

The Advanced Characterization and Structure-Property Correlation of BaMnO₃ for the Oxygen Reduction Reaction Using Electron Microscopy

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The past and future development of 21st century economy and technology relies heavily on the supply of energy. Considering this and the projected doubling of the world's energy consumption within the next 30 years, there is urgent demand for low- and zero-emission energy sources [1,2]. Therefore, the challenge of today's society and researchers is the design of electrochemical technologies that can perform both safely, and at rates and costs competitive with the performance of fossil fuel technologies.

Metal oxides represent one of the most common, diverse and richest class of materials in terms of their electronic, structural, chemical and physical properties [3-5]. In fact, nanostructured metal oxides exhibit an infinite variety of structural motifs and morphological features that make them indispensable in the design and development of energy application devices. Atomic scale characterization and investigations using electron microscopy techniques bridges the gap between the properties and applications of such materials, and their atomic structure and crystallography. Furthermore, aiding in the finer tuning of material properties, and the optimization of environmentally-friendly technological devices. As a result, we combine the use of advanced electron microscopy techniques with spectroscopic analyses to reveal the atomic scale chemical and crystallographic structure of barium manganese oxide (BaMnO₃), a perovskite oxide system.

BaMnO₃ rods were synthesized via a hydroxide composite-mediated method, which is in stark contrast to the high-temperature, high-pressure ceramic methods traditionally used for perovskites [6]. The BaMnO₃ rods display a 2H-hexagonal crystal structure with space group P6₃/mmc and lattice parameters $a = b = 5.6991$ and $c = 4.8148$ Å. Here, the 2H indicates the presence of continuous chains of face-sharing MnO₆ octahedra along the c direction. The crystal structure was successfully characterised using x-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED), and was directly imaged using aberration-corrected high-angle annular dark field scanning transmission electron microscopy (HAADF STEM).

In contrast to the single crystalline nature of the bulk, the surface of the rods was found to be amorphous in nature. Using electron energy loss spectroscopy (EELS) and spectrum imaging, this layer was found to consist of reduced Mn states. This was further confirmed by x-ray photoelectron spectroscopy (XPS), from which the presence of both Mn³⁺ and Mn⁴⁺ states were identified. Due to the presence of mixed transition metal states, the rods were tested for their electrocatalytic activity in the oxygen reduction reaction (ORR). The as-synthesized rods displayed activity for ORR, however, the activity was found to decrease linearly with post-modification annealing temperature, owing to the decrease in the percentage of Mn³⁺ states and associated oxygen vacancies. Therefore, this work offers an insight into the necessity

of atomic-scale structural and chemical analyses via electron microscopy for the process of structure-property correlation, in addition to the successful application of materials.

By taking advantage of the perovskite system and its ability to display countless structural and chemical motifs, the number of avenues for future work are endless. Future research will investigate the atomic scale chemical and crystallographic nature of titanium doped BaMnO_3 , with subsequent structure-property correlation. Additionally, the nucleation of precious metals on the rods with the aim of improving electrocatalytic activity will be explored.

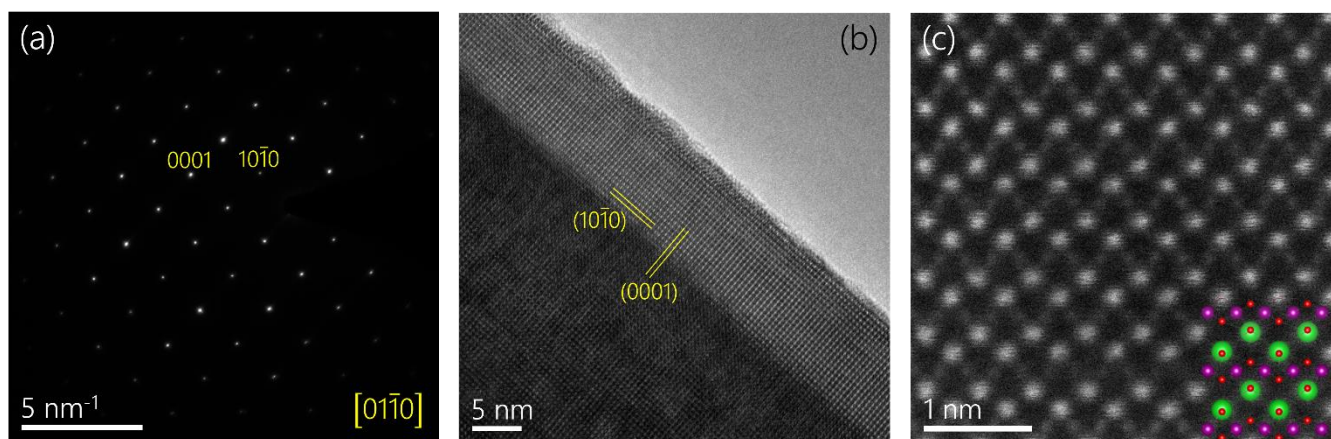


Figure 1. Perovskite BaMnO_3 crystallography and atomic structure. a) SAED pattern and b) corresponding HRTEM image of a BaMnO_3 rod with markings of the plane reflections and lattice fringes, respectively, from the $(10\bar{1}0)$ and (0001) planes. c) HAADF STEM image of BaMnO_3 from the $[10\bar{1}0]$ zone axis, with a schematic illustration of the $(10\bar{1}0)$ 2H- BaMnO_3 crystal structure shown within the inset.

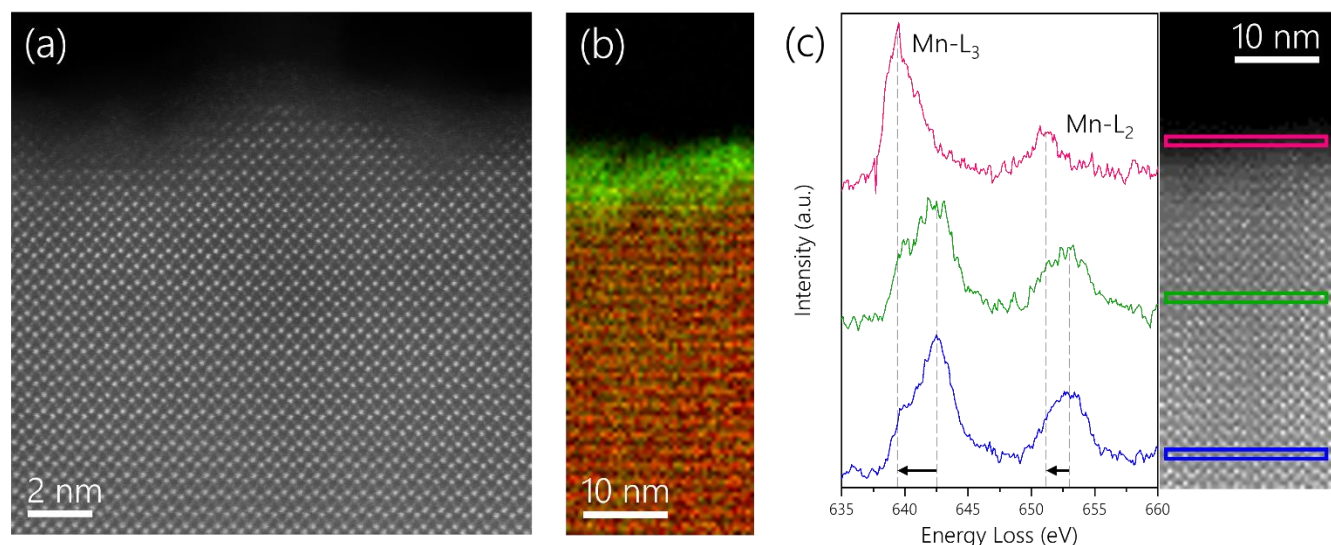


Figure 2. Surface analysis of BaMnO_3 rods. a) HAADF STEM image of BaMnO_3 displaying the bulk crystal structure and the presence of an amorphous surface layer. b) EELS chemical map showing the localization of Mn^{4+} states (red) within the bulk, and reduced Mn states (green) within the surface layer. c) Spatially resolved Mn L-edge EELS spectra from the bulk to the surface of the rods, in which the

black arrows indicate the shift of the Mn-L₃ and Mn-L₂ peaks to lower energy loss when traversing from the bulk to the surface.

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