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Aberration-Corrected STEM Image Simulation of Segregation in Pt_3Co Nanoparticles for PEM Fuel Cells

Brian N. Patrick,* Lawrence F. Allard,** Yang Shao-Horn*** and Paulo J. Ferreira*

*Materials Science and Engineering Program, The University of Texas at Austin, Austin TX 78712
**Materials Science & Technology Division, Oak Ridge National Laboratory Oak Ridge, TN 37831
***Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139

Fuel cells, particularly proton exchange membrane fuel cells (PEMFCs), are promising energy conversion devices for the future. At the heart of these PEMFCs, Pt nanoparticles are currently used as the catalyst to dissociate H_2 at the anode and O_2 at the cathode. However, as Pt is extremely expensive, Pt_3Co nanoparticles are being investigated as a way to reduce cost, as well as increase the overall effectiveness of the fuel cell.

In this work, Pt_3Co nanoparticles, were treated by acid leaching or by a heat treatment at 1000°C. In general, acid leaching produces nanoparticles with a truncated octahedron shape (Fig. 1a). This is typically the equilibrium shape of Pt-alloy nanoparticles. On the other hand, the heat treatment produces nanoparticles with a truncated cuboid shape (Fig. 2a). In order to better understand the relationship between the elemental distribution and the nanoparticle shape and structure, the nanoparticles were characterized by aberration-corrected scanning transmission electron microscopy (STEM), using high-angle annular dark-field (HAADF) imaging [1]. However, as the HAADF-STEM technique is both thickness and atomic number dependent, computer simulations have been employed to match the experimental observations. This is done by first creating an atomic model of the nanoparticles using the VESTA software (freeware 3-D visualization program), followed by computer simulations using the HREM simulation suite (HREM Research).

The nanoparticles treated by acid leaching show pockets of contrast throughout the particle (Fig1b). To infer if these variations of contrast are due to heterogeneities in elemental composition (thickness variations produce also changes in contrast) we have simulated nanoparticles exhibiting either an ordered (space group $Pm\bar{3}m$) or a random solid-solution (space group $Fm\bar{3}m$) structure. The results are shown in Figs. 1(c-g). It is clear that the experimental image (Fig. 1b) does not fit the simulations. Instead, the results show that although the acid leached nanoparticles exhibit a solid solution structure, there are regions within the particle enriched in either Pt or Co. The nanoparticles subjected to heat treatment exhibit an ordered structure throughout the particle except for the first three surface layers where a brighter contrast can be seen (Fig. 2c). From the relative intensities of the atomic columns present in these surface layers, as well as computer simulations carried out to match these relative intensities (Figs. 2d-f), we can infer that there is 85 at% Pt surface segregation in these truncated cuboid nanoparticles [2].

References

[1] S. Chen, W. Sheng, N. Yabuuchi, et. al., *J. Phy. Chem. C.* 113(3) 1109-1125 (2009)
[2] Research at ORNL's High Temp. Materials Laboratory was sponsored by the U. S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Program.

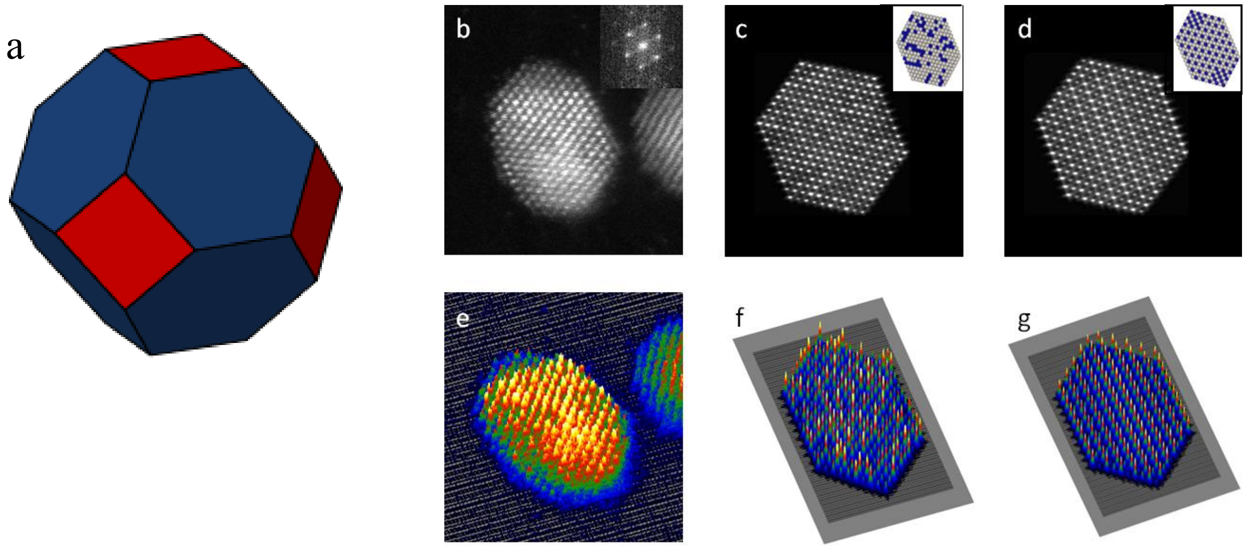
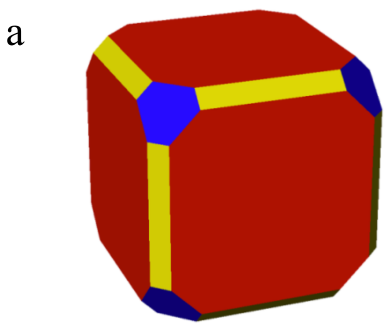


FIG. 1. a) Pt_3Co nanoparticle with a truncated octahedron shape; b) HAADF image of the particle shown in a) with [110] zone axis; c) simulation of the Pt_3Co nanoparticle with random solid solution; d) simulation of a Pt_3Co nanoparticle with an ordered structure; e) surface plot of the image shown in b); f) surface plot of the simulation shown in c); g) surface plot of the simulation in d).



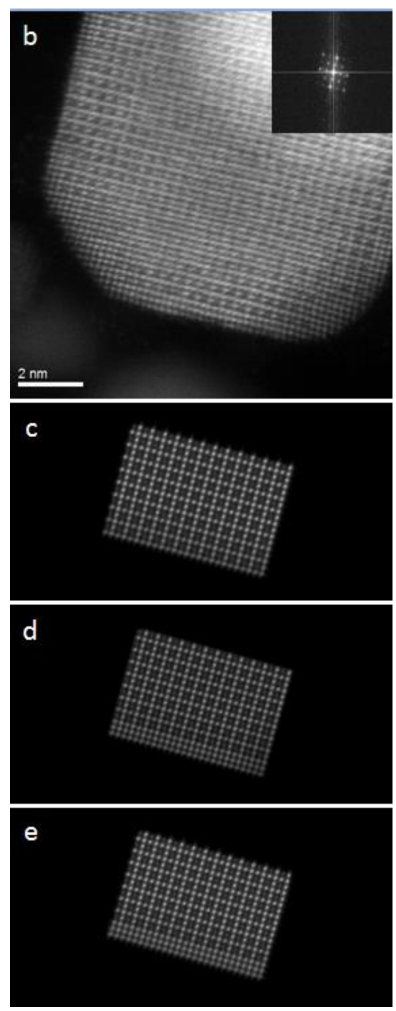


FIG. 2. a) Pt_3Co nanoparticle with a truncated cuboid shape; b) HAADF-STEM image of truncated cuboid particle shown in a) with [001] zone axis; c) simulation of 0% Pt surface segregation; d) simulation of 85% Pt surface segregation, e) simulation of 100% Pt surface segregation.

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