

***Ex Situ* and *In Situ* (S)TEM of Iron Oxide Nanoparticles Synthesized by Decomposition of an Organometallic Precursor**

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Developments in *in situ* Transmission Electron Microscopy (TEM) have enabled the observation of many chemical and materials processes in relevant environmental conditions and at the necessary length and timescales. The understanding of nanoparticle nucleation and growth phenomena is one area that has benefited tremendously from this technology. By encapsulating a liquid sample between impermeable, electron transparent membranes, i.e. Si₃N₄[1] or Graphene[2], nanoparticles can be synthesized inside the TEM and imaged throughout the reaction. In this way platinum[3], gold [4],[5], and lead sulfide[6], for example, have been synthesized *in situ*. In these systems the electron beam facilitates reduction of an aqueous metallic salt precursor, so calibration and control of electron dose is crucial[7]. There has been some investigation of surfactant mediated nanoparticle growth[8], but for the most part *in situ* TEM techniques have not been applied to the wide variety of organic-phase nanoparticle syntheses.

For many nanomaterials, for example the synthesis iron oxide nanoparticles, organic phase reactions provide the necessary synthetic control[9]. Superparamagnetic iron oxide nanoparticles have desirable magnetic properties, combined with general biocompatibility and abundance in nature, making them attractive for a variety of biomedical applications[10]. Because properties are dependent on, for example, particle size, size distribution, morphology, crystallinity, and immediate environment[11], it is important to understand how synthetic conditions affect the growth and nucleation of nanoparticles. The most direct method for characterizing these effects is *in situ* TEM. Comparing the results of *in situ* syntheses, driven by electron beam reduction, to *ex situ* thermal decomposition can provide insight into the relationship between electron dose and temperature. Superparamagnetic iron oxide nanoparticles can also be expected to display unique behavior in solution; in addition to the usual solvation forces and electron beam effects, magnetic forces are also present in this system, increasing the complexity of nanoparticle interactions.

Superparamagnetic iron oxide nanoparticles were synthesized by the thermal decomposition of iron(III) oleate, in 1-octadecene, with excess oleic acid acting as a surfactant. Thermal characteristics of the precursor were evaluated using thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC) (both TA Instruments). Nanoparticle phase has been characterized *ex situ* using $\theta - 2\theta$ powder X-ray diffraction (Bruker F8 Focus), and Raman spectroscopy (Renishaw inVia). Size and size distribution have been determined by fitting Vibrating Sample Magnetometry (VSM) results, and with TEM. Scanning TEM (STEM), bright field TEM, and selected area diffraction were performed on a 300kV Cs-corrected FEI Titan with HAADF detector and GATAN CCD. For *ex situ* syntheses, nanoparticles in organic solvents are deposited on carbon films. *In situ* experiments were performed using a Hummingbird Scientific (Lacey, WA) liquid stage, with 50nm Si₃N₄ chips.

We have characterized size, size distribution, crystallinity, and phase for iron oxide nanoparticles synthesized under a variety of synthetic conditions. Monodisperse particles can be synthesized with size controlled between approximately 2 and 30 nm by varying the excess surfactant (i.e. oleic acid) ratio. Nanoparticles are generally single crystalline, as confirmed by atomic resolution TEM and STEM (Figure 1 A, B), and monodisperse. Monodisperse nanoparticles self-assemble into close packed arrays. We discuss the considerations for imaging nanoparticles in organic solvents *in situ* (Figure 1D), and present some of the first results of iron oxide nanoparticles interacting in their synthetic environment [12].

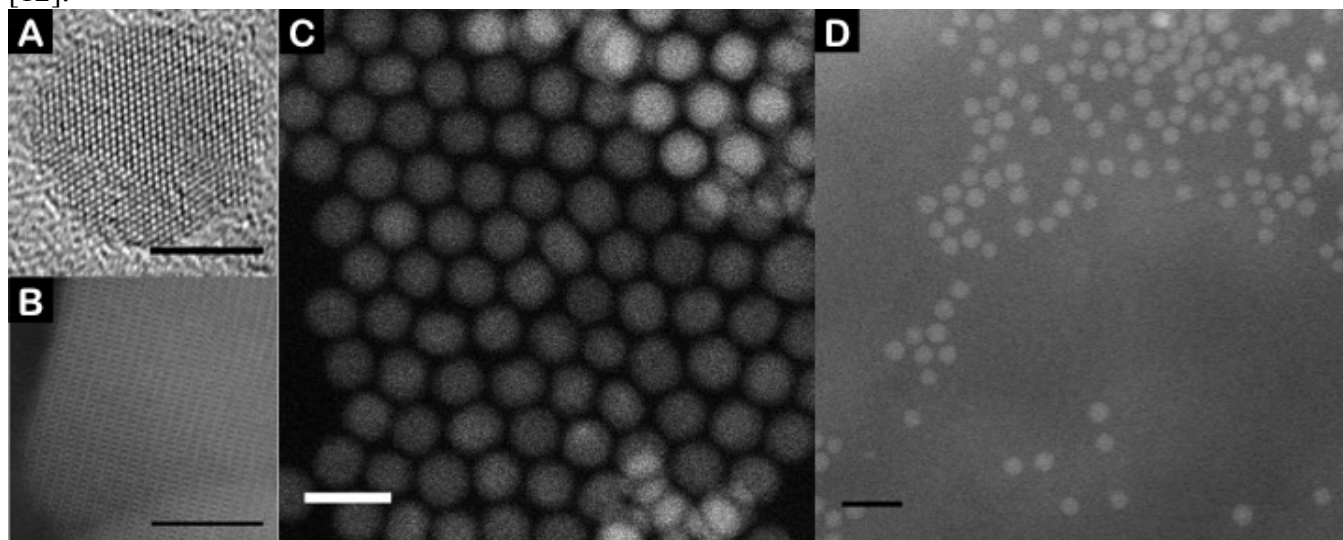


Figure 1. High resolution TEM (A, 5 nm scale bar) and STEM (B, 2 nm scale) images of iron oxide nanoparticles. STEM images of iron oxide nanoparticles self-assembled on a carbon film (C, 50 nm scale), and in solution (iron oleate, 1-octadecene, and oleic acid) in the liquid stage (D, 50 nm scale).

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