Initial Growth of Au Nanoparticles Investigated by Multimode Electron Tomography

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Structural defects in Au nanoparticles have a large impact on their properties.[1,2] Unfortunately, 3D characterization of structural defects in nanoparticles by electron tomography is far from straightforward. Indeed, HAADF-STEM images, typically used for electron tomography do not yield information on defects. On the other hand, diffraction contrast, present in LAADF-STEM images will violate the projection requirement for tomography. Therefore, we propose a multimode approach for electron tomography, during which tilt series of low and high angle ADF-STEM projection images are acquired simultaneously using different detectors. Figure 1.a shows the 3D reconstruction of the morphology of a pentatwinned (PTW) Au decahedron. In Figure 1.b, we present the 3D reconstruction based on a tilt series of LAADF-STEM images that was acquired simultaneously. From the combined reconstruction in Figure 1.c, the location of the twins with respect to the morphology of the decahedron can be investigated.

As an application, we used this approach to investigate the relation between twins in PTW Au bipyramids and the seed from which their growth was initiated. Two different growth mechanisms have been reported for these PTW structures.[4,5] The first pathway involves the nucleation of a PTW seed and its subsequent overgrowth in a layer-by-layer fashion. Alternatively, a single-crystalline seed can develop twin defects during overgrowth, finally resulting in a PTW structure. To gain a better understanding of the growth mechanism, the position of the Au seed inside the final Au nanoparticle and its location with respect to the twins was investigated using the multimode approach. Au bipyramids are grown from Au seeds coated by a thin layer of Pd and from a pure Pd seed.[6] The difference in atomic number between Au and Pd enabled us to accurately find the position of the seed in the final Au nanoparticle, using HAADF-STEM tomography. A proof of concept is illustrated in Figure 2 for a Au bipyramid grown from a relatively large Pd@Au seed and another one grown from a smaller Pd seed, respectively. In both cases, the location of the seed is clear from the HAADF-STEM reconstruction and the twinning planes can be visualized by LAADF-STEM. Our results provide evidence of growth pathway alteration depending on seed size and composition.

As a confirmation of the epitaxial relationship between the Pd@Au seed and the Au shell, high resolution HAADF-STEM images can be acquired along the long axis of the structures. However, for bipyramids, such an analysis is hampered by the relatively large thickness of the investigated structures. Due to the large amount of Au in comparison to Pd, the contrast is not sufficient to identify the position of the seed in a reliable manner. Therefore, the particles were deposited on a Si substrate, and a cross-section cut of the sample was made using focused ion beam milling. In this manner, the Pd layer could be observed in high resolution, clearly showing that the growth of Au on the bimetallic seed is epitaxial.

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[4] Skrabalak et al, ACS Nano. 3 (2009), p 10 - 15

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[6] Midgley et al, Chem. Commun. 10 (2001), p 907 - 908

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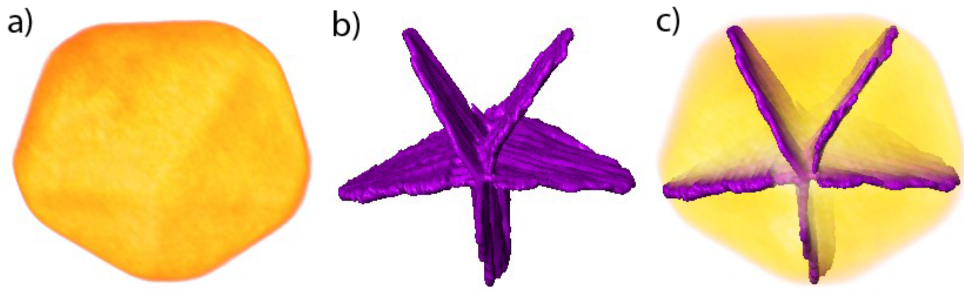

Figure 1. 3D visualization of (a) The HAADF-STEM reconstruction (b) The twin planes segmented from the LAADF-STEM reconstruction (c) Both volumes are superimposed.

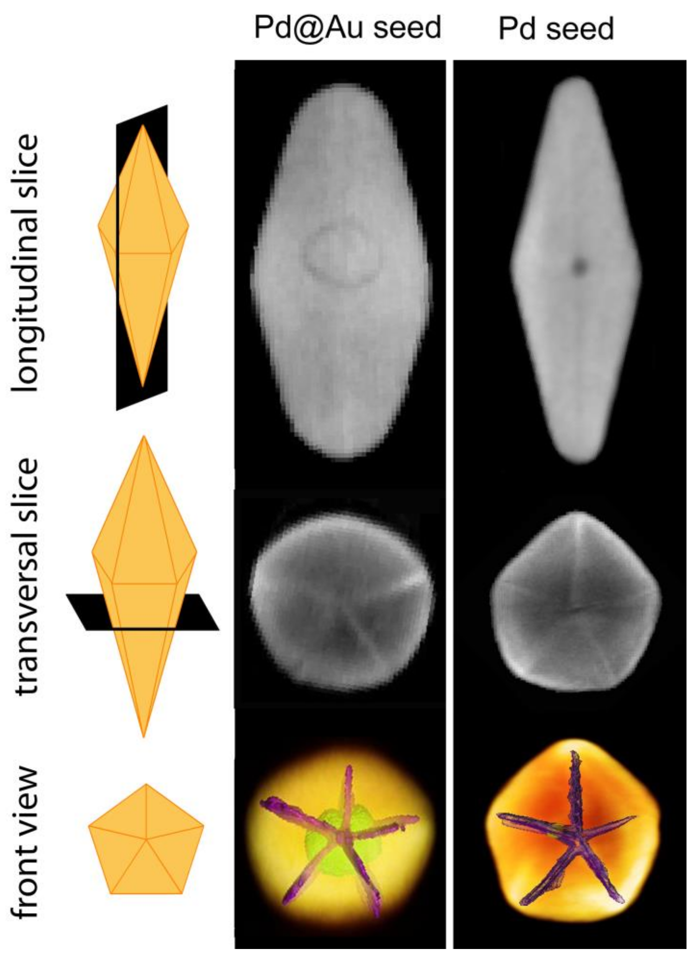

Figure 2. Top row: Longitudional orthoslices through the HAADF-STEM reconstruction of bipyramids from Pd@Au and Pd seed. Middle row: Transversal orthoslices through the LAADF-STEM reconstruction, from which the twins can be segmented. Bottom row: Superposition of the segmented seed and twin planes.