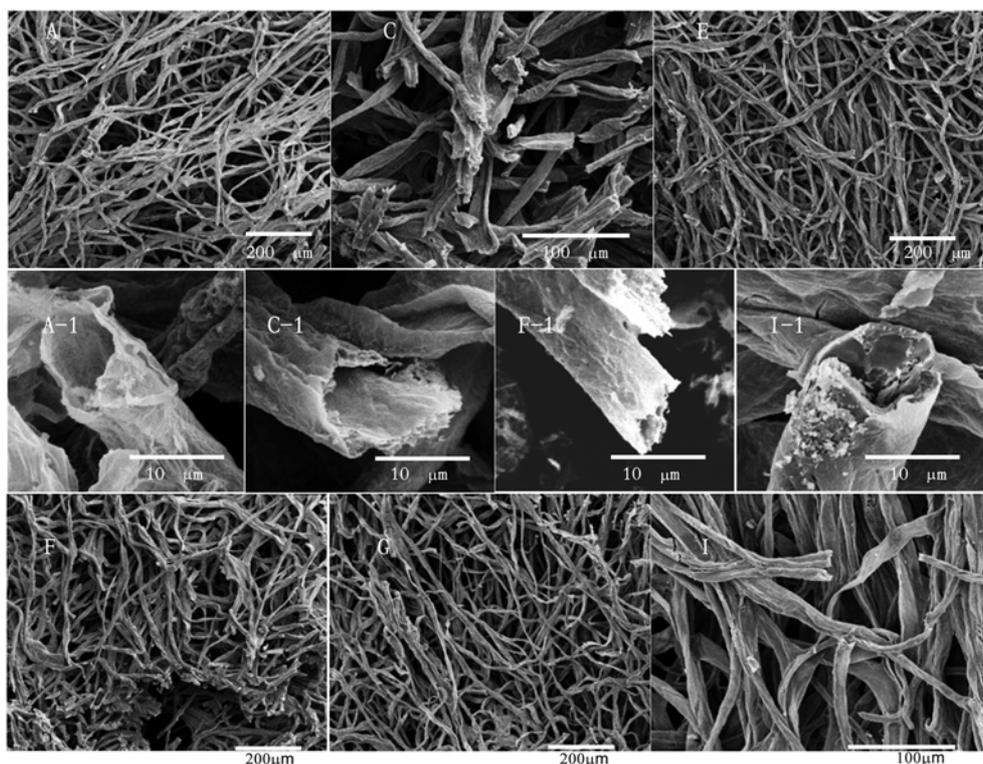
Results and Discussion

The morphology of Fe₂O₃ was studied by SEM. Fig. 1 shows SEM images of the Fe₂O₃ samples. As shown in these images, the samples retained the morphology of the cotton fibers, and Fe₂O₃ microtubules were prepared. The external diameters of Fe₂O₃ microtubules ranged between 8 μm and 13 μm, and the wall thicknesses ranged between 0.5 μm and 2 μm. The microtubules were regular, and some gas cavities were observed in the pipe walls. As is shown in Fig. 1, the effect of the surfactant on the morphology of the Fe₂O₃ microtubules was not very evident. However, a partial Fe(OH)₃ sol was linked together by the complexing effect of the surfactant, resulting in the bonding of partial Fe₂O₃ microtubules.

The mechanism of formation of the microtubules is as follows. In the formation process of Fe₂O₃, Fe³⁺ first

hydrolyzed in the solution to form a Fe(OH)₃ sol with a pH between 1.38 and 2.13. In this study, absorbent cotton was used as the template. There were many –OH on the surface of the absorbent cotton, and the surface of the absorbent cotton appeared to be ragged. Therefore, the solute molecules were prone to be absorbed onto the surface of the absorbent cotton. When the sol was dipped onto the surface of the absorbent cotton, Fe(OH)₃ was adsorbed by it. When the moisture content in the sol was volatilized, Fe(OH)₃ formed hydrogen bonds with the –OH on the surface of the absorbent cotton. On continued evaporation of the moisture content, excessively active groups of the solvent combined through hydrogen bonds to form an annulus-like gel. The absorbent cotton template was carbonized and then gasified in the calcination process. The Fe(OH)₃ gel decomposed to Fe₂O₃ after the calcination process [14]. The sample retained the morphology of the cotton fibers. Finally, Fe₂O₃ microtubules were obtained.

Fig. 2 shows the XRD spectra of the Fe₂O₃ microtubules prepared using the different processes. From the analysis of the XRD characteristic peaks of samples and the standard cards of α-Fe₂O₃ (code: 25-1402) and γ-Fe₂O₃ (code: 33-0644), it can be concluded that the calcination method plays a significant role in the variation of Fe₂O₃ phase in the sol-gel template complexing method. As is shown in Fig. 2, the major phase of the A, D and G samples obtained by a self-propagation process was the γ-Fe₂O₃ phase. Also α-Fe₂O₃ partially appeared in the samples D and G. This suggests that adding DBS effects the purity of the Fe₂O₃ with an absence of an impurity

**Fig. 1.** SEM images of the Fe₂O₃ microtubules prepared by the different processes (see Table 1).

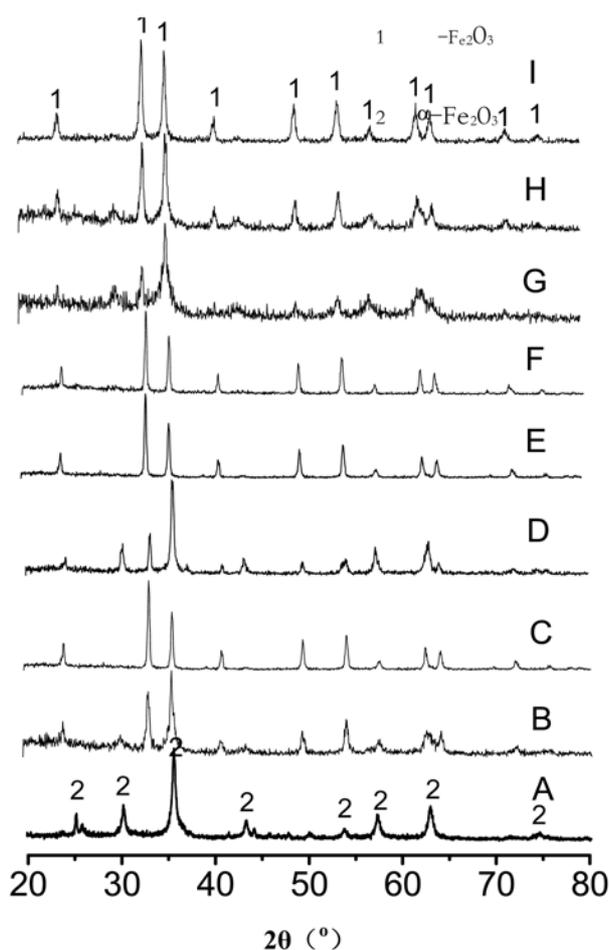


Fig. 2. XRD spectra of Fe₂O₃ microtubules prepared by the different processes.

phase. The sample obtained by the calcination of the precursor at 400 °C for 2 h was pure α-Fe₂O₃. The purity of the samples were improved by the self-propagation process.

As the temperature of self-propagation was relatively low, γ-Fe₂O₃ [15, 16] with a spinel-type structure (the metastable state of α-Fe₂O₃) was formed in the self-propagation process, and it was stabilized. In the calcination process, Fe(OH)₃ decomposed to iron-titanium type α-Fe₂O₃ because of the rapid temperature variation. In the process, where self-propagation was carried out first followed by calcination, the Fe(OH)₃ decomposed to γ-Fe₂O₃; then it stabilized and transformed to α-Fe₂O₃. This indicated that a high temperature is propitious for the formation of α-Fe₂O₃.

The magnetic properties of different samples were measured using the VSM technique and the results are shown in Table 2. As shown in Table 2, the coercivity for samples B, E and H obtained by the calcination of the precursor at 400 °C for 2 h were 40.4 Oe, 20.9 Oe and 24.1 Oe respectively, which represented the properties of a soft magnetic ferrite. The coercivity for samples A, D, F (obtained only by the self-propagation process), C

Table 2. The magnetic performance of the Fe₂O₃ microtubules prepared by different processes

Sample	Coercivity (Hc)/Oe	Saturation magnetization (Ms)/(emu·g ⁻¹)	Remanent magnetization (Mr)/(emu·g ⁻¹)
A	228.8	1.8	7.2
B	40.4	1.1	17.8
C	262.4	2.1	6.7
D	186.8	1.2	10.3
E	20.9	0.8	13.8
F	155.5	1.1	8.8
G	103.2	6.0	15.3
H	24.1	4.1	33.6
I	130.1	11.2	13.7

G, I (obtained by the calcination process after the self-propagation process) were all more than 100 Oe, which represented the properties of a hard magnetic ferrite. According to the literature, γ-Fe₂O₃ is a hard magnetic ferrite and α-Fe₂O₃ is a soft magnetic ferrite [17]. As for the samples obtained by the calcination process after the self-propagation process, the γ-Fe₂O₃ (the metastable phase of α-Fe₂O₃) changed to α-Fe₂O₃ after the stabilization of γ-Fe₂O₃.

The samples obtained by self-propagation and subsequent calcination gave properties of a hard magnetic ferrite. As is seen in Table 2, the coercivity for the samples decreased and the magnetization increased after the addition of a surfactant. As was shown in the XRD spectra, α-Fe₂O₃ partially appeared in the samples obtained by self-propagation after the addition of a surfactant. This indicated that the addition of a surfactant was helpful in the formation of soft magnetic α-Fe₂O₃, resulting in a decrease of the coercivity.

Conclusions

The Fe₂O₃ microtubules (external diameter: between 8 μm and 13 μm; wall thickness: between 0.5 μm and 2 μm) were obtained using an absorbent cotton template. The different calcination methods play a very important part in developing the Fe₂O₃ phase and the variation in the magnetic properties in this sol-gel template complexing method. This indicates that the sample obtained with only the self-propagation of the sol is a hard magnetic γ-Fe₂O₃, the sample obtained by calcination at 400 °C for 2 h is a pure soft magnetic α-Fe₂O₃. The α-Fe₂O₃ obtained by calcination after self-propagation gives hard magnetic properties. The conclusion is that the addition of a surfactant is helpful to the formation of soft magnetic α-Fe₂O₃, resulting in a decrease of the coercivity.

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