Effect of phosphate on the morphology of hydrothermally synthesised β-FeOOH and α-Fe$_2$O$_3$ nanoparticles

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Abstract. β-FeOOH and α-Fe$_2$O$_3$ nanoparticles have been grown from an FeCl$_3$ solution precursor in the presence of an ammonium dihydrogen phosphate surfactant through the process of hydrothermal synthesis. β-FeOOH production varied from small, rounded nanoparticles (~ 45 nm) to larger nanorods (~ 120 nm in length) depending on the stage of synthesis at which the surfactant was added. Larger α-Fe$_2$O$_3$ nanorods (~ 70 nm wide and ~ 450 nm in length) were synthesised from a β-FeOOH suspension at 200°C upon phosphate addition prior to initial β-FeOOH precipitation. The anisotropic growth of α-Fe$_2$O$_3$ was associated with the preferential adsorption of PO$_4^{3-}$ anions onto α-Fe$_2$O$_3$ crystal planes parallel to the c-axis. Phosphate addition to the suspension subsequent to the initial β-FeOOH precipitation inhibited the phase transformation to α-Fe$_2$O$_3$ at 200°C and assisted with increasing the β-FeOOH particle size.

1. Introduction

One-dimensional (1D) nanostructures have attracted considerable attention due to their novel magnetic properties which are greatly dependent on nanorod size and shape [1]. Ferromagnetic hematite (α-Fe$_2$O$_3$), the most thermodynamically stable phase of iron oxide, is of particular interest as a multifunctional nanostructured material with potential applications in catalysis, gas sensing, magnetic recording, water treatment, lithium-ion batteries and pigments; owing to its non-toxicity, low processing cost and high resistance to corrosion [2]. The approach of hydrothermal synthesis (HS), in particular, offers effective control over the size and shape of α-Fe$_2$O$_3$ nanoparticles at relatively low reaction temperatures and short reaction times, providing well-crystallized reaction products with high homogeneity and definite composition. Dilute iron (III) chloride (FeCl$_3$) solution is a simple precursor for the formation of α-Fe$_2$O$_3$ nanoparticles, whereby an intermediate phase of β-FeOOH (akaganeite) is produced prior to α-Fe$_2$O$_3$ precipitation [3]. Chloride, sulphate, phosphate and hydroxide ions have been shown to play a decisive role in the anisotropic growth of hematite [4]. Phosphate anions have been especially effective for the growth of 1D α-Fe$_2$O$_3$ nanorods, despite utilising relatively low concentrations [5]. However, not much has been reported on the effect of phosphate on the initial development of β-FeOOH, in the context of the anisotropic growth of α-Fe$_2$O$_3$ nanostructures. Here, the growth of β-FeOOH and α-Fe$_2$O$_3$ nanostructures is described, produced through the HS of an FeCl$_3$ precursor solution, with the phosphate surfactant added at different stages of the process to appraise its effect on the morphology and growth of the reaction products.

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2. Experimental

β-FeOOH and α-Fe$_2$O$_3$ nanoparticles were prepared through the hydrothermal reaction of 0.2 ml 45% pure FeCl$_3$ aqueous solution, further diluted in 40 ml of distilled water. The reactant solution was mixed with and without 3 mg of ammonium dihydrogen-phosphate (99.999% NH$_4$H$_2$PO$_4$) surfactant (samples S1a and S2a, respectively), mechanically stirred in a 125 ml Teflon-lined steel autoclave, and then sealed and inserted into a temperature controlled furnace at a reaction temperature of 110°C for 2 hours. The autoclave, once removed from the furnace, was allowed to cool down to room temperature naturally. The experiment was repeated and after cooling, sample S1a was reinserted into the furnace again at 200°C for 2 hours (sample S1b), whilst 3 mg of NH$_4$H$_2$PO$_4$ was added to sample S2a before rescaling and reinsertion into the furnace at 200°C for 2 hours (sample S2b). The synthesised reaction products were deposited straight from solution onto single crystal silicon substrates for bulk structural characterisation using a Siemens D500 X-ray diffractometer. For the purpose of TEM investigation, the HS product suspensions were deposited straight onto lacey carbon / copper mesh support grids for conventional diffraction contrast bright field (BF) imaging, performed using a Jeol 2000fx operated at 200 kV. Energy dispersive X-ray (EDX) analysis provided information on the elemental constituents, whilst selected area electron diffraction (SAED) allowed for phase identification and an appraisal of the relationship between nanorod morphology and crystallographic orientation, which was also modelled using Carine software [6].
3. Results

Figure 1 presents a BF TEM image (with associated SAED pattern inset), a crystal structure model, an EDX spectrum and an associated XRD pattern from sample S1b. The XRD pattern (Figure 1d) confirmed that the sample was comprised solely of the $\alpha$-Fe$_2$O$_3$ phase. TEM investigation confirmed the development of lenticular $\alpha$-Fe$_2$O$_3$ nanorods, ~75 nm wide and ~450 nm in length, in this instance (Figure 1a). In all cases, the major axis of these well-defined, single crystalline nanorods was found to be perpendicular to the \{006\} set of crystal planes (Figure 1a). A computer model of the $\alpha$-Fe$_2$O$_3$ crystal structure (Figure 1b) confirmed that the nanorod major axis corresponded to the c-axis of the $\alpha$-Fe$_2$O$_3$ unit cell. Further, EDX investigation indicated the presence of a small amount of phosphorus within the bulk of such nanorods (e.g. Figure 1c), considered to be residual from the phosphate surfactant.

Figure 2. BF TEM images (with associated SAED patterns inset) of the hydrothermal products: (a) sample S1a; (b) sample S2a; and (c) sample S2b. (d) Associated XRD patterns.

BF TEM images of samples S1a, S2a and S2b are presented in Figures 2a, 2b and 2c, respectively. The associated XRD patterns of Figure 2d confirmed all these samples to comprise of $\beta$-FeOOH. Similarly, EDX of sample S1a again revealed a presence of phosphorus. Application of the Scherrer equation suggested an increase in relative average particle size of samples S1a, S2a and S2b, respectively. However, the Scherrer equation does not take into consideration particle morphology.
TEM investigation of sample S1a confirmed this suspension to be a mixture of small and round, as well as larger rod-like, β-FeOOH nanoparticles, up to ~ 15 nm wide and ~ 45 nm in length (Figure 2a). Conversely, sample S2a (Figure 2b) exhibited only the β-FeOOH nanorods (~ 20 nm wide and ~ 60 nm in length). Sample S2b displayed larger, well-crystallised β-FeOOH nanorods, up to ~ 40 nm wide and ~ 120 nm in length (Figure 2c). It is worthy to note the initial precursor of 0.2 ml 45% pure FeCl₃ aqueous solution further diluted in 40 ml distilled water with and without 3 mg of NH₄H₂PO₄ heated straight up to 200°C, under the same HS conditions, produced lenticular and agglomerated rhombohedral α-Fe₂O₃ nanostructures, respectively [7].

4. Discussion
This combined TEM and XRD investigation confirmed that samples grown with and without phosphate at 110°C (samples S1a and S2a), and without phosphate at 110°C then with phosphate at 200°C (sample S2b) all comprised the β-FeOOH phase, whilst only sample S1b grown in the presence of phosphate throughout, at 110°C and then 200°C, comprised the α-Fe₂O₃ phase. Hence, it is evident that the stage at which the NH₄H₂PO₄ surfactant was added to the initial suspension had a dramatic effect on the crystalline phase of the reaction products synthesised at 200°C, i.e. the presence of the phosphate was required at the outset for the efficient formation and development of α-Fe₂O₃ nanorods via the intermediate β-FeOOH phase.

Sample S1a synthesised at 110°C in the presence of the surfactant comprised a mixture of small, rounded nanoparticles and nanorods. Sample S2a, synthesised at 110°C in the absence of a surfactant, mainly consisted of slightly larger nanorods, whilst TEM investigation of sample S2b, synthesised at 200°C subsequent to the addition of NH₄H₂PO₄ to sample S2a, revealed larger still, well-crystallised β-FeOOH nanorods. It is apparent that the initial addition of surfactant to sample S1a acted to inhibit the growth of the developing β-FeOOH nanoparticles, as compared with sample S2a. It is noted that the precursor solution exhibited an initial pH of ~ 2.4, being much lower than the zero point charge of β-FeOOH (pH 8), and hence it is possible that the inhibition of particle growth arises from strong electrostatic attraction and the adsorption of high levels of PO₄³⁻ anions.

Indeed, strong surface PO₄³⁻ anion adsorption onto the β-FeOOH nanorods of sample S2a, after interruption of the HS process, is considered to stabilise these established β-FeOOH nanorods at the elevated reaction temperature of 200°C. This delay to the timing of surfactant addition provides an element of control over the HS process, preventing the phase transformation of β-FeOOH in sample S2b to α-Fe₂O₃, whilst also assisting with increasing the size of the β-FeOOH nanorods.

TEM and SAED investigation and simulation of an individual α-Fe₂O₃ nanorod (sample S1b) showed the major axis to be perpendicular to the {006} set of planes, i.e. coincident with the crystallographic c-axis. It is suggested that the surfactant is preferentially adsorbed onto the faces parallel to the c-axis, thereby promoting anisotropic growth.

In summary, it has been shown that it is possible to control that size and phase of either β-FeOOH or α-Fe₂O₃ nanorods, using HS, through appropriate choice of temperature and the timing of phosphate surfactant addition.

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