

Phase Stability of Iron Oxide Evaluated Through Selected Area Electron Diffraction During In-Situ Heating Experiments

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The phase stability of transition metal oxides and the thermodynamic equilibrium of their reduction-oxidation reactions were previously reported to be size-dependent [1]. As the metal oxide's dimension decreases to the nanoscale, the free energies for redox reactions and phase stability temperatures alter drastically for most compounds, including iron oxides [1]. Navrotsky and colleagues [1] have calculated phase diagrams for nanoscale Fe-O system using calorimetric surface energy data and thermodynamic property values of the bulk systems. It was predicted that γ -Fe₂O₃ nanoparticles smaller than 100 nm undergo reduction to Fe₃O₄ with increasing temperature, before transforming directly to metallic Fe, hence bypassing the formation of the FeO phase.

Bonifacio and colleagues have recently carried out in-situ heating experiments to study the sintering behavior of iron oxide nanochains [2]. γ -Fe₂O₃ nanoparticles with diameters around 40-50 nm were assembled into 1-dimensional chains using a H₂/air diffusion flame inside a magnetic field [3]. The assembled chains were subsequently utilized for in-situ TEM heating experiments using the Protochips Aduro sample holder. The oxidation states of Fe during in-situ heating were probed by electron energy-loss spectroscopy (EELS) measurement. The L₃/L₂ intensity ratios of the Fe L_{2,3} ionization edges were determined from spectra acquired at different temperatures [2]. It was found that consolidation of iron oxide nanochains is accommodated by the stepwise reduction of γ -Fe₂O₃ at room temperature to metallic iron above 900 °C.

In this study, in-situ selected area electron diffraction (SAED) heating experiments were carried out for γ -Fe₂O₃ nanoparticles with an aberration corrected JEOL JEM 2100F/C_s scanning transmission electron microscope. Images and diffraction patterns were acquired in TEM mode under parallel illumination using a Gatan Rio16 camera. Figure 1(a) shows a bright field TEM image recorded at room temperature that displays nanoparticle chains with lengths around 600 to 800 nm. Figure 1(b) shows the same nanochains at 800°C. SAED patterns and bright field TEM images were collected at various temperatures. After holding times of 10 min, no more changes of the diffraction patterns were detected, which suggests completion of any phase transformations. Diffraction patterns recorded at each temperature were subsequently indexed for phase identification. The SAED patterns of the chain-like γ -Fe₂O₃ nanoparticles under room temperature and 800 °C are shown in Figure 2(a) and 2(b), respectively.

The experimental data reveal that during heating γ -Fe₂O₃ initially reduces to Fe₃O₄ for temperatures below 600 °C. As temperature further increases, characteristic diffraction rings of the FeO phase are detected at 800°C. This observation indicates that instead of the direct transformation from Fe₃O₄ to Fe as suggested by Navrotsky [1], the FeO phase is maintained around 800 °C. The FeO phase reduces to metallic Fe once the temperature reaches 900 °C. In summary, the SAED investigations of this study provide direct reciprocal lattice confirmation for FeO phase stability on the nanoscale when particles are arranged in

chain-like morphologies. The results verify earlier EELS results [2] that relied on a qualitative comparison of L_3/L_2 intensity ratios [4].

References:

[1] A Navrotsky et al., *Science* **330** (2010), p. 199.

[2] CS Bonifacio et al., *Journal of applied physics* **122.23** (2017), p. 234303.

[3] GK Das et al., *Journal of Materials Chemistry A* **2** (2014), p. 12974.

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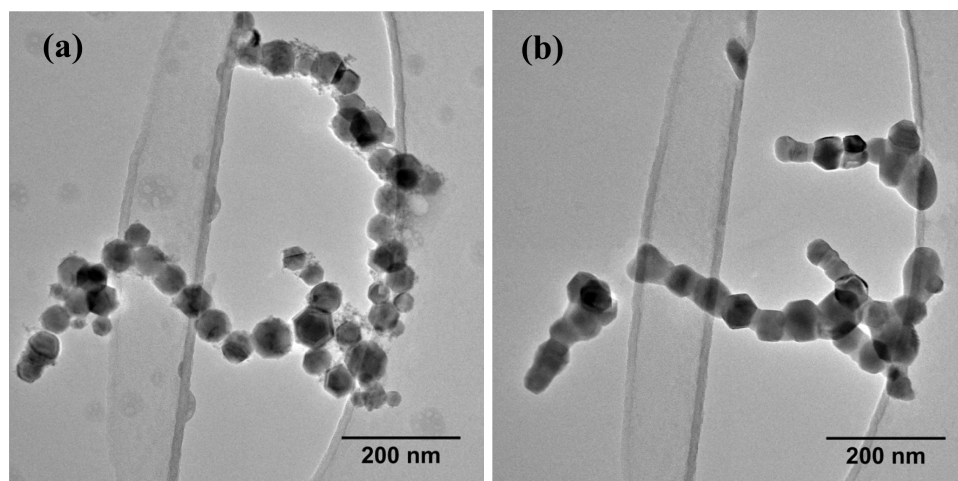


Figure 1. Bright field TEM images of the $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles at (a) room temperature and (b) 800 °C.

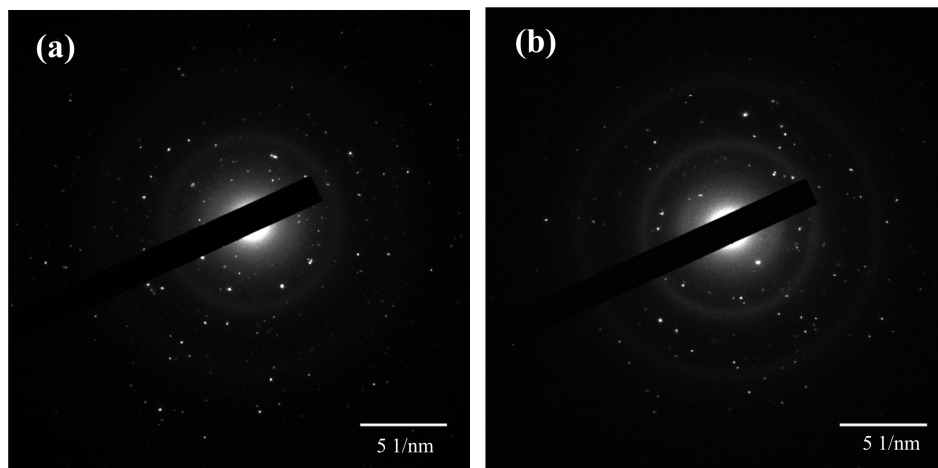


Figure 2. Selected area electron diffraction patterns of the $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles at (a) room temperature and (b) 800 °C.