2D and 3D Oxidation State Mapping in FeO/Fe3O4 Nanocubes Using the Fe-M2,3 EELS Edge

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Background

EELS in the STEM is capable of oxidation state quantification by analyzing the fine structure of the elemental ionization edges. The exact analysis procedure has been1 and continues to be2 a major focus of EELS research. In the last decade, oxidation state mapping at the atomic level 3 has become common and advances in data analysis have enabled 3D oxidation state mapping through tomographic reconstruction of EELS oxidation maps tilt-series4.

To date, most methods of oxidation state analysis involve ionization edges with onset energies above 100 eV. For example, the standard method for iron oxidation state analysis is based on the fine structure of the Fe-L2,3 ionization edges at ~708 eV. However, the small ionization cross-section of these ionization edges presents serious experimental challenges for beam-sensitive samples. For instance, beam damage and contamination issues limited the EELS tilt series in 4 to just half of the angles needed to obtain a full tomograph.

In this context, we explore the new possibilities for oxidation state analysis offered by the new generation of hybrid-pixel direct electron detectors5. Thanks to their almost-perfect DQE and zero read-out noise, using the standard oxidation state analysis methods, the same results can be obtained with a lower electron dose. Less obviously, we show that these detectors' high speed, large dynamic range and small point spread function facilitate EELS analysis using ionization edges that lie below 100 eV. This comes with mainly two advantages with respect to edges situated at higher energies: a much higher signal-to-noise ratio for the same electron dose, and the simultaneous acquisition of the full low-loss spectrum needed for accurate absolute quantification.

To demonstrate the novel oxidation state analysis method, we perform EELS oxidation state tomography on the FeO/Fe3O4 core-shell nanoparticles from 4 by analyzing the Fe-M2,3 ionization edges at ~54 eV.

Methods

FeO/Fe3O4 core-shell nanoparticle EELS spectrum images were acquired on an FEI TITAN Themis 300 S/TEM with a dwell time of 1 ms and a pixel size ranging from 0.2 nm for single maps to 0.4 for tomography studies. EELS maps were taken at 9 different angles ranging from -70 to 70 degrees for these tomographic studies.

Spectrum images were then analyzed using a combination of SVD decomposition of the four-dimensional dataset, blind source separation, and curve fitting EELS quantification.

Results

Figure 1 shows the EEL Fe-M2,3 spectra and maps corresponding to Fe3+ (in blue) and Fe2+ (in green) extracted from the dataset by blind source separation, which has proven successful. Furthermore, the 3D reconstruction of both oxidation states has been achieved, showing a differentiation between the core and the shell of the particle, and with minimal damage to the sample. A frame from this reconstruction can also be seen in Figure 1.

Conclusion

The combination of direct electron detection and the extension of oxidation state analysis to low-energy ionization edges has proven successful in performing EELS oxidation state tomography in beam-sensitive FeO/Fe3O4 core-shell nanoparticles, with a much lower electron dose than standard methods, notably minimizing sample damage and increasing the acquisition speed. This method sets a new standard for EELS analysis of suitable beam-sensitive materials.

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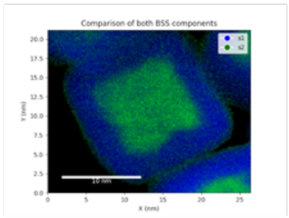
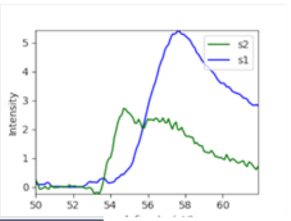
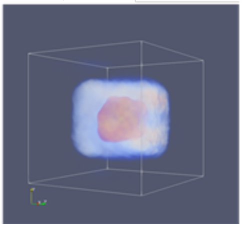
Graphic:







Keywords:

EELS, oxidation states, tomography

Reference:

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