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Morphology-controlled synthesis of α-Fe_2O_3 nanostructures with magnetic property and excellent electrocatalytic activity for H_2O_2

Xiyan Li [a,b], Yongqian Lei [a,b], Xiaona Li [a,b], Shuyan Song [a,b], Cheng Wang [a,b,*], Hongjie Zhang [a,b,*]

[a] State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022 Jilin, China
[b] Graduate School of the Chinese Academy of Sciences, Changchun, 130022 Jilin, China

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ABSTRACT

α-Fe_2O_3 nanocrystals (NCs) with different morphologies are successfully synthesized via a facile template-free hydrothermal route. By simply changing the volume ratio of ethanol to water, we obtained three different α-Fe_2O_3 nanostructures of rhombohedra, truncated rhombohedra and hexagonal sheet. The morphologies and structures of the as-obtained products have been confirmed by varieties of characterizations such as X-ray diffraction (XRD), X-ray photoelectron spectrometry (XPS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The influences of the experimental conditions, such as the amount of NaOH and reaction temperature on the morphologies of the as-prepared α-Fe_2O_3 NCs, have been well investigated. Additionally, magnetic investigations show that the as-obtained α-Fe_2O_3 nanostructures show structure-dependent magnetic properties. Furthermore, the electrochemical experiments indicate that the as-prepared α-Fe_2O_3 hexagonal sheets exhibit strong electrocatalytic reduction activity for H_2O_2.

1. Introduction

Research on the design and synthesis of morphology-controlled functional inorganic materials in the micro- and nano-size has attracted more and more attention in recent years for their unique size and shape-dependent properties, such as optical, electrical, magnetic, catalytic, mechanical and chemical, *etc.* [1]. Therefore, control of morphology and structure is currently a key issue in developing functional micro/nanostructure materials, and much effort has been undertaken for upgrading the characteristics of materials [2]. However, most of earlier works focused on stabilizing specific forms rather than providing a strategy to freely direct the crystal morphology [1c,d]. Direct fabrication a general technique to synthetically control the shape and structures of functional micro-/nanomaterials still remains a challenge.

Hematite (α-Fe_2O_3), based on hexagonal close packing of oxygen with iron in 2/3 of the octahedral vacancy, is the most thermodynamically stable phase of iron oxide under ambient atmosphere. As an important magnetic n-type semiconductor ($E_g = 2.1$ eV), weakly ferromagnetic α-Fe_2O_3 is of special interest and has been investigated extensively for many applications including catalyst supports [3,4], gas sensor [5–7], biological and medical fields [8], photodegradation [9,10], lithium-ion batteries [11], pigments [12], and waste-water treatment [13,14], owing to its environmental safety, low processing cost, and high resistance to corrosion. So far, many of α-Fe_2O_3 micro/nanostructures, such as particles, rods, wires, cables, tubes, and complicated hierarchical Fe_2O_3 nanostructures, and hybrids have already been synthesized [15–19]. As expected, these α-Fe_2O_3 nanocrystals (NCs) lead to interesting shape-dependent properties and a wide variety of potential applications, including electrode materials in lithium secondary batteries and pollution treatment, *etc.* [12,14]. As stimulated by these promising properties and applications of hematite, much effort has been directed toward the synthesis for the preparation of spinel Fe_2O_3 on the micro-/nanoscale, including hydrothermal synthesis [20], microemulsion [21], traditional sol–gel processing [22], and so on. Especially, among the various methods, hydrothermal synthesis has emerged as an attractive and simple route for the processing of such metal oxides. Many researchers have reported the synthesis of Fe_2O_3 by the simple hydrothermal reaction. For example, Zhong et al. [14] have reported the synthesis of flower-like iron oxide nanostructures via a solvothermal route with subsequent calcination. Fu's group [23] reported the synthesis of the urchin-like hematite nanostructures in the solution. Yang and co-workers [24] succeeded in the synthesis of airplane-like α-Fe_2O_3 nanostructures using a mixed solution of ethylene glycol and water as the reaction medium. Zhang et al. [25] reported a series of α-Fe_2O_3

* Corresponding authors. State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022 Jilin, China. Tel.: +86 431 85262127; fax: +86 431 85698041.
E-mail addresses: cwang@ciac.jl.cn (C. Wang), hongjie@ciac.jl.cn (H. Zhang).

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morphologies from snowflake to paired microplates, dumbbell, and spindle microstructures. Nevertheless, it still remains a great challenge to realize the systematically controlled synthesis of various α-Fe_2O_3 micro/nanostructures through a more economic and environmentally friendly way, which will facilitate our understanding on the shape-dependent properties of the products.

Herein, a facile solution-phase route has been successfully developed for the preparation of a series of morphologically different Fe_2O_3 NCs without the help of any surfactants or templates. This method is quite general and simple, by using $FeSO_4\cdot(NH_4)_2SO_4\cdot 6H_2O$ as iron salts, and adjusting the ratio of the solvents ethanol (EtOH) and water, different morphologies including rhombohedra, truncated rhombohedra and hexagonal sheet-like Fe_2O_3 NCs could be controllably synthesized. The influences of the experimental conditions, such as the amount of NaOH and reaction temperature on the morphologies of the as-prepared α-Fe_2O_3 NCs, have been studied. Furthermore, the magnetic and electrochemical experiments have been investigated for the potential use in bioelectrochemical sensing of hydrogen peroxide.

2. Experimental section

2.1. Preparation of Fe_2O_3 NCs

All the reagents are of analytical grade and were used without further purification. In a typical experimental procedure, 0.04 g $FeSO_4\cdot(NH_4)_2\cdot SO_4\cdot 6H_2O$ was added to the mixed solvent of EtOH and distilled water in a particular ratio (see Table 1), the mixture was dispersed to form a homogeneous solution by constant strong stirring. Then, 40 μL NaOH solution (2 M) was added to the above solution at room temperature and was continually stirred for 30 min, and the resulting mixture was transferred into a Teflon-lined stainless-steel autoclave (18 mL capacity). The autoclave was sealed and maintained at 180 °C for 24 h. The system was then naturally cooled to ambient temperature. The final product was collected and washed with distilled water and EtOH several times, vacuum-dried, and kept for further characterization.

2.2. Characterization

The X-ray diffraction (XRD) pattern of the products was collected on a Rigaku-D/max 2500 V X-ray diffractometer with a Cu Kα radiation source ($\lambda = 1.5418$ Å), with an operation voltage and current 40 kV and 40 mA. X-ray photoelectron spectrometry (XPS) analysis was measured by using a Thermo ESCALAB 250 electron spectrometer. Field-emission scanning electron microscopy (FE-SEM) images were obtained with a Hitachi S4800 microscope. Transmission electron microscopic (TEM) images, high-resolution TEM (HRTEM) images and selected area electron diffraction (SAED) patterns were obtained on a HITACHI H-8100 EM with an accelerating voltage of 200 kV. Hysteresis loops were collected on a Magnetic Property Measurement System (MPMS XL-7) at 300 K. The Quantum Design superconducting quantum interference device (SQUID) measurements for all the samples were done on the pure and dried powders.

2.3. Electrocatalytic experiments

Cyclic voltammetric experiments were performed at room temperature with a conventional three-electrode system and an electrochemical workstation (CHI800, USA). A platinum wire was used as the counter electrode. Bare and modified glass carbon electrodes (GCEs) were used as the working electrode. Prior to the surface coating, the GCE was polished carefully with 1.0, 0.3, and 0.05 μm alumina powder, respectively, and rinsed with distilled water followed by sonication in 1:1 nitric acid/water (v/v), acetone, and doubly distilled water successively. The electrode was allowed to dry under nitrogen. After ultrasonicating the suspension of 2.0 mg/mL of hexagonal sheet-like α-Fe_2O_3 NCs solution with the same volume of 0.5 wt% Nafion solution for 20 min, the well-dispersed solution of Nafion/α-Fe_2O_3 mixture was uniformly casted onto the surface of the GCE. The as-modified electrode was dried before electrochemical experiments. The phosphate buffer solution (PBS, 0.1 M, pH 7.4) was used in thoroughly anaerobic conditions by bubbling with high-purity nitrogen.

3. Result and discussion

3.1. Structure and morphology

Samples obtained under different conditions are summarized in Table 1. Fig. 1 shows the XRD patterns of α-Fe_2O_3 NCs representatives with three typical morphologies: (a) rhombohedra (sample 1), (b) truncated rhombohedra (sample 2), and (c) hexagonal sheet (sample 3). It is evident that all of the expected peaks can be indexed to the rhombohedral structure of α-Fe_2O_3 [space group: *R*-3*c* (167)] with lattice parameters of $a = 5.04$ Å, $c = 13.77$ Å, which are in good agreement with the literature values (JCPDS No. 72-0469). No other peaks or impurities are observed. The strong and sharp diffraction peaks indicate the high crystallization of the synthesized samples.

To further ascertain the purity and the phase of the final products, XPS spectra of the three samples are measured (Fig. 2). Fig. 2A shows the present peaks of Fe, O, and C, and the existence of the C1s peak may be caused by the residual solvent absorbing on the surface of the samples. Two distinct peaks at binding energies of ca. 710.8 eV and ca.725.3 eV are observed in the high-resolution spectrum of Fe2p (Fig. 2B). The two peaks can be indexed to $Fe2p_{3/2}$ and $Fe2p_{1/2}$, which is characteristic of Fe^{3+} in Fe_2O_3 [26]. In addition, the O1s core levels show the dominant oxide peaks at around 529.0 eV, which are in good agreement with the literature values of α-Fe_2O_3 [27]. So, combining this result with that of XRD we can make sure that the products are pure α-Fe_2O_3.

Table 1
Summary of the main results on the products obtained under different conditions.

Sample no.	$FeSO_4\cdot(NH_4)_2SO_4\cdot 6H_2O$ (g)	V_{H_2O} (mL)	V_{EtOH} (mL)	V_{NaOH} (2 M, mL)	T/°C	Phase structures	Product's morphology
1	0.04	12	3	40	180	α-Fe_2O_3	Rhombohedra
2	0.04	10	5	40	180	α-Fe_2O_3	Truncated rhombohedra
3	0.04	5	10	40	180	α-Fe_2O_3	Hexagonal plate
4	0.04	12	3	20	180	α-FeOOH	Rods
5	0.04	12	3	80	180	α-Fe_2O_3	Rhombohedra and particles
6	0.04	12	3	100	180	α-Fe_2O_3	Particles
7	0.04	12	3	40	140	α-Fe_2O_3 and α-FeOOH	Rhombohedra and rods
8	0.04	12	3	40	160	α-Fe_2O_3 and α-FeOOH	Cubic and nanotube