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Simultaneous surface and bulk sensitive XAS measurements of magnetic particle clusters

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Abstract. Magnetic iron oxide nanoparticle clusters (mnpc) coated with organic stabilizers were investigated using scanning transmission x-ray microscopy (STXM). Simultaneous surface and bulk sensitive Fe L_3 edge absorption spectra, obtained using a photomultiplier tube and a channeltron, were used to detect subtle changes in the oxidation state in the surface and bulk of Iron Oxide mnpc. The effectiveness of this mode of STXM operation is demonstrated for these nanoparticle clusters.

1. Introduction

The application of magnetic nanoparticles of 5-20 nm diameter and their clusters are actively investigated as Magnetic Resonance (MR) imaging contrast agents due to their low toxicity, high saturation magnetization, high magnetic susceptibility, biodegradability, ease of synthesis and functionalization [1]. However, small particle size also means a decrease in the saturation magnetization [2] and formation of ferromagnetic agglomerates. Stabilizers in a controlled manner are used to overcome the magnetic attraction and to form superparamagnetic clusters.

While the shape, size, agglomeration, coatings and other synthesis parameters are well understood and controlled [3], the interplay and transformation between different iron oxide phases in these nanoparticles clusters is largely uncontrolled and not fully understood. The existence of Fe^{2+} cations in these Fe_3O_4 (magnetite) magnetic nanoparticle clusters (mnpc's) can lead to oxidation and conversion to γ-Fe_2O_3 (maghemite) and finally to α-Fe_2O_3 (hematite) that has no magnetic properties [4]. The iron oxide phase inside the bulk and at the surface of these clusters can have a significant effect on the overall magnetic properties. However, the similar spectroscopic and crystallographic signature of different iron oxides has withheld researchers from correlating magnetic properties with synthesis techniques.

In this paper we present the bulk sensitive and surface sensitive x-ray absorption based characterization of iron oxide (Fe_xO_y) mnpc's coated with dopamine stabilizer. This detection methodology and experimental configuration (Figure 1e) has already been successfully applied for organic materials [5]. Bulk sensitivity was achieved by detection of photons transmitted through the whole samples using a photomultiplier tube. Simultaneous detection of emitted photoelectrons from the sample's surface was achieved using a channeltron. Since the escape depth of Fe 2p photoelectrons at the Fe L-edge is about 4.5 nm for iron oxide [6] the information depth corresponds to the top

surface of the investigated region. We have focused our studies on the Fe L-edge as it is highly sensitive to oxidation state of iron.

2. Experimental

STXM and X-ray absorption spectroscopy (XAS) measurements were performed at the Pollux beamline at the Swiss Light Source (SLS), Villigen, Switzerland [7]. A 35 nm zone plate (ZP) is used to focus the x-rays through an order sorter aperture (OSA) on to the sample. The mnpc's were dropcasted on a 100 nm thick silicone nitride window for measurements. A scintillator coupled with a photomultiplier tube (indicated "PMT") is used to detect the bulk sensitive signal in the form of transmitted photons. Surface sensitivity was made possible by detecting surface photoelectrons using a channeltron (indicated "CT") biased at 2.5 kV (model no. KBL10RS, Dr. Sjuts Optotechnik Gmbh). The CT was mounted adjacent to the PMT and the sample was mounted facing the detectors. A wet-cell sample was also prepared for dopamine coated mnpc's and was measured only using the PMT. This particular sample was prepared by sealing a drop of mnpc solution in a sandwich of two silicone nitride windows with epoxy. The chamber was pumped down to 10^{-6} mbar. The normalization of the CT signal was done by dividing it with the measured photon flux on the PMT. Measurements used in the present work are not intended to be quantitative in nature hence the photon energy dependence of the detector efficiencies was ignored. The PMT signal was normalized using signal from a blank silicone nitride window. The XAS spectra were extracted through line scans after choosing a sample region representative of the whole sample. Plasma treatment was done in an Atto plasma cleaner (Diener electronics GmbH) for 30 min using a H_2/He gas mixture at 0.6 mbar of H_2 and 100% power. Samples were transferred to the STXM experiment station with minimum exposure to ambient air.

3. Results and discussion

3.1. STXM imaging

STXM images obtained at 711 eV from the PMT and the CT are shown in figure 1 for the uncoated, and dopamine coated mnpc's. The thickness of these coatings was calculated in a separated study on core shell nanoparticles to be ca. 1nm [8]. In general large clusters of several hundred nms in size and about 150 nm in thickness was observed in all the cases. Since these samples were drop-cast and air-dried, the analysed clusters are not perfectly dispersed. Several spectra were obtained through a line scan to ensure the chemical homogeneity of the sample before choosing representative spectra.

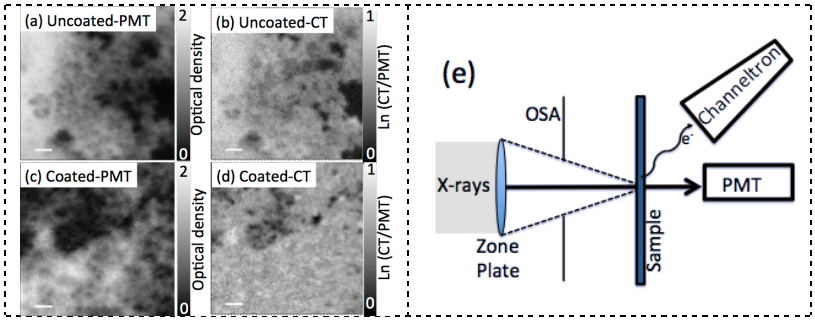

Figure 1 : (a)-(d) STXM optical density images at 711 eV for uncoated and coated mnpc's using PMT and CT. (Scale bar: 500nms) (e) Schematics of the STXM experimental set-up

3.2. Fe L_3 edge Absorption spectra

Figure 2a shows the Fe L_{23} XAS spectra of uncoated and dopamine coated Fe_xO_y mnpc's. Two regions corresponding to the $L_3(2p_{3/2})$ peak around 710 eV and $L_2(2p_{1/2})$ peak around 722 eV can be observed. The ligand field splitting and other atomic interactions form the basis of the fine structure within these regions [9]. We have focussed our discussion on the L_3 region of the spectra as there are significant differences in the PMT and CT signals in this region of the uncoated and dopamine coated mnpc's. The **A**, **B** and **C** energy positions (Figure 2a,b) marked in the L_3 region correspond to site occupancies of Fe cations in the spinel structure. **A** corresponds to Fe^{2+} species at octahedral sites (Fe^{2+} O_h), **B**

corresponds to Fe^{3+} species at tetrahedral sites (Fe^{3+} T_d) and **C** corresponds to Fe^{3+} species at octahedral sites (Fe^{3+} O_h). Relative intensity differences can be observed around the feature **A**. The features **B** and **C** are not clearly resolved. In order to obtain a relative quantification of the oxidation state of iron in the mnpc samples we have used the linear combination of simulated Fe^{2+} and Fe^{3+} spectra using the CTM4XAS software [10].

A linear combination of the simulated spectra of only two species, $Fe^{2+}(O_h)$ and Fe^{3+} (O_h), were used to obtain a consistent fit. The simulations parameters were used according to ref. [9, 10]. A representative fitted spectrum is shown in figure 2b. The integrated intensity of each component is used to estimate the Fe^{2+}/Fe^{3+} ratio. Figure 2c shows the Fe^{2+}/Fe^{3+} ratios as obtained from the fits for all the spectra. These include the measurements on a reference maghemite sample (Fe_2O_3) and from a wet-cell sample wherein the dopamine-coated mnpc's were dispersed in water. Firstly, it is evident that although the reference maghemite (Fe_2O_3) sample, measured in TEY (Total Electron Yield) mode, should be purely Fe^{3+}, it was necessary to introduce the Fe^{2+} component to obtain a reasonable fit. This could be due to reduced sites below the top surface of the reference sample. As expected, the Fe^{3+} phase is the dominant phase in the reference sample. Among the mnpc's, the uncoated clusters show the maximum amount of Fe^{2+} species (Fe^{2+}/Fe^{3+} ~0.9). The bulk and the surface content of the two phases are not very different, with Fe^{3+} content slightly higher in the surface. This observation is expected since the surface is inevitably oxidised. Reduction by H_2 plasma results in an overall decrease in the Fe^{3+} content at the surface as well as in the bulk as illustrated by strong differences in the L_3 region. Figure 2b shows exemplarily the spectra of dopamine coated mnpc's treated with H_2 plasma for 30 minutes.

In the case of dopamine coated mnpc's, it is clear that the bulk content of Fe^{2+} is lower than the surface content of Fe^{2+} indicating a more oxidized bulk compared to the surface. Such behaviour is consistent with initial oxidation behaviour of magnetite as observed by McCarty et al. [11]. In general the transformation of iron oxide starting from magnetite (Fe_3O_4) to maghemite (γ-Fe_2O_3) can be described by the progressive oxidation of octahedral [Fe^{2+}] to [Fe^{3+}] by losing some structural iron and creating cation vacancies [12] according to the following substitutional series $[Fe^{3+}]\{Fe^{3+}_{1+2\delta}\, Fe^{2+}_{1-3\delta}\, \square_{\delta}\}O_4$ where [] indicates tetrahedral sites, {} indicates octahedral sites, $\square$ represents cation vacancies in the spinel structure and $0 \leq \delta \leq 1/3$ [13]. This implies

$$\frac{Fe^{2+}_{(Oh)}}{Fe^{3+}_{(Oh)} + Fe^{3+}_{(Td)}} = \frac{1-3\delta}{2+2\delta} \qquad (1)$$

δ values calculated for different samples are presented in figure 2c along with the theoretical values for pure magnetite and pure maghemite. Values of δ greater than 1/3 and less than 0 indicate the presence of mixed phases not consistent with either magnetite or maghemite phases. The dopamine coated dry samples clearly show a magnetite like composition. The dopamine coated wet-cell sample shows the most maghemite like composition that is very different from dry dopamine mnpc sample. This could be due to the fact that the wet cell sample was significantly older than the dry sample. This could have allowed for sufficient oxidation time for magnetite like mnpc's. The uncoated sample's composition indicates the abundance of Fe^{2+} sites originating from neither magnetite nor maghemite phases but most probably from mixed iron oxide phases. It has to be noted that we have ignored the presence of metallic Fe^0 species in our fitting routine. The energy position of Fe^{2+} is closer to Fe^0 species and some of the contributions of Fe^{2+} species account also for the Fe^0 species, especially in the case of broad L_3 peaks obtained for uncoated mnpcs.

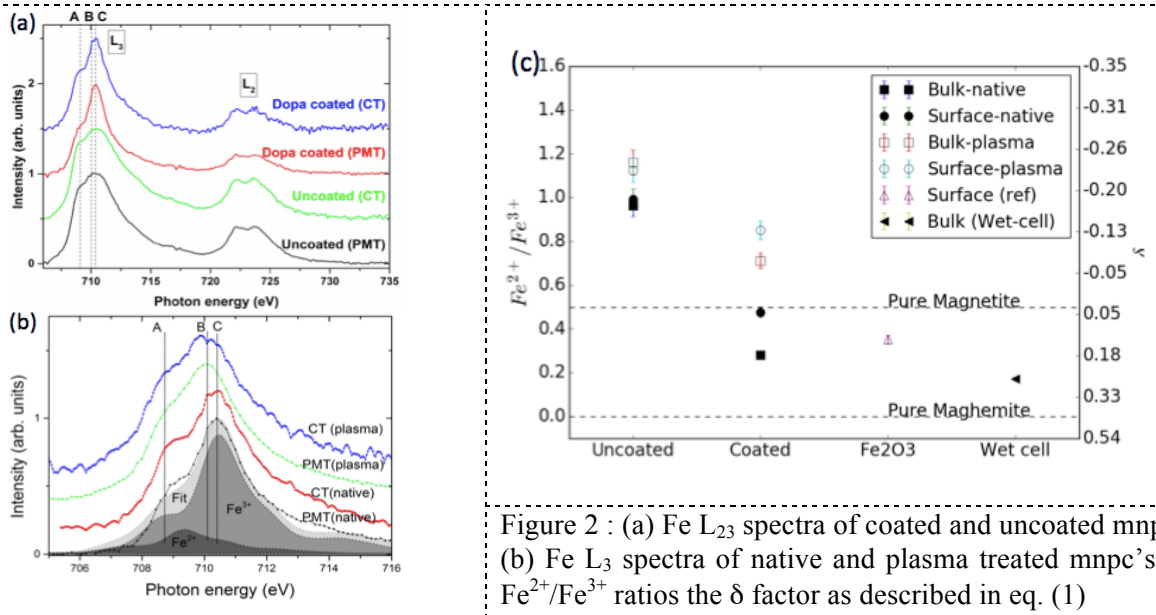

Figure 2 : (a) Fe L_{23} spectra of coated and uncoated mnpc's, (b) Fe L_3 spectra of native and plasma treated mnpc's, (c) Fe^{2+}/Fe^{3+} ratios the δ factor as described in eq. (1)

4. Conclusion

We have shown that using bulk and surface sensitive measurements in STXM, it is possible to disentangle subtle changes in oxidation state of iron oxide mnpc's. Furthermore the applied characterization strategy of iron oxide based nanoparticles combined with computational simulations of Fe L_3 spectra allows distinguishing differently coated iron oxide np's in terms of iron oxide nature, especially of magnetite or maghemite characteristics. Dopamine coatings were found to introduce oxidation state changes leading to increase of Fe^{3+} species. Also mixed Fe_xO_y species were identified by simultaneous bulk and surface sensitive STXM/XAS measurements as demonstrated for the "naked" Fe_xO_y core particles.

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