Supplemental Information for: Observing the Colloidal Stability of Iron Oxide Nanoparticles in situ

Ryan Hufschmid,1 Eric Teeman,1 B. Layla Mehdi,2,3 Kannan M. Krishnan,1 and Nigel D. Browning2,3,4

1Department of Materials Science & Engineering, University of Washington, Box 352120, Seattle, WA 98195-2129, USA
2Department of Mechanical, Materials and Aerospace Engineering, University of Liverpool, Liverpool L69 3GH, UK
3Department of Physics, University of Liverpool, Liverpool L69 3GH, UK
4Physical and Computational Science Directorate, PNNL, Richland, WA 99352, USA

Figure S1 Electron Energy Loss Spectroscopy (EELS) of the low-loss region through TEM liquid cells. The thickness of the specimen can be estimated from the relative intensity of the zero-loss peak.1 This is described by equation 1, where \( t \) is the thickness of the specimen, \( \lambda \) is the mean free path, \( I_0 \) is the intensity of the zero-loss peak and \( I_T \) is the total intensity.

\[
t = \lambda \ln \left( \frac{I_0}{I_T} \right)
\]

For the example spectrum above we calculate 199 nm of H\(_2\)O, including the two 50 nm Si\(_3\)N\(_4\) windows. Experiments are performed near the edge of the window where water thickness is measured to be approximately 100-200 nm. Bulging increases the thickness at center of the window to 1000 nm or more.
Figure S2 A Pourbaix diagram (E vs. pH) for the aqueous Fe-O-H system depicts the equilibrium phase as a function of electric potential and pH. Arrows indicate the extension of the solid phase regions as iron concentration increases from $10^{-5}$ to $10^{-2}$ mol/kg. This diagram was adapted from a web-based application for generating Pourbaix diagrams from The Materials Project (materialsproject.org).
Figure S3 Another ensemble of CPP-PEG coated nanoparticles growing at the expense of dissolving particles.
Figure S4 Post-mortem Energy-Dispersive Spectroscopy (EDS) confirms presence of iron in the nanoparticles (region 2) as well as the high contrast amorphous phase grown in situ (regions 1, 3). No iron was detected in the background (regions 4 and 5). Background copper peaks are from the holder and instrument.
Figure S5 Post-mortem EELS spectra also confirm presence of iron in the particles. HAADF STEM image (top) indicating where spectra were acquired. The iron L edge, onset 708 eV, is apparent both on the particles (2, 4) as well as the growths (1, 3, 5). No iron is detected in the background, captured near the cluster but not over any of the particles or growths.
Supplementary Movie 1 STEM movie of PMAO-PEG coated Fe$_3$O$_4$ nanoparticles at 450kX magnification, sped up 30 times to reduce file size. Dose rate is 24.8 e$^{-}$Å$^{-2}$s$^{-1}$ experiment from main text figure 2.

Supplementary Movie 2 STEM movie of reversible growth of L-cysteine functionalized Fe$_3$O$_4$ nanoparticle, frames shown in main text figure 3.

Supplementary Movie 3 STEM movie of growth of CPP-PEG functionalized Fe$_3$O$_4$ nanoparticles from main text figure 4

Supplementary Movie 4 STEM movie of CPP-PEG coated Fe$_3$O$_4$ nanoparticles dissolving at a dose rate of 14.1 e$^{-}$Å$^{-2}$s$^{-1}$.

References

