

Supporting information for

Preparation of heterogeneous NiCo₂S₄/Ru Composite Electrode Materials and Electrocatalytic Property of Hydrogen Evolution

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Experimental section

Synthesis of bimetallic sulfide NiCo₂S₄ :

According to the atomic percentage of Ni_{1.7}Co_{3.3}Al_{9.5} metal block, Al, Ni, Co blocks were calculated and prepared at analytically pure. After ultrasonic cleaning, vacuum drying, repeated melting three times in the water-cooled copper crucible suspension melting furnace. The obtained alloy ingots were placed in a strip casting tube and sprayed onto a copper rod with a rotating speed of 25r s⁻¹ by magnetic induction melting. The Ni_{1.7}Co_{3.3}Al_{9.5} precursor alloy strips about 3~4 mm in width and 35~45 μm in thickness were obtained. Later on, the alloy strip of about 1.5 g was placed in 5 mol L⁻¹ NaOH solution for 20 h for chemical dealloying and the precipitate after dealloying was collected. The precipitates were washed to neutral by deionized water and anhydrous ethanol, and kept in a vacuum drying oven at 60 °C for 12 h to obtain the nano-porous Ni-Co alloy. 50 mg Ni-Co alloy powder material and 1.5 g sublimated sulfur powder were placed in two porcelain boats and placed in the heating center of the gas deposition furnace. A distance of 10 mm was left between the two porcelain boats and Ar gas was injected into the tubes at a flow rate of 100 mL min⁻¹. The vessels were heated to 550 °C at a rate of 8 °C min⁻¹ and kept for 2 h. After cooling, the vessels were

removed, the substrate material NiCo_2S_4 was obtained.

Synthesis of $\text{NiCo}_2\text{S}_4/\text{Ru}$ electrode :

$\text{NiCo}_2\text{S}_4/\text{Ru}$ heterostructure bimetallic sulfide composite electrode was prepared by solvothermal method and subsequent annealing method. Four groups of NiCo_2S_4 and RuCl_3 samples with the mass ratios of 1:0.89, 1:1.12, 1:1.35 and 1:1.57 respectively, were mixed in benzyl alcohol solution by ultrasound. The solution was poured into a hydrothermal reaction kettle and kept at 180 °C for 8 h in an air-blast drying oven. After cooling, the precipitate was dried in vacuum, and then kept at 350 °C under the protection of Ar gas for 2 h. The heterogeneous $\text{NiCo}_2\text{S}_4/\text{Ru}$ composite electrode material was obtained.

Synthesis of $\text{NiCo}_2\text{S}_4/\text{RuS}_2$ electrode :

30 mg of $\text{NiCo}_2\text{S}_4/\text{Ru}$ (60%) and 1 g of sublimated sulfur powder were placed in two porcelain boats respectively and placed in the heating center of the vapor deposition furnace. At a distance of 10 mm between the two ceramic boats, Ar gas was injected into the tube at a flow rate of 100 mL min^{-1} , and heated to 550 °C at a heating rate of 8 °C \cdot min^{-1} and kept for 2 h. The composite electrode material $\text{NiCo}_2\text{S}_4/\text{RuS}_2$ was obtained as the contrast sample.

Synthesis of working electrode :

The working electrode was prepared by coating method. First for preprocessing of nickel foam with a volume ratio of 20 % dilute hydrochloric acid solution at room temperature of dealing with the surface area of 1 cm^2 nickel foam 18 hours to remove surface oxide and mild etching to increase the effect of surface roughness. Then the treated nickel foam was cleaned by ultrasonic and dried for 8 h in a vacuum at 60 °C. Then take 20 mg of the active substance, 30 μL of anhydrous ethanol and 0.4 μL of poly tetra fluoroethylene, mix thoroughly to get a thick paste liquid. It was uniformly coated on 1 $\text{cm} \times 1 \text{cm}$ nickel foam with a loading capacity of 20 mg/cm^2 and dried at room

temperature for 30 minutes to obtain the prepared working electrode.

Characterization:

The X-ray diffraction spectra (XRD) measurements were performed on a D/Max-2400 instrument utilizing Cu K α radiation ($\lambda=0.154$ nm, I=100 mA, U=40 kV). The XRD patterns were recorded from 10° to 90° with a scanning rate of 5 °/min. Scanning electron microscopy (SEM) measurements were carried out on a field-emission LEI secondary electron scanning electron microscope (JSM-6700) operated at an accelerating voltage of 5.0 KV. Carrying energy spectrum EDS at working voltage 8.0 kV, working distance WD=12 mm. Transmission electron microscopy (TEM) measurements were carried out by using a JEM2010 microscope operated at 200 kV. The element composition was detected by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI), the X-ray source voltage is 16 kV, the tube current is 14.9 mA, and the beam spot diameter is 650 μ m. The full spectrum is 100 eV, and the high-resolution spectrum of elements is 30 eV.

Electrochemical measurements:

Electrolysis experiments were performed in a standard three-electrode cell, which was composed of working electrode, auxiliary electrode (purity graphite rod) and reference electrode (Hg/HgO). 1 M KOH was used as the electrolyte. Before the test, the parametric electrode is corrected, and the test is tested all the way to protect the working electrode.

The linear sweep voltammogram (LSV) curves of the electrodes, with a scan rate of 5 mV s⁻¹, usually compared to the overcurrent density of the current density to measure the catalytic dehydrogenation performance of electrolytic water. A reversible hydrogen electrode (RHE) was used to correct the reference electrode.

$$E_{(RHE)} = E_{(Hg/HgO)} + 0.059 pH + 0.098$$

At the same time, in order to obtain the intrinsic catalytic activity of the electrode material, all the measured potentials are compensated by IR_s to obtain the corrected LSV.

$$E_{correct} = E_{measure} - I \times R_s$$

Among them, $E_{correct}$ is the compensated potential, $E_{measure}$ is the measured potential, R_s is the solution impedance, which is obtained by ac impedance fitting.

According to LSV curve and Tafel equation, the kinetic parameters in the electrocatalytic reaction process can be fitted.

$$\eta = a + b \times \log j$$

Where η is the overpotential, b is the Tafel slope, j is the current density.

The electrochemical impedance spectroscopy (EIS) Nyquist plots were obtained in a 1.0 M KOH aqueous solution at 1.23 V_{RHE} in the frequency range of 10⁻² to 10⁵ Hz. The measured spectra were fitted with ZSimp Win software. The electrochemically active surface areas (ECSAs) were obtained by CV measurement in the non-Faradic region. The range of scanning voltage is 0.2V – 0.3V (vs. RHE). By plotting the interpolation of oxidation current density and reduction current density against the scan rate, the linear slope which is twice of the double-layer capacitance (C_{dl}) is used to represent ECSAs.

Supplemental Figures and Tables

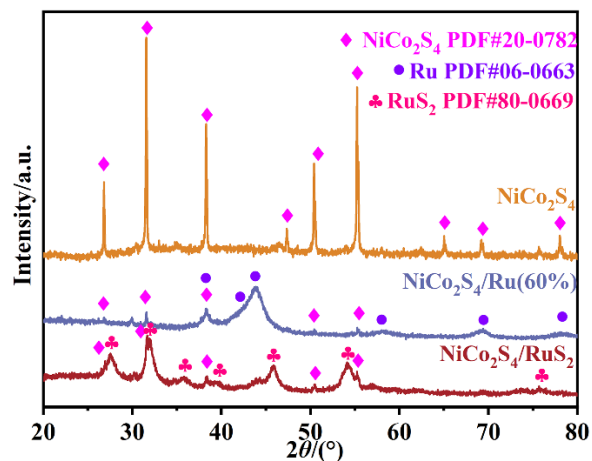


Figure S1. XRD patterns of $\text{NiCo}_2\text{S}_4/\text{Ru}$ and $\text{NiCo}_2\text{S}_4/\text{RuS}_2$ composite electrode materials.

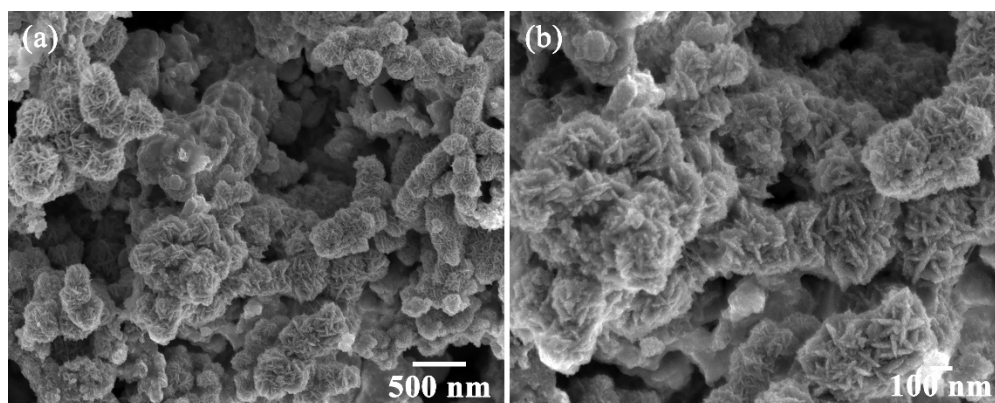


Figure S2. SEM of heterogeneous bimetallic sulfide composite electrode materials of (a, b) $\text{NiCo}_2\text{S}_4/\text{RuS}_2$.

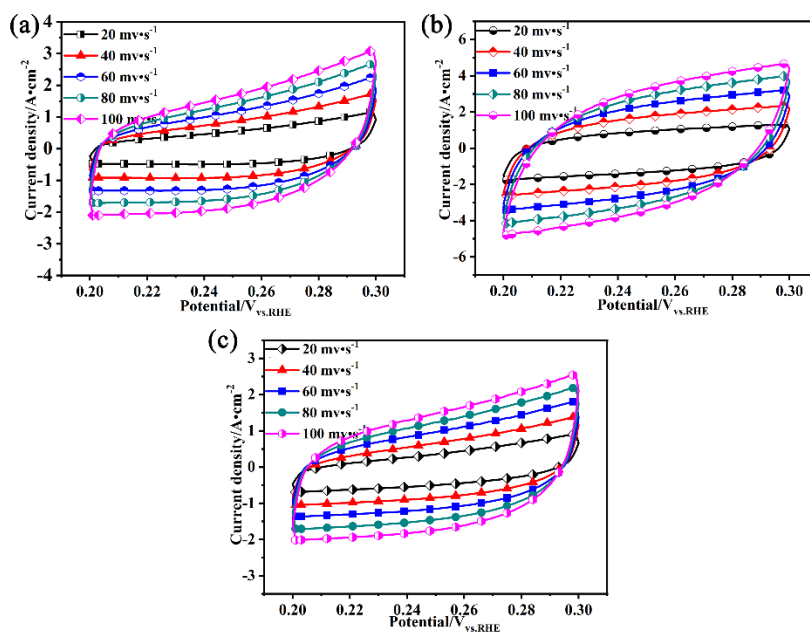


Figure S3. CV curves of (a) NiCo_2S_4 , (b) $\text{NiCo}_2\text{S}_4/\text{RuS}_2$ and (c) $\text{NiCo}_2\text{S}_4/\text{Ru}$ (60%) electrode materials at different sweep speeds

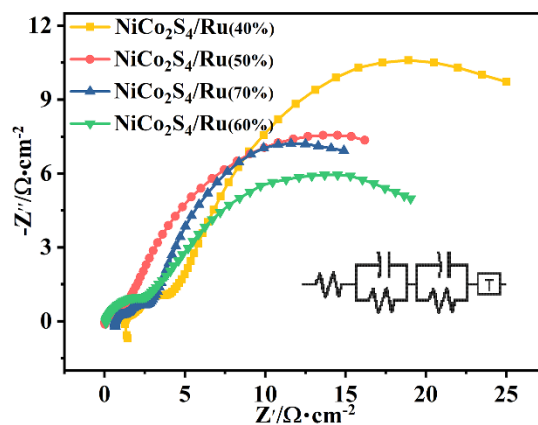


Figure S4. EIS of NiCo₂S₄/Ru (40%, 50%, 70%) electrode at equilibrium potential

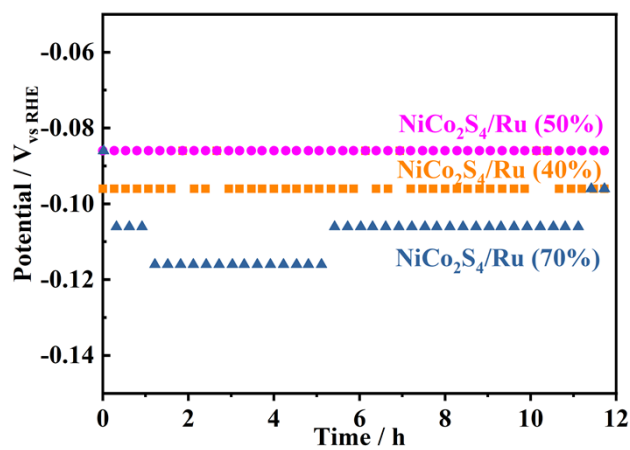


Figure S5. Chronopotentiometry of heterogeneous bimetallic sulfide composite electrode materials

Electrode	Ni		Co		S		O		Ru	
	wt%	at%	wt%	at%	wt%	at%	wt%	at%	wt%	at%
NiCo ₂ S ₄ /Ru(40%)	12.5	10.3	19.7	19.4	25.7	40.2	3.1	11.2	39.0	18.9
NiCo ₂ S ₄ /Ru(50%)	10.8	9.6	16.8	17.8	18.9	31.4	3.2	14.4	50.2	26.8
NiCo ₂ S ₄ /Ru(60%)	7.2	6.5	11.4	10.9	14.1	25.8	3.5	14.9	63.8	41.9
NiCo ₂ S ₄ /Ru(70%)	6.5	7.8	8.4	10.1	9.1	19.9	3.2	11.1	72.8	50.8

Table S1. EDS analysis results of NiCo₂S₄/Ru composite electrode materials with different Ru content

Table S2. Catalytic kinetic parameters of electrode materials

Electrode	a(mV)	b(mV dec ⁻¹)	j ⁰ (mA cm ⁻²)
NiCo ₂ S ₄	363	110	0.50
NiCo ₂ S ₄ /RuS ₂	306	98	0.76
NiCo ₂ S ₄ /Ru (40%)	226	83	1.90
NiCo ₂ S ₄ /Ru (50%)	220	87	2.96
NiCo ₂ S ₄ /Ru (60%)	174	76	5.14
NiCo ₂ S ₄ /Ru (70%)	203	88	5.01

Table S3. Fitting data of components of equivalent circuit diagrams for different electrode materials

Electrode	R _s /Ω·cm ⁻²	CPE1/F	R _{ct} /Ω·cm ⁻²	CPE2/F	R _{sf} /Ω·cm ⁻²	Tanh & Coth Y ₀ /S·sec ^{0.5}
NiCo ₂ S ₄	1.257	2.55×10 ⁻⁴	6.621	—	—	—
NiCo ₂ S ₄ /RuS ₂	1.125	1.179×10 ⁻¹	3.229	2.459×10 ⁻³	0.356	0.325
NiCo ₂ S ₄ /Ru(40%)	1.163	2.933×10 ⁻³	1.651	—	—	0.146
NiCo ₂ S ₄ /Ru(50%)	1.162	1.07×10 ⁻⁴	1.235	—	—	0.183
NiCo ₂ S ₄ /Ru(60%)	1.053	9.73×10 ⁻⁴	0.487	—	—	0.121
NiCo ₂ S ₄ /Ru(70%)	1.181	7.51×10 ⁻⁴	0.891	—	—	0.220