

## Supporting Information:

### **From mixed to three-layer core/shell PtCu nanoparticles: Ligand-induced surface segregation to enhance electrocatalytic activity**

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## Experimental Details

**Chemicals:** Cupric (II) acetylacetonate ( $\text{Cu}(\text{acac})_2$ ) was purchased from TCI. Oleylamine (OAm), oleic acid (OA), benzyl ether (BE), acetic acid, acetone and hexane were purchased from Aladdin. Platinum (II) acetylacetonate ( $\text{Pt}(\text{acac})_2$ , 98%) and commercial platinum/carbon (20% Pt/C) catalyst were purchased from Alfa aesar. High pure nitrogen ( $\text{N}_2$ , 99.999%) was procured from Beijing Ru Yuan Ru Quan Gas Company. Carbon black (Vulcan XC-72R) was obtained from Cabot Company. 5 wt. % Nafion solution was obtained from DuPont Company. All chemicals were used without further purification.

**Synthesis of mixed PtCu NPs:** In a standard synthesis,  $\text{Pt}(\text{acac})_2$  (0.051 mmol),  $\text{Cu}(\text{acac})_2$  (0.039 mmol), OAm (9.0 ml), and OA (1.0 ml) were added into a 3-neck flask, mixed, and heated to 130 °C under an  $\text{N}_2$  atmosphere with magnetic stirring for 20 min. The mixture was then heated to 230 °C quickly and kept at 230 °C for 40 min with  $\text{N}_2$  purging. The reaction mixture was allowed to cool down to room temperature naturally, and the resulting colloidal products were collected by centrifugation and washed with a hexane-ethanol mixture. The resulting mixed PtCu NPs could be easily dispersed in organic solvents such as toluene and hexane.

**Synthesis of three-layer core/shell PtCu NPs:** In a standard synthesis,  $\text{Pt}(\text{acac})_2$  (0.051 mmol),  $\text{Cu}(\text{acac})_2$  (0.039 mmol), OAm (2.0 ml), OA (1.0 ml) and BE (7.0 ml) were added into a 3-neck flask, mixed, and heated to 130 °C under an  $\text{N}_2$  atmosphere with magnetic stirring for 20 min. The mixture was then heated to 230 °C quickly and kept at 230 °C for 40 min with  $\text{N}_2$  purging. The reaction mixture was allowed to cool down to room temperature naturally, and the resulting colloidal products were collected by centrifugation and washed with a hexane-ethanol mixture. The resulting three-layer core/shell PtCu NPs could be easily dispersed in organic solvents such as toluene and hexane.

**Characterization techniques:** Powder X-ray diffraction (PXRD) patterns were recorded using Bruker D8 Advance X-ray diffractometer with CuK $\alpha$  ( $\lambda=0.15418$  nm) radiation source at 40 kV, 40 mA. Transmission electron microscopy (TEM) images were collected on Tecnai G<sup>2</sup> 20 operating at 200 kV. High-Resolution TEM (HRTEM) images were collected on a JEOL JEM-2100 transmission electron microscope. The microstructure was characterized by High-Angle Annular Dark Field (HAADF) imaging in Scanning Transmission Electron Microscopy (STEM) mode. The energy dispersive X-ray spectroscopy (EDX) data were obtained from a Hitachi S-4800 SEM operated at 20 kV. X-ray Photoelectron Spectroscopy (XPS) data were taken on a Thermofisher ESCALAB 250 X-ray photoelectron spectroscopy with a Mg-K $\alpha$  source. UV/Vis spectroscopy was taken in a quartz cuvette on an Agilent Cary 5000 UV-vis-NIR spectrophotometer.

**Catalyst and working electrode preparations:** Carbon black (Vulcan XC-72) was used as support for preparing electrocatalysts. In a typical preparation, the as-prepared product was mixed with 40 mg carbon black in 20 ml hexane. Subsequently, the mixture was sonicated for 30 min and precipitated out by centrifugation. The resulting catalyst was centrifuged at 8,000 rpm for 12 min, and then added into 25ml of acetic acid and heated at 60 °C for 6h. The final catalyst was washed 5 times with ethanol and dried in a vacuum oven overnight before electrochemical measurements.

The procedure of working electrode preparation is as follows: 6 mg carbon support sample was added into a 3 ml mixture of deionized water, isopropanol and Nafion (5%) at a volume ratio of 2:1:0.04. After ultrasonic irradiation for at least 30 min, 10  $\mu$ l catalyst ink was deposited on the glassy carbon-rotating disk electrode (GC-RDE) of 5mmdiameter. The electrode was dried at ambient condition and was used as a working electrode for further electrochemical studies.

**Electrochemical measurements:** CV measurements, ORR, FAOR, MOR and EOR tests were taken on a CHI760e (Chen-Hua, China) electrochemical work station in a

three electrode system at room temperature. A platinum net electrode was used as counter electrode, while a saturated calomel electrode (SCE) was used as reference electrode and a 5 mm diameter glassy carbon electrode modified with catalyst film was used as working electrode. All potentials quoted are referenced to RHE. The CV measurements were performed in N<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> solution at a potential range of 0.05 – 1.10 V and a scanning rate of 50 mVs<sup>-1</sup>. ORR polarization curves were obtained by scanning the potentials from 1.1 to 0.2 V versus RHE at a scan rate of 10 mV s<sup>-1</sup> in oxygen-saturated (O<sub>2</sub>-saturated) 0.1 M HClO<sub>4</sub> with the GC-RDE rotating at 1600 rpm. For ensuring N<sub>2</sub>-saturated or O<sub>2</sub>-saturated, the 0.1 M HClO<sub>4</sub> solution was purged with N<sub>2</sub> or O<sub>2</sub> more than 30 min prior to the electrochemical measurements. In addition, N<sub>2</sub> or O<sub>2</sub> was maintained over the electrolyte during the measurement. The FAOR tests were performed in N<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> + 2 M HCOOH solution at the potential range of 0.05 – 1.30 V and a scanning rate of 50 mVs<sup>-1</sup>. The MOR measurements were performed in N<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> + 0.5 M CH<sub>3</sub>OH solution at the potential range of 0.05 – 1.30 V and a scanning rate of 50 mVs<sup>-1</sup>. The EOR tests were performed in N<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> + 0.5 M CH<sub>3</sub>CH<sub>2</sub>OH solution at the potential range of 0.05 – 1.30 V and a scanning rate of 50 mVs<sup>-1</sup>. The stability tests are performed in N<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> + 0.5 M CH<sub>3</sub>OH solution at 0.9 V.

The ECSA was calculated based on the following relation:

$$ECSA = Q_H / (m \times q_H)$$

where Q<sub>H</sub> is the charge for hydrogen desorption, m is the loading amount of metal in the electrode, and q<sub>H</sub> is the charge required for monolayer desorption of hydrogen on Pt (210 mC cm<sup>-2</sup>). For the ORR at a RDE, the Koutecky-Levich equation can be described by the following relation:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d}$$

where j is the experimentally measured current, j<sub>k</sub> and j<sub>d</sub> are the kinetic and diffusion-

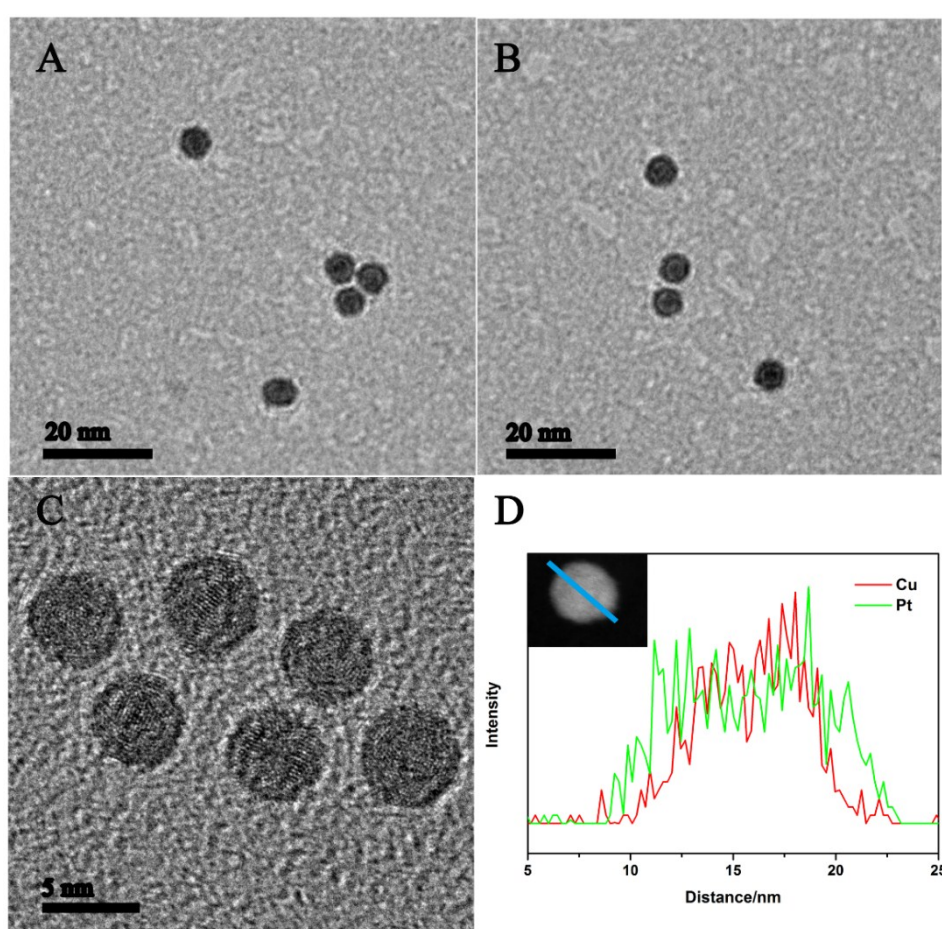
limited current densities, respectively. Then, the kinetic current was calculated based on the following equation:

$$j_k = \frac{j_d \times j}{j_d - j}$$

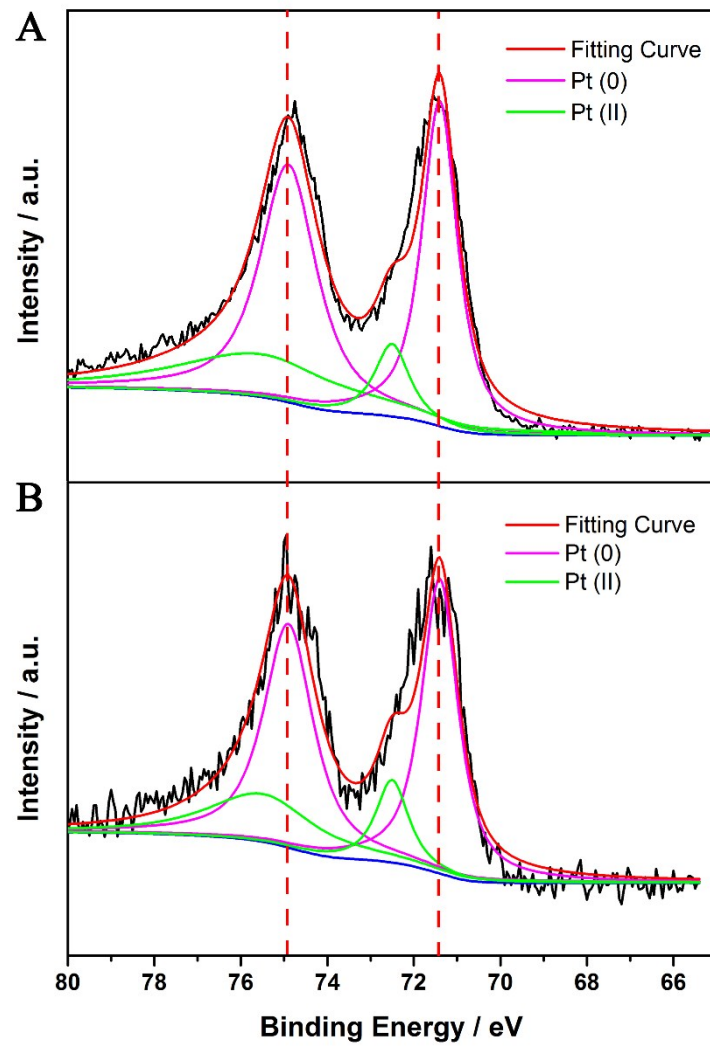
For each catalyst, the kinetic current was normalized to ECSA and the loading amount of metal in order to obtain the specific activity and mass activity, respectively.

**Table S1** Percentage of different structures

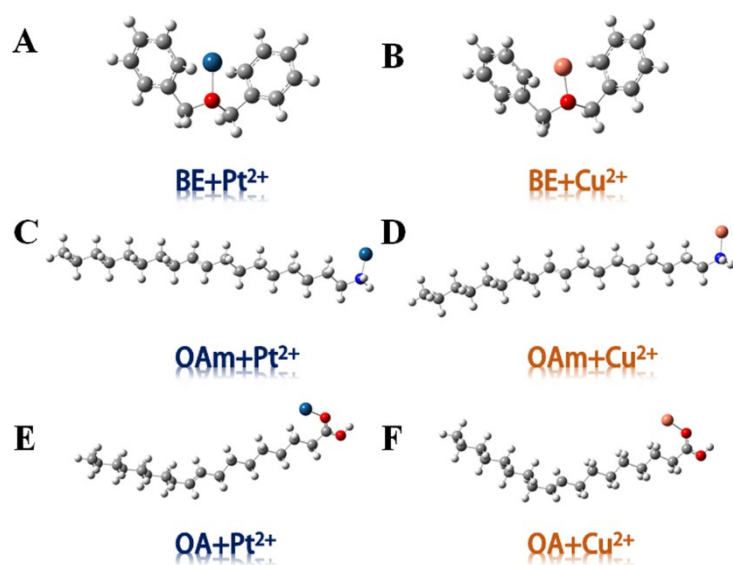
| Structure                        | Percentage |
|----------------------------------|------------|
| three-layer core/shell structure | 72%        |
| defects                          | 15%        |
| concave surface                  | 6%         |
| steps                            | 3%         |
| hollow structure                 | 4%         |



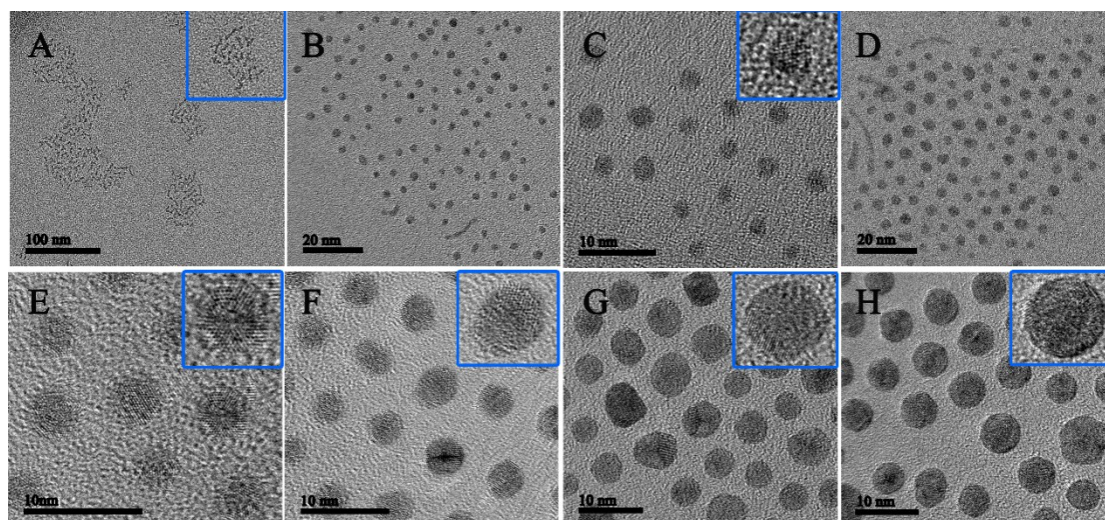
**Fig. S1** Additional(A) and (B) TEM image of three-layer core/shell PtCu NPs. (C) HRTEM image of three-layer core/shell PtCu NPs. (D) EDX line scan profiles recorded from individual three-layer core/shell PtCu NP from Fig. S1A.



**Fig. S2** XPS spectra of Pt4f for (A) mixed PtCu NPs and (B) three-layer core/shell PtCu NPs.

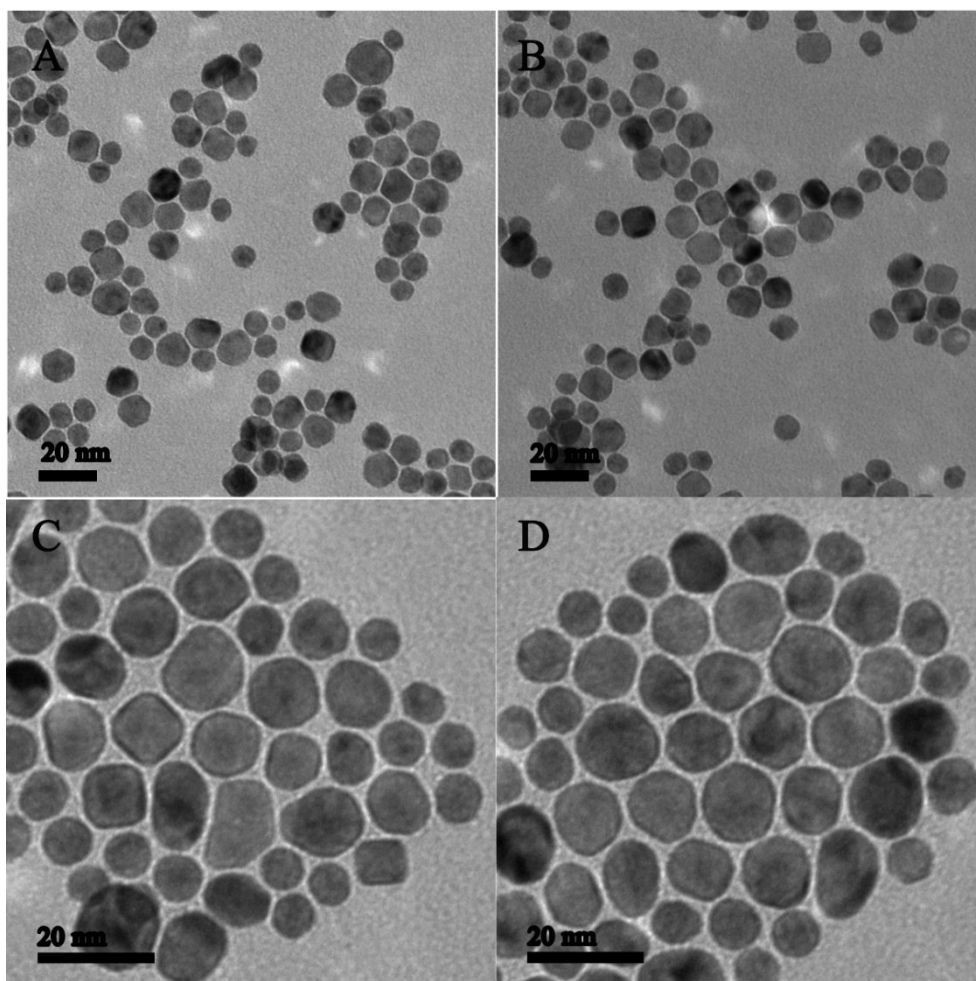


**Fig. S3** Models of (A) BE+Pt<sup>2+</sup>, (B) BE+Cu<sup>2+</sup>, (C) OAm+Pt<sup>2+</sup>, (D) OAm+Cu<sup>2+</sup>, (E) OA+Pt<sup>2+</sup>, and (F) OA+Cu<sup>2+</sup>.



**Fig. S4** TEM images of the products obtained at different reaction time: (A) 210 °C, (B-C) 0min at 230 °C, (D-E) 5min at 230 °C, (F) 10min at 230 °C, (G) 20min at 230 °C, (H) 40min at 230 °C. The inserted image is the HRTEM of individual PtCu NP selected in the corresponding TEM image.





**Fig. S5** (A-B) TEM images PtCu NPs obtained in the solvents mixed with OAm (4.0 ml), OA (1.0 ml) and BE (5.0 ml). (C-D) TEM images PtCu NPs obtained in the solvents consisting of OAm (6.0 ml), OA (1.0 ml) and BE (3.0 ml).