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Hollow α-Fe_2O_3 quasi-cubic structures: Hydrothermal synthesis and gas sensing properties

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ABSTRACT

Hierarchical α-Fe_2O_3 quasi-cubic structures were synthesized through a simple one-step hydrothermal method. The synthesis was performed in a water–isopropanol mixed solvent using ferrous chloride as the precursor free of any templates. The images of field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) indicated that the as-prepared α-Fe_2O_3 quasi-cubes had hollow interior. Moreover, these cubes showed a hierarchical structure, which were composed of densely packed nanoparticles. Subsequently, gas sensors based on the as-prepared hollow cubes were fabricated and their gas sensing performances were investigated. It was found that the gas sensor exhibited high response, good selectivity, fast response and recovery time to acetone at the operating temperature of 250 °C.

1. Introduction

Recently, hierarchical superstructures or complex architectures assembled by nanoscale building blocks have attracted considerable attention owing to their promising applications. Therefore, in order to satisfy the different requirements of such applications, tremendous efforts have been dedicated to the design and synthesis of complex three-dimensional (3 D) micro-/nanostructures. Among them, 3 D hollow structures with low density, large surface area, and good surface permeability have immediately spurred the interest of many scientists all over the world due to their potential applications in a number of areas [1–3]. Up to now, many methods have been developed for the synthesis of hollow nanostructures. A general approach involves the employment of sacrificial or removable templates, either hard ones, such as monodispersed polymer, silica, carbon, and metal oxide nanoparticles, or soft ones, such as micelles. However, the disadvantages of template method are of high cost and tedious synthetic procedures, which will prevent them from being used in large-scale applications. Moreover, in most cases, the resulting hollow structures are spherical in shape. The number of reports on non-spherical hollow structures is significantly limited due to the paucity of suitable templates and difficulty in forming uniform coating. In this regard, there is still a challenge in seeking for simple approaches that enable the general preparation of non-spherical hollow structures.

Hematite (α-Fe_2O_3), an important n-type metal oxide semiconductor with an energy gap of 2.1 eV, has been widely used in many fields [4–6] owing to its characteristics of nontoxic, environment friendly, and low-cost. To highlight some special properties demanded by particular applications, various morphologies and structures of iron oxides have been prepared in the past decades [7–9]. Thus, the design and synthesis of novel morphology α-Fe_2O_3 nanostructures via a facile, mild, and low-cost method still have importantly scientific and practical significance. However, to the best of our knowledge, studies of hollow α-Fe_2O_3 cubes obtained by a template-free hydrothermal route have been rarely reported.

In the current work, we report the synthesis of hollow α-Fe_2O_3 quasi-cubes through a facile one-step hydrothermal method without any templates. The as-prepared products were characterized by various techniques. The XRD pattern showed that the product had high purity and crystallinity. Furthermore, the FESEM and TEM images indicated that the cubes were piled up by nanoparticles. When evaluated as the sensing material for gas sensor, the as-prepared α-Fe_2O_3 hollow cubes manifested good response and recovery characteristics to acetone.

2. Experimental section

All of the reagents used in the experiment were analytical grade and used without any further purification as purchased from Beijing Chemicals Co. Ltd. of China. In a typical experiment, 0.198 g of $FeCl_2 \cdot 4H_2O$ and 0.106 g of $NaClO_3$ were dissolved into a 20 mL water–isopropanol mixture(1:4, v/v) under vigorous magnetic stirring. After stirring for a few minutes, a yellow transparent solution

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was transferred into a 20 mL Teflon-lined stainless steel autoclave which was then subsequently sealed and maintained at 160 °C for 24 h. After being cooled to room temperature naturally, the precipitates were collected by centrifugation and washed several times with deionized water and ethanol alternately, and at last dried in air at 80 °C for 24 h.

X-ray powder diffraction (XRD) pattern of the as-prepared samples was characterized by a Rigaku D/Max-2550 V X-ray diffractometer with high-intensity Cu-Kα radiation (λ=1.54178 Å). Field emission scanning electron microscopy (FESEM) observations were carried out with a JEOL JSM-7500F microscope which was operated at an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) measurements were recorded with JEOL JSM-2100F microscope operated at an accelerating voltage of 200 kV.

The as-synthesized products were mixed with deionized water, and then coated onto the outside of an alumina tube (attached with a pair of gold electrodes at each end) by a small brush to form a thick film. The detail of the sensor fabrication and the testing process were described in our previous works [10]. The gas response was defined as the ratio of R_a to R_g, where R_a and R_g are the resistances measured in air and the tested gas atmosphere, respectively. The response time and recovery time were defined as the time taken by the sensor to achieve 90% of the total resistance change in the case of adsorption and desorption, respectively.

3. Results and discussion

Fig. 1a is the typical XRD pattern of the as-obtained products, from which all of the diffraction peaks were in good agreement with the hexagonal structure of α-Fe_2O_3 (JCPDS card no. 33-0664), unit cell $a=b=5.037$ Å and $c=13.77$ Å. In addition, no diffraction peaks derived from any other impurities could be observed, which indicated the high purity of the sample. The morphology and microstructure of the as-synthesized products were characterized by the FESEM. Fig. 1b shows a low magnification SEM image of the products, from which a number of uniformly dispersed particles with an average size of about 2 μm were clearly observed. The enlarged SEM image (Fig. 1c) provides a clear architecture of the as-prepared α-Fe_2O_3 particles. The quasi-cubic structure was piled up by numerous particles. The average crystal size of α-Fe_2O_3 nanoparticles was calculated to be about 58.6 nm using the Debye–Scherer formula, $D=0.89\lambda/(\beta\cos\theta)$, where λ is the X-ray wavelength (1.5418 Å), θ is the Bragg diffraction angle, and β is the peak width at half maximum. Interior space can be observed directly through a cracked cube as shown in Fig. 1d, from which hollow structure could be clearly discerned.

In addition, more-detailed structure information of the hollow α-Fe_2O_3 quasi-cubes samples was performed by TEM and HRTEM observations, as shown in Fig. 2. As seen from Fig. 2a there are some pale areas in the center, which indicated the hollow internal structure, which was in accordance with the former FESEM observations (Fig. 1d). The HRTEM image (Fig. 2c) of the selected area marked with a white rectangle in Fig. 2b shows a crystalline character, from which the lattice fringes could be observed clearly and the lattice spacing was 0.27 nm, corresponding to the (104) plane of α-Fe_2O_3.

From the perspective of applications, the gas sensing properties of as-synthesized α-Fe_2O_3 hollow cubes, which are of importance for practical applications, were investigated. Based on the common sense that the operating temperature has a dramatic influence on the gas response of a semiconductor gas sensor. Firstly, we explored the influence of temperature to the gas sensor and trying

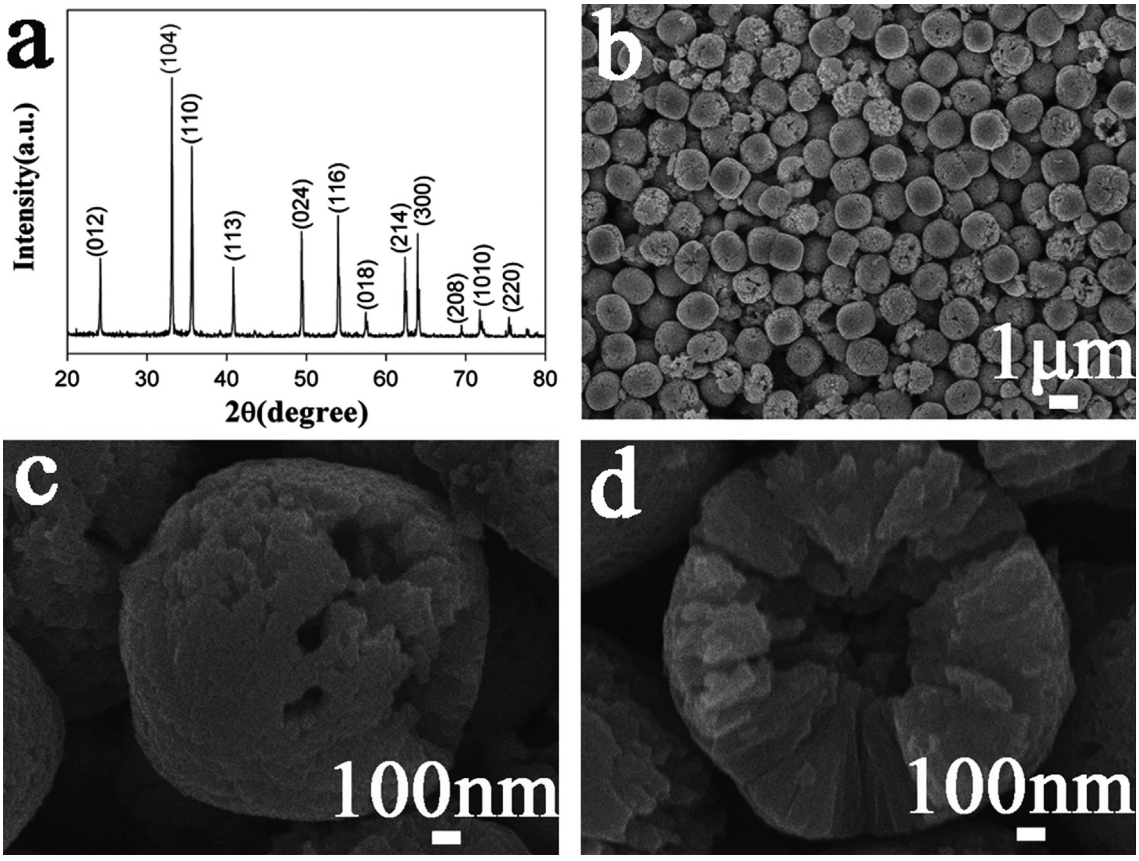

Fig. 1. (a) XRD pattern, (b–d) SEM images of the hierarchical α-Fe_2O_3 hollow cubes.