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LETTER

Gradual phase and morphology transformation of Fe_3O_4 nanoparticles to α-FeOOH nanorods in alcohol/water media in the presence of surfactant F127

Yong Yang · Ji-Sen Jiang

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Introduction

Iron oxide and oxyhydroxide have a wide range of potential applications in the production of pigments, catalysts, gas sensors, magnetic recording media, and raw materials of hard and soft magnets [1–3]. α-FeOOH (goethite) particles were traditionally used as pigments, or starting material in the production of α-Fe_2O_3 (hematite) and γ-Fe_2O_3 (maghemite). Acicular α-FeOOH particles are used in the production of maghemite and in various academic investigations in colloid and surface chemistry. For example, α-FeOOH nanorods have shown potential in mineral liquid crystals. Inspired by the unique properties of the 1-D structure, much work has been concentrated on the synthesis of its nanorods [4, 5]. Fe_3O_4 (magnetite), an important member of spinel-type ferrite, has already been applied in catalysis, ceramics, energy storage, magnetic data storage, ferrofluids clinical diagnosis, and medicine transporters [6–8]. Many methods have been reported for the synthesis of the Fe_3O_4 nanoparticles, such as coprecipitation of ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions by base [9], thermal decomposition of iron pentacarbonyl ($Fe(CO)_5$) in the presence of oleic acid followed by oxidation [10], thermal decomposition of alkaline solution of Fe^{3+} chelate in the presence of hydrazine [11], and direct decomposition of iron Cupferron complexes $FeCup_3$ (Cup: *N*-nitrosophenylhydroxylamine, $C_6H_5N(NO)O^-$) [12].

Some researchers have reported the phase transitions between iron oxide and oxyhydroxide. Xiong et al. [13] reported the synthesis of thermally stable hematite hollow nanowires from FeOOH nanowires by the vacuum–pyrolysis route. Wang and Xin [14] presented a gamma-irradiation-induced chemical change from β-FeOOH to Fe_3O_4. Here, we present a simple coprecipitation way to prepare Fe_3O_4 nanoparticles and α-FeOOH nanorods in alcohol/water media in the presence of Pluronic triblock copolymer F127. By adjusting the volume ratio of alcohol to water, gradual transformation of phase and morphology from Fe_3O_4 to α-FeOOH was clearly observed.

Experimental

F127 was obtained from Sigma-Aldrich. All other chemicals were of analytical grade and purchased from local commercial sources. All chemicals were used as received. Distilled water was used in all the experiments. In a typical synthesis, 1.296 g $FeCl_3 \cdot 6H_2O$, 0.6672 g $FeSO_4 \cdot 7H_2O$, and 1.0 g F127 were dissolved in 50 mL alcohol/water solution. N_2 was bubbled for 30 min to remove dissolved oxygen. Under N_2 protection and vigorous stirring, 1 M NaOH, as the basic agent, was added to the solution drop by drop to adjust the pH value of the system. The pH value was set to about 11. The solution was kept stirring for 2 h, followed by aging for 24 h in air without stirring or shaking. Then, the precipitates were washed with water and alcohol repeatedly, and centrifuged several times. The collected precipitates were dried in vacuum at 50 °C. The X-ray powder diffraction analysis (XRD; Model D/MAX 2550V, Rigaku Co., Tokyo, Japan) was conducted at a scanning rate of 4° per minute with 2θ ranging from 10 to 70, using CuKα radiation ($\lambda = 1.5418$). Transmission electron microscopy observations (TEM; Model JEM-1230, JEOL, Tokyo, Japan) were made at an accelerating

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Y. Yang · J.-S. Jiang (✉)
Department of Physics, Center of Functional Nanomaterials and Devices, East China Normal University, North Zhongshan Rd. 3663, Shanghai 200062, P.R. China
e-mail: jsjiang@phy.ecnu.edu.cn

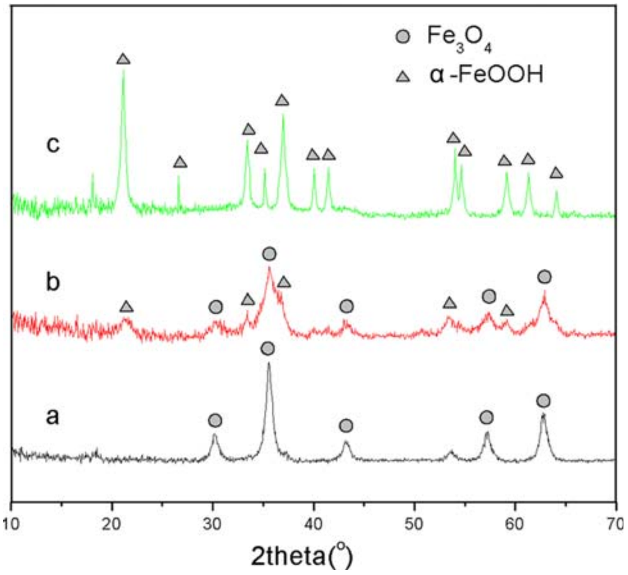

Fig. 1 XRD patterns of the samples prepared in alcohol/water media with various volume ratios of alcohol to water: (a) 0:1, (b) 1:1, (c) 5:1

voltage of 120 kV. Magnetization measurements were carried out with a vibrating sample magnetometer at room temperature.

Results and discussion

Figure 1 shows XRD patterns of the samples prepared in pure water and in alcohol/water media. XRD pattern of Fig. 1a matches cubic Fe_3O_4 (JCPDS card no. 75-0033) well, indicating that the sample prepared in water (sample a) is pure Fe_3O_4. When alcohol is added to water with a volume ratio of 5:1, XRD pattern of the production (sample c, Fig. 1c) confirms α-FeOOH (JCPDS card no. 44-1415) is the only phase. When the volume ratio of alcohol to water is set to 1:1 (sample b), peaks of both Fe_3O_4 and α-FeOOH appear in XRD pattern, as shown in Fig. 1b. It reveals the coexistence of two phases in the product. From the above results, a gradual phase transformation from Fe_3O_4 to α-FeOOH can be seen with increasing volume ratios of alcohol/water.

Figure 2 shows the TEM micrographs of samples prepared in pure water and in alcohol/water media. The production prepared in pure water (sample a) is Fe_3O_4 nanoparticles around 15 nm (Fig. 2a). Figure 2b displays the TEM image of sample b, the coexistence of Fe_3O_4 and α-FeOOH. As shown in Fig. 3c, pure α-FeOOH prepared in 5:1 alcohol/water media consisted of uniform nanorods with diameters around 20 nm and lengths up to 200–300 nm. The results of TEM show the nanoparticles are Fe_3O_4 and nanorods are α-FeOOH. The gradual phase transformation from Fe_3O_4 to α-FeOOH with increasing volume ratios of alcohol/water is consistent with XRD results well.

The magnetism of the samples prepared in pure water and in alcohol/water media is also investigated, as shown in Fig. 3. The value of saturation magnetization of samples a, b, and c is 75.4 emu/g (Fig. 3a), 39.2 emu/g (Fig. 3b), and 0 (Fig. 3c), respectively. The magnetism results also match XRD and TEM results well. Based on the values of saturation magnetization of Fe_3O_4 (75.4 emu/g) and α-FeOOH (0), we can easily deduce that sample b is constituted with 52% of Fe_3O_4 in mass and 48% of α-FeOOH in mass.

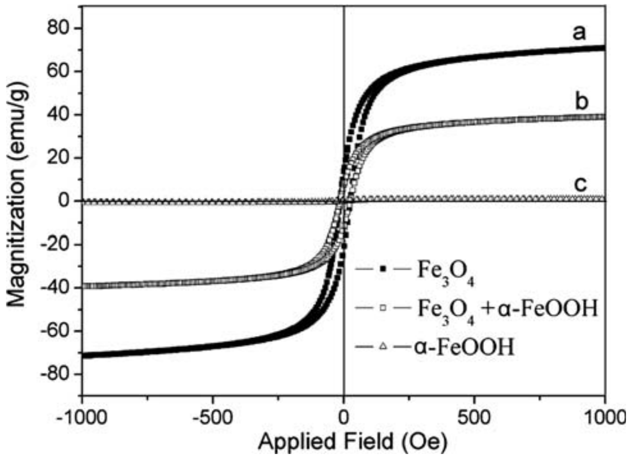

Fig. 3 Hysteresis loops of the samples prepared in alcohol/water media with various volume ratios of alcohol to water: (a) 0:1, (b) 1:1, (c) 5:1

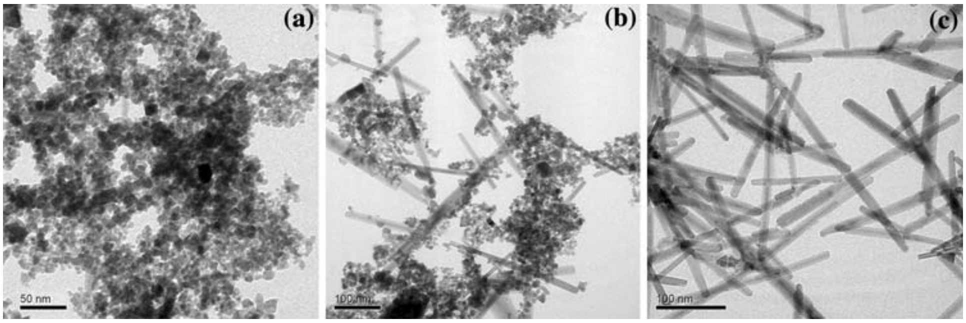

Fig. 2 TEM images of the samples prepared in alcohol/water media with various volume ratios of alcohol to water: (**a**) 0:1, (**b**) 1:1, (**c**) 5:1

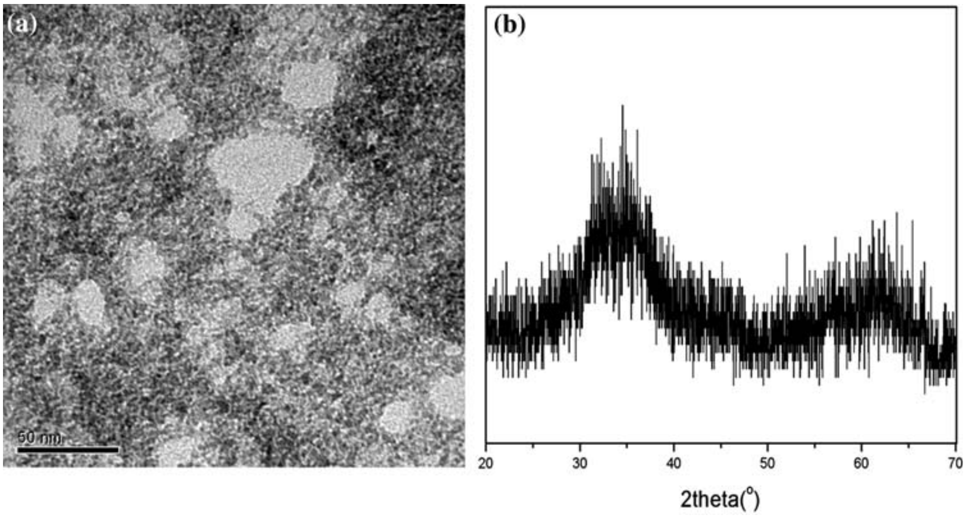

Fig. 4 TEM image and XRD pattern of the sample prepared in alcohol/water (5:1) media without F127: (**a**) TEM image, (**b**) XRD pattern

From the phase transformation from Fe_3O_4 to α-FeOOH, a possible mechanism could be deduced as follows:

$$2Fe^{3+} + Fe^{2+} + 8OH^- \xrightarrow{\text{water}} Fe_3O_4 + 4H_2O, \quad (1)$$

$$Fe^{3+} + Fe^{2+} + OH^- \xrightarrow{\text{F127/alcohol/water}} \text{Fe(II)Fe(III)} \xrightarrow{O_2} \alpha\text{-FeOOH}. \quad (2)$$

As known, Fe^{3+} and Fe^{2+} were easily coprecipitated to form Fe_3O_4 in water when pH value exceeded 9, as shown by Eq. 1. But in alcohol/water media and in the presence of surfactant F127, Fe^{3+} and Fe^{2+} were coprecipitated to form a Fe(II)Fe(III) intermediate [15] as pH of the solution rose to 11. The Fe(II)Fe(III) intermediate was a black precipitate suspended steadily in solution. When the solution was aged in air, a color change from black to yellow was observed, starting from the interface between solution and air. This could be attributed to the oxidation of Fe(II)Fe(III) intermediate to α-FeOOH. The whole chemical reaction route was shown by Eq. 2.

Generally, amphiphilic block copolymer F127 is used as a structure-directing agent to control the mesoscale structure of metal oxides [16–20]. The cooperative assembly route was originally developed for the synthesis of mesostructured silica where the simple and effective control over silicate condensation kinetics has allowed for the creation of an enormous variety of mesostructures [21–23]. In our experiment, the uniform α-FeOOH nanorods were obtained in alcohol/water media in the presence of F127. For comparison, we performed the same coprecipitation processes in alcohol/water media (5:1) without F127. TEM image and XRD pattern of the precipitate are shown in Fig. 4. TEM image (Fig. 4a) represents that the nanoparticles quite differ from samples prepared with F127. Two broad peaks are observed in XRD pattern (Fig. 4b), indicating the amorphous structure of the sample [24–26]. These results show amorphous precipitate was obtained instead of α-FeOOH nanorods in alcohol/water media (5:1) without F127. Obviously, F127 plays an important role in the formation of α-FeOOH nanorods as a structure-directing agent.

Conclusion

Fe_3O_4 nanoparticles and α-FeOOH nanorods were prepared in alcohol/water media in the presence of Pluronic triblock copolymers F127 with a simple coprecipitation way. Fe_3O_4 nanoparticles prepared in water in the presence of F127 were about 15 nm. By adjusting the volume ratio of alcohol to water from 0:1 to 5:1, Fe_3O_4 nanoparticles were completely transformed to α-FeOOH nanorods, which confirmed by TEM images and XRD patterns. α-FeOOH consisted of uniform nanorods with diameters around 20 nm and lengths up to 200–300 nm. Meanwhile, we found F127 played an important role in the formation of α-FeOOH nanorods as a structure-directing agent.

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