

## SUPPORTING INFORMATION

### Vacancy Coalescence During Oxidation of Iron Nanoparticles

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#### *Synthesis.*

Iron nanoparticles were obtained by decomposition of iron pentacarbonyl (99.999 %) in octadecene (90 %) in the presence of oleylamine (70 %) and/or trioctylamine (98 %). All chemicals were purchased from Sigma-Aldrich. Iron pentacarbonyl was stored below its melting point in an argon-filled glovebox. The other chemicals were stored under air at room temperature. In a typical synthesis, 10 ml of organic solvent with the proper amount of amines were heated inside a three-neck flask to 60°C under vacuum for 30 min. While keeping the solution under argon (99.999 %), the temperature was raised to the target set point. A precursor solution of 0.4 ml of iron pentacarbonyl in 2 ml of solvent was prepared separately under Ar. This was rapidly injected through a septum into the hot surfactant solution under vigorous stirring. The decomposition time of the iron carbonyl depends on the temperature and the amount of surfactants used. To oxidize the iron nanoparticles, 20 ml/min of a 20% oxygen mixture in argon were flowed through the heated flask containing the colloidal solution over 1-12h. The reaction temperature was set between 200°C and 250°C. Details on the amount of surfactants and reaction temperatures and times used in the synthesis of the particles in figure 2 are given in table SI 1. The particle size distributions of the oxidized particles are shown in histograms in

figure SI 1. The particle size distribution of the very initial iron particles cannot be exactly determined due to the oxide layer inevitably formed during the transfer of the TEM grid from the glovebox to the electron microscope.

### ***Structural Characterization.***

The crystal structure of the samples was measured using UV-vis spectroscopy and powder X-ray diffraction and absorption. UV-vis spectra were obtained on a Agilent/Hewlett-Packard 8453 spectrometer with the nanoparticles solubilized in toluene (Fig. SI 2A). XRD analyses were obtained on a Bruker AXS diffractometer using Co  $K_{\alpha}$  radiation (1.790 Å) and a general area detector. The instrument resolution was 0.05° in  $2\theta$ , and the acquisition time for each sample was around 1 hour. XRD samples were prepared in air by depositing the precipitated particles on a glass substrate (Fig. SI 2B).

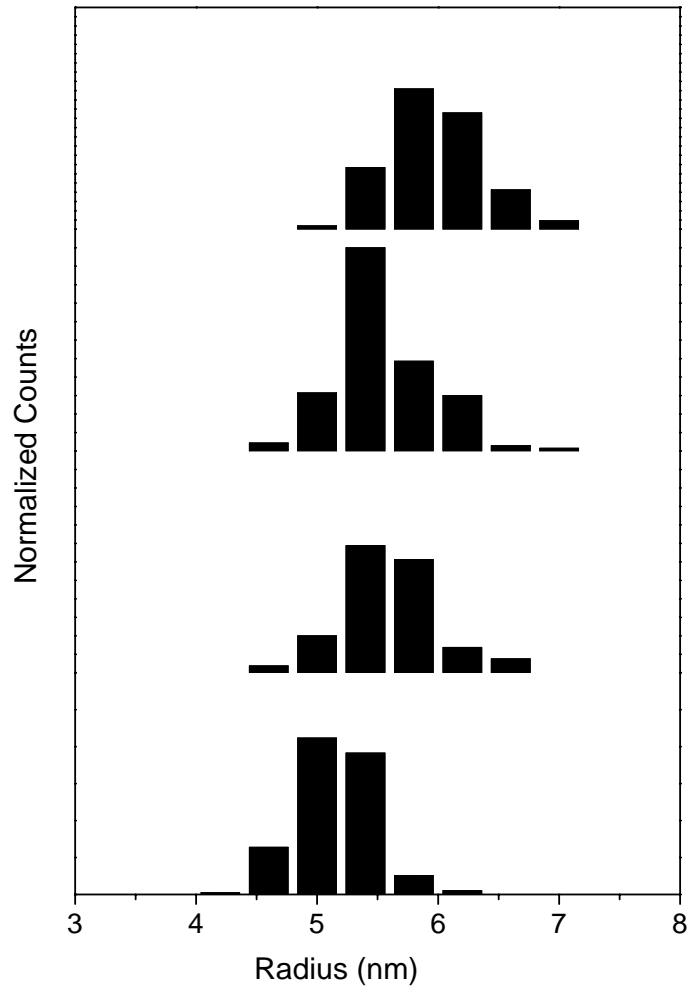
XAS spectra were obtained at the Advanced Light Source at the Lawrence Berkeley National Laboratory, beamline 10.3.2. XANES data was subjected to normalization and background subtraction. For XAS analysis of the as-synthesized iron nanoparticles, the colloidal solution was sealed in air free conditions inside a capillary (Fig. SI 3A). For XAS analysis of the oxidized nanoparticles, the colloidal particles were precipitated and supported on a substrate. The maghemite and magnetite bulk standards were grinded with an agate mortar. Analyses were done at room temperature with the supported powders in air (Fig. SI 3B).

TEM micrographs were obtained using a Tecnai G<sup>2</sup> S-Twin electron microscope (200 kV). TEM samples were prepared by placing a drop of the colloidal solution containing

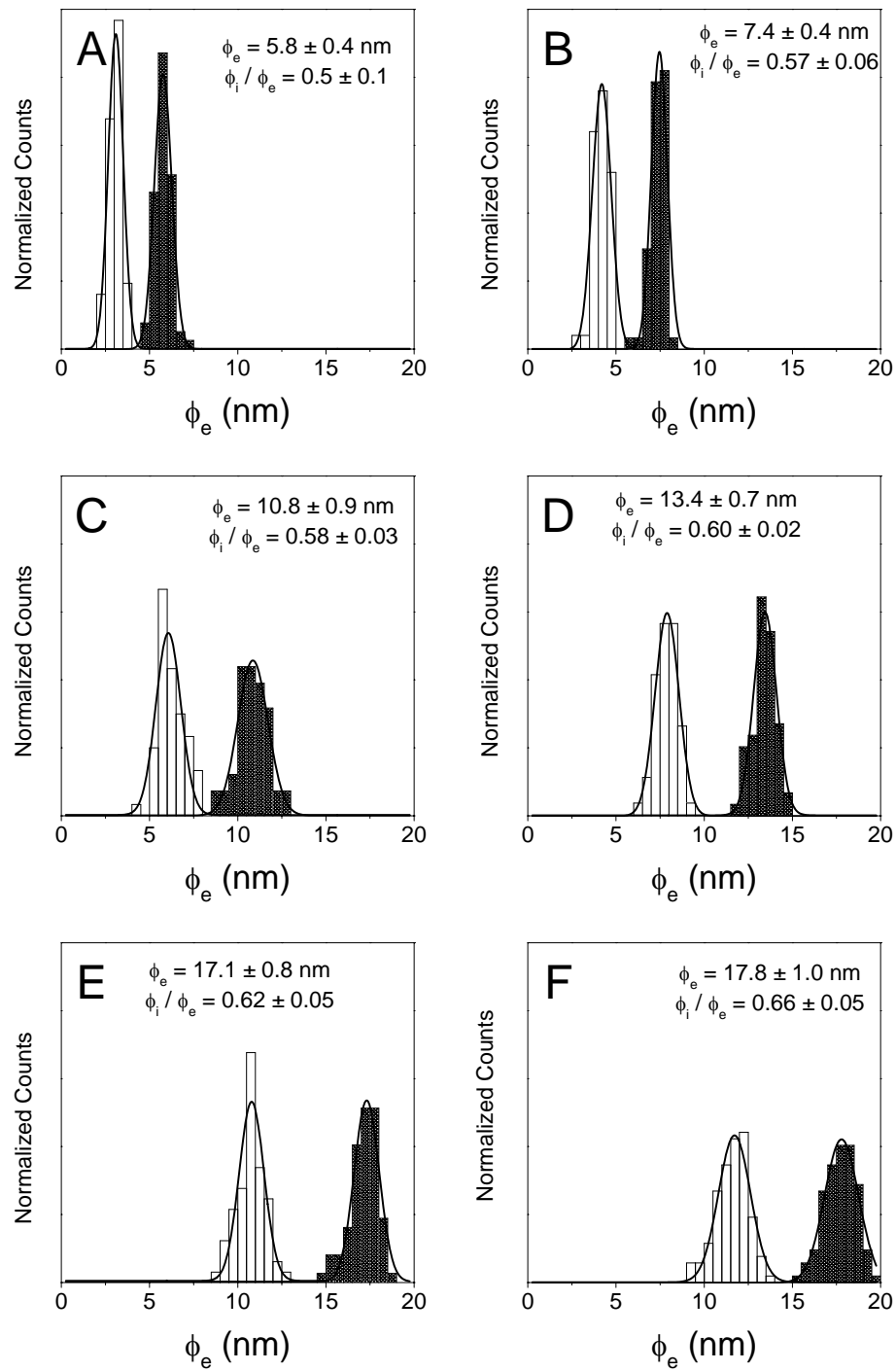
the nanoparticles onto a carbon coated copper grid at room temperature and ambient atmosphere. Only the grid containing the initial iron nanoparticles (Fig. 1A) was prepared and mounted in the TEM holder under an argon atmosphere. This sample was quickly transferred into the TEM, reducing its air exposure to around 20 s.

**Table SI 1.** Reaction conditions for the synthesis of iron nanoparticles by decomposition of 3 mmol of iron pentacarbonyl ( $\text{Fe}(\text{CO})_5$ ) in octadecene. The shell thickness ( $\varnothing_E - \varnothing_I$ ) and the external diameter ( $\varnothing_E$ ) of the fully oxidized particles shown on figure 2 are given. The oxidation at 350°C is performed with the particles supported on a silicon nitride TEM grid.

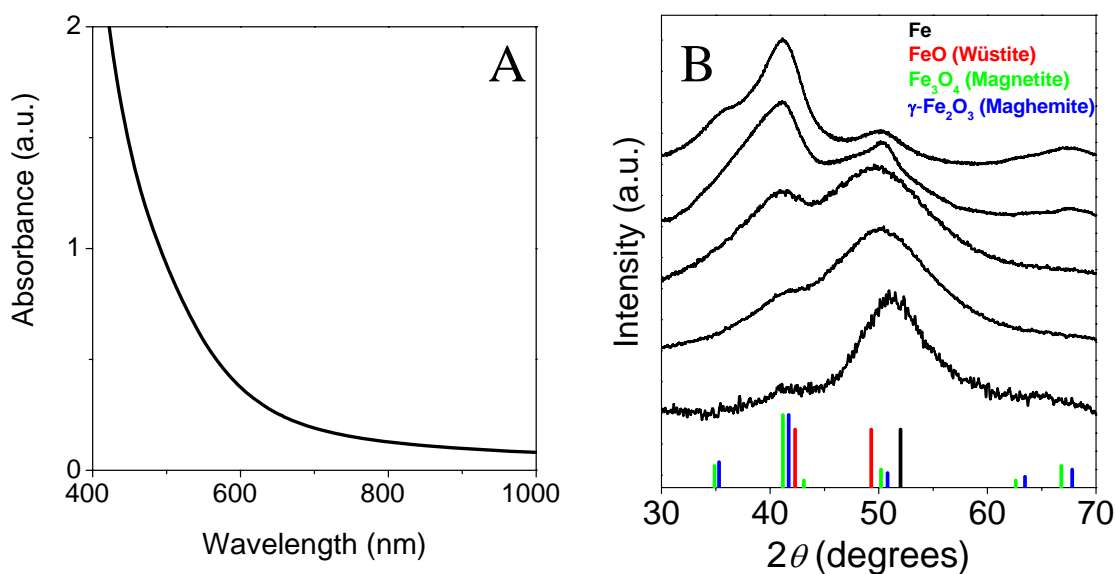
<i>Oleylamine</i> (mmol)	<i>Trioctylamine</i> (mmol)	<i>Vol. Inj.</i> (ml)	$T_{\text{Synthesis}}$ (°C)	$T_{\text{oxidation}}$ (°C)	$\varnothing_E$ (nm)	$\varnothing_E - \varnothing_I$ (nm)
0	0.75	2	220	220	$5.8 \pm 0.4$	$1.5 \pm 0.2$
0	0.38	2	200	220	$7.4 \pm 0.4$	$1.6 \pm 0.2$
0.34	0	2	200	250	$10.8 \pm 0.9$	$2.3 \pm 0.2$
0.34	0	4	220	250	$13.4 \pm 0.7$	$2.8 \pm 0.2$
0.67	0	4	200	250	$17.1 \pm 0.8$	$3.0 \pm 0.2$
0.67	0	2	200	350	$17.8 \pm 1.0$	$3.6 \pm 0.2$



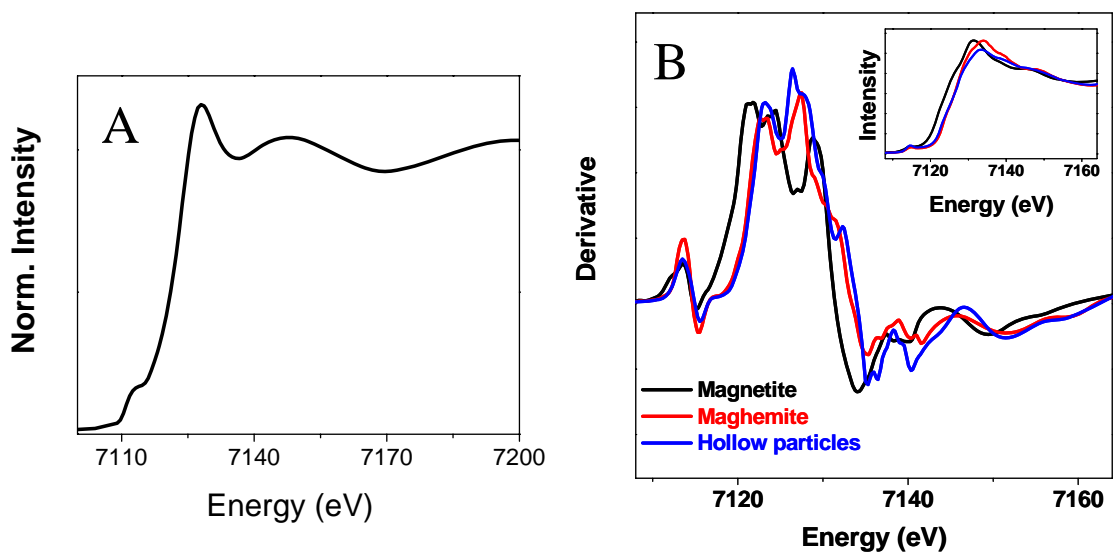
**Fig SI 1.** External diameter distributions of partial oxidized iron oxide particles. From bottom to top histograms correspond to the oxidation state shown in Fig 1 A, B, C, and E.



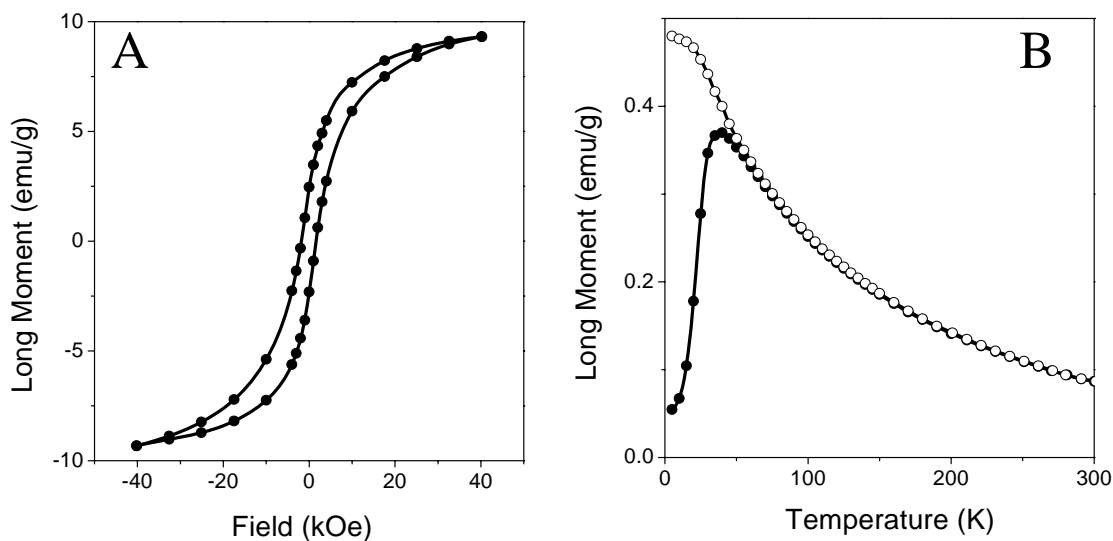
**Fig SI 2.** External (*filled*) and internal (*blank*) diameter distributions of the fully oxidized iron particles shown in figure 2.



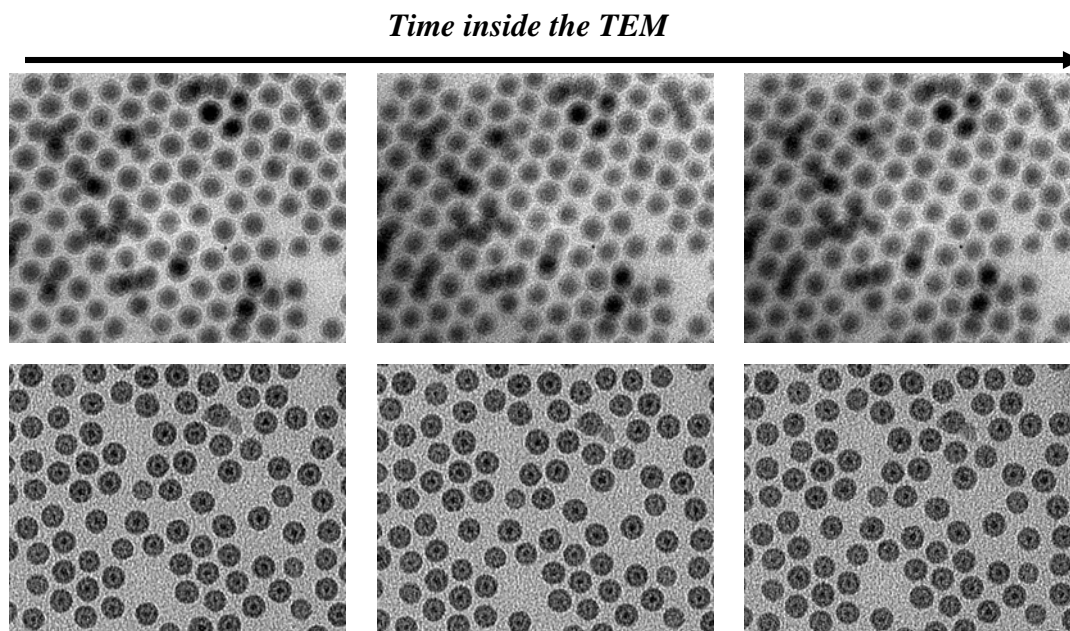
**Fig. SI 3.** A) UV-vis spectrum of 10 nm iron nanoparticles completely oxidized at 200 °C. B) Evolution of the XRD spectra of the dried iron nanoparticles stored at room temperature in air. From bottom to top, the spectra were obtained after 2, 10, 30 min and 24 hr. from exposing the sample to air. The top most spectrum corresponds to the particles totally oxidized at 220°C.



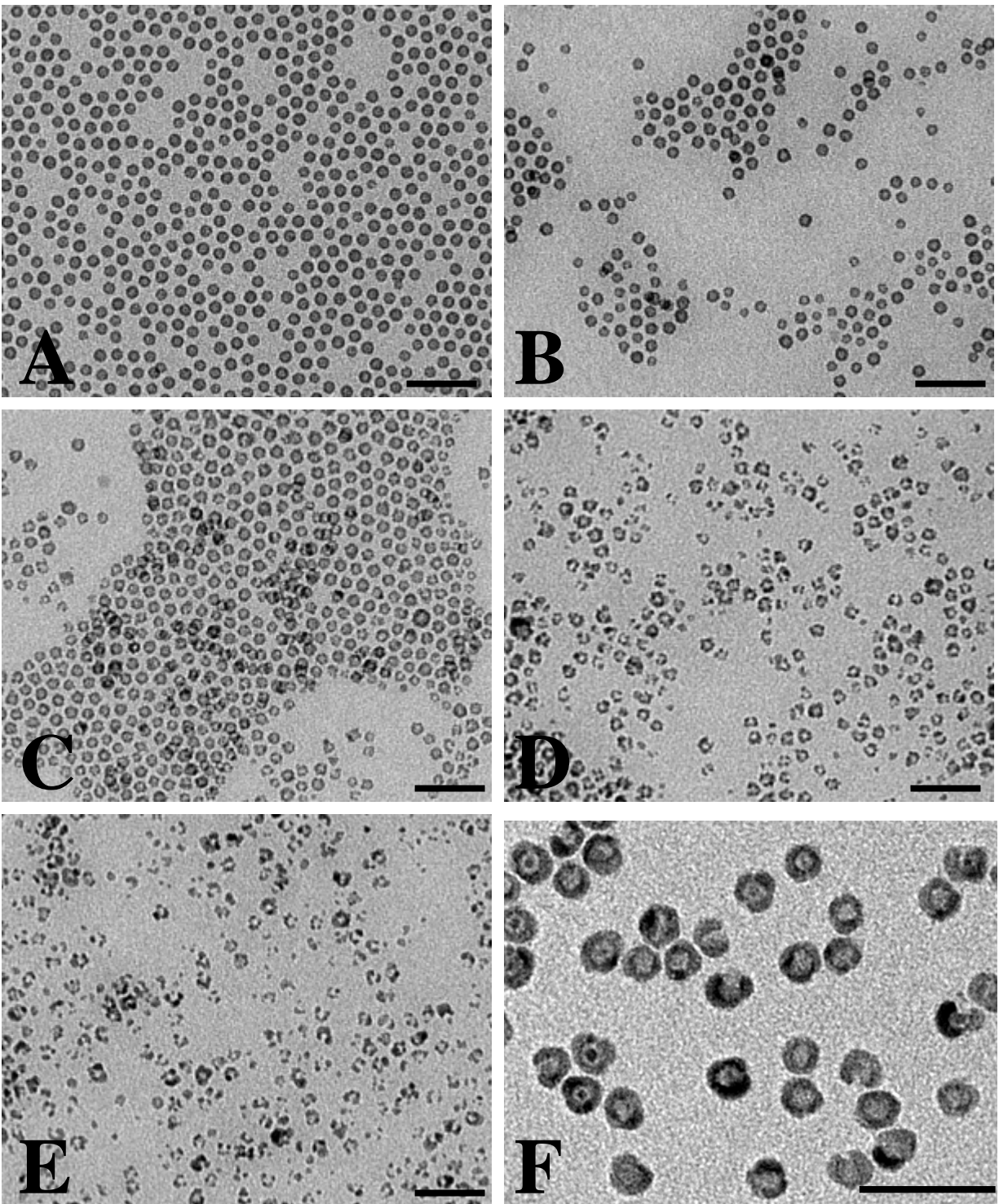
**Fig. SI 4.** A) XANES spectra (Fe, K-edge) of the as-synthesized iron nanoparticles sealed in a capillary. B) Raw (inset) and derivatives of the XANES spectra (Fe, K-edge) of the iron oxide hollow nanoparticles compared with those of maghemite and magnetite reference samples.



**Fig SI 5.** A) Magnetization vs. field at 5 K for ~9 nm completely oxidized nanoparticles. B) Magnetization vs. temperature in a zero-field-cooled/field-cooled (100 Oe) process .



**Fig. SI 6.** TEM micrograph of two different stages of the oxidation of iron nanoparticles synthesized with amines. From left to right micrographs were obtained after exposing the particles to the electron beam for around 30 seconds, 10 minutes and 30 minutes.



*Fig. SI 7.* TEM micrographs of ~7 nm iron oxide nanoparticles oxidized at 150 °C (A) and afterwards heated for 30 minutes at (B) 180 °C; (C) 210 °C; (D) 240 °C; (E) 270 °C. (F) TEM micrographs of ~15 nm iron oxide nanoparticles oxidized at 300 °C in octadecene for 1h. Scale bars correspond to 50 nm.