Magnetic Fe-N Core-Shell Nanoparticles

Nanoscale Analytics in the Transmission Electron Microscope

In this structure-property investigation we analyzed α’’-Fe16N2 and ε-Fe3N core-shell nanoparticles via analytical electron microscopy. Conventional electron microscopy on pristine nanoparticles was done using a vacuum transfer holder. In order to study the effect of oxidation on the nanoparticles a combined experimental and density functional theory (DFT) study of the electron near edge fine-structure (ELNES) was carried out.

Introduction

Alternative magnetic materials have regained attention after the recent rare-earth crisis [1, 2]. Iron nitrides exhibit remarkable physical properties [3-6], which can be of use for several applications, e.g. magnetic recording media [6, 7], catalysis [8], and biomedical applications [9]. These applications demand precise control over the particle size and corresponding magnetic properties on the nanometer scale. Iron nitride nanoparticles are inexpensive, exhibit high saturation magnetizations and large magnetic moments [5, 7]. A main difficulty in the measurement of their magnetic properties is to prepare pure phases in sufficiently large quantities. A recent review discusses the synthesis and properties of iron nitrides at reduced dimensions [10]. A’’-Fe16N2, ε-Fe3N and γ’-Fe4N are important ferromagnetic iron nitrides. Analytical electron microscopy in combination with ab initio density functional simulations is of importance for establishing structure-property correlations in these materials.

Material & Methods

Sample preparation and electron microscopic acquisition conditions can be found in the literature [11, 12]. Ab-initio DFT calculations were carried out using the Wien2k [13] and the FeFF [14] codes. Simulation details are summarized in the supporting information.

Results

Conventional transmission electron microscopy applying diffraction contrast imaging and selected area diffraction was carried out using a vacuum transfer
holder to prevent oxidation and to study the pristine material. The results for $\varepsilon$-Fe$_3$N and $\alpha''$-Fe$_{16}$N$_2$ are shown in figure 1 a,b and figure 1 b,c, respectively.

The selected area diffraction patterns were indexed using the structural parameters from Jacobs et al. [15] and Widenmeyer et al. [16] for $\varepsilon$-Fe$_3$N and $\alpha''$-Fe$_{16}$N$_2$, respectively. It can be seen that both types of nanoparticles agglomerate hampering further atomic resolution image analysis. Nevertheless, the nanoparticle size can be determined from these images as $15.4 \pm 4.1$ nm for $\varepsilon$-Fe$_3$N and $50$ nm for $\alpha''$-Fe$_{16}$N$_2$. This is in good agreement with X-ray measurements. The different values of the particle size are due to the different synthesis method being used.

For any practical application the nanoparticles need to be exposed to ambient air. The result was a partial oxidation, which was then studied by analytical scanning transmission electron microscopy (STEM), since imaging techniques only indicate a shell structure. Analyses using energy-dispersive X-ray spectroscopy (EDX) are not a good option, because of technical and practical limitations such as low energy X-ray absorption and peak overlapping. A better alternative is to use high-angle annular dark-field images (fig. 2 a,b) in combination with electron energy-loss spectroscopy (EELS) maps (fig. 2 c,d). The shell thickness was determined to be $2.5 \pm 1.0$ nm for $\varepsilon$-Fe$_3$N and $7.0 \pm 2.0$ nm for $\alpha''$-Fe$_{16}$N$_2$, respectively. The colored maps were combined by three elemental images using the electron energy-loss ranges $400$-$420$ eV for N-K, $530$-$550$ eV for O-K, and $705$-$730$ eV for Fe-L$_2$ as red, blue and green channel, respectively. This yields a yellow to green core and a blueish shell that can be well separated from each other. In addition, EELS offers the possibility to simultaneously probe the local electronic structure and phase via the ELNES. For example iron oxides can exist as FeO (wuestite), $\alpha$-Fe$_2$O$_3$ (hematite) and Fe$_3$O$_4$ (magnetite). Each of them presents different magnetic properties that interacts differently with the ferromagnetic nitride core. FeO is at room-temperature and ambient pressure paramagnetic [17], $\alpha$-Fe$_2$O$_3$ is antiferromagnetic [18], and Fe$_3$O$_4$ is ferromagnetic [19]. It was not clear from the beginning of the analysis which iron oxide modification is present in the shell or if it is the same for all samples. Iron nitride phases can be treated in a similar way. The exact core-shell combination involves for example effects like spin exchange interactions, which themselves influence macroscopic magnetic measurements such as hysteresis loops [11].

Since only from the oxides experimental EELS reference spectra were available [20] and to check whether the description by bulk properties is still applicable, ab initio DFT calculations were carried out to simulate the ELNES of the N- and O-K edge of the previously mentioned phases, respectively. These simulations were then compared to our experiments. At present time there are two possibilities to do so:
(i) bandstructure based calculations as implemented for example in the Wien2k code [13] and (ii) self-consistent real-space multiple-scattering calculations as implemented for example in the FeFF9 code [14]. The Wien2k code is among the most accurate codes and offers a large number of features like bandstructure, density of states, X-ray emission and absorption spectra, and electron energy loss spectra. Depending on the number of atoms and the symmetry access to a supercomputer is necessary. The FeFF code on the other hand uses a completely different approach, which allows the simulation of doped structures or alloys, voids, interstitials etc. with much less computational effort than needed in Wien2k. A fast desktop computer is for most cases sufficient. Since FeFF has its origin in the calculation of X-ray spectra it offers despite ELNES also the possibility to calculate angular-momentum resolved density of states, X-ray emission spectra and X-ray absorption spectra. Core-holes are also easily introduced without the need to think in detail on supercell geometries like in Wien2k. The interested reader might find more details in [21-24].

Based on the previous considerations we were able to calculate the N- and O-K ELNES. The results of the comparison between experiment and simulation are shown in figure 3. Figure 3a shows the results for a ε-Fe$_3$N core and figure 3b a FeO shell. Distinct peaks labelled p1-p4 can be identified in the spectra. For a better comparison the spectra were normalized. In case of the nitride core differences between experiment and simulation were found in the N-K ELNES indicating that the core is not pure ε-Fe$_3$N anymore. Thus, the blue curve where the N atoms on the 2c position were replaced by O atoms and the 2b position is fully occupied by N atoms in figure 3a was calculated using FeFF. It is closer to the experiment than the pure ε-Fe$_3$N curves. For the shell the case in figure 3b is more clear. When comparing the peaks p1-p4 of the FeO simulation to the experiment, one recognizes deviations of the peak form in p1 and the missing of p4. Furthermore, it might be possible that a second iron oxide phase, e.g. Fe$_3$O$_4$ (fig. 3d), is present in the shell. A more extended study on the oxidation behavior of ε-Fe$_3$N would be of advantage. In the α”'-Fe$_{16}$N$_2$ case, which is shown in figure 3c,d, both Wien2k and FeFF yield a good agreement of simulation and experiment for both core and shell. All peaks (p1-p4) are reproduced by the simulation. The measurement as well as the simulations are in agreement with the O-K ELNES measured by Colliex et al. [20].

**Summary & Conclusion**

In summary, we were able to determine phase and particle sizes of iron nitride nanoparticles via conventional TEM. Furthermore, we were able to characterize partially oxidized core-shell nanoparticles via a combination of analytical TEM and
DFT based ELNES simulations. For the α''-Fe$_{16}$N$_2$ case a good agreement between experiment and simulation was found for both core and shell, whereas for the ε-Fe$_3$N case only the shell fitted and the the experimental core spectrum deviated from the simulation indicating a structural and/or chemical change of the ε-Fe$_3$N core.

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Primitive unit cells of the 4 phases used for ab initio simulations. The plots were generated using XCrysDen [25] but its main function is as a property analyzer program. It can run on most UNIX platforms, without any special hardware or software requirements. Special efforts were made to allow for appropriate display of 3D isosurfaces and 2D contours, which can be superimposed on crystalline structure and interactively rotated and manipulated. XCrySDen is also a graphical user interface for the CRYSTAL95/98 (Saunders, V. R., et al. CRYSTAL98—User’s Manual. University of Torino, Turin, Italy, 1999.

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