Title: Development of superparamagnetism in solutions of nanoparticles studied by means of 1s2p RIXS-MCD

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Introduction

Magnetism of nanoscale materials is in the focus of numerous scientific investigations due to emerging applications in hyperthermia, medical imaging, magnetic storage, ferrofluids, etc. Various analytical methods can be employed to probe their properties. Nevertheless there is a need for techniques allowing for detailed description and characterization of superparamagnetic iron oxide nanoparticles (SPIONs) in solution. Here we show that determining of the first critical radius of SPIONs, namely the diameter at which particles transform from paramagnetic to superparamagnetic, and probing their magnetic and structural properties is possible in solution by means of spin polarized photon-in photon-out X-ray spectroscopy. Important aspect of the study is that presented approach is capable to investigate SPIONs growth in-situ during synthesis.

Experimental methods

We have investigated magnetic nanoparticles obtained from thermal decomposition of iron(III) acetyloacetonate ($Fe(acac)_3$) in a non-aqueous environment of benzyl alcohol. Samples obtained at different stages of the reaction were examined using vibrating sample magnetometry (VSM), transmission electron microscopy (TEM), Mössbauer spectroscopy (MS), and small-angle x-ray scattering (SAXS). TEM and SAXS measurements revealed size distribution of SPIONs as a function of reaction time. Such profiles were recovered from solutions obtained after various intervals of decomposition. Using MINORIM software the 'magnetic' size distribution was determined from VSM hysteresis loops, while Mössbauer spectra probed thermal relaxation of magnetic cores. Finally, magnetic properties and local structure change were examined site-selectively by means of resonant inelastic x-ray scattering employing magnetic circular dichroism (1s2p RIXS-MCD), in-situ, during the reaction in state-of-the-art cell prepared especially for synchrotron experiments.

Results and discussion

Decomposition of $Fe(acac)_3$ and further growth of SPIONs of diameter less than 10 nm was probed in-situ by means of 1s2p RIXS-MCD. Based on diameter vs. time calibration obtained from ex-situ characterization, the valence state of iron ions, an environment of the ions and their magnetic ordering could be tracked as a function of size. High resolution and weak self-absorption give well-defined spectral features, which can be ascribed to specific properties based on reference samples measurements and numerical calculations. Based on pre-edge shape analysis it was possible to study the kinetics of site occupation during particle growth. Main edge evolution provided information on the mean valence state, while MCD signal detected in the pre-edge area allowed to track the projection of iron magnetic moment along external field direction. The latter parameter being proportional to DC magnetic susceptibility provides a good measure of (super)paramagnetic properties. A comparative study of cobalt ferrite nanoparticles, where magnetism depends on cobalt and iron distribution are in progress.

Conclusions

Magnetic nanoparticles were thoroughly examined during the synthesis reaction. 1s2p RIXS-MCD spectra can provide site-selective information on local structure of iron ions and their magnetic ordering, also in-situ, during reaction. Comparison of ex-situ and in-situ measurement results can provide size dependent, comprehensive description of magnetic and structural properties of SPIONs in solution.

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