

Supporting Information

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Pt-Cu and Pt-Pd-Cu Concave Nanocubes with High-Index Facets and Superior Electrocatalytic Activity

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Pt–Cu and Pt–Pd–Cu Concave Nanocubes with High-Index Facets and Superior Electrocatalytic Activity

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Experimental Section

Synthesis

Chemicals. K_2PtCl_4 (AR; Shenyang Research Institute of Nonferrous Metal, China), PdCl₂ (AR; Shenyang Research Institute of Nonferrous Metal, China), CuCl₂ (AR; Beijing Chemical Works, China), KBr (AR; Beijing Chemical Works, China), HCl (36 % - 38%, AR; Beijing Chemical Works, China), and poly(vinylpyrrolidone) (PVP; Mw: ~29,000; Sigma-Aldrich) were used as received. Na₂PdCl₄ solution was prepared by mixing and dissolving 1.0 g of PdCl₂ and 0.66 g of NaCl with 100 mL of H₂O at room temperature under stirring overnight. The water used in all experiments was ultrapure (Millipore, 18.2 MΩ).

Synthesis of Pt–Cu nanocubes (NCs) and concave nanocubes (CNCs). K_2PtCl_4 (0.030 mmol), CuCl₂ (0.030 mmol), KBr (9 mmol), and PVP (100 mg) were dissolved in water. The pH value of the solution was adjusted by adding given amount of 1.0 M HCl solution and the total volume was then adjusted to 15 mL. Typically, Pt–Cu NCs could be obtained when the amount of HCl was kept at 0.15 mmol, and Pt–Cu CNCs could be prepared when the amount of HCl was increased to 0.30 mmol with other synthesis parameters unchanged. Moreover, Pt–Cu CNCs could be synthesized with various amounts of HCl and KBr, as discussed below (Figure S8). The homogeneous yellow-brown solution was transferred to a 25 mL Teflon-lined stainless steel autoclave and sealed. The autoclave was then heated at 160 \degree for 4 hours before it was cooled down to room temperature. The black nanocrystals were centrifuged with importing 45 milliliters of acetone and further washed by water/acetone for several times. The shape and composition of obtained Pt–Cu nanocrystals could be tuned by altering the amount of different reaction agents, as detailed below.

Synthesis of Pt–Pd–Cu CNCs-1. K_2 PtCl₄ (0.030 mmol), Na_2 PdCl₄(0.030 mmol) CuCl₂ (0.060 mmol), KBr (9 mmol), and PVP (100 mg) were dissolved in water. Then, 0.05 mL of 1.0 M HCl solution was added in and the total volume of the mixture solution was adjusted to 15 mL. The homogeneous orange-red solution was transferred to a 25 mL Teflon-lined stainless steel autoclave and sealed. The autoclave was then heated at 160 °C for 4 hours before it was cooled down to room temperature. The black nanocrystals were centrifuged with importing 45 milliliters of acetone and further washed by water/acetone for several times.

Synthesis of Pt–Pd–Cu CNCs-2. The synthesis of Pt–Pd Cu CNCs-2 nanocrystals was similar to that of Pt–Pd–Cu CNCs-1, except that the amounts of K_2 PtCl₄ and Na₂PdCl₄ were adjusted to 0.045 and 0.015 mmol, respectively.

Synthesis of Pt NCs. The synthesis of Pt NCs nanocrystals was similar to that of Pt–Cu NCs, except that no $CuCl_2$ was used and the amount of KBr was 3.0 mmol and the amount of 1.0 M HCl was 0.015 mL.

Instrumentation

XRD. Wide Angle X-ray diffraction (WAXRD) patterns of dry membranes of aqueous dispersions of Pt–Cu and Pt–Pd–Cu nanocrystals on a glass wafer were recorded on a Rigaku D/MAX-2000 diffractometer (Japan) with a slit of $1/2^{\circ}$ at a scanning rate of 4 $^{\circ}$ min⁻¹ using Cu K_a radiation ($\lambda = 1.5406$ Å).

ICP-AES. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis of the obtained samples was performed on a Profile Spec ICP-AES spectrometer (Leeman, USA).

XPS. X-ray Photonelectron Spectroscopy was carried out on an Axis Ultra Imaging Photoelectron Spectrometer (Kratos Analytical Ltd., UK) with a monochromatic Al Ka (1486.7 eV) X-ray source operated at 225 W with 15 kV acceleration voltage.

TEM. Samples for transmission electron microscopy (TEM) observations were prepared by drying a drop of diluted colloid dispersion of obtained nanocrystals in water on copper grids coated by amorphous carbon. Particle sizes and shapes were examined by a TEM (JEM-2100, JEOL, Japan) operated at 200 kV. To get the shape- and size-distributions, more than 100 nanocrystals were counted for each sample.

HRTEM, EDS, HAADF-STEM and single-particle STEM-EDS line-scan. High resolution TEM (HRTEM), energy dispersive X-ray spectroscopy (EDS) analysis, high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and single-particle STEM-EDS line-scans were performed on a FEG-TEM (JEM-2100F, JEOL, Japan) operated at 200 kV with EDS and STEM accessories. For EDS analysis, nickel/iron grid with amorphous carbon membranes and Beryllium specimen holder (EM-31640, JEOL, Japan) were used to avoid the copper signals generated from copper grids and copper specimen holders during the EDS measurements.

Electrochemical measurements

Electrochemical measurements were carried out with a CHI 840B electrochemical analyzer (CH Instrument, TX, USA). A three-electrode cell was used with a glassy carbon (GC) electrode (6 mm in diameter) as the work electrode, a AgCl/Ag/KCl (saturated) electrode as the reference electrode and a Pt wire as the counter electrode. All potentials in this work were converted to values versus reversible hydrogen electrode (RHE) references.

Preparation of working electrode. 5 μ L of the aqueous dispersions of Pt NCs, Pt–Cu NCs, CNCs or Pt–Pd–Cu CNCs were transferred onto a GC electrode. After drying in air for 2 hours, the electrode was illuminated by a homemade UV lamp (10 W, with 185 nm and 254 nm emissions) at the distance of about 5 mm for 4 hours to remove the organic capping agents before electrochemical measurements. The GC electrode was then covered with 5 μ L of 0.2 wt.% Nafion (Alfa Aesar) in ethanol and dried in air for another 1 hour. For commercial Pt/C (20 wt% of Pt nanoparticles (< 3.5 nm) supported on activated carbons, Johnson Matthey) catalysts, 10 μ L of the ethanol dispersitons of Pt/C (1 mg/mL) were transferred onto the GC electrode and no UV/Ozone treatment was used.

Electro-oxidation of methanol. The electrolyte was fresh 0.1 M HClO₄ and 1 M CH₃OH solutions with Millipore ultrapure water (18.2 M Ω) and bubbled with N₂ for 30 min before each electrochemical test. Cyclic voltammetry (CV) measurements were then performed under a N₂ flow at room temperature with a sweep rate of 50 mV s⁻¹. The electrochemically active surface area (ECSA) of each sample was estimated by the O-ad/desorption in CV measurements carried out in fresh 0.1 M HClO₄ solutions with a sweep rate of 50 mV s⁻¹. Before each measurement, several sweeps were cycled until the steady state.

We calculated the ECSA by the O-ad/desorption method (S. W. Han, et al., *Angew. Chem. Int. Ed.* 2011, 50, 8876.). We also calculated the mass activity with reference to the unit weight of total metal or Pt in each sample, as shown in Figure 3 and Figure S16 in SI. For the two kinds of Pd-containing samples (Pt–Pd–Cu CNCs-1and Pt–Pd–Cu CNCs-2), we also used Cu_{upd} method (A. Kucernak, *et al., J. Phys. Chem. B*, **2002**, *106*, 1036;Y. N. Xia, *et al., Chem. Commun.* 2011, 47, 6566.) to measure their ECSA, the results were similar to that measured by O-ad/desorption method, as shown in Figure S17.

Supplementary Data

NCs -		ICP-AES		EDS	VDC**
		before*	after*	EDS	AFS
Pt : Cu	Pt-Cu NCs	88:12	86:14	89:11	95 : 5
	Pt-Cu CNCs	89:11	87:13	89:11	95 : 5
Pt : Pd : Cu	Pt-Pd-Cu CNCs-1	42:46:12	45:41:13	45:43:12	51:42:8
	Pt-Pd-Cu CNCs-2	62:23:15	62:20:18	62:22:16	70:23:7

Table S1 Compositions (molar ratios) of the Pt-Cu and Pt-Pd-Cu nanocatalysts determined by means of ICP-AES, EDS and XPS analyses

* The molar ratio of Pt/Cu or Pt/Pd/Cu before or after electrochemical measurement determined by the ICP-AES method.

** The detection depth of the present XPS analysis is about 2 nm.



Figure S1. TEM images and corresponding EDS spectra of the as-prepared Pt–Cu NCs (a, b) and CNCs (c–e). TEM images of a Pt–Cu CNC projected along the [111] axis (f). The signals of Cr, Fe and Ni in the EDS spectra are from the nickel/iron grid.



Figure S2. XRD patterns of the as-prepared Pt–Cu NCs, CNCs, Pt–Pd–Cu CNCs-1 and CNCs-2 with the standard data for *fcc* Pt (JCPDS Card No.: 01-1194), Pd (JCPDS Card No.: 05-0681), and Cu (JCPDS Card No.: 01-1241) as references. There were very small shifts to high angle in the diffraction peaks for Pt–Cu NCs and CNCs. The Pt (111) peak located at 40.0 degree, and the (111) peaks for Pt–Cu NCs and CNCs located at about 40.1 and 40.2 degree (the (111) peaks for Pt–Pd–Cu CNCs-1 and -2 located at about 40.4 degree). In addition, the (200) and (220) peaks for Pt–Cu NCs/CNCs also shifted from 46.5 and 67.9 degree to about 46.8/46.9 (NCs) and 68.2/68.4 (CNCs) degree. The incorporation of Cu makes the peaks right-shifted a little. But the broadening of the XRD diffraction peaks (due to the small size of the Pt–Cu NCs and CNCs) makes the shift looks not that significant.



Figure S3. HAADF-STEM images of the as-prepared Pt-Cu NCs (a) and CNCs (b), respectively.



Figure S4. TEM images of the Pt nanocrystals prepared under the similar conditions for Pt–Cu NCs (a) or CNCs (b) but without the addition of any Cu(II) precursors, respectively: (a) K_2PtCl_4 (0.030 mmol), KBr (9.0 mmol), PVP (100 mg), 1.0 M HCl (0.15 mL), 160 °C, 4 h; and (b) K_2PtCl_4 (0.030 mmol), KBr (9.0 mmol), PVP (100 mg), 1.0 M HCl (0.30 mL), 160 °C, 4 h.



Figure S5. TEM images of the Pt–Cu nanocrystals prepared under the similar conditions for Pt–Cu NCs (a) or CNCs (b) but with the adding of equivalent amount of KCl instead of HCl solutions, respectively: (a) K_2PtCl_4 (0.030 mmol), CuCl₂ (0.030 mmol), KBr (9.0 mmol), PVP (100 mg), KCl (0.15 mmol), 160 °C, 4 h; and (b) K_2PtCl_4 (0.030 mmol), CuCl₂ (0.030 mmol), KBr (9.0 mmol), PVP (100 mg), KCl (0.30 mmol), 160 °C, 4 h.



Figure S6. TEM images of the Pt–Cu nanocrystals prepared under the similar conditions for Pt–Cu NCs (a) or CNCs (b) but with the adding of equivalent amount HBr instead of HCl and Cu(CH₃COO)₂ instead of CuCl₂, respectively: (a) K₂PtCl₄ (0.030 mmol), Cu(CH₃COO)₂ (0.030 mmol), KBr (8.85 mmol), PVP (100 mg), 1.0 M HBr (0.15 mL), 15 mL, 160 °C, 4 h; and (b) K₂PtCl₄ (0.030 mmol), Cu(CH₃COO)₂ (0.030 mmol), Cu(CH₃COO)₂ (0.030 mmol), KBr (8.7 mmol), PVP (100 mg), 1.0 M HBr (0.30 mL), 160 °C, 4 h.



Figure S7. TEM images of the Pt–Cu nanocrystals prepared under the similar conditions for Pt–Cu NCs or CNCs but with the amount of CuCl₂ precursor increased to 0.090 mmol (a,b) or decreased to 0.010 mmol (c,d), respectively: (a) K₂PtCl₄ (0.030 mmol), CuCl₂ (0.090 mmol), KBr (9.0 mmol), PVP (100 mg), 1.0 M HCl (0.15 mL), 160 \degree , 4 h; (b) K₂PtCl₄ (0.030 mmol), CuCl₂ (0.090 mmol), KBr (9.0 mmol), PVP (100 mg), 1.0 M HCl (0.30 mL), 160 \degree , 4 h; (c) K₂PtCl₄ (0.030 mmol), CuCl₂ (0.010 mmol), KBr (9.0 mmol), PVP (100 mg), 1.0 M HCl (0.15 mL), 160 \degree , 4 h; and (d) K₂PtCl₄ (0.030 mmol), CuCl₂ (0.010 mmol), KBr (9.0 mmol), KBr (9.0 mmol), PVP (100 mg), 1.0 M HCl (0.15 mL), 160 \degree , 4 h; and (d) K₂PtCl₄ (0.030 mmol), CuCl₂ (0.010 mmol), KBr (9.0 mmol), PVP (100 mg), 1.0 M HCl (0.30 mL), 160 \degree , 4 h; and (d) K₂PtCl₄ (0.030 mmol), CuCl₂ (0.010 mmol), KBr (9.0 mmol), PVP (100 mg), 1.0 M HCl (0.30 mL), 160 \degree , 4 h.



Figure S8. TEM images of the Pt–Cu nanocrystals prepared with different amounts of HCl and KBr: (a–d) No HCl and 1.5, 3.0, 6.0 and 9.0 mmol of KBr, respectively; (e–h) 0.15 mmol of HCl and 1.5, 3.0, 6.0 and 9.0 mmol of KBr, respectively; (i–l) 0.30 mmol of HCl and 1.5, 3.0, 6.0 and 9.0 mmol of KBr, respectively; (m–p) 0.60 mmol of HCl and 1.5, 3.0, 6.0 and 9.0 mmol of KBr, respectively; and (q–t) 0.90 mmol of HCl and 1.5, 3.0, 6.0 and 9.0 mmol), 6.0 and 9.0 mmol of KBr, respectively. Other conditions were kept unvaried with K₂PtCl₄ (0.030 mmol), CuCl₂ (0.010 mmol), PVP (100 mg), 160 \degree and 4 h. The scale bar in each panel is 100 nm.



Figure S9. Time sequential TEM images of the Pt–Cu CNCs prepared at 160 $^{\circ}$ C for (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h, and (e) 6 h. The scale bar in each panel is 50 nm.



Figure S10. XPS spectra of the as-prepared Pt–Cu CNCs (a,b) and Pt–Pd–Cu CNCs-1 (c,d). In panels a,c, the XPS peaks of O, N and C would come from the surface capping PVP molecules. Signals from surface adsorbed Br^- species are also detected. The peaks of Cu $2p_{3/2}$ can be divided into a strong peak at 932.4 eV and a much weaker one at 933.6 eV, suggesting that most of the Cu species were of 0 or +1 valence, along with the presence of a small amount of Cu(II) species adsorbed on the CNCs surfaces (panels b, d).



Figure S11. TEM images and corresponding EDS spectra of the as-prepared Pt–Pd–Cu CNCs-1 (a, b) and CNCs-2 (c, d). Inset in panel c is the HRTEM image of a single particle of the Pt–Pd–Cu CNCs-2 with HIFs. The signals of Cr, Fe and Ni in the EDS spectra are from the nickel/iron grid.



Figure S12. HAADF-STEM images (a) and single-particle EDS line-scan profiles (b) of the as-prepared Pt–Pd–Cu CNCs-2.



Figure S13. TEM images of Pd–Cu nanocrystals with the similar conditions for the preparation of Pt–Cu CNCs except of the replacement of Pt(II) with Pd(II) precursors: Na_2PdCl_4 (0.030 mmol), CuCl₂ (0.030 mmol), KBr (9.0 mmol), PVP (100 mg), 1.0 M HCl (0.30 mL), 160 °C, and 4 h.



Figure S14. TEM images of the Pt NCs (a) and Pt/C catalyst (b) used in the methanol oxidation test.



Figure S15. TEM images of Pt-Cu CNCs before (a) and after (b) 12 h of UV/Ozone treatment.



Figure S16. I-t curves (at 0.84 V) of methanol oxidation on (a) Pt/C, Pt NCs, Pt–Cu NCs, Pt–Cu CNCs and (b) Pt–Pd– Cu CNCs in 0.1 M HClO₄/1 M CH₃OH.



Figure S17. Cu stripping curve for a Cu_{upd} monolayer on Pt–Pd–Cu CNCs-1 (a) and Pt–Pd–Cu CNCs-2 (b) in 0.1 M HClO₄ with the scanning rate of 20 mV/s. The ECSA was calculated based on the Cu stripping charge (Q) assuming 460 μ C cm⁻² for full Cu monolayer coverage. The ECSA calculated from Cu stripping method is 0.98 and 1.4 m²/g for CNCs-1 and CNCs-2, respectively, comparable with the results from O-ad/desorption method (0.91 and 1.3 m²/g for CNCs-1 and CNCs-2, respectively).