

## Size-dependent stability of iron oxide evaluated through in-situ heating experiments

Cecile Bonifacio Fittz<sup>1\*</sup>, Hasti Majidi<sup>1#</sup> and Klaus van Benthem<sup>1</sup>

<sup>1</sup> University of California Davis, Department of Materials Science And Engineering, Davis, CA 95616, USA

\* now at: E.A. Fischione Instruments, Inc. Export, PA 15632, USA

# now at: Alta Devices, Sunnyvale, CA 94085, USA

The properties of nanoscale materials can be significantly different from that of their bulk counterparts, which is attributed to increasing surface to volume ratios for continuously decreasing dimensions, and potentially culminating in quantum confinement [1]. For instance, Navrotsky and co-workers suggest considerable errors in oxygen fugacity of 100-200K when using thermodynamic data for bulk phases to calculate reduction-oxidation phase equilibria for various metal oxides at the nanoscale [2].

Iron oxide is ubiquitous in nature and is commonly found in multiple different polymorphs. Potential applications of iron oxides include fuel cells, electrode materials in batteries, and nanoscale magnets. In rocks, FeO acts as a redox buffer coexisting with Fe<sub>2</sub>O<sub>3</sub> to form magnetite, i.e., FeO•Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>3</sub>O<sub>4</sub>. Bulk FeO is stable above 560°C while it remains metastable at lower temperatures in the multiphase configuration. Navrotsky et al. [2] have employed calorimetric techniques to estimate surface energies for various iron oxides as a function of initial particle size. Aided by thermodynamic data for bulk oxides they indirectly concluded that FeO is thermodynamically unstable at or below 100nm.

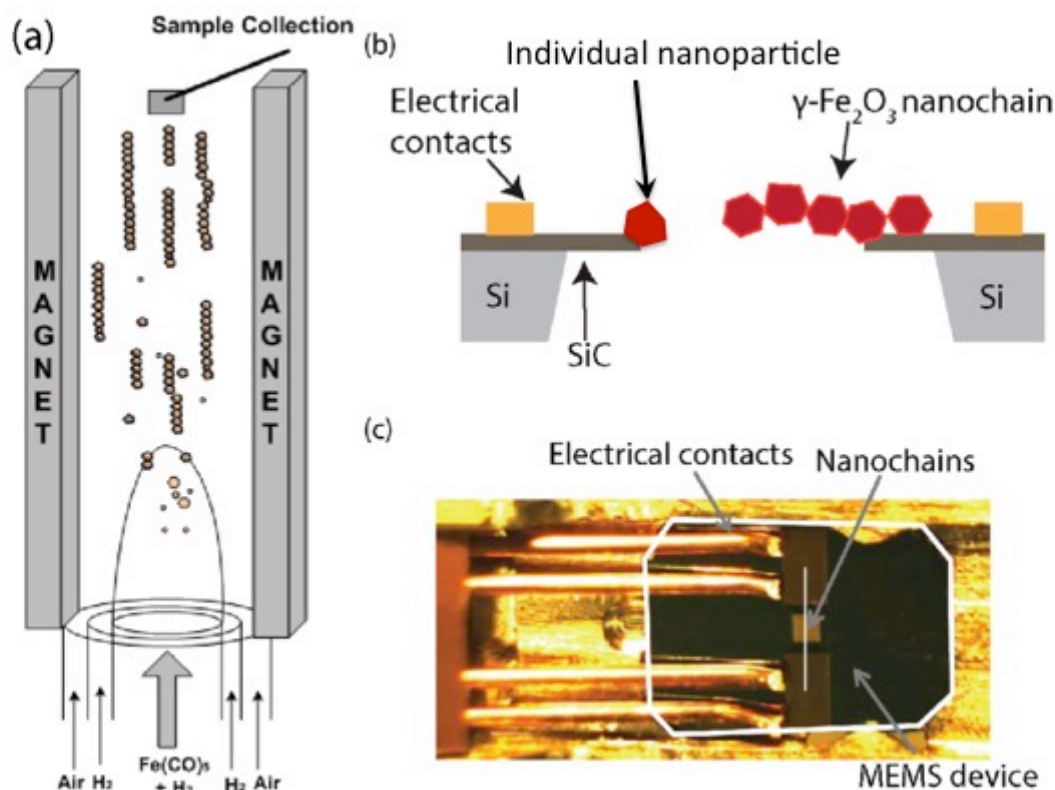
In this study we have gradually reduced individual  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles with diameters of roughly 40-50nm by in-situ heating experiments in the transmission electron microscope. For comparison, 1-dimensional nanochains of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles with various lengths were synthesized with a self-sustaining diffusion flame inside a homogeneous magnetic field (see Figure 1a) [3]. Individual nanochains were caught on Protochips MEMS devices [4] for subsequent in-situ heating experiments (Figure 1b and c). In-situ heating experiments were carried out with an aberration corrected Jeol JEM 2100F STEM instrument, while electron energy-loss spectra of the Fe L<sub>2,3</sub> and O K absorption edges were recorded with a Gatan Tridiem spectrometer. To evaluate the oxidation state for Fe during the continuous reduction experiments, the L<sub>3</sub>/L<sub>2</sub> white line intensity ratios for the Fe L<sub>2,3</sub> edges were obtained for different temperatures, and subsequently compared to data from the literature obtained using identical analysis routines [6].

The experimental results recorded from chains of particles with varying lengths demonstrate that FeO is in equilibrium with Fe<sub>3</sub>O<sub>4</sub> and metallic Fe between 400°C to 800°C. For individual particles, however,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> gradually reduces to Fe<sub>3</sub>O<sub>4</sub> before it transforms directly to metallic Fe [5]. In conclusion, the in-situ TEM studies reported here provide direct experimental evidence that indeed FeO is thermodynamically unstable at the nanoscale. However, the FeO phase can be stabilized by arranging nanoparticles in a 1-dimensional nanochain with a minimal critical length.

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**Figure 1.** (a) shows the diffusion flame utilized for the synthesis of the 1-dimensional nanochains. (b) is a sketch of the Protochips MEMS device (see picture in panel c) onto which either nanochains or individual nanoparticles were deposited.