Evolution of electronic and magnetic properties of iron oxide and cobalt ferrite nanocrystals probed by synchrotron-based X-ray imaging and spectroscopy

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Abstract

Iron oxide-based nanoparticles (NP) have outstanding magnetic properties and promising applications for spin-filter devices, biomedicine, and catalysis. In addition to finite-size effects, a key issue for research is how the intrinsic magnetic properties of the individual particles are modified by their own electronic structure, chemistry, surface termination and crystallinity. In particular, the high-spin polarization predicted for Fe_3O_4 is limited experimentally by structural defects, cation and oxygen vacancies. For spinel ferrites such as $CoFe_2O_4$, the likely size-dependent cation distribution of the tetrahedral and octahedral sites in the close-packed oxygen structure may strongly affect the magnetic properties of the NP.

By combining x-ray absorption spectra (XAS) with photoemission electron microscopy (PEEM), we analyze the electronic structure and chemical bonding of individual, pseudo-spherical $Fe_{3-x}O_4$ and $CoFe_2O_4$ NP in the size range of about 8 to 24 nm, synthesized by thermal decomposition of organometallic precursors [1] and deposited onto either grids or hydrophobic substrates. Both $Fe_{3-x}O_4$ and $CoFe_2O_4$ NP display high crystalline quality and macroscopic bulk-like magnetic properties down to about 5 nm [2,3]. The unique spectral features of the individual particles, such as resonance heights, chemical shifts, oxidation states of the Fe atoms and density of states for the core-hole state, as well as their XMCD asymmetry profiles, are correlated to variations in either the stoichiometry or the lattice geometry of their Fe and Co ions. A quantitative analysis of absorption spectra from *single,* covalently-bonded Fe_3O_4 NP of 15 and 24 nm deposited on bare and C-coated Si substrates, respectively, can be obtained from fitting the spectral characteristics (line-shapes and relative height of peaks L_{3A}/L_2, L_{3A}/L_{3B}) to a weighted sum of reference bulk spectra of different iron-oxide species. Interestingly, our data show that even in the case of the highest crystal quality particles, the *variation* of some synthesis *parameters* may significantly alter the cationic distribution and the uniformity of magnetic phases [4].

Furthermore, spatially integrated XAS and x-ray magnetic circular dichroism (XMCD) spectra, and element-specific hysteresis loops on mono-disperse assemblies of the above nanoparticles, have been performed at high magnetic fields (up to 6T) and variable temperature (2K-300K). By employing both the total-electron-yield and the total-fluorescence-yield modes, we are sensitive to both the surface and inner core regions of the nanoparticles. We will show first results on the evaluation of the cationic distribution, the magnetic contribution of the different magnetic ions, and on the mutual orientation of spins in the Fe and Co sublattices.

All the foregoing indicates the key role of surface chemistry on the physical properties of ferrimagnetic NP and, in turn, on the design of novel NP with optimized magnetic properties.

References

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