

Supporting Information

Bimetallic Pd-Cu nanocrystals and their tunable catalytic properties

Junjie Mao, Yuxi Liu, Zheng Chen, Dingsheng Wang* and Yadong Li

Department of Chemistry, Tsinghua University, Beijing, 100084, China

*E-mail: wangdingsheng@mail.tsinghua.edu.cn

Experimental Details

Materials: Reagents used in this work, including $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, octadecylamine (ODA), ethanol, and cyclohexane, were of analytical grade from the Beijing Chemical Factory. Palladium pentanedionate ($\text{Pd}(\text{acac})_2$, 34.7% Pd basis), Pd black, and Nafion solution were purchased from Alfa Aesar. All the chemicals were used without further purification.

Characterization: The powder XRD patterns were recorded with a Bruker D8-advance X-ray powder diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). 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 measurements were conducted on a computer-controlled electrochemical analyzer (CHI 660D, Chenhua, China) at room temperature. Pd black or Pd-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 μm Al_2O_3 slurry on a polishing cloth and then sonicated in ethanol and water each for several times before 5 μL of each catalyst was dropped on the GC electrode. After the electrode was dried, 5 μL Nafion dilutes (0.05 wt%) was coated on the catalyst surface. Before each test, Pd-Cu nanocrystals were illuminated by a UV lamp (10 W, with 185 nm and 254 nm emissions) at the distance of about 5 mm for 12 h to remove the organic capping agents before electrochemical measurements. Aqueous solutions of 0.5 M KOH and 0.5 M KOH containing 1 M ethanol were used for the electrolytes. All electrochemical experiments were performed at room temperature.

Synthesis of 5.2 nm $\text{Pd}_{0.5}\text{Cu}_{0.5}$ NCs:

In a typical synthesis, 20 mg $\text{Pd}(\text{acac})_2$ and 15.9 mg $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were mixed with 7.5 g ODA and heated at 110 $^\circ\text{C}$ to form a clear solution. Then the temperature was elevated to 240 $^\circ\text{C}$ and maintained at this temperature for 10 min. The reaction mixture was cooled down to 70 $^\circ\text{C}$, followed by addition of 20 mL ethanol. The products were collected at the bottom of the flask by decanting the supernatant and further washed with hexane and ethanol for several times.

Synthesis of 6.8 nm $\text{Pd}_{0.5}\text{Cu}_{0.5}$ NCs:

The synthesis of 6.8 nm $\text{Pd}_{0.5}\text{Cu}_{0.5}$ NCs was conducted under similar conditions to 5.2 nm $\text{Pd}_{0.5}\text{Cu}_{0.5}$ NCs synthesis except 12 g ODA were used.

Synthesis of 8.1 nm $\text{Pd}_{0.5}\text{Cu}_{0.5}$ NCs:

In a typical synthesis, 20 mg Pd(acac)₂ and 15.9 mg Cu(NO₃)₂·3H₂O were mixed with 7.5 g ODA and heated at 110 °C. After the mixture changed into a clear solution, it was then transferred to a 50 mL autoclave at 180 °C for 6 h. The reaction was cooled down to 70 °C, followed by addition of 20 mL ethanol. The products were collected at the bottom of the flask by decanting the supernatant and further washed with hexane and ethanol for several times

Synthesis of 16.4 nm Pd_{0.5}Cu_{0.5} NCs:

In a typical synthesis, 11.6 mg PdCl₂ and 15.9 mg Cu(NO₃)₂·3H₂O were mixed with 3 g ODA and heated at 110 °C to form a clear solution. Then the temperature was elevated to 260 °C and maintained at this temperature for 10 min. The reaction mixture was cooled down to 70 °C, followed by addition of 20 mL ethanol. The products were collected at the bottom of the flask by decanting the supernatant and further washed with hexane and ethanol for several times.

Synthesis of 19.9 nm Pd_{0.5}Cu_{0.5} NCs:

The synthesis of 19.9 nm Pd_{0.5}Cu_{0.5} NCs was conducted under similar conditions to 16.4 nm Pd_{0.5}Cu_{0.5} NCs synthesis except 7.5 g ODA were used.

Composition Control of Pd-Cu NCs: The composition of these Pd-Cu NCs was controlled by the initial metal precursor molar ratio. For instance, in the synthesis of Pd-Cu NCs with the amount of Pd(acac)₂ fixed at 0.066 mmol, 0.330, 0.198, 0.066, 0.022 and 0.0132 mmol of Cu(NO₃)₂ led to the formation of Pd_{0.2}Cu_{0.8}, Pd_{0.3}Cu_{0.7}, Pd_{0.5}Cu_{0.5}, Pd_{0.7}Cu_{0.3}, and Pd_{0.8}Cu_{0.2} NCs, respectively.

Catalytic testing: 0.1 g as-prepared catalysts (Pd-Cu NCs loaded onto La₂O₃, theoretical metal loading = 2 wt %) and 10 mmol styrene were added to 20 mL acetonitrile and refluxed (at 80 °C) for 0.5 h in a two-necked flask under magnetic stirring. The catalytic reaction was initiated by adding 15 mmol tert-butyl hydroperoxide (TBHP) to the mixture in the flask. Resulting product mixtures were analyzed by gas chromatography using tetradecane as an internal standard. Product identification and gas chromatograph calibration were carried out using both gas chromatography–mass spectroscopy and standard solutions of each product identified.

Supplementary Figures

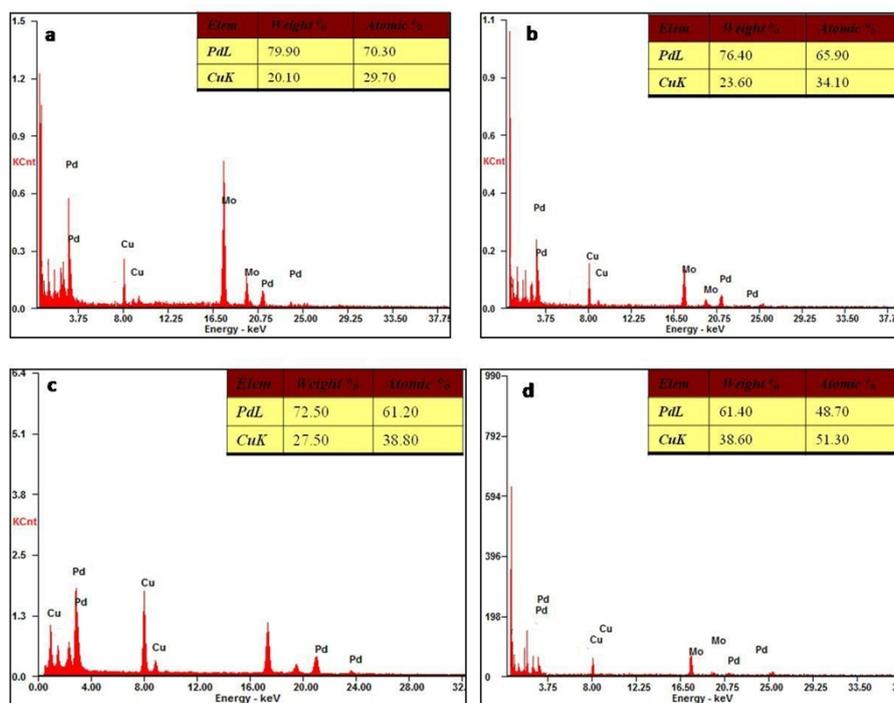


Figure S1. EDX patterns of Pd-Cu NCs obtained at different temperatures: a) 185 °C, b) 220 °C, c) 230 °C, d) 240 °C.

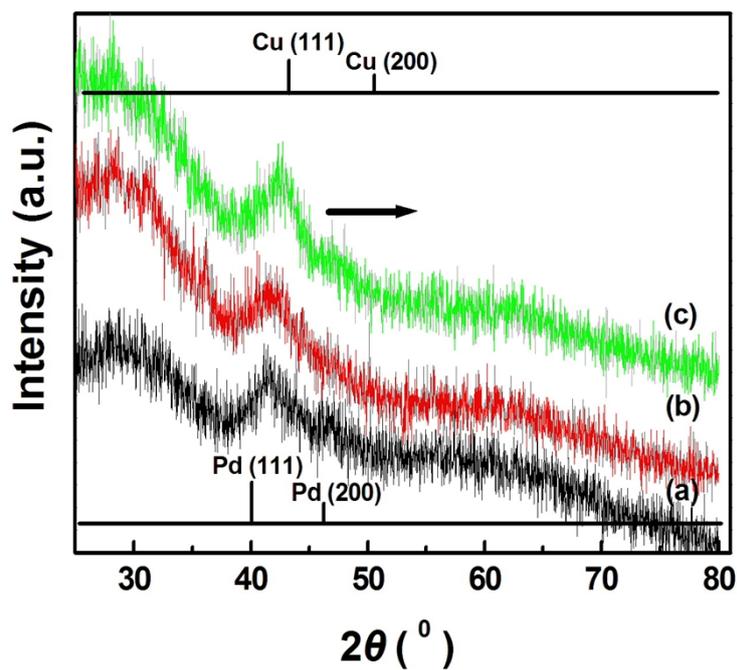


Figure S2. XRD patterns of Pd-Cu NCs obtained at different temperatures: a) 220 °C, b) 230 °C, c) 240 °C.

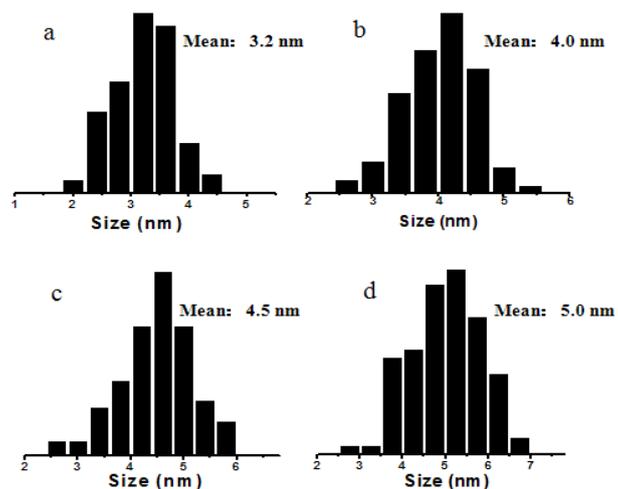


Figure S3. The size distributions of Pd-Cu NCs obtained at different temperatures: a) 185 °C, b) 220 °C, c) 230 °C, d) 240 °C.

Table S1 composition and size of as-prepared Pd-Cu NCs

Entry	Precursor molar ratios (Pd/Cu)	Analyzed molar ratios (Pd/Cu)	Particle size
1	0.83:0.17	0.80:0.20	3.7 nm
2	0.75:0.25	0.71:0.29	4.5 nm
3	0.50:0.50	0.50:0.50	5.2 nm
4	0.25:0.75	0.31:0.69	7.8 nm
5	0.17:0.83	0.20:0.80	11.2 nm

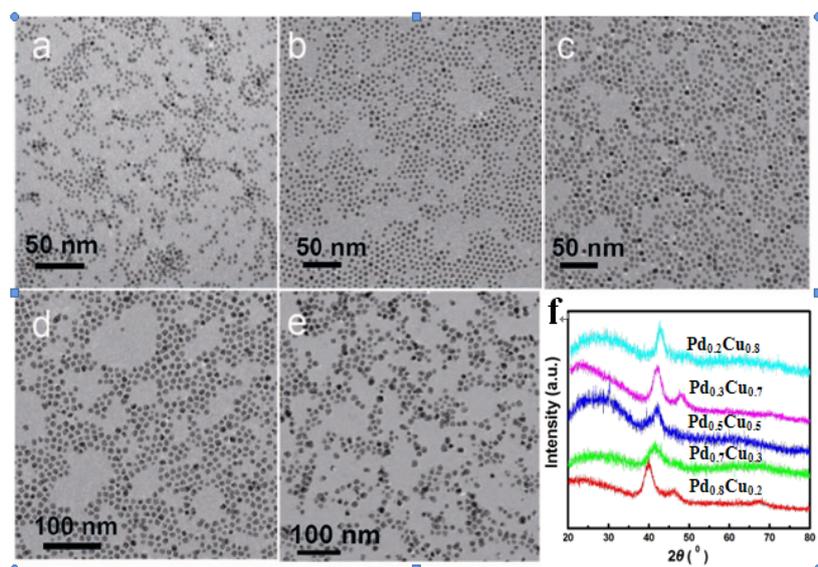


Figure S4. TEM images of Pd-Cu NCs with different compositions: a) Pd_{0.8}Cu_{0.2}, b) Pd_{0.7}Cu_{0.3}, c) Pd_{0.5}Cu_{0.5}, d) Pd_{0.3}Cu_{0.7}, and e) Pd_{0.2}Cu_{0.8}. f) XRD patterns of a series of Pd-Cu NCs.

We have estimated the crystallite size by using XRD data and the Scherrer equation (Table S2). However, the size of Pd-Cu nanocrystals estimated from the XRD peaks is different from that observed from the TEM micrographs. The reason for the difference might be that the nanocrystals were made up of two or more crystallites. There is also the possibility that the XRD estimate is affected by the presence of a range of Pd-Cu particle compositions, which would serve to broaden the diffraction peaks and lead to a smaller crystallite size estimated from the Scherrer equation.

Table S2 the particle size of as-prepared Pd-Cu NCs

Samples	XRD	TEM
Fig. S2a	2.6 nm	4.0 nm
Fig. S2b	3.3 nm	4.5 nm
Fig. S2c	3.7 nm	5.0 nm

Samples	XRD	TEM
Fig. 3a	3.9 nm	5.2 nm
Fig. 3b	4.2 nm	6.8 nm
Fig. 3c	5.4 nm	8.1 nm
Fig. 3d	12.4 nm	16.4 nm
Fig. 3e	14.3 nm	19.9 nm

Samples	XRD	TEM
Fig. S4a	4.0 nm	3.8 nm
Fig. S4b	3.5 nm	4.5 nm
Fig. S4c	3.9 nm	5.2 nm
Fig. S4d	5.2 nm	7.8 nm
Fig. S4e	5.6 nm	11.2 nm

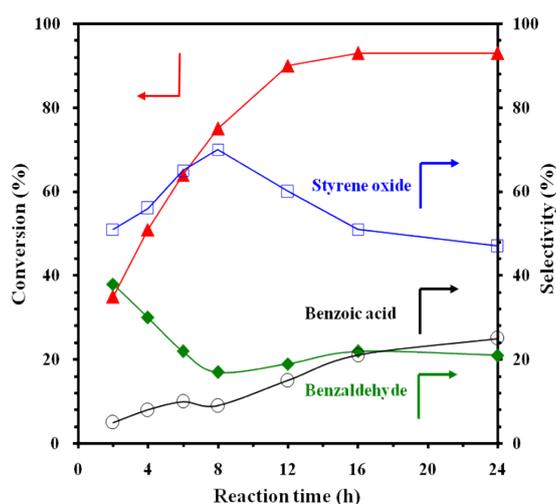


Figure S5. Catalytic performance of as-prepared Pd_{0.3}Cu_{0.7} catalysts for styrene epoxidation.

XPS is an effective technique to gain the information of surface element composition, metal oxidation state, and adsorbed species of a solid material. The Pd 3d_{5/2} XPS spectra of the Pd_{0.3}Cu_{0.7} samples are shown in Figure S6A. The ones at BE = 335.5 eV could be ascribed to the surface metallic palladium (Pd⁰), whereas the ones at BE = 336.2 and 337.7 eV could be attributed to the surface oxidized palladium (Pd²⁺ and Pd⁴⁺) species. As shown in Figure S6B, a broad and asymmetrical Cu 2p_{3/2} XPS peak for the Pd_{0.3}Cu_{0.7} was recorded, indicating the existence of several kinds of surface copper species. The species at BE = 932.5 and 933.5 eV could be assigned to the surface Cu⁰ species and Cu²⁺ species, respectively.

XPS peaks of the Pd 3d_{5/2} and Cu 2p_{3/2} for the used catalyst, as shown in Figure S6C and Figure S6D. The surface Pd^{δ+} and Cu^{δ+} species concentration increased after the catalysis test. The formation of oxidized M^{δ+} species existed in Pd-Cu alloy nanoparticles indicated that part of metal surface might be oxidated by tert-butyl hydroperoxide.

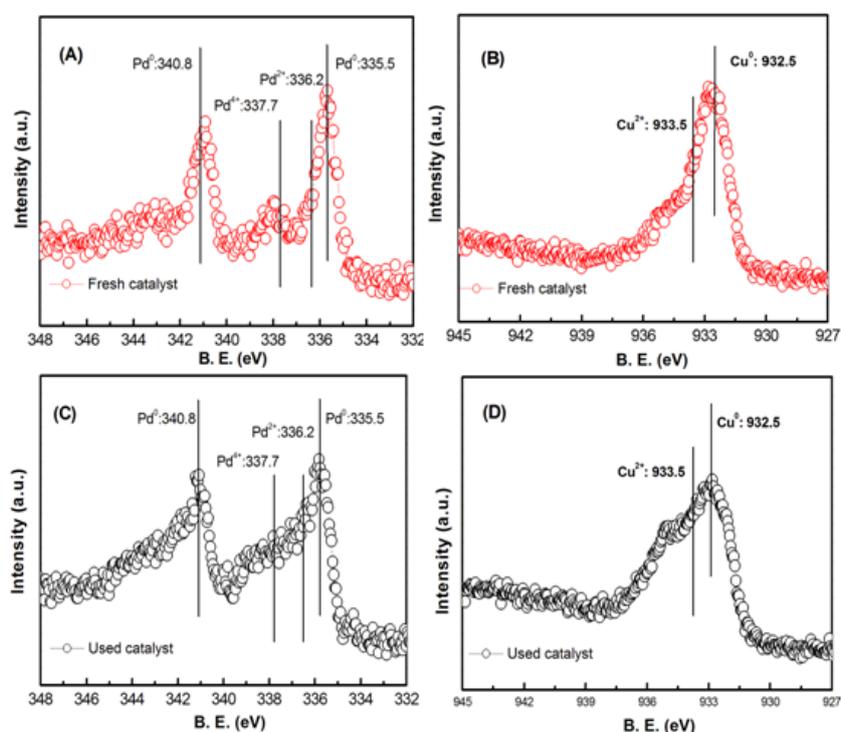


Figure S6. XPS spectra of fresh (A) Pd 3d and (B) Cu 2p; and used (C) Pd 3d and (D) Cu 2p catalysts.