

## Atomic Resolution and *in situ* STEM-EELS of Superparamagnetic Iron Oxide Nanoparticles

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Scanning Transmission Electron Microscopy (STEM) with Electron Energy Loss Spectroscopy (EELS) are powerful techniques for relating the structure and electronic configuration of iron oxide nanoparticles to their magnetic properties. Superparamagnetic iron oxide nanoparticles are used for a variety of biomedical applications requiring control over magnetic and physio-chemical properties.[1] Magnetic performance of iron oxides is dependent on these physio-chemical properties, including size, size distribution, surface chemistry, crystallographic phase, and defects. In this work we use high resolution STEM-EELS to investigate atomic scale structure-properties relationships in iron oxide nanoparticles. These results are complemented by *in situ* STEM movies showing interactions of these nanoparticles in solution.[2]

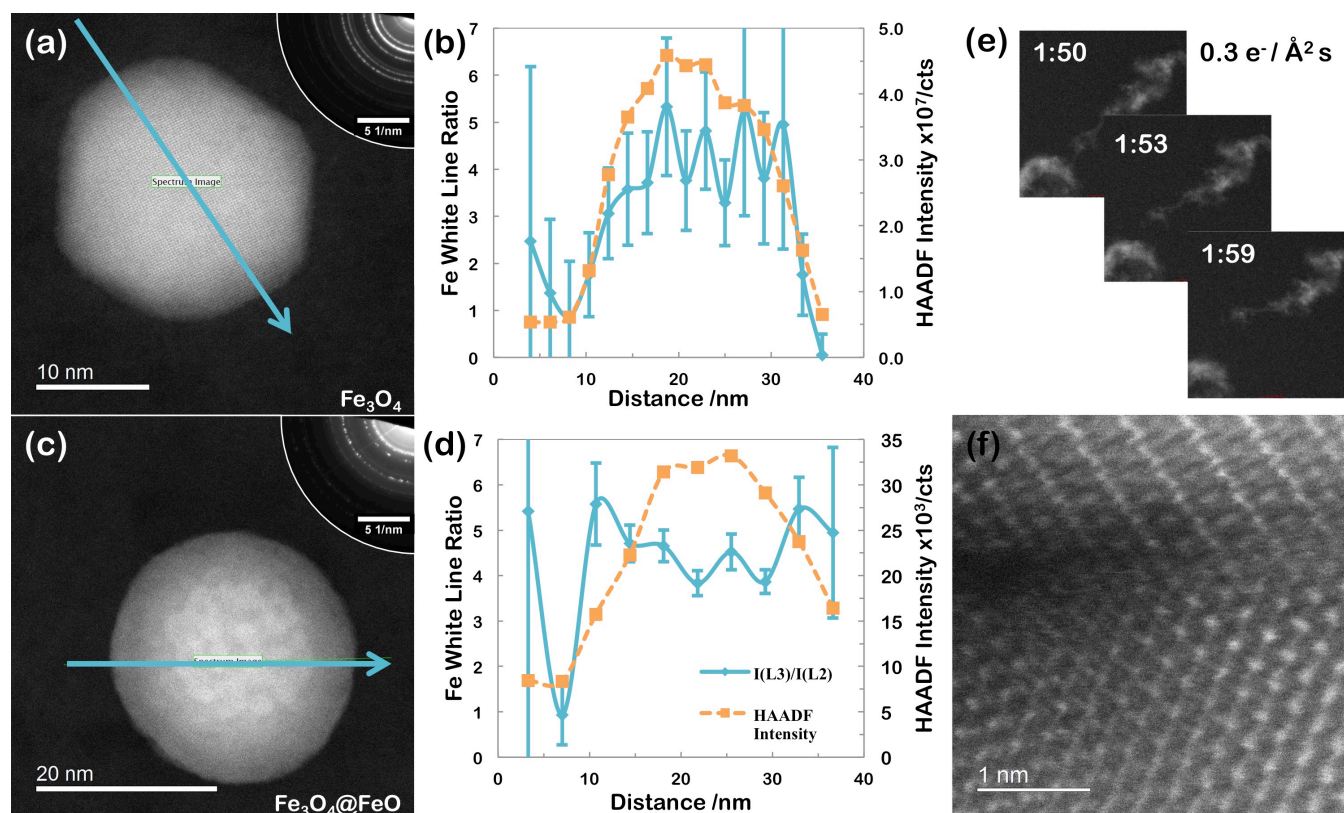
Superparamagnetism is the spontaneous reversal of the magnetic moment and occurs in magnetite ( $\text{Fe}_3\text{O}_4$ ) crystals smaller than approximately 30 nm. This property is used in a variety of applications, for example Magnetic Particle Imaging (MPI).[3] Magnetic properties in iron oxides are dependent on the distribution of iron 3+ and 2+ in the oxide lattice. In the case of stoichiometric wüstite, iron 2+ occupies all octahedral sites between oxygen ions and the symmetry results in no net magnetic moment. As it is oxidized toward inverse-spinel magnetite, iron 3+ occupies tetrahedral sites. This asymmetry produces a net magnetic moment in the crystal. In addition to size and size distribution, the importance of iron oxide phase on magnetic properties has been established.[4] To characterize magnetic and crystallographic properties at relevant length scales we use STEM-EELS. Valence in transition metal oxides, i.e. iron, is proportional to the relative intensities of the  $L_3$  and  $L_2$  core-loss transitions as well as the difference in energy onset between iron L and oxygen K edges. Fine structure, particularly of the oxygen K edge, is sensitive to bonding and coordination.

In this work we use STEM-EELS to characterize magnetic properties and crystallographic phase of iron oxide nanoparticles with atomic resolution. Optimized  $\text{Fe}_3\text{O}_4$  nanoparticles, exemplified in **Figure 1a** are single crystalline, uniform, and faceted. EELS linescans are used to quantify the distribution of iron 3+ and 2+ throughout the particles. For  $\text{Fe}_3\text{O}_4$  nanoparticles, iron valence is uniform throughout the particle within experimental uncertainty. Another sample of comparable size but showing poor magnetic properties is shown in **Figure 1c**. These particles show less pronounced faceting and a core-shell structure. Inset Selected Area Electron Diffraction (SAED) pattern shows presence of wüstite (FeO) in addition to magnetite. However, these particles are still single crystalline as indicated by continuous lattice planes between core and shell. The increased contrast of the core is due to a higher concentration of iron within the continuous oxygen lattice consistent with the wüstite phase. EELS measurements show a larger  $L_3/L_2$  ratio for the particles' shell, indicating a larger proportion of iron 3+. These particles are partially oxidized from the surface, transforming wüstite to magnetite. Annealing after synthesis

optimizes magnetic and crystallographic properties. EELS measurements confirm the importance of iron oxide phase in establishing magnetic properties. In solution, magnetic forces determine *in situ* and *in vivo* performance. [5]

#### References:

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**Figure 1** HAADF STEM images and corresponding EELS line scans measure iron L3/L2 white line ratio of optimized superparamagnetic iron oxide nanoparticle (**a,b**) and core-shell nanoparticle (**c, d**), which show drastically different crystallographic (see inset SAD pattern) and magnetic properties. This is complimented by *in situ* liquid STEM movies showing particle interactions in solution (**e**). Unless stabilized by polymer coatings, oxide particles agglomerate via oriented attachment (**f**).