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Facile synthesis of iron oxide with wormlike morphology and their application in water treatment

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Abstract

A novel and facile synthesis route for the manufacture of transparent and uniform nanocrystalline α-Fe_2O_3 (nc-Fe_2O_3) thin films and equivalent powders with wormlike morphology is reported, utilizing ferric nitrate as the inorganic source and triblock copolymer as the wormlike morphology-directing agent through the evaporation-induced assembly (EIA) method. X-ray powder diffraction (XRD), ellipsometry, thermogravimetry–differential scanning calorimetry (TG–DSC), Raman spectrum, N_2-sorption and scanning electron microscopy (SEM) were used to study the nc-Fe_2O_3 thin films and powders obtained by calcination at different temperatures. The nc-Fe_2O_3 powder samples showed an excellent ability to remove heavy metal ion (Cr(VI)) in water treatment. The possible formation mechanism of the nc-Fe_2O_3 with wormlike morphology was discussed.

Keywords: Morphology; Evaporation-induced assembly (EIA); Iron oxide; Wormlike

1. Introduction

Among transition metal oxides, iron oxides represent a particularly important class of materials that can be used in a wide range of applications, including catalysis, magnetic devices and rechargeable lithium batteries [1–3]. They combine functionality with low cost and low toxicity. Furthermore, interest in hematite (α-Fe_2O_3) has increased owing to its catalytic and sensory activity, magnetic property [4] and use in water treatment [5]. For all of the applications in various fields, α-Fe_2O_3 thin films or powders with high porosity are desirable.

Transition metal oxides with different kinds of morphologies have been synthesized through chemical or electrochemical methods [6–8]. Contrary to traditional bulk metal oxides, it has proved more difficult to synthesize transition metal oxide homogeneous thin films or powders in the form of high-porosity morphology, owing to the difficulty in controlling the fast rate of reaction. Generally, wormlike nc-Fe_2O_3 thin films could not be directly obtained via conventional synthesis routes, such as the chemical vapor deposition (CVD) method, the sol–gel method, etc. [9–11]. Such effects limit the potential applications of wormlike nc-Fe_2O_3.

Based on the above facts, in order to decrease the hydrolysis rate of the inorganic species, we design a one-step synthesis route through the evaporation-induced assembly (EIA) method, and elucidate the reaction processes leading to the formation of homogeneously wormlike iron oxide thin films. As we know, α-Fe_2O_3 thin films or powders with wormlike morphology has not been synthesized through the facile EIA method so far. We used non-ionic amphiphilic triblock copolymer Pluronic F127 as the morphology-directing agent, which can be easily obtained commercially, and ferric nitrate as the inorganic precursor.

The unique feature of the EIA approach is that this novel strategy combines sol–gel dip-coating and organic–inorganic cooperative assembly techniques. In our strategy, the key step of the system is the action of $NH_3 \cdot H_2O$ and surfactant. The surfactant can be first mixed with

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$NH_3 \cdot H_2O$, and then the hydrogen bond may be formed between the hydrophilic block (uncharged water-soluble moieties) and $NH_3 \cdot H_2O$ to decrease the OH^- in the reaction solution. The ferric precursors can hydrolyze slowly to provide relatively smaller inorganic species rather than bulk sediment, which can have a strong interaction with surfactant micelles. At the following stage, the interaction can restrain the transformation from wormlike to bulk morphology when the surfactant is removed.

Chromium has been placed on the top of the priority list of toxic pollutants by the USEPA and is present in aqueous system in both the trivalent form (Cr^{3+}) and hexavalent form (Cr^{6+}). With its high solubility, Cr(VI) is more harmful to living organisms compared to Cr(III) [12]. So the removal capacities of the Cr(VI) ion of the calcined powder samples are investigated. Removal of the adsorbents calcined at different temperatures by a magnet is investigated. The synthesis and characterization of uniform nc-Fe_2O_3 thin films or powders prepared at different temperatures are presented, the formation mechanism of uniform nc-Fe_2O_3 films is discussed, and the water treatment measurements are presented.

2. Experimental

2.1. Materials

Triblock copolymer Pluronic F-127 ($EO_{106}PO_{70}EO_{106}$, MW = 12 600, Product no. P2443-250G) was purchased from Aldrich and used as received without further purification.

2.2. Synthesis of wormlike nc-Fe_2O_3

Isotropic solutions were prepared by dissolving Fe $(NO_3)_3 \cdot 9H_2O$ (4.57 g) precursor and block copolymer F-127 ($EO_{106}PO_{70}EO_{106}$) (0.9 g) in EtOH (23 ml) and H_2O (20 ml; 4.5 ml 26–28% $NH_3 \cdot H_2O$). The solution was refluxed for 1 h. Then they were aged for 24 h at 20–22 °C at ambient environment. Uniform thin films were prepared by dip-coating ITO glass substrates at a constant withdrawal rate ($1\,mm\,s^{-1}$) and relative humidity (50–60%). Alternatively, the sol solutions can be dried to prepare equivalent iron oxide powders. To remove by-products (ammonium nitrate), powder samples were washed with water. The as-prepared layers or powders were calcined at different temperatures for 4 h ($1\,°C\,min^{-1}$ under air).

2.3. Water treatment experiments

Commercial α-Fe_2O_3 nanoparticle powder was purchased from Beijing Chemicals Co. (Beijing, China). For the experiment, $K_2Cr_2O_7$ was used as the source of Cr(VI), and 0.05 g adsorbent samples were stirred in 25 ml solution containing Cr(VI) for 3 h at room temperature (20 °C). Then the solid and liquid were separated and the concentration of chromium in the remaining solution was measured. For desorption, Cr-loaded iron oxides were shaken with 5 ml of 0.01 M NaOH for 24 h and the particles were separated. The initial concentration of Cr(VI) was $10.80\,mg\,l^{-1}$.

2.4. Characterization

Wide-angle X-ray diffraction (XRD) patterns of the iron oxide powder to identify the crystalline phase were recorded on a Rigaku D/max-IIIB (40 kV, 30 mA) diffractometer, using Cu $K\alpha$ radiation with a wavelength of $\lambda = 1.5406$ Å at room temperature. N_2-sorption isotherms of the iron oxide powders obtained on a Micromeritics ASAP 2020 instrument and Brunauer–Emmett–Teller (BET) equation were used to calculate the specific surface area. Thermogravimetry–differential scanning calorimetry (TG–DSC) curves were performed using a NETZSCH STA449C thermal analyzer ($1\,°C\,min^{-1}$ under air atmosphere). Raman spectrum was collected at a HORIBA JY HR 800 spectrometer with a wavelength of $\lambda = 458$ nm (100 ×, 20 mW). The film thickness was estimated by ellipsometry experiments carried out on a SENTECH GmbH/SE400 instrument with a He–Ne laser beam ($\lambda = 632.8$ nm). Atomic absorption spectra to identify the concentration of Cr(VI) were obtained at a Thermo Elemental SOLAAR-M spectrometer with a wavelength of $\lambda = 357.9$ nm. The morphologies of the calcined iron oxide thin films were evaluated by a Hitachi S-4800 Scanning Electron Microscope with an operating voltage of 20 kV.

3. Results and discussions

3.1. Characterization of iron oxides

Wide-angle XRD was used to identify the crystalline phase of the calcined samples and the results are presented in Fig. 1. As shown in Fig. 1, Bragg diffraction peaks in the

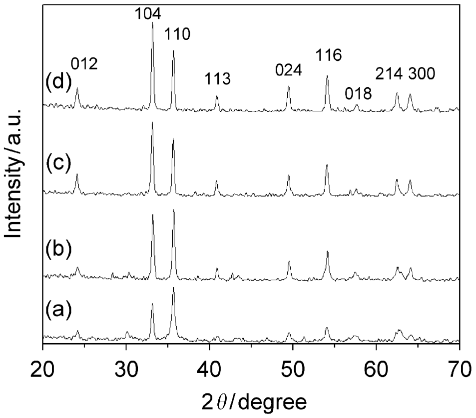

Fig. 1. X-ray powder diffraction patterns of the samples calcined at different temperatures: (a) 350; (b) 400; (c) 450; (d) 500 °C. The XRD patterns are offset for clarity, but the intensity scale is identical for all patterns. I: intensity in arbitrary units.