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A facile solvothermal synthesis of large-grain iron cubes and cuboids with enhanced performances

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ABSTRACT

The cubic and cuboid pure iron particles with particle size ranging from 500 nm to 2 μm have been fabricated using a solvothermal method in ethanol solution. The controlled morphology and size distribution can be easily tuned by adjusting the reaction temperatures. The morphologies of the as-synthesized iron particles can be transformed from cubes to cuboids with the reaction temperature increasing from 100 to 150 °C. Uniform particles with narrow size distribution and good dispersion can be obtained under 120 °C. These chemically synthesized Fe particles exhibit good air stability and very slight surface oxidation. High saturation magnetization of 208–211 A m^2/kg and very low coercivity of 19–26 Oe can be achieved in these micron-level iron particles due to their high purity and small shape anisotropy. The relatively simple preparation process with low cost, good air stability and high saturation magnetization for these large-grain pure iron particles promise their great potential applications in complicated shape and miniaturized Fe-based composite magnetic components.

1. Introduction

Iron-based nanoparticles have always attracted extensive research interests and show a wide range of potential applications in catalysis, data recording and magnetic sensors because of their excellent chemical and magnetic properties such as high reactivity and high saturation magnetization [1–4]. It is known that both the particle sizes and morphologies of magnetic nanoparticles play an important role to determine their overall performances and actual applications [5–8]. Therefore, the rational controlled fabrication of iron-based particles with desirable morphologies and particle size have received considerable attentions. Various chemical methods have been successfully developed to synthesize iron particles with controllable morphologies such as spheres [9,10], nanocluster [11], cubes [12,13], rods [14,15] and wires [16]. Nevertheless, it is still a great challenge to synthesize the iron particles with tunable sizes and morphologies by employing a simple and feasible method under suitable reaction conditions.

Although various iron-based nanostructures show great potential applications for multifunctional materials in catalysis and biomedical fields, they are prone to be oxidized in air with deteriorated performances. Compared with the nanostructures, large-grain iron-based particles with micron-level exhibit enhanced air stability and show better deformability and compactibility [17], which promises their potential use for the full-density and near-net-shape iron-based soft magnetic devices in high-power applications. It has been reported that several methods such as thermal decomposition [18], microemulsion methods [14], reduction by hydroborates [9] and solvothermal approach [13] can be widely used to synthesis nanoscale or micron-scale iron particles. Among the above mentioned methods, solvothermal synthesis shows distinct advantages over the other methods in fabricating size- and shape-dependent iron particles due to its homogeneous nucleation and growth of primary crystals [8].

Although various magnetic iron-based nanoparticles can serve as a promising multifunctional material widely used in biomedical or electromagnetic fields [19,20], for their use in high-power applications such as rotor or stator in motors and generators, these materials often appear as bulk materials or full-density powder cores, which needs high bulk density as one of the key performances. As is known, it is very difficult to compact the nanoparticles to full-density bulk materials by conventional powder metallurgical method, for strong aggregation forces will occur in the compressed nanoparticles [21]. Compared with magnetic nano-sized nanoparticles, the better deformability and compactibility for the micron-sized ones make them easily be densified via traditional powder compacting compacted to full-density magnetic composite materials to form complex-shaped magnetic devices.

In this work, large-grain iron particles with controlled sizes and

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morphologies have been fabricated through a simple solvothermal method. High-purity iron particles with particles size from 500 nm to 2 μm can be directly obtained under the optimal reaction temperatures. The morphologies of the as-synthesized micron-level iron particles can be controlled and varied from cubic to cuboid shape with the reaction temperatures increasing from 100 to 150 °C. The good air stability and improved intrinsic magnetic properties with both high saturation magnetization and low coercivity can be achieved in these large-grain iron particles.

2. Experimental

The high-purity iron particles with cubic and cuboid morphologies have been synthesized by a solvothermal method in ethanol solution. The schematic illustration of the preparation procedure for iron samples is shown in Fig. 1. Typically, $FeCl_2 \cdot 4H_2O$ (2.06 g) was dissolved in ethanol (14 mL) to form a homogeneous solution under magnetic stirring. Then, the mixture of NaOH (7 g) and hydrazine hydrate ($N_2H_4 \cdot H_2O$, 80 wt%, 8 mL) as reducing agent was added into the above ferrous solution to form a homogeneous solution with vigorous stirring. The resulting solution was transferred into a teflon-lined autoclave of 50 mL and then maintained at temperatures of 100 °C, 120 °C and 150 °C for 10 hours, respectively. After the clave was cooled to room temperature naturally, the black precipitates were collected and washed for several times with deionized water and ethanol in sequence. The resulting products were obtained by drying the collected precipitates in a vacuum oven at room temperature for 6–8 h.

The phase structure of the samples was characterized by X-ray diffraction (XRD) using a D/max 2200PC X-ray diffractometer with Cu Kα radiation. The microstructure of the samples was observed by transmission electron microscope (TEM, JEOL JEM-2100) operated at 200 kV. The surface compositions of the samples were investigated by the X-ray photoelectron spectroscopy (XPS, ESCALAB 250 X_i) with an Al Kα excitation source. Magnetic properties for the as-synthesized powder samples were measured with a vibrating sample magnetometer (VSM, Lakeshore 7307) under a maximum magnetic field of 10 k Oe at room temperature.

3. Results and discussion

Fig. 2 shows the XRD patterns of the three samples prepared at reaction temperatures from 100 °C to 150 °C. As shown in Fig. 2, it can be seen that all the samples display three diffraction peaks at 2θ of 44.7°, 65.1° and 82.5° corresponding to the crystal plane of (110), (200) and (211), which are in good agreement with characteristic peaks of the bcc-Fe phase. The strong and sharp diffraction peaks for pure Fe phase indicate their good crystallinity and high purity for these chemically-synthesized iron samples.

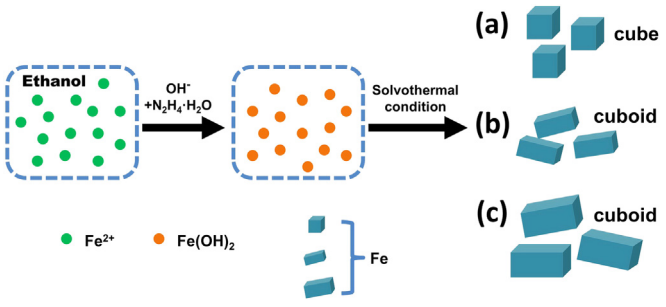

Fig. 1. Schematic illustration of the synthesis procedure for the iron cubes and cuboids prepared at optimal reaction temperatures from 100 °C to 150 °C.

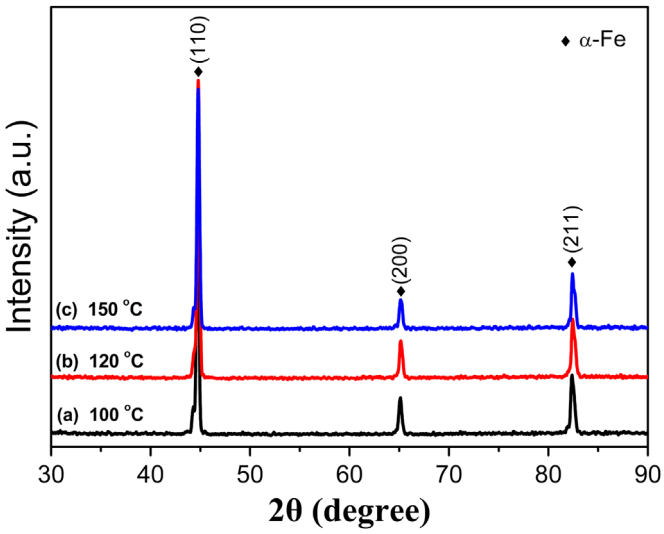

Fig. 2. XRD patterns of the samples prepared at different temperatures: (a) 100 °C, (b) 120 °C and (c) 150 °C.

Moreover, further study shows that no iron phase can be obtained when reaction temperature below 100 °C. It can be seen that reaction temperature shows an obvious effect on the phase compositions of the products and pure α-Fe can be obtained by a solvothermal method at optimal temperature range of 100–150 °C.

Fig. 3 shows the representative TEM micrographs and the corresponding histograms showing the size distribution of the samples prepared at different reaction temperatures. It can be obviously found that the reaction temperature shows significant influences on the morphologies and size distribution of the as-synthesized samples. The average particle sizes for the three samples are also listed in Table 1. As can be seen, the iron particles prepared at 100 °C show a cubic morphology with particle size ranging from 500 nm to 700 nm. While the cuboid-like iron particles with average particle sizes in the range of 500 nm to 1 μm and 1–2 μm can be obtained with increasing the reaction temperature from 120 °C to 150 °C. The higher reaction temperature leads to the much larger cuboid-like iron particles. It can be also found that more uniform iron particles with much better dispersion can be obtained under reaction temperature of 120 °C. The transformation from cubic to cuboid morphology for these chemically-synthesized iron samples with reaction temperature increasing to 120 °C may be ascribed to the combined effects of reaction temperature and ethanol solvent on the reaction process. It has been proved that during chemical reduction reaction the crystallization driving force can be enhanced as the reaction temperature increasing, which can facilitate the nucleation rate of iron primary crystals [7,22]. Furthermore, the selective absorption of ethanol solvent on different crystal planes can kinetically control the growth of certain crystallization facets [23]. Therefore, the combined effects of reaction temperature and ethanol solvent can determine the growth rate of various crystal planes and result in the formation of multi-morphology iron particles. As is known, the formation of Fe particles involves two typical processes including their nucleation and growth of the primary crystals. In this work, the increase of particles size as the reaction temperature increases from 100 °C to 150 °C can be attributed to the coalescence of the iron primary particles [22]. Consequently, the micron-sized morphology-controlled iron particles from cubic to cuboid shape can be synthesized by the solvothermal method under the optimal reaction temperature from 100 °C to 150 °C.

The surface element states of Fe and O atoms in the three samples prepared under different reaction temperatures have