

Atomic resolution imaging of perovskite nanoparticle surfaces exposed to gas environments at elevated temperatures by transmission electron microscopy

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Doped perovskites such as $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ (LSC) are among the most promising materials for intermediate temperature solid oxide fuel cell (SOFC) cathodes¹. However, strontium segregation to the surface of LSC can occur during synthesis, and at exposure to elevated temperatures²⁻³. Strontium surface segregation degrades the ability of LSC to exchange oxygen at the perovskite-gas interface, reducing the activity for oxygen electrocatalysis⁴⁻⁵. Aberration-corrected scanning/transmission electron microscopy (S/TEM) may provide an atomic level understanding of the chemical, crystallographic, and morphological changes that occur at different surfaces of LSC upon exposure to gas atmospheres at elevated temperatures.

Using a molten-salt technique⁶, we have developed a method for synthesizing LSC nanoparticles for TEM characterization using nitrate, nitrite and hydroxide solvents. Figure 1 shows high-angle annular dark-field (HAADF) and bright-field (BF) STEM images of an as-synthesized cubic LSC nanoparticle. In the BF-STEM image, a thin (< 1 nm) layer of material is visible on both the (100) and (110) surfaces of the nanoparticle. X-ray energy dispersive spectroscopy (XEDS) line profiles across the both surfaces show an early onset of the strontium signal, suggesting that the surface layer is strontium rich. Electron energy-loss spectroscopy (EELS), acquired from a second nanoparticle, shows a shift of the cobalt L-edge to lower energies at both the (100) and (110) surfaces (Figure 2). This shift suggests a reduction in the oxidation state of cobalt at the LSC surfaces⁷, which may correspond to an increased concentration of oxygen vacancies at the surfaces.

Our goal is to examine chemical and structural changes to the surfaces of LSC particles under different conditions. Identical location *ex-situ* STEM and EELS, and *in situ* TEM will allow us to track changes in the composition of the surfaces of LSC nanoparticles before, during, and after exposure to oxidising and reducing atmospheres at elevated temperatures. Our results will provide important feedback to help guide the design of more durable perovskite cathodes for SOFCs.

References:

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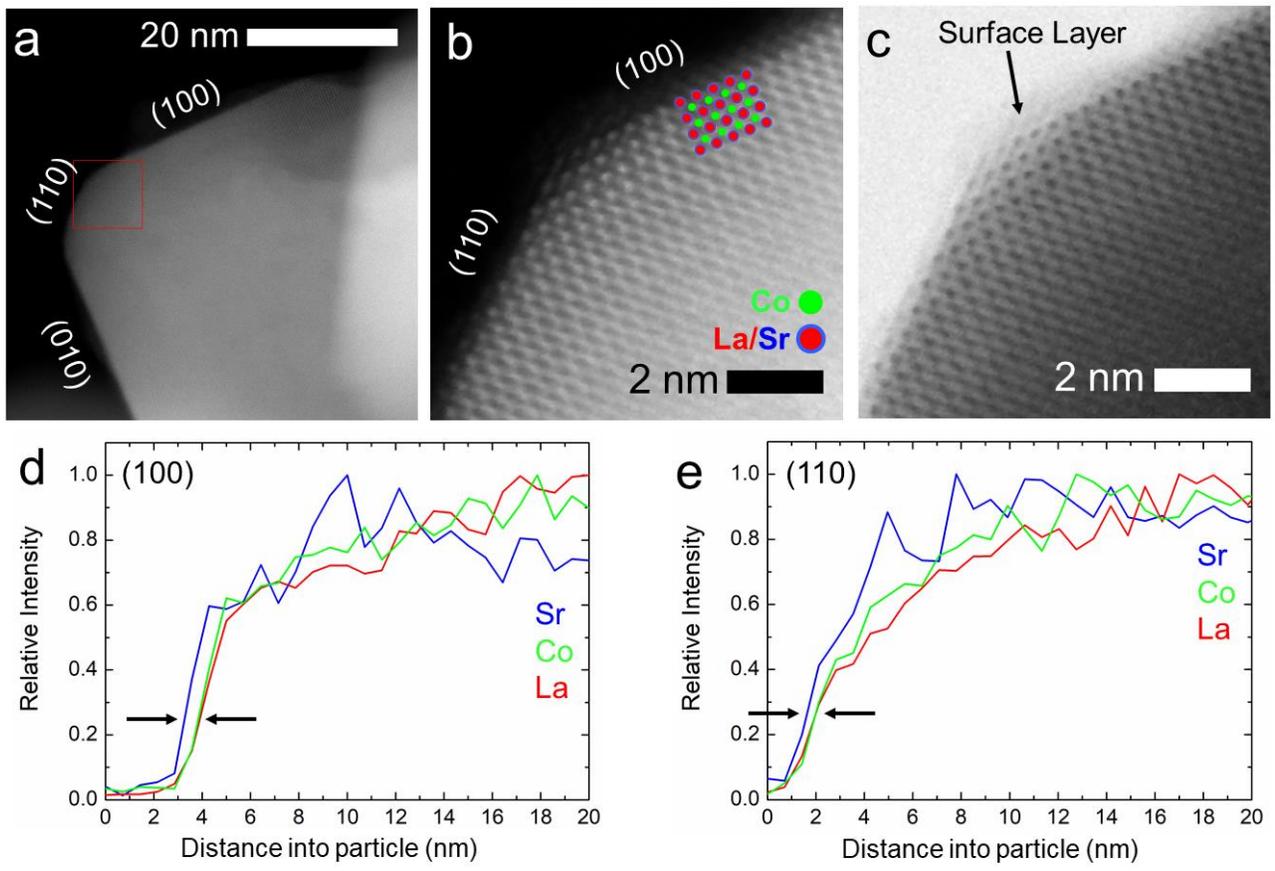


Figure 1. (a) HAADF-STEM image of cubic LSC nanoparticle (b) Magnified HAADF-STEM and (c) BF-STEM image of area from (a) marked by red box. The overlay shows positions of La/Sr and Co columns. (d) and (e) XEDS line profiles across the (100) and (110) surfaces.

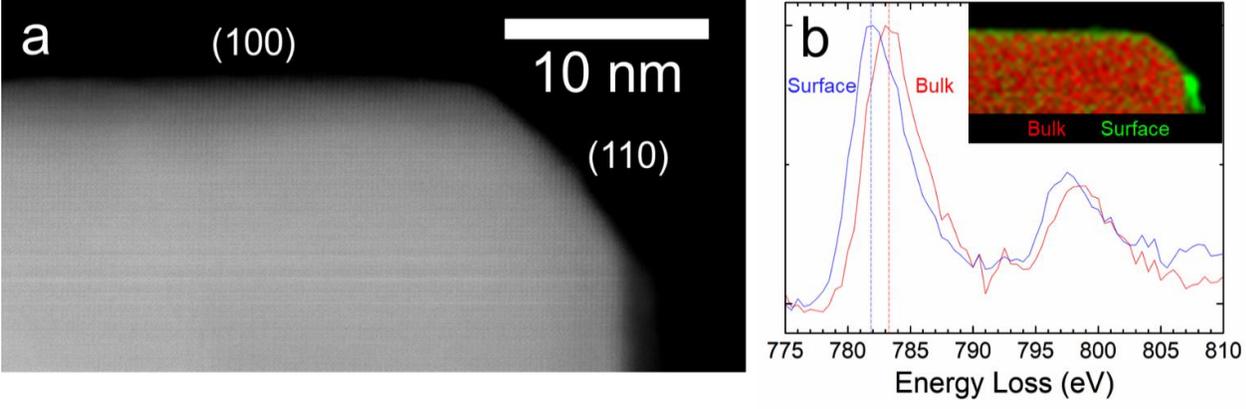


Figure 2. (a) HAADF-STEM image of a second LSC nanocube (b) Cobalt L-edge EEL spectra and spatial map showing different profiles observed on the particle surface, and in the bulk.