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solid state communications

Solid State Communications 140 (2006) 267-269

www.elsevier.com/locate/ssc

A facile biomolecule-assisted approach for fabricating α -Fe₂O₃ nanowires in solution

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Received 3 June 2006; received in revised form 5 August 2006; accepted 29 August 2006 by X.C. Shen Available online 15 September 2006

Abstract

In this study, we present a facile biomolecule-assisted solution-phase approach to fabricating 1D hematite (α -Fe₂O₃) nanowires on a large scale, in which glycine was used as the capping agent in solution. A series of time-dependent experiments reveal that the resulting α -Fe₂O₃ nanowires grow preferentially along the (001) direction possessing the oriented attachment mechanism with the help of glycine. This facile synthetic strategy might be extended to prepare other inorganic nanomaterials with anisotropic morphology. © 2006 Elsevier Ltd. All rights reserved.

PACS: 61.66.Fn; 81.10.Dn

Keywords: A. Nanostructures; B. Chemical synthesis; C. Transmission electron microscopy

1. Introduction

Since the discovery of carbon nanotubes by Iijima in 1991, there has been intensive interest in the synthesis and characterization of one-dimensional (1D) nanoscale structures such as nanowires, nanorods and nanobelts owing to their excellent properties and applications in fabricating electronic, optoelectronic, electrochemical and mechanical devices with dimensionality and size confinement [1,2]. Till now, many synthetic methods have been developed for the synthesis of nanowires, including template [3], electrochemistry [4], laser-assisted catalysis growth [5], solution-phase approach [6], vapour transport [7,8] and so forth.

Hematite (α -Fe₂O₃) is of much scientific and technological importance because it is the most stable iron oxide with ntype semiconducting properties (Eg = 2.1 eV) under ambient conditions. And α -Fe₂O₃ has been extensively utilized in various areas of gas sensors, catalysts, pigments, lithium-ion battery and photoanode, etc. in terms of its low cost and high resistance to corrosion [9,10]. Hitherto, 1D hematite (α -Fe₂O₃) nanowires have been synthesized through different routes such as direct thermal oxidation of iron substrates under the

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0038-1098/\$ - see front matter © 2006 Elsevier Ltd. All rights reserved. doi:10.1016/j.ssc.2006.08.040 flow of O₂ at 600–700 °C [11,12], iron–water reaction at 350–450 °C [13], aluminium membranes [14], pyrolysis from FeOOH nanowires at 520 °C [15]. However, how to explore a convenient solution-based approach to fabricate hematite (α -Fe₂O₃) nanowires is still a challenge to chemistry and material scientists at present.

Meanwhile, bio-molecules have special structures and fascinating self-assembling functions as life's basic building blocks, which make them templates for the design and synthesis of complex structures [16,17]. For instance, DNA has been confirmed to be useful in the assembly of nanoparticles to 2D- or 3D structures [18], in the alignment of discrete 1D nanomaterials [19], and nanoscale Pd metallization by electroless deposition of metal [20].

Herein, a facile biomolecule-assisted solution-phase approach has been developed to synthesize hematite (α -Fe₂O₃) nanowires on a large scale. The strategy in this study is the application of glycine acting as the capping agent in the solution. Furthermore, the formation mechanism of 1D hematite nanowires is briefly discussed.

2. Experimental section

All the chemicals are of analytical grade from Shanghai Chemical Reagents Company and used as received without

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Fig. 1. Typical XRD pattern of the resulting Fe₂O₃ sample.

further purification. In a typical procedure for preparing 1D hematite nanowires, $FeCl_3 \cdot 6H_2O$ (4 mmol) and glycine (4 mmol) were first added to 30 mL distilled water and dispersed to form a homogeneous solution under constant stirring. Then 10 mL distilled water containing NaOH (30 mmol) was poured into the above solution to obtain a mixture, which was transferred into a 40 mL Teflon-lined stainless steel autoclave. The autoclave was further sealed and maintained at 140 °C for 10 h. After cooling to room temperature naturally, the resulting products with deeply brickred colour were filtered off, washed with distilled water and absolute ethanol several times, and dried *in vacuo* at 50 °C for 6 h.

In this study, X-ray powder diffraction (XRD) pattern was recorded on a Japan Rigaku D/max- γ B X-ray diffractometer with Cu K α radiation ($\lambda = 1.54187$ Å). Transmission electron microscopy (TEM) images were obtained on a Hitachi H-800 transmission electron microscope with an accelerating voltage of 200 kV.

3. Results and discussion

The crystal structure and phase composition of the resulting sample were characterized using X-ray powder diffraction (XRD) technique. Fig. 1 displays the typical XRD pattern of the Fe₂O₃ sample obtained at 140 °C for 12 h. The obvious and sharp reflection peaks in Fig. 1 can be indexed as hexagonal hematite (α -Fe₂O₃) (JCPDS Card no. 33-0664).

Fig. 2 shows the representative TEM images of the samples obtained at 140 °C for 12 h with different molar ratio (FeCl₃/glycine). When the initial molar ratio of starting materials (FeCl₃/glycine) is 1:1, the obtained TEM image is shown in Fig. 2(a). It clearly reveals that there exist a large number of 1D Fe₂O₃ nanowires with the average diameter of 60 nm and length ranging from several hundred nanometers to several micrometers. When increasing the initial molar ratio (FeCl₃/glycine) to 2:1 in the solution, the corresponding TEM image of the sample is taken on Fig. 2(b). The corresponding sample in Fig. 2(b) is also composed of 1D Fe₂O₃ nanowires. It is noticeable that the possible growth direction of the assynthesized α -Fe₂O₃ nanowires is (001) according to the corresponding SAED pattern in Fig. 2(b), which is taken from an individual single α -Fe₂O₃ nanowire. Similarly, when



Fig. 2. Representative TEM images of the samples obtained at 140 °C for 12 h with different initial molar ratio (glycine/FeCl₃): (a) 1:1; (b) 2:1; (3) 3:1; (d) 4:1.

increasing the molar ratio (FeCl₃/glycine) to 3:1 or 4:1 in the initial solution, the resultant samples always consist of a large quantity of 1D Fe₂O₃ nanowires, which are shown in Fig. 2(c) and (d).

Several time-dependent experiments were carried out by quenching the Teflon-lined autoclave with tap water at different reaction stages to investigate the intermediate products as well as the growth mechanism. A series of TEM images in Fig. 3 show the morphology at different reaction stages corresponding to the reaction time of 2 h, 4 h, 6 h, 8 h. When the reaction was carried out at 140 °C for 2 h, the resulting sample is shown in Fig. 3(a), consisting of irregular nanoparticles. When prolonging the reaction time to 4 h (shown in Fig. 3(b)), some 1D nanostructures appear in the products. Fig. 3(b) and (c) are the corresponding samples obtained at 140 °C for 6 h and 8 h, indicating that the proportion of 1D Fe₂O₃ nanowires increases dramatically. As a result, 1D Fe₂O₃ nanowires can be obtained under present reaction conditions.

In order to explore the effect of glycine in the reaction system, some contrast reactions were conducted in the absence of glycine while keeping other reaction conditions unchanged. However, only irregular Fe₂O₃ nanoparticles can be synthesized (in Fig. 4) at 140 °C for 12 h with the initial molar ratio (glycine/FeCl₃) of 1:1. In terms of the experimental results, we can conclude that glycine indeed exerts a crucial role of fabricating 1D Fe₂O₃ nanostructures in the present reaction system.

It is known that hematite (α -Fe₂O₃) has a rhombohedrallycentred hexagonal structure of the corundum type with a close-packed lattice in which two-thirds of the octahedral sites are occupied by Fe³⁺ ions. The surface hydroxy groups of (001) planes of hematite are doubly coordinated, whereas other planes such as (100), (110), (012) are singly coordinated by surface hydroxyl groups [21]. Meanwhile, as for the hematite



Fig. 3. Representative TEM images of the samples obtained at different reaction time: (a) 2 h; (b) 4 h; (c) 6 h; (d) 8 h with the initial molar ratio (glycine/FeCl₃) of 1:1.



Fig. 4. Typical TEM images of the sample obtained at 140 $^\circ C$ for 12 h in the absence of glycine.

structure, adsorption is considered to involve only the singly coordinated surface hydroxyl groups, and the doubly and triply coordinated hydroxyl groups are relatively unreactive [22]. Yan et al. has reported that phosphate ions can be selectively adsorbed on the other surfaces of hematite owing to the less adsorption affinity on (001), leading to the tubular growth along (001) direction [21]. In this study, the possible formation mechanism of 1D Fe₂O₃ nanostructures can be elucidated as follows: First, the freshly-synthesized Fe (III)-glycine complex in the solution will react with NaOH at 140 °C for 2 h to form nanoparticles as the nuclei (in Fig. 3(a)). It is assumable that glycine will give rise to the adsorption phenomena on the surfaces of hematite except for (001) planes in terms of the above-mentioned knowledge, which will be beneficial to the preferential growth of hematite along the (001) direction. With increasing the reaction time, the oriented nanoparticles will further grow into anisotropic nanostructures along the *c* axis with the help of glycine as the capping agent (in Fig. 3(b)–(d)). Based on the intermediate morphologies obtained at different reaction time, the present reaction process of 1D Fe_2O_3 nanostructures in solution is in accordance with the oriented attachment mechanism [23,24].

4. Conclusions

In summary, glycine was used as the capping agent in solution to fabricate 1D hematite (α -Fe₂O₃) nanowires on a large scale. The oriented attachment mechanism is adopted for the present solution system based on time-dependent experiments. It might open up an opportunity to prepare other metal oxides such as CuO, ZnO and so forth with anisotropic structures using the present synthetic method.

Acknowledgements

Financial support from Hefei University of Technology is greatly appreciated. The authors would gratefully thank Prof. Shupei Tang and Mr Anping Liu at HFUT for their kind assistance with the XRD and TEM characterization.

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