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Facile route to the synthesis of porous α-Fe_2O_3 nanorods

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ABSTRACT

The requirements of simple and reliable protocols for the synthesis of anisotropic structures with controlled morphology continue to be a major challenge in nanoscience. In this paper we describe the facile synthesis of porous hematite (α-Fe_2O_3) nanorods using anionic surfactant as a rod-like template. α-FeOOH nanorods with diameters of 170–210 nm and lengths up to 3–5 μm were synthesized in high yield via hydrothermal method using sodium dodecyl sulphate as a template. The porous α-Fe_2O_3 was obtained after solvent extraction and calcining the as-obtained α-FeOOH nanorods at 500 °C for 6 h. Even after removal of template by solvent extraction and calcination the shape of the nanorods was intact except the generation of pores on the nanorods. The porous nanorods were analysed by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, transmission and high-resolution transmission electron microscopy (TEM & HRTEM), scanning electron microscopy (SEM) and superconducting quantum interference device (SQUID) measurements. SEM and TEM images showed that the morphology of hematite nanostructure is homogeneous in the shape of rods and full of porosity and magnetization measurements of the porous α-Fe_2O_3 nanorods showed weak ferromagnetic behavior. The surfactant SDS (sodium dodecyl sulphate) plays a key role in controlling the nucleation and growth of the nanorods and their use as a new class of inorganic scaffolds for the synthesis of nanomaterials are salient features of the work with implications in crystal engineering and nanocomposites design for various applications.

1. Introduction

An important area of research in nanotechnology is the development of reliable synthesis protocols for nanostructured materials over a range of chemical compositions, shapes and sizes. Over the past few years, the synthesis of inorganic nanoscale materials with special morphologies has been of great interest in material science [1,2] because the intrinsic properties of nanoscale materials are mainly determined by their composition, structure, crystallinity, size, and morphology [3]. Compared with nondimensional nanoparticles, one-dimensional (1D) nanomaterials are more interesting because of their potential high technological applications for electronics, photonics, and magnetic materials [4].

In recent years, the preparation of magnetic nanomaterials is under scrutiny for potential applications in information storage [5], color imaging [6], magnetic refrigeration [7] bioprocessing [8], gas sensors [9], ferrofluids [10], and so on. In particular, hematite (α-Fe_2O_3), the most stable iron oxide, with n-type semiconducting properties under ambient conditions, is of scientific and technological importance because of its usage in catalysts [11], sensors [12], and lithium-ion batteries [13]. Because of their nontoxicity, low cost, and hue, they are also widely used as polishing materials and roof tiles and for colorants in the pigment and paint industry [14]. α-Fe_2O_3 nanorods, nanotubes and nanowires represent a class of 1D magnetic materials, in which carrier motion is restricted in two directions so that they can exhibit unique behavior which is significantly different from that of the bulk material and expected essentially to improve photochemical, photophysical, and electron-transport properties and make it an ideal candidate as a photocatalyst and as a photoelectrode in solar energy conversion applications [15]. In addition to the preparation of 1D nanomaterials, many efforts have been developed for the fabrication of porous nanostructures with hollow interiors, owing to their specific structure, interesting properties that differ from their solid counter parts [16–19]. The structural attribute, such as pores of the materials can be applied as gas and heavy metal ion adsorbents, selective separation, support for artificial cells, light fillers, low-dielectric-constant prosthetic materials as well as inorganic carriers for enzyme immobilization and controlled drug delivery [20–30]. Therefore, by combining the porous 1D nanostructure with magnetic property, the magnetic porous nanorods can be an ideal candidate for the multifunctional nanomaterials such as photonic crystals, host materials, accustic insulation, chemical reactors, biomedical diagnosis agent and targeting drug delivery with MRI

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capability [31–35]. Many synthesis methods have been developed for generating 1D α-Fe_2O_3 nanostructures, such as nanorods [36], nanowires [37], nanobelts [38], and nanotubes [39] using various methods such as vapor–solid (VS) reaction [40], vapor–liquid–solid growth technique [41], metalorganic chemical vapor deposition (MOCVD) technique [42], sol–gel process [43], hard porous templates [44], γ-irradiation method [45]. However, all these reported methods either produced solid nanorods, nanowires or hollow nanotubes but without pores on the wall.

To the best of our knowledge, very few reports on the synthesis of porous α-Fe_2O_3 nanorods have been published to date [46]. Owing to their specific characteristics and promising applications exploring proper methods for the synthesis of nanoscale porous α-Fe_2O_3 rods proves to be stimulating and valuable. Therefore, it is important to develop the methods to regulate both the pore and particle morphology in a one-dimensional structure of these materials. Surfactant-assisted methods have been widely used in the preparation of one-dimensional structure of materials. The surfactant plays an important role in determining the morphology of the products, as surfactants have proved to be useful and versatile soft templates that can form different conformations by self assembly and lead to the formation of different nanostructures. The presence of a rod-like micelle of the surfactant in solution promoted the formation of one-dimensional rod-like structures.

Herein, we report a new method for the preparation of porous α-Fe_2O_3 nanorods using rod-like surfactant template and removing the template by solvent extraction and calcination.

2. Experimental section

A surfactant-assisted synthesis procedure adopted to prepare iron oxide nanorods with a high aspect ratio via hydrothermal process is described in the following sections. All chemicals were analytical grade, purchased from Merck Chemicals and used without further purification.

A typical approach employed by us is as follows: 1.28 mmol of $FeCl_3$ and 0.04 mmol of $FeCl_2{\cdot}4H_2O$ were dissolved in 1.5 mL of purified, deoxygenated water with constant magnetic stirring for 10 min. Then this solution was added to 2.5 mL of a 33 wt.% aqueous solution of SDS (sodium dodecyl sulphate) under N_2 atmosphere and followed by vigorous stirring for 2 h. After 2 h stirring, 5 mL of 3M NaOH solution was introduced into the mixed solution under N_2 atmosphere with vigorous stirring for 2 h more. After adding the NaOH solution into the reaction mixture a brownish black-colored reaction mixture appears instantaneously. The next step for the hydrothermal treatment, 2.5 mL of the brownish black-colored reaction mixture was transferred into a 25 mL Teflon-lined autoclave and the autoclave was sealed and heated at 120 °C for 24 h without shaking or stirring during the heating period and allowed to cool to room temperature naturally. After the reactions were completed, the final yellow solid products were centrifuged and washed with distilled water and absolute ethanol several times, and then dried at 40 °C under a vacuum for 4 h. The obtained yellow solid products were collected for the following experiments and characterization. To prepare porous hematite nanostructures, the as-prepared rod-like iron oxide nanostructures were treated/stirred with acidic (hydrochloric)–ethanolic solution at temperature 65 °C for 24 h, followed by calcination at 500 °C with a ramping rate of 5 K min^{-1} and then maintained at 500 °C for 6 h. A red-brown precipitate was collected and then washed with distilled water and absolute ethanol for further characterization. To check the role of surfactant SDS as template in the growth process of the colloidal particles, we carried out the same experiment without surfactant as control experiment.

Powder X-ray diffraction (XRD) measurements of each sample were performed on a PANalytical X-Pert Pro MRD instrument consisting of a rotating anode generator with a copper target (Cu Kα radiation) operating at 45 kV and 40 mA. The XRD patterns of the samples were recorded in the range from 2θ = 20 to 70° with a 0.04° 2θ step size and a 100 s count time. Fourier transform infrared (FTIR) spectra of the as synthesized and calcined samples were recorded in the diffuse reflectance mode on a Bruker IFS 66 V in the range of 600–4000 cm^{-1} and at a resolution of 4 cm^{-1}. The as-synthesized and calcined samples were directly imaged using a LEO 1530 field emission scanning electron microscope (FE-SEM) with a resolution of 1 nm. Samples for field emission scanning electron microscopy (FE-SEM) were prepared by solution-casting films onto Si wafers. Samples for TEM (transmission electron microscopy) analysis were prepared by placing drops on carbon-coated copper TEM grids after dispersing the samples in 2-propanol. The films on the TEM grids were allowed to stand for 2 min, following which the extra solution was removed using a blotting paper and the grid was allowed to dryprior to measurement. TEM measurements were performed on a Zeiss CEM 902 Model instrument operated at an accelerating voltage at 80 kV. High-resolution transmission electron microscopy (HRTEM) measurements were performed on a LEO-922 model instrument operated at an accelerating voltage at 200 kV. The magnetic properties of the porous nanorods were examined using SQUID (superconducting quantum interference device) (Quantum Design, MPMS-7).

3. Results and discussion

Fig. 1A shows the XRD patterns recorded in the 2θ range 20–70° of the samples before (curve 1) and after calcination (curve 2). Well-defined XRD patterns were observed and all diffraction peaks were perfectly indexed, which are in agreement with the data of α-FeOOH (curve 1) (JCPDS 29-713) and α-Fe_2O_3 (hematite, curve 2) (JCPDS 33-664). The strong and sharp peaks indicate that the α-FeOOH and α-Fe_2O_3 powders are highly crystalline.

Fig. 1B shows FTIR spectra of as-prepared sample, before solvent extraction and calcination (curve 1) and sample after solvent extraction and calcination (curve 2) in the spectral region 2700–3100 cm^{-1}. The C–H symmetric and antisymmetric stretch-

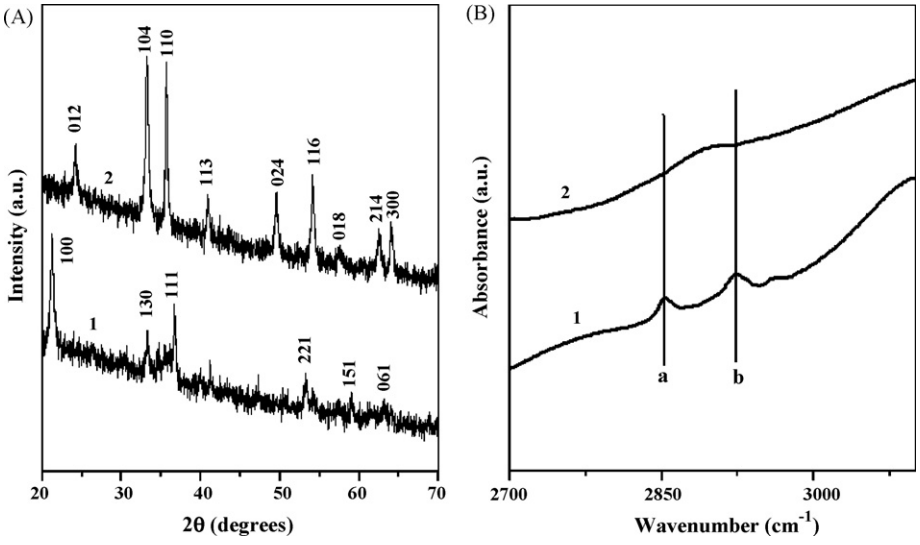

Fig. 1. (A) The XRD patterns recorded from the as-prepared sample (curve 1) and after calcination sample (curve 2). (B) The FTIR spectra of as-prepared sample, (curve 1) and sample after solvent extraction and calcination (curve 2).