Environmental TEM investigation of the reduction of $\alpha$-Fe$_2$O$_3$ nanorods under H$_2$ atmosphere

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Abstract. The thermal reduction of hydrothermally synthesised $\alpha$-Fe$_2$O$_3$ nanorods (NRs) to Fe$_3$O$_4$ NRs under hydrogen is investigated. Complete reduction of $\alpha$-Fe$_2$O$_3$ NRs to Fe$_3$O$_4$ NRs was achieved during in situ XRD under 1 bar H$_2$ atmosphere at 360ºC. Complementary environmental transmission electron microscope investigation at high resolution, during in situ heating under an H$_2$ pressure of 5 mbar at 500ºC, provided evidence for the very first stages of transformation, supporting a model for the migration of oxygen along favoured $\alpha$-Fe$_2$O$_3$ lattice planes during the templated thermal reduction of $\alpha$-Fe$_2$O$_3$ NRs to Fe$_3$O$_4$ NRs.

1. Introduction

One-dimensional (1D) nanostructures have attracted considerable attention due to their novel magnetic properties which are greatly dependent on nanostructure size and shape [1]. Ferrimagnetic magnetite (Fe$_3$O$_4$) is of particular interest as a multifunctional nanostructured material with potential application in ferrofluids, magnetic recording and magnetic resonance imaging [2]. Acicular hematite ($\alpha$-Fe$_2$O$_3$) nanorods (NRs) may be used as a precursor for the synthesis of Fe$_3$O$_4$ NRs, through a process of partial reduction [3]. Hydrothermal synthesis (HS) constitutes an ideal method for the production of $\alpha$-Fe$_2$O$_3$ NRs from dilute iron (III) chloride (FeCl$_3$) precursor solution, via the formation of an intermediate $\beta$-FeOOH (akaganeite) phase. The addition of phosphate anions has been shown to play a decisive role in the anisotropic growth of $\alpha$-Fe$_2$O$_3$ NRs, defining their acicular shape by mediating the process of oriented attachment of primary $\alpha$-Fe$_2$O$_3$ nanoparticles (NPs) [4]. X-ray diffractometry (XRD) investigation of $\alpha$-Fe$_2$O$_3$ NRs heated in situ under a reducing atmosphere may be used to gain insight into the process of bulk phase transformation to Fe$_3$O$_4$. However, in order to elucidate the intricate details of this phase transformation process, it is necessary to visualise the reduction process at high resolution. Spherical aberration (Cs) correction combined with environmental TEM (ETEM) enables the detailed investigation of localised chemical reactions under gas atmospheres with interpretable spatial resolution at the sub-angstrom level [5, 6]. In this context, a high resolution ETEM investigation of the partial reduction of $\alpha$-Fe$_2$O$_3$ NRs to Fe$_3$O$_4$ under conditions of high temperature and reducing atmosphere is presented.

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2. Experimental

Acicular \( \alpha \)-Fe\(_2\)O\(_3\) NRs (Sample H) were prepared through the hydrothermal synthesis of 0.2 ml FeCl\(_3\) aqueous solution (45% pure FeCl\(_3\); Riedel-de Haen, Germany) in the presence of ammonium dihydrogen-phosphate (99.999% NH\(_4\)H\(_2\)PO\(_4\); Sigma-Aldrich, UK) surfactant, further diluted in 40 ml distilled water and mechanically stirred in a 125 ml Teflon-lined steel autoclave. The autoclave was sealed and inserted into a temperature controlled furnace at a reaction temperature of 200\(^\circ\)C for 2 hours. The autoclave, once removed from the furnace, was allowed to cool down to room temperature naturally.

The heating of Sample H under a reducing atmosphere in the ETEM provided insight into the progressive reduction of \( \alpha \)-Fe\(_2\)O\(_3\) on the localised scale. No change occurred after 30 min at 360\(^\circ\)C, as seen during \textit{in situ} XRD, and hence the temperature was increased to 500\(^\circ\)C with a view to accelerate the reduction process. Figure 2 presents BF diffraction and phase contrast TEM images of Sample H acquired at 500\(^\circ\)C under an H\(_2\) atmosphere of 5 mbar. The BF TEM image of Figure 2a shows large \( \alpha \)-Fe\(_2\)O\(_3\) NRs located near the edge of the gold TEM grid. The phase contrast image of Figure 2b illustrates the fine details of an individual \( \alpha \)-Fe\(_2\)O\(_3\) NR surface (Figure 2a, boxed region), as identified by (d\(_{104}\) = 2.70Å) (inset). Selected images from a time-lapse series acquired at 500\(^\circ\)C provided evidence for the localised development of an Fe\(_3\)O\(_4\) NP on the \( \alpha \)-Fe\(_2\)O\(_3\) NR surface (Figures 2c–i), as evidenced by the \{220\} (d\(_{220}\) = 2.96Å) and \{111\} (d\(_{111}\) = 4.83Å) lattice fringes (Figures 2e & f). Figure 2j shows the newly
developed Fe3O4 NP (outlined) and reveals the presence of additional Fe3O4 NPs (arrowed) developed on the α-Fe2O3 NR surface during heat treatment.

Figure 3 similarly presents phase contrast ETEM images from Sample H acquired at 500°C under an H2 atmosphere of 5 mbar. Figure 3a presents a close examination of the tip of an α-Fe2O3 NR, as identified by \{104\} lattice fringes (d_{104} = 2.70Å) (inset). The defects in the α-Fe2O3 NR are an effect of the coalescence of α-Fe2O3 particles during growth [4]. Figures 3b,c show the localised development of an Fe3O4 NP (arrowed), as identified by \{220\} lattice fringes (d_{220} = 2.96Å, Figure 3c, inset).

Figure 4 presents BF diffraction contrast and HAADF images of Sample H acquired after 5 hours of heating under a reducing atmosphere within the ETEM. The BF TEM of Figure 4a shows a single crystalline α-Fe2O3 NR (~ 420 nm long, ~ 70 nm wide), as identified by SAED (inset). Figures 4b & 4c present HAADF images of α-Fe2O3 NRs before and after heating in the ETEM, respectively, with a porous structure of the annealed α-Fe2O3 NR revealed in Figure 4c.

4. Discussion

In situ heating of α-Fe2O3 NRs in the XRD at 360°C under an H2 atmosphere of 1 bar for 30 minutes promoted their complete transition to Fe3O4. This is consistent with the reduction of precursor α-Fe2O3, being a recognised method for the production of Fe3O4, as summarised by the equation: 3Fe2O3 + H2 → 2Fe3O4 + H2O. The H2 atmosphere interacts with the oxygen of the α-Fe2O3 NR surfaces to form water, whilst heating to 360°C provides sufficient thermal energy to promote oxygen diffusion from inside the α-Fe2O3 NRs to restore the equilibrium oxygen concentration at the surface, resulting in partial reduction to Fe3O4. SAED combined with TEM imaging of individual NRs showed that the major axes of the α-Fe2O3 (Figure 4a) and Fe3O4 NRs (Figure 1c) were <006>, and <111>, respectively. This orientation relationship between α-Fe2O3 and Fe3O4 is consistent with previous reduction studies, with oxygen considered to migrate along \{006\} planes [7]. Here, the restacking to Fe3O4 is not so severe as to affect the NR acicular morphology (Figure 1c), hence, the α-Fe2O3 NRs act as templates for the topotactic transformation to Fe3O4 NRs.

BF TEM imaging and SAED (Figure 4a) during ETEM investigation demonstrated that α-Fe2O3 NRs were only reduced to Fe3O4 at the NR surfaces, under an H2 atmosphere of 5 mbar at 500°C for 5 hours, with the caveat that the achievable H2 pressure of 5 mbar in ETEM was significantly lower than the 1 bar used during in situ XRD investigation. This low H2 pressure was found to be insufficient to promote the thermal reduction of complete α-Fe2O3 NRs during in situ heating in the ETEM. Thermal effects, however, did lead to the development of porosity in the α-Fe2O3 NRs through the release of trapped water and phosphate [8], as revealed by HAADF imaging (Figure 4c). Nevertheless, it is recognised that the time-lapse imaging at 500°C during ETEM provided for direct observation of the very first stages of...
after heating at 500ºC under an H$_2$ atmosphere of 5 mbar for 5 hours, as identified by SAED (inset, indexed). (b,c) HAADF images of the localised development of Fe$_3$O$_4$ NPs (Figure 2j, arrowed). Likewise, formation of the Fe$_3$O$_4$ NPs contributed to the development of the Fe$_3$O$_4$ NPs in this low pressure H$_2$ environment. In Figures 2b-i, the electron beam was converged on an area slightly larger than the field of view, which included the location of the newly formed NPs (Figure 2j, arrowed). Likewise, formation of the Fe$_3$O$_4$ NP on the tip of the Fe$_3$O$_4$ NR (Figure 3c) occurred during high resolution imaging. Further, the surface of the Fe$_3$O$_4$ NR shown in Figure 2j became noticeably eroded. Hence, the high current density of the electron beam acted to destabilise the α-Fe$_2$O$_3$ NR surface, allowing oxygen to react with H$_2$ and form water, leaving an oxygen deficiency in the α-Fe$_2$O$_3$ NR surface, whilst remaining unstable iron and oxygen supplied the growth of Fe$_3$O$_4$ NPs.

Considering the relationship between the orientation of the α-Fe$_2$O$_3$ NRs and the growth of the initial Fe$_3$O$_4$ NPs, Figures 2 and 3 illustrate the formation of Fe$_3$O$_4$ NPs on the side and tip of α-Fe$_2$O$_3$ NRs, respectively. Closer examination reveals the growth interface of the tip Fe$_3$O$_4$ NP to be parallel to the major axis of the α-Fe$_2$O$_3$ NR (Figure 3c, inset), and hence, in both cases, the Fe$_3$O$_4$ NPs grow on surfaces parallel to the α-Fe$_2$O$_3$ <006> direction. Elemental supply to developing Fe$_3$O$_4$ NPs through an interface parallel to the α-Fe$_2$O$_3$ c-axis reinforces the notion that α-Fe$_2$O$_3$ {006} planes are favourable for oxygen diffusion during the thermal reduction of α-Fe$_2$O$_3$ NRs to Fe$_3$O$_4$ NRs. The α-Fe$_2$O$_3$ {006}; or Fe$_3$O$_4$ {111} planes may become unstable and collapse during oxygen diffusion, resulting in defects.

In summary, fine details of the reduction of α-Fe$_2$O$_3$ NRs to Fe$_3$O$_4$ NRs during in situ XRD were examined. ETEM experiment provided evidence to support a model for oxygen migration along favoured α-Fe$_2$O$_3$ lattice planes during templated thermal reduction of α-Fe$_2$O$_3$ NRs to Fe$_3$O$_4$ NRs.

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