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Controlled Growth of High-Index Faceted Nanoparticles Using the Gas Phase Environmental Cell TEM

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Nanoparticles having exposed high-indexed facet have gathered significant interests as a high-throughput catalyst. Exposed high-indexed planes tends to have higher coordination number with the reactant materials compared to the low-indexed planes. However, fabrication of the high-index faceted nanoparticles are challenging due to the favorable thermodynamic stability of the lower index planes. Recently, various high-index faceted tetrahexahedral (THH) nanoparticle were successfully synthesized by using the two-step alloying and dealloying method. In this two-stage method, metallic elements with relatively low melting temperatures (Sb, Bi, Pb, and Te) are alloyed with refractory metals (Pt, Pd, Rh, Ni, and Co) at intermediate temperature followed by dealloying at elevated temperature [1-2].

Recent developments in the environmental cell S/TEM allows for constructing of isolated micro-reactors inside the TEM column. The gas cell environmental TEM gathers broad interests among the *in situ* and *operando* microscopists as it requires relatively lower investment compared to conventional open-cell gas environmental microscopes. Especially, for *in situ* high-temperature nanoparticle generation experiments, continuous flow of reducing gas for extended periods must be achieved to prevent unwanted oxidation. The reducing environment can be easily achieved with an environmental cell as compared to the environmental S/TEM, where the light gas molecules, such as hydrogen, cannot be efficiently pumped with differential pumping mechanism [3].

Here, we demonstrate the formation process of high-index facet exposed nanoparticles during two-stage synthesis procedure using *in situ* environmental cell microscopy (Figure 1a). The liquid state Pt acetylacetonate and Bi precursors dispersed on the methanol are drop-cast on the SiN_x MEMS chip equipped with ceramic heater membrane. The heater membrane chip with the precursor is then sandwiched with another SiN_x membrane chip to form an isolated environmental cell within the commercial gas-supplying specimen rod. Hydrogen gas is then gently flowed through the environmental cell and the temperature is elevated to 600°C to form Bi-Pt bimetallic alloy. After the alloy formation, dealloying and the facet development is performed at 900°C (Figure 1b-c). The results show that quasi-liquid state molten alloyed platinum nanoparticle is mobile on the SiN_x substrate and undergoes the coarsening with neighboring particles until it reaches to the critical size. Next, the dealloying and facet development occurs after the critical size nanoparticle is immobilized at the surface (Figure 2). We have also found that particles formed during the experiment were identical to products from bulk synthesis with a CVD (Chemical vapor deposition) setup, which implies good correlation between our experiment and conventional growth processes. [4].

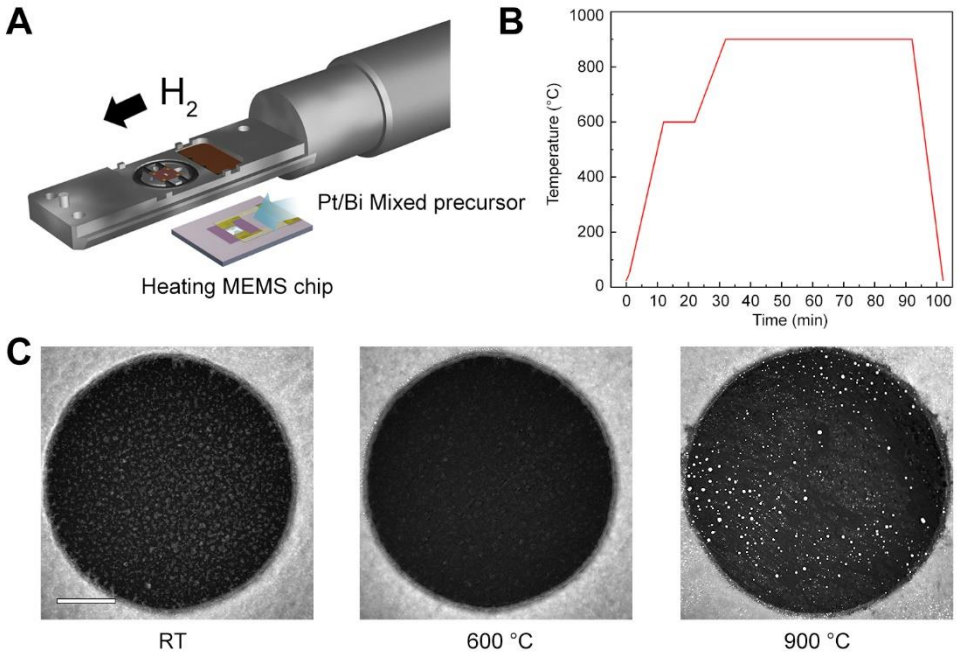

Figure 1. (A) Experimental schematic for *in situ* growth of high-indexed platinum nanoparticle using environmental cell TEM. (B) Profile of system temperature during the experiment. (C) Low magnification image of the precursor salt and nucleated nanoparticles during each heating stage. The scale is 2 μm.

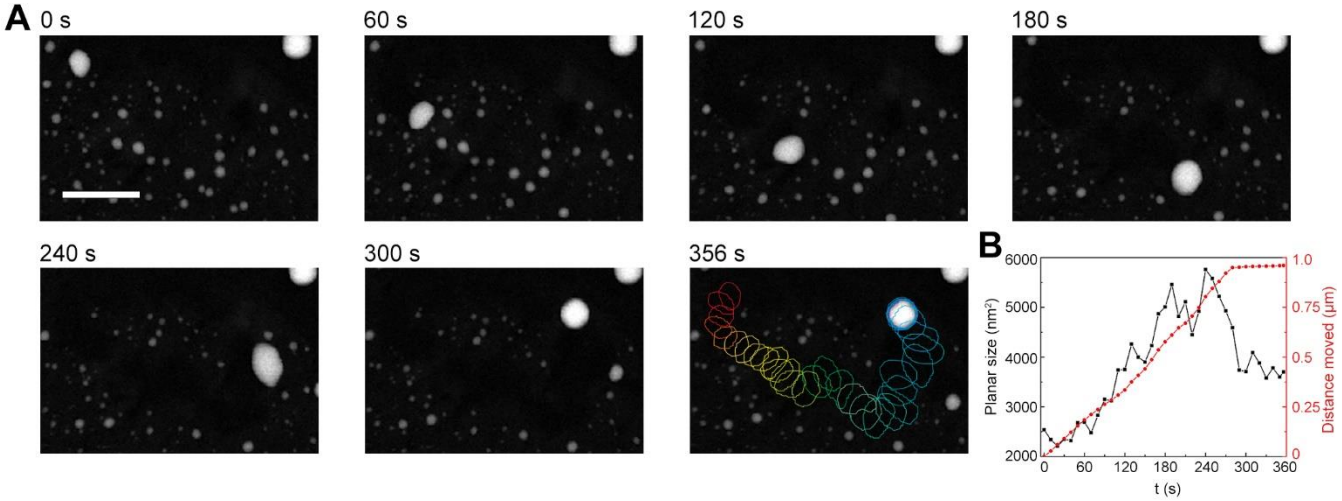

Figure 2. (A) Time-series images showing coalescence and facet development of platinum nanoparticle at 900°C in hydrogen condition. The scale bar is 200 nm. (B) Planar size of the tracked platinum nanoparticle and accumulated total distance traveled. The particle during the coalescence has constant velocity and stopped during the facet development stage.

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