

Supporting information for

Highly Open Rhombic Dodecahedral PtCu Nanoframes

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1: Materials and methods

1.1 Chemicals: Platinum(II) acetylacetonate (Pt(acac)₂, 97%), copper(II) acetylacetonate (Cu(acac)₂, 97%), cetyltrimethylammonium chloride (CTAC, AR), oleic acid (CH₃(CH₂)₇CH=CH(CH₂)₇COOH, ≥99%) and oleylamine (CH₃(CH₂)₇CH=CH(CH₂)₇CH₂NH₂, 68-70%) were all purchased from Sigma-Aldrich. Copper (II) chloride dihydrate (CuCl₂•2H₂O, reagent grade), ascorbic acid (C₆H₈O₆, AA, reagent grade), glucose (C₆H₁₂O₆, reagent grade) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All the chemicals were used as received without further purification. The water (18 MΩ/cm) used in all experiments was prepared by passing through an ultra-pure purification system (Aqua Solutions).

1.2 Preparation of PtCu nanoframes: In a typical preparation of PtCu nanoframes, platinum(II) acetylacetonate (Pt(acac)₂, 5.0 mg), copper(II) chloride dihydrate (CuCl₂•2H₂O, 50.0 mg), glucose (60.0 mg), 2 mL of oleic acid and 8 mL of oleylamine were added into a vial (volume: 30 mL). After the vial was capped, the mixture was ultrasonicated for around 2 hours. The resulting homogeneous mixture was then heated at 180 °C for 3 hours in an oil bath, before it was cooled to room temperature. The resulting colloidal products were collected by centrifugation and washed three times with an ethanol/cyclohexane mixture.

1.3 Characterizations: Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) were conducted on an FEI Tecnai F20 transmission electron microscope at an acceleration voltage of 200 kV. Scanning electron microscopy (SEM) images were taken with a Zeiss scanning electron microscopy. The samples were prepared by dropping ethanol dispersion of samples onto carbon-coated copper TEM grids using pipettes and dried under ambient condition. Powder X-ray diffraction (PXRD) patterns were collected on a Shimadzu XRD-6000 X-ray diffractometer. The

concentration of catalysts was determined by the inductively coupled plasma atomic emission spectroscopy (710-ES, Varian, ICP-AES).

1.4 Methanol electrooxidation measurements: A three-electrode cell was used to perform the electrochemical measurements. The working electrode was a glassy-carbon rotating disk electrode (RDE) (diameter: 5 mm, area: 0.196 cm²) from Pine Instruments. Ag/AgCl (3 M KCl) was used as reference electrode. Pt wire was used as counter electrode. 10 μ L of ethanol dispersion of PtCu nanoframes on C (0.265 mg Pt/mL) was deposited on a glassy carbon electrode to obtain the working electrodes, and dried in the air. The electrochemical active surface area (EASA) was determined by integrating the hydrogen adsorption charge on the cyclic voltammetry (CV) at room temperature in nitrogen-saturated 0.1 M HClO₄ solution. Before cyclic voltammetry measurements, 200 cycles of potential sweeps between -0.25 V and 0.96 V were applied. Methanol electrooxidation measurements were conducted in a 0.1 M HClO₄ + 1.0 M CH₃OH solution. The scan rate for methanol electrooxidation was 50 mV/s. For comparison, commercial Pt black and Pt/C were used as the benchmark catalysts. The Pt loadings were 10 μ g for commercial Pt black and 3 μ g for commercial Pt/C, respectively.

2: Supplementary Figures

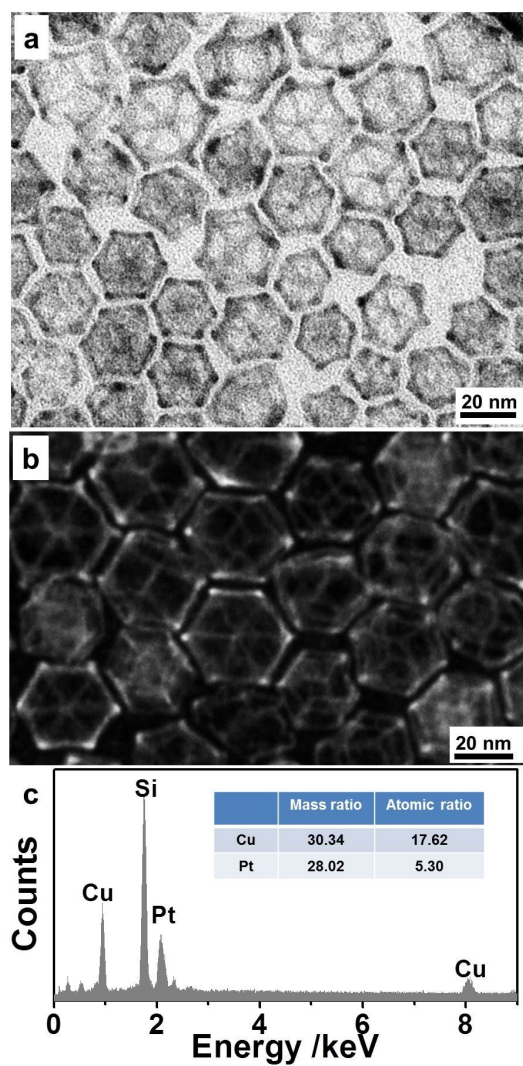


Figure S1. Additional low-magnification (a) TEM, (b) HAADF-STEM images, and (c) SEM-EDX of PtCu nanoframes.

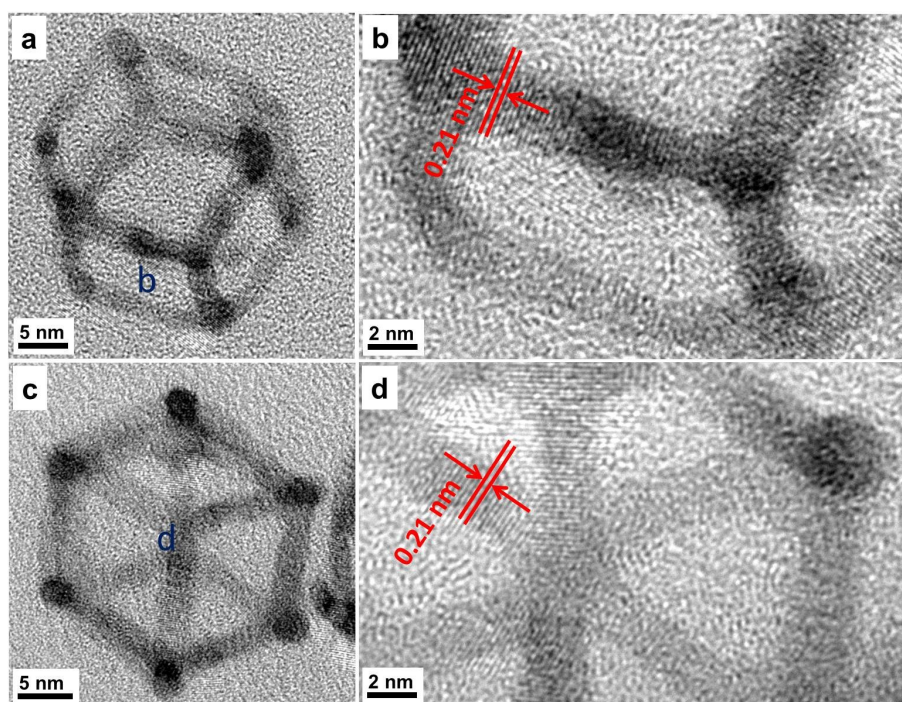


Figure S2. (a) High-magnification TEM of PtCu nanoframe and (b) HRTEM images of the indicated region in (a). (c) High-magnification TEM of PtCu nanoframe and (d) HRTEM images of the indicated region in (c).

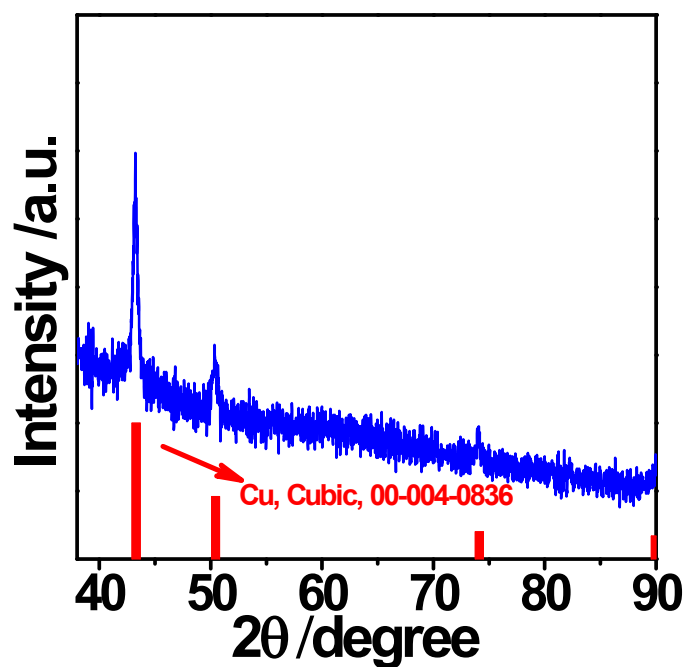


Figure S3. PXRD pattern of the intermediate product when the reaction time was 0.5 h.

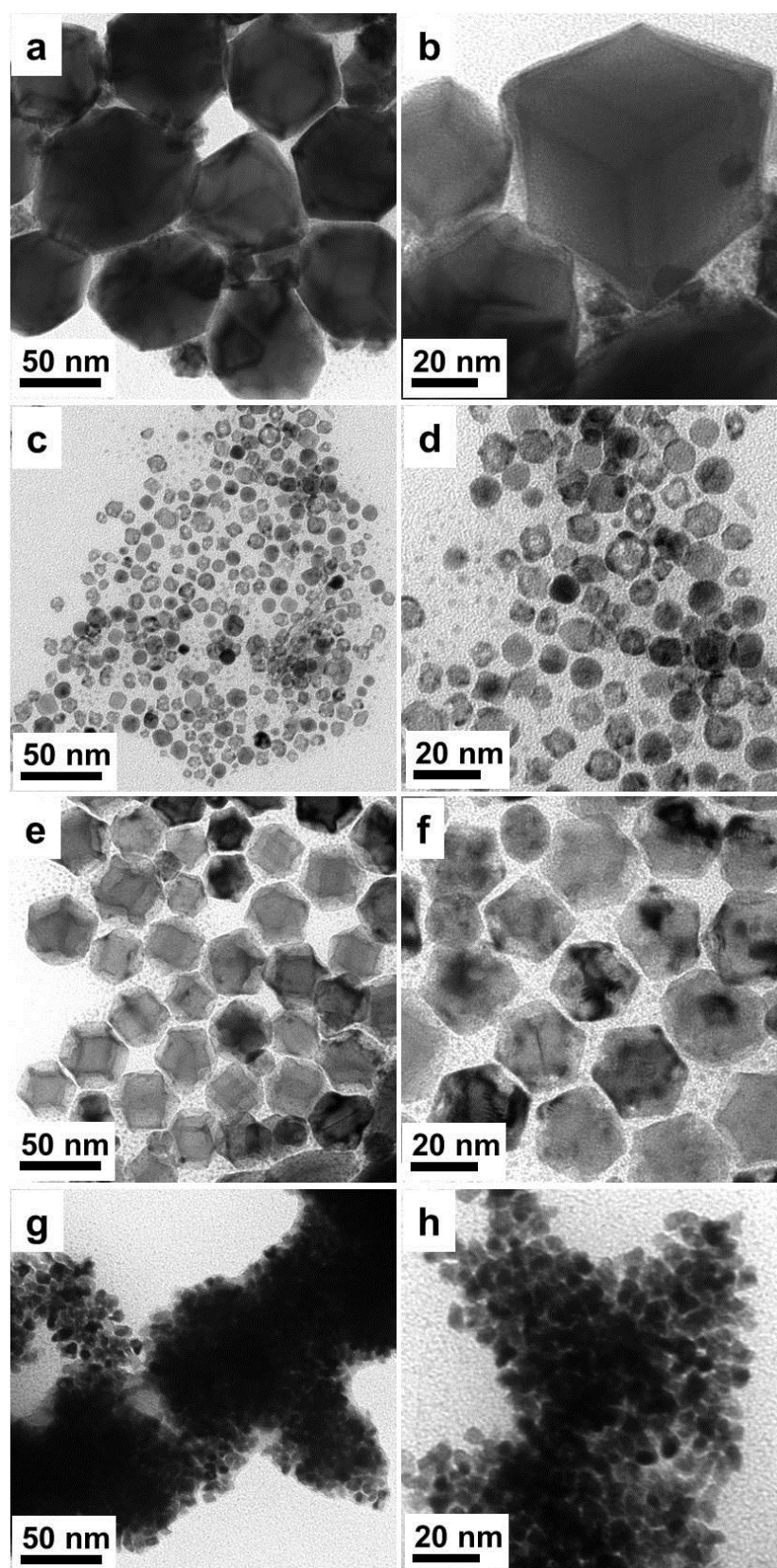


Figure S4. Representative TEM images of the products collected from the reaction with the same condition used in the synthesis of rhombic dodecahedral PtCu nanoframes but changing the solvent with (a, b) oleylamine:oleic acid=10: 0, (c, d) oleylamine:oleic acid=6:4, (e, f) oleylamine:oleic acid=1 : 9 and (g, h) oleylamine:oleic acid=0:10.

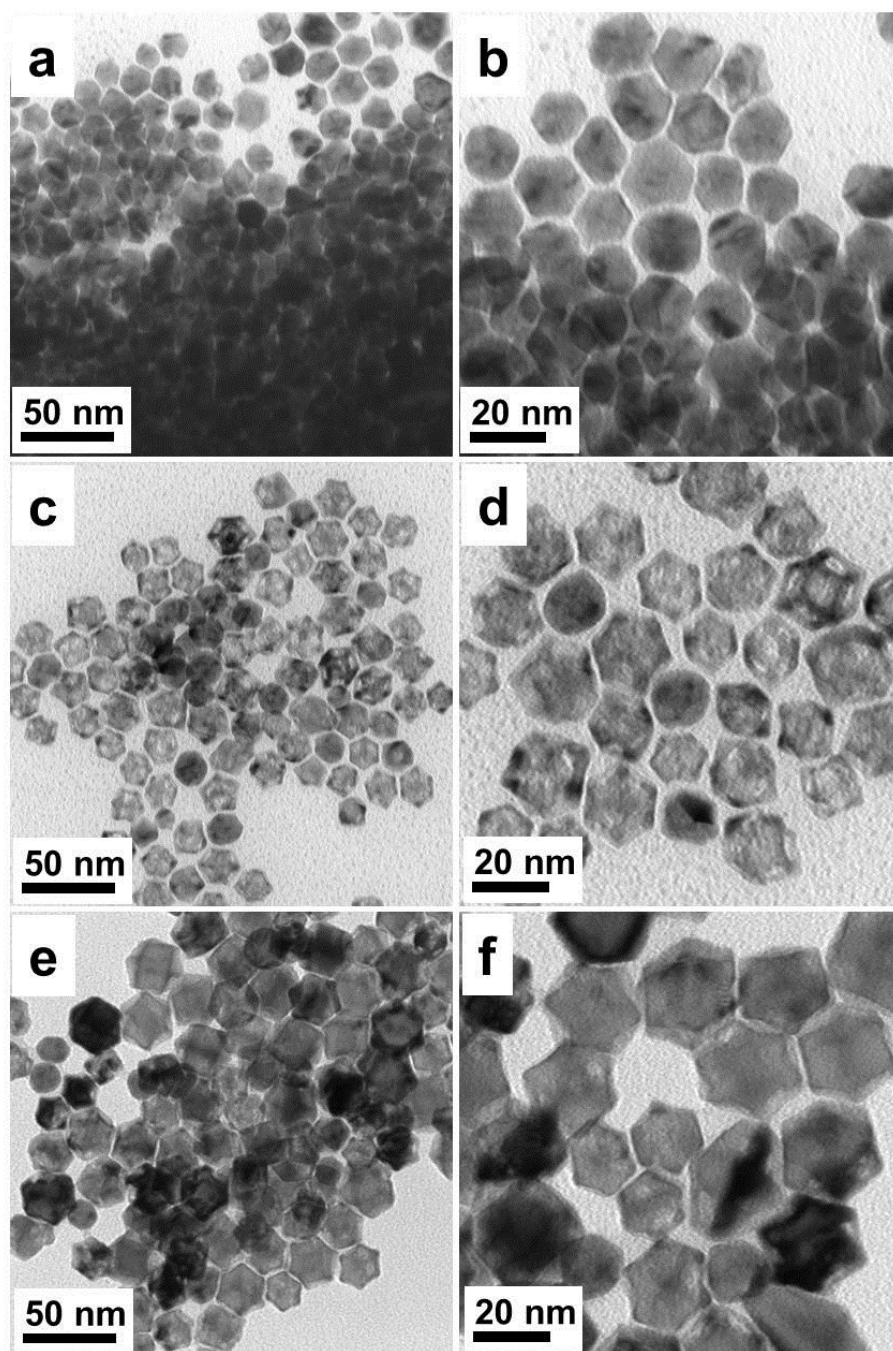


Figure S5. Representative TEM images of the products collected from the reaction with the same condition used in the synthesis of unique PtCu nanoframes but with different amount of glucose: (a, b) 0 mg, (c, d) 30 mg and (e, f) 90 mg.

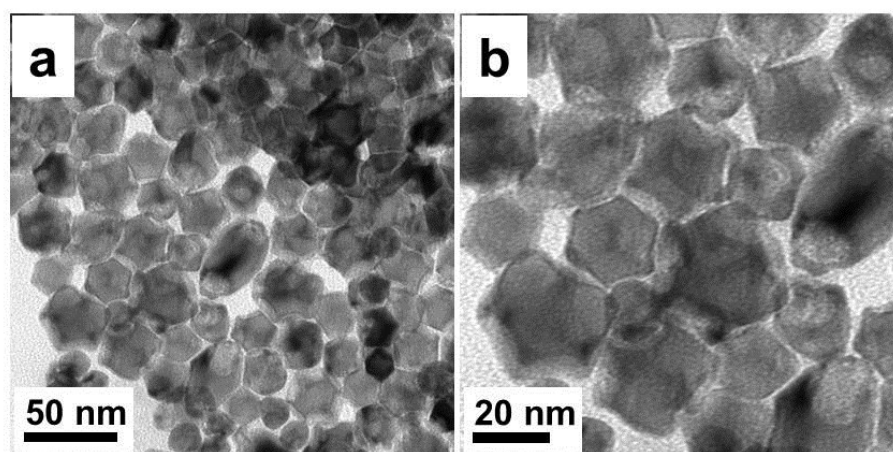


Figure S6. Representative TEM images of the products collected from the reaction with the same condition used in the synthesis of unique PtCu nanoframes but changing glucose with ascorbic acid.

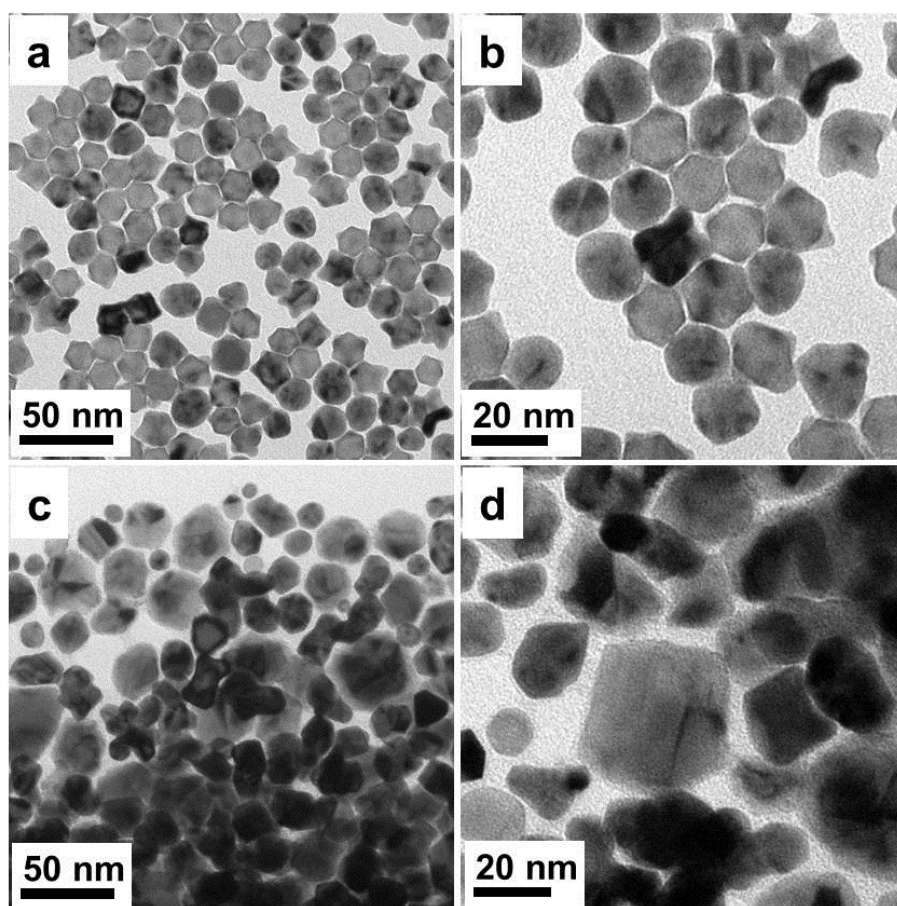


Figure S7. Representative TEM images of the products collected from the reaction with the same condition used in the synthesis of unique PtCu nanoframes but (a, b) changing $\text{Pt}(\text{acac})_2$ with H_2PtCl_6 and (c, d) changing CuCl_2 with $\text{Cu}(\text{acac})_2$.

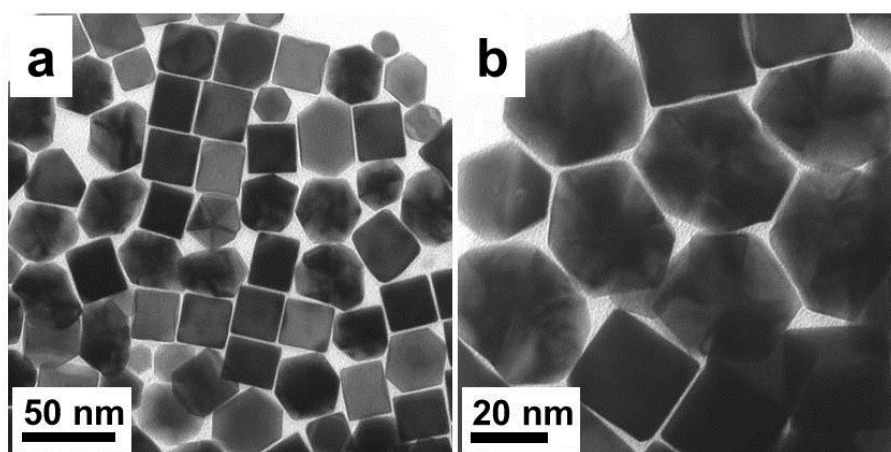


Figure S8. Representative TEM images of the products collected from the reaction with the same condition used in the synthesis of unique PtCu nanoframes but in the absence of any CuCl_2 .

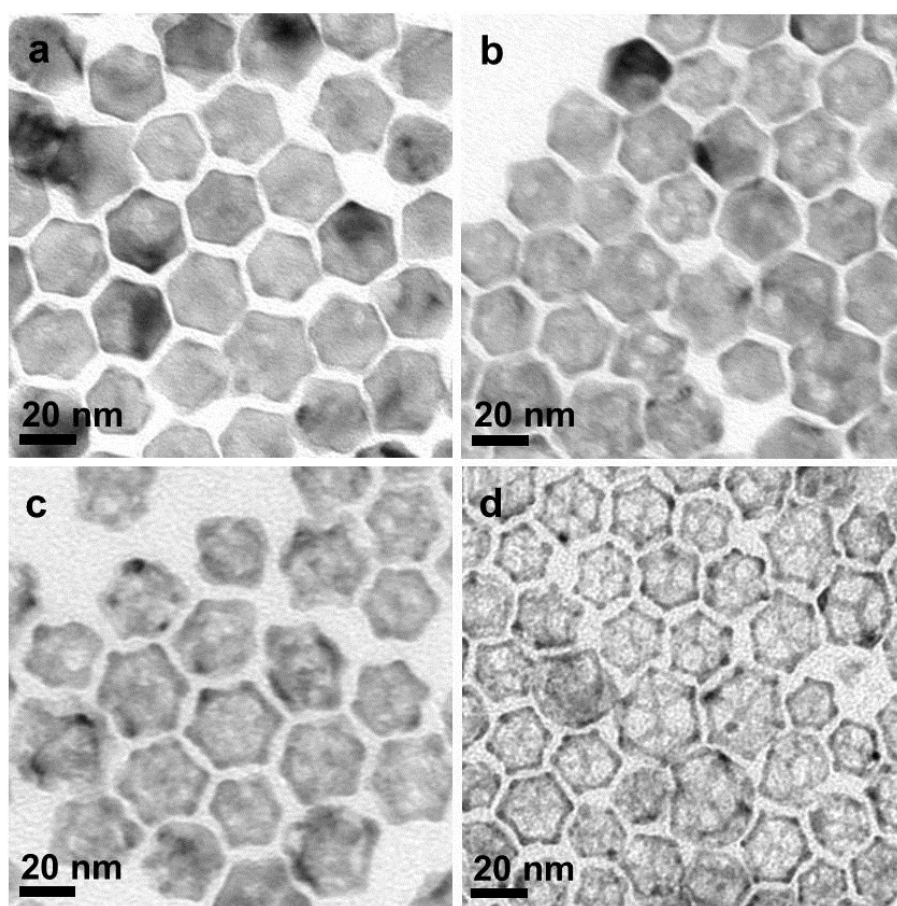


Figure S9. Representative TEM images of nanostructures prepared using the standard procedure, except for the use of different amount of CuCl_2 : (a) 12.5 mg, (b) 25.0 mg, (c) 37.5 mg, and (d) 50.0 mg.

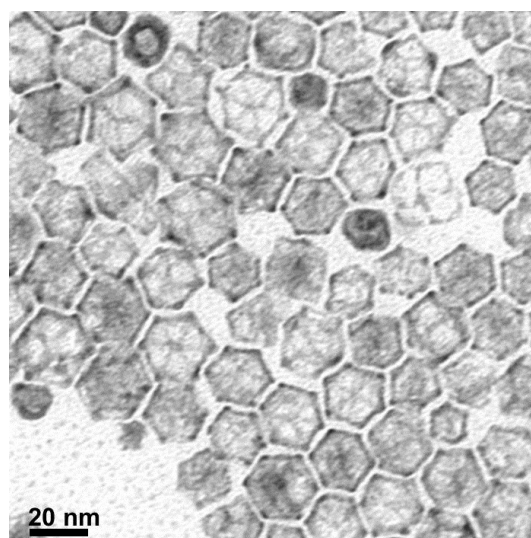


Figure S10. Representative TEM image of nanostructures prepared using the standard procedure, except for the use of different amount of CuCl_2 (25.0 mg) and additional CTAC (94.1 mg).

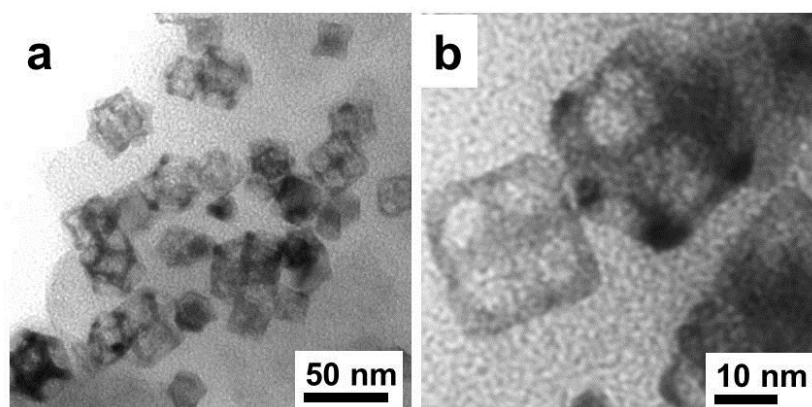


Figure S11. Representative TEM images of PtCu nanoframes on commercial carbon.

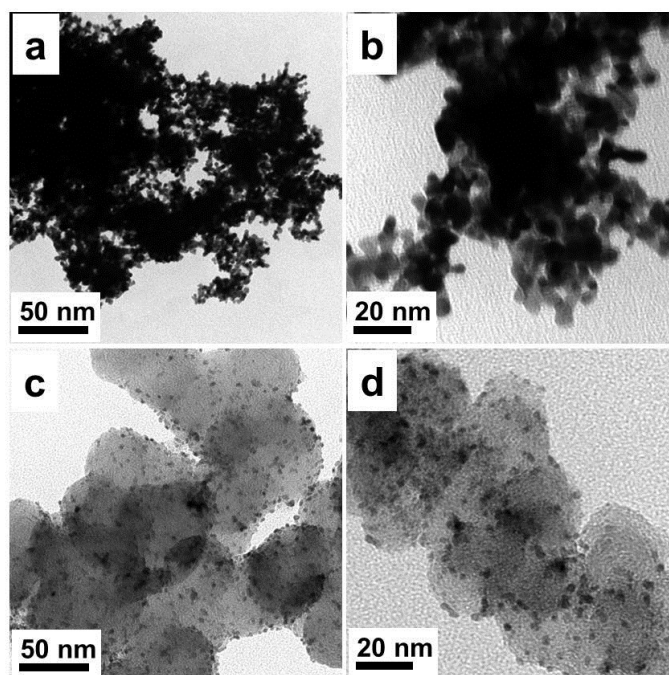


Figure S12. Representative TEM images of (a, b) commercial Pt black and (c, d) commercial Pt/C.

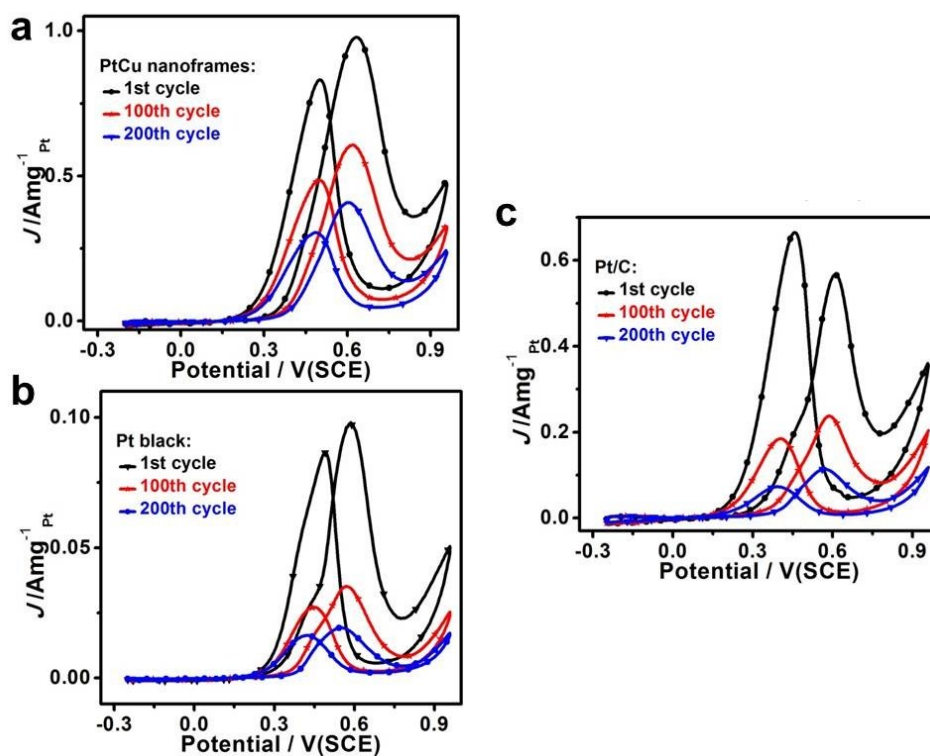


Figure S13. Cyclic voltammograms (1st, 100th and 200th cycle) of (a) PtCu nanoframes, (b) commercial Pt black and (c) commercial Pt/C for methanol electrooxidation. Potential was continuously scanned between -0.25 and 0.96 V for 250 cycles at 20 mV s⁻¹ in 0.1 M HClO₄ containing 1.0 M methanol.