Magnetic properties of Co$_3$O$_4$ nanoparticles mineralized in Listeria innocua Dps

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Temperature-dependent magnetic measurements are reported for 4.34 nm antiferromagnetic Co$_3$O$_4$ nanoparticles mineralized in the Listeria innocua Dps protein cage. ac measurements show a superparamagnetic blocking temperature of roughly 5.4 K and give an extracted anisotropy energy density of $(7.6\pm0.4) \times 10^{4}$ J/m$^3$. The Néel temperature for the Co$_3$O$_4$ nanoparticles, determined with dc magnetometry, was determined to be roughly $15\pm2$ K. © 2006 American Institute of Physics. [DOI: 10.1063/1.2163839]

I. INTRODUCTION

Recently magnetic nanoparticles have become the focus of many studies. In particular, antiferromagnetic nanoparticles have shown a stunning array of emergent properties reminiscent of the variation of bulk materials when created as magnetic films. In the case of magnetic thin films, low dimensionality and interface effects played a significant role. For magnetic nanoparticles, when the number of atoms that make up the surface become of the order that make up the remaining volume, the surface spins compete with the core spins, resulting in unusual magnetic properties with a multiple assortment of technological applications which include biomedical and hard-drive densifying technologies.

In this study, biological containers of Listeria innocua Dps proteins, LDps, were used as the growth and constraining vessels for the synthesis of Co$_3$O$_4$ nanoparticles. Nanoparticles were synthesized inside of these biological containers in order to produce uniform and monodisperse spherical Co$_3$O$_4$ nanoparticles separated by a nonmagnetic buffer to help mute any magnetic interparticle interactions.

LDps is composed of 12 identical 18 kDa subunits, which self-assemble into an empty cage having a 2-3 symmetry. LDps has an outer diameter of 8.5 nm and an inner diameter of 5 nm with 0.8 nm pores at subunit interfaces allowing molecular access to the interior. These pores allow Co ions to penetrate into the interior for the size constrained synthesis of Co$_3$O$_4$ nanoparticles. It has been found that protein cages can be emptied of their contents and mineralized with a multitude of different materials, forming monodisperse and highly uniform nanoparticles.

II. EXPERIMENT

The expression and purification of the Listeria innocua Dps protein as well as the synthesis of the Co$_3$O$_4$ nanoparticles inside these protein cages are described in detail elsewhere. Transmission electron microscopy (TEM) measurements showed Co$_3$O$_4$ spherical-like particles with an average diameter of roughly 4.34±0.55 nm. Electron diffraction measurements in the TEM showed these nanoparticles to have a similar structure and $d$ spacings as Co$_3$O$_4$.

The chemical environment of the Co atoms was also identified by x-ray absorption spectroscopy (XAS), acquired at the Co L$_{2,3}$ edges (770–800 eV). Measurements were performed on microgram quantities of Co$_3$O$_4$ mineralized cages dried out on formvar-coated TEM grids, at the Advanced Light Source beamline 4.01. Figure 1 shows the Co L$_{2,3}$ XAS measurements in transmission. The characteristic two-peak...
structure in the $L_3$ cobalt edge is consistent with Co$_3$O$_4$.\cite{21}

For comparison, the $L_{2,3}$ XAS spectra for a bulk sample Co$_3$O$_4$, obtained from Sigma-Aldrich, is also shown. The small differences in the nanoparticle’s spectrum compared to the bulk’s may be due to the sudden termination of the Co$_3$O$_4$ structure on the surface. Since transmission XAS probes equally over all Co atoms, the sample is almost entirely Co$_3$O$_4$.

ac and dc magnetometry measurements were performed on 3.5 mg of dried out Co$_3$O$_4$ mineralized cages, immobilized with epoxy into a small pellet form, with the alternating current magnetic susceptometer (ACMS) and vibrating sample magnetometer (VSM) options for the Quantum Design physical properties measurement system. The ac magnetometry measurements were taken at 100, 200, 300, 500, 1000, 2000, 3000, 5000, and 10,000 Hz with an oscillation amplitude of 10 Oe, while being cooled in a zero dc field down to 2 K. The dc magnetometry measurements shown in this study were taken between 0 and 8 T at several temperatures between 2 and 15 K.

III. RESULTS AND DISCUSSION

Antiferromagnetic Co$_3$O$_4$ nanoparticles of the size used in this study are thought to possess single domains with small moments that have a collective superparamagnetic behavior. The Co$_3$O$_4$ nanoparticle moments are ascribed to uncompensated spins, which are attributed to structural inhomogeneities, defects, and finite size effects. For superparamagnetic particles thermal fluctuations flip the magnetization between two states along the anisotropy axis by overcoming an anisotropy energy barrier. The relaxation time, $\tau$, between the two states is given by\cite{22}

$$\tau = \tau_0 \exp \left( \frac{E_a}{k_B T} \right),$$

where $\tau_0$ is the attempt time of the material, $E_a$ is the anisotropy energy, $k_B$ is Boltzmann’s constant, and $T$ is the temperature of the particle. There is typically a broad peak in the ac susceptibility, which is associated with the blocking temperature, $T_B$. Taking the log of Eq. (1) gives the Néel–Arrhenius relation, which has worked well for protein-encapsulated nanoparticles:\cite{23}

$$\ln \left( \frac{1}{f} \right) = \ln \left( \frac{1}{\Gamma_0} \right) + \left( \frac{E_a}{k_B T_B} \right),$$

where $f$ is the measurement frequency of the oscillating ac field, and $\Gamma_0(=\langle T_B \rangle^{-1})$ is the attempt frequency. Figure 2 shows the imaginary parts to the ac susceptibility at the different frequencies. The peaks shift down and to the right as the frequency increases, corresponding to higher extracted blocking temperatures for higher frequencies, a characteristic superparamagnetic behavior. By fitting the peak in the imaginary or out-of-phase susceptibility, we determine that the superparamagnetic blocking temperature of these particles at 1000 Hz is roughly 5.4 K.

Plotting the blocking temperatures with frequency, the anisotropy energy and attempt frequency can be determined from a Néel–Arrhenius plot. The insert in Fig. 2 shows this plot for the out-of-phase component of the ac susceptibility. $E_a$ and $\Gamma_0$ were determined to be $3.3 \times 10^{-21}$ J and $1.4 \times 10^{23}$ Hz, respectively. $E_a$ is the product of the anisotropy energy density, $K$, and the volume of the particles, $V$, which are taken to be spherical. Using an average diameter, determined by TEM to be 4.34 nm, the anisotropy energy density for the Co$_3$O$_4$ nanoparticles is $(7.6 \pm 0.4) \times 10^4$ J/m$^3$. This is slightly below the reported value of the anisotropy energy density of $9 \times 10^4$ J/m$^3$ measured on 3 nm Co$_3$O$_4$ nanoparticles with a SQUID magnetometer.\cite{24} However, a difference in the anisotropy energy density is not unexpected since the affect of a reduced size on a magnetic material should enhance its anisotropy.\cite{25,26}

Figure 3 shows initial magnetization curves of the Co$_3$O$_4$ nanoparticles from 2 to 30 K. The data was well fit to a simple Langevin model with an added offset and linear susceptibility term given by

$$m = m_R + m_s L(x) + \chi H,$$

where $m$ is the measured magnetic moment of the sample, $m_R$ is taken to represent the remnant moment, $m_s$ is the saturation moment of the sample, $\chi$ is the linear susceptibility.
attributed to the antiferromagnetic nature and spin canting of the material, and

\[ L(x) = \coth(x) - \frac{1}{x} \]  

is the Langevin function, where \( x = \mu H/k_B T \). \( \mu \) is the magnetic moment of a single particle, \( H \) is the external applied magnetic field, \( k_B \) is Boltzmann’s constant, and \( T \) is the temperature of the sample.

Figure 4 shows the susceptibility extracted from the fits. The peak in the susceptibility suggests a Néel temperature of \( 15 \pm 2 \) K. This is significantly lower than the reported values for bulk \( \text{Co}_3\text{O}_4 \) (40 K),\(^{23}\) for 20 nm \( \text{Co}_3\text{O}_4 \) particles (>25 K),\(^{27}\) and for 8 nm particles (30 K).\(^{28}\) The significantly lower Néel temperature can be accounted for by the effect of finite-size scaling that has been thought to change the critical ordering temperatures of both ferro- and antiferromagnetic nanoparticles\(^{29}\) and thin films.\(^{30}\) Quantitatively finite-size scaling can account for this reduction by using a characteristic length scale of roughly 2.6 nm and a correlation length exponent of 0.8 in the finite-size scaling model. These values are similar to values found in other reduced systems.\(^{29,30}\)

**IV. CONCLUSION**

Both an elevated anisotropy energy density and a lower Néel temperature point to surface or finite-size effects playing a major role in the magnetism of these antiferromagnetic \( \text{Co}_3\text{O}_4 \) nanoparticles. Further studies of the finite-size and surfaces effects on a multiple assortment of different size \( \text{Co}_3\text{O}_4 \) nanoparticles is needed in order to further probe and understand these interesting effects.

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