Complexing-reagent assisted synthesis of α-Fe and γ-Fe_2O_3 nanowires under mild conditions†

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α-Fe and γ-Fe_2O_3 nanowires were successfully synthesized from $FeCl_2$ solution with 1,10-phenanthroline as complexing reagent *via* a simple, mild reduction or reduction–oxidization process. It was found that there existed some folded ribbon-like nanostructures as well as nanowires in the obtained α-Fe and γ-Fe_2O_3 products. Magnetic behavior of as-prepared α-Fe and γ-Fe_2O_3 nanowires was investigated by the temperature dependence of magnetization. The formation mechanism of α-Fe and γ-Fe_2O_3 nanowires was also proposed.

Over the past several years, the areal density in magnetic storage media increased at a very high rate[1] and the development of uniform magnetic nanoparticles became a very important issue in their application to ultrahigh-density magnetic storage devices.[2] α-Fe and γ-Fe_2O_3, due to their dominant role in magnetic storage media, have been of interest recently.[3,4] Highly dispersed γ-Fe_2O_3 nanoclusters possess unique magnetic and electronic characteristics, such as superparamagnetism and macroscopic quantum tunneling associated with size quantization and electronic quantum confinement effects,[5–8] which can be used in magnetic inks and magnetic fluids. Many studies have focused on the synthesis of uniform spherical forms and the control of their particle sizes.[9–11]

Recently, anisotropic magnetic nanoparticles were recognized to exhibit interesting magnetic properties because of shape anisotropy.[12] Therefore, the preparation of 1-dimensional (1D) magnetic nanomaterials is crucial to the magnetic science and technology. Xu *et al.*[13] and Yang *et al.*[3] prepared iron nanowires using polyaniline nanotubules and anodic aluminium oxide (AAO), respectively, as solid templates, as well as preventing oxidization of iron nanowires. In these methods, the main problem is how to remove the template. As for the iron oxide nanomaterials, to the best of our knowledge, few reports have been published about the preparation of γ-Fe_2O_3 nanowires. Herein, α-Fe and γ-Fe_2O_3 nanowires were successfully synthesized from $FeCl_2$ solution with 1,10-phenanthroline as complexing reagent *via* a simple, mild reduction or reduction–oxidization process, without using solid templates.

Experimental

The α-Fe and γ-Fe_2O_3 nanowires were prepared *via* the following process: analytical grade $FeCl_2$ (0.500 g, 2.5 mmol) and 1,10-phenanthroline (1.485 g, 7.5 mmol) were loaded into a three-necked round bottom flask that was then filled with 50 mL H_2O. Subsequently, the flask was heated at about 4 °C s^{-1} from 25 to 60 °C and kept at 60 °C for 6 h, exhibiting a red solution which slowly turned blue, then red. This indicated that $[Fe(phen)_3]^{2+}$ was firstly oxidized to $[Fe(phen)_3]^{3+}$ in the air and then hydrolyzed to β-FeOOH. The flask was then cooled to room temperature naturally, and in a nitrogen atmosphere 5 mL HCl and 2 mL 2.0 M aqueous sodium borohydride solution were added drop-wise and the Fe colloids formed. (1) If the reaction mixture was allowed to continue for 20 minutes in this reductive environment, the Fe colloids turned into α-Fe. The precipitate of α-Fe was filtered off, washed twice with distilled water then twice with acetone, and then dried under vacuum at room temperature for 4 h, and the final products of α-Fe nanowires were conserved in a N_2-protecting container. (2) If the Fe colloids were blown slowly with compressed air for 2 days, they were oxidized to γ-Fe_2O_3. Red–brown powders precipitated, which were washed with distilled water, and then the final γ-Fe_2O_3 nanowires were dried under vacuum at room temperature for 3 h. All the reaction steps above were carried out with magnetic stirring.

X-Ray diffraction (XRD) patterns were carried out with a Japan Rigaku D/max γA X-ray diffractometer equipped with graphite monochromatized high-intensity Cu-Kα radiation ($\lambda = 1.54178$ Å). Field emission scanning electron microscopy (FE-SEM) images were taken on a JEOL JSM-6700F SEM. The transmission electron microscopy (TEM) images and electronic diffraction (ED) patterns were performed on a Hitachi Model H-800 instrument with a tungsten filament, using an accelerating voltage of 200 kV. High-resolution transmission electron microscopy (HRTEM) images were carried out on a JEOL-2010 TEM at an acceleration voltage of 200 kV. Mössbauer spectra were recorded using an MS-500 Mössbauer spectrometer and $^{57}Co/(Pd)$ (25 mCi) radiation source at 25 °C.

Results and discussion

The phase and purity of as-prepared α-Fe and γ-Fe_2O_3 products were determined by the X-ray diffraction (XRD) pattern, shown in Fig. 1(a) and (b), respectively. In each XRD pattern, all the reflection peaks can be indexed to those of the correspondent pure phases (JCPDS cards 6–696, $a = 2.8664$ Å; 4–755, $a = 8.350$ Å). However, for the case of γ-Fe_2O_3, the XRD pattern cannot provide enough evidence to confirm the successful formation of γ-Fe_2O_3, since there is little difference

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† Electronic supplementary information (ESI) available: Mössbauer spectrum of as-prepared γ-Fe_2O_3 nanowires. See http://www.rsc.org/suppdata/nj/b2/b209856c/

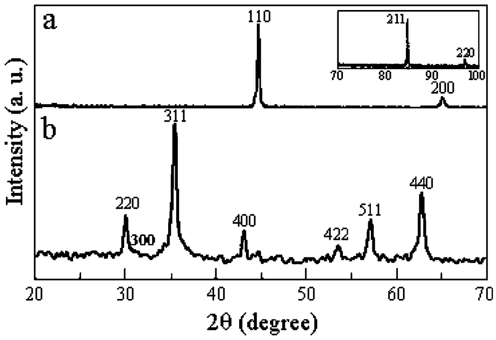

Fig. 1 The XRD patterns of (a) α-Fe (the inset shows the XRD pattern in the 2θ range of 70 to 100°; the two peaks correspond to the (211) and (220) diffraction of α-Fe), (b) γ-Fe_2O_3.

between the two XRD patterns of Fe_3O_4 and γ-Fe_2O_3. However, red–brown is the characteristic color of γ-Fe_2O_3 (the characteristic color of Fe_3O_4 is black) and Mössbauer spectrum analysis of the product gave more concrete evidence that our product was γ-Fe_2O_3 rather than Fe_3O_4 (see ESI†). The corresponding hyperfine parameters are $\delta = 0.328$ mm s^{-1}, $\langle QS \rangle = 1.032$ mm s^{-1}, which are typical of iron(III).[14] No peak characteristic of Fe(II) is present in the spectrum. The broad lines of the magnetic sextets and the smooth inner slopes suggest the existence of a wide size distribution of the obtained iron oxide, corresponding to the difference between diameter and length of nanowires.

The panoramic morphologies of as-obtained α-Fe and γ-Fe_2O_3 were examined by field emission scanning electron microscopy (FE-SEM) (Fig. 2(a) and (d)), in which the solid samples were mounted on a copper mesh without any dispersion treatment, revealing that most of the as-prepared products are wire-like nanostructures with typical lengths in the range of 3–6 μm and width of *ca.* 20 nm. More careful observations in the enlargements of FE-SEM images (Fig. 2(b) and 2(e)) show that some folded ribbon-like nanostructures also exist in the as-obtained products of α-Fe and γ-Fe_2O_3. It indicates that this route might provide a new mild approach to metal and metal oxide nanoribbons. It is a pity that we cannot observe their cross-section and measure their thickness, due to the low content of nanoribbons in the products. High-resolution transmission electron microscopy (HRTEM) images (Fig. 2(c) and 2(f)) reveal that the α-Fe and γ-Fe_2O_3 nanowires are structurally uniform. ED patterns (inset in Fig. 2(c) and 2(f)) can be indexed to be $[1\bar{1}\bar{1}]$ zone axis of α-Fe and [001] of γ-Fe_2O_3, respectively, and the axis growth plane of both the nanowires of α-Fe and γ-Fe_2O_3 is (110).

Further magnetic studies were conducted on a Lakeshore vibrating sample magnetometer (VSM). The temperature dependence of magnetization (Fig. 3) was measured in an applied magnetic field of 100 Oe between 5 and 300 K using zero-field-cooling (ZFC) and field-cooling (FC) procedures. The blocking temperatures of α-Fe and γ-Fe_2O_3 nanowires were found to be 110 and 120 K, respectively, much higher than those of spherical nanoparticles.[13,15] These characteristics result from their shape anisotropy. This indicates that the as-prepared α-Fe and γ-Fe_2O_3 nanowires are magnetic nanocrystals. Since the ultrahigh-density magnetic storage devices have attracted attention, the as-prepared magnetic nanowires are expected to assemble into high-density storage devices, resulting in more potential applications in magnetic science and technology.

Possible mechanism

A mechanism for the formation of α-Fe and γ-Fe_2O_3 nanowires is proposed in which the complexing reagent plays an important role in the nanowire growth. Without adding 1,10-phenanthroline, no α-Fe and γ-Fe_2O_3 nanowires can be obtained. Fe^{2+} could be combined with 1,10-phenanthroline to form the complex $[Fe(phen)_3]^{2+}$, which would be spontaneously oxidized to $[Fe(phen)_3]^{3+}$ in air. $[Fe(phen)_3]^{3+}$ could be hydrolyzed to form β-FeOOH before starting the reduction process, which was identified by the XRD pattern of the precipitates at this step. The color change of the solution also confirms this process. Then, *via* a reduction process, β-FeOOH would be transformed into Fe colloids,[16] which could form α-Fe or γ-Fe_2O_3, depending upon their subsequent treatment. However, what factor led to the orientated growth of their nanowires? The complexing reagent increased the solubility and slowed down the hydrolysis, so that the reactions proceeded more slowly to provide enough time for the crystal to grow, or it can adsorb to specific surfaces to affect the morphology of the crystals. Moreover, $[Fe(phen)_3]^{3+}$ with an octahedral structure is well known to firstly degrade to $[Fe(phen)_2]^{3+}$ when hydrolyzing and the resulting $[Fe(phen)_2]^{3+}$ has a planar structure due to the rigidity of phen. The first degradation would result in a structural

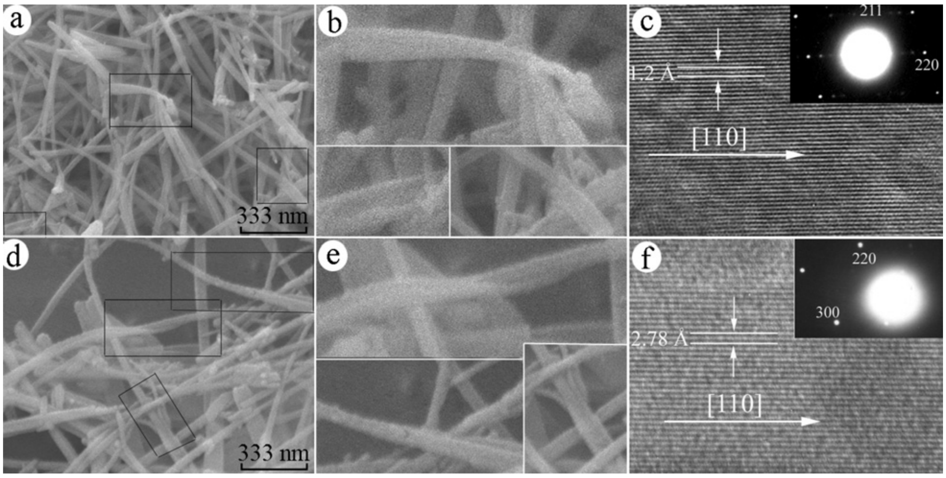

Fig. 2 (a) FE-SEM image of as-obtained α-Fe nanowires without any dispersion treatment. (b) Enlargements of the boxed regions in Fig. 2(a), revealing some twisted α-Fe ribbon-like nanostructures. (c) HRTEM image of an α-Fe nanowire, showing its uniform structure. The inset shows the ED pattern. (d) FE-SEM image of as-obtained γ-Fe_2O_3 nanowires without any dispersion treatment. (e) Enlargements of the boxed regions in Fig. 2(d), revealing some twisted γ-Fe_2O_3 ribbon-like nanostructures. (f) HRTEM image of a γ-Fe_2O_3 nanowire, showing its uniform structure. The inset shows the ED pattern.

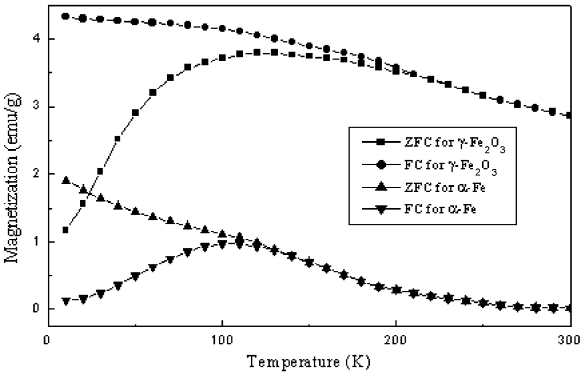

Fig. 3 Magnetization normalized by mass *versus* temperature for the as-prepared α-Fe and γ-Fe_2O_3 nanowires in an applied field of 100 Oe.

transformation from 3D to 2D, thus the bare *z* direction would be first exposed to oxygen when hydrolyzing. Under further hydrolysis, $[Fe(phen)_2]^{3+}$ would gradually lose the two phen ligands on the *xy* plane, and finally would be hydrolyzed to β-FeOOH, in which degradation and hydrolysis occured on the symmetrical *xy* plane and thus had no effect on orientated growth of β-FeOOH. Thus, we speculated that the hydrolysis of $[Fe(phen)_3]^{3+}$ to β-FeOOH along the *z* axis was faster than other directions, leading to the 1D orientated growth of β-FeOOH and even resulting in the nanowire growth of α-Fe and γ-Fe_2O_3 . The 1D orientated growth of β-FeOOH was also identified by the TEM images of the precipitates at this step before the reduction process.

Conclusions

In summary, α-Fe and γ-Fe_2O_3 nanowires were successfully synthesized from $FeCl_2$ solution with 1,10-phenanthroline as complexing reagent *via* a simple, mild reduction or reduction–oxidization process. It was found that there existed some folded ribbon-like nanostructures as well as nanowires in the obtained α-Fe and γ-Fe_2O_3 products, which indicates that this route might provide a new mild approach to metal and metal oxide nanoribbons. Magnetic behavior of as-prepared α-Fe and γ-Fe_2O_3 nanowires was investigated by the temperature dependence of magnetization, showing that the as-prepared α-Fe and γ-Fe_2O_3 nanowires perhaps have more applications in magnetic science and technology, due to their shape anisotropy. The formation mechanism of α-Fe and γ-Fe_2O_3 nanowires was also proposed.

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