Hollow Echinus-like PdCuCo Alloy for Superior Efficient Catalysis of Ethanol

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Experimental Section

1 Material

Palladium (II) chloride ($PdCl_2$, 60%) was purchased from Sigma-Aldrich. Sodium hydroxide (NaOH, reagent grade) and Cobalt (II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$, reagent grade) were bought from Sinopharm Chemical Reagent Co., Ltd., China. Ethanol (CH_3CH_2OH, reagent grade) was obtained from Jiangsu strong and powerful features chemical Co., Ltd. Copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$), sodium borohydride ($NaBH_4$) and potassium citrate ($K_3C_8H_5O_7.H_2O$, reagent grade) were obtained from Shanghai Qingxi Chemical Science Co. Commercial 20% Pd/ C was obtained from Alfa Aesar. Deionized water (18.2 MΩ cm) was used throughout the work.

2 Synthesis of PdCuCo HENSs

To synthesize PdCuCo HENSs, 1.0 mL of 0.2 $mol \cdot L^{-1}$ $Co(NO_3)_2$, 1.0 mL of 0.2 $mol \cdot L^{-1}$potassium citrate, and 100 mL of water were mixed together and purged with highly purified N_2 for more than 40 min. Then, 10 mL of aqueous 0.05 $mol \cdot L^{-1}NaBH_4$ was dropwise to the above solution under stirring. After aged for 15 min, quickly added into 600 μL of 0.034 $mol \cdot L^{-1}$ H_2PdCl_4 and then 200 μL of 0.1 $mol \cdot L^{-1}CuCl_2$ was dropped to the above solution with a pipette, respectively. And then the resulting mixture was kept stirred at 25 °C for 1 h. The products were collected by centrifugation and washed several times with water. Different compositions of PdCuCo HENSs as control experiments were also prepared just by tuned the volume of precursors, 760 μL of 0.034 $mol \cdot L^{-1}H_2PdCl_4$ and 130 μL 0.1 $mol \cdot L^{-1}$ $CuCl_2$, 450 μL

of 0.034 mol·L^{-1} H_2PdCl_4 and 300 μL 0.1 mol·L^{-1} $CuCl_2$, respectively. The exact composition of PdCuCo were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

3 Characterization

The chemical compositions of the samples were analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa Probe). The crystal structures were also identified by X-ray diffraction (XRD, Rigacu D/Max-2000, monochromatic Cu Kα radiation). Scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) were carried out by using a Hitachi S-4800 scanning electron microscope. The microstructures of the products were characterized by a JEOL JEM-2100 transmission electron microscope (TEM). The composition of PdCuCo HENSs was determined through inductively coupled plasma-atomic emission spectrometry (ICP-AES, Varian VISTA-MPX).

4 Electrochemical Measurement

Cyclic voltammetry (CV) and chronoamperometry (CA) measurement were performed with a CHI660D electrochemical workstation at room temperature and at ambient pressure. For the electrochemical cell, a glassy carbon electrode (GCE) with a diameter of 3 mm was used as the working electrode. A platinum wire was employed as a counter electrode, and an Ag/AgCl (in 3 mol·L^{-1} KCl solution) as the reference electrode. The GCE were respectively coated with 7 μL of PdCuCo HENSs and commercial 20% Pd/C at same mole, and dried at 25 °C. The ethanol oxidation reaction (EOR) activities and stabilities of the catalysts were studied in a 1.0 mol·L^{-1}

NaOH and 1.0 $mol \cdot L^{-1}$ C_2H_5OH aqueous solution at a sweep rate of 50 mV/s. The chronoamperometric (CA) results were measured in a solution containing 1.0 $mol \cdot L^{-1}$ ethanol and 1.0 $mol \cdot L^{-1}$ NaOH, while applied the potential at -0.25 V.

For the CO stripping experiments, CO was pre-adsorbed on the catalyst modified electrode by bubbling in the electrolytes for 30 min while keeping the electrode potential at 0.1V (vs Ag/AgCl) in 1.0 $mol \cdot L^{-1}$ NaOH. And then passed through high purity nitrogen for 30 minutes to remove the dissolved CO in the electrolyte. The CO stripping voltammetry patterns were recorded at a potential scan rate of 50 mV/s.

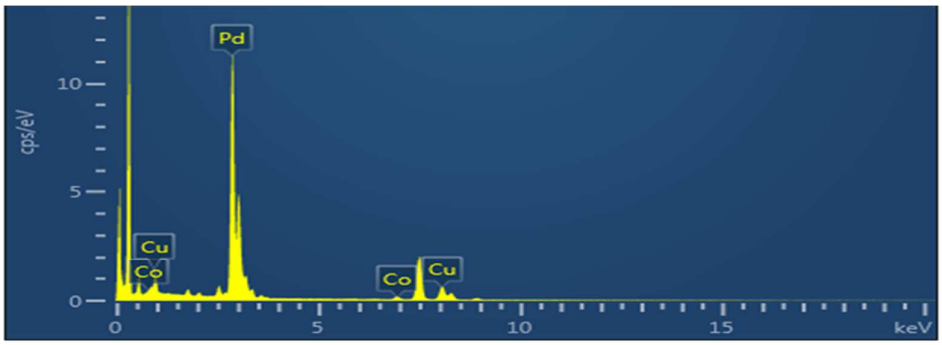

Figure S1 TEM-EDS result of $Pd_{75}Cu_8Co_3$ HENSs.

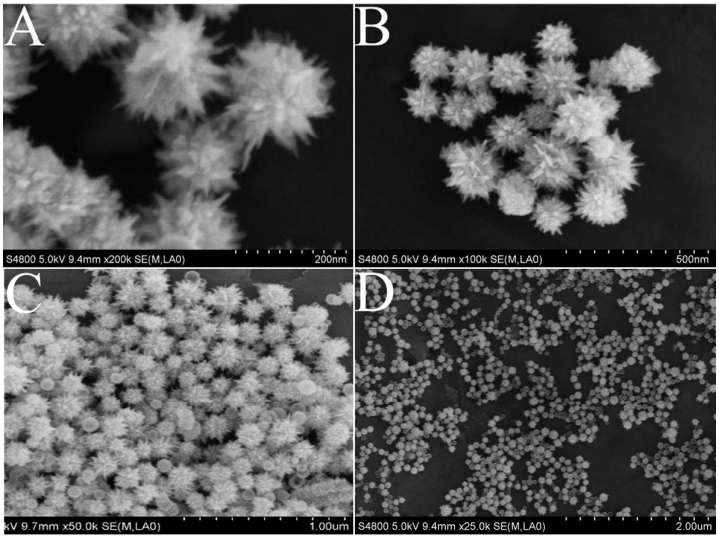

Figure S2 (A, B, C, and D) SEM images at different magnifications of $Pd_{75}Cu_8Co_3$ HENSs.

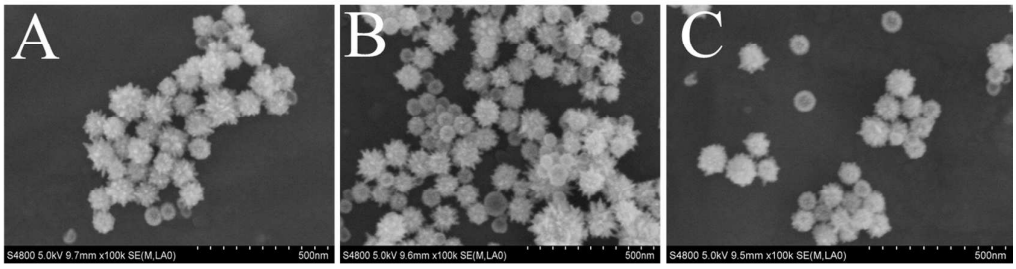

Figure S3 SEM images of the prepared PdCuCo HENSs with different compositions: $Pd_{94}Cu_3Co_2$ (A), $Pd_{52}Cu_5Co_3$ (B)， $Pd_{78}Co_2$ (C).

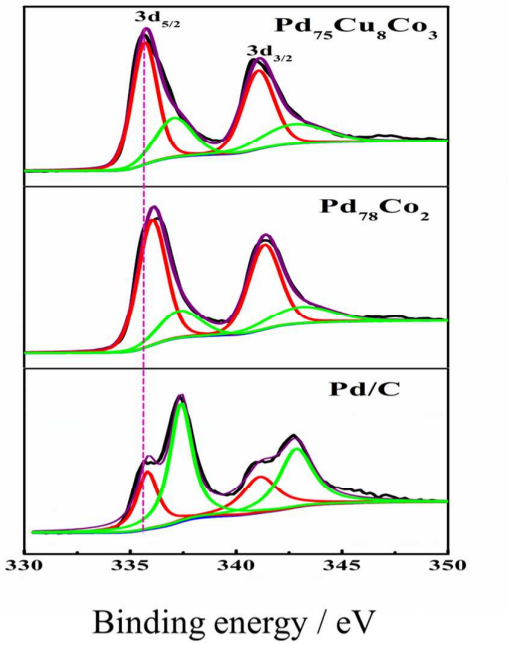

Figure S4 XPS spectra of Pd 3d regions in $Pd_{75}Cu_8Co_3$ HENSs, $Pd_{78}Co_2$ HENSs and commercial 20% Pd/C.

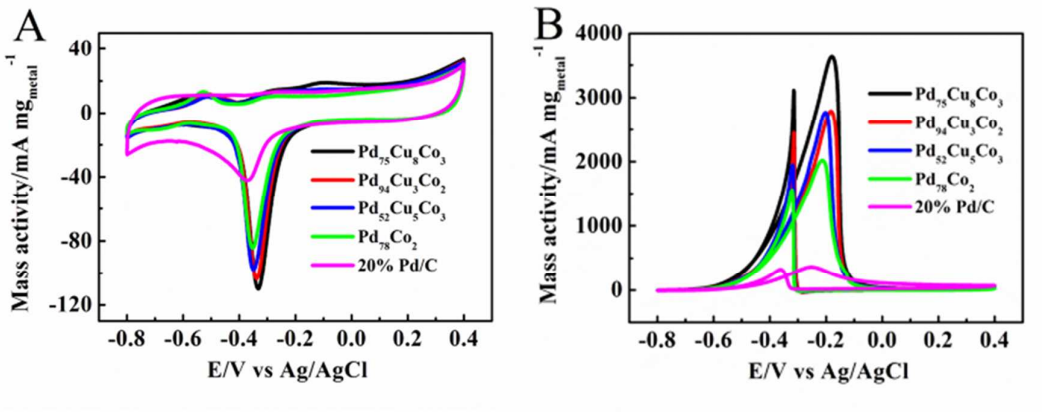

Figure S5 (A and B) the current density is normalized by total metal mass of Pd, Cu, and Co in catalyst. (A) CV curves of various PdCuCo HENSs and commercial 20% Pd/C catalysts in 1.0 M NaOH at the scan rate of 50 mV/s. (B) Total mass activity in 1.0 M NaOH and 1.0 M C_2H_5OH solution at the scan rate of 50 mV/s.

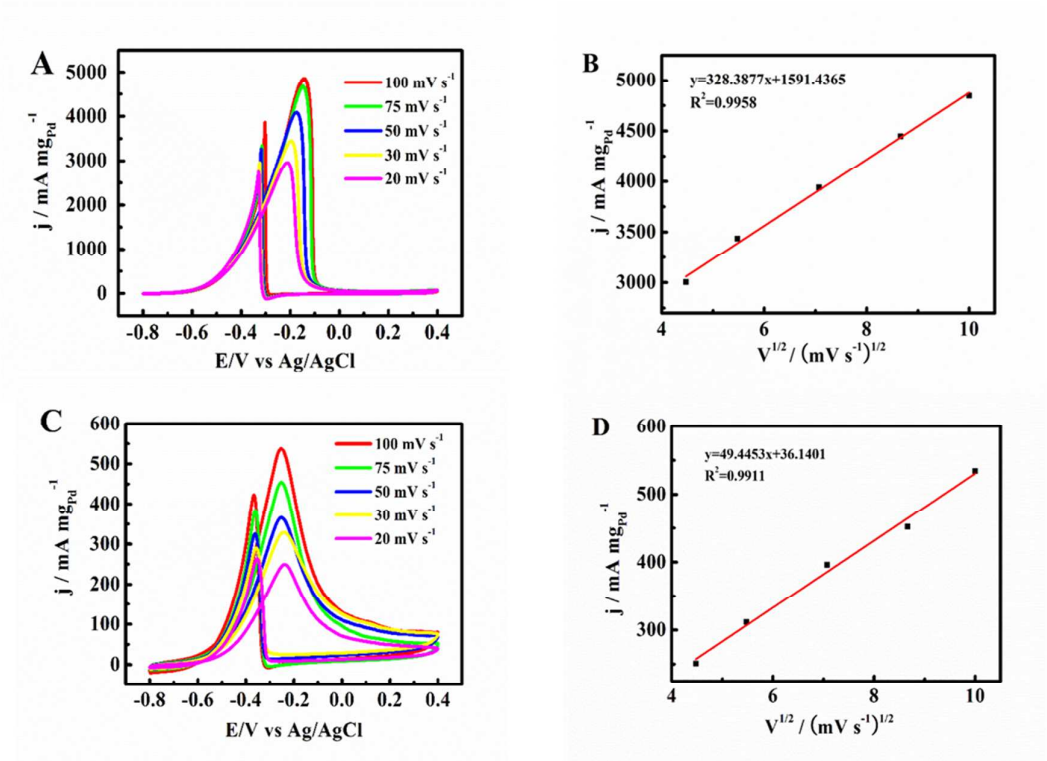

Figure S6 CV plots of ethanol electrooxidation on $Pd_{75}Cu_8Co_3$ HENSs modified GCE electrodes at different scan rates (A) and the corresponding plot of forward peak current (j_p) versus the square root of the scan rate ($V^{1/2}$) (B). CV plots of ethanol electrooxidation on commercial 20% Pd/C modified electrodes at different scan rates (C) and the corresponding plot of j_p versus the $V^{1/2}$ (D).

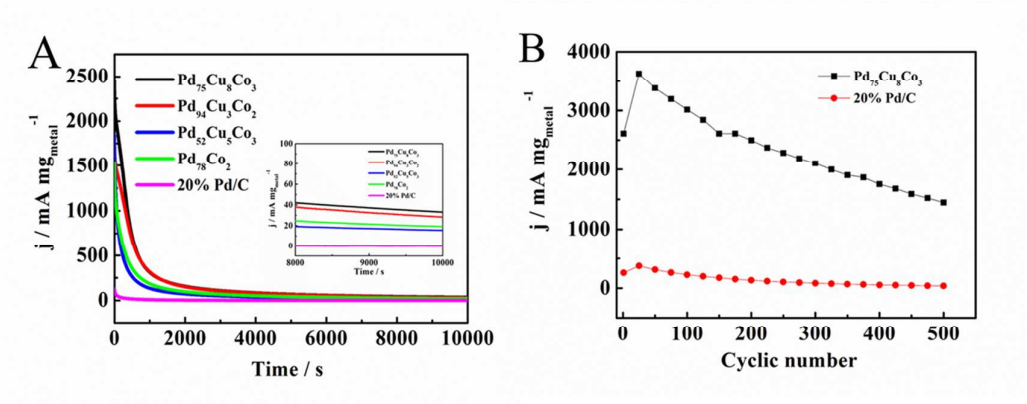

Figure S7 (A) Total-metal-mass normalized Chronoamperometry curves of EOR. (B)The long-term durability of $Pd_{75}Cu_8Co_3$ HENSs and commercial 20% Pd/C catalysts referring to peak current densities for ethanol oxidation for 500 circles. The current density is normalized by total-metal-mass.

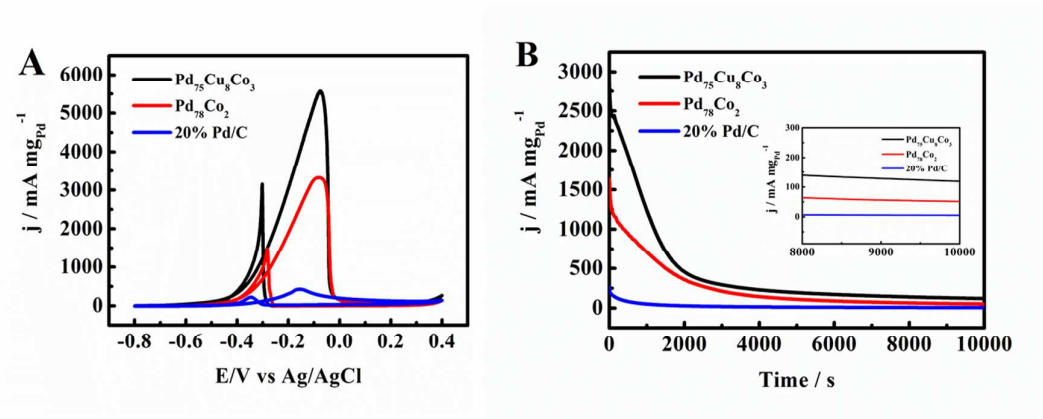

Figure S8 (A) CV curves of the prepared $Pd_{75}Cu_8Co_3$ HENSs, $Pd_{78}Co_2$ HENSs and commercial 20% Pd/C for ethylene glycol electrooxidation. (B) current-time curves recorded at -0.15 V. All the measurements were conducted in 1.0 $mol \cdot L^{-1}$ ethylene glycol + 1.0 $mol \cdot L^{-1}$ NaOH.