Supporting Information

One-pot Synthesis of Cubic PtCu\textsubscript{3} Nanocages with Enhanced Electrocatalytic Activity for the Methanol Oxidation Reaction

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Experimental Section

Preparation of PtCu\textsubscript{3} nanocages. In a typical synthesis, 131 mg of H\textsubscript{2}PtCl\textsubscript{6} solution (8 wt\%) and 20 mg of Cu(acac)\textsubscript{2} were added into a solution containing 8 mL of oleylamine and 50 mg of cetyltrimethylammonium bromide (CTAB). After about 30 min of ultra-sonication, the solution was transferred into a 15 mL Teflon-lined autoclave. The autoclave was maintained at 170 °C for 24 h, and then cooled down to room temperature. The black precipitate was washed by centrifugation and re-dispersion into ethanol and toluene for several times before drying at 80 °C overnight.

Materials Characterization. Powder X-ray diffraction (XRD) patterns were recorded using a Bruker diffractometer (D8 Advance X-ray diffractometer, Cu K\textsubscript{α}, $\lambda = 1.5406$ Å, 40 kV and 40 mA) to study the crystallographic information of the samples. Field-emission scanning electron microscopy (FESEM; JEOL, JSM-6700F, 5 kV) equipped with energy dispersive X-ray spectroscopy (EDX) was used to analyze the morphology and elemental composition of the samples. The morphology and microstructure of the products were further studied by transmission electron microscopy (TEM; JEOL, JEM-2010, 200 kV) and high-resolution transmission electron microscopy (HRTEM; JEOL, JEM-2100F, 200 kV). Selected-area electron diffraction (SAED) was performed to study the
crystallinity and structure of the samples.

*Electrochemical Measurements.* The electrochemical activities of the PtCu₃ nanocages and commercial Pt (20 wt%; JM) electrocatalysts were characterized by cyclic voltammetry (CV) and chronoamperometry (CA) techniques. The measurements were performed using a three-electrode cell with a CHI660 electrochemical workstation at ambient temperature. Typically, the catalyst dispersion was prepared by mixing 8 mg of catalyst in 2.5 mL of solution containing 2.4 mL of ethanol and 100 µL of 5 wt % Nafion solution followed by untrasonication for 30 min. Glassy carbon (GC) disk electrode (5 mm in diameter) served as the substrate for the support. Prior to use, the GC electrode was polished using aqueous alumina suspension. And then the catalyst suspension was pipetted using a micropipettor onto the GC surface to make a Pt loading of about 0.2 mg cm⁻². The working electrode was dried under N₂ flow at room temperature. A saturated calomel electrode (SCE) and a large-area Pt plate were used as the reference electrode and the counter electrode, respectively. The electrochemical dealloying process was carried out at a scan rate of 100 mV s⁻¹ within the potential range from -0.241 to 1 V vs. SCE in a 0.1 M HClO₄ solution. After 200 cycles, the stable CV profile with a scan rate of 20 mV s⁻¹ was recorded. Methanol oxidation experiments were carried out in a solution containing 0.1 M HClO₄ and 1.0 M CH₃OH with a scan rate of 20 mV s⁻¹. CA curves were recorded at 0.75 V in a solution containing 0.1 M HClO₄ and 1.0 M CH₃OH for 1000 s to investigate the stability of the electrocatalysts.
Figure S1. a, b) Typical FESEM images of PtCu$_3$ cubic nanocages. The inset of Figure S1b shows the 3D architecture of PtCu$_3$ nanocages. c) A representative EDX spectrum of the PtCu$_3$ nanocages. The additional Si signals arise from the substrate.
Figure S2. Powder X-ray diffraction (XRD) pattern of PtCu₃ cubic nanocages. The standard diffraction peaks for Pt and Cu metals are also shown for comparison.

Figure S3. TEM image (a) and corresponding elemental mapping for Cu (b) and Pt (c).
**Figure S4.** TEM images of Cu-Pt products obtained with addition of different amounts of CTAB in the synthesis while keeping other conditions unchanged; a) 0 mg, b) 10 mg, c) 50 mg and d) 150 mg.

**Figure S5.** a, b) TEM images of Pt-Cu nanocages after the electrochemical dealloying process.
Figure S6. EDX spectrum of Pt-Cu cubic nanocages after the electrochemical dealloying process, which shows that the atomic ratio of Pt and Cu is about 3:1.

Figure S7. a) XRD pattern and b) TEM image of the commercial Pt (JM, 20 wt%) electrocatalyst.
**Figure S8.** Powder X-ray diffraction (XRD) pattern of PtCuₓ nanoparticles. The standard diffraction peaks for Pt and Cu metals are also shown for comparison.

**Figure S9.** EDX spectrum of PtCuₓ nanoparticles showing that the atomic ratio of Pt and Cu is about 1:9.
**Figure S10.** Cyclic voltammetric (CV) profiles of solid PtCu$_x$ nanoparticles.

**Figure S11.** EDX spectrum of PtCu$_x$ nanoparticles after the electrochemical dealloying process, which shows that the atomic ratio of Pt and Cu is about 1:3. Initially, x is ~9 from energy dispersive X-ray analysis.