

## Supporting Information

### **PtCu nanodendrite-assisted synthesis of PtPdCu concave nanooctahedra for efficient electrocatalytic methanol oxidation†**

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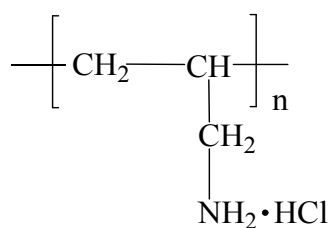
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## Experimental section

### *Reagents and Chemicals*

Potassium tetrachloroplatinate(II) ( $K_2PtCl_4$ ), cupric chloride ( $CuCl_2$ ), potassium tetrachloropalladate(II) ( $K_2PdCl_4$ ), sulfuric acid ( $H_2SO_4$ ), methanol ( $CH_3OH$ ) and formaldehyde (HCHO) solution (40%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Polyallylamine hydrochloride (PAH, Scheme S1, average molecular weight  $M_w=15\ 0000$ ) was supplied from Nitto Boseki Co., Ltd. (Tokyo, Japan). Commercial Pt black was purchased from Johnson Matthey Corporation. Other reagents were of analytical reagent grade and used without further purification. All the aqueous solutions were prepared with Millipore water having a resistivity of 18.2 M $\Omega$ .



**Scheme S1.** The molecular structure of PAH.

### *Preparation of PtPdCu alloy concave nanooctahedra*

Platinum-copper alloy nanodendrites was firstly synthesised according to our previous work<sup>1</sup>. Briefly, 2.0 mL of 0.5 M PAH, 1.0 mL of 0.05 M  $K_2PtCl_4$ , and 2.0 mL of 0.05 M  $CuCl_2$  aqueous solutions were added into the 3 mL  $H_2O$ . After adjusting solution pH to 3.0, 2.0 mL of HCHO solution (40%) was added into the mixture solution. Then, the mixture solution was heated at 140 °C for 4 h. After being cooled to room temperature, 1.0 mL of 0.05 M  $K_2PdCl_4$  added into the obtained PtCu alloy nanodendrites solution and heated at 140 °C for another 4 h. Lastly, the products were separated by centrifugation, washed with water for several times, and dried at 60 °C for 5 h in a vacuum dryer.

### *Apparatus*

Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), selected area diffraction (SAED), high-angle annular dark-field scanning TEM (HAADF-STEM) and EDX mapping images were performed on a JEOL JEM-2100 instrument operated at 200 kV. The X-ray (EDX) analysis of samples were carried on a JEOL JSM-7600F SEM instrument. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo VG Scientific ESCALAB 250 spectrometer. The binding energy was calibrated by means of the C 1s peak energy of 284.6 eV. X-ray diffraction (XRD) patterns of samples were obtained from Model D/max-rC X-ray diffractometer (Cu K $\alpha$  radiation source,  $\lambda=1.5406$  Å, operating at 40 kV and 100 mA).

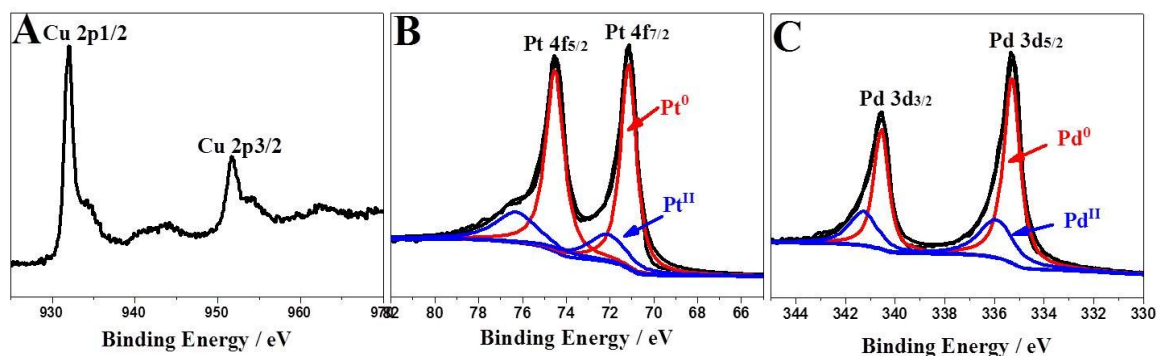
### *Electrochemical measurements*

Cyclic voltammetry and chronoamperometry experiments were performed on a CHI 660D electrochemical work station (CH Instruments, Shanghai, Chenghua Co.) at  $30 \pm 1$  °C using conventional three-electrode system. A saturated calomel electrode as the reference electrode, a pure platinum wire as the counter electrode, and the sample modified glassy carbon (3 mm diameter) electrode as the working electrode.

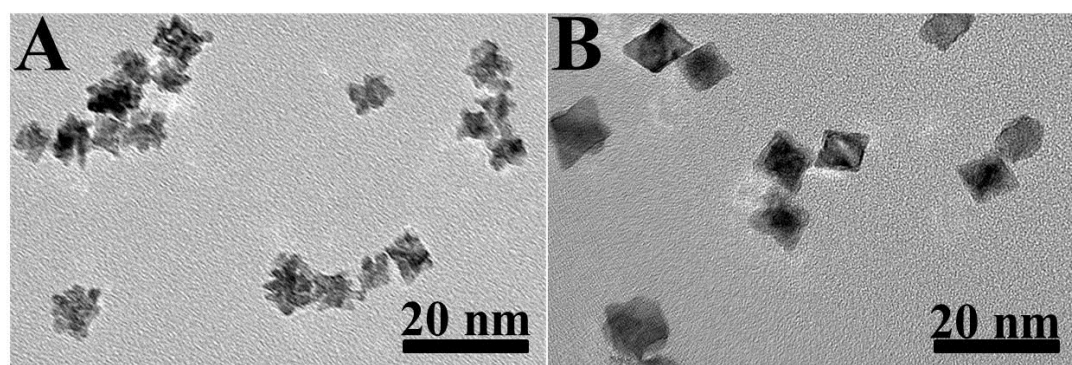
For the preparation of the working electrodes, 2.0 mg of catalyst was dispersed into 2.0 mL of water to form a homogeneous suspension by ultrasonication for 1 h. Then 6  $\mu$ L dispersion was covered onto the surface of the glassy carbon electrode and drying naturally, 2.0 $\mu$ L of 5.0 wt% Nafion solution was spread on the surface of the catalyst layer. The Pt metal loading on the electrode surface was about 3.289, 3.657, and 6.0  $\mu$ g, respectively. The electrochemically active surface areas (ECSA) of Pt electrocatalysts were calculated from the following equation by collected the charge in CO adsorption oxidation region and assuming a value of 420  $\mu$ C cm<sup>-2</sup> for the adsorption of a CO monolayer.<sup>2</sup>

$$ECSA = \frac{Q}{m \times C} \quad (1)$$

Where  $Q$  was the charge collected in the CO adsorption oxidation region,  $m$  was the loading amount of Pt metal,  $C$  ( $420 \mu\text{C cm}^{-2}$ ) was the charge required for monolayer adsorption of CO on Pt and Pd surface.



**Fig. S1.** XPS spectra of PtPdCu ACNOs in (A) Cu 2p region, (B) Pt 4f region, and (C) Pd 3d region, indicating the Cu, Pt and Pd exist prominently as metallic state.<sup>3</sup>



**Fig. S2.** TEM images of (A) PtCu alloy nanodendrites and (B) PtPdCu ACNOs after chronoamperometry test.

*References:*

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2. X. Y. Liu, Y. Zhang, M. X. Gong, Y. W. Tang, T. H. Lu, Y. Chen and J. M. Lee, *J. Mater. Chem. A*, 2014, **2**, 13840.
3. J. Moulder, W. Stickle, P. Sobol and K. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, Physical Electronics Division: Eden Prairie, MN, 1992.