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3D Structure Determination of Pt-based Nanocatalysts at Atomic Resolution

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The Pt based catalysts have shown the prominent enhanced selectivity, activity, and stability. The field of Pt based catalysis such as Pt and Pt heterogeneous catalysts has seen many advances over the past few decades. Recent studies have shown that introducing earth-abundant metals such as Ni and Cu into Pt can not only significantly enhance the oxygen reduction reaction (ORR) activity of the catalysts, but also lower the cost [1, 2]. Among these nanoalloys, bimetallic platinum-nickel (PtNi) nanostructures represent an emerging class of candidates for ORR catalyst in fuel cells. More recently, a new nanoalloy catalyst of carbon-supported PtNi with Mo doped on the surface (PtNi-Mo) has been reported, demonstrating 80-fold enhancements compared with commercial Pt-C catalyst [3]. To understand the structure and performance of these nanoalloy catalysts, it is essential to fully characterize the surface structure of these nanoalloy catalysts in 3D with atomic resolution. An ideal method to achieve this challenging goal is atomic electron tomography (AET) [4], which retrieves 3D atomic structure information from a tilt series of high-resolution 2D images. In recent years, AET has been used to image the 3D structure of grain boundaries, stacking faults, and the core structure of edge and screw dislocations at atomic resolution [5, 6] as well as map out the 3D strain tensor with high precision [7]. More recently, we have determined the 3D atomic arrangement of chemical order/disorder in an FePt nanoparticle with 22 pm precision [8] and captured nucleation at 4D atomic resolution [9]. Here, we apply AET to probe the 3D surface atomic structure of PtNi-Mo nanoalloy catalysts. By using the TEAM microscope at the National Center for Electron Microscopy at LBNL, several series of atomic-resolution tomographic images of PtNi-Mo nanoparticles have been acquired. Combining the high-quality tomographic images with the GENeralized Fourier Iterative REconstruction (GENFIRE) algorithm [10], we have performed 3D reconstruction of four PtNi-Mo nanoparticle datasets with atomic resolution. The individual Pt, Ni and Mo atoms can be distinguished based on the intensity contrast due to Z contrast in STEM image. Figure 1a-c show the 1.4-Å-thick atomic slices along three <100> directions, where the large and small dots represent Pt and Ni atoms, respectively. We can clearly see the feature of segregation of the Pt and Ni atoms. Figure 1d-f show the summation of reconstruction along the same direction, which is the same as measured projections. Using an advanced polynomial atomic tracing method, we successfully locate and identify of the accurate 3D positions and species of each atom in PtNi-Mo nanoalloys without the assumption of crystallinity. Coupled with first principles calculations, the full surface oxygen binding energy map can be derived from the 3D atomic structure, providing essential information to precisely tailor and optimize the catalytic behavior for various applications [10].

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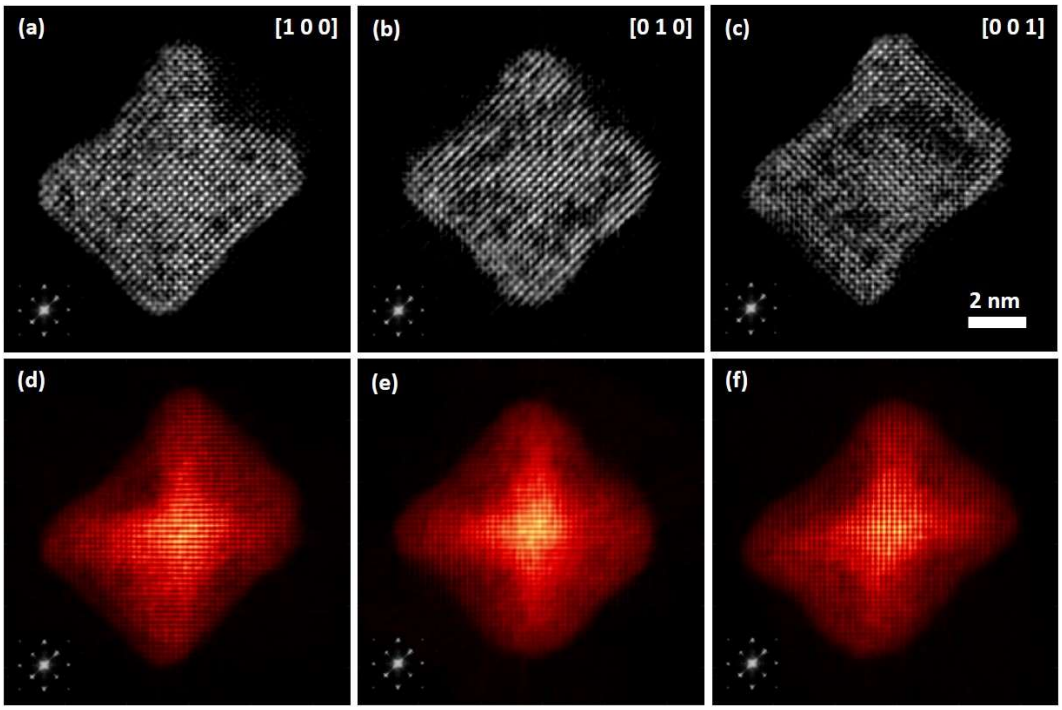

Figure 1. (a-c) Three central 1.4-Å-thick atomic slices along the [100], [010] and [001] direction, respectively, showing clear atom structures. Pt, Ni and Mo can be distinguished by the intensity contrast, and segmentation of Ni atoms and Pt atoms is observed. (d-f) The summation of reconstruction along the same direction, which is the same as measured projections.

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