Differentiating the structures of PtNi octahedral nanoparticles through combined ADF and EDX simulations

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Pt-based bimetallic nanoparticles demonstrate great promise as catalysts for the oxygen reduction reaction (ORR) in hydrogen fuel cells.[1] The addition of a second transition metal, such as Ni or Co, not only reduces the cost of the catalyst due to the reduction in Pt metal loading, but also provides an increase in activity. Recently, octahedral PtNi nanoparticles have attracted considerable interest, as it was reported that the Pt_3Ni (111) alloy surface has exceptionally high activity for the ORR[2]. Its activity has been reported to be 10 times higher than that of the Pt (111) surface and 90 times higher than that of state-of-the-art Pt/C catalysts. Therefore, there is great benefit to understanding the structures and compositions of the near-surface layers on such nanoparticles. Although previous studies have proposed a variety of possible models for octahedral PtNi nanoparticles, it is highly challenging to obtain an exact atomic-scale understanding of their structure in three dimensions.

Although energy-dispersive X-ray spectroscopy (EDX) can be used to study local variations in the compositions of individual supported nanoparticles on the atomic scale in the scanning transmission electron microscope (STEM), electron-beam-induced damage and contamination can preclude the use of long exposure times and tomographic approaches. Here, we perform simulations of annular dark-field (ADF) STEM images and EDX maps of seven different octahedral PtNi nanoparticle model structures for a selection of crystallographic orientations and tilts, in order to evaluate which of them can be distinguished from elemental mapping and imaging performed in only one orientation, allowing for better experimental design.

(1) Holton, O. T.; Stevenson, J. W. The Role of Platinum in Proton Exchange Membrane Fuel Cells. *Platin. Met. Rev.* **2013**, *57*, 259 - 271.

(2) Stamenkovic, V. R.; Fowler, B.; Mun, B. S.; Wang, G.; Ross, P. N.; Lucas, C. A.; MarkoviÄ, N. M. Improved Oxygen Reduction Activity on Pt3Ni(111) via Increased Surface Site Availability. *Science* **2007**, *315*, 493 - 497.