Supporting Information

Two-Dimensional Porous PtPd Nanostructure Electrocatalysts for Oxygen Reduction Reaction

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Experimental Section

1. Synthesis of catalysts

Silica synthesis and array: In the synthesis of silica spheres with diameter of 200 nm, 10 ml of distilled water and 3 ml of ammonia were dissolved in 75 ml of ethanol firstly, then magnetic stirred for 1 hour at 30℃ till the homogeneous solution was formed. Subsequently, 6 ml of tetraethylorthosilicate (TEOS) was add to the solution and stirred for another 3 hours till the solution became milky white. Then the silica spheres were separated by centrifugating the solution at 10,000 rpm for 5 min. After that, the obtained solid was re-dispersed in 20 ml of ethanol. Then the quartz substrate was inserted vertically into the solution for 30 seconds and kept at 60℃ in vacuum until all solvent vaporized. The synthesis of silica spheres with diameter of 100 and 300 nm were prepared as above, except by using 3 and 9 ml of TEOS respectively.

Impregnation of metal precursors: The aqueous solution mixed with $PdCl_2$ (5mM, 2.5 mL) and H_2PtCl_6 (0.1M, 5.0 mL) was slowly dropped onto the silica template until the entire template was covered. After drying naturally, continue to repeat the above operation several times until the template dyed to yellow color. After solvent vaporization in vacuum at 50 ℃, the as-prepared composite was subsequently heat-treatment in a tube furnace for 3 hours at 500 ℃ in H_2 atmosphere to obtain PtPd alloys.

Removal of templates: The SiO_2 templates were leaching by 20wt.% hydrofluoric acid by stirring for 24 hours. Finally, the PtPd alloying catalysts were collected by centrifugation. For comparison, the pure Pt porous structure was prepared by the same method only used H_2PtCl_6 (0.1M, 5.0 mL) impregnated template.

2. Characterization

X-ray diffraction (XRD) analysis was tested on Rigaku Ultima IV diffractometer using Cu Ka radiation (λ = 1.54056 Å). Scanning electronic microscopy (SEM) and transition electronic microscopy (TEM) investigations were carried out on a Hitachi S-3400 and JEOL JEM-2100F, respectively. X-ray photoelectron spectroscopy (XPS) was conducted by a Thermo scientific (Escalab 250Xi).

3. Electrochemical measurements

The electrochemical tests were conducted using an electrochemical workstation (CHI 760E, Shanghai Chenhua). A Pt wire was used as the counter electrode and a saturated Ag/AgCl electrode was used as the reference electrode. All the potentials in this work were calibrated by referencing to the reversible hydrogen electrode (RHE). Vulcan-72 commercial carbon black were added into PtPd alloys to ensure that the metal mass is 20wt.% of the final catalysts. Then the mixture was dissolved in 10ml ethyl alcohol and ultrasonicated for 2 h at room temperature to ensure uniform dispersion. Afterward, the precipitates were dried at 60 ℃ in a vacuum oven for 12 h to obtain the final catalyst sample. To prepare the catalyst ink, 3 mg of the catalyst was ultrasonically mixed for 30 min with 40 μL of a 5 wt% Nafion solution (Aldrich), 660 μL of water, and 300 μL of ethanol. From this homogeneous catalyst ink, 10 μL was deposited onto the surface of the GC electrode.

Electrochemically active surface areas (ECSAs) were calculated from the CV curves according to the following equation:

$$E^{CSA} = \frac{Q}{C \times m} \#(1)$$

Where Q is the Coulombic charge of the hydrogen desorption peak area, C is the hydrogen adsorption constant, and m is the mass of the catalyst (Pd, Pt and PdPt). For Pd, C=4.2 C/m^2; for Pt, C=2.1 C/m^2; and for Pd_xPt_y, C=4.2x/(x+y) + 2.1y/(x+y).

Koutecky-Levich (K-L) plots were analyzed at different potentials according to Koutecky-Levich equation:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \#(2)$$

$$B = 0.2NFC_0D_0^{2/3}\nu^{-1/6}\,; J_K = nFkC_0 \#(3)$$

Where J is the measured current density, J_k and J_L are the kinetic and limiting current densities, respectively, ω is the angular velocity, n is transferred electron number, F is the Faraday constant, D_0 is the diffusion coefficient of oxygen in 0.1 M KOH, C_0 is the bulk concentration of oxygen, ν is the kinetic viscosity of the electrolyte and k is the electron-transfer rate constant.

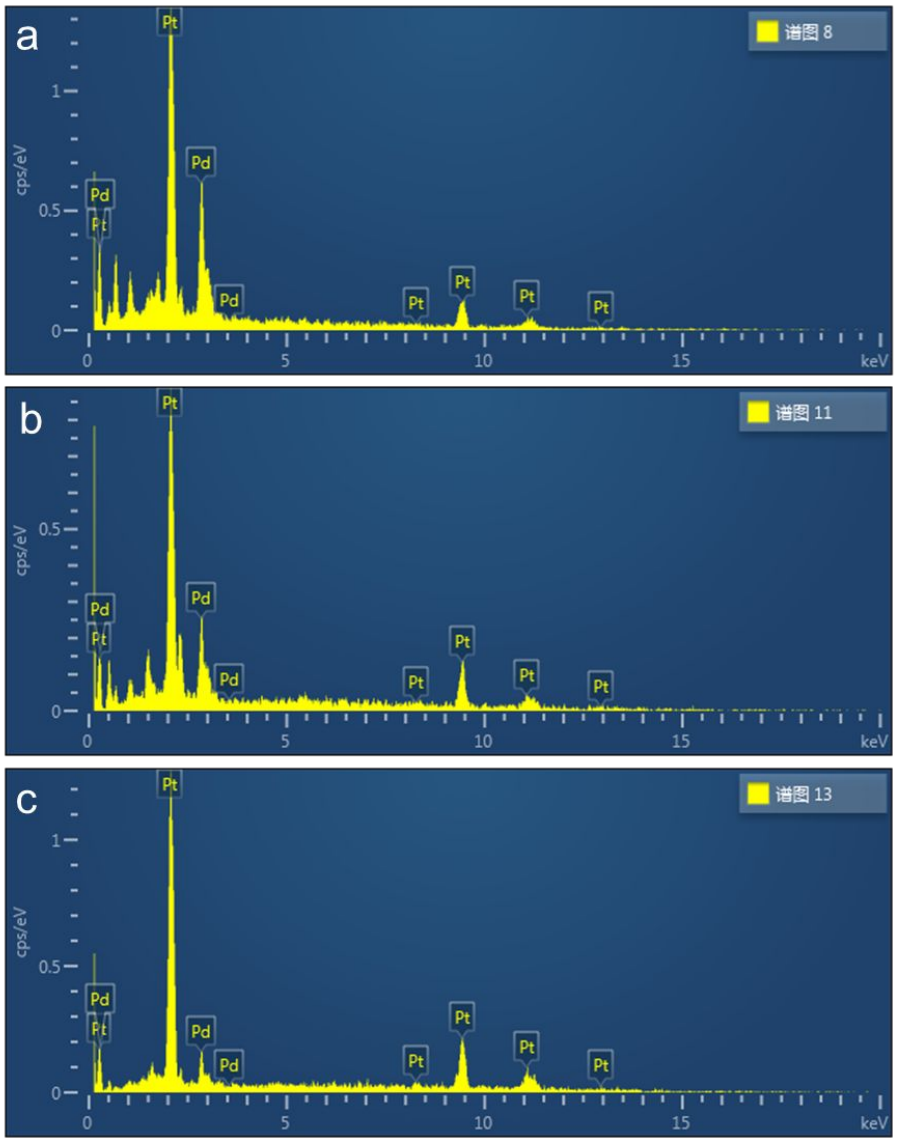

Figure S1. The EDS composition analysis of (a) Pt_1Pd_1, (b) Pt_2Pd_1 and (c) Pt_3Pd_1 respectively.

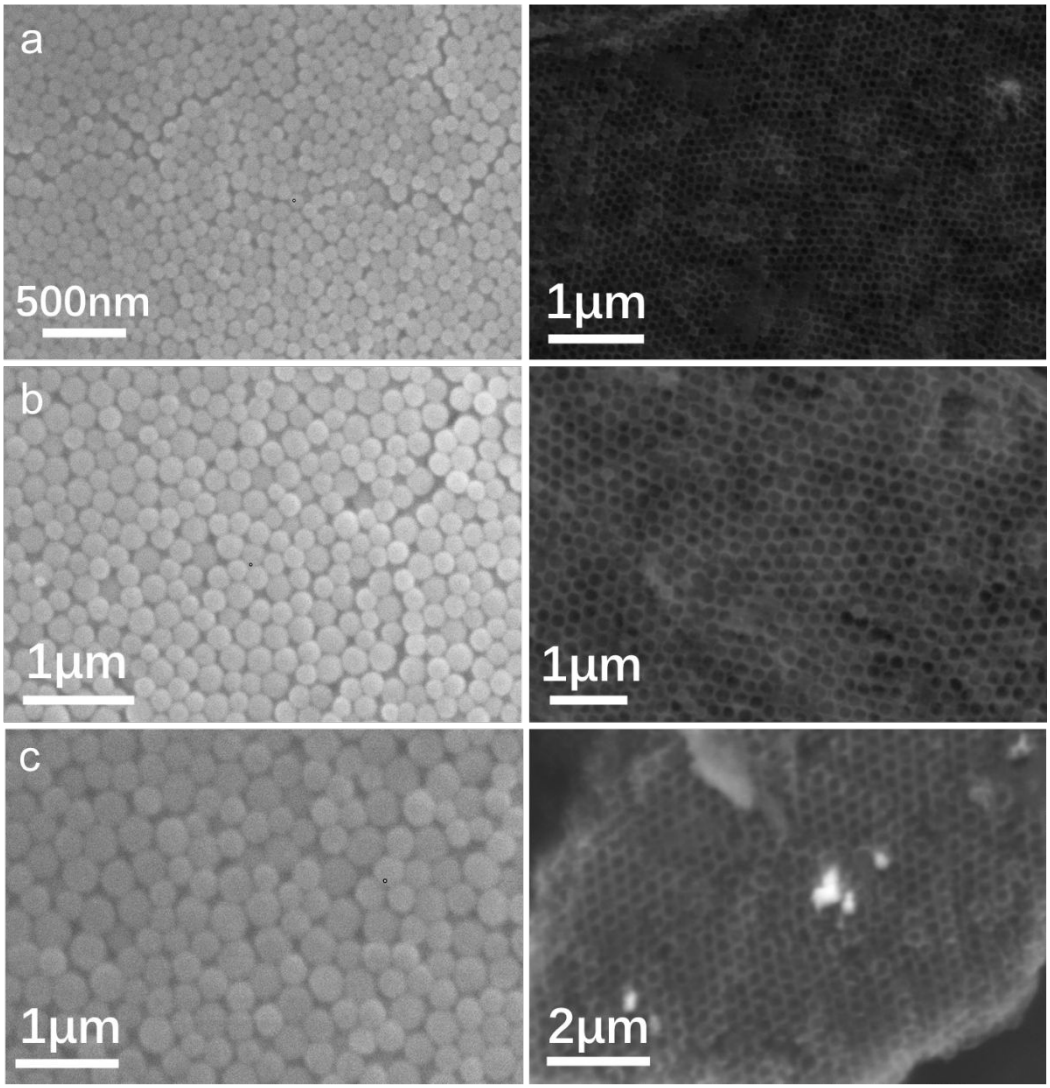

Figure S2. SEM images of SiO_2 template with diameter of (a) 100 (b) 200 (c) 200 nm and corresponding TEM images of Pt_2Pd_1 alloys.

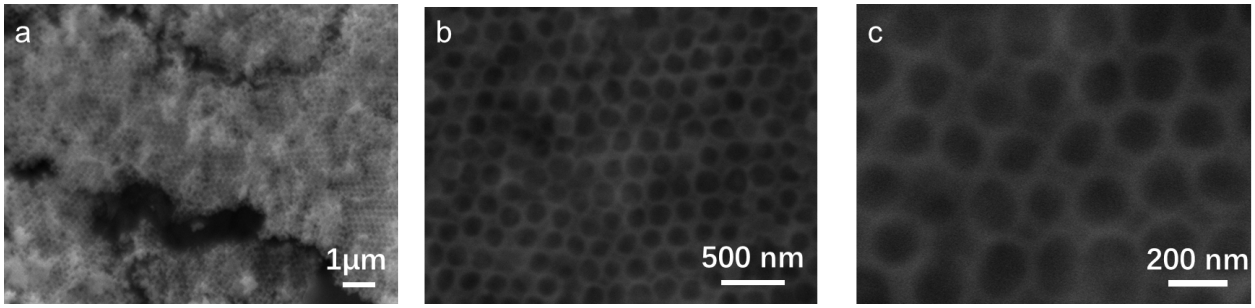

Figure S3. The low- (a), medium- (b), and high-resolution (c) SEM images of Pt_2Pd_1 alloys.

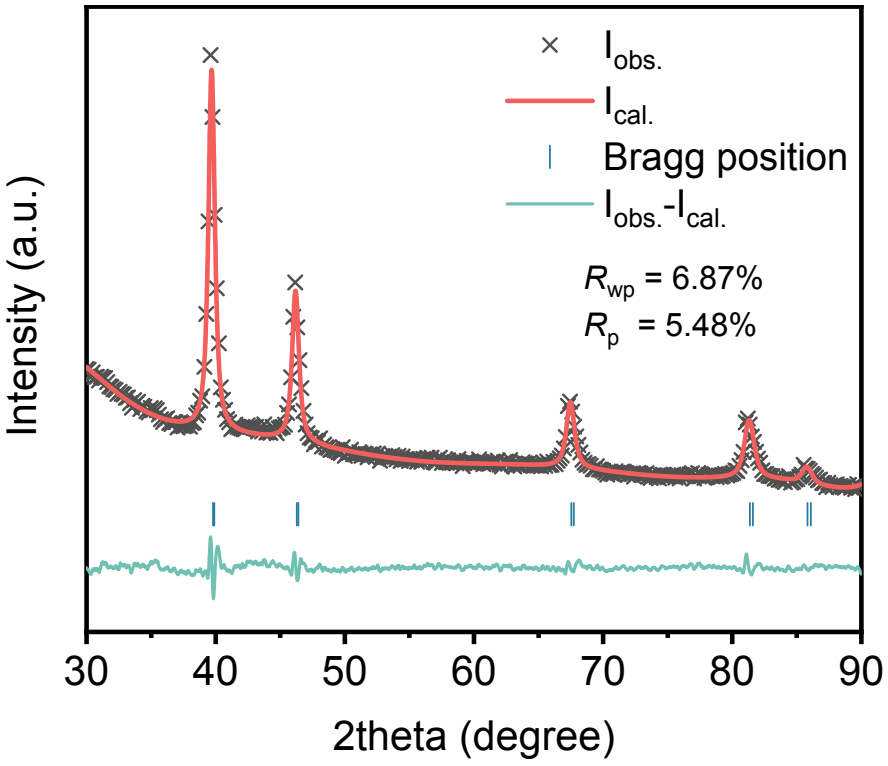

Figure S4. Rietveld refinement of Pt_1Pd_1 alloy.

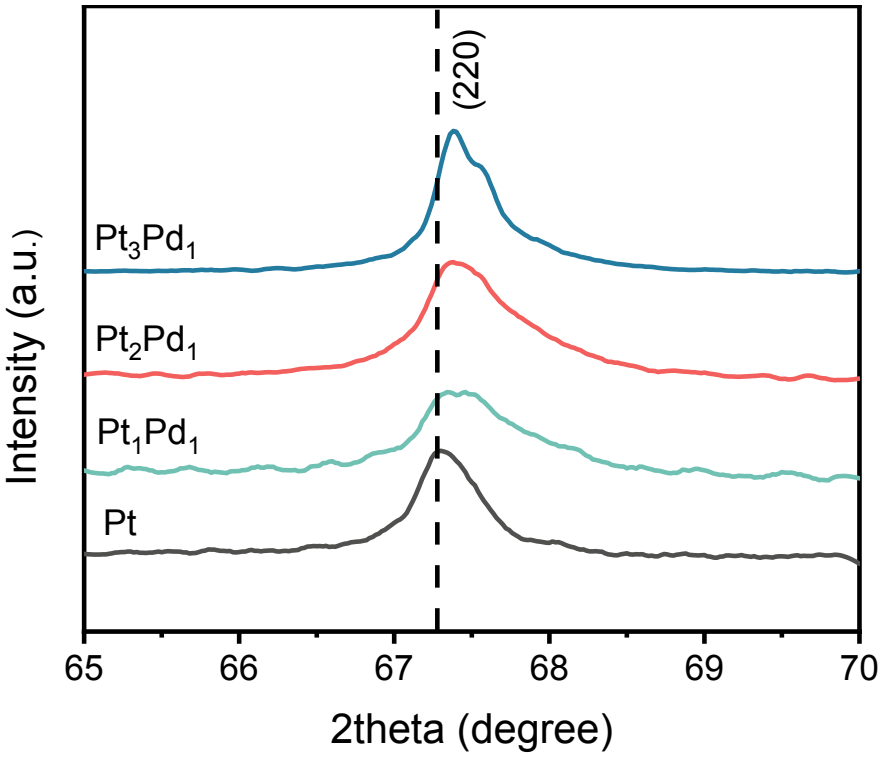

Figure S5. XRD results of the (220) reflection for PtPd alloys.

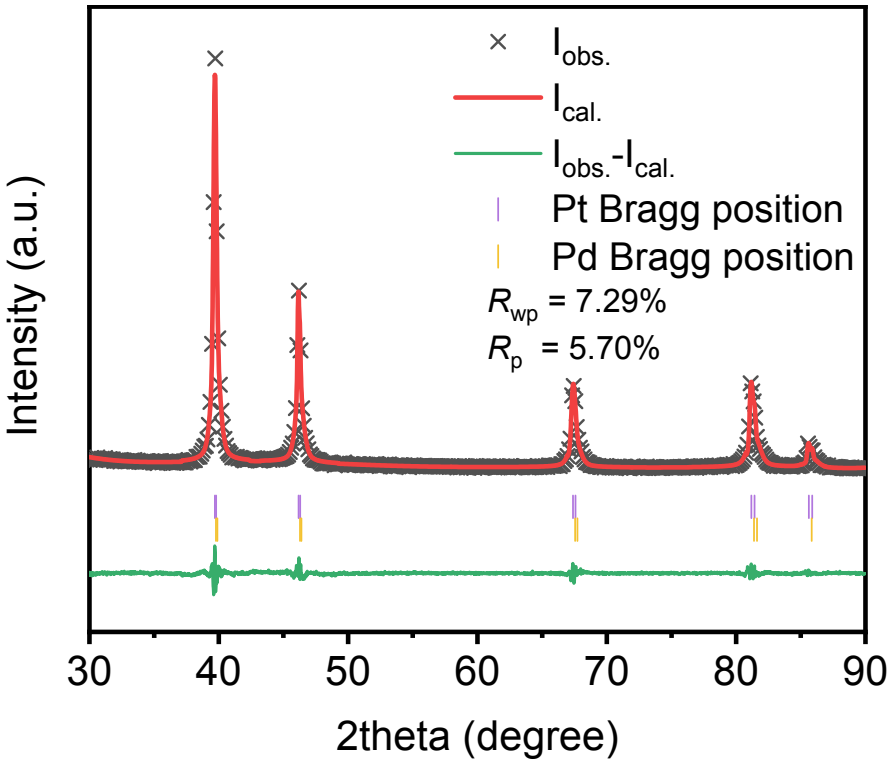

Figure S6. Rietveld refinement of Pt_3Pd_1 alloy.

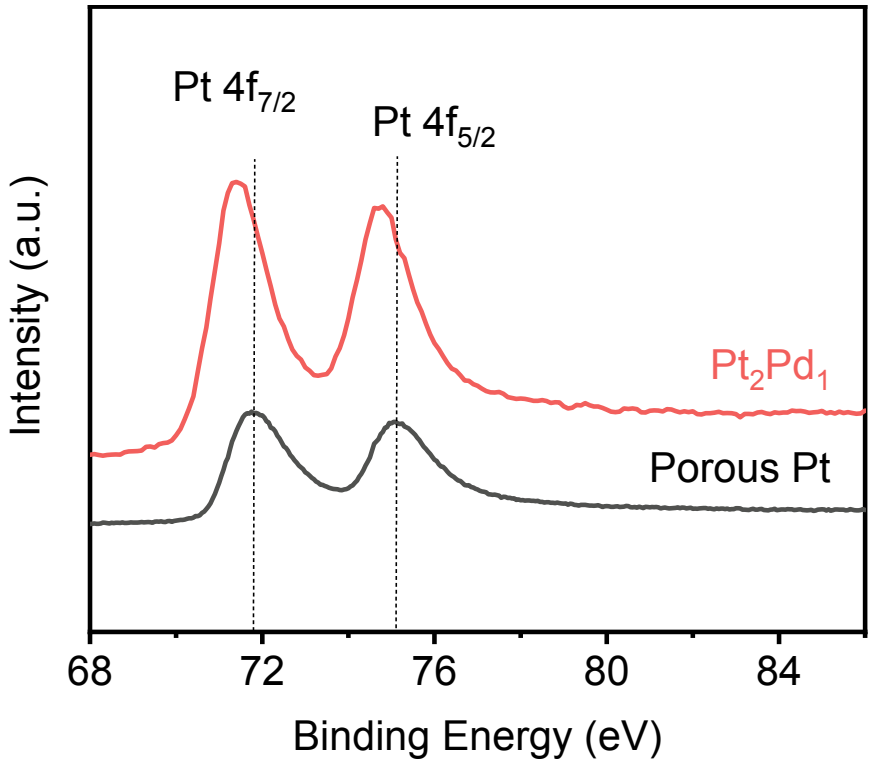

Figure S7. XPS spectrums of Pt 4f for Pt_2Pd_1 alloy and porous Pt nanostructure.

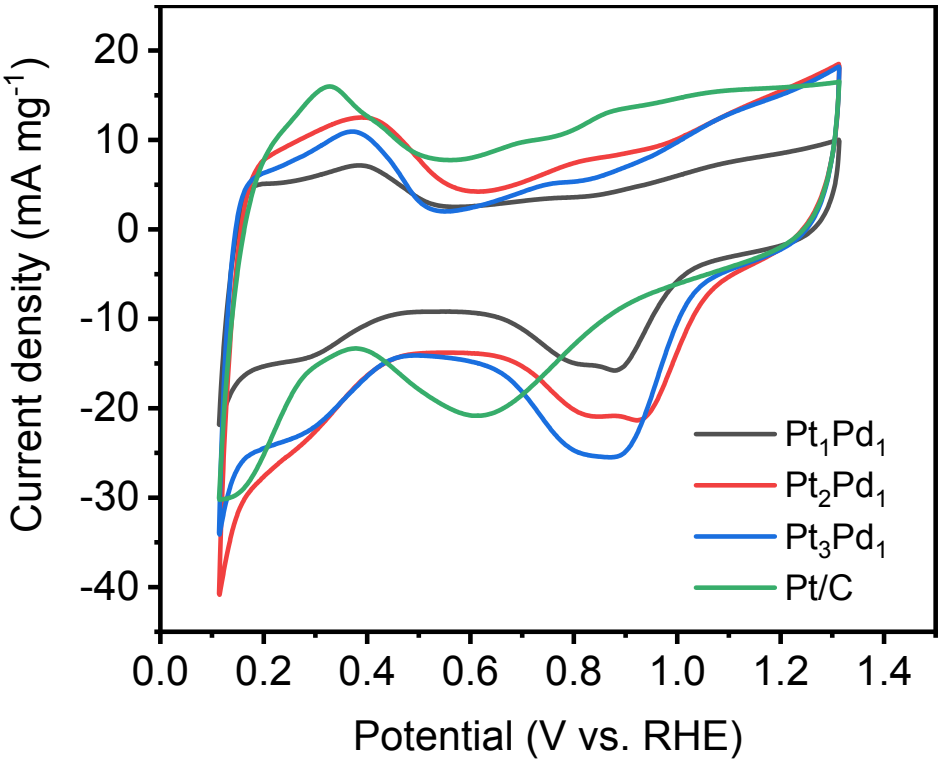

Figure S8. CVs of the PtPd catalysts in 0.1M KOH at a scan rate of 20 mV s^{-1}.

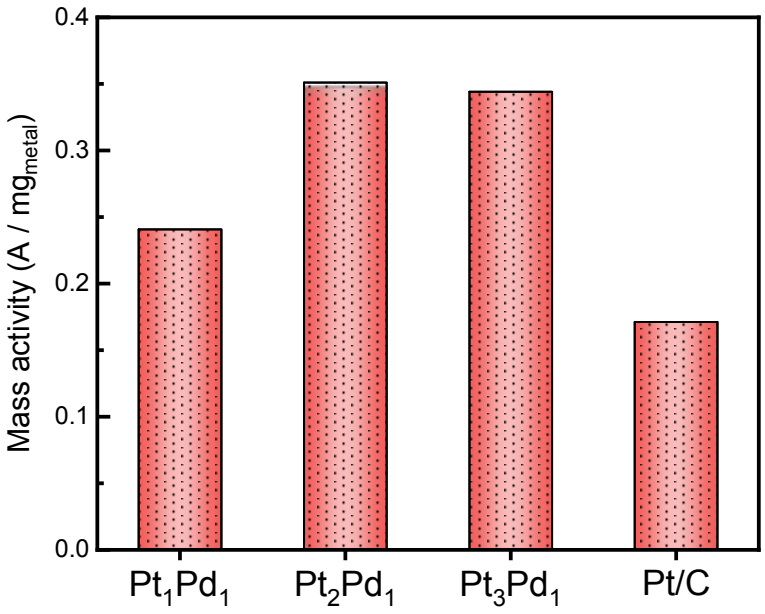

Figure S9. MA of the PtPd catalysts and commercial Pt/C in O_2-saturated 0.1M KOH.

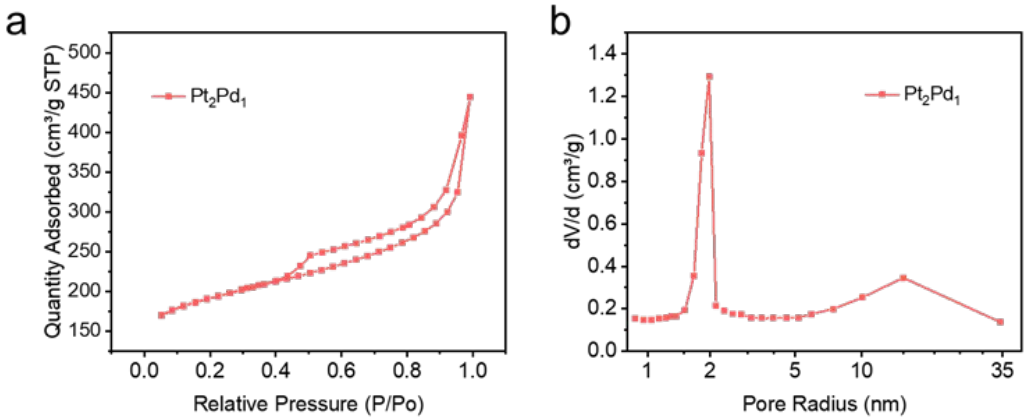

Figure S10. (a) N_2 adsorption-desorption isotherms and (b) pore size distribution of Pt_2Pd_1.

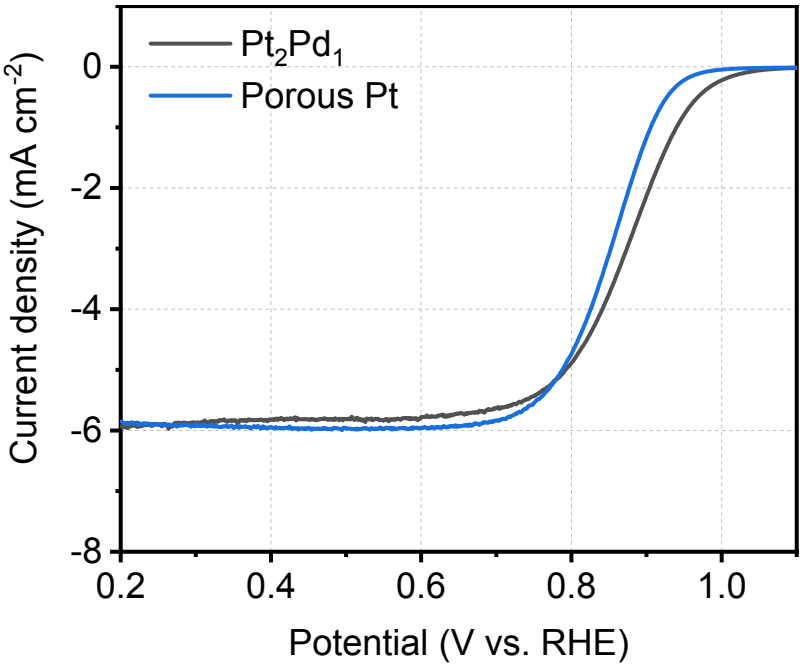

Figure S11. LSVs of Pt_2Pd_1 and porous Pt in 0.1M KOH with a scan rate of 5 mV s^{-1} at 1600rpm.

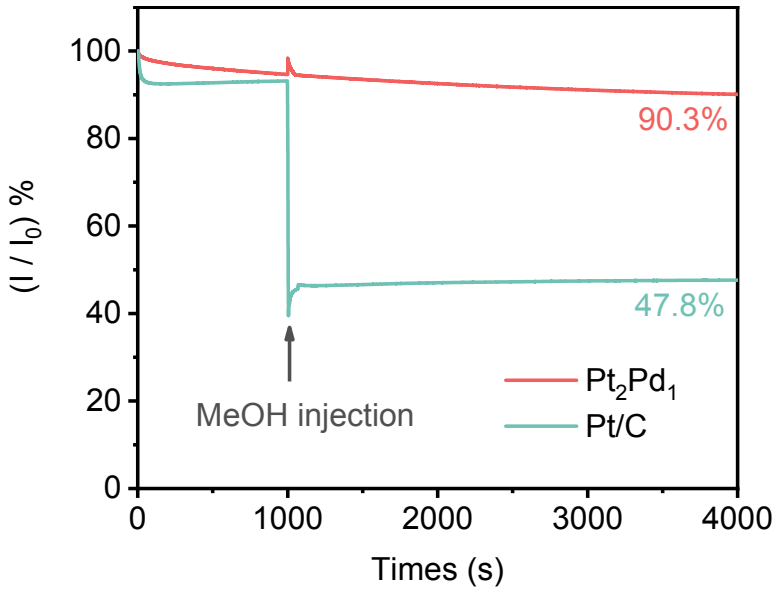

Figure S12. The methanol tolerance test of Pt_2Pd_1 and Pt/C catalysts.

Table S1 The average content of Pt and Pd from EDS results.

Sample name	Pt wt.%	Pd wt.%	Pt/Pd molar ratio
Pt_1Pd_1	61.41	38.59	0.89
Pt_2Pd_1	75.12	24.88	1.65
Pt_3Pd_1	83.20	16.80	2.7

Table S2 The molar ratio of Pt and Pd calculated from ICP results.

Sample name	Pt/Pd molar ratio
Pt_1Pd_1	0.92
Pt_2Pd_1	1.85
Pt_3Pd_1	2.97

Table S3 The on-set and half-wave potentials for the catalysts in our work and other reported literatures.

Catalyst	$E_{on\text{-}set}$ (V vs. RHE)	$E_{1/2}$ (V vs. RHE)	Reference
Pt_2Pd_1	0.967	0.889	This work
$Pt_{46}Pd_{54}$	0.9	0.72	Ref.1
Pt_2Pd_3/CKN		0.821	Ref.2
PtPd NSs		0.879	Ref.3

PtPd NRs/C		0.889	Ref.4
PtPd/(rGO:MWCNT)	0.86		Ref.5
PtPd nanocube–rGO		0.829	Ref.6

Reference

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