Electronic Supplementary Information (ESI) for Shape-control of super-branched PdCu alloy with enhanced electrocatalytic performance for ethylene glycol oxidation

Experimental

1. Chemicals and materials

Copper(II) acetate, (Cu(OAc)₂.H₂O) was purchased from Sinopharm Chemical Reagents Co., Ltd. (China). Potassium chloropalladite (99.9%, K₂PdCl₄), 1methylimidazole, (\geq 99.0%, C₄H₆N₂) and ethylene glycol (98%, C₂H₆O₂) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (China). Vulcan carbon powder XC-72 was purchased from Cabot Co. (USA). Nafion solution (5%) was purchased from Dupont Co. (USA). 10 wt% Pd/C was purchased from J&K Scientific Ltd. (China). All the chemicals were of analytical grade and used as received. Ultrapure water (resistivity: $\rho \geq$ 18 M Ω cm) was used to prepare the solutions.

2. Synthesis of self-supported sea cucumber-like PdCu alloy

The super-branched PdCu alloy was synthesized via a one-pot solvothermal process. Briefly, 0.01 g Cu(OAc)₂·H₂O (0.5 mmol) and 0.163 g K₂PdCl₄ (0.5 mmol) was dissolved into 50 mL ethylene glycol solution with 12 mL 1-methylimidazole. After stirring for 1 h at room temperature, the prepared solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave and maintained at 160 °C for 6 h. After cooled down to room temperature naturally, the product was centrifuged and washed with ethanol absolute repeatedly, and dried at 60 °C in an oven overnight. Based on the contents of Pd and Cu in the super-branched PdCu alloy, as measured by ICP-MS, the mass ratio (Pd : Cu) was calculated to be 64 : 36, and the obtained sample was denoted as PdCu. Other samples with different mass ratio were prepared just by changing the amount of the Cu(OAc)₂·H₂O. Typically, 0.125 mmol, 1 mmol and 2 mmol of Cu(OAc)₂·H₂O was added, respectively. Based on the contents of Pd and Cu

in the samples, as measured by ICP-MS, the mass ratio (Pd : Cu) was calculated to be 88 : 12 , 46 : 54 and 31 : 69, respectively. The obtained samples were denoted as $Pd_{88}Cu_{12}$, $Pd_{46}Cu_{54}$ and $Pd_{31}Cu_{69}$, respectively. The pure Pd and pure Cu nanoparticles was prepared as discussed in the above method without the addition of $Cu(OAc)_2$.H₂O and K₂PdCl₄, respectively.

3. Characterization

The crystal structure of samples was examined by X-ray diffractiion (XRD) using a Rigaku ultima IV diffractometer with Cu $K\alpha$ radiation. Scanning electron microscopy (SEM) images were obtained using a JEOL JFC1600 microscope at 10 kV. Transmission electron microscopy (TEM) characterization was completed by using a JEOL JEM-2100 instrument with operating voltage at 200 kV. The exact compositions of the products were examined by inductively coupled plasma-optical emission spectrometry (ICP-OES, X Series 2, Thermo Scientific USA). N₂ adsorption-desorption isotherms were measured by using ASAP 2020 at liquid nitrogen temperature 77 K with prior degassing at 120 °C for 8 h. The specific surface areas were calculated by the BET method.

4. Electrochemical measurements

All the electrochemical measurements were performed on a CHI 660E electrochemical workstation (Chenhua Instruments Corp, Shanghai, China) system with a typical three-electrode cell at room temperature. Hg/HgO electrode and Pt wire were used as reference electrode and counter electrode, respectively. In briefly, the catalytic ink is prepared by ultrasonically dispersing 3 mg of electrocatalyst and 7 mg of Vulcan XC-72 in 1 mL ethanol containing 50 μ L 5 wt.% Nafion solution for 30 min, then 6 μ L ink was coated on the surface of glassy carbon electrode (GCE, 4 mm in diameter), resulting in a catalyst loading of 0.455 mg cm⁻². The commercial Pd/C were used for comparison with the same powder loading.

The electrochemically active surface area (ECSA) was calculated according to the area of Pd-oxides reduction peak, and the formula was shown as following:

$$ECSA = \frac{Q}{SL}$$

Where Q (μ C) represents the total charge calculated by integral area of Pd-oxides reduction peak, S (μ C cm⁻²) represents the charges required to reduce the Pd-oxides monolayer, assuming a value of 405 μ C cm⁻² for monolayer Pd oxide reduction, and L (mg) is the total quality of palladium on the surface of working electrode.

Possible formation mechanism of branched PdCu alloy

Various control experiments were conducted to explore the possible formation mechanism of the branched PdCu alloy. Firstly, we introduced the same volume of acetic acid instead of 1-methylimidazole, irregular pure Pd nanoparticles were produced and no branched Pd were obtained (Fig. S11, ESI⁺). When we kept all the other synthetic conditions unchanged, only used the same molar amount of $Pd(OAc)_2$ to replace K₂PdCl₄, the products were still in sapling-like with a few long, thick branches (Fig. S12, ESI⁺). These observations strongly demonstrate the essential role of 1-methylimidazole as a structure-directing agent in the formation of 3D superbranched nanostructures. Besides, to further confirm the Cu²⁺ can effectively control the morphology of Pd, we chose different copper salts, but kept all the other synthetic conditions unchanged. When the same molar amount of CuCl₂ or Cu(NO₃)₂ instead of Cu(OAc)₂ was added, similar 3D branched PdCu alloy were synthesized (Fig. S13, Fig. S14, ESI[†]), These results further confirm that the presence of Cu²⁺, instead of the anions (e.g., Cl⁻, NO₃⁻, OAc⁻), takes the central role in the formation of 3D branched nanostructures. Compared with using Cu(OAc)₂ as the precursor, the branches of the products become shorter, owing to the variation of reduction kinetics using different precursors.¹ It is well established that 1-methylimidazole as a structure-directing agent can selectively adsorb on the (111) planes of Pt-Pd alloy and cause hierarchy growth along the (111) planes.² Our XRD result also confirms the main exposed planes for pure Pd are (111) planes (Fig. S6, ESI⁺). When the Cu²⁺ is introduced into the synthesis, partial (111) planes of Pd will be blocked by the generated of Cu, and

growth will only be allowed at the uncovered (111) planes to generate a 3D superbranched structure.

Sample name	Surface area (m ² g ⁻¹)
PdCu alloy (Pd : Cu = 4 : 1)	7.81
PdCu alloy (Pd : Cu = 1 : 1)	11.62
PdCu alloy (Pd : Cu = 1 : 4)	6.11

Table S1. Comparison the surface area of PdCu alloy with different morphology.



Fig. S1 SEM image of pure Cu.



Fig. S2 SEM image of pure Pd.



Fig. S3 SEM image of PdCu with small amount of Cu^{2+} (Pd : Cu = 4 : 1).



Fig. S4 SEM image of PdCu with large amount of Cu^{2+} (Pd : Cu = 1 : 4).



Fig. S5 XRD patterns of pure Cu.



Fig. S6 XRD patterns of pure Pd.



Fig. S7 XRD patterns of PdCu alloy with different mass ratio.



Fig. S8 CV curves of PdCu alloy with different mass ratio in N_2 -saturated 1.0 M KOH with the scan rate 100 mV s⁻¹.



Fig. S9 CV curves of PdCu alloy with different mass ratio in 1.0 M KOH + 0.5 M EG with the scan rate of 100 mV s^{-1} for EG electrooxidation.



Fig. S10 TEM image of PdCu after the durability test.



Fig. S11 SEM image of pure Pd (acetic acid instead of 1-methylimidazole).



Fig. S12 SEM image of pure Pd (Pd(OAc)₂ instead of K_2PdCl_4).



Fig. S13 SEM image of PdCu (copper salts: Cu(NO₃)₂).



Fig. S14 SEM image of PdCu (copper salts: CuCl₂).

- 1 X. Huang, H. Zhang, C. Guo, Z. Zhou and N. Zheng, *Angew Chem Int Ed Engl*, 2009, **48**, 4808-4812.
- 2 J. J. Lv, L. P. Mei, X. Weng, A. J. Wang, L. L. Chen, X. F. Liu and J. J. Feng, *Nanoscale*, 2015, **7**, 5699-5705.