Designed multimetallic Pd nanosponges with enhanced electrocatalytic activity for ethylene glycol and glycerol oxidation

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1. Experimental section

1.1 Materials

PdCl₂, NaBH₄, HAuCl₄, NiCl₂ and ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA) were purchased from Sinopharm Chemical Reagent Co.Ltd. (Shanghai, China). Nafion (10%) was purchased from Sigma-Aldrich. Commercial state-of-the-art 40 wt% Pt/C was obtained from Johnson Matthey Company. All chemicals were analytical-reagent grade and used without further purification.

1.2 Instrumentation

Scanning electron microscopy (SEM) images were recorded in a FEI XL30 ESEM FEG Scanning Electron Microscope operated at 25 kV. TEM images were all obtained using a FEI Tecnai G2 F20 microscope operated at 200 kV. Energy dispersive spectrometer (EDS) spectrums were collected in a Hitachi S-4800 Scanning Electron Microscope operated at 20.9 KV. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer (Cu K α radiation) in the 30 to 80° 2theta range. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. Electrochemical experiments were performed in a CHI 660C electrochemistry workstation (Shanghai CHI Instruments Company, China) using modified glassy carbon working electrodes ($\phi = 3$ mm), an Ag/AgCl reference electrode (saturated KCl), and a platinum wire counter electrode.

1.3 Preparation of PdAuNi nanosponge

In a typical synthesis, $Pd_{62}Au_{21}Ni_{17}$ nanosponges were synthesized via a simple method. In a typical synthesis, 5 mL EDTA (0.06 M) aqueous solution was mixed with 5 mL of the metal precursors containing 3.0 mL H₂PdCl₄(0.1 M) solution, 1.0 mL NiCl₂(0.1 M) solution and 1.0 mL HAuCl₄ (0.1 M) solution. The resulting mixture was quickly injected into 20 mL of an aqueous solution of 0.1 M NaBH₄ with stirring under N₂ atmosphere. Trimetallic nanosponges could be formed within 5 min accompanying by the release of hydrogen. The final product was obtained for further use. The resulting black colloidal solutions were collected by centrifugation at 8000 rpm for 3 min, and washed with water several times. The final materials were redispersed in water. Furthermore, we varied the mole ratios of Pd, Au and Ni sources in the precursor solutions to prepare PdAuNi nanosponges with various mole ratios. As such, the monometallic Pd, bimetallic PdAu and PdNi nanosponges could be also obtained through the same way mentioned above.

1.4 Preparation of Pt/Pd catalysts modified electrodes

The Pt/Pd catalysts were then resuspended in a mixture containing water and Nafion (10%) (v:v 5:0.05) to form a 0.5 mg/mL catalyst ink. 2 μ L catalyst inks were deposited on the glassy

carbon working electrode that was polished prior to catalyst deposition by $0.3 \ \mu m$ and $0.05 \ \mu m$ alumina powders and rinsed by sonication in ethanol and in deionized water. The final Pt/Pd catalysts modified electrode was then dried at ambient condition prior to its use in the electrochemical reaction.

1.5 Electrochemical measurements

The test solutions were 0.5 M H_2SO_4 , 0.5 M KOH + 0.5 M EG, and 1 M KOH + 0.1 M glycerol. In the CV measurements, the electrode potential was scanned in the range of -0.8-0.4 V versus Ag/AgCl. Chronoamperometry was carried out at the constant potential of -0.1 V in 0.5 M KOH + 0.5 M EG, and -0.2 V in 1 M KOH + 0.1 M glycerol. All the catalyst electrodes were cleaned before datum collection with a CV in the range of -0.8-0.4 V versus Ag/AgCl at 50 mV/s.



Figure S1. HAADF-STEM images of $Pd_{62}Au_{21}Ni_{17}$ nanosponges and corresponding EDX elemental mapping images.



Figure S2. EDX spectrum of $Pd_{62}Au_{21}Ni_{17}$ nanosponges.



Figure S3. FESEM image of $Pd_{61}Au_{31}Ni_8$ (A) and $Pd_{64}Au_4Ni_{32}$ (B) nanosponges.



Figure S4. FESEM image of Pd (A), PdAu (B) and PdNi (C) nanosponges.



Figure S5. Typical FESEM images of the PdAuNi products prepared without adding EDTA.



Figure S6. CV curves of EG (A) and glycerol (B) electrooxidation on Pd, PdAu, PdNi nanosponges materials modified electrodes, the test conditions are same to the PdAuNi nanosponges.

Figure S7. Mass activity (measured by the forward peak current density) of the various materials for EG (A) and glycerol (B) electrooxidation.

Figure S8. Cyclic voltammograms of Pt/C, Pd, PdAu, PdNi and different PdAuNi nanosponges-modified glassy carbon electrodes in 0.5 M H₂SO₄ solution (scan rate: 50 mV/s).

Figure S9. Cyclic voltammogram of Cu UPD for Pt/C, Pd, PdAu, PdNi and different PdAuNi nanosponges-modified glassy carbon electrodes in a solution containing 50 mM H_2SO_4 and 50 mM CuSO₄. The scanning rate was 5 mV s⁻¹.

Figure S10. CV curves of EG electrooxidation before and after the long-time current-time experiments on various materials modified electrodes: A) Pd₆₂Au₂₁Ni₁₇ nanosponges; B) Pd₆₁Au₃₁Ni₈ nanosponges; C) Pd₆₄Au₄Ni₃₂ nanosponges and D) Pt/C.

Figure S11. CV curves of glycerol electrooxidation before and after the long-time current-time experiments on various materials modified electrodes: A) Pd₆₂Au₂₁Ni₁₇ nanosponges; B) Pd₆₁Au₃₁Ni₈ nanosponges; C) Pd₆₄Au₄Ni₃₂ nanosponges and D) Pt/C.

Catalysts	Lattice	crystallite
	parameter (Å)	size (nm)
Pd	3.8928	8.2
PdNi	3.8911	7.1
PdAu	3.9666	5.0
$Pd_{64}Au_4Ni_{32}$	3.9053	6.5
$Pd_{61}Au_{31}Ni_8$	3.9401	5.6
$Pd_{62}Au_{21}Ni_{17}$	3.9308	4.9

Table S1. Parameters of Catalysts Obtained from XRD.