Title

Site Determination of Mn Doping in Protein Encapsulated gamma-Fe2O3 Nanoparticles

Permalink

https://escholarship.org/uc/item/78s2k8r4

Authors

Pool, V. L.
Klem, M. T.
Arenholz, E.
et al.

Publication Date

2009-11-01

Site Determination of Mn Doping in Protein Encapsulated γ-Fe_2O_3 Nanoparticles

V. L. Pool[1, 4]; M. T. Klem[2, 4]; E. Arenholz[5]; C. Jolley[2, 4]; T. Douglas[2, 4]; M. Young[3, 4]; Y. U. Idzerda[1, 4]

1. Physics, Montana State University, Bozeman, MT, USA.
2. Chemistry and Biochemistry, Montana State University, Bozeman, MT, USA.
3. Plant Sciences and Pathology, Montana State University, Bozeman, MT, USA.
4. Center for Bio-inspired Nanomaterials, Montana State University, Bozeman, MT, USA.
5. Advanced Light Source, LBNL, Berkeley, CA, USA.

Separately controlling the properties of iron oxide nanoparticles without modifying their size is important for actualizing many of the exciting applications of protein encapsulated magnetic nanoparticles. In addition, determining the effect that the nanoparticle size has on material properties is fundamentally interesting. One important way to make these modifications is through doping with other magnetic transition metals.

In this study, Mn has been doped (0-33%) into 6.7 nm, γ-Fe_2O_3 nanoparticles grown inside the horse-spleen ferritin (HSF) protein and compared to similarly protein encapsulated pure γ-Fe_2O_3 and Mn-oxide nanoparticles to quantify the variation in magnetic behavior and to determine the Mn doping site [1]. By using soft-X-ray absorption spectroscopy (XAS), soft-X-ray magnetic circular dichroism (XMCD), hard X-ray scattering position distribution functions (PDFs), and frequency dependent Alternating Current Magnetic Susceptibility (ACMS), we have ascertained that the Mn dopant is substituting preferentially as Mn^{2+} and prefers the octahedral site in the γ-phase Fe_2O_3 spinel structure. The measured Mn L_{23} XAS spectra (shown in Figure 1) are compared to measured reference powders and molecular-orbital calculations supporting this conclusion of the Mn dopant substitution site [2]. We find that the Mn L_{23} XAS multiplet structure for the nanoparticles is simpler than for our bulk standards, complicating this identification but suggesting that the nanoparticle lattices are relaxed from the distortions present in the bulk. These Mn XAS spectra are nearly identical to those for similarly prepared Mn-oxide nanoparticles synthesized in HFN. For these nanoparticles, hard X-ray scattering position distribution functions (PDFs) identify that these Mn-oxide particles have formed into the spinel structure.

A simple picture of the effect of doping into the various Fe-sites of the γ-Fe_2O_3 spinel structure suggests that there will be a significantly different magnetic moment per iron lattice position depending on the site favored by the dopant atom. By performing Fe L_{23} edge XMCD on the particles, it is possible to obtain the magnetic moment per iron lattice position and provide insight into the site occupation of the remaining Fe atoms. (It should be noted that straight-forward magnetometry measurements cannot be properly mass normalized due to the presence of empty protein shells.) This result (shown as dots in Figure 2) displays a rapid decline in the average Fe moment, more rapid than a simple substitution model would predict (dashed line). Moreover, both the Fe L_3 XMCD lineshape (INSET of Figure 2) and the Mn L_3 XAS lineshape show that as the Mn concentration increases, the occupation by Fe of the Fe^{3+} octahedral site decreases while that of Mn in the octahedral site increases [3]. Finally, from a Neel-Arrhenius plot of the frequency dependent ACMS measurements we conclude that these particles are non-interacting and that the anisotropy energy for each particle is linearly reduced with increasing Mn concentration. For 33% Mn doping, the anisotropy energy is nearly one half that of pure γ-Fe_2O_3.

Supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

[1] T. Douglas and M. Young, Nature 393, 152 (1998).
[2] J.-S. Kang, et al, Phys. Rev. B 77, 035121 (2008).
[3] S. Brice-Profeta, et al, Physica Scripta, T115, 626 (2005).

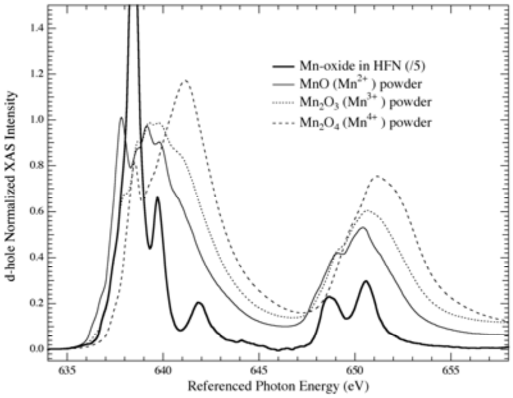

FIGURE 1: Mn L_{23} XAS spectra for Mn doped into 6.7 nm diameter γ-Fe_2O_3 nanoparticles (heavy line) and for Mn oxide reference powders (for comparison).

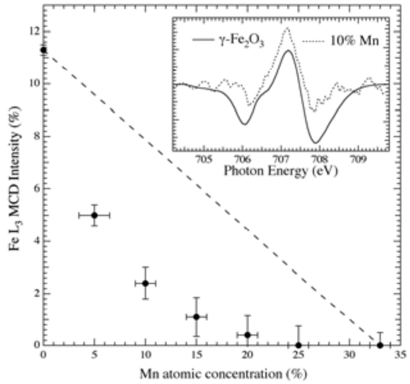

FIGURE 2: Fe L_3 XMCD intensity as a function of Mn concentration (exp. – circles, model – dashed line). INSET: Normalized XMCD spectra for 0% and 10% Mn doping.