Supporting Information

Monitoring the Shape Evolution of Pd Nanocube to Octahedron by PdS Frame Marker

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Experimental Section

Synthesis of Pd nanocubes: In a typical synthesis, 8.0 ml of an aqueous solution containing 105 mg PVP (Mw ≈ 55,000), 60 mg AA, 600 mg KBr in a 20-ml vial was heated for 10 min at 80 °C under magnetic stirring. Subsequently, 3.0 ml of an aqueous solution of Na₂PdCl₄ (57 mg) was added with a pipette. After that, the reaction was allowed to continue at 80 °C for 3 h. The product was collected by centrifugation, washed three times with water to remove excess PVP, and dispersed in 11 mL water.

Preparation of polysulfide (Na₂Sₓ) aqueous solution: The Na₂Sₓ solution was prepared by reacting aqueous Na₂S with sulfur powders. In a typical process, 32 mg of sulfur powders were mixed with 9 ml of 2.22 mM Na₂S aqueous solution in a 20 mL vial. The solution reacted at 90 °C without stirring for 3 days. The final product was obtained by diluting the solution for 100 times.

Sulfuration reaction: In a standard procedure for sulfuration, different volume of the Na₂Sₓ solution was added to 1ml of the aqueous suspension of Pd nanocubes (1.8mg/L in terms of elemental palladium) at room temperature without stirring. The reaction was conducted for 6h. After that, the product was collected by centrifugation, washed three times with water to remove excess Na₂Sₓ, and dispersed in 1 mL water to make a seed solution.

Synthesis of PdS marked Pd octahedrons: In a standard procedure, 3 mL of aqueous Na₂PdCl₄ solution (32 mM) was introduced into 8 mL of an aqueous solution containing 105 mg PVP, 100 mL HCHO, and 0.3 mL of an aqueous suspension (1.8 mg/mL in concentration) of sulfurized Pd cubic seeds which had been heated at 60°C for 5 min under magnetic stirring in a capped vial. The reaction was allowed to proceed at 60°C for 3 h. To acquire a better understanding of the growth process, we did a series of experiments with different reaction times. The reaction was quenched at a specific time point by centrifuging the solution. The product was then precipitated twice with water by centrifugation and decantation. The final product was re-dispersed in water for further structural analysis.

Synthesis of PdS cubic nano-frames via Galvanic Replacement: In a standard procedure, 1 mL of the aqueous suspension of the proper sulfurized Pd nanocubes (the concentration of Na₂Sₓ is 0.15 mM) and 7 mL of an aqueous solution containing PVP (33.3 mg) and KBr (300 mg) were mixed in a glass vial. The mixture was heated to 90°C in air under magnetic stirring. Meanwhile, 3.5 mg of H₂PtCl₆ was dissolved in 3 mL deionized water. This aqueous solution was then injected into the solution containing PVP, KBr, and Pd nanocrystals using a syringe pump at a rate of 1 mL/min. The reaction
mixture was then heated to 90°C for 12 h in air. Finally, the solution was centrifuged and washed three times with water to remove PVP before characterization.

**Figure S1.** TEM images of nanocrystals obtained at different stages during the shape evolution from cube to octahedron: (a) truncated nanocubes; (b) cuboctahedrons; (c) truncated octahedrons; (c) octahedrons.

**Figure S2.** (a) STEM and (b-d) elemental mapping of the as-prepared Pd octahedrons marked with PdS.
frames: (b) Pd-K, (c) Pd-L, and (d) S-K.

**Figure S3.** TEM and HRTEM images of cubic seeds with different sulfuration ratio by adding different volume of Na$_2$S$_x$ solution: (a, d) 250 μl; (b, e) 750 μl; (c, f) 5 ml;

**Figure S4.** TEM images of the Pd polyhedrons obtained by adding 1.5 mg of Na$_3$PdCl$_4$ to the reaction solution.
Figure S5. HRTEM images of PdS cubic nano-frames obtained by selectively etching away the Pd cores via the galvanic replacement.