

Supporting Information for:

TEM-Induced Structural Evolution in Amorphous Fe Oxide Nanoparticles

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Experimental.

Chemicals and Materials. All chemicals and solvents were acquired from commercial sources and used as received without further purification. Trioctylphosphine oxide (TOPO) and hexadecylamine (HDA) were both of technical grade (90%).

Synthesis of Crystalline Fe₂O₃ Nanoparticles. The synthesis of crystalline Fe₂O₃ nanoparticles followed slightly modified literature preparations.¹ Briefly, lauric acid (3.05 mmol) was added to 25 mL octyl ether. Under a N₂ atmosphere, the reaction temperature was increased to 120 °C. Upon injection of Fe(CO)₅ (3.05 mmol), the temperature was held at 120 °C for 1 hr then increased to reflux (~287 °C). After 90 min, the reaction was cooled to 80 °C and aerated for 14 hours to completely oxidize the nanoparticles. Once complete, the reaction was cooled to room temperature and the particles were precipitated with ethanol. A minimum of three dissolution in hexane and precipitation with ethanol steps were required to purify the nanoparticles. The final crystalline sample was stored in hexane.

Synthesis of Amorphous Fe Nanoparticles. TOPO (6.5 mmol, 2.5 g) and HDA (29.0, 7.0 g) were combined in a flask and the temperature was increased to 100 °C for 1.5 hours to thoroughly degas the mixture. The reaction was then placed under N₂ and Fe(CO)₅ (1.52 mmol) was injected. The reaction temperature was increased to 250 °C and after 30 min cooled to room temperature and the particles precipitated with methanol. A minimum of three dissolution in chloroform and precipitation with methanol steps were required to purify the nanoparticles. The final amorphous Fe nanoparticle sample was immediately analyzed to prevent significant surface oxidation.

Synthesis of Amorphous Fe Oxide Nanoparticles. TOPO (6.5 mmol, 2.5 g) and HDA (29.0, 7.0 g) were combined in a flask, and the reaction temperature was increased to 100 °C under a N₂ atmosphere. Upon injection of Fe(CO)₅ (1.52 mmol), the temperature was increased to 250 °C. After 30 min, the reaction was cooled to 80 °C and aerated for 14 hours to completely oxidize the nanoparticles. Once complete, the reaction was cooled to room temperature and the particles precipitated with methanol. A minimum of three dissolution in chloroform and precipitation with methanol steps were required to purify the nanoparticles. The final amorphous Fe oxide nanoparticle sample was stored in chloroform.

Instrumentation.

Transmission Electron Microscopy (TEM). TEM samples were prepared by slow evaporation of dilute hexane or chloroform solutions of nanoparticles directly onto a grid (300-mesh Cu, EM Science). Images were obtained using a JEOL-1200EXII microscope operating at 80 keV equipped with a high-resolution Tietz F224 digital camera. Particle sizes are reported as the mean \pm the standard deviation, based on a statistical analysis of at least 300 particles taken from different areas on the TEM grid. High-resolution TEM analysis was performed on a JEOL-2010F field emission microscope operating at 200 keV equipped with a Gatan (GAT-776D.US1000) Enfina™ 1000 electron energy loss spectroscopy (EELS) system and a $2,000 \times 2,000$ CCD sensor.

SQUID Magnetometry. Magnetization measurements were obtained using a Quantum Design MPMS SQUID magnetometer. SQUID samples were prepared by evaporating solutions of nanoparticles in gelatin capsules.

Magnetization curves are normalized to the particle sample mass. The estimated mass per particle is 4.1 and 7.5 ag for the 8.5 nm diameter crystalline Fe₂O₃ and 10.5 nm diameter amorphous Fe oxide particles, respectively. Masses are likely overestimates because they assume a close-packed ligand shell, therefore the magnetizations are not calculated per individual particle.

Powder X-ray Diffraction (XRD). XRD patterns were obtained using a Philips X'Pert X-ray diffractometer operating at 40 kV. Samples were prepared by evaporating hexane or chloroform solutions of nanoparticles directly onto a glass slide.

BET Surface Adsorption/Porosity Analysis. Nitrogen adsorption-desorption curves were obtained using a Micromeritics Multi-point BET model ASAP 2000.

Figure S1. Particle size histograms for (A) crystalline as well as amorphous Fe oxide nanoparticles (B) before and (C) after electron beam irradiation. Red bars indicate outer diameter.

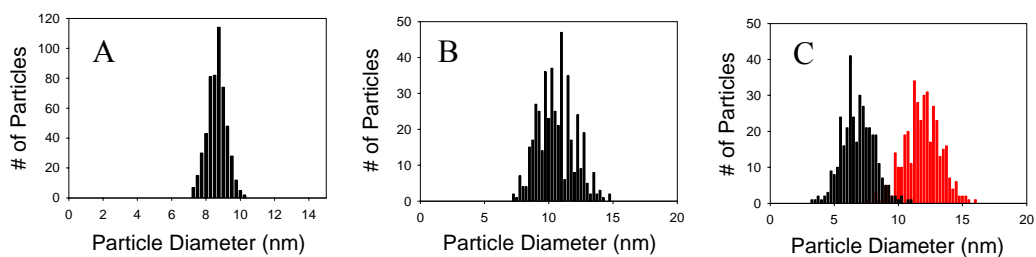


Figure S2. Variable-tilt TEM image of amorphous Fe oxide nanoparticles at angles of (A) 0°; (B) 25°; and (C) 35°. Scale bars are 100 nm.

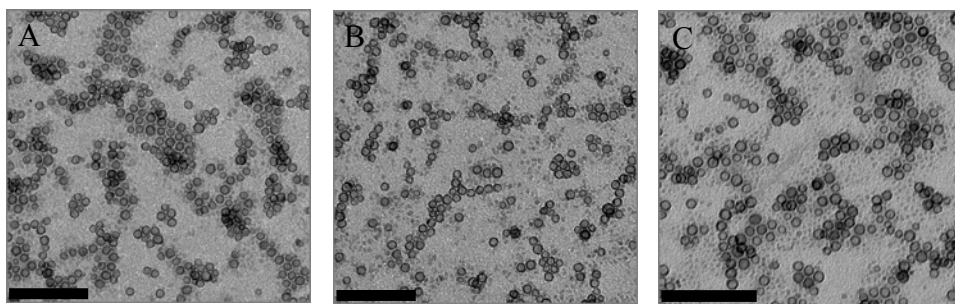


Figure S3. TEM images of crystalline Fe_2O_3 nanoparticles (A) before and (B) after 15 min of electron beam irradiation and amorphous Fe oxide nanoparticles (C) before and (D) after 2 min of electron beam irradiation. Scale bars are 100 nm. Minor particle translocations such as we observe are typical in TEM.²

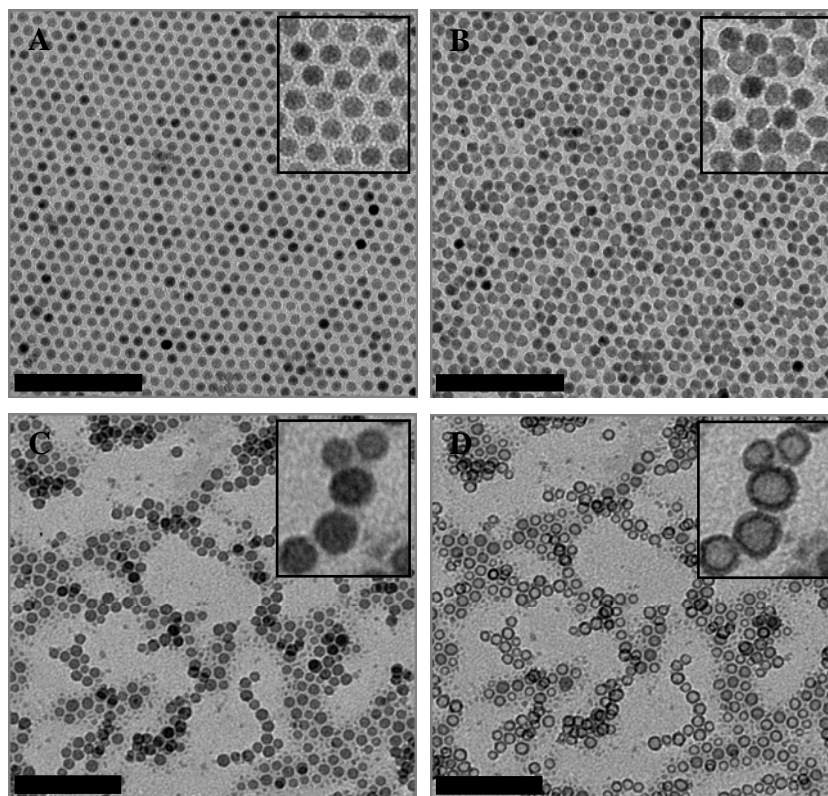


Figure S4. Selected area electron diffraction pattern of the hollow Fe oxide nanoparticles.

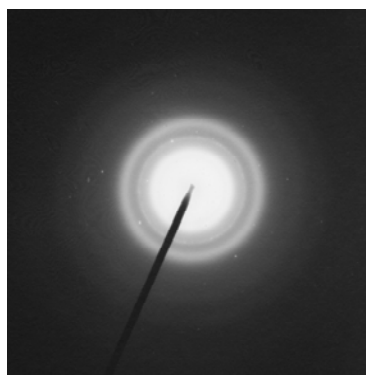


Figure S5. Low resolution TEM images of amorphous Fe oxide particles acquired at approximately (A) 0 sec; (B) 10 sec; (C) 20 sec; (D) 30 sec; (E) 40 sec; (F) 50 sec; (G) 60 sec; (H) 120 sec; and (I) 180 sec exposure in the 80 keV beam. Scale bar is 15 nm.

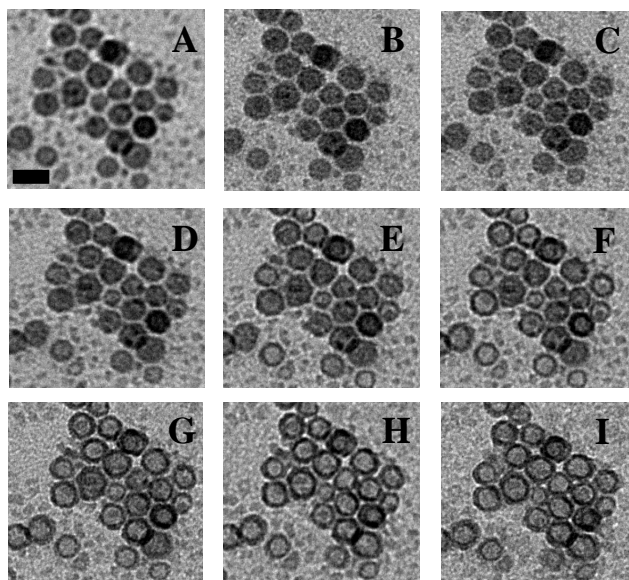


Figure S6. Examples of low resolution TEM images of different amorphous HDA/TOPO coated Fe nanoparticles samples.

Top: particles exposed to the beam for approximately (A) 30 and (B) 210 sec. Scale bar is 50 nm.

Middle: images acquired at approximately (A) 0 sec; (B) 10 sec; (C) 20 sec; (D) 30 sec; (E) 40 sec; (F) 60 sec; (G) 80 sec; and (H) 120 sec exposure in the 80 keV beam. Scale bar is 15 nm.

Bottom: images acquired at approximately (A) 0 sec; (B) 10 sec; (C) 20 sec; (D) 30 sec; (E) 40 sec; (F) 60 sec; (G) 80 sec; and (H) 120 sec exposure in the 80 keV beam. Scale bar is 25 nm.

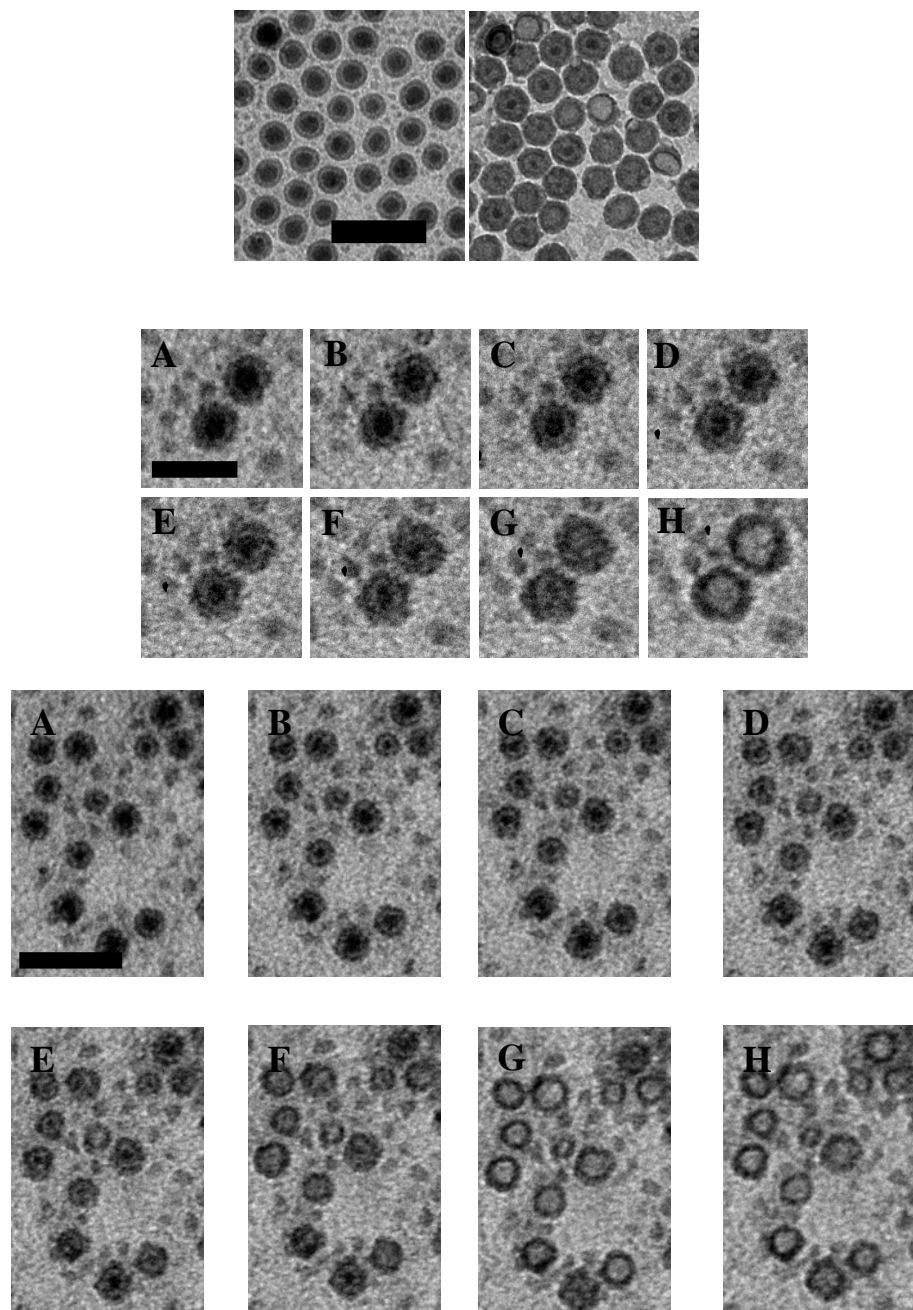


Figure S7. TEM image (exposure time = 10 sec) acquired after the grid had already been exposed to the electron beam and then slightly translated in the microscope. The dashed line roughly indicates the area previously imaged, in which amorphous Fe oxide particles were exposed to 80 keV for 2 min. Scale bar is 100 nm.

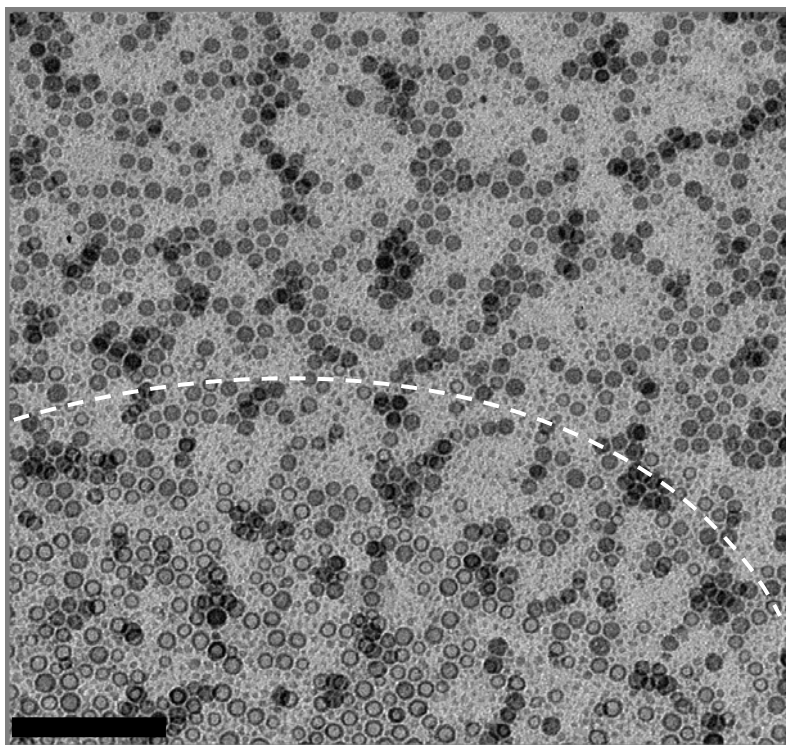


Figure S8. High-resolution TEM image of hollow Fe oxide nanoparticles (A-B) showing the presence of lattice fringes suggesting nanocrystallinity in the TEM irradiated particles. Inset is the electron diffraction pattern for the particle shown. Scale bars are 5 nm.

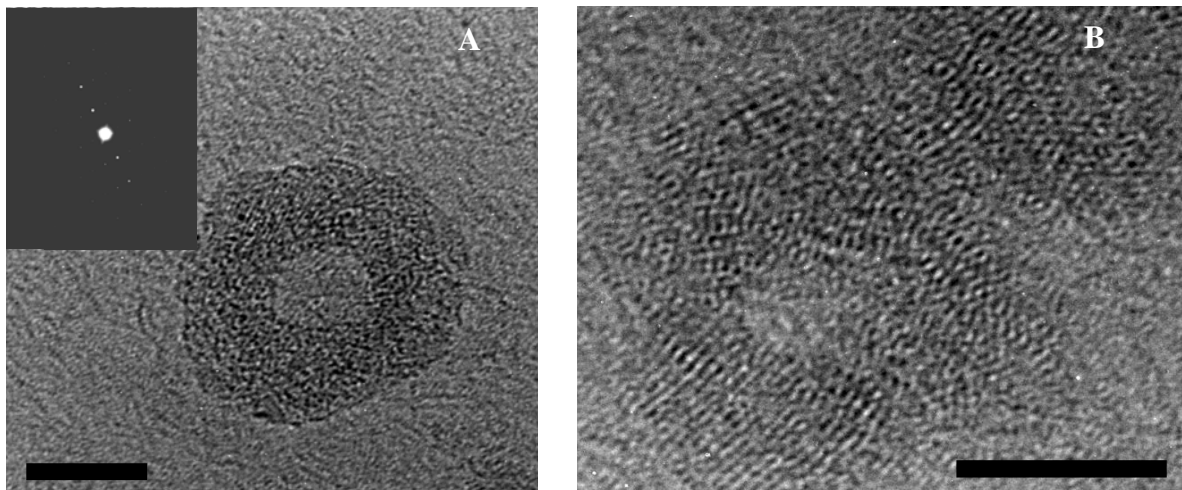


Figure S9. ADF-STEM image showing the location of recorded EELS spectra (A) with arrows indicating the location of selected spectra (B-D). There is no detectable O or Fe signal when the probe is positioned off the particle.

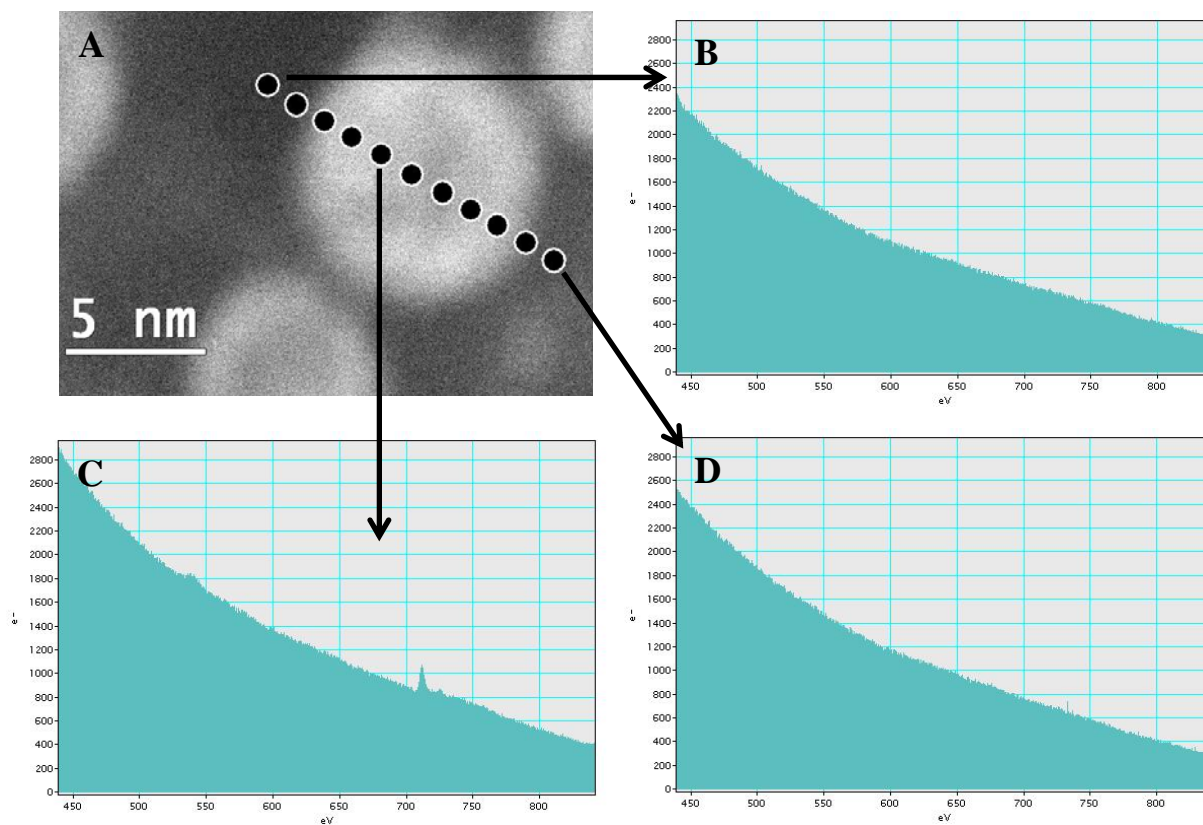


Figure S10. BET nitrogen adsorption-desorption curves for (●) crystalline and (■) amorphous Fe oxide nanoparticles.

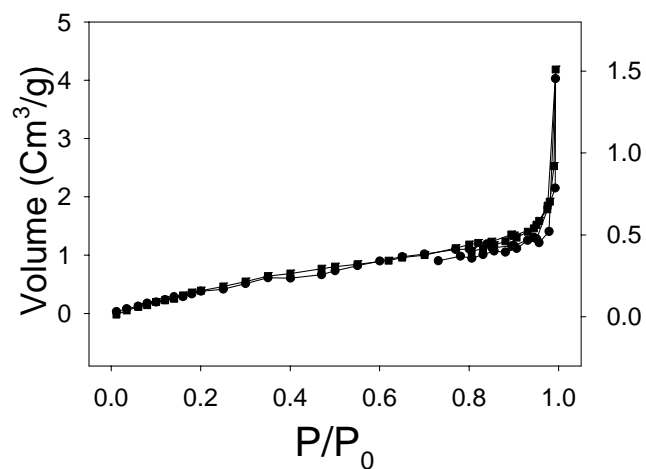


Figure S11. Magnetization measurements as a function of temperature after cooling in a zero field (■,●) and in a 100 Oe field (□,○) for (●) crystalline and (■) amorphous Fe oxide particles.

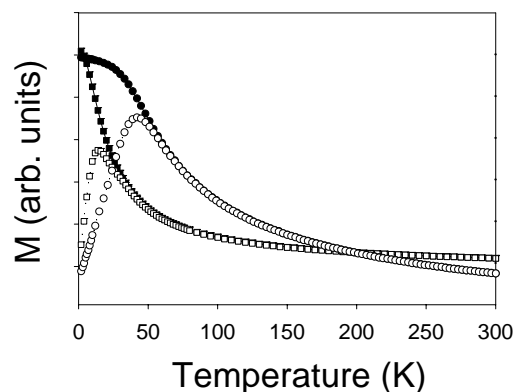
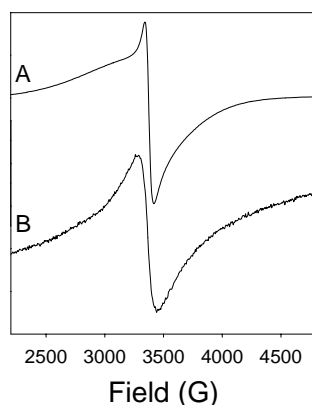


Figure S12. Room temperature solution EPR spectra of the as-prepared crystalline Fe_2O_3 (~13 mg/mL) and amorphous Fe oxide (~5 mg/mL) particles in chloroform solutions.



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References.

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- S2. (a) Marks, L.D.; Zhang, J.P. *Ultramicroscopy* **1992**, *41*, 419-422. (b) Iijima, S.; Ichihashi, T. *Phys. Rev. Lett.* **1986**, *56*, 616-619. (c) Smith, D.J.; Petford-Long, A.K.; Wallenberg, L.R.; Bovin, J.O. *Science* **1986**, *233*, 872-875.