Decoupling of valence and coordination number contributions at perovskite surfaces

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Perovskite oxide nanostructures are on the forefront of technology due to the wide spectrum of possible applications pertinent to renewable energy sources, such as water-splitting, solar cells, fuel cells, batteries, and catalysis. In particular, the exceptional properties for the oxygen reduction reaction in catalysis have been detailed recently in a volcano plot and the results reveal that orthorhombic, Jahn-Teller distorted $LaMnO_3$ perovskite nanoparticles are the leading, non-noble metal candidate for enhanced catalytic activity on the cathode electrode of fuel cells [1]. Since the functional properties of these nanoparticles lie on their active surfaces, our approach involves a detailed structural and chemical evaluation of the surfaces on the atomic scale to determine what/where the reaction centres are. Subsequently, the morphology of the particles can be optimised to maximise the number of these reaction centres, allowing us to attain the highest possible performance of perovskite catalysts.

From structural transmission electron microscopy (TEM) data it was determined that polar facets exist on crystallites, which lead to assumptions on possible surface reconstruction/relaxation. However, high resolution TEM indicated that the atomic terminations of several surfaces remained defect-free up to the very surface with no visible reconstruction taking place [2], as shown in Figure 1. Next, the surface and subsurface of the working perovskite catalyst was probed by high spatial and temporal resolution electron energy-loss spectroscopy (EELS) in scanning TEM mode. The results revealed that the surface shows different character than the bulk. Tan *et al.* has previously shown that different oxidation states of Mn can be probed at neighbouring sites in the same compound [3] but it was also theoretically predicted that such a change can be attributed to coordination number differences as well [4]. Indeed, the extracted experimental information by EELS for the pristine $LaMnO_3$ powder was analysed utilising density functional theory calculations under the optic matrix elements approximation, as shown for the Mn L_3 peak in Figure 2, and the shift to lower energies of the Mn $L_{3,2}$ edge was found to be a convolution of both changes in oxidation state and in the number of nearest neighbours (coordination).

References:
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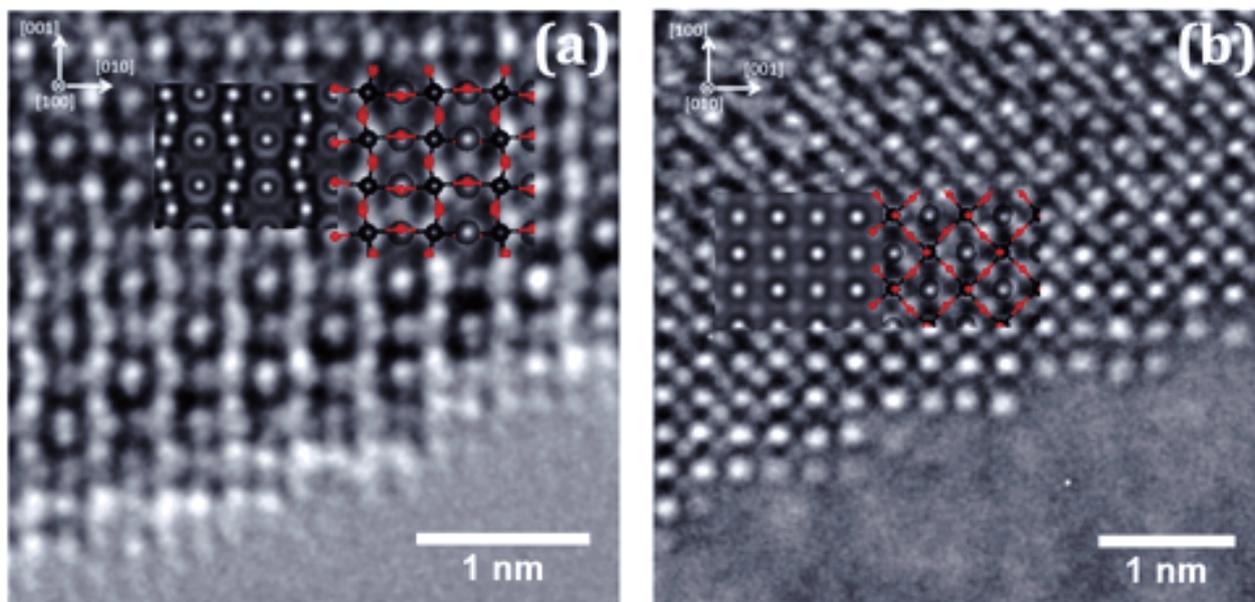
Figure 1. TEM image of a LaMnO3 particle edge showing the Jahn− Teller distortion at the exposed surface of the (001) plane (a) and the surface termination on the [010] zone axis (b). In the overlaid schematics, a simulated HRTEM image is shown along with simulations of the atomic positions where La is grey, Mn is black, and O is red.
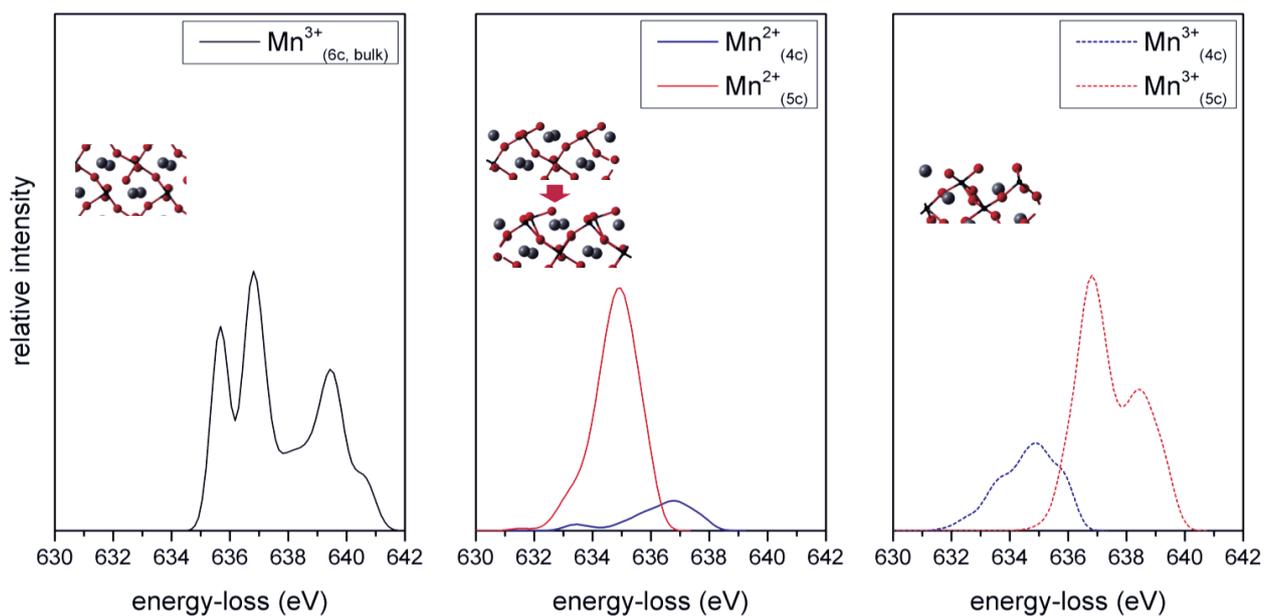

Figure 2. Optical matrix elements calculations for (a) the MnO6 as found in bulk, (b) the reduced case in two coordination configurations, and (c) the MnO4 and MnO5 contributions for the Mn3+.