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Cooperative effect of pH value and anions on single-crystalline hexagonal and circular α-Fe_2O_3 nanorings

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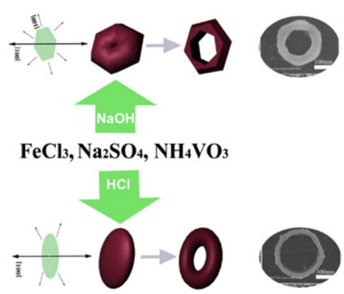
HIGHLIGHTS

- ► Single-crystalline α-Fe_2O_3 nanorings were synthesized by a solvothermal approach.
- ► The cooperative action of the VO_4^{3-} and SO_4^{2-} is a crucial factor in the formation of the ring-like structures.
- ► The H_c value of circular nanorings is larger than that of the hexagonal ones.

GRAPHICAL ABSTRACT



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ABSTRACT

Ring-like materials have attracted intense research interests because of their intriguing structural features and promising applications. In this work, we report an effective solvothermal method to prepare single-crystalline α-Fe_2O_3 nanorings with different morphologies without using any templates. Hexagonal nanorings and circular nanorings have been obtained just by varying the pH of initial solution with HCl or NaOH. On the basis of a series of experiments and characterizations, the growth mechanism of these kinds of nanorings is explained by the influence of the pH values and different anionic ligands. Here the cooperative action of the VO_4^{3-} and SO_4^{2-}, involving adsorption and coordination, is a crucial factor in bringing about the formation of the ring-like structures.

1. Introduction

In recent years, ring-like materials have attracted intense research interests because of their intriguing structural features and promising applications. Many rings have been successfully fabricated and some progresses in controllable synthesis and applications have been made [1]. For example, Xie and co-workers prepared a new magnetic semiconductor $Ag_{1.2}V_3O_8$ nanoring structure in solution. The $Ag_{1.2}V_3O_8$ nanoring structures are obtained by the spontaneous self-coiling of polar nanobelts which reveals the highly anisotropic internal structure [2]. Gao et al. reported the fabrication of Co–Sn–O nanoring structures, which show a strong magnetic response to a varying magnetic field. The interdiffusion between CoO and SnO_2 is considered to be the main reason for the formation of such nanoring structures [3].

As an n-type semiconductor, α-Fe_2O_3 (hematite) is a very important multifunctional material with peculiar physicochemical properties, high resistance to corrosion, environmentally-friendly and a wide variety of potential uses, such as catalysis [4], sensors [5], water treatment [6], pigments [7], water splitting [8] and electrode materials in lithium secondary batteries [9]. In order to highlight some special properties demanded by particular

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technological applications, iron oxides with different dimensional structures, such as uniform nanocrystals [10], nanocubes [11], one-dimensional spindle-like structures [12], nanowires [13], nanorods and nanotubes [14,15] and hollow [16,17] as well as other hierarchical nanostructures [18,19] have been synthesized. Ring-like α-Fe_2O_3 materials have especially attracted tremendous attention recently due to their unique properties. For instance, Yu et al. have prepared ring-like α-Fe_2O_3 in solution by a simple and rapid microwave-assisted hydrothermal method [20]. Unlike above results, Yan group synthesized uniform α-Fe_2O_3 dodecagonal prismatic nanorings with various heights (nanorings, short nanotubes, and long nanotubes) through hydrothermal method [21]. No doubt, previous research on ring-like α-Fe_2O_3 is an excellent prelude, but it has remained a challenge to find a simple, efficient and controllable synthesis method to fabricate ring-like α-Fe_2O_3 structures. In addition, some properties of ring-like structures are mainly influenced by the size and quality of rings [22,23], which still needs systematic investigation in order to explore their applications. However, little systematic work has been done concerning controllable synthesis of uniform α-Fe_2O_3 nanoring with various sizes and shapes and their experimental conditions.

In this paper, we report a solvothermal approach to synthesize single-crystalline α-Fe_2O_3 nanorings with different morphologies without using any template. It is well-known that template-dependant methods always suffered from the time-consuming process and low-scale preparation, which seriously limits the practical usage of the materials. Consequently, the template-free approach is significant for the large-scale preparation of ring-like α-Fe_2O_3 nanostructures. In our system, both circular and hexagonal rings are formed just by adjusting the pH of the initial solution. In addition, the effect of the experimental parameters on the final morphologies and sizes of α-Fe_2O_3 nanocrystals is also investigated in detail, and the results may provide an insight into the growth mechanism of ring-like structure of α-Fe_2O_3. Finally, the addition of low concentration of anionic ligands (SO_4^{2-} and VO_4^{3-}) in the solution is proved to play an important role in the whole process of the reaction. Herein, the best reaction conditions have been investigated for the two typical morphologies of the ring-like α-Fe_2O_3, and crystallization, Ostwald ripening and subsequent oriented dissolution give rise to the formation of ring-like α-Fe_2O_3 nanostructures. The results would be significant for the future research in design, modification and controllable synthesis of ring-like structures.

2. Experimental

2.1. Materials

All chemicals are of analytical grade and used without further purification: Ferric chloride ($FeCl_3\cdot 6H_2O$, China Medicament Co.), sodium sulfate (Na_2SO_4, China Medicament Co.), ammonium metavanadate (NH_4VO_3, China Medicament Co.). Double-distilled water and ethanol are used throughout the experiment. The pH of the solution is adjusted by NaOH or HCl.

2.2. Synthesis

In a typical synthesis, $FeCl_3\cdot 6H_2O$ (0.4 mmol), Na_2SO_4 (0.02 mmol) and NH_4VO_3 (0.007 mmol) were dissolved in a mixed solution of distilled water (12 mL) and ethanol (12 mL). After intense sonication with an ultrasonic cleaner for 5 min, the pH of the solution was adjusted to the range of 1.7–3.0. Then, the mixture solution was vigorously stirred for 15 min. After that, the precursor solution was transferred into the Teflon-lined stainless autoclave with the total volume of 30 mL and then heated to and maintained at 200 °C. After 24 h, the autoclave was cooled naturally to room temperature. The products were collected and washed several times with deionized water and ethanol and then dried in a vacuum oven at 60 °C for 4 h. Finally the red powders were obtained.

2.3. Characterization

The as-synthesized iron oxide nanostructures were characterized by field emission SEM (FESEM, Hitachi S-4800), transmission electron microscopy (TEM; Tecnai G2 20 S-TWIN, Holland), and high-resolution TEM (HRTEM, Tecnai G2 20 S-TWIN, Holland). X-ray diffraction (XRD) patterns were recorded on a Shimadzu XD-3A (Japan), using filtered Cu Kα radiation. An energy-dispersive X-ray spectroscopic (EDS) detecting unit was used for the element analysis. Magnetic measurements were performed with a Quantum Design MPMS-7 SQUID magnetometer at 301 K.

3. Results and discussion

3.1. Structure and morphology analysis

By adjusting the experimental parameters, the ring-like products with different shapes and sizes have been prepared. As the typical morphologies, hexagonal nanorings and circular nanorings have been systematically discussed, respectively.

Fig. 1a shows a typical morphology of the as-prepared α-Fe_2O_3 hexagonal nanorings. It can be clearly seen that ring structure with uniform size are obtained. The typical α-Fe_2O_3 hexagonal nanoring is 180–200 nm in outer diameter, and the thickness of the wall is 40 nm–60 nm. The typical circular nanoring shown in Fig. 1b is 0.8–1.0 μm in outer diameter and the thickness of the wall is about 100 nm. It is noteworthy that the rings have circular inner holes instead of hexagonal holes. Insets in Fig. 1a and b show the obtained single nanorings, respectively.

The powder X-ray diffraction (XRD) was used to determine the crystalline phase characteristics and composition of the obtained products. As shown in Fig. 1c, both the XRD patterns of the obtained products can be well indexed to corundum structure of hematite α-Fe_2O_3, according to the reference data JCPDS 33-0664, without any impurities. The strong and sharp diffraction peaks indicate that the as-obtained samples are well crystallized and the amount of adsorbed anionic ligands is too small to be detected by XRD. To confirm the existence of anionic ligands, EDS was adopted to analyze the element composition of the synthesized α-Fe_2O_3 nanorings. As shown in Fig. 1d, the EDS spectra reveal that the nanorings are mainly composed of Fe and O, which is consistent with the XRD results. It is noted that there are two weak peaks for V and S in the EDS spectra, which could be attributed to the surface adsorption of SO_4^{2-} and VO_4^{3-}. By coordination with surface hydroxy groups, SO_4^{2-} and VO_4^{3-} were adsorbed on hematite to form a monodentate or bidentate innersphere complex. Similar results were reported in the literature for α-Fe_2O_3 nanotubes [20,21]. The signals of C are generated from the carbon support film.

In order to provide further insights into the microstructure and morphology, a systematic transmission electron microscopy (TEM) investigation was carried out in detail. Fig. 2a shows the TEM image of a hexagonal ring. The nanoring exhibits a hexagonal prismatic morphology and both the outer profile and the inner hole of the nanoring are hexagonal. As can be seen from the SEM and TEM images, hexagonal ring is very thick, so it is not very easy to obtain the ideal microstructure and morphology of hexagonal ring. Fig. 2b is its corresponding selected area electron diffraction (SAED) pattern, which indicates its single crystal structure with a ring axis of [001]. An analysis of the SAED pattern indicates that the diffraction spots are due to the (110) (120) (210) planes and/or their