Supporting Information

Enhanced Bifunctional Fuel Cell Catalysis via Pd/PtCu Core/Shell Nanoplates

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Experimental section

Materials. Palladium(II) acetylacetonate ($Pd(acac)_2$, 99%), platinum(II) acetylacetonate ($Pt(acac)_2$, 97%), PVP(MW ≈ 24000), hexadecyltrimethylammonium bromide (CTAB), oleylamine (OAm) and tungsten hexacarbonyl ($W(CO)_6$) were all purchased from Sigma-Aldrich company. Copper (II) acetylacetonate ($Cu(acac)_2$, 95%), citric acid (CA) and commercial Pt/C (20 wt%) were purchased from Alfa Aesar. Benzyl alcohol (BA) and N,N-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent.

Synthesis of 10 nm Pd nanoplates. In a standard synthesis of Pd nanosheets with an average edge length of 8 nm and thickness of ~1.1 nm, 16 mg of $Pd(acac)_2$, 30 mg of PVP, 60 mg of CTAB and 120 mg of CA were dissolved in 10 mL of DMF and stirred for 1 h at room temperature. The homogeneous orange-red solution was then transferred into a 50 mL glass flask, and 100 mg of $W(CO)_6$ was added into the flask under an N_2 atmosphere. The sealed flask was heated at 80℃ under magnet stirring for 1 h, and then cooled to room temperature. After the reaction, the Pd nanoplates were isolated by centrifugation using acetone, and then washed three times with acetone and ethanol.

Synthesis of Pd/PtCu nanoplates. In a standard procedure for the synthesis of the Pd/PtCu nanoplates, 400 mg of PVP, 0.020 mmol of $Pt(acac)_2$ and 0.020 mmol of $Cu(acac)_2$ were dissolved in 10 mL of BA containing Pd seeds sealed into a 15 mL Teflon-lined stainless steel autoclave, and further stirred for 2 h. The autoclave was heated at 200 ^oC for 12 h and then cooled at room temperature. The final product was collected by centrifugation, washed with a sufficient amount of acetone and ethanol for three times.

Morphological, structural and elemental characterization. Transmission electron microscopy (TEM) images were taken using a Tecani-G2 T20 operated at 200 kV. High-resolution TEM (HRTEM), selected-area electron diffraction (SAED) and energy-dispersive X-ray (EDX) were performed using a JEOL 2100F TEM (200 kV). The concentration of catalysts was determined by inductively coupled plasma emission spectrometry (ICP-AES) on a Prodigy.

Electrochemical test. A three-electrode cell was used to take the electrochemical measurement using a Pt wire as the counter electrode, an Ag/AgCl as the reference electrode, and a glassy carbon (GC) electrode (5 mm in diameter) as the working electrode. To prepare catalyst-coated GC working electrodes, the Pd/PtCu-C NPs or commercial Pt/C was dispersed in a mixture of water/propanol/Nafion (v/v/v = 15/5/0.080) under sonication to form a 1 mg/mL catalyst ink. And 10 μL of this ink was casted on the surface of electrode, and dried at ambient condition. Electrolyte was freshly made and all working electrodes were cleaned by a steady-state potential sweeping from 0.05 to 1.15 V *vs.* RHE at 200 mVs^{-1} in N_2-saturated 0.1 M $HClO_4$ solution. CV measurements were scanned from 0.05 to 1.15 V *vs.* RHE at a sweep rate of 50 mVs^{-1}. The ECSA of each sample was determined by integrating the area surrounded by the hydrogen desorption curve and CV baseline. The ORR scan rate and rotation rate were 50 mVs^{-1} and 1600 rpm, and the MOR scan rate was 50 mVs^{-1}. The ORR and MOR kinetic currents were normalized to the amount of Pt and to ECSA to get mass and specific activities of the catalysts, respectively.

Table

Table S1 ECSA values of different electrocatalysts

	$Pt_{65}Cu_{35}$	$Pt_{50}Cu_{50}$	$Pt_{35}Cu_{65}$	Commercial Pt
ECSA/m^2 g^{-1}	33.9	39.1	62.3	60.8

Figures

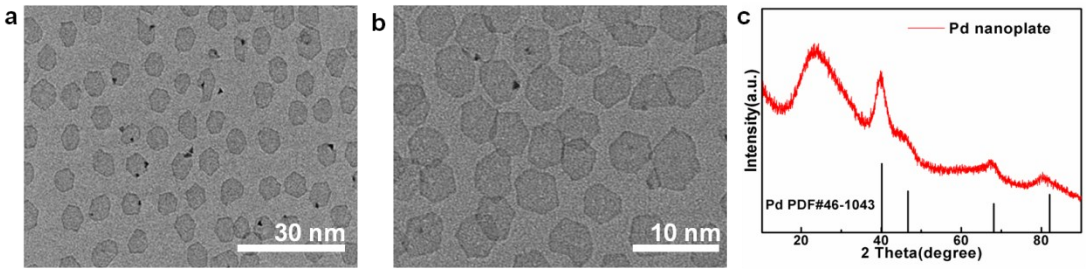

Figure S1. (a, b)TEM images and (c) XRD pattern of the Pd nanoplates.

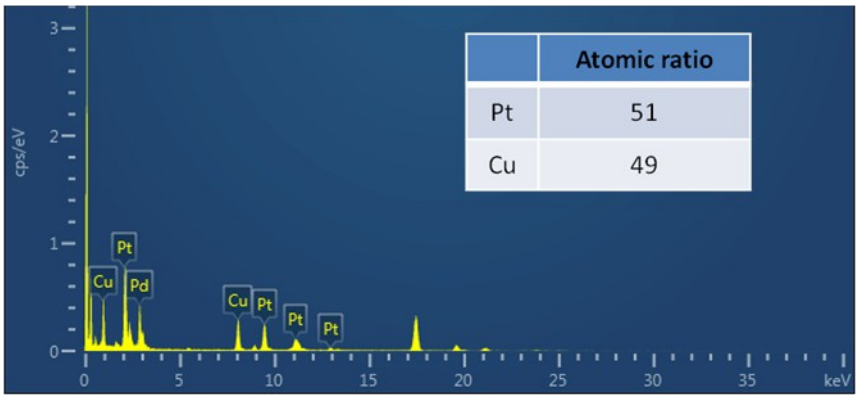

Figure S2. Representative TEM-EDX image of Pd@$Pt_{50}Cu_{50}$ NPs and the atomic ratio (inside).

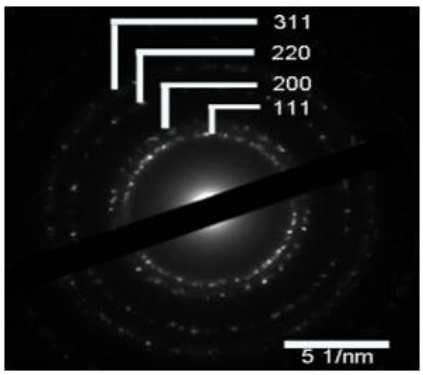

Figure S3. SAED pattern of Pd/$Pt_{50}Cu_{50}$ NPs.

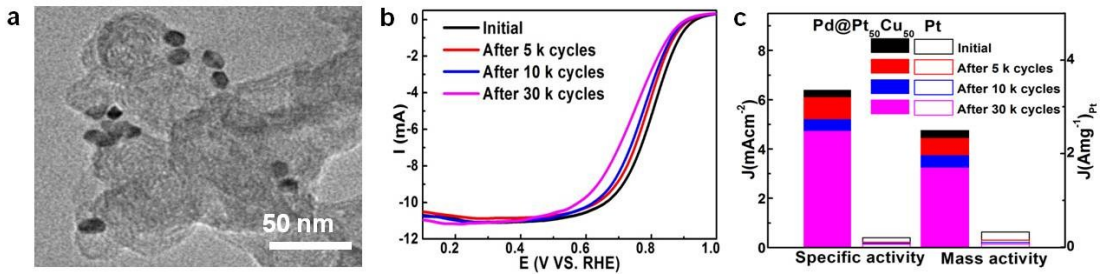

Figure S4. (a) Representative TEM image of $Pd/Pt_{50}Cu_{50}$ NPs loaded on commercial carbon. (b) ORR polarization curves of commercial Pt before and after 5,000 10,000 and 30,000 potential cycles. (c) Specific and mass activities of $Pd/Pt_{50}Cu_{50}$ NPs and commercial Pt before and after 5000, 10,000 and 30,000 potential cycles.

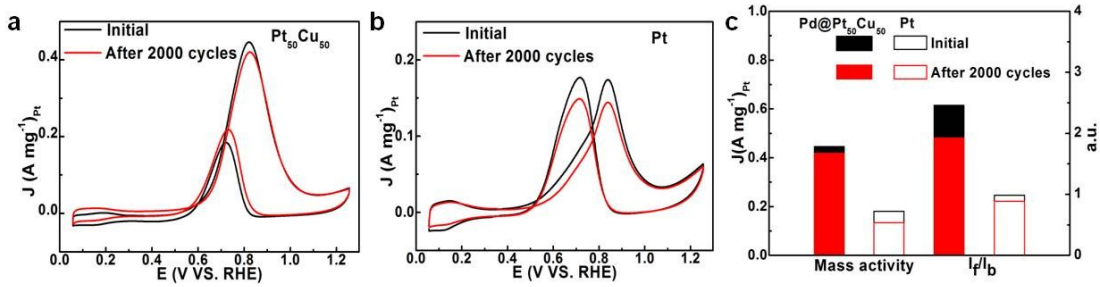

Figure S5. Cyclic voltammetric curves for MOR mass activity of (a) $Pd/Pt_{50}Cu_{50}$ NPs and (b) commercial Pt before and after 2,000 cycles. (c) Mass activities at 0.8 V *vs.* RHE and I_f/I_b of $Pd/Pt_{50}Cu_{50}$ NPs and commercial Pt before and after 2,000 potential cycles.