

Spectroscopic characterization of nano-magnetite: Facts and mystery about an illusive mineral phase

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The non-destructive spectroscopic characterization of structural and electronic properties of nano-forms (< 50 nm crystallite size) of Magnetite (Fe₃O₄) and related iron-based phases has become of utmost importance, because of their great potential for new applications in a variety of different fields. Biosensors, magnetic storage devices and environmental remediation are just a few examples of promising applications and new markets for such materials.

We've used a suite of surface and bulk sensitive microscopic and spectroscopic techniques (TEM, HREELS, XPS, XRD and synchrotron L-edge STXM) to study nano-magnetite particles coming from different sources (bio-synthesis, wet chemical synthesis routes (Gee et al.)). We have found that the application of non-microscopic techniques, such as XPS or conventional powder XRD can yield incomplete information because of particle size dependant variations in structural and electronic composition and because of effects of aggregation. The soft X-ray absorption signature of L-edge spectra taken from individual particles or sub-micron clusters of crystallites indicates a size dependant variation in oxidation states of iron. As confirmed by TEM-HREELS, spectra of the smallest particles (<5 nm) show a higher content of reduced iron, whereas those averaged over single larger crystallites (>7 nm) resemble spectra of partially or fully oxidized isomorphs (e.g. γ -Fe₂O₃). Also, the outer surface layers (<1 nm) of the bigger particles appear more reduced than the corresponding core volumes indicating surface stabilized forms of reduced iron in nano-magnetite. Our results are discussed in the context of recent results by Park et al., possible quantum confinement effects, probe damage and charge localization in nano-magnetite as compared to more extended crystals or thin films.

References

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Mapping of metal species in biofilms using scanning transmission X-ray microscopy

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Metals, even at low concentrations, can pose a hazard to ecosystems. Both quantity and the chemical form of the metal are critical determinants of risk. To understand metal dynamics in the environment we must define oxidation state, ligands and elemental quantitation. X-ray absorption spectroscopy at the metal 2p edges can provide this information. The ALS STXM11.02 provides both speciation and quantitation at 50 nm spatial resolution in microbial biofilms. We have combined results obtained with STXM on the ALS Molecular Environmental Sciences beamline 11.0 with those from STXM 532 to detect, speciate, and quantitatively map the oxidation state of metals in the context of microbial biofilm microstructure and chemistry. We have shown that Mn, Fe, and Ni 2p signals provide metal speciation and quantitative spatial distributions of the identified species, with a sensitivity equivalent to a monolayer of the metal species. Spectra from STXM 532 facilitate the mapping of biomolecular structure and allow correlation of metal species with protein, lipid, carbohydrate and nucleic acid components of the biofilm. The resultant observations are relevant to metal dynamics and biotechnological applications of biofilms for remediation of metal contaminated environments.