Supporting Information for

Two-dimensional Heterogeneous Structured Ni_3Se_2@MoO_3 Catalyst for Seawater Electrolysis

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1. Experimental

1.1 Materials

All chemicals were analytical grade, including, and potassium hydroxide (KOH, 85%), $NiCl_2 \cdot 6H_2O$ (AR, 99%), SeO_2 (AR, 99%), $C_6H_8O_7 \cdot H_2O$ (AR, 98.5%), and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (AR, 98%) were used in the experiments. The commercial porous copper foam (CF) (Type: PPI, 1 cm × 2 cm, 1 mm thickness, and purity>99.99%) All test solution was prepared with distilled water purified.

The CF was ultrasonically cleaned in 3.0 mol hydrochloric (HCl) for 10 min to remove the copper oxides layer on the surface, ultrasonically cleaned in absolute ethanol (C_2H_6O) for 10 min to remove the oil stain layer, and deionized (DI) water rinsing and finally vacuum drying.

1.2 Preparation of Ni_3Se_2@MoO_3/CF Catalyst

Ni_3Se_2@MoO_3/CF, Ni_3Se_2/CF, and MoO_3/CF were synthesized by a fast one-step electrodeposition process, which was a standard three-electrode system in the CHI660D electrochemical workstation. The solvent was synthesized by ethaline ethylene glycol (EG), choline chloride (ChCl, 99 %) (EG and ChCl at a molar ratio of 2:1), 300 mmol L^{-1} $NiCl_2 \cdot 6H_2O$, 200 mmol L^{-1} $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 200 mmol L^{-1} $C_6H_8O_7 \cdot H_2O$, and 200 mmol L^{-1} SeO_2, followed by stirring at 343 K for eight hours until a balanced mixture was obtained.

CF was used as the working electrode, a silver wire was the reference electrode, and a platinum column was the counter electrode. At 343 K, the voltage at constant potential was −0.85 V. The deposition time was approximately 1000 s, and the charge amount was 10 C cm^{-2}.

1.3 Preparation of Pt/C and RuO_2 catalyst

Synthesis of Pt/C electrode: Prepare the catalyst solution and mix 5 mg of Pt/C catalyst uniformly into the ethanol (0.990 mL) and Nafion solution (0.010 mL) mixture, the mixed solution was sonicated for two hours to obtain a homogeneous catalyst ink. Then 100 μL of the catalyst ink was loaded onto a 2 cm×1 cm CF.

Synthesis of RuO_2 electrode: Prepare the catalyst solution and mix 5 mg of RuO_2 catalyst uniformly into the ethanol (0.990 mL) and Nafion solution (0.010 mL) mixture, the mixed solution was sonicated for two hours to obtain a homogeneous catalyst ink. Then 100 μL of the catalyst ink was loaded onto a 2 cm×1 cm CF.

1.4 Structural and Microstructure Characterization

The phase structures of $Ni_3Se_2@MoO_3$ was probed by powder X-ray diffraction (XRD) patterns recorded on a Rigaku D/Max-2200 diffractometer with Cu Ka radiation (λ = 1.5418 Å). They detected X-ray Photoelectron Spectroscopy (XPS) analysis on a PHI5000 Versaprobe-II. Scanning Electron Microscope (SEM) also measured the microstructures and chemical compositions of $Ni_3Se_2@MoO_3$ deposits recorded on an FEI Nova, Nano SEM 450 equipped with an Energy Dispersive Spectrometer (EDS) system. Transmission Electron Microscope (TEM) measurements were carried out using the JEM-2100 instrument. Gas products from the decoupled water electrolytic cell during OER and HER were respectively analyzed using a GC-2014 (Shimadzu). The variation of ClO^- concentration during exposure was monitored at 430 nm wavelength by UV–Vis spectrophotometer (MAPADA UV-1100). Raman instrument type: WITec alpha 300R, Germany; laser: 532 nm. Raman instrument type: WITec alpha 300R, Germany; laser: 532 nm.

1.5 Electrochemical measurements

The seawater was collected from the local coast in Sanya city, pH ≈ 8.7 (Fig. S1). The prepared catalytic materials were used as working electrodes in an electrochemical workstation recorded on Autolab three-electrode system). The counter electrode was a graphite rod electrode, while Hg/HgO electrode served as a reference electrode. The reference electrode is corrected as in Fig. S2. Potential correction CV curve of Hg/HgO electrode under 1.0 M KOH, E (RHE) = E (Hg/HgO) + 0.896 V. Potential correction CV curve of Hg/HgO electrode under 1.0 M KOH + 0.5 M NaCl, E (RHE) = E (Hg/HgO) + 0.840 V. Potential correction CV curve of Hg/HgO electrode under 1.0 M KOH + seawater, E (RHE) = E (Hg/HgO) + 0.852 V.

To evaluate the activity of each electrocatalyst, linear sweep voltammetry (LSV) at a scan rate of 5 mV s^{-1}, and the linear portion of the Tafel polarization curve was fitted according to the following Tafel Eq. (2):[1]

$$\eta = a + b\log|j| \quad (1)$$

where η is the overpotential, b is the Tafel slope, and *j* indicates the current density.

Through CV, electric double layer curves were obtained from open circuit potential (OCP) ± 0.05 V. The corresponding current density was estimated using Eq. (3):[2]

$$j = 1/2\ (j_a + j_c) \quad (2)$$

The *j* parameter and the scan rate linear slope were used to calculate electrochemical double-layer capacitance, C_{dl}.

The electrochemical impedance spectra (EIS) were recorded at an overpotential of 10 mA cm^{-2} in the frequency range from 10^{-1} to 10^{5} Hz.[3] For testing stability with ISTEP Multi-Current Steps, the current densities were successively raised from 20 to 100 mA cm^{-2} with 20 mA cm^{-2} per 1 h for OER and HER. Long-term stability of catalyst was tested through the chronoamperometric curve.

The Faradaic efficiency was calculated by comparing the experimentally produced gas volume with the theoretically calculated one:[4]

$$FE\% = V_{Experimental} / V_{Theoretical} \quad (3)$$

The experiment volume of H_2 was measured by drainage. The theoretical volume can be calculated using the formula:

$$V_{Theoretical} = I \cdot t \cdot V_m / n \cdot F \quad (4)$$

Where I is the electrolysis current, t is the electrolysis time, V_m is molar volume of H_2 of gas (24.5 L mol^{-1}, 298 K, 101 kPa), n is the number of electrons required for one molecule of H_2 and F is the Faraday's constant (96485 $Cmol^{-1}$).

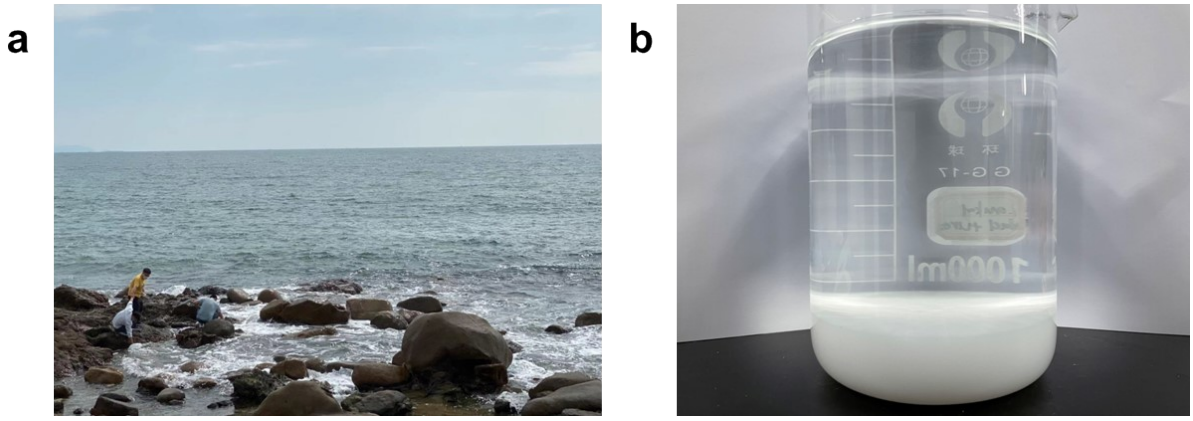

Fig. S1. (a) The photo is taken in Yazhou bay of Sanya, China. (b) Photograph of the alkaline seawater electrolyte.

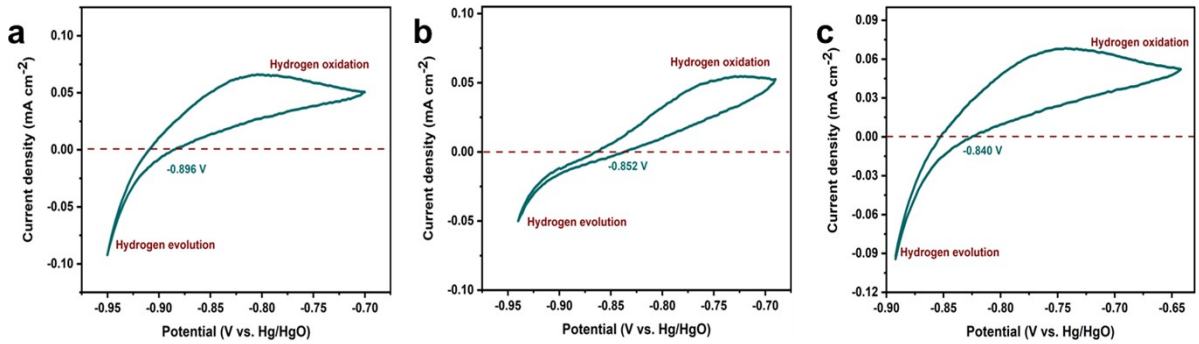

Fig. S2. (a-c) Potential correction CV curve of Hg/HgO electrode under 1.0 M KOH, 1.0 M KOH + seawater, and 1.0 M KOH + 0.5 M NaCl.

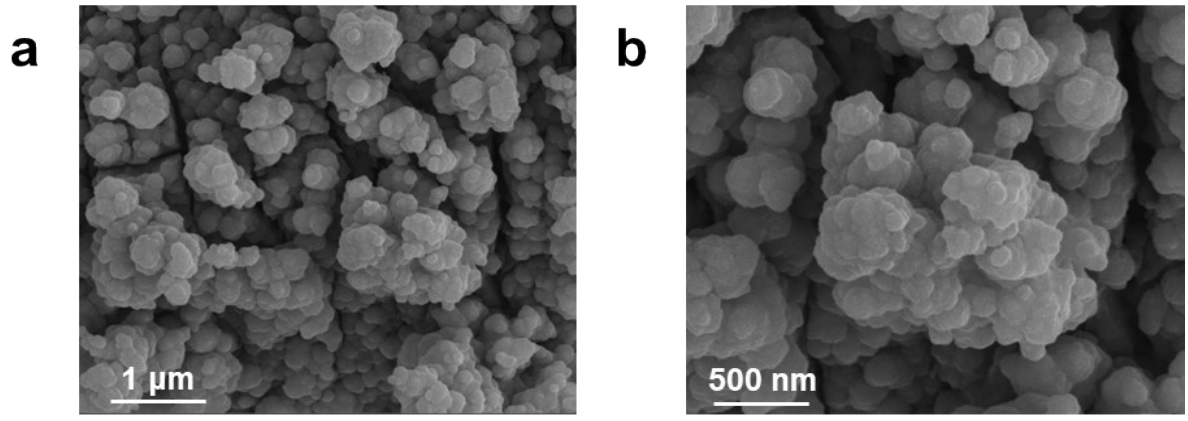

Fig. S3. (a, b) The SEM image of Ni_3Se_2@MoO_3/CF.

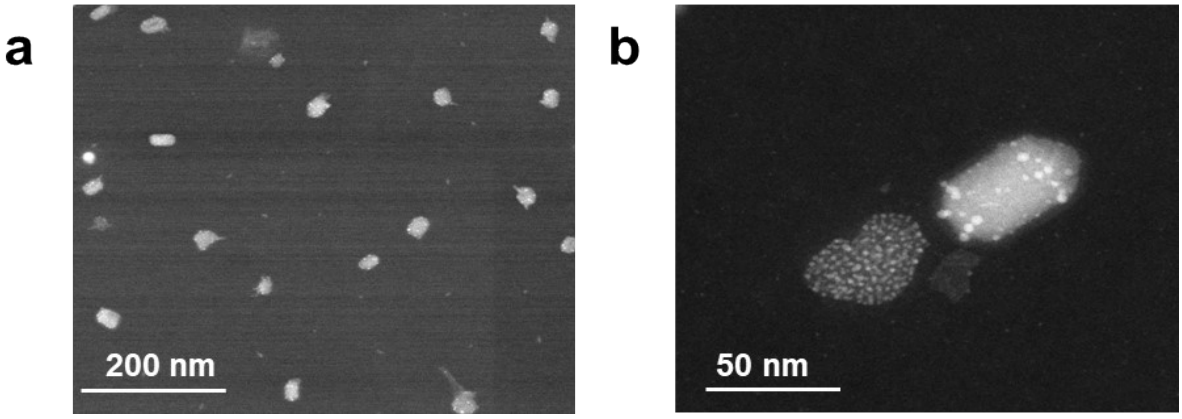

Fig. S4. (a, b) The TEM image of Ni_3Se_2@MoO_3.

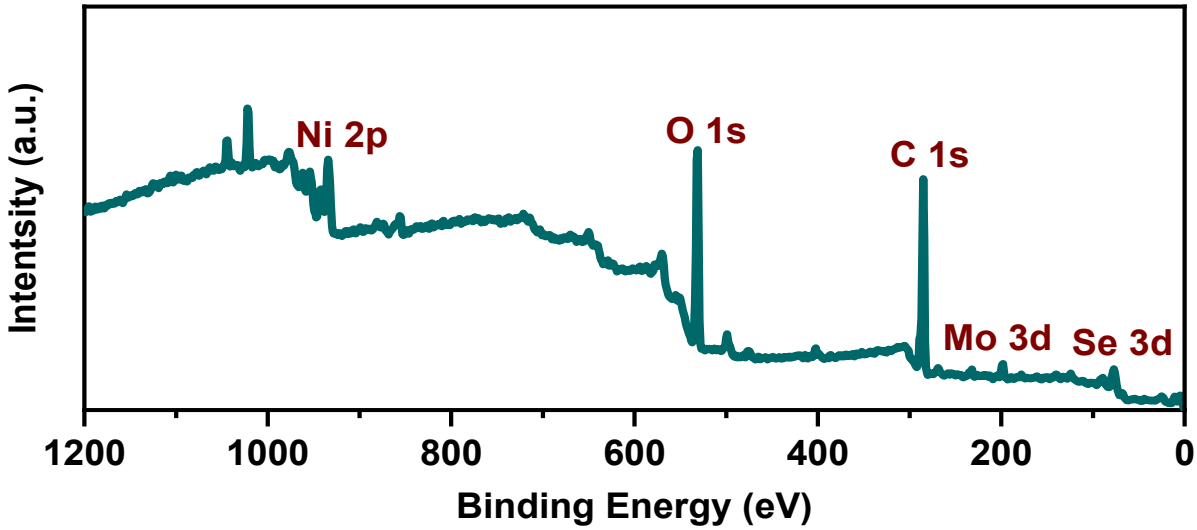

Fig. S5. XPS survey spectra of initial Ni_3Se_2@MoO_3/CF.

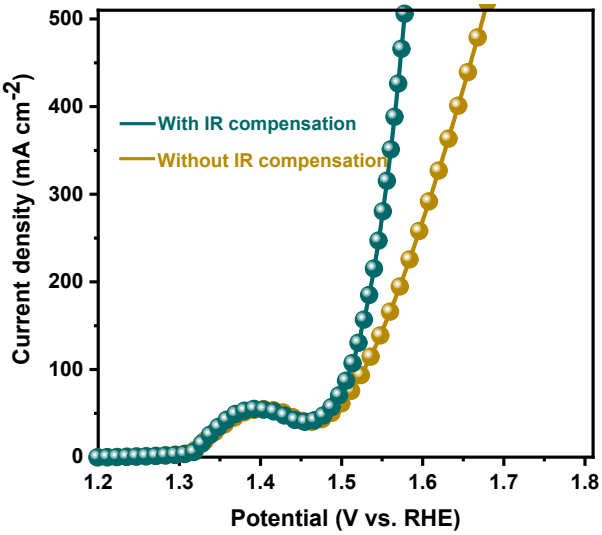

Fig. S6. Activity comparison between with iR and without iR compensation. Electrolyte: 1.0 M KOH + Seawater (resistance: ~ 0.5 Ω); temperature: 25 ℃. The catalytic activity of different catalysts in consistent-nation the LSV with 85% IR compensation.

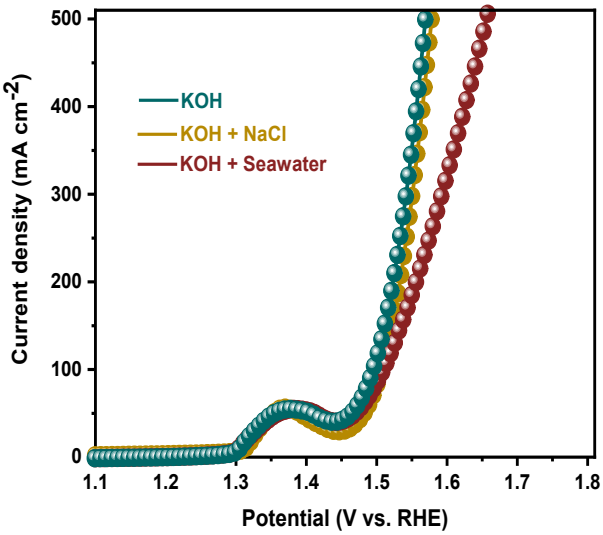

Fig. S7. Comparison of the activity of Ni_3Se_2@MoO_3/CF in different electrolytes.

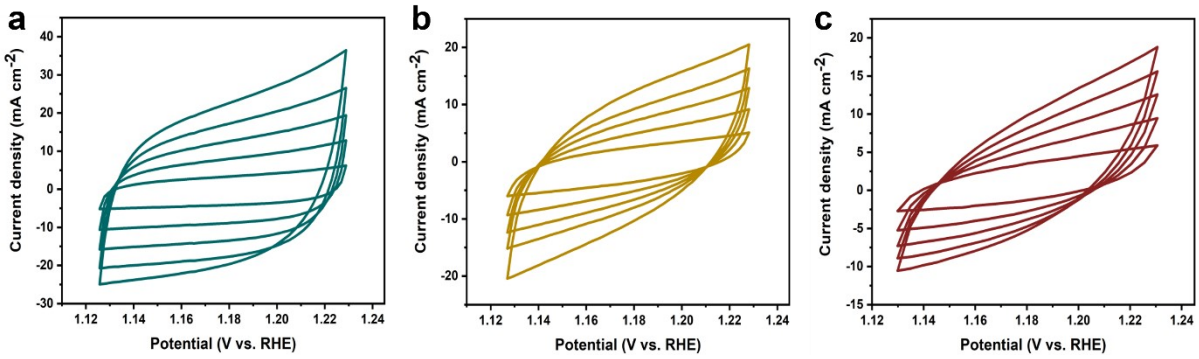

Fig. S8. (a-c) CVs recorded in a non-faraday region of different catalysts for OER.

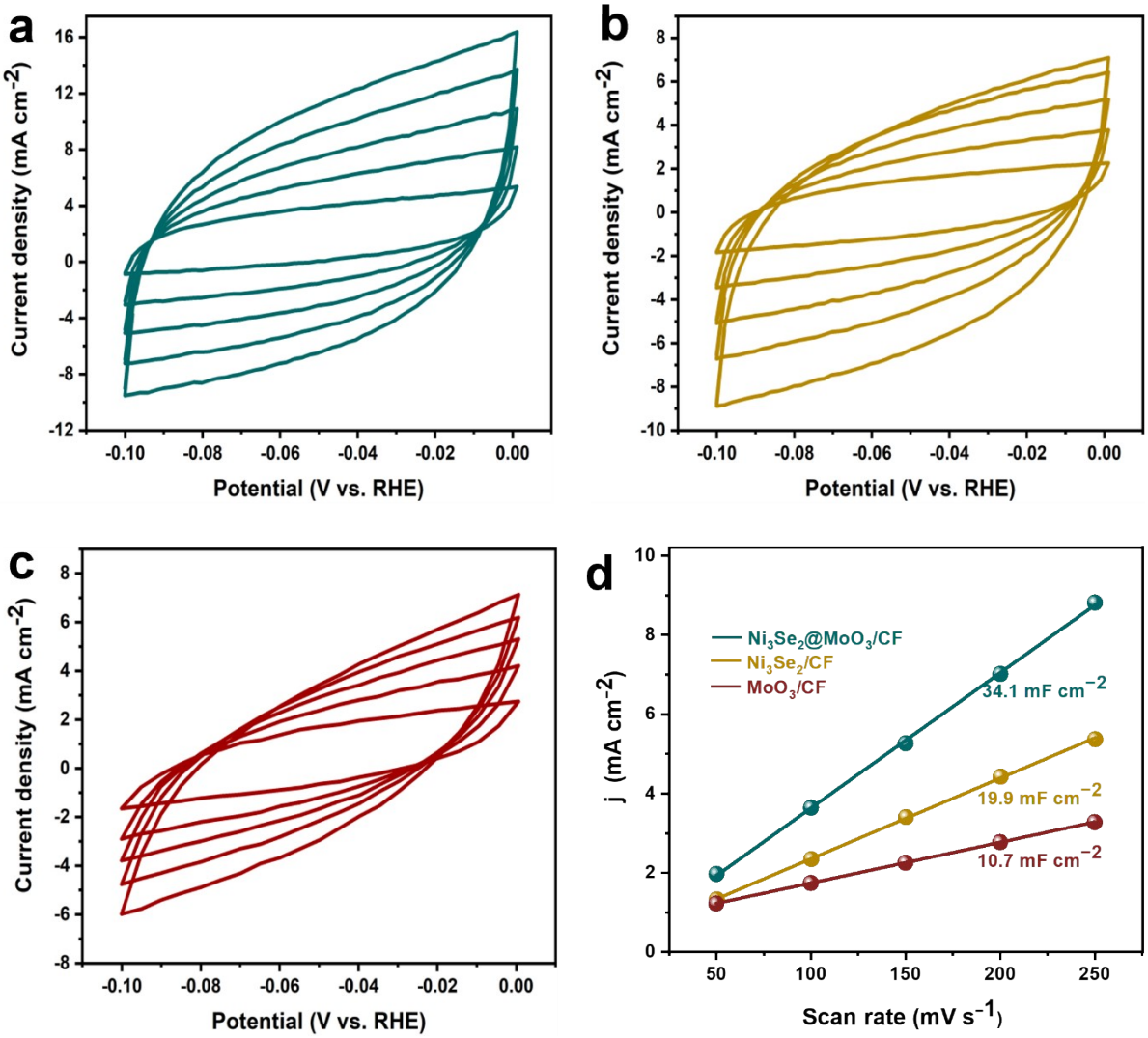

Fig. S9. (a-c) CVs recorded in a non-faraday region of different catalysts for HER. (d) The estimation of C_{dl}.

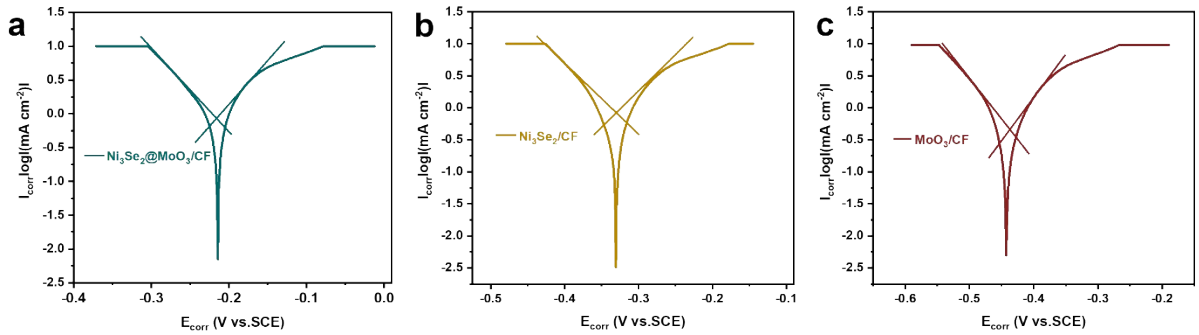

Fig. S10. (a-c) Corrosion polarization curves of the Ni_3Se_2@MoO_3/CF, Ni_3Se_2/CF, and MoO_3/CF catalysts in 1.0 M KOH + seawater.

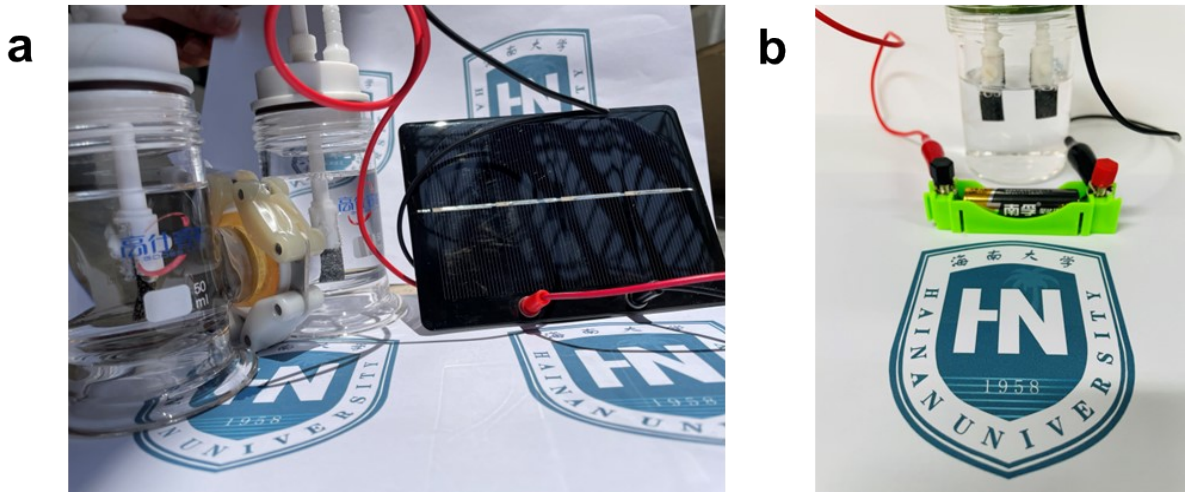

Fig. S11. (a) Photograph of solar cell driven seawater electrolysis. (b) Photograph showing the O_2 and H_2 bubbles produced from overall seawater splitting driven by a 1.5 V AA battery. Electrolyte: 1.0 M KOH + Seawater; temperature: 25 ℃.

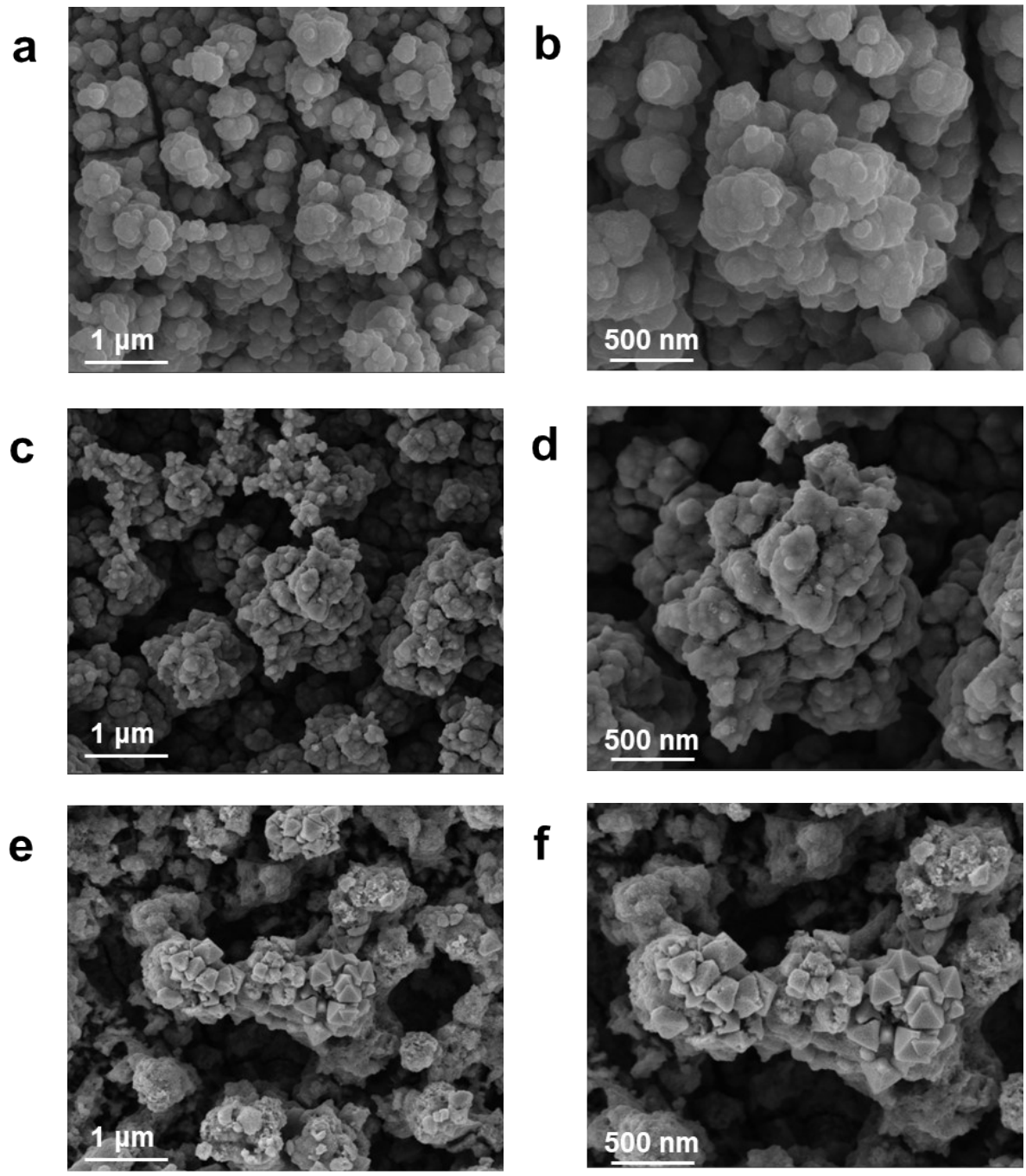

Fig. S12. The SEM images (a, b) initial and after 200 h v-t testing for (c, d) OER and (e, f) HER.

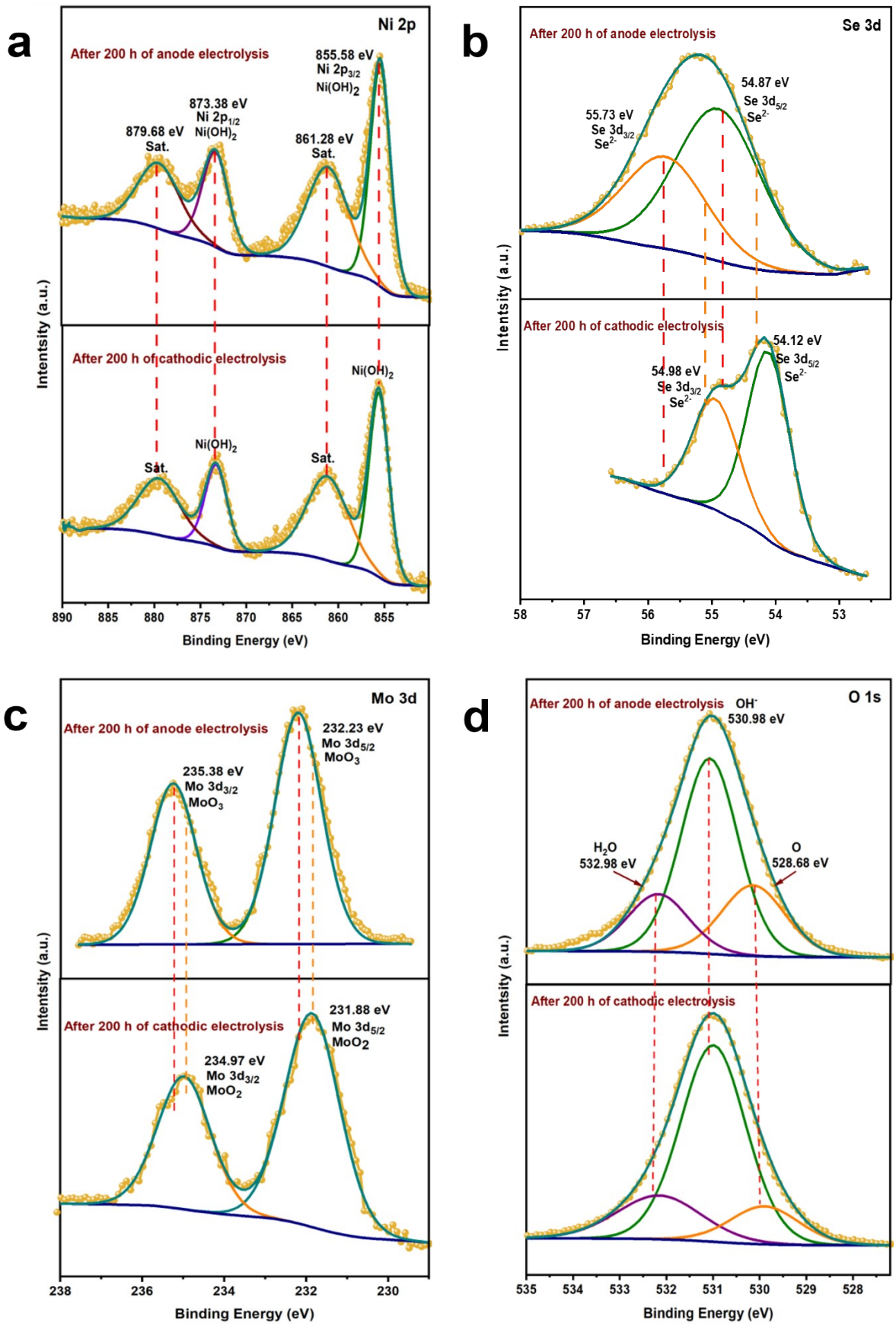

Fig. S13. XPS survey spectrum (a) Ni 2p, (b) Se 3d, (c) Mo 3d, and (d) O 1s after 200 h v-t testing.

Table. S1. OER activity, types of solutions, and potential of typical materials reported in the literature.

OER Catalysts	Solution	Potential(mV) @100 mA cm^{-2} @Stability (h)	Reference
Ni_3Se_2@MoO_3/CF	**1.0 M KOH + 0.5 M NaCl**	**277 mV**	**This work**
Ni_3Se_2@MoO_3/CF	**1.0 M KOH + Seawater**	**280 mV@200h**	
NiMoN@NiFeN	1.0 M KOH + 0.5 M NaCl	277 mV@100h	Nat. Commun., 2019, 10(1): 1-10.
S doped (Ni,Fe)OOH	1.0 M KOH + Seawater	300 mV@100h	Energy Environ. Sci, 2020, 13(10): 3439-3446.
NiCoS/NF	1.0 M KOH + 0.5 M NaCl	270 mV@100h	Appl. Catal., B, 2021, 291: 120071.
Ni_xFe_yN@C@NF	1.0 M KOH + 0.5 M NaCl	270 mV@100h	J. Mater. Chem. A, 2021, 9(23): 13562-13569.
Pt-Co_3O_4/CP	1.0MNaOH + 3.5%NaCl	370 mV@20h	J. Mater. Chem. A, 2021, 9(10): 6316-6324.
Fe_2O_3/NiO/NF	1.0 M KOH + Seawater	339 mV@50h	ACS Appl. Mater. Interfaces, 2021, 13(31): 37152-37161.
Ni_2P-Fe_2P/NF	1.0 M KOH + Seawater	305 mV@48h	Advanced Functional Materials, 2021, 31(1): 2006484.
B-Co_2Fe LDH	1.0 M KOH + Seawater	310 mV@100h	Nano Energy, 2021, 83: 105838.
NiFe LDH/FeOOH	1.0 M KOH + 0.5 M NaCl	286.2 mV @105h	Inorganic Chemistry, 2021, 60(22): 17371-17378.
NiPS/NF	1.0 M KOH + Seawater	329 mV @60h	Journal of Energy Chemistry, 2022, 75: 66-73.
$Ni_3B_2S_2$@NF	1.0 M KOH + 0.5 M NaCl	390 mV @36h	Small, 2022, 18(12): 2106868.
1D-Cu@Co-CoO/Rh	1.0 M KOH + 0.5 M NaCl	400 mV @12h	Small, 2021, 17(50): 2103826.

Table. S2. Comparison of the performance of the Ni_3Se_2@MoO_3/CF catalyst with some representative electrocatalysts reported recently for HER.

Catalyst	Overpotential HER (mV) @10 mA cm^{-2} @stability	Electrolyte	Reference
Ni_3Se_2@MoO_3/CF	**242@100 mA cm^{-2} 120@10 mA cm^{-2}**	**1.0 M KOH + Seawater 1.0 M KOH + Seawater**	**This work**
CoMnCH	180@10h	1.0 M KOH	J. Am. Chem. Soc., 139 (2017) 8320-8328.
NGQDs-Ni_3S_2	218@16.7h	1.0 M KOH	Small, 13 (2017) 1700264.
$NiCo_2S_4$	210@200h	1.0 M KOH	J. Mater. Chem. A, 4 (2016) 16394-16402.
Ni/Ni_xM_y	130@24h	1.0 M KOH	Adv. Funct. Mater., 26 (2016) 3314-3323.
Co@Co-P@CNTs	160	1.0 M KOH	Small, 10 (2014) 66-72.
Co-Se4	268@100 mA cm^{-2}@12h	1.0 M KOH	Adv. Energy Mater., 8 (2018) 1801926.
Ni_3FeN-NPs	320@100 mA cm^{-2}@~9h	1.0 M KOH	Adv. Energy Mater., 6 (2016) 1502585.
200-SMN/NF	287@100 mA cm^{-2}	1.0 M KOH	J. Mater. Chem. A, 5 (2017) 1595-1602.
Ni-Co-P	156@20h	1.0 M KOH	J. Mater. Chem. A, 6 (2018) 12506-12514.
$Ni(OH)_2/MoS_2$	290100 mA cm^{-2}	1.0 M KOH	Nano Energy, 37 (2017) 74-80.
$Ni_xCo_{3-x}S_4/Ni_3S_2$	258@100 mA cm^{-2}	1.0 M KOH	Nano Energy, 35 (2017) 161-170.
Ni/NiP NPs	130@24h	1.0 M KOH	J. Am. Chem. Soc., 136 (2014) 7587-7590.
CoP/CC	210@22h	1.0 M KOH	Int. J. Hydrogen Energy41 (2016) 10688-10694.
$Ni_{0.85}Se$/GS	200@15h	1.0 M KOH	Electrochim. Acta., 365 (2021) 137384.
Fe-Co-CN/rGO-700	215@45h	1.0 M KOH	ACS Catal., 9 (2019) 2956-2961.
$Fe_{0.5}Co_{0.5}P$	143@12h	1.0 M KOH	J. Alloys Compd., 847 (2020) 156514.
Ni_1Co_1-P	169@30h	1.0 M KOH	J. Mater. Chem. A, 9 (2021) 27639-27650.
Ni_3S_2/Cu-NiCo LDH/NF	156@12h	1.0 M KOH	

Table. S3. EIS simulating parameters of equivalent circuit element for OER.

Type	R_s (Ω)	R_{ct} (Ω)	Chi squared
Ni_3Se_2@MoO_3/CF	0.52	4.5	1.3×10^{-4}
Ni_3Se_2/CF	0.51	9.7	2.4×10^{-3}
MoO_3/CF	0.53	13.4	2.8×10^{-4}
CF	0.59	64.1	3.9×10^{-3}

Table. S4. EIS simulating parameters of equivalent circuit element for HER.

Type	R_s (Ω)	R_{ct} (Ω)	Chi squared
Ni_3Se_2@MoO_3/CF	0.53	1.9	1.4×10^{-4}
Ni_3Se_2/CF	0.54	3.2	2.9×10^{-4}
MoO_3/CF	0.51	12.4	2.5×10^{-3}
CF	0.79	19.8	5.1×10^{-4}

Reference

1.X. Wang, J. Wang, B. Yu, W. Jiang, J. Wei, B. Chen, R. Xu and L. Yang, *J. Hazard. Mater.*, 2022, **428**, 128212.

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3.X. Wang, J. Wang, W. Jiang, C. Chen, B. Yu and R. Xu, *Sep. Purif. Technol.*, 2021, **272**, 118916.

4.Z. Liu, X. Yu, H. Xue and L. Feng, *J. Mater. Chem. A*, 2019, **7**, 13242-13248.