

Facile hydrothermal route to the controlled synthesis of α -Fe₂O₃ 1-D nanostructures

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Abstract. Single-crystalline α -Fe₂O₃ 1-D nanostructures can be obtained via a facile one-step hydrothermal synthetic route. It was found that the introduction of SnCl₄ played a key role in determining the composition and morphology of α -Fe₂O₃. The addition of SnCl₄ favours the formation of Fe₂O₃ rather than FeOOH, and the morphology can be tuned from nanorod to double-shuttle as the increase of SnCl₄ concentration. The products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and selected-area electron diffraction (SAED). This simple method does not need any seed, catalyst, or template, thus is promising for large-scale and low-cost production.

Keywords. Fe₂O₃; hydrothermal; morphology; nanostructure.

1. Introduction

Iron oxides represent an important type of materials capable of use in a wide range of applications, such as catalysis (Rumyantseva *et al* 2006), sensors (Kotsikau *et al* 2004; Chen *et al* 2005; Wu C Z *et al* 2006), in magnetic devices (Cao *et al* 2005; Wu J J *et al* 2006), and in rechargeable lithium batteries (Wu C Z *et al* 2006). The properties of Fe₂O₃ are determined predominantly by crystal structure, composition, particle size and morphology. Therefore, the synthesis of Fe₂O₃ with well controlled composition, size and shape is of great significance for their applications. Since the discovery of carbon nanotubes in 1991, one-dimensional (1-D) nanostructures have aroused intensified interest because of the unique size- and shape-dependent properties for future technological applications. α -Fe₂O₃ is the most stable iron oxide under ambient conditions. It is expected that 1-D nanostructures of Fe₂O₃ will find new applications or improve the performance of existing applications.

There have been many reports on the preparation of α -Fe₂O₃. α -Fe₂O₃ nanowire arrays were grown by a vapour-solid route via the tip-growth mechanism (Chueh *et al* 2006). Large arrays of aligned α -Fe₂O₃ nanotubes were prepared by a templating technique through thermal decomposition of an analytical Fe(NO₃)₃ precursor within an anodic alumina membrane. Tang *et al* (2006) reported the synthesis of α -Fe₂O₃ nanorods through the calcination of FeOOH nanorods precursor. Ordered mesoporous

α -Fe₂O₃ with crystalline walls was prepared through silica template (Jiao *et al* 2006). Zhu *et al* (2006) reported the synthesis of novel 3D urchin-like α -Fe₂O₃ superstructures. However, there are a few reports dedicated to the synthesis of α -Fe₂O₃ 1-D aggregated nanostructures.

Herein, we demonstrate that α -Fe₂O₃ nanorods and double-shuttles consisting of nanoparticles can be synthesized through the introduction of SnCl₄ by one-step hydrothermal method, which avoids the subsequent procedure for the removal of the surfactant or template to synthesize one-dimensional aggregated nanostructures.

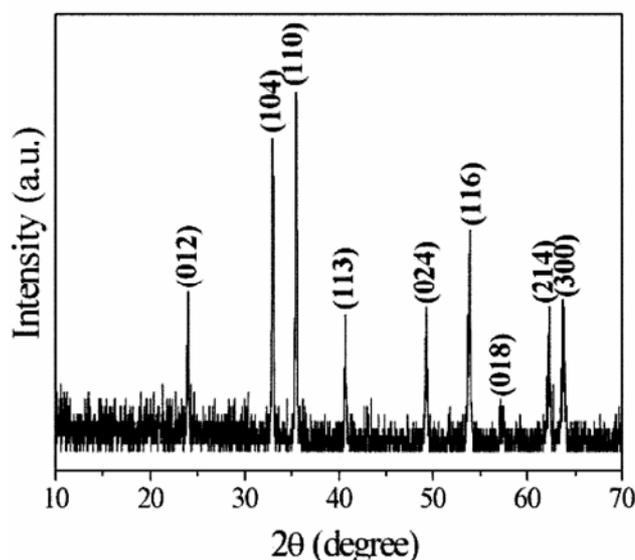


Figure 1. XRD pattern of the obtained product.

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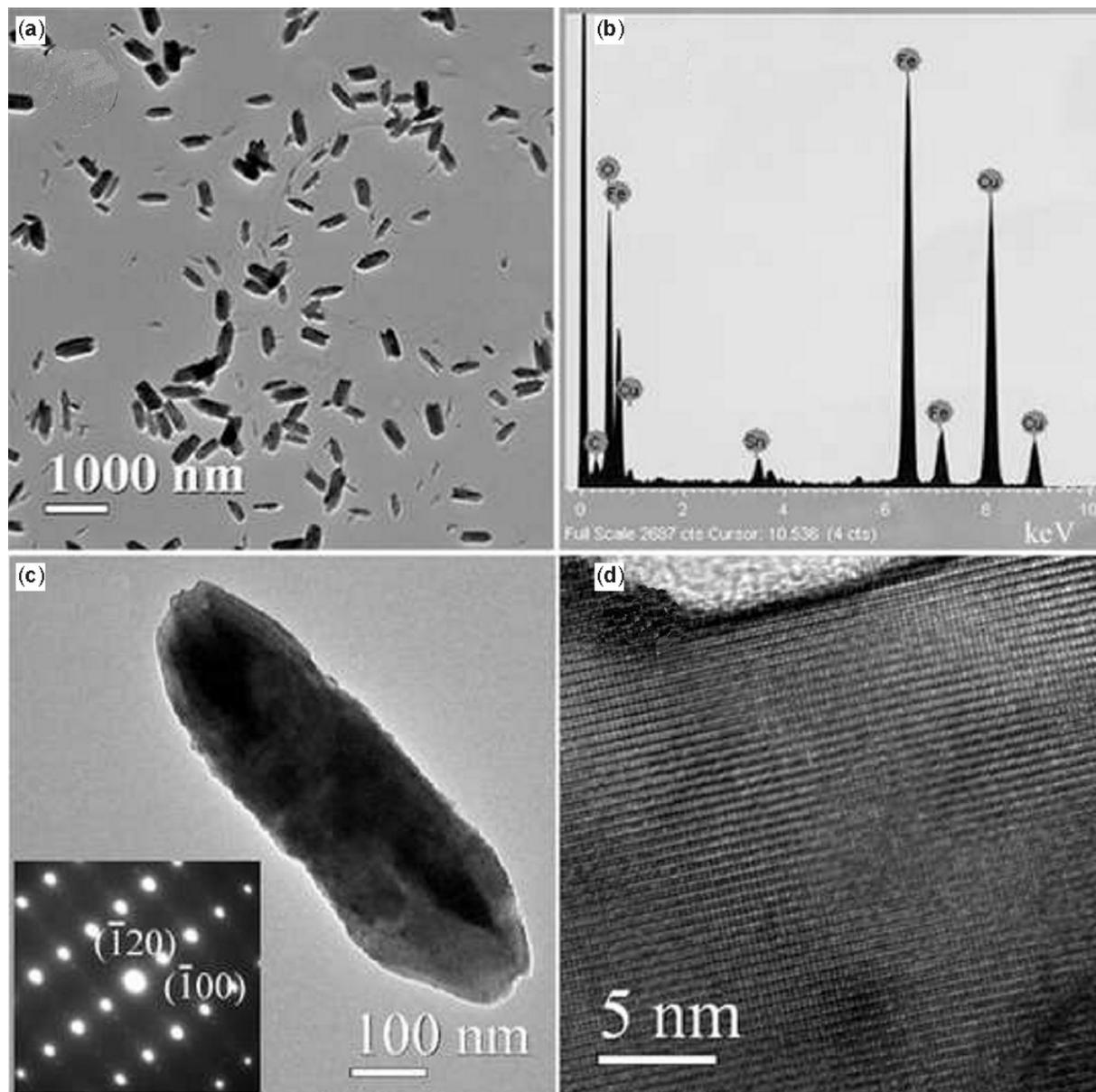


Figure 2. (a) TEM image of the product, (b) EDS pattern, (c) a single nanorod of the product and (d) HRTEM image from (c) and the inset of (c) is the corresponding SAED pattern.

2. Experimental

Hydrous ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), hydrous tin chloride ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) and sodium hydroxide (NaOH) were of analytical grade and used as received without further purification. In a typical experimental procedure, 0.33 mmol SnCl_4 and 0.33 mmol FeCl_3 were dissolved in 30 mL distilled water at room temperature. 10 mL 2M NaOH solution was added to the above solution and yellow-brown precipitates occurred immediately. Then the mixture solution was transferred into a commercial stainless steel Tef-

lon-lined autoclave of 50 mL capacity. The autoclave was maintained at a temperature of 180°C for 12 h without stirring and shaking during heating and then was allowed to cool to ambient temperature naturally. The products were collected by centrifugation, washed twice with distilled water and absolute ethanol respectively, and finally dried in air at 60°C .

The XRD pattern of prepared powder sample was collected using a Rigaku D/Max-2200PC X-ray diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) and a graphite monochromator. Transmission electron microscopy (TEM)

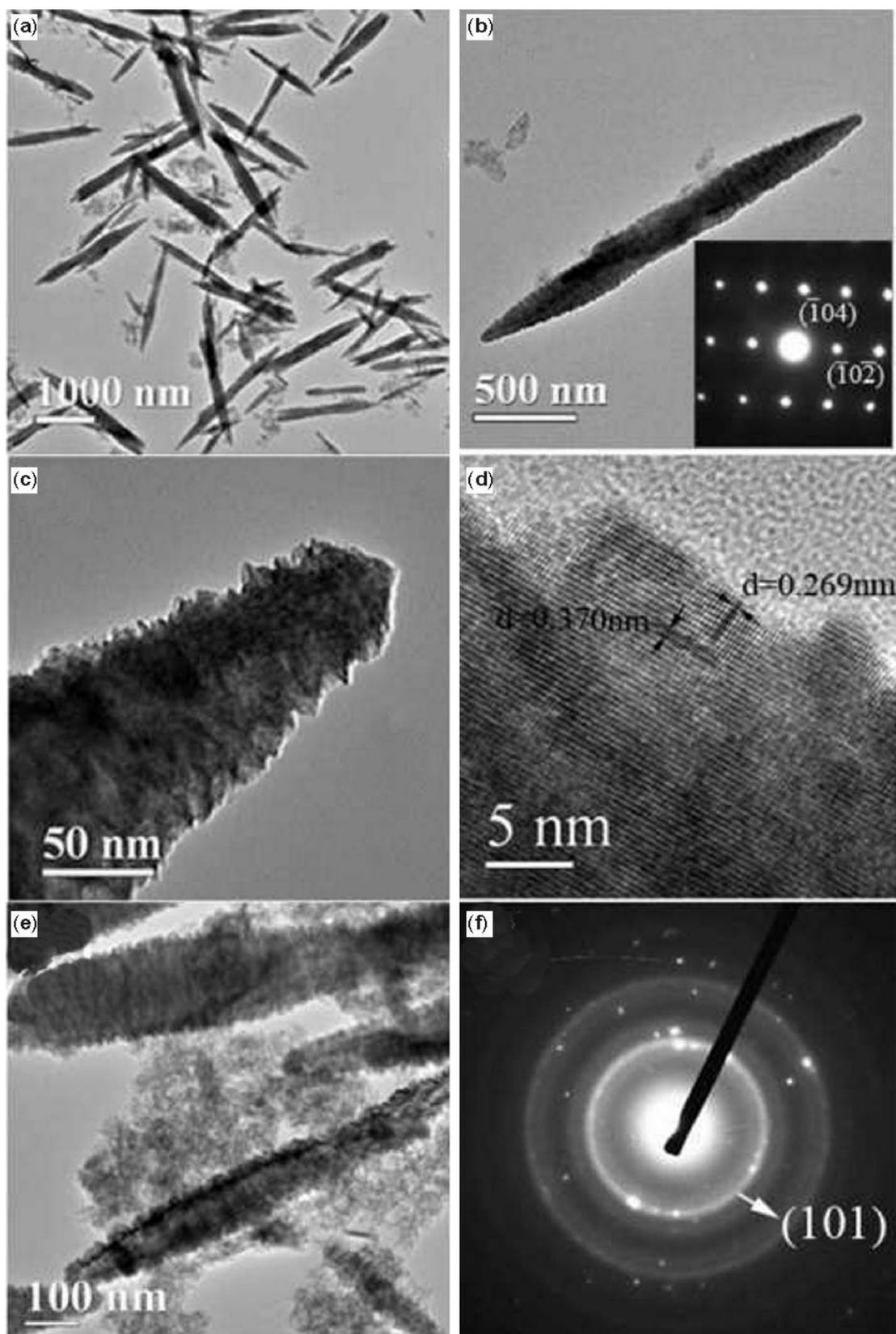


Figure 3. (a, e) TEM images of the products prepared by the addition of 0.66 mmol SnCl_4 , (b) a single double-shuttle of the product, (c) higher magnification of part of (b); (d) HRTEM image from (c); the inset of (b) is the corresponding SAED pattern and (f) is the corresponding SAED pattern of (e).

and selected-area electron diffraction (SAED) were obtained using a JEOL JEM-2100F field emission transmission electron microscope.

3. Results and discussion

Figure 1 shows the typical XRD pattern of the product. All the reflections of the XRD pattern can be indexed to the single phase of α -Fe₂O₃ with hexagonal structure (JCPDS Card No. 86-0550). No other phases of SnO₂ or FeOOH were found in the XRD pattern.

The morphology of the as-prepared sample was investigated by TEM, as shown in figure 2. One can see α -Fe₂O₃ nanorods with diameters of \sim 100 nm and lengths up to 1 μ m. Each nanowire is straight and has relatively sharp tips at the two ends. Energy dispersive spectroscopy (EDS) shows that the nanorods consisted of tin, iron and oxygen (copper came from copper grid of TEM sample holder) (as shown in figure 2b). Selected area electron diffraction (SAED) patterns taken from different positions from an individual nanorod or different α -Fe₂O₃ nanorods were essentially the same, indicating that α -Fe₂O₃ nanorods were single-crystalline. Figure 2c shows a typical single nanorod and its corresponding SAED pattern (inset of figure 2c). The SAED pattern can be indexed as the [00-1] zone axis of hexagonal α -Fe₂O₃, which is consistent with the XRD result (figure 1). Figure 2d shows the high-resolution TEM (HRTEM) micrograph of an individual nanorod. The visible lattice fringes further confirm that the as-obtained nanorods are single crystals.

The addition of SnCl₄ played a key role in the controlled formation of α -Fe₂O₃ nanorods. We carried out the experiment without the use of SnCl₄ with equal amounts of FeCl₃ and NaOH concentrations at 180°C for 12 h. Only FeOOH nanobelts formed, which means that the introduction of SnCl₄ caused the formation of α -Fe₂O₃ instead of FeOOH. We also tried to increase the addition of SnCl₄ concentration to 0.66 mmol, and a single phase of α -Fe₂O₃ was still obtained, with the occurrence of Sn as evidenced by EDS. However, the morphology of α -Fe₂O₃ was double-shuttle as shown in figure 3, and the shuttles have a rough surface with sawtooth structure (figure 3c). It is amazing that SAED pattern taken along the [010] zone axis reveals that the double-shuttles are single-crystalline in nature. Shown in figure 3d is the corresponding high-resolution transmission electron microscopy (HRTEM) image and the corresponding SAED pattern. Like the XRD profile, the HRTEM image and the SAED pattern may also be indexed to hexagonal phase of α -Fe₂O₃. The observed lattice spacings of 0.370 and 0.269 nm correspond to the (012) and (104) planes of hexagonal α -Fe₂O₃, respectively. It is different from the product prepared by adding 0.33 mmol SnCl₄, which gives single crystal nanorod morphology. From the sawtooth morphology we can speculate that the formation of 1-D

nanostructure may have come from the nanoparticle aggregation, at the same time oriented aggregation and particle fusion may have occurred in the process since the SAED pattern shows a single crystal diffraction pattern and no obvious particle boundary was found from HRTEM. In addition, the formation of double-shuttles of α -Fe₂O₃ nanostructures accompanied by the occurrence of some tidy nanoparticles, are as shown in figure 3e.

The effect of SnCl₄ addition on the morphology of α -Fe₂O₃ is obvious, but what is the existence of Sn? it is clear that Sn is present with the formation of α -Fe₂O₃ phase on the basis of EDS, but XRD diffraction peaks give no diffraction peaks of Sn or corresponding oxides. From the corresponding SAED pattern (figure 3f) focused on the areas of large amount of nanoparticles, one can see the intense diffraction rings of polycrystals, which indicates the formation of well-crystallized product. According to the index calculation and the EDS result, we believe that the nanoparticle phase was SnO₂. Due to the low content of SnO₂, the diffraction peaks cannot be found in the XRD pattern. Hence, the final products should be a mixture of α -Fe₂O₃-SnO₂, with α -Fe₂O₃ as the main phase. $(1-x)\alpha$ -Fe₂O₃- x SnO₂ composite has been reported by Sorescu *et al* (2004), but the morphology of α -Fe₂O₃ was different from the present study. It is believed that the addition of SnCl₄ has a key influence on both the composition and morphology of the products. However, detailed formation mechanism of α -Fe₂O₃ nanostructures still needs to be further studied.

4. Conclusions

In summary, we have successfully developed a facile hydrothermal synthetic route to single-crystalline Sn-doped α -Fe₂O₃ nanostructure. The introduction of SnCl₄ has a key influence on both the composition and morphology of α -Fe₂O₃. The addition of SnCl₄ favours the formation of Fe₂O₃ rather than FeOOH, and the morphology can be tuned from nanorod to double-shuttle as the increase of SnCl₄ concentration. This simple method does not need any seed, catalyst, or template, thus is promising for large-scale and low-cost production. The method demonstrated in this paper may also be extended to the fabrication of other doped materials.

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