Supporting Information

Galvanic replacement mediated morphological adjustments boost nanoparticle performance in electrocatalytic alcohol oxidation

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Experimental section

1. Materials Synthesis

Materials and reagents. Oleylamine (OAm, C18: 80-90%) was bought from Aladdin Biochemical Technology Co., Ltd. Cobalt(II) acetylacetonate ($C_{10}H_{16}CoO_4$) and platinum acetylacetonate ($C_{10}H_{14}O_4Pt$) were purchased from J&K Scientific Co., Ltd. Absolute ethanol, n-Hexane and hydrochloric acid (HCl) were received from Sinopharm Chemical Reagent Co., Ltd. Hexadecyltrimethylammonium bromide (CTAB) was bought from Adamas. All chemicals and materials used in this study were obtained from commercial suppliers and were directly used without purification. The water used in all experiments was ultrapure (18.25 $M\Omega \cdot cm^{-1}$).

Preparation of $Pt_{47}Co_{53}$ Alloy. In the synthesis process, 40 mg of Pt(acac)$_2$, 20 mg of Co(acac)$_2$, and 500 mg of CTAB were added to a flask containing 50.0 mL of OAm. The flask was then sealed and stirred at 60°C for 4 hours to obtain a homogeneous solution. The resulting light yellow solution was transferred to a stainless steel Teflon-lined autoclave and subjected to solvothermal reaction in a constant temperature forced-air drying oven at 180°C for 8 h. After the reaction was completed, the product was repeatedly washed by centrifugation with ethanol and n-hexane. The centrifuged product was then dispersed in 10 mL of ultrapure water and 10 mL of anhydrous ethanol for subsequent use.

Preparation of $Pd_xPt_yCo_z$. The product dispersed in a mixture of ultrapure water and anhydrous ethanol (volume ratio of 1:2) is subjected to ultrasonic treatment for 30 minutes. Anhydrous ethanol is used during the dispersion process to ensure the effective removal of residual organic solvents and to prevent the aggregation of nanoparticles. Followed by rapid addition of 200 μL of 0.05 M H_2PdCl_4, and then sonicated at room temperature for 30 minutes. The product was separated by centrifugation at 8000 rpm/min, washed several times with ethanol, and vacuum dried at 60°C for 8 h. By varying the amount of H_2PdCl_4 (400 μL, 600 μL, and 800 μL of 0.05 M H_2PdCl_4), catalysts with compositions of $Pd_5Pt_{46}Co_{49}$, $Pd_{12}Pt_{43}Co_{45}$, and $Pd_{23}Pt_{47}Co_{30}$ were obtained, respectively.

2. Characterization.

The morphology of as-prepared samples was studied by using transmission electron

microscopy (TEM) on a Talos F200X, USA and high-angle angular dark-field scanning transmission electron microscopy (HAADF-STEM) on a ARM200F. X-ray diffraction patterns (XRD) patterns of samples were examined by X-ray diffraction on a Rigaku MLtima IV-185 X-ray diffractometer using Cu Kα radiation in a region of 2θ = 10-90°, operating with a scanning rate of 10° min^{-1}. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a ESCALAB-210 using an Al Kα X-ray source. The mass loadings of metal on the UCN were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) on a PerkinElmer 8300.

3. Electrochemical Measurements.

All electrochemical tests were performed on the CHI 760E electrochemical analyzer at room temperature. A three-electrodes system was used for all electrochemical tests, in which glassy carbon electrode (GCE, 0.1256 cm^{-2}) was used as the working electrode, a carbon rod as the counter electrode, and a Hg/HgO electrode as the reference electrode. An ink of the catalysts was prepared by mixing 3 mg of nanocatalysts, 7 mg of Valcan XC-72 carbon, 700 uL of isopropanol and 300 uL of H$_2$O. After that, 50 μL of Nafion solution (5 wt. % in isopropanol and H$_2$O) was added and sonicated for 0.5 h. Then, 6 μL of above-prepared ink solution was dropped on the GCE electrode and dried at room temperature before test. The cyclic voltammograms (CVs) were then scanned until the stabilized curves were obtained for further removal of the surfactant in 1.0 M KOH. The EOR tested with a scan rate of 50 mV s^{-1} at room temperature in 1.0 M KOH + 1.0 M CH$_3$CH$_2$OH, other alcohols were tested as above.

In addition, the ECSA of the catalysts was further analyzed by CV plots and calculated in the region of the PdO/PtO$_x$ reduction peak as follows:

$$ECSA = \frac{Q_{redox}}{Q_{ref} \times m}$$

For Pd/Pt catalysts, the PdO reduction peaks are typically at 0.4 - 0.6 V vs. RHE, and the PtO$_x$ reduction peaks are typically at 0.5 - 0.8 V vs. RHE. Integrate the reduction peaks to obtain the redox charge Q$_{redox}$.   Pd: Q_{ref} = 405 μC/cm²,   Pt: Q_{ref} = 420 μC/cm². Specifically, Q_{redox} : charge of the hydrogen desorption or redox peak (C). m: loading of Pd or Pt on the electrode (mg).

Product Analysis: Chronoamperometry experiments were conducted at 0.9 V vs. RHE, with an

electrolysis duration of 7 h, aiming to identify the products resulting from polyalcohol oxidation and subsequently compute the corresponding selectivity and faradaic efficiencies. The products were analyzed by ^{1}H nuclear magnetic resonance (NMR). ^{1}H NMR spectra were recorded on an Avance III HD 600MHz (Bruker). 50 μL D_2O and 10 μL dimethyl sulfoxide (DMSO) used as internal standard were added to 0.5 mL electrolyte. The concentration of products was calculated based on the equation given below:

$$C_{product} = \frac{A_{product}}{A_{DMSO}} \times \frac{N_{DMSO}}{N_{product}} \times C_{DMSO}$$

(1)

Where $C_{product}$ is the concentration of the liquid product, $N_{Product}$ and N_{DMSO} are the number of protons for the individual NMR peak of the liquid product and DMSO, respectively, and C_{DMSO} is the concentration of DMSO.

Taking ethylene glycol oxidation as an example, the selectivity of product is calculated by the following equation:

$$Selectivity_{glycolate} = \frac{C_{glycolate}}{C_{glycolate} + C_{formate}} \times 100\%$$

(2)

The Faradaic efficiency was calculated using Equation:

$$Faradaic\ Efficiency = (n \times z \times F/Q) \times 100\%$$

(3)

where n is the yield of product (mol), z is the number of electrons required to form a molecule of product, Q is the total amount of charge consumed during the i-t test (C), and F is the Faraday constant (96485 C mol^{-1}).
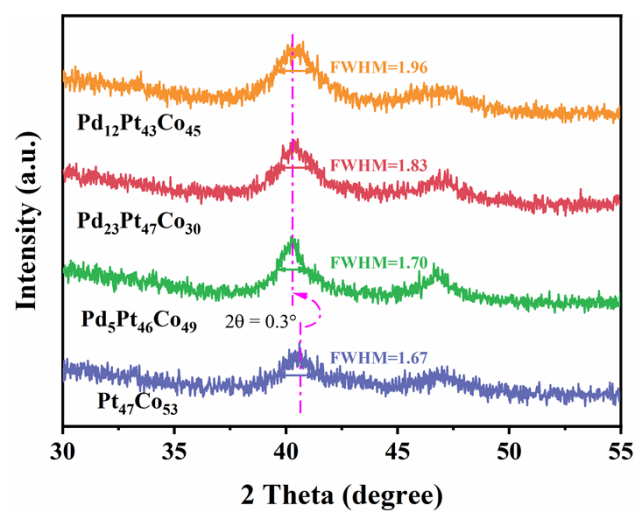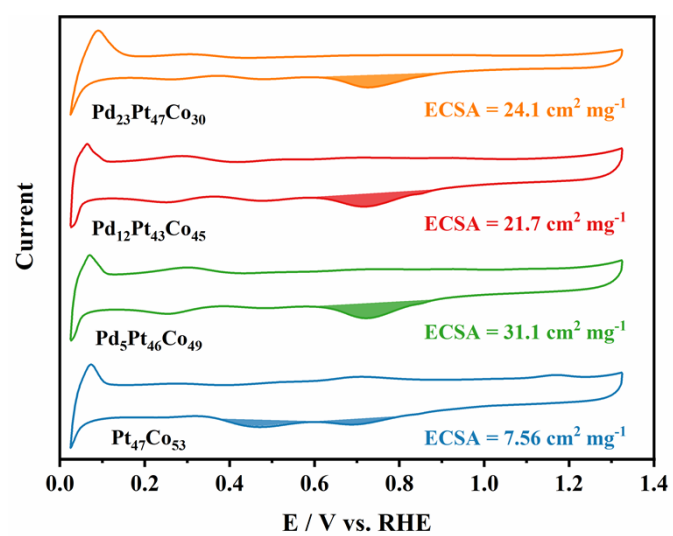
Fig. S1 Partial magnification of XRD.
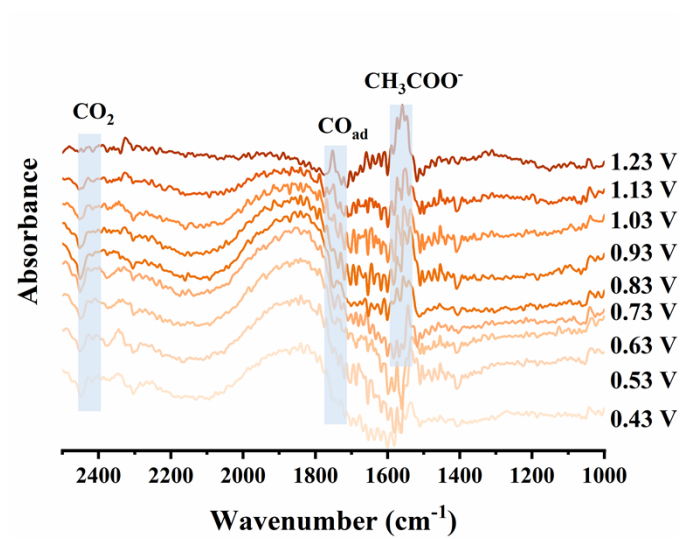
Fig. S2 CV curve in 1.0 M KOH solution.

Fig. S3 FTIR image of $Pd_{12}Pt_{43}Co_{45}$ tested in 1.0 M KOH + 1.0 M ethanol solution.

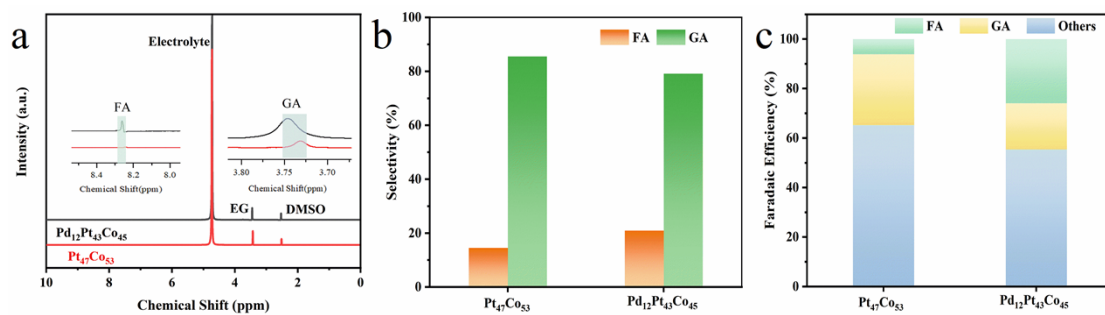Fig. S4 (a) ^{1}H NMR-spectrum of the products analysis test of $Pd_{12}Pt_{43}Co_{45}$ and $Pt_{47}Co_{53}$ towards EGOR at 0.9 V vs. RHE in electrolyte after completing 7-hour electrolysis. Comparison of products (b) selectivity values and (c) faraday efficiency.
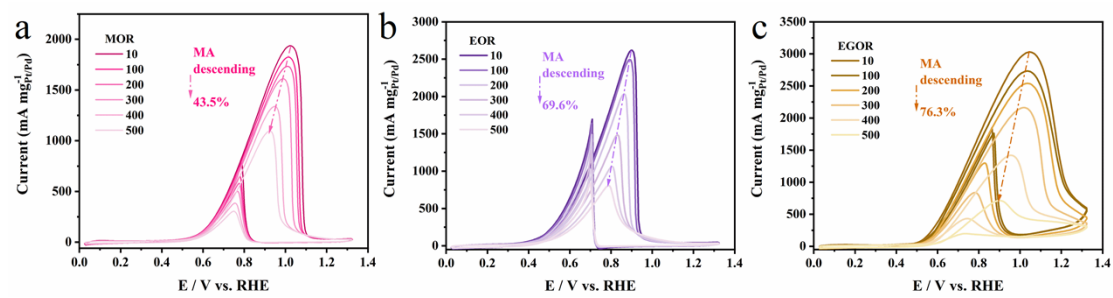
Fig. S5 Stability of Pt$_{43}$Co$_{57}$ in 1.0 KOH + 1.0 M ethanol solution.

Table S1. Comparisons of EGOR activity of $Pd_{12}Pt_{43}Co_{45}$ with previously reported the-state-of-the-art Pd/Pt based catalysts.

Catalysts	Electrolyte		Mass Activity	Ref.
	KOH (M)	EG (M)	(A mg^{-1})	
$Pd_{12}Pt_{43}Co_{45}$	1.0	1.0	3.90	This work
PtCu nanospheres (NSs)	1.0	1.0	2.15	J. Colloid Interface Sci. 2019, 551, 81
Pd/CoO-NiO	1.0	1.0	2.98	Electrochim. Acta 2022, 408, 139965
PdNiRuNSs	1.0	1.0	3.86	Nano Research 2024, 17, 3777
Pd/CoTe	1.0	1.0	3.92	J. Colloid Interface Sci., 2022, 616, 316-325
Doughnut-shaped Pd-Bi$_2$Te$_3$	1.0	1.0	2.42	Inorg. Chem., 2022, 61(10), 4533-4540
Pd$_1$Ni$_1$HNs	1.0	1.0	3.15	Electrochimica Acta, 2008, 268, 383-391
Pt$_{81}$Rh$_{19}$ NDs	0.5	0.5	1.5	J. Colloid Interf. Sci., 2020, 579, 250-257
PtRuPd NSs	0.5	0.5	1.368	J. Colloid Interf. Sci., 2020, 560, 467-474
AuPt core-shell structures	1.0	0.75	0.973	Electrochim. Acta, 2015, 180, 1075-1084
PdPt nanowire	0.5	0.5	3.37	Energy Environ. Sci., 2015, 8, 2910-2915
Pt$_3$Mn	0.5	0.5	0.24	Appl. Catal. B-Environ., 2019, 253, 11-20
PtRh$_{0.02}$@Rh	0.1	0.5	1.25	J. Mater. Chem. A, 2022, 10, 20571-20579
Pt-Co EDNC	0.5	0.5	2.5	Appl. Catal. B- Environ., 2019, 258, 117951