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3D Characterization of Faceted Core/Shell Nanoparticles by STEM Tomography with TEAM I

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The shape of nanoparticles is known to greatly influence their function, because the performance of some chemical reactions is enhanced at certain crystal faces. Therefore, control of nanoparticle surface structure can lead to greatly enhanced reaction rates. Direct, quantitative analysis of the final three-dimensional shape of such particles can help tune the growth parameters to produce optimum particles for a certain reaction. In particular, it has been shown that Pt/Pd core/shell nanoparticles with a controllable Pd surface structure (cube, cube-octahedral or octahedral) can be synthesized from uniformly {100}-faceted Pt seeds. The overgrowth of the Pd shell is predicted to proceed layer-by-layer, and the final shape is precisely controlled by selectively inhibiting growth rates along {100} or {111} directions. The resulting binary nanoparticles are highly faceted and provide tunable physical and chemical properties [1-2].

Previous two-dimensional analysis by high-resolution TEM/STEM projection images show the epitaxial Pt/Pd interface and indirectly confirm the overall shell surface structure [1], but direct quantitative determination of shell shape and thickness benefits from three-dimensional analysis. Therefore, three-dimensional electron tomography with HAADF-STEM imaging was used to determine the resulting Pd surface structure and Pd shell thickness for corresponding Pt seed particles. A cluster of ~25nm Pt/Pd nanoparticles were reconstructed from 129 projections acquired over a tilt-range of ±64° using the 300keV TEAM I aberration-corrected microscope operated in HAADF-STEM mode and equipped with the tilt-rotate TEAM stage. The tilt range was limited only by the sample grid bars. HAADF-STEM imaging minimizes diffraction contrast during tilting and provides *Z*-contrast imaging $I \propto Z^2$ which differentiates elements by scattering intensity [3]. Thus, the shape, size and orientation of the core and shell for each particle can be determined quantitatively in three-dimensions.

Each particle was segmented using the Amira 5 software package to distinguish regions of Pt and Pd throughout the reconstruction for quantitative analysis. Figure 1a and 1b show two reconstructed nanoparticles with dissimilar Pt seeds (solid color), but a surrounding cubic Pd shell structure (transparent) of similar thickness. Figure 2a-b) shows that the shell thicknesses perpendicular to <100> faces for both particles is ~7nm, although the Pt seeds differ in size by over $2\times$ (4.5nm and 10nm respectively). The thick carbon support obscures some measurements on the underside of the particles indicating the advantage of graphene as a substrate in nanostructured characterization [4]. The limited tilt range produces a stretching artifact along the original beam direction. Still, all other reconstructed particles show the same results, which indicates that Pd overgrowth on faceted Pt seeds proceeds layer-by-layer to produce a cubic shell independent of initial seed shape/size. Also, some particles exhibit nanopores 2-3nm in diameter at the Pt/Pd interface, but they do not affect the final shell shape. Quantitative analysis using three-dimensional electron tomography is capable of determining the shape, thickness, orientation, etc. of nanoparticles and is readily applied to many other similar systems. [5]

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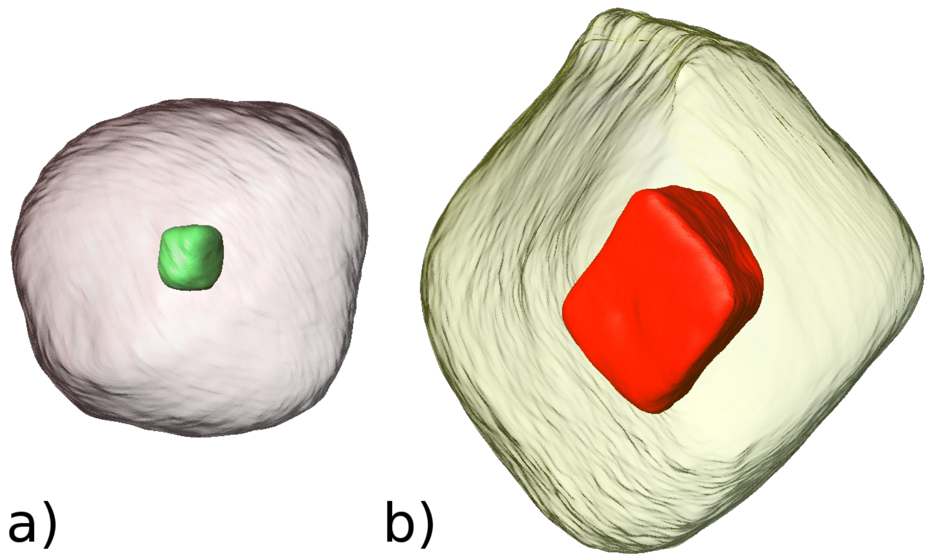

FIG 1: Three-dimensional electron tomography reconstructions of two Pt/Pd core/shell nanoparticles. The Pd shell thickness is ~7nm for both particles perpendicular to the <100> faces even though the Pt seed particles have different shapes and sizes (4.5nm and 10nm). This indicates the Pd overgrowth occurs layer-by-layer and results in a similar cubic Pd shell shape regardless of the Pt seed shape. Electron tomography allows the direct quantification of layer thicknesses along any direction and determination of seed/shell surface area and volume.

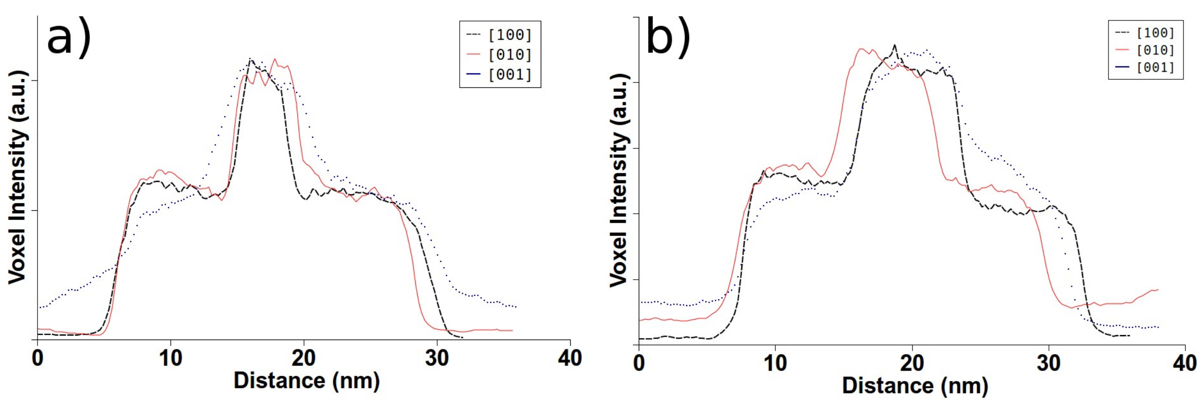

FIG 2: Line plots of the voxel intensities through a) the small particle and b) the large particle in Fig. 1a-b. The Pt seeds of the two particles are very different in size, but the thickness of the Pd shell - which exhibits medium intensity - is ~7nm for each. This shows that the Pd shell grows layer-by-layer as expected.

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