

Low-dose STEM-EELS as a tool to investigate nanoscale redox processes: the case of uranium oxides.

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Nanoscale redox processes are challenging to observe as the tools typically employed (e.g., synchrotron-based approaches) do not have the necessary resolution. Here, we have used STEM-EELS (scanning transmission electron microscopy - electron energy loss spectroscopy) to probe the valence state of 2 to 3 nm thick uranium (U) oxide nanowires with the goal to decipher the mechanism of their formation through hexavalent U reduction. Obtaining EELS spectra from such samples at the needed spatial resolution required extensive method development. Indeed, because of sample susceptibility to electron beam-induced damage, it was necessary to use very low beam currents of 10-50 pA. These low beam current called for adapting the spectrometer-detector alignment to optimize sensitivity, dose rate per pixel, and the signal-to-noise ratio. We collected low-loss and high-loss spectrum images of O K-edge and U N_{6,7} edges for UO_{2+x} standards and samples.

STEM-EELS measurements were obtained for the following U oxide standards that included various combinations of the three main U oxidation states: UO₂ U(IV), U₄O₉ 50% U(IV) and 50% U(V), U₃O₇ 33% U(IV) and 66% U(V), KUO₃ U(V), U₃O₈ 66% U(V) and 33% U(VI), and BaUO₄ U(VI) (Figure 1). To obtain statistically reliable results, 8 to 12 measurements were acquired for each standard.

It was therefore crucial to set up automated processing for the EELS data cubes. The processing included: zero loss alignment, automatic spike removal, principal component analysis denoising (using pyEELSMODEL [1]), background removal with edge model-based deconvolution, and smoothing. Spectra from sample regions including nanowires and U oxide nanocrystals were extracted and compared to those from the above U oxides standards.

Both the O K-edge and the U N_{6,7} edges were used to fit the sample spectra with standard spectra. Fitting confirmed the presence of U(V) in the nanowires. This work illustrates the potential of low dose STEM-EELS in investigating nanoscale redox processes and ultimately unravelling the underlying

electron transfer mechanisms.

[1] D. Jannis and J. Verbeeck (2024), BIO Web of Conferences 129, 10035.

Fig. 1: U N_{6,7} edge and O K-edge spectra for U_xO_y oxides standards.

