Supporting Information: Synthesis of nanosized vanadium(V) oxide clusters below 10 nm

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In the Supporting Information we present a detailed analysis of the EEL spectra presented in the main article.

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1 EELS Analysis

Figure 1 shows a comparison between an EEL spectrum (black, normalized to the L2/L3 peak maximum) of the deposited nanoparticles and literature spectra taken from Ref. 1. The EEL spectrum represents the mean over 5 selected nanoparticles, a background obtained from an area that does not contain a nanoparticle has been subtracted. The background corresponds to an oxygen feature originating, presumably, from a contamination of the carbon TEM grid. Note that the same measured EEL spectrum is plotted for all four cases. The shown spectrum features the region containing both the V L-edge at 513 eV (L_3 $2p_{3/2}$) and 521 eV (L_2 $2p_{1/2}$) as well as the O K-edge at 532 eV (K 1s). As described above, the resolution in our experiment is lower than in previous bulk experiments where typical reported values are around 0.5 - 1 eV.[2] In order to account for this difference we convoluted the literature spectra with a Gaussian function such that the gap between the L2 and L3 peak matches our experimental spectrum. The employed FWHM of the Gaussian varies and lies between 1.4 and 2.4 eV. In addition to the convolution the literature spectra have been red-shifted by 0.75 eV.

To determine the oxidation state of vanadium oxides from EEL spectra, two characteristic O 1s pre-edge peaks located around round 530 eV serve as fingerprint features. They are associated with transitions into unoccupied t_{2g} and e_g energy levels, which emerge from a hybridization of V 3d and O 2p orbitals. However, from the modified literature spectra in Figure 1 it becomes obvious that the oxidation state can not be identified in the case of our nanoparticles because the characteristic features are blurred and appear only as a high-energy shoulder due to the relatively low energy resolution. Furthermore, even though the L2/L3 peak ratio is approximately 1 in the recorded EEL spectrum, suggesting a higher oxidation state such as V_2O_5,[1,3] the limited resolution demands care and we refrain from taking this as a definite evidence for a V_2O_5 stoichiometry.

Based on the above discussion we conclude that EELS as the standard method in transmission electron microscopy for the identification of oxidation states is not sufficiently sensitive in the case of our deposited nanoparticles. However, the results would agree with V_2O_5 as possible stoichiometry but for a confirmation additional methods have to be employed, which are presented in the main manuscript.

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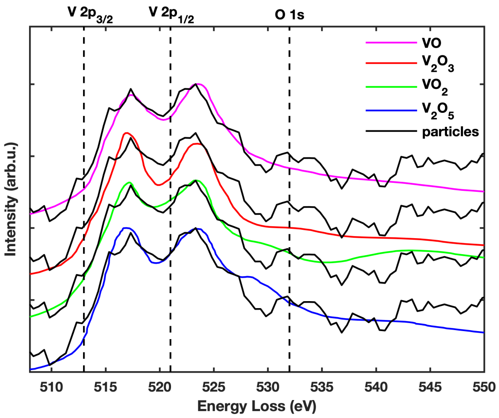

Figure 1: EEL spectrum normalized to the L2/L3 peak maximum obtained by averaging over 5 different nanoparticles (black) and compared to literature reference spectra for V_2O_5 (blue), VO_2 (green), V_2O_3 (red) and VO (purple) taken from Ref. 1. The literature spectra have been convoluted by a Gaussian function in order to match the energy resolution.

References

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