

## Supporting Information

### Kinetically Controlled Synthesis of Pt-Cu Alloy Concave Nanocubes with High-Index Facets for Methanol Electro-Oxidation

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## Experimental Section

**Chemicals and Materials.** Platinum(II) acetylacetone (Pt(acac)<sub>2</sub>, Sigma-Aldrich, 97%), copper(II) acetylacetone (Cu(acac)<sub>2</sub>, Sigma-Aldrich, 99.99%), oleylamine (OAm, Aladdin), cetyltrimethylammonium bromide (CTAB, Aladdin, 99%), trioctylphosphine oxide (TOPO, Sigma-Aldrich, 99%), n-butylamine (Sigma-Aldrich, 99.5%), Pt/C (20 wt% of 3.2-nm Pt nanoparticles on Vulcan XC-72 carbon support, Premetek Co.) were all used as received. All syntheses were carried out in a glass vial (25 mL, Shuniu).

**Synthesis of Pt-Cu Concave Nanocubes.** Pt-Cu concave nanocubes were synthesized by co-reducing Pt(acac)<sub>2</sub> and Cu(acac)<sub>2</sub> with OAm in the presence of CTAB and TOPO. In a standard synthesis, 5 ml of OAm containing 30 mg CTAB and 100 mg TOPO was added to a glass vial, and pre-heated to 180 °C in air under magnetic stirring for 10 min. Meanwhile, 15.7 mg Pt(acac)<sub>2</sub> and 5.3 mg Cu(acac)<sub>2</sub> with a Pt<sup>2+</sup>/Cu<sup>2+</sup> ions molar ratio of 2:1 were dissolved in 3 mL of OAm. Subsequently, this precursor solution was dropped into the pre-heated vial with a pipette. The reaction was maintained at 180 °C for 3 h. After the reaction, the Pt-Cu concave nanocubes were isolated by centrifugation using a sufficient amount of ethanol, and then re-dispersed in anhydrous hexane to remove the excess CTAB, TOPO, and OAm. This process was repeated three times. We also systematically investigated the effects of the amount of CTAB and TOPO, reaction temperature, precursor concentration, as well as the duration of reaction on the final morphology of resultant Pt-Cu alloy nanocrystals.

**Synthesis of Pt-Cu Multipods.** Pt-Cu multipods were synthesized by varying the amount of Pt and Cu salt precursors (e.g., 21.2 mg Pt(acac)<sub>2</sub> and 1.6 mg Cu(acac)<sub>2</sub> with a Pt<sup>2+</sup>/Cu<sup>2+</sup> ions molar ratio of 9:1) with all other parameters being the same as in the standard procedure.

**Preparation of Carbon-Supported Catalysts.** Carbon black (Vulcan XC-72) was used as support for making Pt-Cu catalysts (Pt-Cu/C) according to a previous report with some minor modifications.<sup>[1]</sup> In a standard preparation, carbon black particles were dispersed in chloroform and sonicated for 30 min. A designed amount of Pt-Cu alloy nanocrystals were added to this dispersion with a Pt-Cu/C mass ratio of 20:80. This mixture was further sonicated for 10 min and stirred for 12 h. The resultant solids were precipitated out by centrifugation and re-dispersed in n-butylamine at a concentration of 0.5 mg/mL. The mixture was kept under stirring for 3 days, and then centrifuged and washed three times with methanol.

**Morphological, Structural, and Elemental Characterizations.** The obtained samples were characterized by transmission electron microscopy (TEM) images using a Philips CM 200 microscope operated at 160 kV. High-resolution transmission electron microscopy (HRTEM) was performed using a FEI Tecnai F30 G2 microscope operated at 300 kV. High-angle annular dark-field scanning TEM (HAADF-STEM) and Energy dispersive X-ray (EDX) mapping analyses were taken on a Cs-corrected STEM (TitanG2 80-200 ChemiSTEM equipped with a Super-X EDX detector system), operated at 200 kV using a probe with 50 pA beam current and a converge angle of 21.4 mrad. The percentages of Pt and Cu in the samples were determined using inductively coupled plasma mass spectrometry (ICP-MS) (Perkin-Elmer Elan DRC IIICP-MS).

**Electrochemical Measurements.** The electrochemical measurements were performed at room temperature using a rotating disk electrode (RDE, Pine Research Instrumentation, United States) connected to a PARSTAT 283 potentialstat (Princeton Applied Research, United States). A Ag/AgCl electrode was used as the reference. The as-received data were finally converted to reversible hydrogen electrode (RHE) as the reference. The counter electrode was a Pt mesh ( $1 \times 1 \text{ cm}^2$ ) connected to a Pt wire. To prepare the working electrode, 1.5 mg of the Pt-Cu/C or 2.0 mg of commercial Pt/C catalysts was dispersed in 1 mL of water, and then 20  $\mu\text{L}$  of the ink suspension was deposited on the pre-cleaned glassy carbon substrate. The geometric area of each RDE was  $0.196 \text{ cm}^2$ . Upon drying under air for 2 h, the electrode was covered with 50  $\mu\text{L}$  of 5 wt% Nafion (Aldrich) dispersed in water. The capping agent was removed by using a nondestructive method of holding the electrode potential, for example, -0.05 V (vs RHE) for 1000 s. After removing, each electrode was further cycled in a  $\text{N}_2$ -saturated 0.1 M  $\text{HClO}_4$  solution for 100 cycles between 0.08 and 1.1 V at a sweep rate of 100 mV/s. The cyclic voltammetry curves were recorded on the working electrode by cycles between 0.08 and 1.1 V at 50 mV/s in a  $\text{N}_2$ -saturated 0.1 M  $\text{HClO}_4$  solution. For the electrooxidation of methanol, cyclic voltammograms were recorded in an  $\text{N}_2$ -purged (ultrahigh purity, Airgas) 0.1 M  $\text{HClO}_4$ /1.0 M  $\text{CH}_3\text{OH}$  solution at a sweep rate 50 mV/s in the range of 0.08 V to 1.2 V. Chronoamperometric measurements of methanol oxidation were obtained at 0.8 V for 1000 s.

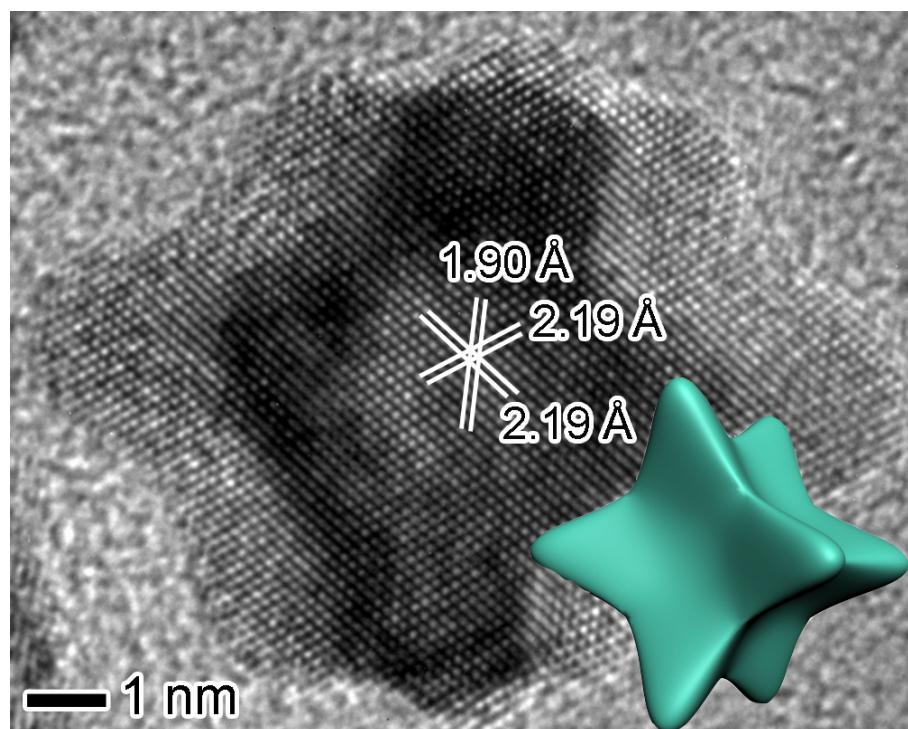
## References

- [1] J. Wu, J. Zhang, Z. Peng, S. Yang, F. Wagner, H. Yang, *J. Am. Chem. Soc.* **2010**, *132*, 4984.

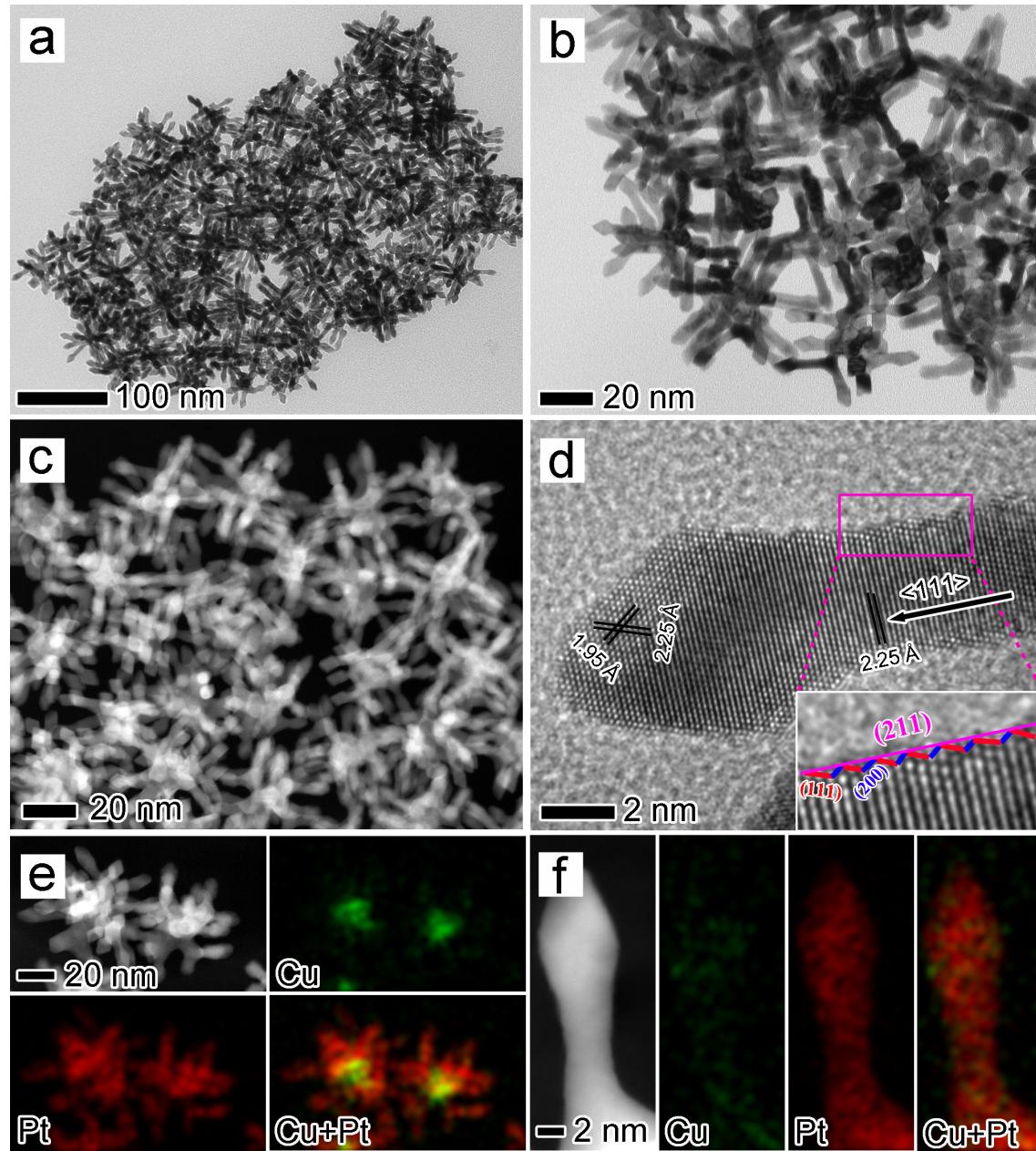
**Table S1.** ICP-MS data and ECSA of the carbon supported Pt-Cu alloy concave cubes and spherical NPs, including commercial Pt/C.

Catalysts	Pt/Cu ratio	metal wt% on Carbon	ECSA ( $\text{m}^2/\text{g}_{\text{metal}}$ )
Pt-Cu Concave Cubes	1.45/1	20.1	13.45
Pt-Cu Spherical NPs	2.8/1	15.1	14.13
Pt/C*	/	20.0	66.9

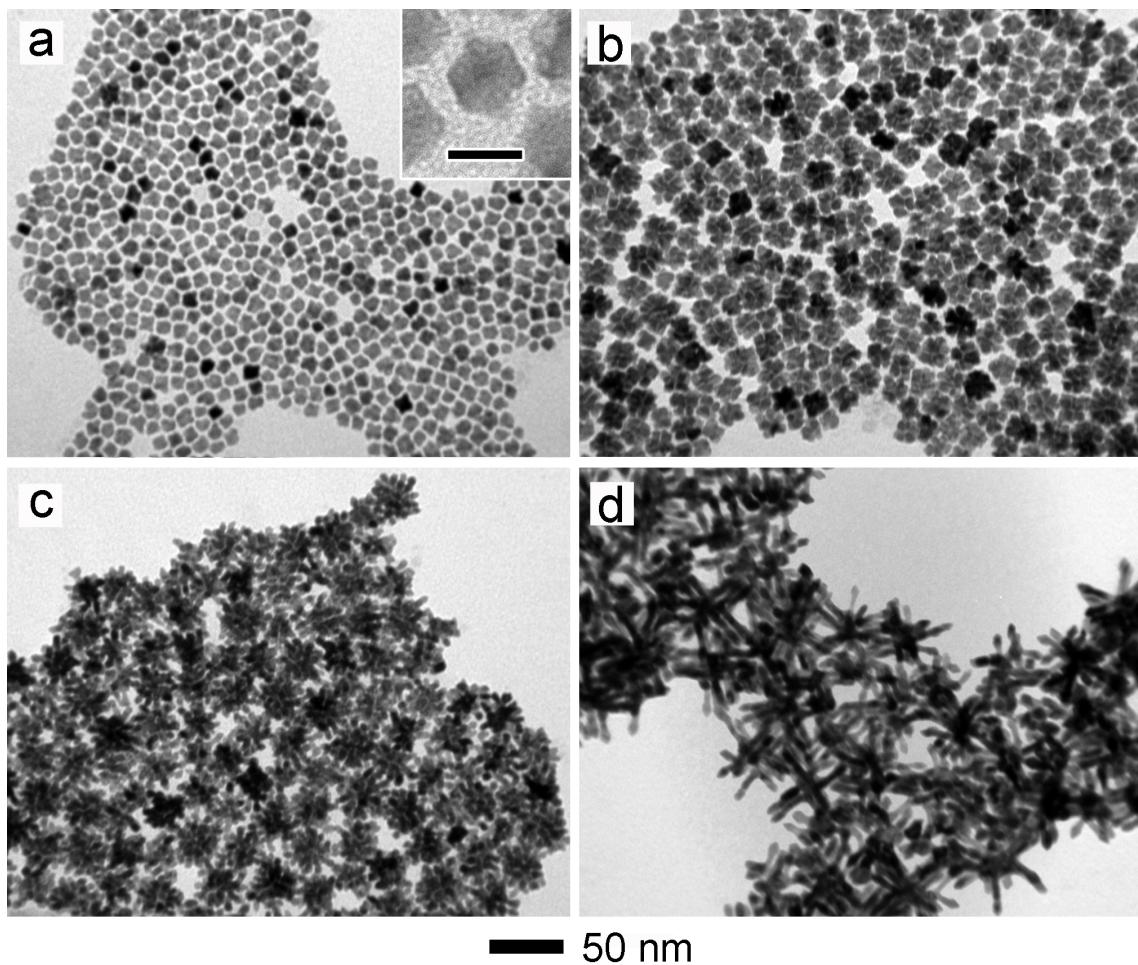
\*20 wt% of 3.2-nm Pt nanoparticles on Vulcan XC-72 carbon support (Premetek Co.).



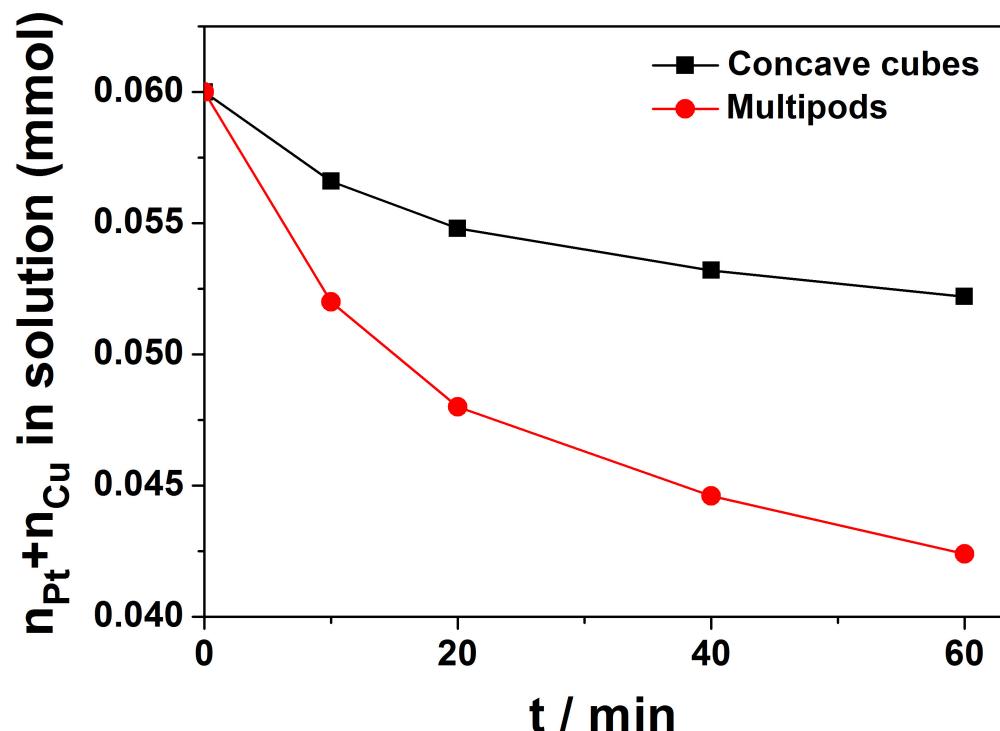
**Figure S1.** Typical HRTEM image of the Pt-Cu concave nanocubes prepared using the standard procedure. The inset shows the corresponding 3D model of the Pt-Cu concave nanocubes. The fringes with lattice spacing of 2.21 and 1.91 Å can be indexed to the {111} and {200} planes of face-centered cubic (*fcc*) Pt-Cu alloy, respectively.



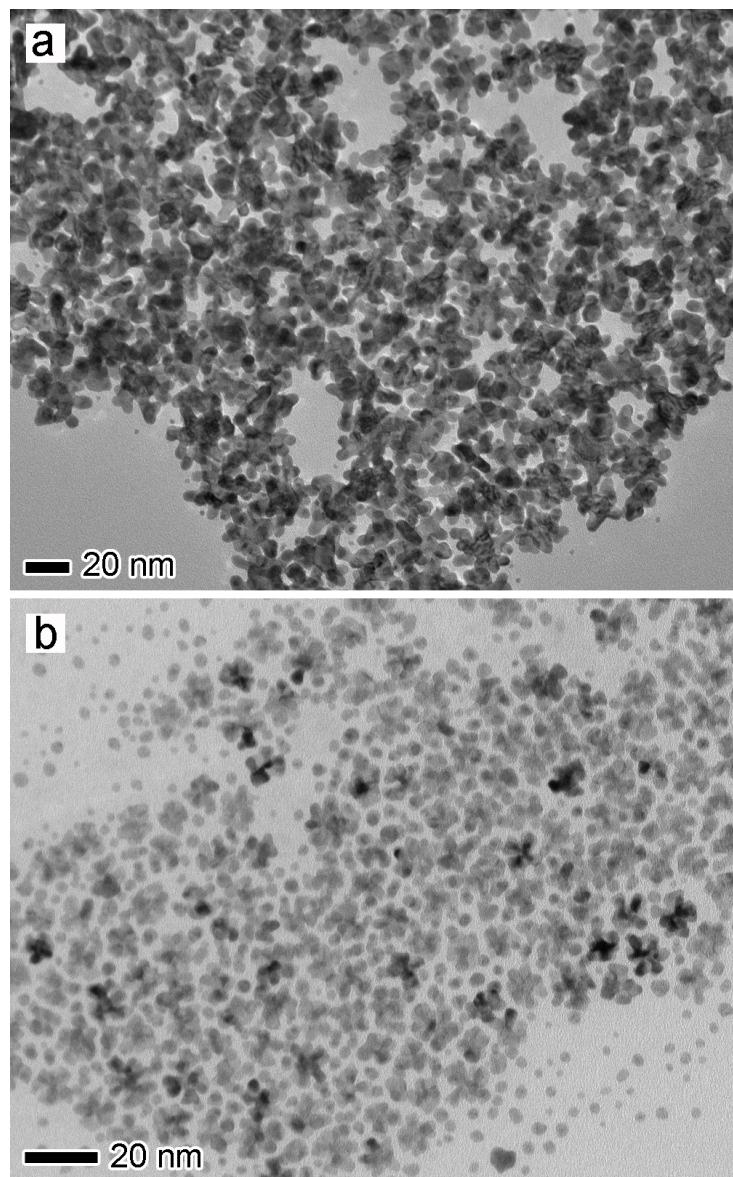
**Figure S2.** Morphological, structural, and compositional characterizations of the Pt-Cu alloy multipods prepared using the standard procedure except for the difference in the molar ratio of Pt to Cu salt precursors (9:1). (a, b) TEM images, (c) HADDF-STEM image, (d) HRTEM image, and (e, f) HAADF-STEM-EDX mapping. The inset in (d) shows the magnified HRTEM image of the edge region (as marked by red box) recorded along the [011] zone axis.



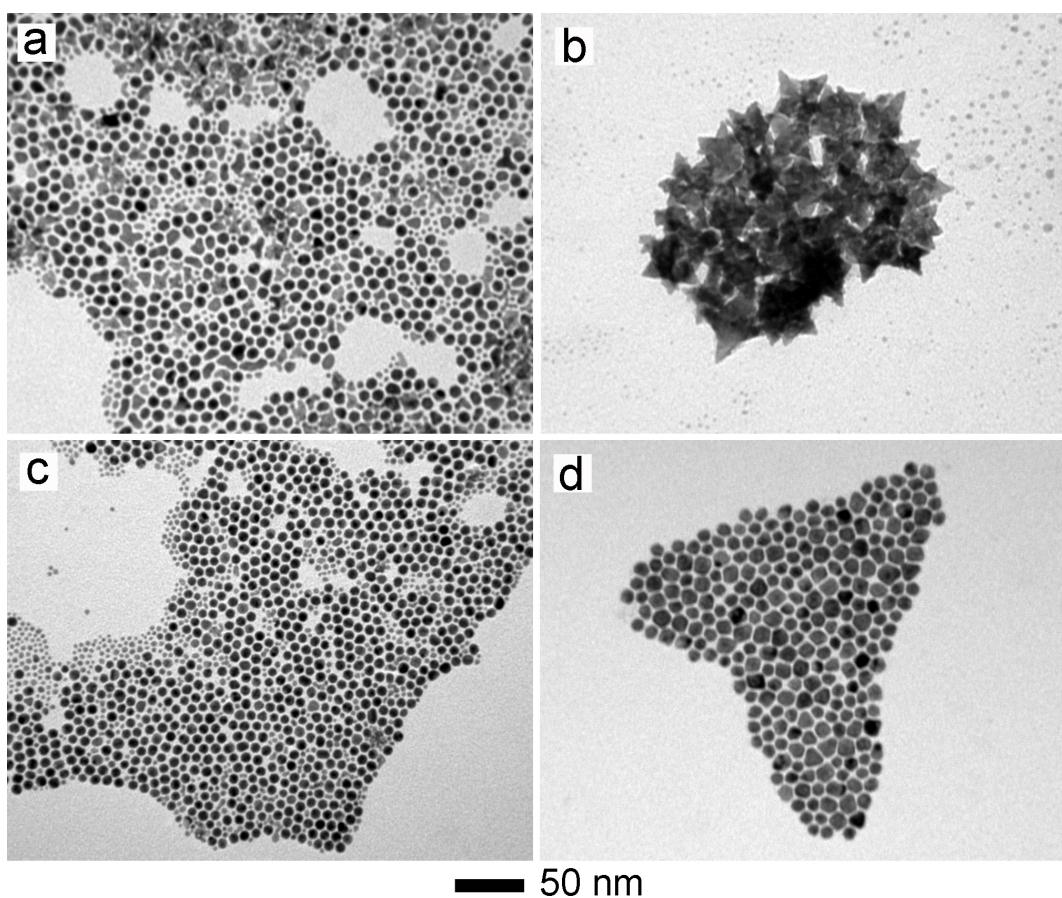
**Figure S3.** TEM images of Pt-Cu alloy nanocrystals prepared using the standard procedures for the syntheses of multipods, except for the difference in the reaction time: (a) 15 min, (b) 30 min, (c) 1 h, and (d) 6 h. The insets show TEM images of individual nanocrystals at a higher magnification. The scale bars in the insets are 10 nm.



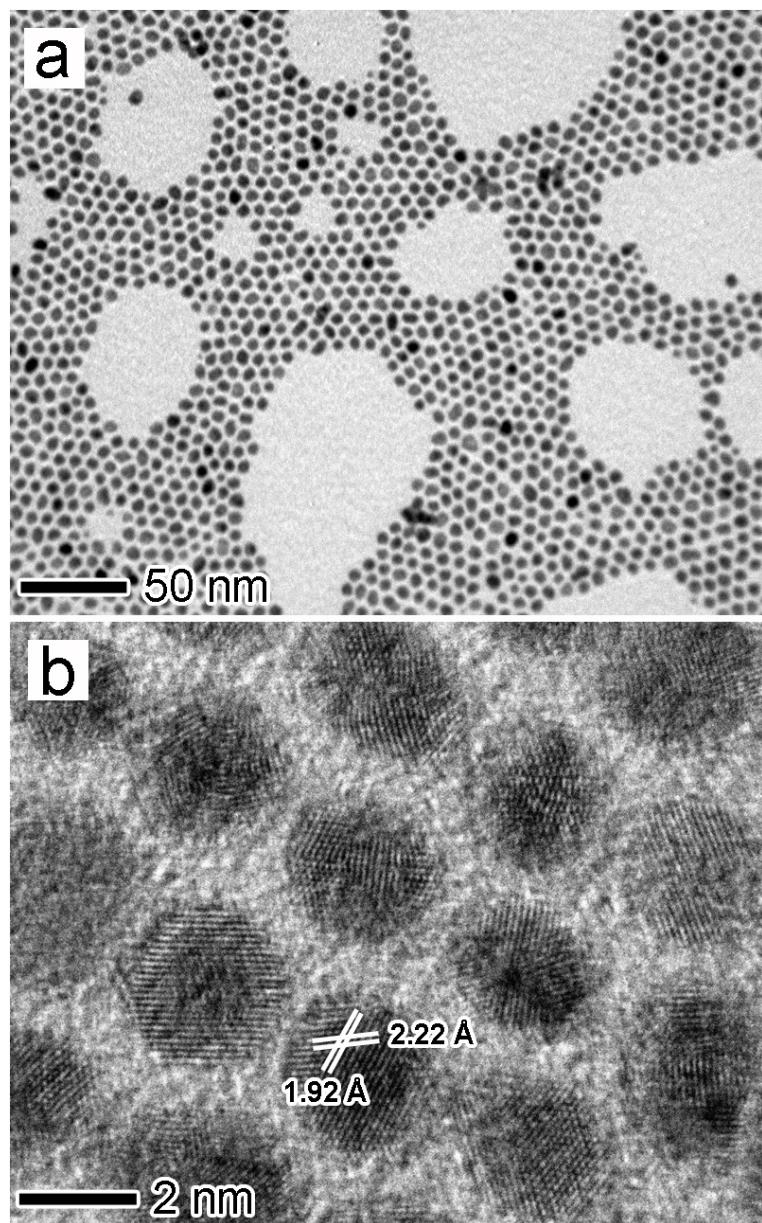
**Figure S4.** The variation of the amount of Pt plus Cu salt precursors with reaction time in the typical synthesis of the Pt-Cu concave cubes and multipods.



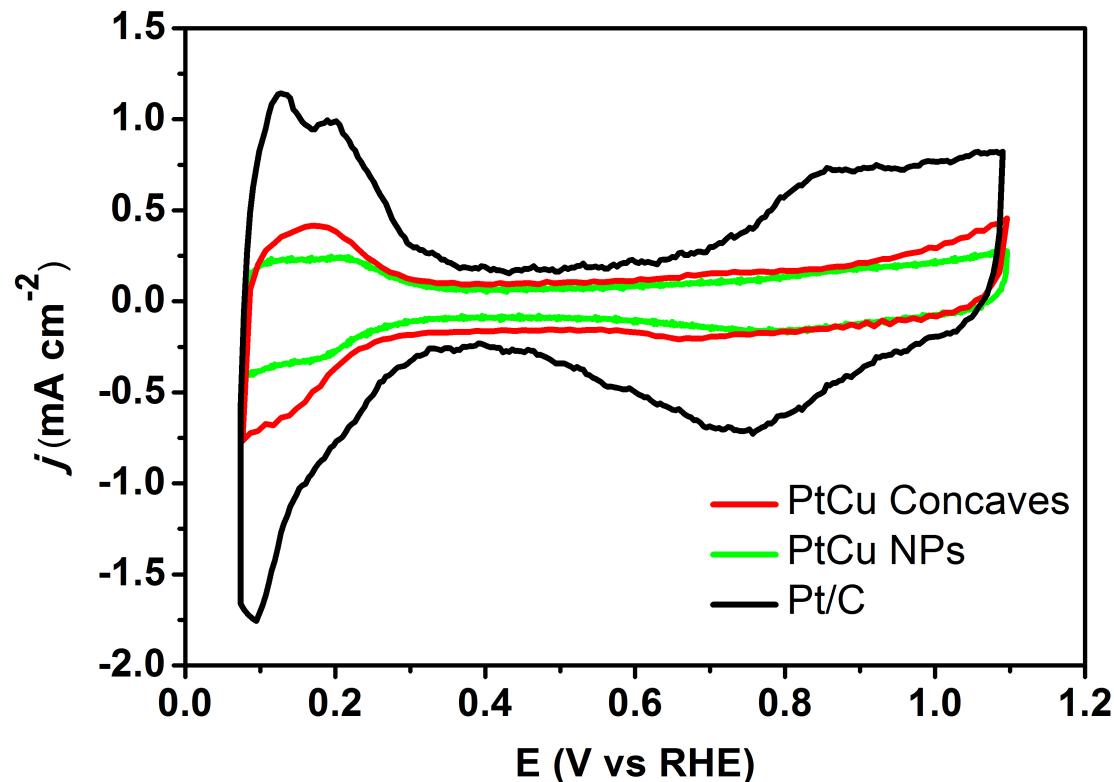
**Figure S5.** TEM images of the Pt-Cu nanocrystals prepared using the standard procedure except for: (a) reaction temperature at 220 °C and (b) precursor concentration in double.



**Figure S6.** TEM images of Pt-Cu nanocrystals that were prepared using the standard procedure, except for the difference in the amounts of CTAB and TOPO added in the reaction: (a) in the absence of CTAB and TOPO, (b) only 30 mg of CTAB, (c) only 100 mg of TOPO, and (d) 15 mg of CTAB and 100 mg of TOPO.



**Figure S7.** (a) TEM and (b) HRTEM images of the Pt-Cu alloy spherical nanocrystals that were prepared in an OAm solution containing 17.7 mg of  $\text{Pt}(\text{acac})_2$ , 4.0 mg of  $\text{Cu}(\text{acac})_2$ , and 100 mg of TOPO at 180 °C for 3 h.



**Figure S8.** Cyclic voltammograms (CVs) of Pt-Cu concave cubes (red), Pt-Cu spherical particles (green), and commercial Pt/C (black) in a  $\text{N}_2$ -saturated 0.1 M  $\text{HClO}_4$  solution at a sweep rate of 50 mV/s. The CV was recorded after 100-potential cycles with a scan rate of 100 mV/s.