Aberration-Corrected STEM and Tomography of Pd−Pt Nanoparticles: Core−Shell Cubic and Core−Frame Concave Structures

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Nanosize bimetallic particles have long been recognized as important heterogeneous catalytic materials. Platinum (Pt) is an inestimable material due to its excellent catalytic performance. To reduce the use of Pt and lower overall cost, depositing a thin layer of Pt on the surfaces of less expensive metal cores, such as Palladium (Pd), is an effective approach. Controlling the shape, morphology, and chemistry of the outer Pt layer has been widely accepted as a critical factor to realize the specific applications. Our studies show that the growth shape of nanocrystals can be controlled by adjusting the ratio between the rates of atom deposition and surface diffusion ($V_{deposition}/V_{diffusion}$).[1] Herein, we provide a comprehensive study of the atomic structures, composition, and 3D morphology of the Pt shell layer in Pd-Pt nanoparticles with core-shell cubic and core-frame concave structures by aberration (Cs) - corrected high angle angular dark field (HAADF) - scanning transmission electron microscopy (STEM), energy dispersive X-ray spectroscopy (EDS), and HAADF tomography.

Core-shell cubic and core-frame concave Pd-Pt nanoparticles were synthesized by site-specific growth.[2] TEM, HAADF-STEM, EDS mapping, and HAADF tomography were performed in a JEOL ARM200F with a STEM Cs corrector operated at 200 kV. A Fischione 2030 ultra-narrow gap tomography holder was used in the tilt range of ±72° with 2° step. A low dose mode at 1 M× magnification was used via SerialEM software. The 3D reconstructions were achieved by simultaneous iterative reconstruction algorithm (SIRT) of 2D projections in IMOD. Visualization was performed with AMIRA 3.1.

Atomic resolution Cs-corrected HAADF imaging combined with EDS line scanning can identify the atomic level differences in layer-by-layer thickness.[3] Figure 1 shows the results of EDS line scanning indentifies Pt atomic layers in Pd-Pt core-shell nanocubes. Figure 1a is an atomic HAADF image of a Pd-Pt core-shell nanocube, where the red arrow indicates the direction of EDS line scanning. The intensity profiles (Figure 1b) shows outer 7 atomic layers have higher intensity than inner layers, implying that the 7 atomic layers are Pt, based on HAADF imaging contrast theory. The corresponding line profile of EDS scanning (Figure 1c) confirms the structure of Pt shell/Pd core. The distance between half-intensity of Pt EDS signal is about 1.25 nm, which is in good agreement with the measured peak distance between the 7 Pt layers (1.22 nm) in Figure 1b. It is worth noting that the most outset surface Pt layer is not fully covered, while the interfacial layer is a mixed Pt and Pd layer at the atomic scale due to the termination of growth steps under a two-dimensional growth mechanism. 3D electron tomography

confirmed that the Pd-Pt core-frame concave nanoparticle has high index crystallography facets on its surfaces, as shown in Figure 1d.

In this work, we investigated the structural and chemical characteristics of the Pt shell layer in the core-shell cubic and core-frame concave Pd-Pt nanoparticles at the atomic scale. Our results reveal the deposition and growth mechanism of Pt ad-atoms onto Pd cubic seeds under various growth conditions. The characterization methodology developed in this work provides important insights that will serve to guide the analyses of nano and atomic structures, and the design of Pd-Pt nanoparticles for specific catalytic functionality.[4]

References:
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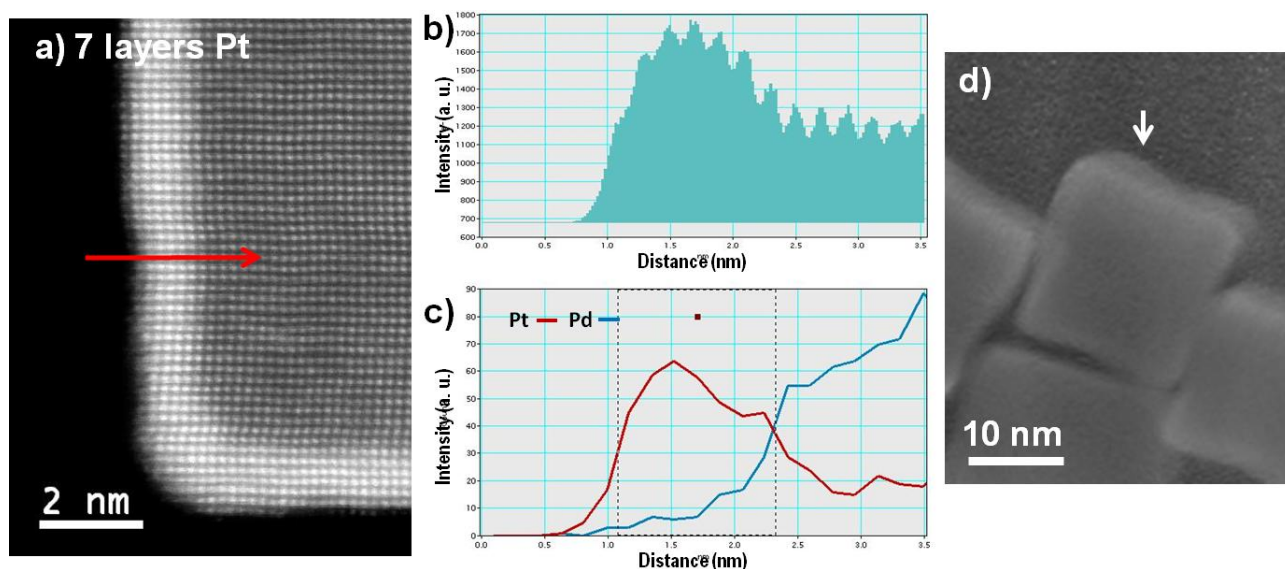

Figure 1. EDS line scanning indentifies Pt atomic layers in Pd-Pt core-shell nanocube (a-c) and 3D tomography of Pd-Pt core-frame concave nanoparticle (d). (a) Atomic HAADF image. (b) Intensity profiles along the red lines indicated in (a). (c) EDS line scan profiles of Pt and Pd acquired along the red lines indicated in (a). (d) 3D tomography of Pd-Pt core-frame concave nanoparticle.