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Tailorable magnetic properties of ε-Fe_2O_3/SiO_2 hybrid via alkaline etching

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ABSTRACT

In this study, conventional silicon alkaline-etching procedure was utilized to tailor magnetic properties of ε-Fe_2O_3/SiO_2 hybrid. It was found that the saturation magnetization, coercivity and exchange bias field can be readily changed and tailored by altering the etching time and frequency in a set of sodium hydroxide solutions. The relative quantity of ε-Fe_2O_3 phase, the proximity or pinning effect derived from SiO_2 phase as well as the phase transformation from ε-Fe_2O_3 to α-Fe_2O_3 during etching treatment were three main factors to its controllable magnetic properties. This work will shed new light on the development of functional ε-Fe_2O_3/SiO_2 composites with tailorable magnetism in practical magnetically-relevant applications.

1. Introduction

Development of high-performance magnetic materials with desirable and controllable magnetic properties is highly demanded for magnetic recording and magnetic resonance imaging. During the last decade or so, many of these research activities [1–7] were devoted to singular synthetic routes for magnetic materials with tailorable magnetic properties. As a result, a substantial amount of information is now available on crystallography, structural chemistry, magnetic ordering, proximity effect, and other new properties [8–12] that make materials have an enormous technological impact in the new generation of ultrahigh density magnetic information storage devices, magnetic sensors, refrigerant materials and permanent magnets [13–17]. Compared to the above topical areas, nonetheless, much less attention has been paid to their magnetism controls after fabrication, although it has been well conceived that suchlike robust and facile post-treatment can enhance stability and reproducibility of the final product.

ε-Fe_2O_3, a polymorph of iron oxide, features the merits of giant coercive field (H_c) as large as 20 kOe at room temperature, coupled magnetoelectric properties, and ferromagnetic resonance capability [18–23], whereas its pure phase can be hardly synthesized due to the presence of silicon phase [24–26] that imposes space restriction and serves to limit the size of ε-Fe_2O_3 nanoparticles [8,24]. In this work, we tailor-make various ε-Fe_2O_3/SiO_2 nanosystems with controllable ferromagnetism by alkaline-etching silicon after fabrication. This synthetic route is not only highly feasible, cost-effective and reproducible, but also enables new insights into the fundamental understanding of the related magnetic effects in ε-Fe_2O_3 phase.

2. Experimental

2.1. Syntheses of ε-Fe_2O_3/SiO_2 hybrids

All chemicals were analytical grade and used as received without further purification. In a typical experimental procedure [27], 2.9 mmol of $Fe(NO_3)_3{\cdot}9H_2O$ and 0.18 mmol of $Ba(NO_3)_2$ were dissolved into 30 mL of water, while 7 mL of ammonia was dissolved into 23 mL of water. These two solutions were mixed together with vigorous stirring before 7 mL of tetraethyl orthosilicate (TEOS) being injected. After stirring for another 12 h, the light yellow precipitate was separated by centrifugation, washed successively with distilled water and absolute ethanol, and finally calcined at 1100 °C in the air for 4 h to form brown products.

In order to modify the ferromagnetism of the resultant product, a set of sodium hydroxide solutions (1 mol/L) were utilized to etch silicon phase for 3, 6, 12, 24, 36, 72 and 120 h. On the other hand, with the total etching time of 72 h held constant, the raw product was etched by 1 mol/L of NaOH solution for 1, 2, 3, 4, and 6 times with time intervals of 72, 36, 24, 18 and 12 h, respectively. After each time interval, NaOH solution was renewed and its concentration was maintained at 1 mol/L prior to the following etching procedure. All these dark red precipitates were separated by centrifugation, washed successively with distilled water and absolute ethanol, and finally dried in the vacuum at 60 °C for 4 h.

2.2. Characterization

The XRD patterns were recorded on a powder X-ray diffractometer

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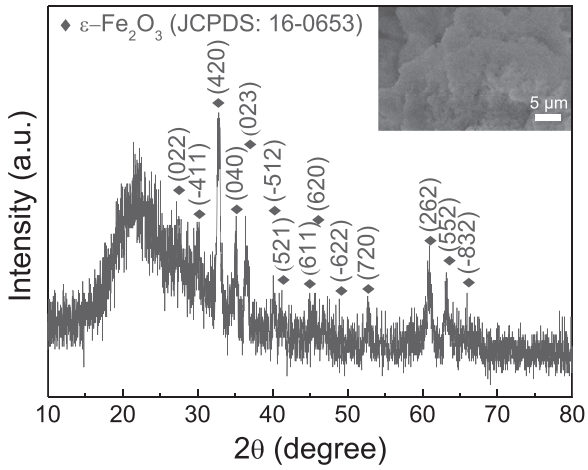

Fig. 1. XRD pattern of the as-synthesized ε-Fe_2O_3/SiO_2 hybrid product. The typical SEM image is shown as an inset.

(Rigaku D/max-rA) equipped with a rotating anode and a Cu $K_{\alpha1}$ radiation source (λ = 1.5406 Å) at a step width of 0.02°. Field emission scanning electron microscope (FE-SEM) images were collected on a JEOL JSM-6700F FE-SEM. Fe^{3+} ion concentrations were determined by inductively coupled plasma-optic emission spectrometry (ICP-OES, Perkin-Elmer Optima 8000). Magnetic measurements were carried out using a commercial superconducting quantum interference device magnetometer (SQUID MPMS-XL5, U.S.A).

3. Results and discussion

The chemical composition of the as-synthesized product is shown in Fig. 1, in which the diffraction peaks at 27.50°, 30.20°, 32.94°, 35.14°, 36.40°, 40.08°, 41.24°, 45.58°, 45.74°, 48.90°, 52.72°, 60.96°, 63.16°, 65.94° can be unambiguously indexed to (022), ($\bar{4}$11), (420), (040), (023), ($\bar{5}$12), (521), (611), (620), ($\bar{6}$22), (720), (262), (552), ($\bar{8}$32) of monoclinic structure ε-Fe_2O_3 (JCPDS PDF No. 16–0653), respectively. Besides, a hump located around 22° demonstrates the presence of amorphous silicon in the product. The morphology of the ε-Fe_2O_3/SiO_2 hybrid is shown in the inset of Fig. 1, from which it mainly composes of heavily aggregated ε-Fe_2O_3 nanoparticles dispersed in flocculent SiO_2 matrix. Its microstructure is clearly presented by the lowly- and highly-magnified TEM images in Fig. 2, from which iron oxide nanoparticles with an average diameter of ca. 10 nm are dispersively distributed in the amorphous silica matrix.

After alkaline-etching this pristine ε-Fe_2O_3/SiO_2 product for various time, the flocculent SiO_2 matrix is getting inconspicuous (Fig. 3) due to the reaction of $SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$ to yield soluble sodium silicate. In stark contrast, the boundaries of ε-Fe_2O_3 nanoparticles are becoming distinct and well-defined because of the relatively inert nature of ε-Fe_2O_3 phase in alkaline aqueous solution.

Fig. 4a is XRD patterns of etched products for different time. In general, diffraction peaks at 27.40°~27.62°, 29.72°~30.02°, 32.70°~32.98°, 34.86°~35.14°, 36.40°~36.72°, 39.90°~40.20°, 41.36°~41.48°, 45.22°~45.58°, 45.66°~45.86°, 48.86°~48.98°, 52.46°~52.84°, 60.70°~60.88°, 63.00°~63.18°, 65.74°~66.04° can be assigned to (022), ($\bar{4}$11), (420), (040), (023), ($\bar{5}$12), (521), (611), (620), ($\bar{6}$22), (720), (262), (552), ($\bar{8}$32) of monoclinic structure ε-Fe_2O_3 (JCPDS PDF No. 16–0653), respectively. Notably, the intensity of diffraction peak of amorphous silicon around 22° was nearly unchanged in the initial etching stage, while it significantly decreases as prolonging the etching time beyond 12 h. The magnetic hysteresis loops of these products measured at room temperature are shown in Fig. 4b, in which the saturation magnetization (M_S) is virtually unchanged when the etching time is below 12 h. Further increasing etching time to 72 h, the M_S value monotonically increases to 8.7 emu/g, which is 3.6 times as large as that below 12 h. This M_S increment can be ascribed to the ever-decreasing amount of silicon phase during alkaline etching procedure. As prolonging the etching time to 120 h, the M_S value is almost unchanged and located around 9 emu/g, indicating complete consumption of sodium hydroxide etching agent after 72 h. It is noteworthy that all magnetic hysteresis loops in Fig. 4b exhibit a sudden magnetization falloff near the origin, which has also been observed in many previous literatures due to the presence of weak ferromagnetic α-Fe_2O_3 and non-ferromagnetic SiO_2 phases [19,26].

The presence of SiO_2 has profound effect on coercive fields (H_c) at different etching time. Fig. 5a shows all etched products exhibit large H_c values (> 12.5 kOe) and they increase as prolonging the etching time to 36 h. This variation tendency of coercivity bears striking similarities with that of weight percent of Fe_2O_3 as observed in Fig. 5b. The weight percent of Fe_2O_3 is estimated on the basis of Fe^{3+} ion concentration. Typically, 10 mg of etched products were separately dispersed in 70 mL of hydrochloric acid aqueous solutions (12 wt%) and sonicated for 5 days. Then the concentrations of iron ions in supernatant (marked as C) were determined by ICP-OES. The weight percent of Fe_2O_3 (denoted as W_{Fe2O3}) is given by

$$W_{Fe2O3} = \frac{C \times 70(mL) \times M_{Fe2O3}}{2 \times M_{Fe} \times 10(mg)} \times 100\% \quad (1)$$

here M_{Fe} and M_{Fe2O3} denote the molar mass of iron and Fe_2O_3,

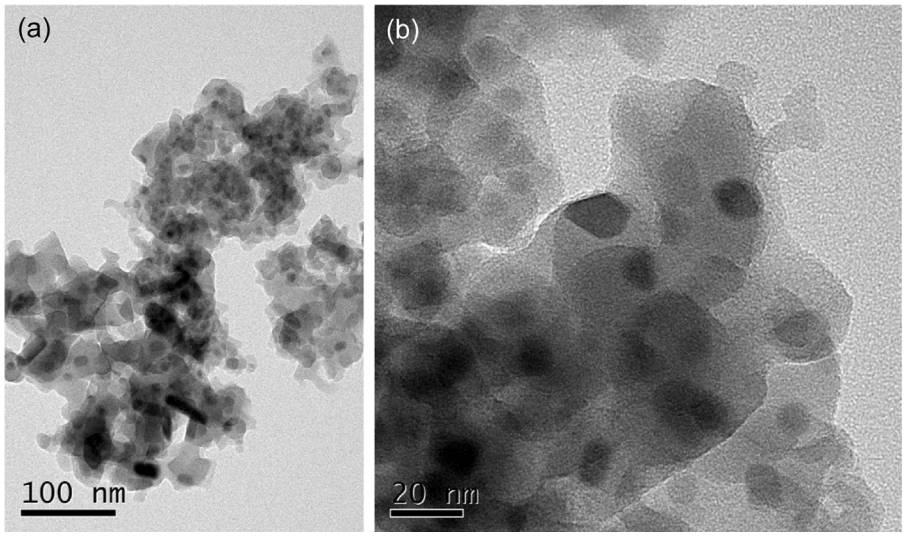

Fig. 2. TEM images of the as-synthesized ε-Fe_2O_3/SiO_2 hybrid product with (a) low- and (b) high- magnifications.