Supporting Information

Experimental Details

Materials: Platinum (II) pentanedionate (Pt(acac)₂, \geq 48.0% Pt basis), Copper (II) 2,4pentanedionate (Cu(acac)₂), and Nafion solution (5% w/w) were purchased from Alfa Aecar. Other materials were obtained from Beijing Chemical Reagents, China. All the chemicals were used without further purification.

Characterization: The powder XRD patterns were recorded with a Bruker D8advance X-ray powder diffractometer with CuK α radiation ($\lambda = 1.5406$ Å). The size and morphology of as-synthesized samples were determined by using Hitachi model H-800 transmission electron microscope and JEOL-2010F high-resolution transmission electron microscope. The composition of the product was measured by the inductively coupled plasma-mass spectrometry and energy dispersive X-ray spectrometer.

Electrochemical were conducted measurements on а computer-controlled electrochemical analyzer (CHI 660D, Chenhua, China) at room temperature. Pt/C or Pt-Cu modified glassy carbon (GC) electrodes were used as working electrodes, platinum spiral wire as counter electrode and Ag/AgCl (KCl-saturated) electrode as reference electrode. GC substrate electrodes were first polished with 0.3 and 0.05 um Al₂O₃ slurry on a polishing cloth and then sonicated in ethanol and water each for several times. After the electrode was dried, 5 µL Nafion dilutes (0.05 wt%) was coated on the catalyst surface. Aqueous solutions of 0.5 M H₂SO₄ and 0.5 M H₂SO₄ containing 1 M methanol were used for the electrolytes. All electrochemical experiments were performed at room temperature. The specific electrochemical surface area (ECSA) of each sample was calculated based on the following equation : EASA = $Q_H/0.21m_{[Pt]}$, where Q_H is the amount of charge exchanged during the adsorption or desorption of hydrogen atoms on Pt, the correlation constant of 0.21 (mC/cm²) represents the charge required to oxidize a monolayer of hydrogen onto a Pt surface; m_[Pt] represents the platinum loading.

Catalytic Properties: For a typical run, p-chloronitrobeneze (0.5 mmol) and PtCu/C or Pt/C catalyst (0.01 mmol catalyst based on Pt) were placed in a 10 mL flask with ethanol (3 mL) as the solvent. A H₂ balloon was introduced after the flask was purged with H₂ for 5 minutes. The reaction was performed at room temperature (25°C) for the specified time then the catalyst was separated from the mixture by centrifugation. Liquid samples were analyzed by gas chromatography with a Thermo Finnigan chromatograph equipped with a flame ionization detector and a DB-WAX capillary column (J&W, 30 m, 0.25 mm i.d.) with nitrogen as the carrier gas.

Synthesis of Pt_{0.5}Cu_{0.5} NCs:

 $Pt(acac)_2$ (0.025 mmol), $Cu(acac)_2$ (0.025 mmol), benzoic acid (1.64 mmol) and CTAB (0.069 mmol), were dissolved in 5 mL of N, N-dimethylformamide, followed by 20 min vigorous stirring. The resultant homogeneous solution was transferred into a Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 120 °C

for 20 h. The resulting products were collected by centrifugation and washed several times with ethanol. The as-obtained octahedral Pt-Cu NCs were dispersed in ethanol. Synthesis of $Pt_{0.30}Cu_{0.70}$ NCs:

Pt(acac)₂ (0.025 mmol), Cu(acac)₂ (0.075 mmol), benzoic acid (1.64 mmol), heptanol (500 μ L) and CTAB (0.069 mmol), were dissolved in 5 mL of N, N-dimethylformamide, followed by 20 min vigorous stirring. The resultant homogeneous solution was transferred into a Teflon-lined stainless-steel autoclave. The sealed vessel was then heated at 150 °C for 12 h. The resulting products were collected by centrifugation and washed several times with ethanol. The as-obtained octahedral Pt-Cu NCs were dispersed in ethanol.

Synthesis of multi-octahedral Pto.5Cu0.5 NCs:

The synthetic protocols for the preparation of multi-octahedral Pt-Cu NCs were similar to that of octahedral $Pt_{0.5}Cu_{0.5}$ NCs except for replacing benzoic acid with decalin.

Supplementary Figures



Figure S1. The size distributions of $Pt_{0.50}Cu_{0.50}$ NCs, mean:9.8 nm.



Figure S2. EDX patterns of Pt-Cu NCs with different compositions.



Figure S3. TEM images and XRD patterns of as-prepared NCs.



Figure S4. XRD patterns of Pt-Cu NCs with different compositions (a) $Pt_{0.65}Cu_{0.35}$, (b) $Pt_{0.50}Cu_{0.50}$, (c) $Pt_{0.30}Cu_{0.70}$.



Figure S5. TEM images of as-prepared (a) Pt_{0.65}Cu_{0.35}, (b) Pt_{0.30}Cu_{0.70} NCs.



Figure S6. The size distributions of (a) $Pt_{0.65}Cu_{0.35}$, mean:9.1 nm; (b) $Pt_{0.30}Cu_{0.70}$ NCs, mean:6.6 nm.



Figure S7. (a) Color evolution during the reaction process at different time. (b) EDX patterns of Pt-Cu NCs with different reaction time.



Figure S8. TEM images show the effect of CTAB amount on the formation of Pt-Cu octahedral NCs. The amounts of CTAB used were a) 0 mmol, b) 0.027 mmol, and c) 0.137 mmol.



Figure S9. XRD pattern of products collected from the reaction without adding CTAB, the ratio of precursor between $Cu(acac)_2$ and $Pt(acac)_2$ is 3:1.



Figure S10. TEM images of the NCs prepared by replacing CTAB into a) SDBS, b) DDAB, and c) PVP.



Figure S11. TEM images of the NCs prepared by replacing DMF with different solvents (a) formamide, (b) ethylene glycol.



Figure S12. TEM images of the NCs prepared by replacing (a, b) Cu(acac)₂ into CuCl₂ and (c, d) Pt(acac)₂ into H₂PtCl₆.



Figure S13. TEM images of the NCs prepared without adding benzoic acid.



Figure S14. XRD patterns of multi-octahedral Pt-Cu NCs.



Figure S15. EDX patterns of multi-octahedral Pt-Cu NCs.



Figure S16. TEM images of the NCs prepared by adding (a, b) 200 μ L and (c, d) 2 mL decalin into the reaction.



Figure S17. Cyclic voltammetry curves of Pt-Cu NCs and commercial Pt/C catalyst in $0.5~M~H_2SO_4.$



Figure S18. Representative TEM images of the recycled (a) Pt-Cu octahedral NCs, (b) Pt-Cu multi-octahedral NCs.



Figure S19. XPS spectra of the fresh (black line) and recycled catalyst (red line).