Supporting Information

Interstitial Nitrogen Modified Rh Nanocrystal for Efficient and CO-Resistant Alkaline

Hydrogen Oxidation Electrocatalysis

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Reagents and materials

Rhodium (III) acetylacetonate (Rh(acac)₃, 97%, Wuhan, Changcheng Chemical Co., Ltd.), oleylamine (OAm, 80%~90%, Shanghai, Aladdin Industrial Co., Ltd.), urea (CN₂H₄O, 99%, China, Sinopharm Chemical Reagent Co., Ltd.), polyvinylpyrrolidone (PVP, MW \approx 40000, Shanghai, Aladdin Industrial Co., Ltd.), acetic acid (AR, China, Sinopharm Chemical Reagent Co., Ltd.), ethanol and hexane (>99%, China, Sinopharm Chemical Reagent Co., Ltd.), isopropanol (~99.5%, China, Sinopharm Chemical Reagent Co., Ltd.), and nafion solution (5%, Sigma-Aldrich) were obtained. Carbon black (Vulcan, XC-72R) was used as support material. The water used in all experiments was prepared by passing through an ultra-pure purification system.

Synthesis of N-Rh/C nanoparticles.

Typically, 40 mg Rh(acac)₃ and 4 mL OAm were put into the two-necked glass bottle under stirring. The mixture was heated to the 60 °C and purged with nitrogen after forming a uniform solution. Then the reaction temperature remained constant for 0.5 h. After purging with nitrogen, the reaction temperature was further elevated to 300 °C with a speed of 5 °C min⁻¹ and kept for 1 h. The cooled product was washed with hexane and ethanol to remove impurities for at least five times, and collected by centrifuging at 9800 rpm. The as-prepared products and acetic acid are evenly mixed and stirred at 70 °C for 24 h, and then washed with ultra-pure water and ethanol to obtain the Rh precursor. 10 mg Rh precursor, 240 mg urea, 340 mg PVP, and 24 mL ultra-pure water were thoroughly mixed and stirred for 20 minutes to homogenize, and the mixture is transferred to a 50 mL a Teflon-lined stainless-steel autoclave, heating at a rate of 2 °C min⁻¹ to 180 °C and keeping for 1 h. The cooled product was washed with ethanol and ultra-pure water to remove impurities for at least five times, and collected by centrifuging at 9800 rpm. The sample was dried to obtain N-Rh. Finally, the ethanol solution of Rh was dropwise added into the ethanol solution of XC-72, with a catalyst loading of ~20% wt.

The corresponding catalysts N-Rh/C-300 and N-Rh/C-400 were prepared by changing the urea input from 240mg to 300mg and 400mg, respectively.

Synthesis of Rh/C nanoparticles.

40 mg Rh(acac)₃, 40 mg XC-72, and 4 mL OAm were put into the two-necked glass bottle under stirring. The mixture was heated to the 60 °C and purged with nitrogen after forming a uniform solution. Then the reaction temperature remained constant for 0.5 h. After purging with nitrogen, the reaction temperature was further elevated to 300 °C with a speed of 5 °C min⁻¹ and kept for 1 h. The cooled product was washed with hexane and ethanol to remove impurities for at least five times, and collected by centrifuging at 9800 rpm. The as-prepared products and acetic acid are evenly mixed and stirred at 70 °C for 24 h, and then washed with ultra-pure water and ethanol to obtain the Rh/C nanoparticles.

Physical characterizations

The X-ray powder diffraction (XRD) patterns were performed on a Rigaku Miniflex600 X-ray powder diffractometer equipped with a Cu K α radiation source ($\lambda = 0.154178$ nm). All the diffraction data were collected in a 2θ range from 10° to 80° at a scanning rate of 8 ° min⁻¹. The transmission electron microscopy (TEM) images were performed with FEI Tecnai G20 U-Twin operated at 200 kV. The high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were obtained on a JEOL JEM ARM200CF transmission electron microscope operated at an acceleration voltage of 200 kV, equipped with a probe spherical aberration corrector. X-ray photoelectron spectroscopy experiments were collected with Thermo Fisher ESCALAB 250Xi using Al Ka radiation source. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) were conducted on a Thermo IRIS Intrepid II XSP atomic emission spectrometer. X-ray absorption spectroscopy (XAS) including both X-ray absorption near-edge structure (XANES) and extended Xray absorption fine structure (EXAFS) at Rh K-edge were collected in total-fluorescence yield mode at ambient air at the BL11B beamline of the Shanghai Synchrotron Radiation Facility (SSRF). In situ surface-enhanced infrared absorption spectroscopy (SEIRAS) was carried out with Bruker Invenio R equipped with a liquid nitrogen-cooled detector. A homemade IR cell with a polished Si prism was employed as experimental apparatus.

Electrochemical measurements

All the electrochemical measurements were conducted by the CHI 760E electrochemical analyzer (CH Instruments, Chenhua Co., Shanghai, China). The standard three-electrode-system were adopted. Glass carbon electrode (GCE, diameter: 5 mm) with catalysts coating were used as the working electrode. The Hg/HgO electrode (MOE) (in 0.1 M KOH or 1.0 M KOH) and the graphite rod were served as reference electrode in alkaline electrolytes and the counter electrode, respectively. All measured potentials were reported versus the reversible hydrogen electrode (RHE) potential.

To prepare catalyst ink for HOR experiments, 4 mg catalysts were dispersing in 2 ml isopropanol solution containing 0.05% Nafion. The mixture solvent was ultrasonicated for 1h to form homogeneous solution. Then, 5 μ L ink was pipetted onto the surface of glassy carbon electrode (GCE, 5 mm in diameter) resulting in a total mass loading of ~ 0.05 mg cm_{geo}⁻². The accurate loading of catalysts and elements contents were originated from the ICP-AES results listing in Table S1.

Cyclic voltammetry (CV) was conducted in 0.1 M KOH solution with Ar-saturated at a scanning rate of 50 mV s⁻¹ from -0.18 V to 0.72 V. The HOR polarization curves were recorded by a rotation disk electrode (RDE) with a rotation speed of 1600 rpm in a H₂-saturated 0.1 M KOH and the potential range is from -0.08 V to 0.72 V at a scanning rate of 10 mV s⁻¹.

The HOR polarization under the rotation speed of 2500, 2025, 1600, 1225, 900, and 625 rpm were collected at a scanning rate of 10 mV s⁻¹. The kinetic current density (j^k) of each electrocatalyst could be calculated from the Koutecky-Levich equation (Eq. S1)^[1]

$$\frac{1}{j} = \frac{1}{j^k} + \frac{1}{j^d} = \frac{1}{j^k} + \frac{1}{Bc_0 \omega^{1/2}}$$
.....Eq. S1

where *j* and *j*^d are the measured and diffusion limited current density, and *B* represents the Levich constant, c_0 represents the solubility of H₂ (7.33 × 10⁻⁴ mol L⁻¹), ω is the rotating speed. Among them, *B* could be obtained from Eq. S2

 $B = 0.2nFD^{2/3}v^{-1/6}$ Eq. S2

where *n* is the numbers of electron transferred, *F* is the Faraday constant (96485 C mol⁻¹), *D* is the diffusivity of H₂ (3.7×10^{-5} cm² s⁻¹), and *v* represents the kinematic viscosity (1.01×10^{-2} cm² s⁻¹).^[2]

Exchange current density (j^0) could be deduced from the Butler–Volmer equation in Eq. S3,

$$j^{k} = j^{0} \left[e^{\frac{\alpha F}{RT} \eta} - e^{\frac{-(1-\alpha)F}{RT} \eta} \right] \qquad \dots \text{Eq. S3}$$

where α is the transfer coefficient, *R* represents the universal gas constant (8.314 J mol⁻¹ K⁻¹), *T* stands the operating temperature (303.15 K), η is the overpotential. ^[3]

For Ru-based catalysts, the hydrogen underpotential deposition (H-UPD) method is unsuitable for confirming the electrochemically active surface areas (ECSAs) owing to the adsorption of OH* in H-UPD area. ^[4] Correspondingly, the Cu-UPD method is employed to determine the ECSA for the catalysts. The catalysts modified electrode were cycled between 0.20 and 0.70 V in Ar-saturated solution of 0.1 M H₂SO₄ with 2 mM CuSO₄ to obtain a complete CV containing the UPD and overpotential deposition (OPD) of Cu. Since the stripping peaks of Cu-UPD and Cu-OPD are recorded separately, after eliminated the effect of Cu-OPD in the manner of performing the CV from 0.25 V, the region of Cu-UPD is used to calculate the ECSA. Before the deposition fo Cu, the modified electrodes were cycled between 0 and 0.70 V in pure 0.1 M H₂SO₄ as the background. The surface charge density of 420 μ C cm⁻² is assigned as a monolayer adsorption of Cu on catalysts. All the values of ECSAs are exhibited in Table S2. The value of ECSAs could be calculated via Eq. S4:

$$ECSA\left(\frac{cm_{metal}^{2}}{g_{metal}}\right) = \frac{Q_{Cu}}{M_{metal} \, 420C \, cm^{-2}} \qquad \dots \text{Eq. S4}$$

where M_{metal} is the mass loading of metals on the electrode.

For the CO stripping experiments, the samples were kept at 0.1 V versus RHE for 10 min in the saturated CO to adsorb CO on the metal surface, ^[5] followed by pumping Ar for 20 min to remove residual CO in the electrolyte. The CO stripping current was collected through cyclic voltammetry in a potential range from 0 to 0.9 V at a scanning rate of 5 mV s⁻¹.

The stability of catalyst was appraised by the accelerated durability tests by scanning the potential between -0.08 and 0.72 V for 1000 cycles at the scanning rate of 500 mV s⁻¹. Then, the HOR polarization curve was recorded in H₂-saturated 0.1 M KOH electrolyte at 10 mV s⁻¹ from 0.92 to - 0.08 V via the comparison with the initial curve. The loading of catalyst is around 30 μ g cm_{disc}⁻².

In this work, all the potentials in HOR tests were referred to reversible hydrogen electrode (RHE) with *iR*-compensation. The uncompensated resistance (R_u) was measured by the electrochemical impedance spectra (EIS) tests. EIS tests were measured from 200 kHz to 0.1 kHz at a voltage perturbation of 5 mV after each RDE measurement. The *iR*-free potential ($E_{iR-free}$) was obtained by

using the value of the real part of the resistance at 1 kHz, according to the following equation, Eq. S5,

$$E_{iR-free} = E - iR_u$$
 Eq. S5

where E, i are the measured potential and the corresponding current.

Computational methods

Density functional theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) and generalized gradient corrected approximation (GGA) was carried out for electronic structure calculations. ^[6-7] The cutoff energy was 400 eV and the self-consistent field (SCF) tolerance was 1×10^{-5} eV. The Brillouin zone was sampled by the Monkhorst-Pack scheme with a $4 \times 4 \times 1$ k-points mesh for all of the surfaces. The four-layers of Ru (001) surface were modelled with 4*4 supercell and a vacuum width of 10 Å was added in the z axis. For all the optimization calculations, the bottom two layers were fixed while the topmost two layers and the adsorbates were allowed to relax. The binding energies of H* were determined by the following formula $\Delta E_{H*} = E(\text{surf} + \text{H}) - E(\text{surf}) - 1/2E(\text{H}_2)$. The binding energies of OH* were determined by the following formula $\Delta E_{OH*} = E(\text{surf} + \text{OH}) - E(\text{surf}) - E(\text{H}_2\text{O}) + 1/2E(\text{H}_2)$.

 E_{sub-H} and E_{sub-OH} represent total energies of the model with hydrogen and hydroxyl adsorption. E_{sub} represents total energy of the model. E_{H2} and E_{H2O} represent the energy of molecular H_2 and H_2O in gas phase.

The Gibbs free energy of H* adsorption was calculated as follows:

 $\Delta G_{H^*} = \Delta E_{H^*} + \Delta ZPE$ - T ΔS

 Δ ZPE and Δ S represent the zero point energy correction and entropy change of hydrogen adsorption, respectively. And We refer to the previous work for the related values.^[8]



Fig. S1 The TEM image and size distributions of the Rh/C.



Fig. S2 The line scanning EELS spectra of Rh M₃-edge and N K-edge for different positions on one N-Rh nanoparticle.



Fig. S3 Linear fitting curves in the micro-polarization region.



Fig. S4 (a) HOR polarization curves of N-Rh/C, Rh/C, N-Rh/C-300, and N-Rh/C-400 in H₂-saturated 0.1 M KOH. (b) Linear fitting curves in the micro-polarization region.



Fig. S5 (a) Polarization curves of N-Rh/C in H₂-saturated 0.1 M KOH solution at the rotating speeds

varied from 2500 to 625 rpm. (b) The Koutecky-Levich plot.



Fig. S6 (a) Polarization curves of Rh/C in H₂-saturated 0.1 M KOH solution at the rotating speeds varied from 2500 to 625 rpm. (b) The Koutecky–Levich plot.



Fig. S7 (a) Polarization curves of Pt/C in H_2 -saturated 0.1 M KOH solution at the rotating speeds varied from 2500 to 625 rpm. (b) The Koutecky–Levich plot.



Fig. S8 Exchange current densities normalized by corresponding metal mass of Pt/C, N-Rh/C and Rh/C.



Fig. S9 Cu stripping voltammograms of the N-Rh/C (a), Rh/C (b), and Pt/C (c).



Fig. S10 Comparison of $j^{0,s}$ of N-Rh/C with those of recently reported advanced platinum-group metal (PGM) based catalysts.



Fig. S11 HOR polarization curves of N-Rh/C measured in H_2 -saturated whole pH electrolytes with a scan rate of 10 mV s⁻¹ at a rotating rate of 1600 rpm.



Fig. S12 (a) HOR polarization curves of Rh/C measured in H_2 -saturated whole pH electrolytes at the rotating rate of 1600 rpm. (b) Non-monotonously relation between the exchange current density and the pH of different electrolyte Rh/C.



Fig. S13 Zeta potentials of N-Rh/C and Rh/C.



Fig. S14 (a) HOR polarization curves for N-Rh/C before and after 1000 cycles. The inset shows the linear fitting curves in the micro-polarization region before and after 1000 cycles. (b) CVs in Arsaturated 0.1 M KOH at a scan rate of 50 mV s⁻¹ before and after 1000 CVs of N-Rh/C.



Fig. S15 (a) HOR polarization curves and (b) the linear fitting curves in the micro-polarization region of Rh/C in H₂-saturated 0.1 M KOH at a rotating speed of 1600 rpm before and after 1000 CVs.



Fig. S16 (a) XRD pattern, (b) TEM image, and (c) the size distributions of N-Rh/C after HOR stability test in 0.1 M KOH solution.



Fig. S17 XPS spectra of N 1s in N-Rh/C after the stability test.



Fig. S18 HOR polarization curves in H_2 -saturated 0.1 M KOH before (solid line) and after (dashed line) a chronoamperometry test with 1000 ppm CO of Rh/C.



Fig. S19 In situ CO-adsorption SEIRAS of the Rh/C.



Fig. S20 bridge-bounded CO on N-Rh/C and Rh/C as a function of potential. The Stark tuning rates are labeled.



Fig. S21 Deconvolution of the O-H stretching vibration features of in situ SEIRAS spectra recorded at potentials from 0 V to 0.2 V vs RHE for Rh/C in 0.1 M KOH.



Fig. S22 Potential-dependent proportion of interfacial water for (a) N-Rh/C and (b) Rh/C from in situ SEIRAS spectra.



Fig. S23 The Rh (111) (a) and N-Rh (111) (b) surface models. The Rh and N atoms are colored in pink and blue.



Fig. S24 The charge density difference on N-Rh. Charge accumulation and depletion are illustrated by yellow and blue regions.



Fig. S25 The optimal theoretical structures of H^* on the Rh (111) (a) and N-Rh (111) (b).



Fig. S26 The optimal theoretical structures of OH* on the Rh (111) (a) and N-Rh (111) (b).



Fig. S27 Cyclic voltammograms of N-Rh/C and Rh/C in 0.1 M KOH solution.



Fig. S28 The optimal theoretical structures of CO* on the Rh (111) (a) and N-Rh (111) (b).



Fig. S29 The adsorption energy of CO* on the Rh and N-Rh.



Fig. S30 (a) The charge density difference on N-Rh (charge accumulation and depletion are illustrated by yellow and blue regions) and (b) the slice of charge density difference. (c) The Bader charge distribution of N-Rh.

Catalyst	Rh (Atomic %)	N (Atomic %)
N-Rh/C	16.58	2.97

Table S1. The atomic proportion of Rh and N in N-Rh/C from XPS.

Table S2. The EXAFS fitting results for N-Rh/C.

Sample	Shell	Ν	R (Å)	σ ² (Å ² 10 ⁻³)	ΔE_0 (eV)	R factor
N Dh/C	Rh-Rh	7.9	2.69	5.4	4.00	0.0024280
IN-KII/C	Rh-O/N	2.7	1.98	13.7	4.09	0.0024389

Catalyst	Rh (wt. %)
N-Rh/C	13.16
Rh/C	18.73

Table S3. ICP-AES results of the contents of Rh.

Table S4. HOR activities of the reported PGM-based catalysts in alkaline media.

Catalust	Loading	$j^{0,s}$	<i>j</i> ^{k,m} @50 mV	Defenerae	
Catalyst	$(\mu g_{PGM} cm^{-2})$ (mA cm _{metal} ⁻²)		$(\mathrm{mA}\mu\mathrm{g}_{\mathrm{metal}}^{-1})$	Kelerence	
N-Rh/C	6.7	0.729	1.013	This work	
Ir-Ru@C	17.5	0.133	0.750	9	
Ru/Meso C	25.4	/	0.54	10	
$\operatorname{Ru-Cr}_1(\operatorname{OH})_x$ -1.1	60	0.28	0.425	11	
Ru _{0.7} Ni _{0.3} /C	14	0.13	0.14	12	
Ru _{0.95} Fe _{0.05} /C	14	0.11	0.16	12	
$(Pt_{0.9}Pd_{0.1})_3Fe/C$	5	0.99	0.330	13	
Ru-Ir(2/3)/C	10	0.283	0.210	14	
Rh@Pt _{0.83} NBs	10.2	0.592	0.214	15	
$Pd_{0.33}Ir_{0.67}/N-C$	10	0.45	0.481	16	
RuRh-Co	250	/	0.011	17	
PtRu/Mo ₂ C-TaC	13	0.2	0.291	18	
PtRh	25.5	0.34	0.322	19	
Ru colloidosomes	57	0.045	/	20	
D-PdFe@Pt/C	5	0.076	0.077	21	
O-PdFe@Pt/C	5	0.243	0.248	21	
Rh NBs	10	0.146	0.361	22	

Rh NP/PC	54.8	0.164	0.163	23
Ru NP/PC	50.1	0.227	0.263	23
Ni ₁ Ru ₁ /C	12.5	0.078	0.224	24
Sub-2 nm Ru/HC	14.7	/	0.30	25
PtMo NPs/C	~9.43	0.63	0.805	26
Ru@C-400	10	0.31	0.64	27
Pd ₃ Co@Pt/C	1.87	0.57	0.685	28

 Table S5. Preparation of different pH buffers.

	Acid			Base	Valuera	
Electrolytes	Reagent	Mole weight (mmol)	Reagent	Mole weight (mmol)	(mL)	рН
H_2SO_4	H_2SO_4	50	/	/		~ 1.0
H ₃ Ci/KH ₂ Ci	H ₃ Ci	100	КОН	50		~ 2.8
HAc/KAc	HAc	50	KAc	50		~ 4.6
KH ₂ PO ₄ /K ₂ HPO ₄	$\mathrm{KH}_{2}\mathrm{PO}_{4}$	16.67	K ₂ HPO ₄	16.67	500	~ 6.7
H ₃ BO ₃ /KB(OH) ₄	/	/	$K_2B_4O_7$	25		~ 9.1
K ₂ HPO ₄ /K ₃ PO ₄	K ₂ HPO ₄	10	K ₃ PO ₄	10		~ 11.5
КОН	/	/	КОН	50		~ 13.0

 Table S6. CO tolerance of the reported PGM-based catalysts in alkaline media.

		Attenuation	
Catalyst	CO content	degree	References

Rh ₂ Sb NBs/C	100ppm	5000 s, 11.2%	Adv. Mater. 2021, 33, 2105049
Ru/VOC	1000 ppm	1800 s, 9.1%	J. Am. Chem. Soc. 2023 , 145, 27867- 27876
La ₁ Pt@HCS	1000 ppm	1000 s, 39%	Nat. Commun. 2023, 14, 3767
HEA SNWs	1000 ppm	2000 s, 26.4%	Nat. Commun. 2021, 12, 6261
Ru@TiO ₂	1000 ppm	1900 s, 12.4%	Nat. Catal. 2020, 3, 454-462
(Pt _{0.9} Rh _{0.1}) ₃ V/C	1000 ppm	2400 s, 15%	Angew. Chem. Int. Ed. 2024 , e202402496
RuGa/C-600	1000 ppm	1000 s, 21.4%	J. Mater. Chem. A 2025, 13, 7158-7167
Ni-Ir(BCS)/G	1000 ppm	4000 s, 20.4%	J. Am. Chem. Soc. 2023 , 145, 13805- 13815
Pt ₂ -Rh NSs	1000 ppm	2000 s, 18.9%	ACS Catal. 2023, 13, 6974-6982
Pb _{1.04} -Ru ₉₂ Cu ₈ /C	1000 ppm	2000 s, 57.2%	Angew. Chem. Int. Ed. 2023 , 62, e202311722
N-Rh/C	1000 ppm	4000 s, 30%	This work

Table S7. The number of electrons of $2\tilde{\pi}^*$ (N($2\tilde{\pi}^*$)), the integrated overlap populations up to the Fermi level (ICOHP) of C-O and Pt-C bonding for gas phase CO, CO/Rh (111) and CO/N-Rh (111). The more negative ICOHP indicates the stronger interaction.

/	CO	CO/Rh (111)	CO/N-Rh(111)
N(2π*)	0	0.59	0.54
ICOHP (C-O)	-20.32	-15.28	-15.87

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