

Supporting Information

Tailoring Electronic Environments of Dispersed Ru Sites for Efficient Alkaline Hydrogen Evolution

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Experimental section

Chemical reagents and materials

Anhydrous ethanol (≥ 99.7 wt.%) was purchased from Sinopharm Chemical Reagent co. Ltd. (Shanghai, China). Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ≥ 99.0 wt.%), Ruthenium carbon (Ru/C, 5%) and potassium hydroxide (KOH) were supplied by Macklin Biochemical Co., Ltd. (Shanghai, China). Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ≥ 98.5 wt.%), hydrochloric acid, and acetone were obtained from Xilong Science Co., Ltd. (Guangzhou, China). Urea ($\text{N}_2\text{H}_4\text{CO}$, ≥ 99.5 wt.%) and anhydrous ruthenium (III) chloride (RuCl_3 , 45-55 wt.%) were purchased from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). Ammonium fluoride (NH_4F , ≥ 96.0 wt.%) was supplied by Sinopharm Chemical Reagent co. Ltd. (Shanghai, China). Deionized water used in the experiment was always ultrapure water ($18.2 \text{ M}\Omega \cdot \text{cm}$). Platinum, nominally 20% on carbon black (Pt/C 20%) was purchased from Thermo Scientific Co., Ltd. (Shanghai, China).

Synthesis of NiCo-OH/CC

The carbon cloth ($3 \times 4 \text{ cm}^2$) was ultrasonically cleaned sequentially in acetone, 3 M hydrochloric acid, deionized water, and ethanol. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (348.0 mg) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (162.5 mg) were dissolved in 35 mL of deionized water and stirred for 30 minutes. Subsequently, 180 mg of $\text{CO}(\text{NH}_2)_2$ and 44.4 mg of NH_4F were added to the solution. The mixture was transferred to a 50 mL Teflon-lined autoclave, and a piece of pretreated carbon cloth was immersed in it. The autoclave was sealed and heated at $120 \text{ }^\circ\text{C}$ for 5 hours. After cooling to room temperature, the sample was washed several times with deionized water and dried in an oven at $60 \text{ }^\circ\text{C}$.

Synthesis of NiCo₂O₄/CC

The as-prepared NiCo-OH/CC was placed in the center of a tube furnace and heated at $400 \text{ }^\circ\text{C}$ for 3 hours in air to obtain NiCo₂O₄.

Synthesis of Ru-NiCoO₂/CC

The Ru-NiCoO₂ catalyst was fabricated using a facile galvanostatic deposition strategy

in the electrochemical workstation (CHI760E, Inc. China). Typically, the as-prepared NiCo₂O₄/CC served as the working electrode, and a high-purity graphite rod was used as the counter electrode. Ru deposition was carried out in an electrolyte containing RuCl₃ (3×10^{-3} M) and NH₂SO₃H (30×10^{-3} M) under a current density of -0.2 mA cm⁻² for 1200 seconds.

Synthesis of Ru-NiCo₂O₄/CC

Co(NO₃)₂·6H₂O (348.0 mg) and Ni(NO₃)₂ · 6H₂O (162.5 mg), were dissolved in 35 ml of deionized water and stirred for 30 min, followed by the addition of CO (NH₂)₂ (180 mg), NH₄F (44.4 mg), RuCl₃·xH₂O (24.7 mg) and NH₂SO₃H (105 mg), and stirred for another 10 min. The solution was then transferred to a Teflon-lined autoclave (50 ml), and a piece of pretreated CC (3×4 cm²) was immersed in the solution and placed vertically. The autoclave was sealed and kept at 120 °C for 5 h, after which it was allowed to cool naturally. Washing the obtained CC several times with deionized water and anhydrous ethanol and dried at 60 °C. At last, placed it in the center of the tube furnace and annealed at 400 °C in air for 3 h at a ramp rate of 5 °C min⁻¹ to obtain Ru-NiCo₂O₄/CC.

Synthesis of Ru/CC

Using a facile galvanostatic deposition strategy in the electrochemical workstation (CHI760E, Inc. China). Typically, the CC served as the working electrode, and a high-purity graphite rod was used as the counter electrode. Ru deposition was carried out in an electrolyte containing RuCl₃ (3×10^{-3} M) and NH₂SO₃H (30×10^{-3} M) under a current density of -0.2 mA cm⁻² for 1200 seconds.

Electrochemical Measurements

HER electrochemical tests were conducted in an alkaline medium (1 M KOH / 1 M KOH + seawater) using a CHI 760E electrochemical workstation in a three-electrode system. A reversible hydrogen electrode (RHE) served as the reference electrode, and a graphite rod was used as the counter electrode. Linear sweep voltammetry (LSV) was performed with 95% iR compensation at a scan rate of 5 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) measurements were taken over a frequency range of 0.1

to 100 kHz with an AC amplitude of 5 mV. All stability tests were carried out without iR compensation. Using a RuO₂|| Ru-NiCoO₂/CC electrolytic cell, the generated gas was collected by the drainage method, and the Faradaic efficiency was estimated.

Physical characterization

The morphologies were observed using a scanning electron microscope (SEM) Hitachi S-4800. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) measurements were performed using an FEI Tecnai G20 with a 200 kV acceleration voltage. Energy-dispersive X-ray spectroscopy (EDS) mapping was also conducted with the FEI Tecnai G20 (200 kV). The purity and crystal properties of the catalysts were evaluated by Rigaku D/max-2500 pc X-ray diffraction (XRD) using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) at a scan rate of 2° s^{-1} . The chemical states of the samples were analyzed using Thermo Fisher Scientific II X-ray photoelectron spectroscopy (XPS) with an Al K α source. Contact angle measurements were performed using a Dataphysics-OCA100. Raman spectra were obtained with a LabRAM HR Evolution using an excitation wavelength of 532 nm.

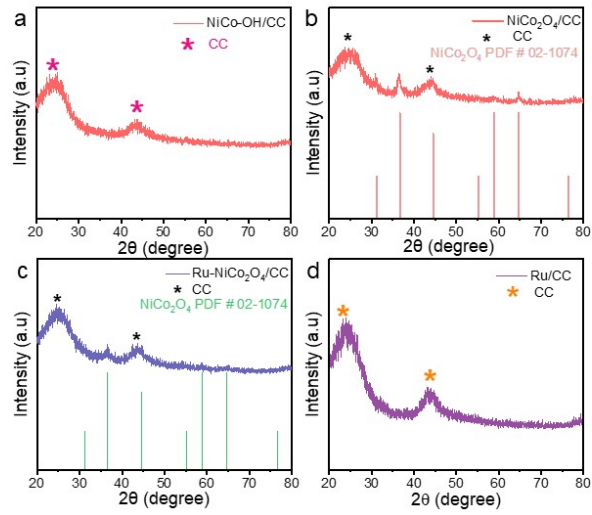


Fig. S1 The XRD patterns of (a) NiCo-OH/CC , (b) $\text{NiCo}_2\text{O}_4/\text{CC}$, (c) $\text{Ru-NiCo}_2\text{O}_4/\text{CC}$ and (d) Ru/CC .

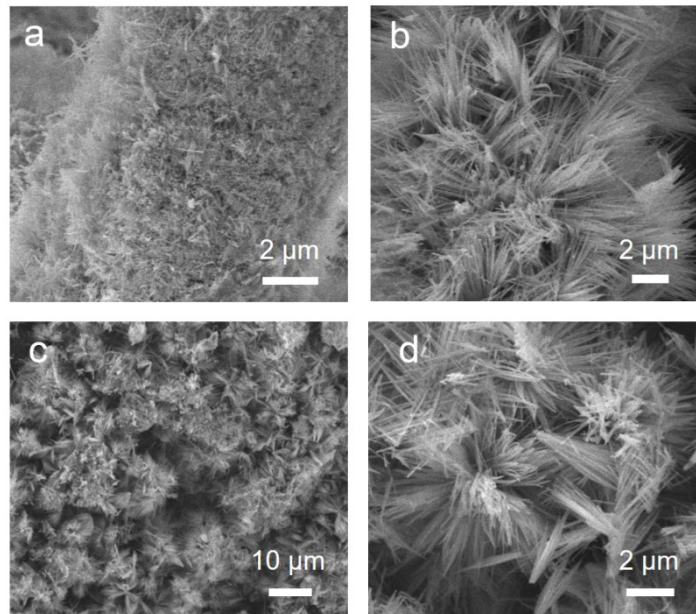


Fig. S2 SEM images of (a, b) NiCo-OH/CC , (c, d) $\text{NiCo}_2\text{O}_4/\text{CC}$.

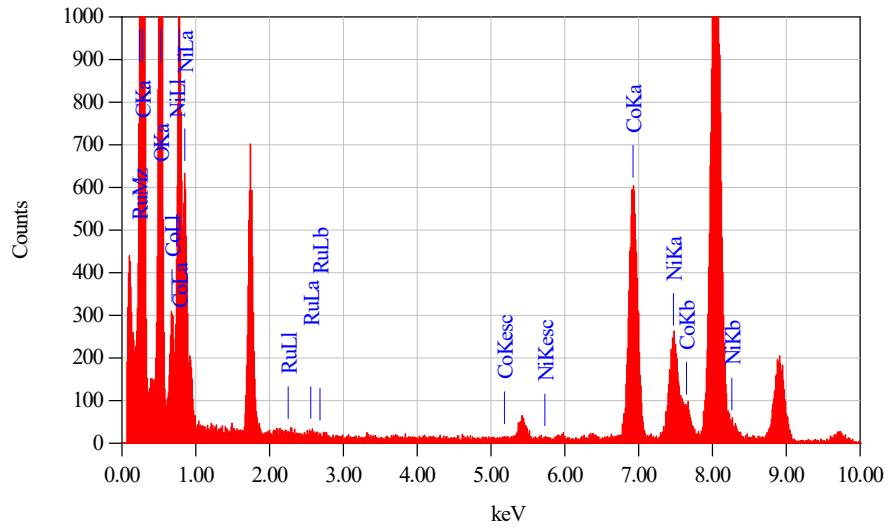


Fig. S3 Elemental maps obtained by point-scanning the energy spectrum for a position of Ru-NiCoO₂/CC.

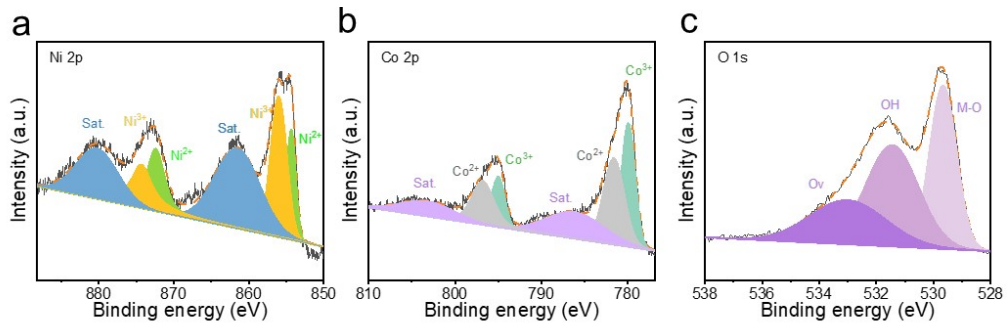


Fig S4. XPS spectrum of (a) Ni 2p, (b) Co 2p and (c) O 1s of NiCo₂O₄/CC.

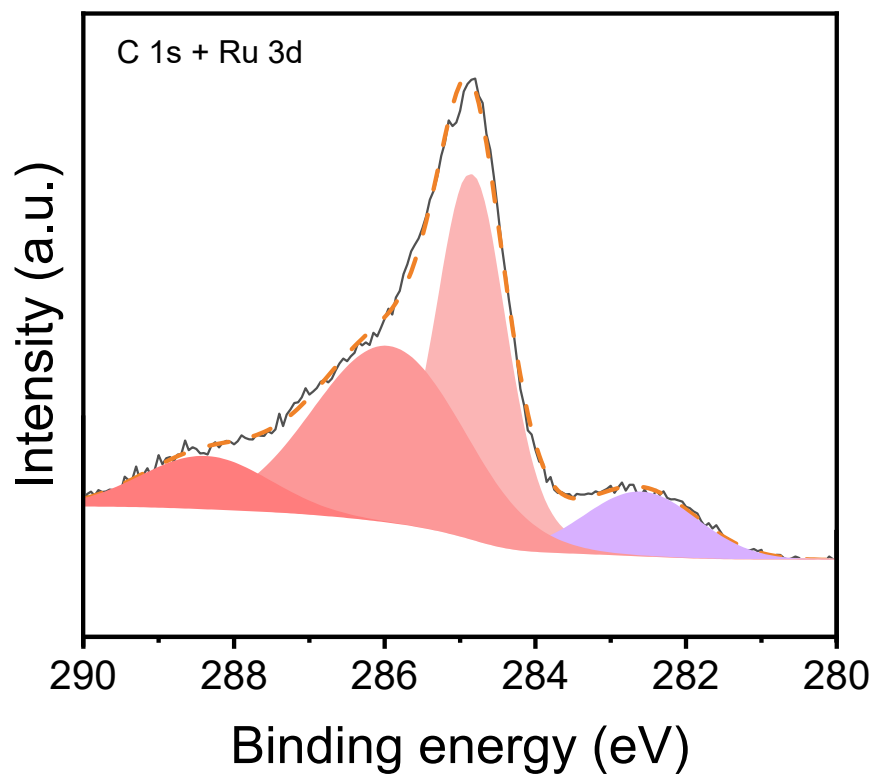


Fig S5. XPS spectrum of C 1s of Ru-NiCoO₂/CC.

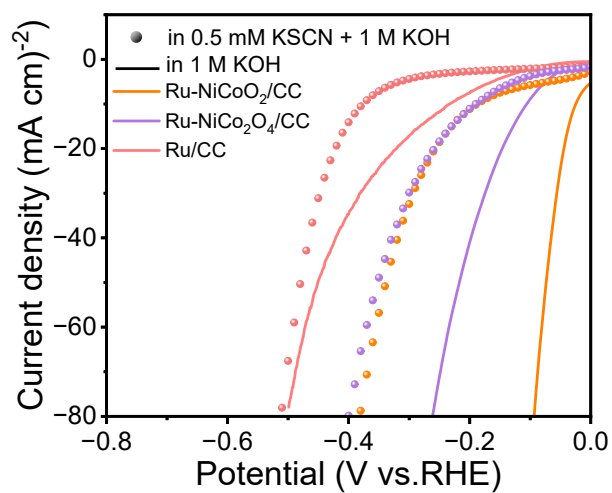


Fig S6. Poisoning experiment of Ru-NiCoO₂/CC, Ru-NiCo₂O₄/CC and Ru/CC in 1 M KOH with the addition of 0.5 mM of potassium thiocyanate.

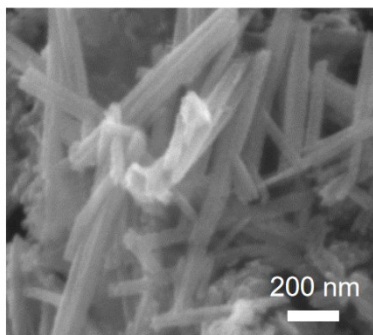


Fig S7. SEM image of Ru -NiCoO₂/CC after i-t test in 1 M KOH.

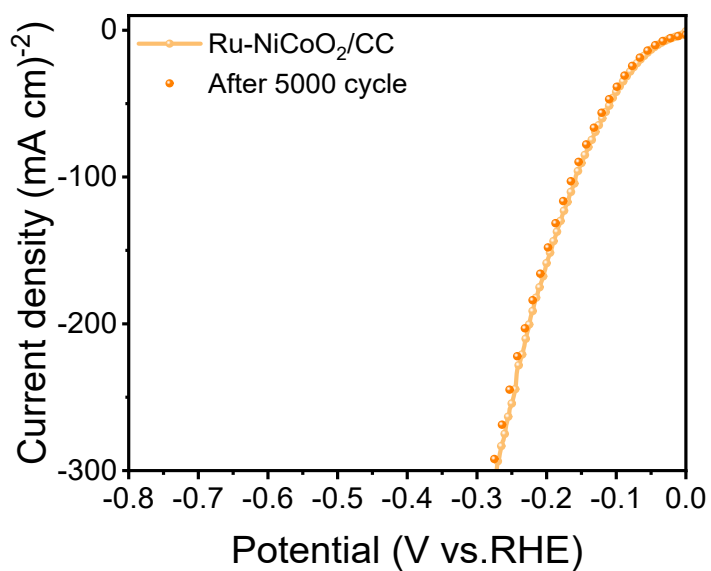


Fig S8. LSV curves before and after 5000CV cycle in 1 M KOH.

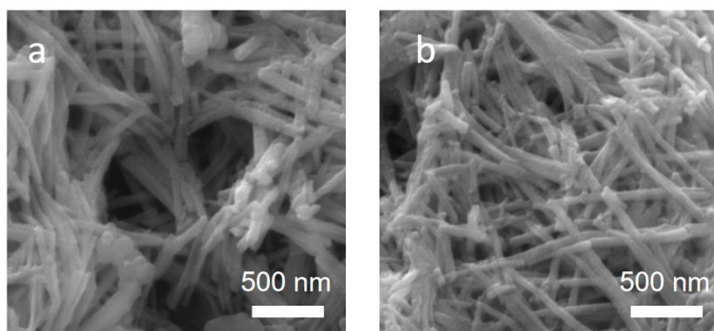


Fig S9. SEM images of Ru-NiCoO₂/CC after i-t test in 1 M KOH + seawater.

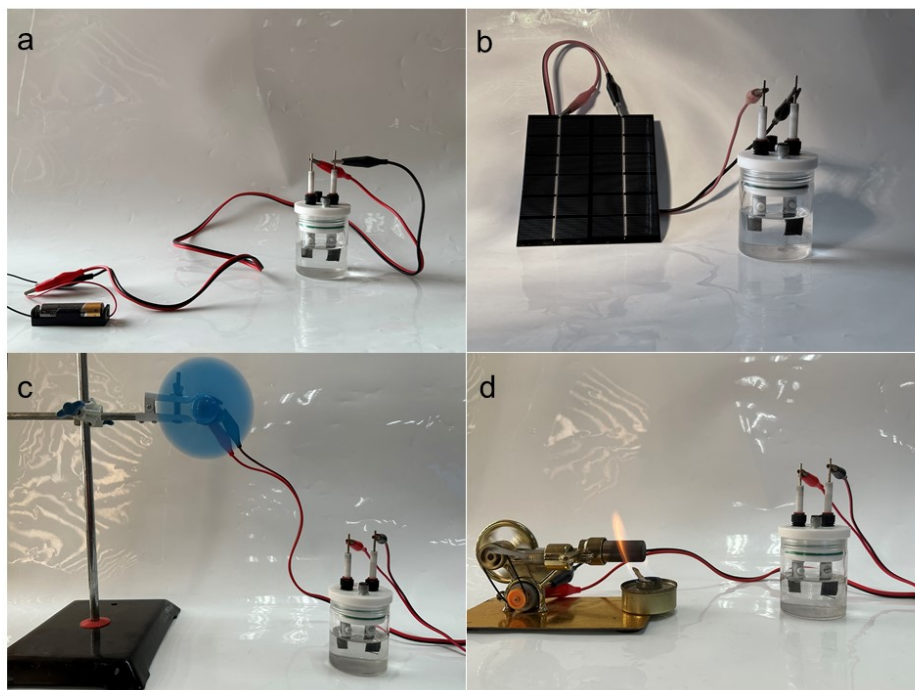


Fig S10. Schematic of overall water splitting powered with the electric energy generated by (a) a single AAA battery, (b) solar energy, (c) wind and (d) thermal.



Fig. S11. The device of collecting gas by the drainage method.

Table S1. Relative elemental content of Ru-NiCoO₂/CC.

Element	Line Type	Absorption Correction	wt%	wt% Sigma
C	K series	1.00	80.37	88.64
O	K series	1.00	11.52	9.54
Co	K series	1.00	5.80	1.30
Ni	K series	1.00	2.24	0.50
Ru	L series	1.00	0.07	0.01
Total:			100.00	100.00

Table S2. Comparison of the HER performance of the Ru-NiCoO₂/CC with other previously reported electrocatalysts with overpotential versus Tafel slope in 1.0 M KOH.

Catalyst	η_{10} / mV	Tafel slopes (mV dec ⁻¹)	Ref.
Ru-NiCoO₂/CC	37	63.7	This work
RuNiCo_{0.5}-600 °C	42	62	[1]
NiCoP/CC	62	68	[2]
Ru/CoO	55	70	[3]
RuNi-0	69	7	[4]
Ni-Co-P-00	150	60	[5]
Co-RGO	156	70	[6]
CoP	226	76	[7]
Ni₀.Co_{0.67}S₂	88	91	[8]
Ru-CoP CC	45	98	[9]
RuNi-alloy@SC	9	96	[10]

Table S. Comparison of the HER performance of the Ru-NiCoO₂/CC with other previously reported electrocatalysts with overpotential in 1.0 M KOH + seawater.

Catalyst	η_{10} / mV	Ref.
Ru-NiCoO₂/CC	50	This Work
Ru/B-Ni₂P/Ni₅P₄	57	[11]
Ru_{1+NPS}/N-C	58	[12]
Co@RuCo-	59	[13]
Ru₂₂NiMoP₂/NF	60	[14]
Pt-Ru-Ni	65	[15]
RuFe-Ni₂P@NF	81	[16]
NiFeRuO_x/NF	98	[17]
Mo-Ni₂P/CC	154	[18]
NiCoN NixP NiCoN	165	[19]
Ru-WO_x	218	[20]
Ru-W-NiSe₂/NF	5	[21]

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