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Unraveling the Coarsening Mechanism of Palladium Nanoparticles Using *in situ* High Resolution Transmission Electron Microscopy

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In the past decades, extensive interests have emerged in the controllable synthesis of nanocrystals, ranging from metals to semiconductors and insulators, with tailored morphologies, from spheres to rods or even heterostructures, to allow large-scale use of nanotechnology [1-4]. The classical crystal coarsening kinetics, Ostwald ripening (OR) theory, is usually used to explain the diffusion-controlled growth process, in which larger particles grow at the expense of smaller particles [5-7]. Recently, intense research indicates that the Ostwald ripening kinetics cannot explain all coarsening behaviors of nanocrystals. Thus a significant mechanism named "oriented attachment (OA)" was proposed, in which the adjacent nanoparticles are aggregated by sharing a common crystallographic orientation [8-10]. Despite some work has been performed to track growth trajectories *in situ* [11-14], many critical questions on the underlying mechanism of nanoparticles interaction and coarsening remain unresolved due to the lack of real-time atomic-scale observation of such progress.

Therefore, *in situ* high resolution transmission electron microscopy (HRTEM) is used in our study to follow the dynamic evolution of palladium nanoparticles during heating in vacuum. The Pd nanoparticles have cubic shape with side lengths distributing narrowly around 10 nm and flat {100} facets. *In situ* experiments are performed in Hitachi H-9500 environmental TEM at 300 kV with two kinds of *in situ* heating holder. One is Hitachi double-tilt heating holder, and the other is Protochips Aduro heating holder. Both can allow high-resolution imaging at elevated temperatures up to ~1000 °C.

The HRTEM images (see Figure 1) display the particle coarsening process during heating. Figure 1a (at lower temperature) shows two adjacent but independent nanocubes while Figure 1b (at higher temperature) demonstrates a coalesced single crystal nanoparticle. The high-resolution image indicates that it really becomes single crystal while the contrast along the boundary may result from strain effects. On the other hand, during continuous electron beam irradiation without external heating, two palladium nanocubes coalesced gradually at a planar interface, as shown in Figure 2, but did not recrystallize into a single crystal like those after heating. These evidences directly demonstrate that this kind of nanoparticle coalescence and coarsening is motivated by the oriented attachment kinetics. More details will be reported during presentation to finally unravel the mechanism of such coarsening progress.

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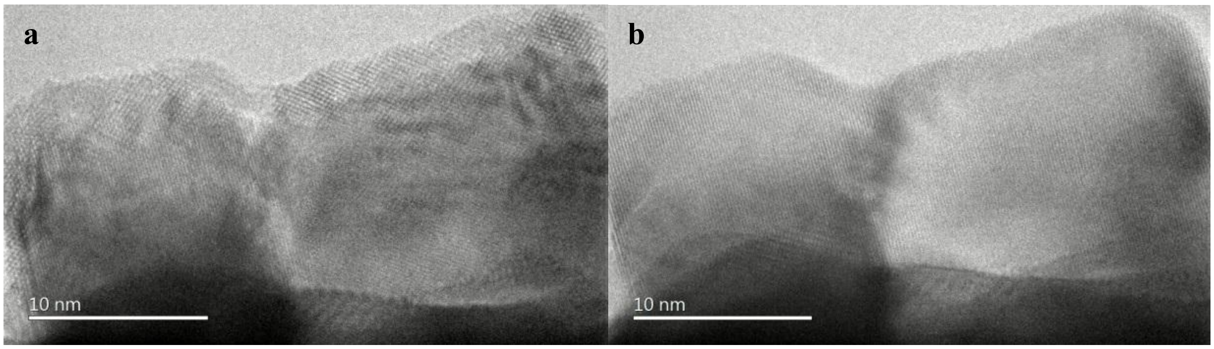

Figure 1. HRTEM images showing coarsening process of Pd nanocubes during heating. Figure 1a shows two adjacent but independent nanocubes at lower temperature, while Figure 1b displays they became a coalesced single crystal nanoparticle after heating to higher temperature.

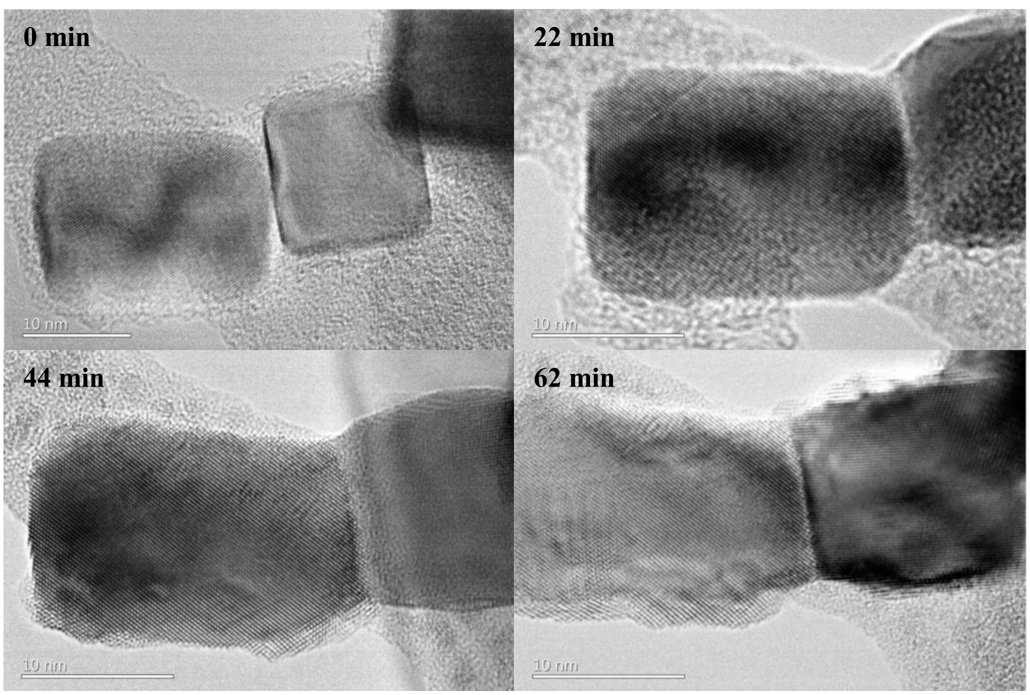

Figure 2. HRTEM images extracted from movies showing dynamic process of Pd nanocubes coalescence during electron beam irradiation without external heating. The upper left figures indicate the irradiation time of the sample.