## **Electronic Supplementary Information**

# One step synthesis of a hierarchical dendritic Pt nanostructure with the building unit of Pt concave octahedron via simultaneous vertex growth and facet etching

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### **Material Characterizations**

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed on a TECNAI G2 20 S-Twin operated at 200 kV and TECNAI G2 F30 operated at 300 kV. Elemental mapping and energy dispersive X-ray spectra (EDX) were obtained with a FEI Titan Cubed 60-300 with Chemi-STEM technology and a JEOL ARM200F Cs STEM. X-ray diffraction (XRD) patterns were collected with a Rigaku Ultima III diffractometer system using a graphite-monochromatized Cu-Kα radiation at 40 kV and 40 mA.

### **Experimental Section**

#### Preparation of hierarchical dendritic Pt nanostructure with the building unit of Pt concave octahedron

In a typical synthesis of Pt nanocrystals, a solution of  $Pt(acac)_2$  (0.02 mmol, Aldrich, 97%), CTAB (Cetyltrimethyl ammonium bromide) (0.10 mmol, Aldrich, 99%) in octadecylamine (15 mmol, Aldrich, 90%) was prepared in 100 mL Schlenk tube. After removing gas in the solution under vacuum 10 minutes at 100°C, mixed gas (O<sub>2</sub> 20%, N<sub>2</sub> 80%) was charged into the tube. Then the tube was directly injected to hot oil bath at 165°C. After 11 hours, the reaction mixture was cooled down to room temperature. The product was purified by multiple centrifugal separation with added toluene and methanol.



Fig. S1 TEM images of Pt nanocrystals at different reaction temperature. a) 145°C, b) 165°C, c) 185°C, d) 210°C



Fig. S2 Low resolution TEM images of synthesized Pt nanocrystals at various condition in Fig. 3.



**Fig. S3** TEM temporal images of side product hierarchical nanocrystals with different structural features. a) 3 h, b) 4 h, c) 10 h, d) 5 h.