Supplementary Information

N-Coordinated PdRh Synergy for High-Selective Ethylene Glycol Oxidation and Efficient Hydrogen Evolution

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Experimental section

1. Chemicals

Nickel foam (NF) was purchased from Delve Metal Material Technology Co., LTD. Rhodium acetate dimer (($C_2H_3O_2$)_4Rh_2) was received from Shanghai Titan Technology Co., LTD. Palladium acetate ($C_4H_6O_4Pd$, AR) and diethylenetriamine (DETA, 99%) were supplied from Shanghai Maclin Biochemical Technology Co., LTD. Acetonitrile (ACN, \geq 99.5%) and *N*, *N*–dimethylacetamide (DMA, \geq 99.0%) were obtained from Sinopharm Chemical Reagent Co., LTD. Noticeably, acetonitrile, DMA and DETA are all analytical grade and used without further purification. All of the aqueous solutions were prepared with distilled water throughout the whole experiments.

2. Characterizations

The morphology and structure of the samples were characterized by scanning electron microscopy (SEM) with a Hitachi S-4800 scanning electron microanalyzer and an accelerating voltage of 15 kV, transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) measurements on a JEM-2100F microscope operated at an acceleration voltage of 200 kV. X-ray diffraction (XRD) spectra were acquired on a Philips PW3040/60 diffractometer by using Cu Ka radiation source (1 ¼ 0.15405 nm). The metal content of the sample was measured by atomic absorption spectroscopy (AAS, PinAAcle900T). X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo VG ESCALAB 250 spectrometer with an Al Ka X-ray irradiation (1486.6 eV photons) for excitation operated at 120 W. The ultraviolet photoelectron spectroscopy (UPS) and XPS tests were conducted on the same instrument, with the primary distinction being that UPS utilizes a UV light source for excitation. The in situ EPR measurement was carried out using Bruker EPR EMXplus-9.5/12

spectrometer. The EPR spectrometer was coupled with a computer for data acquisition and instrument control. The magnetic parameters of the radicals were obtained from direct measurements of the magnetic field and the microwave frequency.

3. Electrochemical measurements

Electrochemical measurements were performed on a CHI 760e electrochemical workstation (CH Instrument, Chenhua Co., Shanghai, China). A conventional three-electrode system was adopted, including a glassy carbon rotating disk electrode (RDE) as the working electrode, a graphite rod as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The relevant potentials were converted to a reversible hydrogen electrode (RHE) by the follow-up equation (1):

$$E_{\rm RHE} / V = E_{\rm SCE} / V + 0.059 \times \rm{pH} + 0.244$$
 (1)

The ethylene glycol oxidation reaction (EGOR) and hydrogen evolution reaction (HER) were conducted at the electrochemical workstation with the three-electrode configuration. Before the test, a 1.0 M KOH aqueous solution was initially bubbled with N_2 for 30 min and maintained throughout the HER process. The cyclic voltammetry (CV) curves of the investigated electrocatalyst were acquired by scanning at a scan rate of 50 mV s⁻¹ for 20 cycles until the electrochemical signals were stable. Then, the linear sweep voltammetry (LSV) measurements were carried out with a rotation rate of 1600 rpm and a scan rate of 10 mV s⁻¹ to assess the electrochemical performance of the HER. After the LSV curves were stabilized, the alkaline electrolyte containing 1.0 M EG was adopted to acquire the LSV curves towards EGOR.

4. Electrolytic cell tests

The bifunctional EGOR//HER system was carefully assembled by the flow cell (Gaoss Union) at room temperature. The N-PdRh worked as both anodic and cathodic catalysts. The non-membrane flow cell was constructed, where a 3.0 M KOH aqueous solution with/without 1.0 M EG performed as anodic and cathodic electrolyte simultaneously.

The liquid products were analyzed by nuclear magnetic resonance (NMR) spectroscopy. ¹H spectra were recorded on a 600 MHz/AVANCE 400 (Bruker), in which 300 μ L of the electrolyte was mixed with 300 μ L of D₂O, coupled by introducing 30 μ L of dimethyl sulfoxide (DMSO) used as an internal standard. The EG conversion efficiency and GA selectivity were evaluated using the follow-up equations (2-3):

EG conversion efficiency =
$$[n (EG \text{ consumed}) / n (EG \text{ initial})] \times 100\%$$
 (2)

GA selectivity =
$$[n (GA \text{ formed}) / n (EG \text{ consumed})] \times 100\%$$
 (3)

The Faraday efficiency (%) of the GA formation can be determined by the following equation (4):

$$FE = \{n (GA formed) / [total charge passed / (4 \times 96485)]\} \times 100\%$$
(4)

In the formula, n is the amount of GA, which is obtained by ¹H NMR quantitative analysis.

The cathodic hydrogen was quantitatively analyzed by the drainage method. The cathodic counterpart was connected into a graduated cylinder, which was filled with water and submerged inversely into a water-filled beaker. Once hydrogen was produced at the cathode, the pressure in the cathodic counterpart increased and forced the gas into the inverted graduated cylinder to replace the water. The volume of water discharged was equal to that of the produced hydrogen. The Faraday efficiency (FE) of H_2 was calculated according to the follow-up equation (5):

$$FE = (n_{\text{measured}} / n_{\text{theoretical}}) \times 100\%$$
(5)

where *n* is the mole number of generated H_2 . The theoretically produced amount of the product was calculated based on the following equation (6):

$$n_{\text{theoretical}} = Q / (n \times F) \tag{6}$$

where Q is the transferred charges, n is the number of electrons transferred for H₂, and F is Faraday's constant (96485 C mol⁻¹).

The electricity consumption per m^3 of H_2 produced (*W*, kWh per m^3 H_2) was calculated based on the below equation (7):

$$W = Q \times U / (V \times 3.6 \times 10^6) \tag{7}$$

where U is the applied potential, and V is the actual volume of hydrogen produced.

5. Theoretical calculations

The first-principle DFT calculations were performed using the projector augmented wave (PAW) method. The exchange functional is processed using the generalized gradient approximation (GGA) of the Perdew-Burke-Emzerhof (PBE) functional.^{1, 2} The energy cutoff for the plane-wave basis expansion was set to 450 Ev,³ and the convergence criterion for the geometric relaxation was set to force less than 0.03 eV/Å per atom. Dispersive interactions were described using Grimme's DFT-D3 method.⁴ Throughout the calculations, the Brijulin area was sampled with a Monkhorst grid of $3 \times 3 \times 1$. A convergence energy threshold of 10^{-5} eV was applied from the coherent calculations. To avoid interactions between two adjacent images, a 15 Å vacuum space along the *z* direction was added. Additionally, the adsorption energies (E_{ads}) were calculated as $E_{ads} = E_{ad/sub} - E_{ad} - E_{sub}$, where $E_{ad/sub}$, E_{ad} , and E_{sub} were the optimized

adsorbate/substrate system, the adsorbate in the structure, and the clean substrate, respectively.



Fig. S1 TEM image of N-Ni(OH)₂.



Fig. S2 Standard curves of (a) Pd and (b) Ni for AAS.



Fig. S3 (a) E_{fermi} and (b) E_{cutoff} values of the UPS spectra, where the work function (Φ) can be calculated by $\Phi = hv - (E_{\text{cutoff}} - E_{\text{fermi}})$, and hv is the incident photon energy of 21.2 eV.



Fig. S4 Calculated charges transfer within (a) N-Pd, (b) N-Rh, and (c) O-PdRh



Fig S5. LSV curves of the N-PdRh and N-Ni(OH)₂ towards EGOR in the 1.0 M KOH + 1.0 M EG at 10 mV s⁻¹ with 90% *iR* compensation.



Fig. S6 Calculated adsorption energies of *OH and *CO on the surfaces of N-PdRh and N-Pd.



Fig. S7 (a-c) LSV curves with different metal ratios, reaction temperature and time in the 1.0 M KOH + 1.0 M EG at 10 mV s⁻¹ with 90% *iR* compensation.



Fig. S8 Nyquist plots of the N-PdRh and N-Pd acquired at 0.9 V_{RHE} .



Fig. S9 CV curves of (a) N-PdRh, (b) N-Pd, (c) N-Rh, and (d) NF acquired at 20, 40, 60, 80, and 100 mV s⁻¹ in the 1.0 M KOH + 1.0 M EG solution.



Fig. S10 Potential-dependent EIS spectra. Bode phased plots over the N-PdRh acquired in 1.0 M KOH + 1.0 M EG.



Fig. S11 Potential-dependent EIS spectra. Bode phased plots over the N-PdRh without EG in the 1.0 M KOH electrolyte.



Fig. S12 CV curves of N-PdRh, N-Pd and N-Rh in 1.0 M KOH.



Fig. S13 LSV curves of N-PdRh at 10 mV s⁻¹ in the 1.0 M EG solution by varying the KOH concentrations.



Fig. S14 ¹H NMR spectra of the electrolyte after the electrolysis test.



Fig. S15 Representative ¹H NMR-spectra of the N-PdRh electrocatalyst in the EG oxidation recorded (a) at 0.7 V_{RHE} , (b) 0.9 V_{RHE} , (c) 1.1 V_{RHE} , (d) 1.3 V_{RHE} , (e) 1.5 V_{RHE} and (f) 1.7 V_{RHE} , along with (g) the test of N-Pd electrocatalyst at 0.9 V_{RHE} .



Fig. S16 The Gibbs free energy required for converting EG to FA.



Fig. S17 GA selectivity for N-PdRh and N-Pd at 0.9 V_{RHE} in the 1.0 M KOH + 1.0 M EG solution.



Fig. S18 Stability test with 1.0 M EG. Electrolyte: 1.0 M KOH.



Fig. S19 Nyquist plots of (a) N-PdRh, (b) N-Pd, (c) N-Rh, and (d) NF acquired at -0.1, -0.2, -0.3 and -0.4 V_{RHE} in the 1.0 M KOH solution.



Fig. S20 LSV curves of N-PdRh and N-Ni(OH)₂ recorded in the N₂-saturated 1.0 M KOH solution at 1600 rpm and 10 mV s⁻¹ with 90% *iR* compensation.



Fig. S21 (a) LSV curves of N-PdRh and O-PdRh recorded in the N₂-saturated 1.0 M KOH solution at 1600 rpm and 10 mV s⁻¹ with 90% *iR* compensation. (b) The corresponding Tafel plots.



Fig. S22 (a) Nyquist plots of O-PdRh at -0.1, -0.2, -0.3 and -0.4 V_{RHE}. (b) EIS-derived Tafel plots of the catalysts obtained from the *H adsorption resistance R_2 . (c) Nyquist plots of the catalysts measured at -0.2 V_{RHE}. Electrolyte: 1.0 M KOH.



Fig. S23 CV curves of (a) N-PdRh, (b) N-Pd, (c) N-Rh, and (d) NF acquired at 20, 40, 60, 80, and 100 mV s⁻¹ in the 1.0 M KOH solution.



Fig. S24 High-resolution Pd 3d, and Rh 3d XPS spectra of N-PdRh before and after EGOR (a and b) and HER (c and d).



Fig. S25 HRTEM image of the N-PdRh after EGOR.

E / V _{RHE}	$R_{ m ct}\left(\Omega ight)$
0.7	71.52
0.8	12.80
0.9	6.651
1.0	4.214
1.1	3.096
1.2	2.311
1.3	1.840
1.4	1.656
1.5	1.653

Table S1. Fitting results of the EIS spectra depicted in EGOR at different potentials.

Table S2. Comparison of the energy consumption required for hydrogen production using theN-PdRh and earlier catalysts.

Catalysts	Energy consumption / kWh per m ³ H ₂	References
N-PdRh	2.52	This Work
NiCo/MXene	2.75	5
MSM/CC	2.69	6
NiSe	2.63	7
$H_6[PV_3Mo_9O_{40}]$	2.90	8
SSCAS	2.96	9
Au/Ni(OH) ₂	3.20	10

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