Growth and degradation of octahedral Pt-alloy nanoparticle catalysts

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Shape control can be effective for tuning the physical and chemical properties of inorganic nanoparticles. As a result of their extraordinarily high activity for the oxygen-reduction-reaction (ORR), octahedral Pt-Ni nanoparticles have become highly attractive as fuel-cell catalysts. A deep understanding of their atomic-scale structure, degradation and formation is a prerequisite for their use as rationally designed nanoparticle catalysts with high activity and long-term stability.

We have used aberration-corrected high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) combined with electron energy-loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (EDX) to reveal element-specific anisotropic growth in Pt-Ni nanoctahedra, in which compositional anisotropy couples to geometric anisotropy. During solvothermal synthesis, a Pt-rich nucleus evolves into precursor nanohexapods, followed by the slower step-induced deposition of Ni on the concave hexapod surface, to form octahedral facets [1]. The compositional anisotropy of the Pt-Ni octahedra leads to complex structural degradation during ORR electrocatalysis. The Ni-rich (111) facets are preferentially etched, resulting in the formation of first concave octahedra and then Pt-rich skeletons that have less active facets [2]. In order to tune the atomic-scale microstructure of the octahedra for long-term stability, we illustrate the effect of varying the growth conditions on morphology and compositional segregation by producing trimetallic PtNiCo nanoctahedra and comparing “one-step” and newly-developed “two-step” synthesis routes [3].

Figure 1: a) Microstructural study comprising high-resolution TEM, HAADF STEM and EELS mapping of the element-specific compositionally anisotropic growth of octahedral PtNi nanoparticles. The images and corresponding models show the elemental distribution of Pt (red) and Ni (green) in alloy nanoparticles measured at different stages of growth after 4, 8, 16 and 42 hours of solvothermal synthesis.

References