Research Article

Hydrothermal Synthesis and Characterization of Single-Crystalline α -Fe₂O₃ Nanocubes

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Single-crystalline α -Fe₂O₃ nanocubes were successfully obtained in large quantities through a facile one-step hydrothermal synthetic route under mild conditions. In this synthetic system, aqueous iron (III) nitrate (Fe(NO₃)₃ · 9H₂O) served as iron source and triethylamine served as precipitant and alkaline agent. By prolonging reaction time from 1 h to 24 h, the evolution process of α -Fe₂O₃, from nanorhomboheda to nanohexahedron, and finally nanocube, was observed. The products were characterized by Powder X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), High-resolution Transmission Electron Microscopy (HRTEM), Selected-Area Electron Diffraction (SAED), and Fourier Transform Infrared Spectrometry (FTIR). The possible formation mechanism was discussed on basis of the experimental results.

1. Introduction

Iron oxides are conventional semiconductor materials, mainly in forms of α - and γ -Fe₂O₃. The unit cell of α -Fe₂O₃ (hematite) is hexagonal, containing only octahedral coordinated Fe³⁺ atoms (corundum structure), while γ -Fe₂O₃ (magnetite) particles have cubic unit cells with both octahedral and tetrahedral coordinated Fe³⁺ sites (defect spinel structure) [1]. They are both technologically important because of their special magnetic and electrical properties, and potential applications in sorbents [2], ion exchangers [3], information storage [4], and magnetic refrigeration [5]. Controlling the morphologies of these materials during synthetic process is of great importance because of their shape-dependent properties. Various synthetic methods are continually being improved. To date, a variety of novel shapes of iron oxides nanocrystals have been successfully synthesized via various approaches. Magnetite nanorods with high aspect ratio have been synthesized by one-step wet chemistry process that a surfactant, polyethylene glycol, served as the template, and a ferrous ammonia sulphate served as iron source [6]. Uniform α -Fe₂O₃ particles within the nanometer range (100–300 nm) have been obtained by precipitation of iron (III) perchlorate in the presence of urea.

Different morphology, from spheres to ellipsoidal particles with axial ratio up to 10, was obtained by adding to the initial solution increasing amounts of phosphate anions up to 7 mM [7]. Plate-shaped γ -Fe₂O₃ nanocrystals have been successfully prepared in a water system by a simple reduction-oxidation method at room temperature and under ambient pressure. The reactions contain two steps: first, Fe(II) is reduced into Fe atoms by γ -ray irradiation in nitrogen atmosphere; then, Fe atoms are oxidized into γ -Fe₂O₃ in air [8]. Continuous iron oxide gel fibers were prepared by the sol-gel method using ferric alkoxide and acetic acid as starting materials and alcohol as solvent, and continuous hollow α -Fe₂O₃ fibers produced after the gel fibers were heat treated at 400 degrees C for 1 hour [9]. Vertically aligned iron oxide nanobelt and nanowire arrays have been synthesized on a large-area surface by direct thermal oxidation of iron substrates under the flow of O₂. It was found that nanobelts (width, tens of nanometers; thickness, a few nanometers) were produced in the low-temperature region (similar to 700°C) whereas cylindrical nanowires which are tens of nanometers thick are formed at relatively higher temperatures (similar to 800°C) [10]. Sphere-like maghemite (γ -Fe₂O₃) nanocrystals are formed by utilizing a solution-based one-step thermolysis method; modulating

the growth parameters, such as the type and amount of capping ligands as well as the growth time, is shown to have a significant effect on the overall shape and size of the obtained nanocrystals and on the ripening process itself [11]. Hou et al. report a facile organic-phase synthesis of monodisperse FeO nanoparticles through high-temperature reductive decomposition of iron (III) acetylacetonate ($[\text{Fe}(\text{acac})_3]$) with oleic acid (OA) and oleylamine (OAm) both as surfactants and solvents; the sizes of the particles are tuned from 14 to 100 nm by controlling the heating conditions and the shapes of the particles are controlled to be either spherical or truncated octahedral depending on the volume ratio of OA and OAm used in the reaction. Thermal annealing under an argon atmosphere converted these FeO nanoparticles into composite Fe-Fe₃O₄ nanoparticles, while controlled oxidation of the FeO nanoparticles resulted in the formation of Fe₃O₄, γ -Fe₂O₃, or α -Fe₂O₃ nanoparticles [12]. The highly crystalline and monodisperse γ -Fe₂O₃ nanocrystallites are fabricated from the controlled oxidation of uniform iron nanoparticles which are generated from the thermal decomposition of iron complex. Particle size can be varied from 4 to 16 nm by controlling the experimental parameters [13]. Nevertheless, the production of Fe₂O₃ nanocubes has not been realized ever. Nanocubes exposed a specific surface, which provided an ideal model for the study of surface related properties [14, 15].

In this paper, we demonstrated that single-crystalline α -Fe₂O₃ nanocubes could be successfully synthesized via a facile hydrothermal synthetic method under mild conditions. The morphologies of α -Fe₂O₃ samples could be easily controlled via simply varying the reaction time, and the probable formation mechanism was proposed to explain their growth processes. Moreover, this synthetic approach provided a simple and economical route to synthesize nanocrystals, some of which have a variety of potential applications.

2. Experimental Procedures

The aqueous iron (III) nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was purchased from Sinopharm Chemical Reagent Co., Ltd. The triethylamine was purchased from Beijing Chemical Factory, China. Both $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and triethylamine were of analytical grade and no further purification was conducted. Deionized water was used throughout the experiment.

2.1. Synthesis. In a typical procedure, 0.404 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 3 mL triethylamine were dissolved in deionized water (10 mL) to form a homogeneous solution and then the solution was stirred vigorously for 5 minutes. After that, the solution was sealed in a 50 mL teflon-lined autoclave filled with deionized water till up to 80% of the total volume, and the container was maintained at 160°C for 1–24 hours without shaking or stirring. The resulting products were filtered and then washed successively with deionized water and anhydrous ethanol for several times, and finally, the product was dried for 5 h under vacuum at a temperature of 50°C.

FIGURE 1: X-ray powder diffraction pattern of various as-prepared sample.

2.2. Characterization. The obtained samples were characterized by powder X-ray diffraction (XRD) with a D/max2550 VB+, and Cu K α ($\lambda = 1.54178 \text{ \AA}$) was used as the radiation source, while the operation voltage and current were kept at 40 kV and 40 mA, respectively. Particle size and morphology of the as-synthesized products were observed using field emission scanning electron microscopy (FESEM) with Philips XL30 S-FEG at an accelerating voltage of 20 kV and transmission electron microscopy (TEM) with JEM-200CX at an accelerating voltage of 160 kV and high-resolution transmission electron microscopy (HRTEM) with JEOL JEM-2010F at an accelerating voltage of 200 kV. Meanwhile, selected area electron diffraction (SAED) was performed to identify the crystallinity. The Fourier transform infrared (FTIR) spectra was recorded on a Nicolet Impact 410 infrared spectrophotometer, and, as for sample preparation, the synthesized powder was added into KBr to press a KBr pellet for FTIR analysis.

3. Results and Discussion

3.1. Crystal Structure. XRD pattern of the sample obtained at 160°C for 24 hours was shown in Figure 1. It could be concluded that all the diffraction peaks could be readily indexed as the pure rhombohedral α -Fe₂O₃ ($a = 5.038 \text{ \AA}$, $c = 13.772 \text{ \AA}$) (JCPDS file Card, no. 33-0664). The XRD diffraction patterns peaks of α -Fe₂O₃ became narrower with prolonging the reaction time, and the narrower peaks suggested that the α -Fe₂O₃ samples were higher crystalline, and it testified that iron oxide nanocrystallines could be synthesized through this method. No other peaks were observed, indicating high purity of the as-prepared samples.

The characteristic peaks of orthorhombic α -FeOOH ($a = 4.6048 \text{ \AA}$, $b = 9.9595 \text{ \AA}$, $c = 3.023 \text{ \AA}$) (JCPDS file Card, no. 81-0464) were observed in Figure 1 when the reaction time was 1 hour, 3 hours, 6 hours, and 12 hours, but the characteristic peaks of α -FeOOH decreased with prolonging

FIGURE 2: (a) TEM image of Fe_2O_3 nanocubes prepared at 160°C for 24 hours with 3 mL triethylamine, and the Inset is the SAED image. (b) HRTEM image of the Fe_2O_3 nanocubes. (c), (d) SEM images of the Fe_2O_3 nanocubes. The Inset in (d) is the high magnification image taken from the highlighted section marked by the circle, which indicates that these particles are nanocubes.

the reaction time, and there were only the characteristic peaks of $\alpha\text{-Fe}_2\text{O}_3$ when the reaction time was 24 hours. The narrow sharp peaks suggested that the $\alpha\text{-Fe}_2\text{O}_3$ samples were highly crystalline.

3.2. Morphology. TEM data and analyses of the iron oxide particles prepared at 160°C for 24 hours using 3 mL triethylamine were illustrated in Figure 2(a). These cubes had a regular cubic structure and a uniform width of about 100 to 200 nm. The surfaces of the cubes were equal and the boundaries of them are evident. The SAED pattern in Figure 2(a), which was parallel to uprightness axis of cube surface, indicates that the cubes were single crystallines. The fringe spacing measured 3.62 Å and 2.49 Å (Figure 2(b)), which concurred well with the interplanar spacing of (012) and (110).

Figure 2(c) was a typical SEM image of the Fe_2O_3 nanocubes obtained at 160°C for 24 hours using 3 mL triethylamine and Figure 2(d) is the magnified image of Figure 2(c). Both images showed that the regular Fe_2O_3 nanocubes could be prepared by this approach. The nanocubes were 100 to 200 nm in width and the nanocube

morphology was more evident in Figure 2(d). The inset in Figure 2(d) was the high-magnification image of a typical particle in the highlighted section marked with a white colored circle, which indicates that these particles possess regular cubic morphology and had smooth facies.

The influence of reaction time on the morphology of the products was also investigated and TEM images of iron oxides nanocubes obtained at 160°C using 3 mL triethylamine for 1, 3, 6, and 12 hours were displayed in Figures 3(a), 3(b), 3(c), and 3(d), respectively. For a short reaction time of 1 hour, as shown in Figure 3(a), most of the synthesized particles were in irregular shape and the particle size varied a lot. Yet, by prolonging the reaction time, a tendency was deduced that the particles became more and more regular in size and morphology, and, gradually, these particles formed into cubic patterns, as shown in Figures 3(b), 3(c), and 3(d). Compared with these TEM data, prolonging the reaction time was helpful to the formation of iron oxides nanocubes.

3.3. FTIR Spectrum. Figure 4 represented the FTIR spectrum between 4000 to 400 cm^{-1} of $\alpha\text{-Fe}_2\text{O}_3$ nanocubes. The peaks

FIGURE 3: TEM images of Fe_2O_3 nanocubes were prepared at 160°C using 3 mL triethylamine for 1 hour (a), 3 hours (b), 6 hours (c) and 12 hours (d).

FIGURE 4: FT-IR image of Fe_2O_3 sample at 160°C using 3 mL triethylamine for 24 hours.

at 420 and 576 cm^{-1} attributed to the Fe-O bond vibration of the Fe_2O_3 . The spectrum showed the bands at 899 and 803 cm^{-1} corresponds to the out-of-plane C-H vibration

caused by the remnant of triethylamine on the surface of particles and the peaks at around 1629 cm^{-1} were tentatively assigned to the vibration of C-N bond [16]. The peaks at 3134 cm^{-1} were assigned to the $\nu(\text{N}^+-\text{H})$ vibrations [17], and peaks at 3448 cm^{-1} were assigned to the O-H stretching vibration of absorbed water.

4. Discussion and Conclusion

Iron oxide nanocubes were prepared by a hydrolysis reaction of Fe^{3+} in triethylamine at the temperature of 160°C and the triethylamine provides OH^- to form the $\text{Fe}(\text{OH})_3$ deposition. After reacting in hydrothermal environment, the $\text{Fe}(\text{OH})_3$ translated into $\alpha\text{-FeOOH}$ through heat decomposition at first, and then the $\alpha\text{-FeOOH}$ translated into $\alpha\text{-Fe}_2\text{O}_3$ through heat decomposition (Figure 1). With the Fe_2O_3 crystal particles growing, the cubes were formed because triethylamine influenced the growth rate of some crystal faces. Furthermore, the iron oxide cubes' formation was influenced by reaction time. The formation mechanism and influenced factors of iron oxide cubes will be discussed thoroughly in our further investigation.

In summary, iron oxide nanocubes were successfully synthesized via hydrothermal synthetic route under mild conditions. It is expected that the iron oxide of uniform nanocrystallines may be promoted to some important applications in fields, for example, sensors, magnetic media, and catalytic, and so forth. This synthetic approach provided a simple and economical route to synthesize Nanocrystals. We have also discovered that many of our synthesis techniques could be utilized in the preparation of other nanostructured metal oxides, which will be reported later.

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