Synergetic optimization promoted full water splitting performance of CoSe@NiSe₂@MoS₂ heterostructured composites

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Experimental section

Reagents and chemicals

Cobaltous chloride (CoCl₂), nickel chloride (NiCl₂), (NH₄)₂MoS₄, Se powder (>99%), potassium hydroxide (KOH, 85%), Nafion solution (5 wt%) and carbon fiber paper (CFP) were obtained from Sinopharm Chemical Reagent Co., Ltd. (China, Shanghai). All reagents are used as received without any purification. The detailed characterization information and electrochemical measurements are presented in supporting information.

Preparation of CoSe@NiSe2@MoS2-xy nanostructures

CoSe@NiSe₂@MoS₂-*xy* nanostructures were prepared by a simple selenide process. To prepared CoSe@NiSe₂@MoS₂-12, CoCl₂ (0.8 mmol), NiCl₂ (0.8 mmol), (NH₄)₂MoS₄ (0.4 mmol) and Se powder (8 mmol) were heated at 300 °C for 2 h in a quartz boat under a flow of nitrogen atmosphere. After the pyrolyzed process, the resultant product was washed with absolute ethanol and deionized water for several times, and then was dried under vacuum at room temperature for 10 h to afford the desired CoSe@NiSe₂@MoS₂-12 sample. To prepare control samples with different Mo:Co molar ratios, we fixed the amount of (NH₄)₂MoS₄ at 0.4 mmol while changing the CoCl₂ amount, and the other preparation processes were unchanged. The obtained samples were named as CoSe@NiSe₂@MoS₂-11 and CoSe@NiSe₂@MoS₂-13 with the Mo:Co molar ratios of 1:1 and 1:3, respectively.

Physicochemical characterization

The crystal structures of the as-prepared samples were recorded by the XD-3 diffractometer with Cu Ka radiation. The chemical composition and bonding states were determined by the X-ray photoelectron spectroscopy (XPS, a RBD upgraded PHI-5000C ESCA). The morphology and nanostructure of the samples were investigated by the scanning electron microscopy (SEM, a Model S4800, Hitachi) equipped with energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM, a JEM-2100 HR, JEOL system).

Electrochemical measurements

The electrochemical measurements including hydrogen evolution (HER) and oxygen evolution reaction (OER) were carried out on a CHI 614E electrochemical workstation (CH Instrument, China) with 1.0 M KOH solution as the electrolyte. The scan rate for all electrochemical measurements is 2 mV/s. The mercury/mercury oxide electrode (MOE) was employed as the reference electrode, the Pt gauze $(1 \times 1 \text{ cm}^2)$ was used as the counter electrode, and the samples covered carbon fiber paper (CFP) was conducted as theworking electrode. The preparation of working electrode is described as follows. The as-prepared samples (3 mg) was added into the mixed solution of Nafion solution (5 wt%, 40 μ L), CH₃CH₂OH (0.5 mL) and deinonized water (0.5 mL). And then the obtained suspension was sonicated for 0.5 h to afford the homogeneous ink. Lastly, the obtained homogeneous ink (20 µL) was dropped onto the CFP, and then dried at room temperature and retained for use. The overall water splitting was carried out with a two-electrode system with the as-prepared working electrode as both anode and cathode. The electrochemical impedance spectroscopy (EIS) measurements for HER and OER were performed over the frequencies ranging from 100KHzto 0.01Hz in 1.0 M KOH. The time-dependent current density, i.e. the long-term stability of the samples, was recorded with a chronoamperometry method by using the same electrolyzer. The cyclic voltammograms in the non-Faradaic potential window of 0.1-0.2 V vs. RHE was recorded with different scan rates (20, 40, 60, 80, and 100 mV/s) to determine the double-layer capacitance, and thus the electrochemical surface areas

(ECSA) was obtained. All potentials in this work was calibrated with the reversible hydrogen electrode potential (RHE) according to the Nernst equations. All measurements were conducted at the room temperature.

The volume of H₂ and O₂ during a potentiostatic electrolysis experiment was monitored by the water displacement method. If the initial height of water in the gas gathering tube before the gas gathering experiment is h₀, and after the potentiostatic electrolysis experiment the generated gas is gathered into the tube and the final height of water in the gas gathering tube become h_1 , then the volume of generated gas (V) should be $s(h_0-h_1)$, where s is the inner cross-sectional area of the gas gathering tube. At the initial status, the pressure inside the gas gathering tube (P_0) is P - ρgh_0 , where P is the atmospheric pressure, ρ is the density of water, and g is the acceleration due to gravity. The output voltage of the differential pressure transducer would be $U_0 = k(P - P)$ P_0 = kpgh₀, where k is the sensitivity of the differential pressure transducer (1 mV/Pa for a Freescale MPXV7002DP). When the height of water in the gas gathering tube decreases to h_1 , the pressure inside the gas gathering tube becomes P_1 , and $P_1 = P$ - ρgh_1 . Then, the output of the differential pressure transducer is $U_1 = k(P - P_1) = k\rho gh_1$. Accordingly, the volume of generated gas can be computed by $V = s(h_0 - h_1) = s(U_0/k\rho g$ - $U_1/k\rho g$) = s(U₀ - U₁)/k ρg = C(U₀ - U₁), where C is a coefficient that can be calibrated by injecting a known volume of gas into the gas gathering tube and recording the variation of output voltage of the differential pressure transducer.

Kinetic analysis based on the dual-pathway kinetic model

We performed kinetic analyses to evaluate the standard activation free energies for the three elementary reaction steps of HER following the procedure of Wang et al¹⁻² and Hu et. al.³ There are three elementary reaction steps for the alkaline HER on the catalysts' surfaces, including Volmer step (H₂O + e⁻ \rightarrow H_{ad} + OH⁻), Heyrovsky step (H₂O + H_{ad} + e⁻ \rightarrow H₂ + OH⁻) and Tafel step (2H_{ad} \rightarrow H₂). Under steady-state conditions, d $\Theta/dt = v_T + v_H - v_V = 0$ ($v_T + v_H = v_V$), where v is the reaction rate, and Θ is the surface coverage of the active reaction intermediate. The current is directly proportional to the sum of the reaction rates for the two single electron-transfer reactions ($j_i = 2Fv_i$). Thus, the total kinetic currents (j_k) can be expressed as below:

$$j_{k} = F(v_{V} + v_{H}) = (j_{V} + j_{H})/2$$

=2F(v_{T} + v_{H}) = j_{T} + j_{H}
=2F(v_{V} - v_{T}) = j_{V} - j_{T} (S1)

The kinetic currents for each individual step are:

$$j_{\rm T} = j * e^{-\Delta G + T/kT} [(1 - \theta)^2 - e^{2\Delta G \frac{\theta}{ad}/kT} \theta^2]$$
(S2)

$$j_{\rm H} = j * e^{-\Delta G + \theta / kT} [e^{0.5\eta/kT} (1 - \theta) - e^{(\Delta G_{ad}^0 - 0.5\eta)/kT} \theta]$$
(S3)

$$j_{V} = j * e^{-\Delta G * \frac{\theta}{-V}/kT} \left[e^{(\Delta G_{ad}^{0} + 0.5\eta)/kT} \Theta - e^{-0.5\eta/kT} (1 - \theta) \right]$$
(S4)

where ΔG represents the free energies of Volmer step (ΔG_{-V}^{*0}), Heyrovsky step (ΔG_{H}^{*0}), Tafel step (ΔG_{T}^{*0}) and H*adsorption (ΔG_{ad}^{0}).

The calculation of the adsorption isotherm (Θ) is given as below:

$$\Theta = \frac{-B - \sqrt{B^2 - 4AC}}{2A} \tag{S5}$$

$$A=2T_{p}-2T_{m} \qquad (S6)$$

$$B=-4T_{p}-H_{p}-H_{m}-V_{p}-V_{m}$$
 (S7)

$$C=2T_{p}+H_{p}+V_{m} \qquad (S8)$$
$$T_{p}=e^{-\bigtriangleup G \stackrel{* 0}{+}T/kT} \qquad (S9)$$

$$T_{m} = e^{-(\triangle G + T + 2 \triangle G_{ad}^{0}/kT)}$$
(S10)

$$H_{p} = e^{-(\bigtriangleup G \stackrel{* 0}{+} H - 0.5\eta)/kT}$$
(S11)

$$H_{\rm m} = e^{-(\triangle G_{+H}^{*0} - \triangle G_{ad}^{0} + 0.5\eta)/kT}$$
(S12)

$$V_{p} = e^{-(\bigtriangleup G_{-V}^{*0} - \bigtriangleup G_{ad}^{0} - 0.5\eta)/kT}$$
(S13)

$$V_{\rm m} = e^{-(\triangle G_{-V}^{*0} + 0.5\eta)/kT}$$
(S14)

The kT is 25.51 meV at 300 K. The kinetic current, $j_k(\eta) = f(\bigtriangleup G_{-V}^{*0}, \bigtriangleup G_{+H}^{*0}, \bigtriangleup G_{+T}^{*0}, \bigtriangleup G_{ad}^{*0}, j, \Theta)$ can be determined by equations of S1-S4, in which the adsorption isotherm, $\Theta(\eta) = f(\bigtriangleup G_{-V}^{*0}, \bigtriangleup G_{+H}^{*0}, \bigtriangleup G_{+T}^{*0}, \bigtriangleup G_{ad}^{0})$ can be obtained from equations of S5-S14.



Figure S1. XRD patterns of CoSe@NiSe₂@MoS₂-11, CoSe@NiSe₂@MoS₂-12 and CoSe@NiSe₂@MoS₂-13.



Figure S2. SEM images of (a) CoSe@NiSe₂@MoS₂-11, and (b) CoSe@NiSe₂@MoS₂-13; EDS spectra of CoSe@NiSe₂@MoS₂-11, CoSe@NiSe₂@MoS₂-12 and CoSe@NiSe₂@MoS₂-13; Corresponding Mo, S, Co, Ni and Se elemental mapping images of (d-h) CoSe@NiSe₂@MoS₂-11 and (i-m) CoSe@NiSe₂@MoS₂-13.



Figure S3. XPS spectra of $CoSe@NiSe_2@MoS_2-12$: (a) Mo 3d, (b) S 2p, (c) Co 2p, (d) Ni 2p, (e) Se 3d and (f) O 1s.



Figure S4. (a) HER LSV curves and (b) OER LSV data of the as-prepared samples. All potentials were corrected with the *iR* drop.



Figure S5. Free energy diagram of the as-prepared samples in 1.0 M KOH.



Figure S6. The amount of H₂ and O₂ experimentally measured and theoretically calculated as a function of time for CoSe@NiSe₂@MoS₂-12.



Figure S7. (a) Electrolytic cell activity for overall water splitting and (b) chronopotentiometric curve of CoSe@NiSe₂@MoS₂-12, (c) Plots of current density as a function of scan rates and (d) Nyquist plots of the as-prepared samples. All potentials were corrected with the *iR* drop.



Figure S8. CV curves of (a) CoSe@NiSe₂@MoS₂-11, (c) CoSe@NiSe₂@MoS₂-12 and (c) CoSe@NiSe₂@MoS₂-13 at different scan rates of 20-100 mV/s.



Figure S9. Exchange current density (j_0) of the as-prepared samples for (a) HER and (b) OER.



Figure S10. Mott-Schottky plots of the as-prepared samples.



Figure S11. (a) XRD patterns of CoSe@NiSe₂@MoS₂-12 after HER and OER, and (b) Raman spectrum of CoSe@NiSe₂@MoS₂-12 after OER.



Figure S12. High-resolution XPS spectra of (a) Mo 3d, (b) S 2p, (c) Co 2p, (d) Ni 2p, (e) Se 3d and (f) O 1s for CoSe@NiSe₂@MoS₂-12.

Electrocatalysts	Overpotential (mV@10 mA cm ⁻²)	Ref.
MoS ₂ /Co ₉ S ₈ /Ni ₃ S ₂ /Ni	113 (1.0 M KOH)	4
CoSe/MoSe ₂	115 (1.0 M KOH)	5
CoS ₂ /CoSe@C	164 (1.0 M KOH)	6
Co _{0.8} Mo _{0.2} Se	87.6 (1.0 M KOH)	7
Porous C/Ni ₂ SeS	121 (0.5 M H ₂ SO ₄)	8
Ni ₂ P/Ti ₃ C ₂ T _x /NF	135 (1.0 M KOH)	9
Ni ₂ P@NiFeAlO _x	105 (1.0 M KOH)	10
Co _{0.9} Ni _{0.1} Se	186 (1.0 M KOH)	11
CoSe@NCNT/NCN	197 (0.5 M H ₂ SO ₄)	12
CoSe@NiFe-LDH/NF	98 (1.0 M KOH)	13
NiSe ₂ -Ni ₂ P	102 (1.0 M KOH)	14
NiSe ₂ /Ni-NSC	116 (1.0 M KOH)	15
Cu ₃ Se ₂ @CoSe ₂ -NiSe ₂ /PNCF	42 (1.0 M KOH)	16
CFP/NiSe ₂ /MoS ₂	143 (1.0 M KOH)	17
NiSe ₂ /Ni ₂ P@FeP	113 (1.0 M KOH)	18
NiSe ₂ -Ni ₂ P/NF	102 (1.0 M KOH)	19
Fe _{0.09} Co _{0.13} -NiSe ₂	92 (1.0 M KOH)	20
NiSe ₂ @N-doped carbon	162 (1.0 M KOH)	21
A-NiSe ₂ P	111 (1.0 M KOH)	22
NiSe ₂ @NG	201 (0.5 M H ₂ SO ₄)	23
Ni ₃ S ₂ /MoS ₂	78 (1.0 M KOH)	24
MoO ₂ @MoS ₂ @Co ₉ S ₈	160 (1.0 M KOH)	25
Co ₉ S ₈ @MoS ₂	239 (1.0 M KOH)	26
MoS ₂ /Gr/CC	91 (0.5 M H ₂ SO ₄)	27
Co-Ni-P/MoS ₂	116 (1.0 M KOH)	28
Co,Nb-MoS ₂ /TiO ₂	58.8 (1.0 M KOH)	29
CoSAs-MoS ₂ /TiN NRs	131.9 (1.0 M KOH)	30
Ni(OH) ₂ /MoS ₂	139 (1.0 M KOH)	31
Mo _{0.29} Co _{0.71} P ₂ /MWCNTs	85 (1.0 M KOH)	32
FeO _x -MoP@MWCNT	78 (1.0 M KOH)	33
PdSe ₂	138 (1.0 M KOH)	34
CuSN@MoS ₂ -Pt	102.6(1.0 M KOH)	35
CoSe@NiSe2@MoS2-12	81	This work

 Table S1. Comparison of HER performance of CoSe@NiSe2@MoS2-12 with some other reported electrocatalysts.

HEK.						
Sample	ΔG^{*0}_{-V}	$\Delta G \stackrel{* 0}{+ H}$	$\Delta G \stackrel{* 0}{+ T}$	$\Delta G_{ad}^{\ 0}$	R^2	$\Delta G \stackrel{* 0}{+ H} - \Delta G \stackrel{0}{ad}$
	(meV)	(meV)	(meV)	(meV)	(%)	(meV)
MoS ₂ @CoSe	112	286	965	98	99.7	188
MoS ₂ @NiSe ₂	123	299	996	106	99.7	193
CoSe@NiSe ₂	138	331	921	115	99.6	216
CoSe@NiSe2@MoS2-12	104	253	1064	86	99.8	149

 Table S2. The fitting results of free energies corresponding to different steps during

 LIED

 ΔG_{-V}^{*0} : the standard activation free energy for Volmer step.

 $\Delta G \stackrel{* 0}{_{+ H}}$: the standard activation free energy for Heyrovsky step.

 $\Delta G \stackrel{* 0}{+ T}$: the standard activation free energy for Tafel step.

 ΔG_{ad}^{0} : the standard free energy of adsorption for the reaction intermediate.

Electrocatalysts	Overpotential (mV@10 mA cm ⁻²)	Ref.
MoS ₂ /Co ₉ S ₈ /Ni ₃ S ₂ /Ni	166	4
Ni ₂ P@NiFeAlO _x	210	10
CoSe@NCNT/NCN	301	12
CoSe@NiFe-LDH/NF	201	13
Cu ₃ Se ₂ @CoSe ₂ -NiSe ₂ /PNCF	240	16
NiSe ₂ /Ni ₂ P@FeP	202	18
Fe _{0.09} Co _{0.13} -NiSe ₂	251	20
Ni ₃ S ₂ /MoS ₂	260	24
MoO ₂ @MoS ₂ @Co ₉ S ₈	310	25
Co ₉ S ₈ @MoS ₂	230	26
Co-Ni-P/MoS ₂	235	28
Co,Nb-MoS ₂ /TiO ₂	260	29
CoSAs-MoS ₂ /TiN NRs	340.6	30
Ni(OH) ₂ /MoS ₂	360	31
Mo _{0.29} Co _{0.71} P ₂ /MWCNTs	220	32
FeO _x -MoP@MWCNT	229	33
O-MoS ₂ @Pt	244	36
Co-Fe-Cr(oxy)hydroxides	232	37
Fe ₃ O ₄ -decorated Co ₉ S ₈	340	38
Co(OH) ₂ /NiMo CA@CC	267	39
RuO ₂ -decorated FeOOH	230	40
2D CoNC@Co2N	217	41
Co ₄ N-CeO ₂	239	42
V-CoP@ a-CeO ₂	225	43
CoSe@NiSe2@MoS2-12	170	This work

 Table S3. Comparison of OER performance of CoSe@NiSe2@MoS2-12 with other reported electrocatalystsin alkaline electrolyte.

Electrocatalysts	Cell voltage (V@10 mA cm ⁻ ²)	Ref.
MoS ₂ /Co ₉ S ₈ /Ni ₃ S ₂ /Ni	1.54	4
Ni ₂ P@NiFeAlO _x	1.52	10
CoSe@NiFe-LDH/NF	1.53	13
NiSe ₂ -Ni ₂ P	1.50	14
Cu ₃ Se ₂ @CoSe ₂ -NiSe ₂ /PNCF	1.52	16
NiSe ₂ /Ni ₂ P@FeP	1.55	18
NiSe ₂ -Ni ₂ P/NF	1.50	19
Fe _{0.09} Co _{0.13} -NiSe ₂	1.52	20
A-NiSe ₂ P	1.62	22
Ni ₃ S ₂ /MoS ₂	1.53	24
MoO ₂ @MoS ₂ @Co ₉ S ₈	1.62	25
Co ₉ S ₈ @MoS ₂	1.49	26
Co-Ni-P/MoS ₂	1.53	28
Co,Nb-MoS ₂ /TiO ₂	1.57	29
CoSAs-MoS ₂ /TiN NRs	1.65	30
FeO _x -MoP@MWCNT	1.51	33
Co(OH) ₂ /NiMo CA@CC	1.52	39
RuO ₂ -decorated FeOOH	1.46	40
2D CoNC@Co2N	1.52	41
Co ₄ N-CeO ₂	1.507	42
V-CoP@ a-CeO ₂	1.56	43
CoSe@NiSe2@MoS2-12	1.48	This work

Table S4. Comparison of the overall water splitting performance of $CoSe@NiSe_2@MoS_2-12$ with other reported electrocatalysts in alkaline electrolyte.Cell voltage (V@10 mA cm⁻)

Table S5. The fitting results of EIS spectra for HER in basic solution.

Samples	$R_s(\Omega$	n	$R_1(\Omega$	n _{ct}	$R_{ct}(\Omega$
)	п1))
CoSe@NiSe ₂ @MoS ₂	0.25	0.7	2.65	0.7	10 51
-13	0.25	1	2.65	2	18.51
CoSe@NiSe2@MoS2	0.28	0.6	3.16	0.6	20.53

-11		9		0	
CoSe@NiSe ₂ @MoS ₂	0.21	0.5	2 27	0.7	15 ()
-12	0.21	9	2.37	2	15.02

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