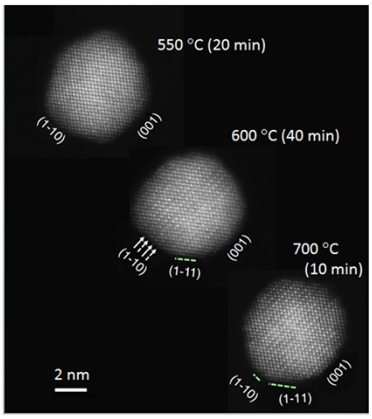
In situ microscopy explains why Pt-Co nanoparticles outperform commercial Pt fuel cell catalysts



Tracking a single nanoparticle in the STEM at different temperatures and annealing times. The ordered Pt_3Co structure is visible as alternating bright-dark contrast (arrows); the particle is fully ordered at 700 °C. Labels refer to surface facets.

Work performed at the Center for Nanophase Materials Sciences, Argonne National Laboratory, Johns Hopkins University, and the University of Pittsburgh.

Scientific Achievement

Individual Pt_3Co catalyst nanoparticles (NPs) were imaged during *in situ* thermal annealing from 350-800°C in a scanning transmission electron microscope (STEM) to track structural and chemical changes at the atomic level.

Significance and Impact

***In situ* STEM annealing coupled with simulations reveal the dynamic interplay between elemental diffusion and crystallographic faceting and demonstrate that Pt_3Co NPs exhibit distinct stages of atomic rearrangement at specific temperatures.**

Research Details

- Individual Pt_3Co NPs were imaged via Z-contrast STEM using a Protochips Aduro™ *in situ* TEM heating holder.
- *In situ* STEM annealing conditions were identical to those used for post-synthesis annealing of catalyst NPs and provide atomic-scale insight for precisely tuning NP structure towards optimized catalytic performance.

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Narrative Highlight Text:
This study directly reveals the dynamic structural and chemical evolution of Pt_3Co NPs during thermal annealing. The nanocatalysts exhibit distinct elemental diffusion behavior at critical annealing stages: the formation of a Pt-rich shell with a randomly alloyed core; the preferential nucleation of ordered domains associated with specific surface facets; the establishment of a fully ordered L12 phase and, finally, pre-melting. The dynamic coupling of surface faceting and elemental inter-diffusion during annealing was also discovered, which should be carefully considered during catalyst design. The major facets, {111}, {110} and {100}, play differing roles during NP evolution. Our results provide insight regarding the rational design of NPs at the atomic scale aimed at creating enhanced catalytic activity and stability through optimizing the surface structure and elemental distribution using thermal annealing. Finally, our studies demonstrate the power of directly tracking the atomic configurations, including both atomic position and chemical distribution, within single particles during *in situ* annealing using sub-Å-resolution HAADF-STEM imaging.

Reference

"Surface Faceting and Elemental Diffusion Behavior at Atomic Scale for Alloy Nanoparticles During *In Situ* Annealing"
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