Electronic Supplementary Information for :

Bimetallic PdPt nanowire networks with enhanced electrocatalytic activity for

ethylene glycol and glycerol oxidation

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1. Experimental Section

Chemicals. Polyvinylpyrrolidone (PVP, K30) was obtained from Sinopharm (Shanghai, China). H₂PtCl₆, PdCl₂ and KBr were commercially purchased from Beijing Chemical Corp (China). NaBH₄ and nafion ethanol solution (5 wt.%) were obtained from Sigma-Aldrich. Na₂PdCl₄ and commercial Pt/C catalyst were purchased from Alfa Aesar. Commercial Pd/C (10 wt.%) were purchased from Aladdin Chemistry Co. Ltd (Shanghai, China). All the reagents used in this experiment were of analytical grade and used without any further purify process. The water used in the experiment refer to the Milli-Q ultrapure water (Millipore, $\geq 18.2 \text{ M}\Omega \text{ cm}$).

Apparatus. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) measurements, high-angle annular dark-field scanning (HAADF-STEM), and energy dispersive X-ray spectrum (EDS) investigations were carried out on a JEM-2100F high-resolution transmission electron microscope operating at 200 kV. Low resolution TEM images were analyzed with a

HITACHI H-600 Analytical TEM with an accelerating voltage of 100 kV (all the TEM images in ESI except Fig. S1). Inductively coupled plasma-mass spectroscopy (ICP-MS, X Series 2, Thermo Scientific USA) was used to determine the exact compositions of the products. X-ray diffraction (XRD) results of the as-prepared samples were recorded on a D8 ADVANCE (BRUKER, Germany) diffractometer using Cu–K α radiation with a Ni filter ($\lambda = 0.154059$ nm at 30 kV and 15 mA). X-ray photoelectron spectroscopy (XPS) measurements of the products were taken out on an ESCALAB-MKII spectrometer (VG Co., United Kingdom) with Al K α X-ray radiation as the X-ray source for excitation. The whole electrochemical experiments were measured with a CHI 832B electrochemical workstation (Chenhua Instruments Corp, Shanghai, China).

Synthesis of PdPt nanowires networks. For the synthesis of Pd₁Pt₁ NNWs, 30 mg PVP, 0.2 mL of Na₂PdCl₄ (60 mM), 0.063 mL of H₂PtCl₆ (193 mM) and 1 mL KBr (2.5 M) were mixed Into 15 mL of water under stirring. After that, 4 mL of NaBH₄ (2 mg/mL) were added into the above mixture slowly. About 30 min later, the reaction can be completed. Another two types of PdPt NNWs were prepared just by changing volume of the precursors and NaBH₄: 0.2 mL of Na₂PdCl₄ (60 mM), 0.031 mL of H₂PtCl₆ (193 mM) and 3 mL of NaBH₄ (2 mg/mL); 0.1 mL of Na₂PdCl₄ (60 mM), 0.062 mL of H₂PtCl₆ (193 mM) and 11 mL of NaBH₄ (2 mg/mL) respectively. Finally, the products were centrifuged at 11000 rpm for 15 and washed with Milli-Q water for several times.

Electrocatalytic measurements. A common three-electrode cell was used, which containing a KCl saturated Ag/AgCl electrode as reference electrode, a platinum wire as counter electrode and modified glassy carbon electrode (GCE) as working electrode respectively. Before the modifications, GCE was polished carefully with alumina powder to obtain a mirror-like surface, and then followed by sonication in ethanol and Milli-Q water respectively. Then, certain amount of commercial Pt/C or the as-prepared catalysts solution was dropped on the surface of the GCE with a pipette and dried under an infrared lamp, the loading mass of noble-metals (metal_{*Pd+Pt*}) was controlled at 25.5 μ g/cm². Finally, 4 μ L of Nafion (0.02%) was coated onto surface of GCE and dried carefully before electrochemical tests.



Fig. S1 Large-area TEM (a) and HRTEM images of the prepared PdPt NNWs.



Fig. S2 EDS of the prepared PdPt NNWs. The inset is the digital photo of the prepared PdPt NNWs.



Fig. S3 (A) TEM images of the prepared PdPt NNWs with different compositions: $Pd_{55}Pt_{30}$ (A) and $Pd_{22}Pt_{41}$ (B).



Fig. S4 (A) Typical TEM images of the products prepared without adding KBr, the products were consisted of small nanoparticles as marked by the red circles and arrows. (B) The products (denoted as Pt NNWs) prepared without adding Pd precursors.



Fig. S5 Typical TEM images of the products collected at different time: (A) 1, (B) 2, (C) 5 and (D) 8 min respectively. The scale bar represents 100 nm.



Fig. S6 Pd 3d XPS of PdPt NNWs with different compositions and Pd NNWs.



Fig. S7 CV curves of EG (A) and glycerol (B) electrooxidation on Pd NNW, Pt NNWs and commercial Pd/C materials modified electrodes, the test conditions are same to the PdPt NNWs.



Fig. S8 Mass activity (measured by the forward peak current density) of the various materials for EG (A) and glycerol (B) electrooxidation.



Fig. S9 CV curves of different PdPt NNWs and Pt/C in 0.5 mol/L H_2SO_4 . The ECSA (m²/g) of these materials was measured as follows by using the hydrogen adsorption/desorption method reported in literature,¹⁻²

$$ECSA=100*(Q_{adsorption}+Q_{desorption})/(2*210*m_{Pd+Pt})$$

 $Q_{adsorption}$ and $Q_{desorption}$ (unit: C) represents the charge of hydrogen adsorption/desorption area obtained after deducted the double-layer area. m_{Pd+Pt} (unit: g) represents the mass of Pd and Pt for PdPt NNWs, and mass of Pt for Pt/C, respectively.

Equation S1

$$j_p = (2.99 \times 10^5)n(an_a)^{1/2}AC_0^*D_0^{1/2}v^{1/2}$$

For a diffusion-controlled total irreversible electrooxidation reaction, the relationship between the forward peak current (j_p) and the square root of scan rates $(v^{1/2})$ complies with the above Equation (see book: Allen J. Bard; Larry R. Faulkner; ELECTROCHEMICAL METHODS Fundamentals and Applications. 1980, by John Wiley& Sons, Inc. Page 222).

In the equation, n represents the total number of electrons involved in the reactions; a represents the electron transfer coefficient for the rate-determining step; n_a represents the electron transfer number in the rate-determining step; A represents the surface area of the electrode, which is a constant; C_0^* represents the initial bulk concentration of the reactant; D_0 represents the diffusion coefficient. For the same solution and reactant, C_0^* and D_0 are the same. So the slope of j_p versus $v^{1/2}$ is determined by $n(an_a)^{1/2}$, while $n(an_a)^{1/2}$ is related to the electron transfer involved in the electrooxidation, hence the higher slope value indicates the improved electrooxidation kinetics (enhanced electron transfer kinetics).



Fig. S10 CV curves of EG electrooxidation before and after the long-time current-time experiments on various materials modified electrodes: A) Pd₅₇Pt₆₁ NNWs; B) Pd₅₅Pt₃₀ NNWs; C) Pd₂₂Pt₄₁ and D) Pt/C.



Fig. S11 CV curves of glycerol electrooxidation before and after the long-time current-time experiments on various materials modified electrodes: A) Pd₅₇Pt₆₁ NNWs; B) Pd₅₅Pt₃₀ NNWs; C) Pd₂₂Pt₄₁ and D) Pt/C.

Reference

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