

Supporting Information Available

One-Pot Fabrication of Single-Crystalline Octahedral Pt–Cu Nanoframes and Their Enhanced Electrocatalytic Activity

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Experimental Details

Reagents: Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) was analysis reagent (A.R.) and purchased from Beijing research institute for nonferrous metals. Copper chloride (CuCl_2), Poly(vinylpyrrolidone) (PVP; MW= 30000), glycine, NaI, ethanolamine, amino-1-butanol, isopropanol amine, ethylene glycol, ethylenediamine, methanol, and ethanol were A. R. and purchased from Sinopharm Chemical Reagent Co. Ltd. Sulfuric acid was A.R. and purchased from Beijing Chemical Reagent Company. All reagents were used as received without further purification. The water used in all experiments was ultrapure (Millipore, 18.2 M Ω).

Synthesis of octahedral Pt–Cu nanoframes: In a typical synthesis of oct ahedral Pt–Cu nanoframes, PVP (400mg), NaI (75 mg), glycine (300 mg), 1 mL of 20 mM CuCl_2 aqueous solution, 1 mL of 20 mM H_2PtCl_6 aqueous solution, and 0.75mL ethanolamine was added into 3.25 mL deionized water, respectively. The mixture was magnetically stirred for 5 minutes at room temperature until it turned transp arent. The result ant homogeneous yellowish-green solution was transferred to a T eflon-lined stainless-steel autoclave. Then the sealed v essel was kept at 200 °C for 2 h and finally cooled down to room temperature. At last, the resulting black product was sep arated via centrifugati on at 11000 rpm for 15 minutes and further purified by water and ethanol for several times.

Characterization: The X-ray dif fraction (XRD) p atterns were p erformed on a Bruker D8-advance X-ray powder diffractometer operated at 40 kV voltage and 40 mA current with $\text{CuK}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$). The morphology and size of the products were determined by a HITACHI H-7700 transmission electron microsc ope (TEM) at 100 kV , and a FEI Tecnai G2 F20 S-Twin high-resolution transmission electron microscope (HRTEM) equipped with energy dispersive X-ray spectroscopy (EDS) at 200 kV. TEM samples were prepared by using ethanol dispersion of final product s onto carbon-coat ed Mo or Ni grids followed by the solvent

evaporation. EDS and the high-angle annular dark-field scanning TEM (HAADF-STEM) were determined by a FEI Tecnai G2 F20 S-Twin HRTEM operating at 200 kV. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine the concentration of octahedral Pt-Cu nanoframes.

Electrochemical measurements: Electrochemical experiments were carried out using a CHI 650D electrochemical analyzer (CHI Instrument, USA). A conventional three-electrode cell was used, including a saturated calomel electrode (SCE) as the reference electrode, a Pt wire as the counter electrode, and a glassy carbon (GC) electrode (3 mm in diameter) as the working electrode. All the electrode potentials in this paper are quoted versus the SCE.

A GC electrode was carefully polished with Al_2O_3 paste, and washed with ethanol and deionized water before use. After the electrode was dried in the air, the water dispersion of Pt-Cu alloy NCs was cast onto the surface of the pretreated GC electrode using a microsyringe with the Pt loading of ca. 3.2 μg . It should be noted that the concentration of octahedral Pt-Cu nanoframes dispersed in aqueous solution was determined by ICP-OES measurements. The solvent was allowed to evaporate under an IR lamp. Then the electrode was covered with 2 μL of 0.5 wt% Nafion alcohol solution (Alfa Aesar) and dried in air for 0.5 h. For Pt black or Pt/C catalysts, 8 μL of the aqueous dispersion of Pt black (Alfa Aesar; 0.75 mg mL^{-1}) or Pt/C (20 wt% of Pt nanoparticles supported on carbon black, Alfa Aesar; 0.75 mg mL^{-1}) was transferred onto the GC electrode.

The electrolyte was fresh made 0.5 M H_2SO_4 + 0.25 M CH_3COOH solutions and bubbled with N_2 for 30 min before electrochemical measurements. Cyclic voltammetry (CV) measurements were performed under a N_2 flow at room temperature, and the potential was scanned from -0.2 to 1.0 V (vs. SCE) at a sweep rate of 50 mV s^{-1} . The electrochemically active surface area (ECSA) of each sample was estimated by CV measurements carried out in fresh nitrogen-saturated 0.5 M H_2SO_4 solution, and the potential was scanned from -0.24 to 1.0 V (vs. SCE) at a sweep rate of 50 mV s^{-1} .

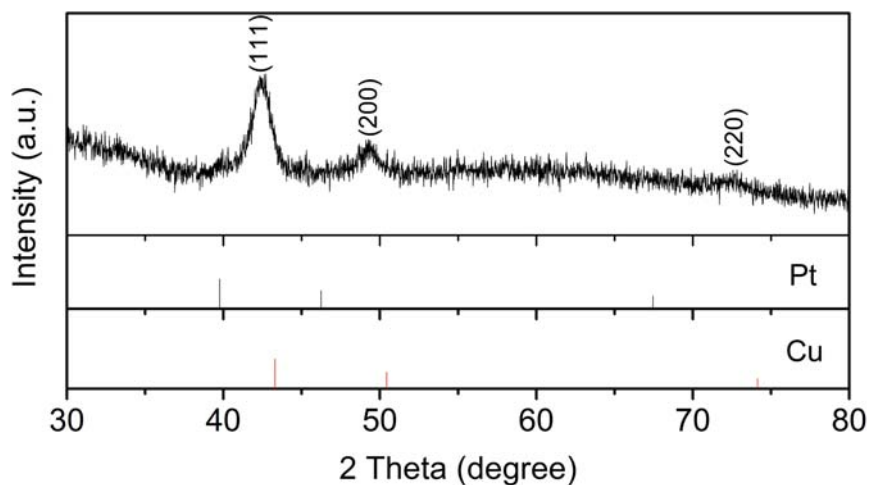


Figure S1. XRD pattern of as-prepared octahedral Pt-Cu nanoframes.

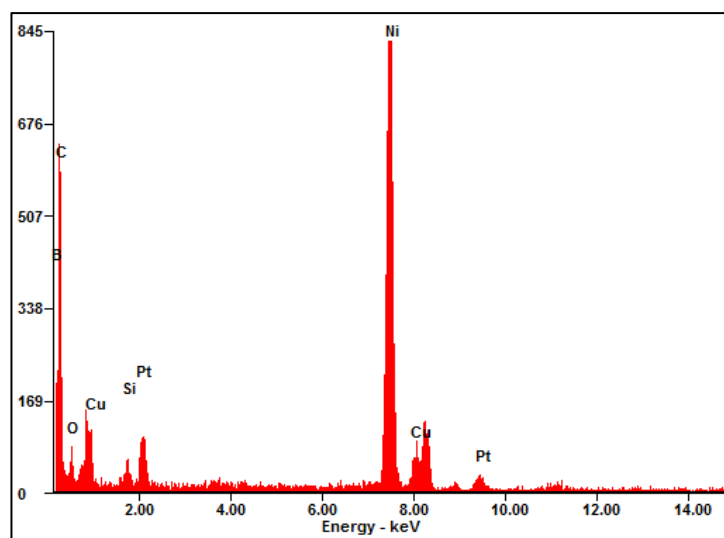


Figure S2. A representative EDS spectrum of as-prepared octahedral Pt-Cu nanoframes, which shows that the atomic ratio of Cu and Pt is about 2:1.

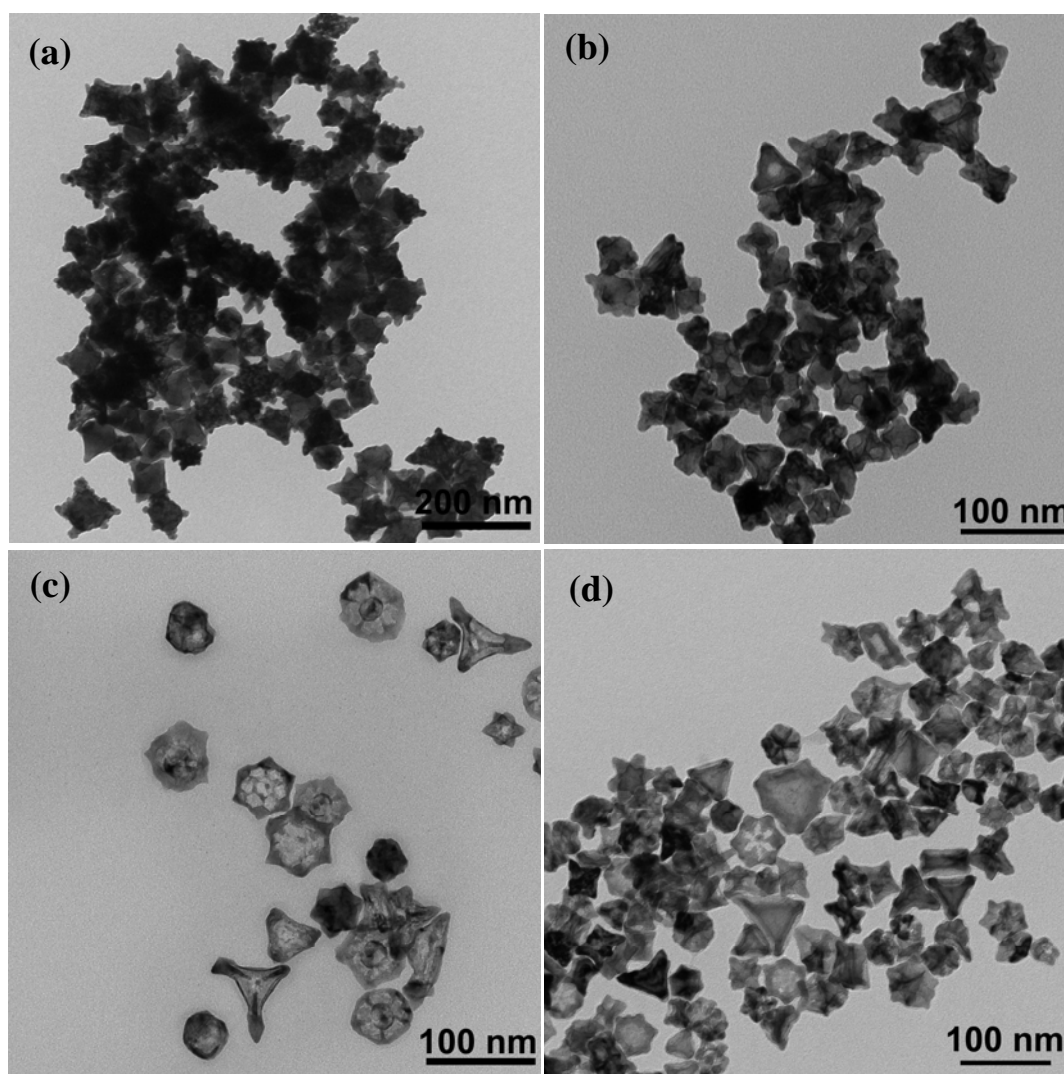


Figure S3. TEM images of octahedral Pt-Cu nanoframes synthesized by the standard procedure, except the change in amount of glycine: (a) 0 mg, (b) 50 mg, (c) 150 mg, (d) 400 mg.

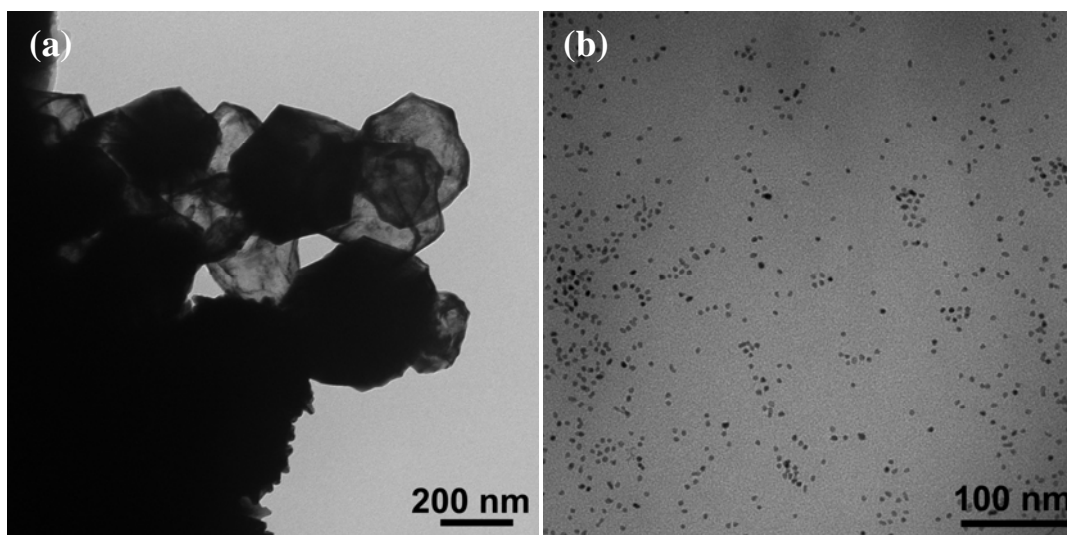


Figure S4. TEM image of octahedral Pt-Cu nanoframes synthesized using the standard procedure but in absence of: (a) NaI, and (b) ethanolamine, respectively.

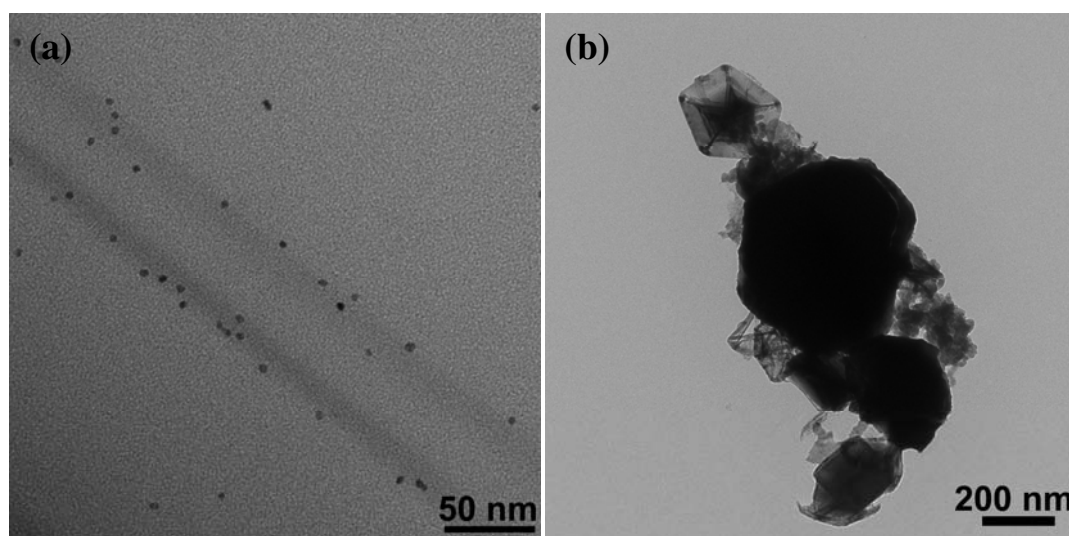


Figure S5. TEM images of the product synthesized using the standard procedure, but using other reagents instead of ethanolamine: (a) ethylene glycol, (b) ethylenediamine.

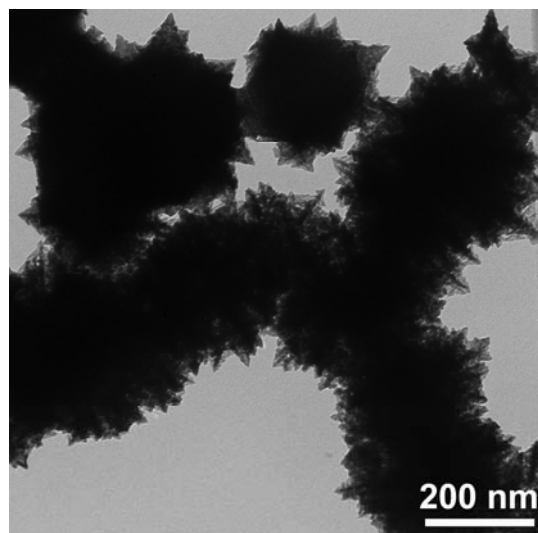


Figure S6. TEM image of octahedral Pt-Cu nanoframes synthesized using the standard procedure but without PVP.

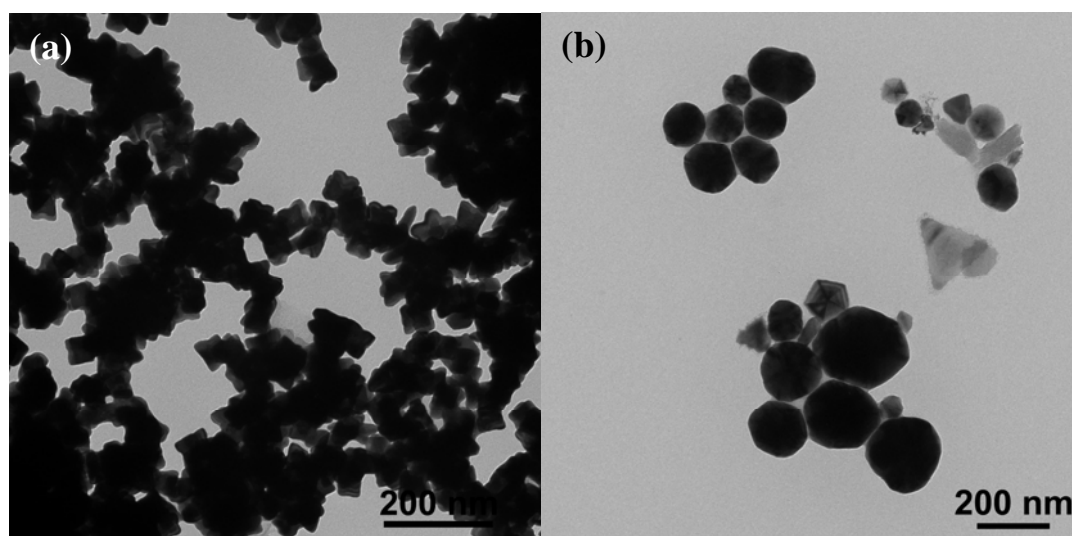


Figure S7. TEM image of octahedral Pt-Cu nanoframes synthesized using the standard procedure but without: (a) CuCl_2 , (b) H_2PtCl_6 . It is worth noting that total volume of solution was kept 6 mL in all experiments.

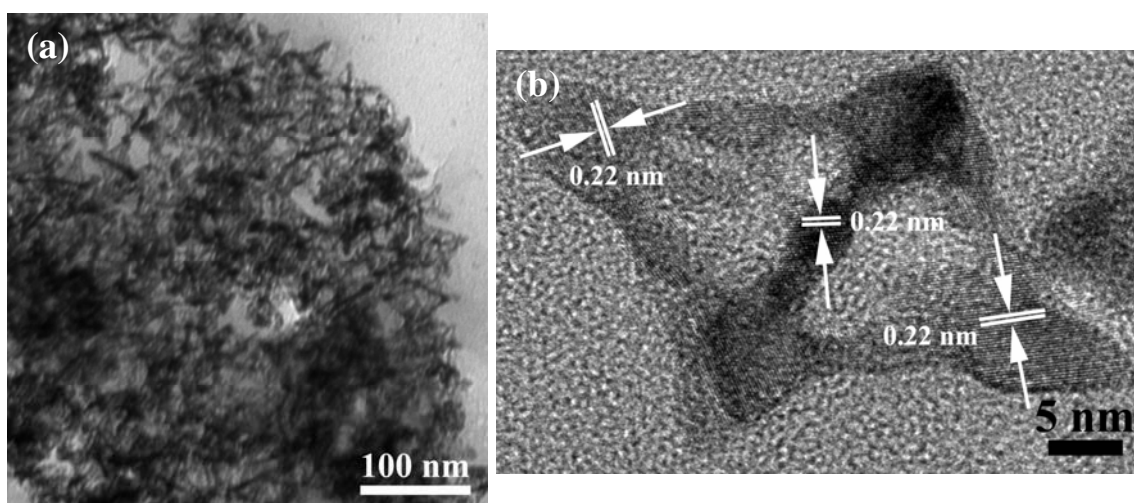


Figure S8. TEM (a) and HR TEM (b) images of octahedral Pt-Cu nanoframes after the electrochemical dealloying process. It is worth noting that the crystal structure of octahedral nanoframes could be well maintained after the electrochemical measurement.

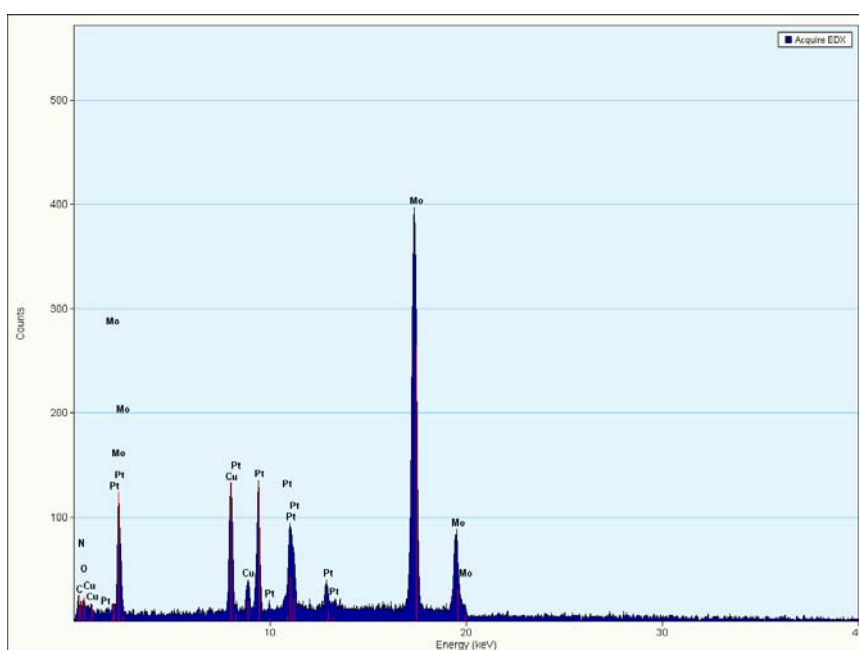


Figure S9. EDX spectrum of octahedral Pt-Cu nanoframes after the electrochemical dealloying process. The result shows that the atomic ratio of Pt and Cu is about 2: 1.

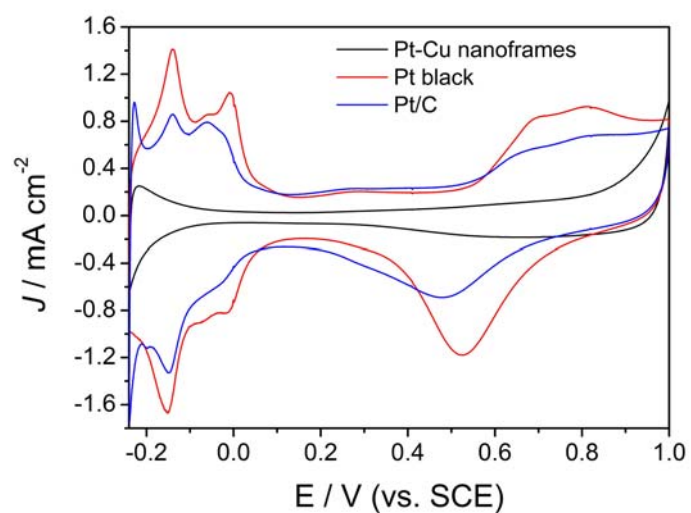


Figure S10. CVs of octahedral Pt-Cu nanoframes, commercial Pt black and Pt/C catalysts. It is noted that the Pt loading of octahedral Pt-Cu nanoframes, commercial Pt black and Pt/C is 3.2, 6, 1.2 μg , respectively; While for the catalyst loading, it is 5.3, 6, 6 μg , respectively.