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Supporting Information

Spin configuration modulation of Co₃O₄ by Ru-doping for boosting overall water splitting and hydrazine oxidation reaction

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Materials

All chemicals were of analytical grade and directly used without further purification in the experiments. Hydrochloric acid (HCl), potassium hydroxide (KOH), anhydrous ethanol, acetone, ruthenium(III) chloride hydrate (RuCl₃·3H₂O) and cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O) were purchased from Sinopharm Chemical Reagent Co., Ltd. Cobalt foam (CF) was obtained from the Kun Shan Kunag Xun Electronics Co., Ltd. Pt/C (20 wt % Pt), ruthenium(IV) oxide (RuO₂) and Nafion (5wt%) were purchased from Aladdin Ltd. The deionized (DI) water used in all experiments with a resistivity of 18.2 M Ω ·cm⁻¹ was purified through a Millipore system.

Experimental synthesis

Preparation of a-Co(OH)₂/CF nanosheet arrays

Prior to the electrodeposition, a piece of cobalt foam (CF, 2 cm \times 3 cm) was ultrasonically cleaned with acetone and 3 M HCl for 15 min in sequence to remove oil stains and oxides, then rinsed with deionized (DI) water and ethanol several times, next, dried at 60 °C for standby use. The electrodeposition process was carried out using the three-electrode system, with a mercury oxide electrode (Hg/HgO) as the reference electrode, a carbon rod as the counter electrode, and the cobalt foam as the working electrode. The electrolyte only consists of 0.05 M Co(NO₃)₂. The experiments were performed at a deposition potential of -1.0 V (vs. Hg/HgO) with a deposition time of 20 min. After electrodeposition, the as-prepared sample was washed with DI water several times and dried overnight. The obtained sample was denoted as a-Co(OH)₂/CF.

Preparation of Ru-Co₃O₄|V₀/CF and Ru/CF

Typically, first, RuCl₃·3H₂O as a source of Ru was dissolved in DI water to form a homogeneous solution. Subsequently, the as-obtained a-Co(OH)₂/CF was directly immersed into 25 mL freshly prepared RuCl₃·3H₂O aqueous solution with different concentrations (20, 40, 60, 80, 100 and 120 mM) for 5 min at room temperature. Afterwards, the resultant samples were taken out and dried in an oven at 60 °C for 12 h, then followed by annealing in air at 300 °C for 30 min with a heating rate of 5 °C·min⁻¹. Depending on the different etching concentration, we labeled the final samples as Ru₂₀-Co₃O₄|V₀/CF, Ru₄₀-Co₃O₄|V₀/CF, Ru₆₀-Co₃O₄|V₀/CF, Ru₈₀- $Co_3O_4|V_0/CF, Ru_{100}-Co_3O_4|V_0/CF$ and $Ru_{120}-Co_3O_4|V_0/CF$, respectively. Since Ru_{80} -Co₃O₄|V₀/CF has the best performance for both HER and OER with a mass loading of around 10 mg, we chose it as the final catalyst and simplified the label to Ru- $Co_3O_4|V_0/CF$. For comparison, the synthesis approach of the control electrode of Co₃O₄/CF was the same as that of Ru-Co₃O₄|V₀/CF except without RuCl₃·3H₂O immersion. In addition, Ru/CF was also obtained though the same procedure (including immersion and calcinations steps) except without the first hydrothermal step.

Characterization

X-ray diffraction (XRD) patterns were obtained by X-ray diffractometer (Bruker D8-Advance) equipped with a Cu K α radiation source ($\lambda = 1.5418$ Å) to record the

crystal diffraction patterns of samples. The morphology and structure of all samples were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi, SU-8010) and high-resolution transmission electron microscopy (HR-TEM, JEM-2100, 200 kV) with X-ray energy-dispersive spectroscopy. The inductively coupled plasma emission spectrometer (ICP-MS Agilent-720) analysis was conducted to analyze the elemental content in the samples. The surface composition and valence state of the samples were characterized by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD). Raman spectra were acquired by a Renishaw-inVia Raman spectrometer with a 532 nm excitation length. The electron paramagnetic resonance (EPR) spectra were performed to display lone pair electron content using a Bruker E-500 spectrometer. The BET specific surface area was evaluated by a Micromeritics ASAP 2020 instrument.

Electrochemical measurements

All electrochemical data tests were achieved by CHI 760E electrochemical workstation (CH Instruments, China) with a three-electrode system in an O₂ saturated 1.0 M KOH. The as-prepared samples supported on Co foam, a mercury oxide electrode (Hg/HgO) and a carbon rod (4 mm in diameter) were employed as the working, reference and counter electrode, respectively. All the potentials with regard to Hg/HgO were calibrated to the reversible hydrogen electrode (RHE) according to the following equation: E (RHE) = E (vs. Hg/HgO) + 0.059 × pH+ 0.098. All the measurements above were corrected by manual *iR* compensation using the current and the solution resistance. Furthermore, all experiments were repeated at least three times

to ensure reliability and reproducibility. Cyclic Voltammetry (CV) measurements for OER and HER were scanned in the potential range from 0 to 1 V (vs. Hg/HgO), -1.5 to -1 V (vs. Hg/HgO) at a scanning rate of 200 mV·s⁻¹, respectively. And the corresponding polarization curves were obtained by using Linear Sweep Voltammetry (LSV) with a scan rate of 5 mV·s⁻¹, respectively. The stability test was implemented using chronopotentiometric method at certain potentials. In addition, the polarization curve of the OWS was measured from 1.0 to 2.0 V at a sweep rate of 5 mV s⁻¹ via a two-electrode configuration in 1 M KOH, and the chronopotentiometric curve was recorded at a constant potential of 1.79 V. The electrochemical data were not collected until the signals of working electrodes stabilized after scanning several times. Electrochemical impedance spectroscopy (EIS) experiments were conducted in the frequency range from 100 KHz to 1 Hz with an amplitude potential of 5 mV.

Turnover frequency (TOF) is defined as the number of reactant that a catalyst can convert to a desired product per catalytic site per unit of time, which can exhibit the intrinsic activity of each catalytic site. It can be estimated by the following equation:

$$TOF = \frac{|J| \times N_A}{m \times F \times n}$$

where j is current density at defined overpotential; N_A denotes the Avogadro number; m is the number of the consumed electrons forming one H₂ or O₂ molecule from water, F is the Faraday constant. The number of surface active sites (n) can be calculated with the formula: n = $Q/(1 \times 1.602 \times 10^{-19})$, and assume a one-electron transfer process for both reduction and oxidation herein. While charge (Q) can be

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obtained from the reductive negative scan peak areas of cyclic voltammetry (CV) curves at a specific scan rate, for example 200 mV/s. Q can be obtained with the formula: Q= peak area/200 mV/s.

DFT calculations

In this study all calculations were performed by using density functional theory (DFT) with the Vienna ab-initio simulation package (VASP). The projectoraugmented wave (PAW) potentials were adopted to treat the electron-ion interaction. And we applied the generalized gradient approximation (GGA) with the Perdew, Burke, and Ernerhof (PBE) realization to characterize the exchange and correlation potential. The DFT-D3 method of Grimme was employed to correct the intermolecular van der Waals (vdW) interaction. The Co₃O₄ (111), obtained by cutting the Co_3O_4 bulk along the (111) direction, is selected as the activity surface. A (2×2) supercell is employed, while a vacuum of 15 Å is employed to avoid the periodic interaction. A Ru atom will replace the Co atom to model the Ru-doped configuration. For O vacancy, the O atom will be removed. The plane wave energy cutoff was set as 400 eV. The Gaussian scheme was employed for electron occupancy with an energy smearing of 0.1 eV. The first Brillouin zone was sampled in the Monkhorst-Pack grid. The $3 \times 3 \times 1$ k-point mesh is used for the calculations. The energy (converged to $1.0 \times 10-5$ eV/atom) and force (converged to 0.02 eV/Å) were set as the convergence criterion for geometry optimization.

For HER, activity is evaluated by plotting a three state HER free energy diagram. The diagram includes an initial pair of e^- and H^+ , an intermediate adsorbed H (H*)

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and final $\frac{1}{2}E(H_2)$ product, where the Gibbs free energy change of the intermediate state ΔG^*_H can be obtained. The Gibbs free energy change can be expressed as below:

$$\mathrm{H}^{+} + \mathrm{e}^{-} + ^{*} \to \mathrm{H}^{*} \qquad \qquad \mathrm{S}(1)$$

$$\Delta G_{H}^{*} = E_{H} - E_{sub} - \frac{1}{2} E(H_{2}) + E_{ZPE} - T\Delta S \qquad S(2)$$

where ΔE_{H} and E_{sub} are the energies of the surface with and without H adsorption, respectively, $E(H_2)$ is the energy of isolated H_2 , ΔE_{ZPE} and ΔS are the adsorption energy of atomic hydrogen on the surface, zero-point energy correction and entropy change of H* adsorption, respectively. The zero-point energy correction can be estimated by the equation

$$\Delta E_{ZPE} = E_{ZPE} (H^*) - \frac{1}{2} E_{ZPE} (H_2)$$
 S(3)

where E_{ZPE} (H *) and E_{ZPE} (H₂) are obtained by vibrational frequency calculation. The T Δ S is estimated to be -0.2 eV at 1 bar and 300 K.

The OER performance of the catalysts was determined by the adsorption free energy change (ΔG_{ads}) of the intermediates OH, O, OOH and O₂ in alkaline environments. Eq. S(4) - S(7) were adopted to express the mechanism of OER, as the four-electron transfer reaction pathway in the calculation

 $H_2O + * \rightarrow *OH + H^+ + e^-$ S(4)

$$*OH \rightarrow *O + H^+ + e^-$$
 S(5)

 $H_2O+*O \rightarrow *OOH + H^+ + e^- \qquad S(6)$

*OOH
$$\rightarrow$$
 * + O₂ + H⁺ + e⁻ S(7)

Here, the * represents the catalytic active sites on the surface of the samples, and the oxygen-containing groups (*OH, *O, and *OOH) express the adsorbed intermediates on the active sites. The free energy of the adsorbed intermediates was calculated based on the standard hydrogen electrode, defined as Eq. S(5), where E, ZPE, ΔH_t , T, and S represented the total energy, zero-point energy, the change in the heat capacity, thermal correction energy (298.15 K), and entropy, respectively. The Gibbs free energy in the OER process were obtained according to the formulas Eq. S(8) - S(15).

$$G = E + ZPE + \Delta H_{t} - T \cdot S$$

$$S(8)$$

$$ZPE = \frac{h}{2} \sum_{i=1}^{3N} V_{i}$$

$$S(9)$$

$$\sum_{i=1}^{3N} \frac{hV_{i}}{\frac{hV_{i}}{k_{B}T} - 1}}{\Delta H_{t}}$$

$$S(10)$$

$$\sum_{i=1}^{3N} \left[\frac{hV_i}{e^{\frac{hV_i}{k_B T} - 1}} - k_B T \ln\left(1 - e^{-\frac{hV_i}{k_B T}}\right) \right]$$

T·S = S(11)

$$\Delta G_1 = G(*OH) + \frac{1}{2}G(H_2) - G(H_2O) - G(*) - eU - k_BT \ln(10) \times pH \quad S(12)$$

$$\Delta G_2 = G(*O) + \frac{1}{2}G(H_2) - G(*OH) - eU - k_BT \ln(10) \times pH$$
 S(13)

$$\Delta G_3 = G(*OOH) + \frac{1}{2}G(H_2) - G(H_2O) - G(*O) - eU - k_BT \ln(10) \times pH$$

S(14)

$$\Delta G_4 = 4.92 - i = 1$$

$$- eU - k_B T \ln(10) \times pH$$
S(15)

where U, e, and k_B are the applied electrode potential, the transferred charge and the Boltzmann constant, respectively. The overpotential (η) was defined as below: \Box

$$\Box \qquad \eta = \max \{ \Delta G_1 \ , \ \Delta G_2 \ , \ \Delta G_3 \ , \ \Delta G_4 \}_{/e} - 1.23 V \Box \qquad S(16)$$

Here, 1.23 V represents the balanced potential.

		■ #国 2 ■ 10 12 14 16 18 kcV
element	wt%	At%
Со	20.25	49.44
0	71.41	47.34
Ru	8.34	3.22
Total	100	100

Fig. S1 EDX pattern of Ru-Co₃O₄ $|V_0/CF$.



Fig. S2 (a) N_2 adsorption-desorption isotherms and (b) Pore distribution of Ru- $Co_3O_4|V_0/CF$ and $Co_3O_4/CF.$



Fig. S3 Representative SEM images of Ru-free Co₃O₄/CF.



Fig. S4 Representative SEM images of the Ru/CF.



Fig. S5 Contact angles of a water droplet on different substrates (a) CF; (b) Co_3O_4/CF ; (c) Ru-Co₃O₄|V₀/CF.



Fig. S6 EPR spectra of Co_3O_4/CF and $Ru-Co_3O_4|V_0/CF$.



Fig. S7 LSV curves with different etching concentration.



Fig. S8 CV curves of (a) Ru-Co₃O₄ $|V_0/CF$, (b) Ru/CF, (c) a-Co(OH)₂/CF, (d) Co₃O₄/CF in the non-faradaic region with different scanning rates from 20 to 140 mV·s⁻¹.



Fig. S9 Reduction peaks recorded at 200 mV s⁻¹ of (a) $a-Co(OH)_2/CF$; (b) Co_3O_4/CF ; (c)Ru/CF; (d) Ru-Co₃O₄|V₀/CF.



Fig. S10 TOF curves of a-Co(OH)₂/CF, Co₃O₄/CF, Ru/CF, and Ru-Co₃O₄ $|V_0$ /CF for HER at different overpotentials.



Fig. S11 Representative SEM images of the Ru-Co₃O₄|V₀/CF catalyst after continuous 100 h for HER.

		Ru 3 10 12 14 16 18 keV
element	wt%	At%
Со	31.34	64.41
0	56.96	31.78
Ru	11.70	3.81
Total	100	100

Fig. S12 EDX pattern of Ru-Co₃O₄ $|V_0$ /CF after HER stability test at 100 mA cm⁻² for 100 h.



Fig. S13 (a) XPS full survey spectrum of $Ru-Co_3O_4|V_0/CF$ after continuous 100 h HER electrolysis. High-resolution XPS spectrum: (b) Ru 3p, (c) Co 2p, and (d) O 1s.



Fig. S14 (a,c) Nyquist and (b,d) Bode phase plots of Ru-Co₃O₄ $|V_0/CF$ and Co₃O₄/CF

for OER at different potentials versus RHE, respectively.



Fig. S15 (a,c) Nyquist and (b,d) Bode phase plots of Ru-Co₃O₄|V₀/CF and Co₃O₄/CF for HER at different potentials versus RHE, respectively.

In situ EIS at different voltages was employed to explore the electron transfer resistance and electrocatalytic kinetics at the electrode-electrolyte boundary during HER and OER process. The obtained Nyquist plots illustrates the different electrochemical behaviours of Co_3O_4/CF and Ru- $Co_3O_4|V_0/CF$. For OER, at the low potentials from 1.152 to 1.352 V versus RHE for Ru- $Co_3O_4|V_0/CF$, the Nyquist

spectra present steep straight lines, which indicates the infinite charge transfer resistance (R_{ct}), as provided in figure S14a and 14c. An evident semicircle appears when the applied potential exceeds 1.402 V, which suggests the electrocatalytic OER has appeared, while the initial OER potential for Co₃O₄/CF is much higher. In addition, the corresponding Bode phase plots depict the trend of phase angle variation with change of frequency in figure S14b and 14d. Ordinarily, the peaks of phase angle in high frequency and low frequency region could be ascribed to the electron conduction of catalyst inner-layer and the interface reaction charge transfer on the electrolyte-catalyst interface, respectively. As shown by the dotted arrow in the low frequency region (potential from 1.402 to 1.552 V), the smaller phase peak angles of Ru-Co₃O₄|V₀/CF demonstrates the facilitating of interface reaction charge transfer and the faster OER kinetics because of Ru doping compared with undoped Co₃O₄/CF. At high frequency region, the phase angle starts to decrease, signifying the oxidation of the electrocatalyst. For HER as shown in figure S15, both in situ EIS and Bode phase plots show the same results. The phase angel in low frequency area decreases more quickly, which means faster electron transfer rate with the Ru doping in Ru-Co₃O₄|V₀/CF catalyst.



Fig. S16 TOF curves of a-Co(OH)₂/CF, Co₃O₄/CF, Ru/CF, and Ru-Co₃O₄|V₀/CF for OER at different overpotentials.



Fig. S17 Representative SEM images of the Ru-Co₃O₄ $|V_0/CF$ catalyst after continuous 100 h at 100 mA·cm⁻² for OER.



Fig. S18 (a) XPS full survey spectrum of Ru-Co₃O₄|V₀/CF after OER test for 100 h. High-resolution XPS spectrum: (b) Ru 3p, (c) Co 2p, and (d) O 1s.

		■ 33 1 2 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
element	wt%	At%
Со	33.27	65.19
0	63.68	33.86
Ru	3.07	0.95
Total	100	100

Fig. S19 EDX pattern of Ru-Co₃O₄ $|V_0$ /CF after OER stability test at 100 mA cm⁻² for 100 h.



Fig. S20 Formation energy calculation of Ru-doping in Co₃O₄ at different sites.



Fig. S21 Formation energy calculation of oxygen vacancy in Ru-Co₃O₄ at different



Fig. S22 The side view and top view of the optimized geometry of adsorption structure of *OH, *O and *OOH intermediates on Co₃O₄ (111).



Fig. S23 The side view and top view of the optimized geometry of adsorption structure of *OH, *O and *OOH intermediates on Ru-Co₃O₄ (111).



Fig. S24 The side view and top view of the optimized geometry of adsorption structure of *OH, *O and *OOH intermediates on $Ru-Co_3O_4|V_0$ (111).



Fig. S25 XRD patterns of Ru-Co $_3O_4|V_0/CF$ after stability tests for HzOR.



Fig. S26 SEM images of Ru-Co₃O₄|V₀/CF after stability tests for HzOR.

		H3 10 12 14 15 18 10
element	wt%	At%
Со	41.40	74.24
0	44.95	21.89
Ru	13.65	3.87
Total	100	100

Fig. S27 EDX pattern of Ru-Co₃O₄|V₀/CF after stability tests for HzOR.



Fig. S28 Quantitative H_2 and N_2 measurement via water displacement.

Table S1 Contents of Ru and Co elements in the Ru-Co $_3O_4|V_0/CF$ as determined by ICP-MS analysis.

Sample	Element	W (wt.%)
Ru-Co ₃ O ₄ V _O	Ru	0.25%
Ru-Co ₃ O ₄ V _O	Со	73.81%

Table. S2 Comparisons of HER catalytic activity of Ru-Co3O4|V0/CF with someprevious reported catalysts in 1 mol/L KOH solution.

		Overpotential	Overpotential	
Material and	Substrate	HER@	HER@	Reference
content of Ru (wt.%)		10mAcm ⁻²	100mA cm ⁻²	
Ru-Co ₃ O ₄ V ₀ /CF	Co foam		48	This work
(0.25%)				
MoNi@Mo-NiO	NGF	56	-	1
RuBx-Ru@BNPCH		5	52	2
(2.09%)	-	3		2
Co ₃ O ₄	-	77.9	-	3
Co/WN	Ni foam	27	-	4
V-CPNA	Carbon Cloth	87	-	5
C-Ni _{1-x} O	Ni foam	27	-	6
Al-CoP	Carbon Cloth	38	-	7
NiFe NTAs	Ni foam	181	-	8
Co _{6.25} Fe _{18.75} Ni ₇₅ O _x	Ni foam	84	-	9
FF-Na-Ru	Iron foam	30	230	10
Ru-NiCoP	Ni foam	44	-	11
(0.270) RuO ₂ /NiO	Ni foam	22		12
Ru/Cu-doped RuO2	-	22		12
CoMnCH	Ni foam	180		13
Fe-Ni ₂ S ₂	Ni foam	-	314	15
	Carbon Cloth	152	-	16
Cr-doped FeNi–P	Carbon Nanotube	190	-	17
Ru@Co ₃ O ₄ (7.53%)	-	49	-	38
Ru-Co ₃ O ₄ (13.77%)	-	97	-	39
Ru-CoP (13.26%)	-	47	-	39
RuNiFe-O@SS (0.17%)	Stainless steel	331	-	40
Ru-VOx/Ni ₃ S ₂ (2.49%)	Ni foam	7	-	41
Ru-NiCo ₂ O ₄ (1.4%)	Ni foam	25	-	42
Ru@FeP ₄ /Fe ₂ PO ₅ (3.55%)	Ni foam	49	-	43
Ru _{9.1} -NiFe-MOF/NFF	Nickel-iron	17	-	45

(9.1%)	foam			
Ru-NiCoP (0.64%)	Ni foam	32.3	-	47
Ru, Ni-CoP (6.3%)	-	45	-	49

Table. S3 Comparison of OER catalytic performance of Ru-Co $_3O_4|V_0/CF$ with otherrecently reported non-precious metal electrocatalysts in 1 mol/L KOH solution.

Material and content of Ru (wt.%)	Substrate	Overpotential OER@ 10mAcm ⁻²	Overpotential OER@ 100mA cm ⁻²	Reference
Ru-Co ₃ O ₄ V ₀ /CF (0.25%)	Co foam		270	This work
MoNi@Mo-NiO	NGF	-	-	1
Co ₃ O ₄	-	301.2	-	3
Co/WN	Ni foam	232	-	4
Al-CoP	Carbon Cloth	265	-	7
$Co_{6.25}Fe_{18.75}Ni_{75}O_x$	Ni foam	186	-	9
FF-Na-Ru	Iron foam	174	-	10
RuO ₂ /NiO	Ni foam	250	-	12
Ru/Cu-doped RuO ₂	-	241	-	13
Fe-Ni ₃ S ₂	Ni foam	-	269	15
Co/CoO@NC	Carbon Cloth	284	-	16
Cr-doped FeNi–P	Carbon Nanotube	240	-	17
MoO ₃ /Ni-NiO	Carbon Cloth	-	347	18
FeCoNiB@B-VG	Graphene Oxide	387	-	19
Co-NixPy@Co ₃ O ₄	Ni foam	120	260	20
Co/CoO@NC	Carbon Cloth	284	-	21
CoS _{1.097} /NGF-750	Graphene Oxide	240	-	22
Co _{0.13} Ni0 _{.87} Se ₂	Ti foam	100	-	23
Ru@Co ₃ O ₄ (7.53%)	-	290	-	38
Ru-Co ₃ O ₄ (13.77%)	-	269	-	39
Ru-CoP (13.26%)	-	328	-	39
RuNiFe-O@SS (0.17%)	Stainless steel	310	-	40

Ru-VOx/Ni ₃ S ₂ (2.49%)	Ni foam	215	-	41
Ru-NiCo ₂ O ₄ (1.4%)	Ni foam	249	-	42
Ru@FeP ₄ /Fe ₂ PO ₅ (3.55%)	Ni foam	249	-	43
a/c CoNiRuOx-1 (2.5%)	-	245	-	44
Ru _{9.1} -NiFe-MOF/NFF (9.1%)	Nickel–iron foam	202	-	45
Ru@CoFe/D-MOF (1.5%)	-	265	-	46
Ru/NiFe(OH)x/NiFe-MOF (2.8%)	-	242	-	48
Ru, Ni-CoP (6.3%)	-	251	-	49

Table S4. Comparison cell voltage of hierarchical Ru-Co $_3O_4|V_0/CF$ with otherbifunctional electrocatalysts in 1 mol/L KOH solution.

Catalyst	Substrate	cell voltage (V) @ j=10 mA·cm ⁻²	Reference
Ru-Co ₃ O ₄ V ₀ /CF	Co foam	1.47	This work
MoNi@Mo-NiO	NGF	1.53	1
Co ₃ O ₄	-	1.60	3
Co/WN	Ni foam	1.51	4
Al-CoP	Carbon Cloth	1.62	7
NiFe NTAs	Ni foam	1.62	8
Co _{6.25} Fe _{18.75} Ni ₇₅ O _x	Ni foam	1.583	9
FF-Na-Ru	Iron foam	1.46	10
Ru-NiCoP	Ni foam	1.515	11
RuO ₂ /NiO	Ni foam	1.50	12
Ru/Cu-doped RuO ₂	-	1.47	13
CoMnCH	Ni foam	1.68	14
Fe-Ni ₃ S ₂	Ni foam	1.58	15
Co/CoO@NC	Carbon Cloth	1.66	16
Cr-doped FeNi-P	Carbon Nanotube	1.54	17
MoO ₃ /Ni-NiO	Carbon Cloth	1.55	18
CoO _x -RuO ₂	Ni foam	1.49	24
P-Co ₃ O ₄	Ni foam	1.63	25
NiS-NiS ₂ -Ni ₃ S ₂	Ni foam	1.46	26

Catalyst	Electrolyte	Tafel slope (mV dec ⁻¹)	Reference
Ru-Co ₃ O ₄ V ₀ /CF	0.5M N ₂ H ₄ +1M KOH	100 mA cm ⁻² at -96 mV	This work
Co ₉ S ₈ @S-C-600	0.5M N ₂ H ₄ +1M KOH	376 mA cm ⁻² at 300 mV	27
NiCoP/NF	0.2M N ₂ H ₄ +1M KOH	1511mA cm ⁻² at 300 mV	28
Cu _x Se/CF	0.5M N ₂ H ₄ +1M KOH	20 mA cm ⁻² at 530mV	29
Ni(Cu)@NiFeP	0.5M N ₂ H ₄ +1M KOH	1017 mA cm ⁻² at 300 mV	30
Ni-Fe/NF	0.5M N ₂ H ₄ +1M KOH	907mA cm ⁻² at 300 mV	31
CoP/Co-20	0.5M N ₂ H ₄ +1M KOH	100 mA cm ⁻² at 177 mV	32
Co/LaCoOx@N-C-1	0.1M N ₂ H ₄ +1M KOH	69.2 mA cm ⁻² at 300 mV	33
Ni ₃ S ₂ /NF-2	0.2M N ₂ H ₄ +1M KOH	100 mA cm ⁻² at 415 mV	34
Cu _x Se/CF	0.2M N ₂ H ₄ +1M KOH	20 mA cm ⁻² at 530 mV	35
Au1Pt8	0.5M N ₂ H ₄ +1M KOH	10 mA cm ⁻² at 502 mV	36
RhIr MNs	0.5M N ₂ H ₄ +1M KOH	100 mA cm ⁻² at 117 mV	37

Table S5. Comparisons of HzOR catalytic activity of Ru-Co₃O₄|V₀/CF with the previous HzOR catalysts in alkaline solutions.

Table S6 Contents of Ru and Co elements in the Ru-Co₃O₄|V₀/CF after stability testsfor HzOR as determined by ICP-MS analysis.

Sample	Element	W (wt.%)
Ru-Co ₃ O ₄ V _O	Ru	0.19%
	Со	72.57%

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