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Three-dimensional Imaging of Surface Structural Transformations on Electrocatalyst Nanoparticles Using Multi-slice Electron Ptychography

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Surface structural transformations are important in electrocatalysis as reactions take place at surfaces [1,2]. Many electrocatalysts such as metal alloy, metal oxide, and metal nitride nanoparticles undergo surface transformations and generate a different phase on the surface, forming a core-shell structure [3–5] altering the expected surface chemistry [6]. Measuring the structure, coverage and continuity of the shell, and how it coupled to the core requires a method that can provide atomic-resolution information with a depth-sensitivity beyond that of conventional imaging modes, and at a lower dose than tilt-series tomography. Multi-slice electron ptychography can in principle meet this challenge by providing a dose-efficient, high-spatial-resolution reconstruction of the scattering potential with depth information [7].

Here we studied MnN nanoparticles that are of interest as cathode electrode catalysts for anion-exchange membrane fuel cells (AEMFCs) [8]. As with many other metal nitrides, MnN nanoparticles generate a layer of manganese oxide (*e.g.*, Mn_3O_4) on their surface in the presence of air or during alkaline oxygen reduction reaction (ORR) electrochemical testing. Here, the combination of high angle annular dark field (HAADF) images along the [110] zone axis of MnN nanoparticles and electron energy-loss spectroscopy (EELS) demonstrated island-like growth of Mn_3O_4 layers with different thicknesses after 10k ORR cycles (Figure 1 a-b). With less electron dose, the reconstructed ptychography stack provides the position of Mn, O, and N atoms, with an improved resolution compared to HAADF (Figure 1c).

Moreover, without dose-intensive tomography, HAADF images lack the depth sensitivity to resolve the complex surface structures with overlapping nanoparticles along the Z axis and tilting often occurring in nano-domains. By changing the defocus value in HAADF, we get some sense that the some overlapped trapezoidal Mn_3O_4 nano-islands nucleated heterogeneously on the MnN nanoparticle surface (Figure 2 a). Nonetheless, the overlap greatly complicates prospects for obtaining physically meaningful strain maps from the HAADF images.

Here we apply multi-slice electron ptychography [7] to characterize the electrocatalyst surface in 3D, imaging with both heavy and light elements at sub-Angstrom lateral resolution. A single ptychographic reconstruction shows details of different MnN/Mn_3O_4 interfaces at different depths of view (Figure 2b). Within a single ptychography stack, we separate the structural information from two different Mn_3O_4 nano-islands at different depths of view even when overlapped with sufficient details to allow us to study lattice displacements and strain separately from each grain. The heterogenous nucleation of the Mn_3O_4 nano-islands is visible in the orthogonal XZ slices. The misregistration between the two Mn_3O_4 grains can be seen in slices 2–5, and is a consequence of the degeneracy of possible registrations between the Mn-O unit and O-Mn-O unit in Mn_3O_4 unit cells. These quantitative insights into three-dimensional atomic structures of electrocatalyst surface layers, especially continuity, uniformity and strain help us better understand reaction mechanisms and durability of the catalyst nanoparticles. [9]
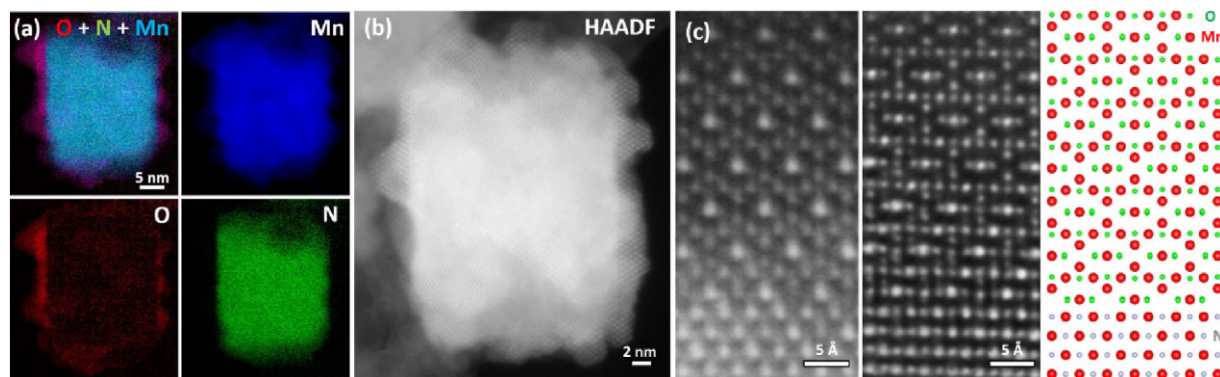

Fig. 1. (a) EELS spectra and (b) HAADF image of the MnN nanoparticle along the [110] zone axis showing islanding of the oxide shell. (c) comparison between a HAADF image showing only Mn, ptychography slice showing Mn, N and O, and a schematic atomic model of MnN/Mn_3O_4 interface.
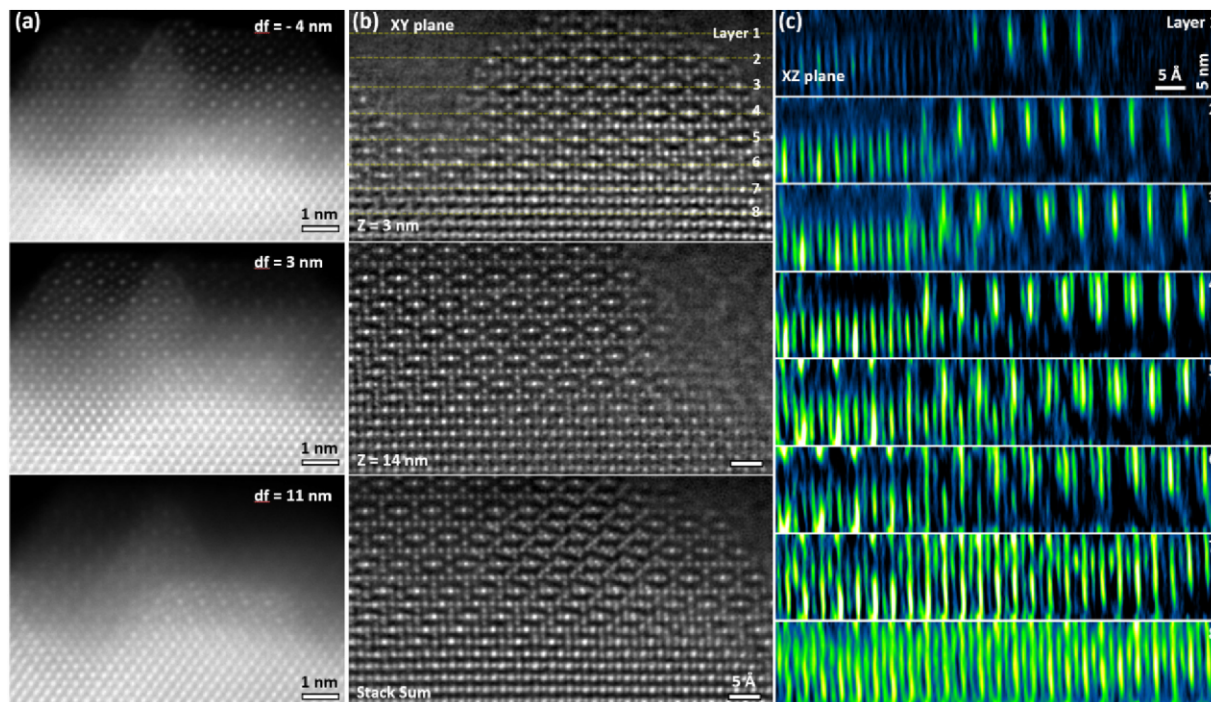
Fig. 2. (a) HAADF images of the MnN/Mn$_3$O$_4$ interface at different defocus values (df = -4 nm, 3 nm and 11 nm, respectively) and (b) multi-slice ptychography reconstruction of the same MnN/Mn$_3$O$_4$ interface at different depth slices, and the summed stacked image of all 16 ptychography slices, showing the oxide islands are not in registry. (c) XZ plane slices at for the different y positions labelled with the yellow dotted lines in the top panel of (b), showing positions of the Mn-O and O-Mn-O units in Mn3O4 for the two oxide islands and the Mn-N unit in MnN. Layer 2-5 show the 2 islands misregistration along Z.

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