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Observation of Simultaneous Successive Twinning Using Atomic Electron Tomography

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Electron microscopy is the characterization method of choice to observe atomic-scale and microstructural local features within materials that play a critical role in material performance. With resolution that can be deeply sub-angstrom, a single image from a high-resolution electron microscope can measure atomic positions, defects, and strain. Electron tomography extends these characterization capabilities to three dimensions, enabling isolation of individual atoms in nanomaterials, which in turn gives the ability to map defects, strain, and chemical composition in three dimensions [1-3].

Electron microscopy characterization has been particularly important to our understanding of the structure-property relationships in nanomaterials, for example multiply twinned nanoparticles (MTPs). These structures are common in solution-based synthesis of face centered cubic (FCC) materials, such as palladium, gold, and platinum, that have application in catalysis, optoelectronics, and lithography. In particular, the ability to tune catalytic activity by controlling the exposed facet of a nanoparticle is highly desirable, and much effort has gone into understanding how to control the size and shape of FCC MTPs for this purpose [4].

MTPs frequently adopt shapes that can be thought of, in an idealized way, as decahedra or icosahedra, comprised of tetrahedral subunits (Fig. 1), and many synthetic protocols aim to select for one of these shapes [4]. One observation from static and *in-situ* studies of MTP growth is the phenomena of successive twinning during growth of decahedral or icosahedral MTPs: during growth, additional twin planes form, adding new tetrahedral subunits in the multiply twinned structure [5,6]. This process can transform single tetrahedra to multiple tetrahedral structures, such as decahedra and eventually icosahedra, forming transient multi-tetrahedron structures along the way (Fig. 1 (a-b)). Most previous electron microscopy observations of successive twinning studies have been limited to two-dimensional imaging, such that many of the multi-tetrahedron structures present during successive twinning appear ambiguous [5,6].

Atomic electron tomography (AET) uses high-resolution scanning transmission electron microscopy (HR-STEM) data sets to reconstruct the atomic-scale 3D structure of materials. Previously, AET has been used to determine the structure, local defects, and strain in icosahedral and decahedral metal nanoparticles [2, yongsoo7], and it is therefore ideally suited to characterize Pd MTPs. In this work, we have applied conventional HR-STEM to a population of Pd nanoparticles to determine the relative abundance of decahedra, icosahedra, and multi-tetrahedron structures [8]. AET was then used to determine the atomic-scale structure of a representative particle undergoing successive twinning [7]. To analyze the twinning structure in detail, we developed a classification protocol to determine the local coordination environment of the atoms in the reconstruction. By mapping whether the atoms are in an FCC or hexagonal-close packed (HCP) environment (Fig. 1(c)), the twinning structure of the particle could be deduced. This protocol revealed a *simultaneous* successive twinning process in the atomic-scale 3D reconstruction, meaning the particle was captured transitioning from a decahedron to an icosahedron *via* addition of multiple tetrahedra simultaneously (Fig. 1(d)). We also observe many defects within the crystal grains of the particle.

Tetrahedron by tetrahedron growth has been demonstrated before in prior work, under different synthetic conditions [6]. However, the structure we observe is more consistent with a simultaneous twinning process, where the tetrahedra comprising the center portion of the icosahedra grow at the same time. This process has been predicted to occur in small metal nanoclusters through the coordinated formation of an HCP layer on the surface of a decahedra [9]. Based on the HR-STEM studies, we hypothesize that this growth route is only viable for small decahedra, as above a certain size regime the structure-directing action of the surfactant ligands used in synthesis will play a larger role.

Our observations confirm addition of multiple tetrahedra to a decahedral particle as a growth route toward an icosahedral shape. The observation of the successively twinned structure has implications for the functionality of Pd nanoparticles, as the lack of <111> terminated facets would be expected to alter catalytic activity. The large number of defects with the particle could also alter the surface strain states and therefore performance as well. Ultimately, the combination of HR-STEM and AET used in this study provide important insight into the structure and functionality of MTPs [10].

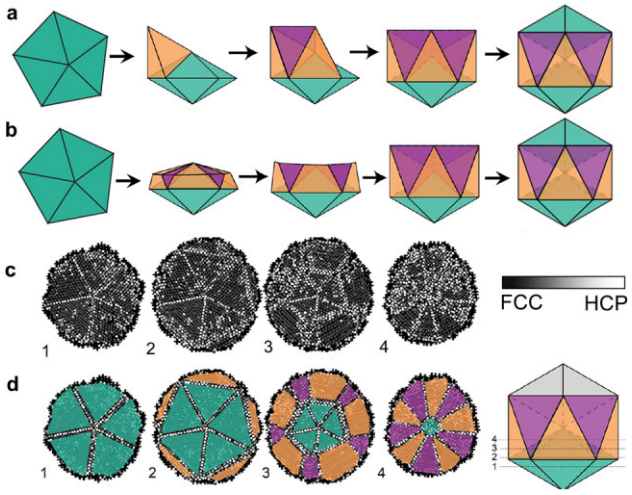

Fig. 1. Successive twinning in MTPs. (a) Successive twinning occurs when tetrahedra are added to a twinned nanostructure, in this case one by one. (b) Simultaneous successive twinning. (c) Thin slices from the AET-reconstructed atomic coordinates, with the coordinates classified according to their coordination environment. Slices 1-4 are taken from the bottom (1) towards near the top (4) of the particle. (d) An overlay has been added to thin slices from the AET reconstruction, illustrating the additional tetrahedra growing on top of the decahedra, consistent with the idealized simultaneous successive twinning shown in (b).

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