Supporting Information

High Performance Electrocatalyst: Pt-Cu Hollow Nanocrystals

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Experimental Details

Preparation of hollow Pt-Cu nanocrystals. In a typical synthesis, 0.0125 g of K_2PtCl_6 was added into a solution containing 5 ml of oleylamine and 0.05 g of hexadecyl trimethyl ammonium bromide (CTAB) at 60 ^oC. After about 20 minutes of stirring, 0.02 g of $Cu(acac)_2$ was put into the reaction system and then the solution was transferred into a Teflon cup in a stainless steel-lined autoclave. The autoclave was maintained at 170 °C for 24 hours and then allowed to cool to room temperature. The final products were collected and washed with ethanol for several times.

Preparation of Pt Nanoparticles. 0.01g of $Pt(acac)_2$ was added into 5 mL of oleylamine at 60 ^oC. The resulted homogeneous solution was then treated under the same conditions as those used in the preparation of hollow Pt-Cu nanocrystals.

Characterization of the synthesized nanocrystals. The powder X-ray diffraction (XRD) patterns were recorded with a Bruker D8-advance X-ray powder diffractometer with Cu Kα radiation (λ= 1.5406 Å). Transmission electron microscopy (TEM) images were obtained with a Hitachi H-7650B transmission electron microscope operating at 100 kV. High-resolution TEM (HR-TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) characterizations were performed with a FEI Technai G2 F30 Super-Twin transmission electron microscope operating at 200 kV after placing a drop of the synthesized nanocrystals on carbon-coated Mo grids (200 mesh). Energy dispersive spectroscopies (EDS) were recorded to determine the compositions of the obtained products. The contents of hollow Pt-Cu nanocrystals were determined by inductively coupled plasma mass spectrometry (ICP-MS, X Series). Fourier transform infrared spectra (FT-IR) were measured by using a Nicolet 5700 FT-IR spectrometer. X-ray photoelectron spectra (XPS) were acquired with a PHI-5300 ESCA1610 SAM instrument equipped with Mg Kα X-ray exciting source (1253.6 eV) operating at 10 kV and 10 mA. To prepare the samples, Si wafers were washed thoroughly with ethanol and de-ionized water. After dropping the products on these cleaned Si wafers, they were dried under room temperature. To correct for charging, the binding energies (BE) were referred to the C1s peak at 284.8 eV.

Electrochemical measurement

The weight loading of carbon black supported precursor catalyst was 20 wt%. The catalyst was prepared by mixing Pt-Cu hollow nanoparticles and carbon black in 20 mL of hexane and then sonicated for 2 hours (to ensure complete adherence of the nanoparticles onto the carbon support). After evaporation of hexane, 20 mL of acetic acid was added to the dispersion and heated for 12 hours at 70 ^{o}C. The nanoparticles on the carbon support were separated by centrifugation and re-dispersed in de-ionized water to form a 1 mg/mL suspension. For comparison, the concentrations of commercial Pt/C and Pt black are equal to that of Pt-Cu hollow nanoparticles.

Electrochemical measurements were conducted in an electrochemical cell with a three-electrode configuration at room temperature. A Pt wire was used as the counter electrode, and a silver chloride electrode (Ag/AgCl) was used as the reference electrode. The working electrode was a glassy carbon disk with a diameter of 3.0 mm, polished with Al_2O_3 paste, and washed thoroughly with de-ionized water before 5 μL of each catalyst was dropped on the glassy carbon electrode. After the electrode was dried, 5 μL Nafion dilutes (0.1 wt%) was coated on the catalyst surface. Aqueous solutions of 0.5 M H_2SO_4 and 0.5 M H_2SO_4 containing 1 M methanol were used for the electrolytes.

The electrochemical surface area (ECSA) was estimated by measuring the charges associated with H_{upd} adsorption/desorption (Q) between -0.15 and 0.1 V after double-layer correction and assuming a value of 210 mC/cm^2 for the adsorption of a monolayer of hydrogen onto a Pt surface (qH). Then, the specific ECSA was calculated based on the following relation: specific ECSA=0.5Q/(mqH), where Q is the charge associated with H_{upd} adsorption or desorption, m is the mass of loaded metal, and qH is the charge required for the adsorption of a monolayer of hydrogen on a Pt surface.

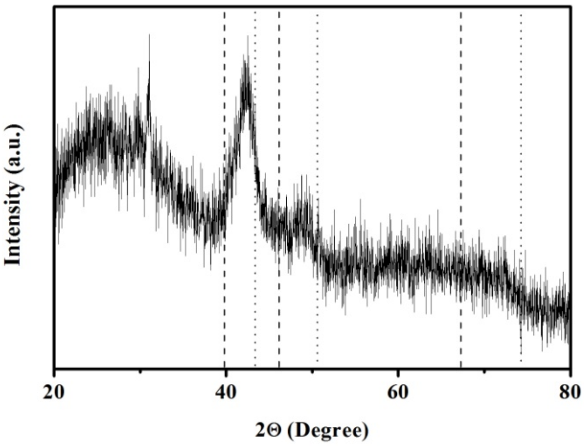


Fig. S1 XRD pattern of the synthesized Pt–Cu hollow nanocrystals. (------ Pt (111), (200) and (220); ……Cu (111), (200) and (220)).

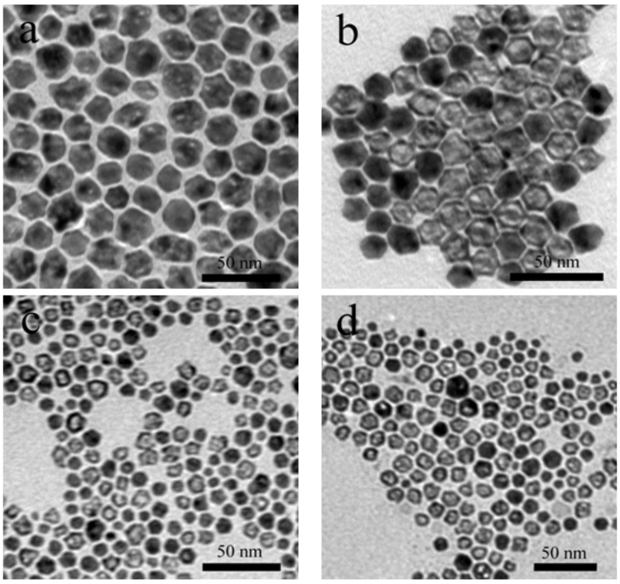


Fig. S2 TEM images of the nanoparticles synthesized by using different amounts of CTAB: a) 0; b) 0.025 g; c) 0.05 g; d) 0.075 g.

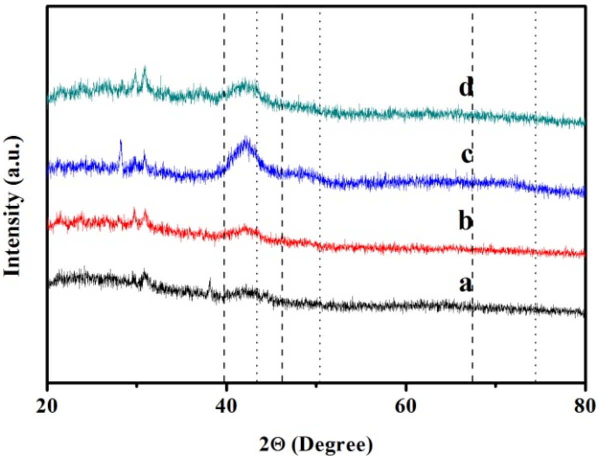


Fig. S3 XRD of the nanoparticles synthesized by using different amounts of CTAB: a) 0; b) 0.025 g; c) 0.05 g; d) 0.075 g. (------ Pt (111),(200) and (220); …… Cu (111), (200) and (220)).

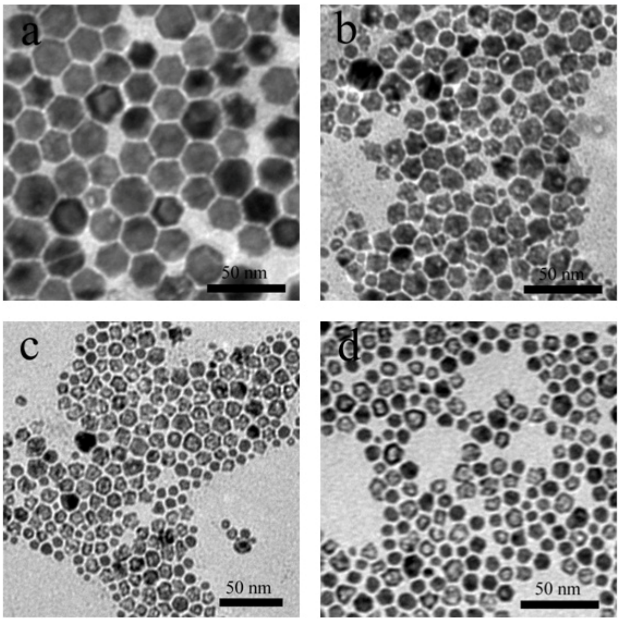


Fig. S4 TEM images of the synthesized nanoparticles collected at different reaction times: a) 4 h; b) 12 h; c) 16 h; d) 24 h during 24 h of reaction.

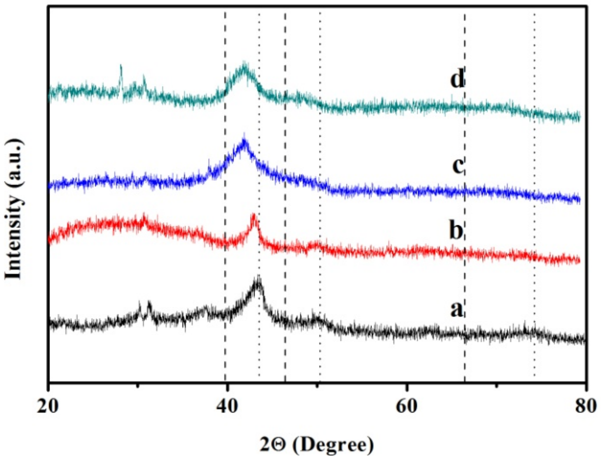
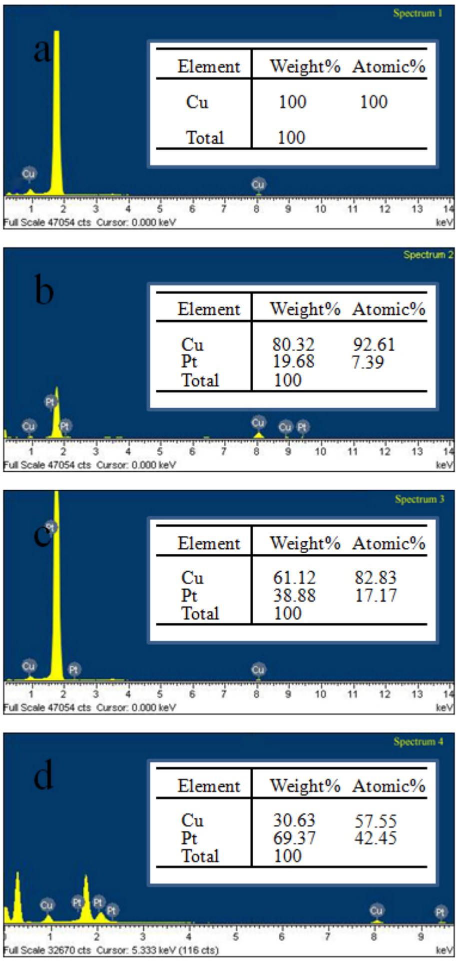


Fig. S5 XRD of the synthesized nanoparticles collected at different reaction times: a) 4 h; b) 12 h; c) 16 h; d) 24 h during 24 h of reaction. (------Pt (111), (200) and (220); …… Cu (111), (200) and (220)).



Element	Weight%	Atomic%
Cu	100	100
Total	100	

Element	Weight%	Atomic%
Cu	80.32	92.61
Pt	19.68	7.39
Total	100	

Element	Weight%	Atomic%
Cu	61.12	82.83
Pt	38.88	17.17
Total	100	

Element	Weight%	Atomic%
Cu	30.63	57.55
Pt	69.37	42.45
Total	100	

Fig. S6 EDS of Pt-Cu nanocrystals and analytical results of their chemical compositions obtained at different reaction times: a) 4 h; b) 12 h; c) 16 h; d) 24 h.

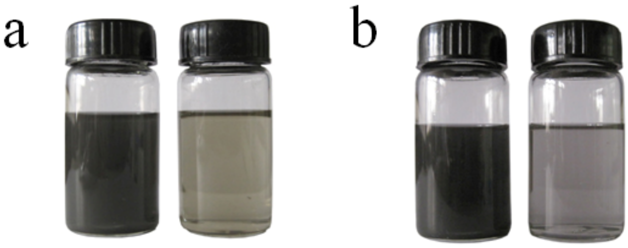


Fig. S7 The dark color indicating a lot of K_2PtCl_6 reduced in OAm and the light color implying only a very small part of K_2PtCl_6 reduced in OAm and CTAB. a) Before washing the product with ethanol for three times; b) After washing the product with ethanol for three times.

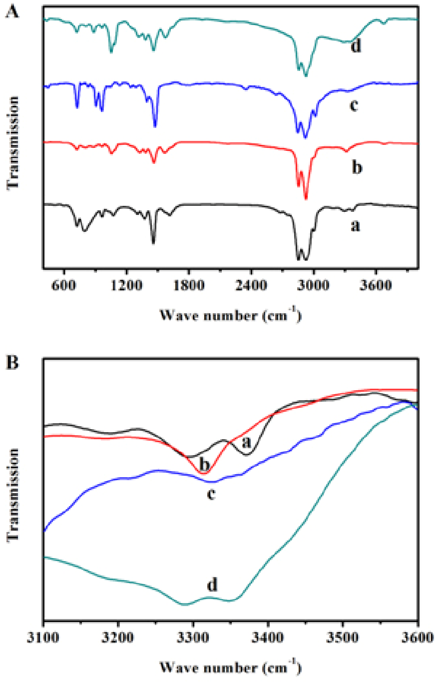


Fig.S8 FT-IR spectra: A) OAm (a), K_2PtCl_6 dissolved in OAm (b), CTAB (c) and K_2PtCl_6 dissolved in OAm-CTAB (d); B) Part of the spectra of (A).

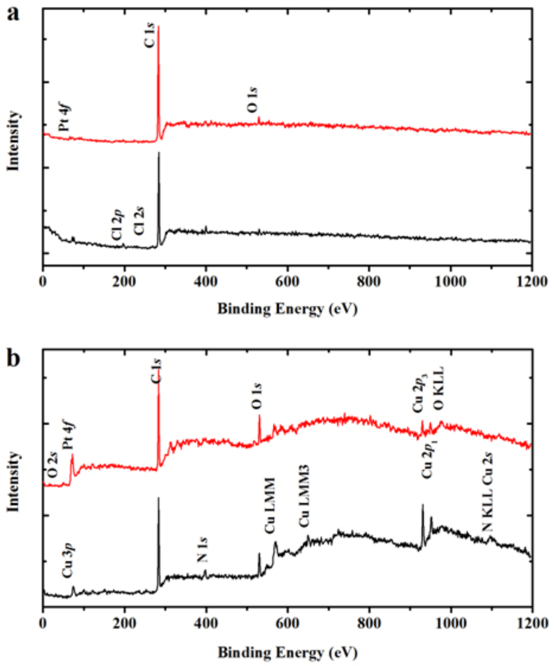


Fig. S9 XPS spectra: a) K_2PtCl_6 dissolved in OAm (black) and OAm-CTAB (red); b) Pt-Cu nanoparticles prepared in OAm (black) and OAm-CTAB (red).

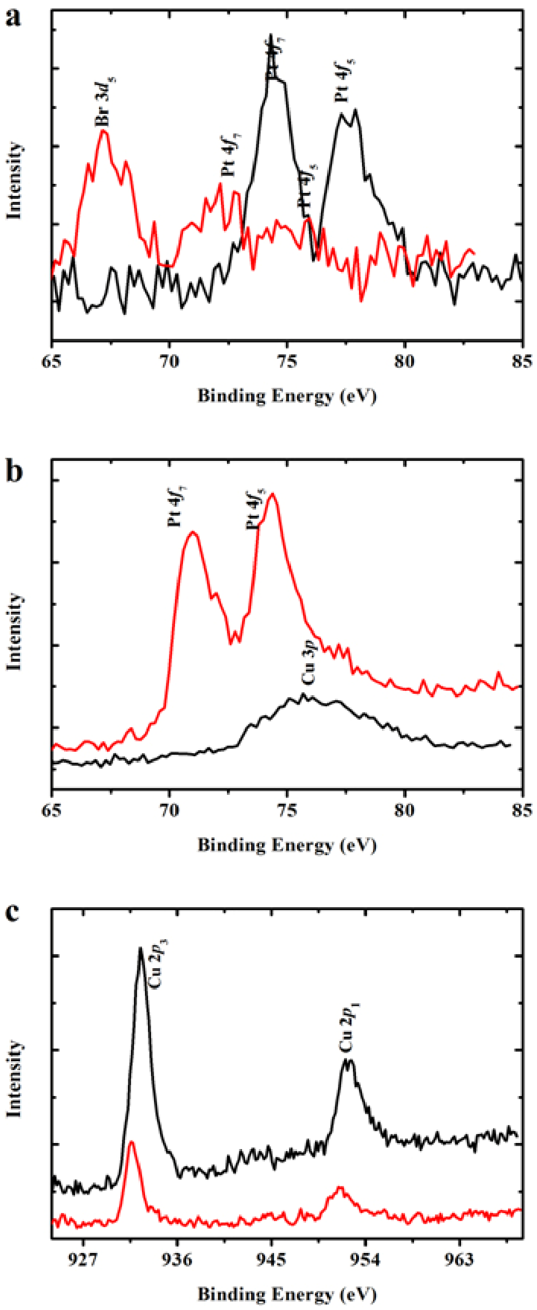


Fig. S10 Representative high-resolution XPS pectra: a) Pt 4f of K_2PtCl_6 in OAm (black) and OAm–CTAB (red); b) Pt 4f of Pt-Cu nanoparticles obtained with (red) or without (black) CTAB; c) Cu 2p of Pt-Cu nanoparticles obtained with (red) or without (black) CTAB.

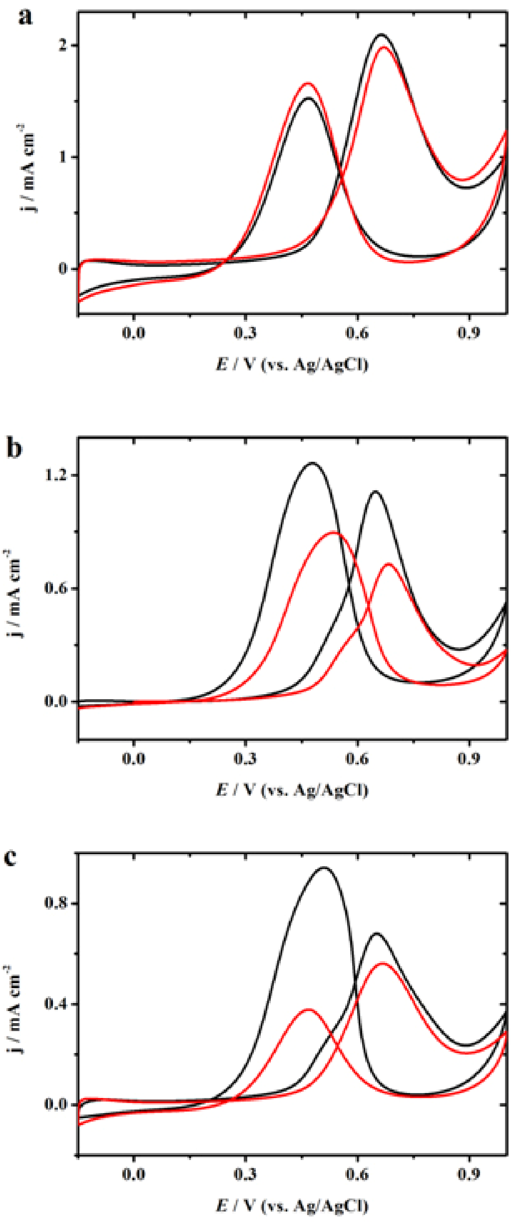


Fig. S11 Electrocatalytic stability test of hollow Pt-Cu nanocrystals, commercial Pt/C and Pt black. CV curves for (a) hollow Pt-Cu nanocrystals, (b) commercial Pt black and (c) commercial Pt/C before and after 1000 cycles of accelerated stability tests. The tests were carried out in 0.5 M H_2SO_4 containing 1 M methanol solutions with the cyclic potential between -0.15 and 1.0 V at a scan rate of 200 mV/s. The current of Pt-Cu nanocrystals drops less than commercial Pt/C and Pt black.