Supporting Information

Branch-leaf-like Hierarchical Self Supporting Electrode as a

Highly Efficient Catalyst for Hydrogen Evolution

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1. Experimental section

1.1. Materials and chemicals

Ni foam (NF, thickness: 0.3 mm) was purchased from Changsha Lyrun Material Co., Ltd. Ni foam first was cleaned with diluted HCl, acetone, and deionized water for three times to remove surface oil and oxide layers. Then the cleaned NF is cut into a rectangle of 4*0.5 cm. Nickel(II) Chloride Hexahydrate $Ni(Cl)_2 \cdot 6H_2O$, Cobaltous chloride hexahydrate $Co(Cl)_2 \cdot 6H_2O$, Sodium Molybdat Dihydrat, methenamine $Na_2MoO_4 \cdot 2H_2O$, Nickel(II) nitrate hexahydrate $Ni(NO_3)_2 \cdot 6H_2O$, Ammonium molybdate tetrahydrate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, Carbamide $CO(NH_2)_2$, Potassium hydroxide (KOH) were purchased from Shanghai Aladdin Bio-Chem Technology Co.,LTD. Commercial 20% Pt/C was purchased from Shanghai Macklin Biochemical Co., Ltd. Highly purified water (> 18 MΩ*cm resistivity) was provided by a PALL PURELAB Plus system. Commercial 20% Pt/C electrocatalyst deposited on nickel foam (weight density: 1 mg/cm^2) using Nafion as a binder.The simulated seawater was prepared by mixing26.73 g of NaCl, 2.26 g of $MgCl_2$, 3.25 g of $MgSO_4$, 1.12 g of $CaCl_2$, 0.19 g ofNaHCO$_3$, 3.48 g of Na_2SO_4 and 0.72 g of KCl in 1 L of ultrapure water.

1.2. Preparation of NiCo$_2$O$_4$@NF composite

NiCo$_2$O$_4$ nanowires arrays were grown on Ni foam by simple hydrothermal method. Briefly, NiCl$_2 \cdot 6H_2O$ (2.5 mmol), urea (15 mmol) and CoCl$_2 \cdot 6H_2O$ (5 mmol) were dissolved in 80 mL distilled water. After stirring for 30 min, this solution was transferred to PTFE stainless steel autoclave. The cleaned Ni foam with size about 4*0.5 cm was vertically placed in the autoclave. NiCo$_2$O$_4$ nanoneedle arrays were obtained after heated the solution at 150 ºC for 12 h. After cooled down to room temperature, the as-prepared sample was cleaned with distilled water and further dried at 80 ºC. Subsequently, the sample was heated to 300 °C at a heating rate of 2 °C min^{-1} for 2 h under air atmosphere.

1.3. Synthesis of NiMoO$_4$/NiCo$_2$O$_4$@NF

2 mmol NiSO$_4$ and 2 mmol $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were dissolved in 80 mL distilled water. After stirring for 30 min, this solution was transferred to PTFE stainless steel autoclave. NiCo$_2$O$_4$@NF was vertically placed in the autoclave. NiMoO$_4$/NiCo$_2$O$_4$@NF was obtained after heated the solution at 120 ºC for 6 h. After cooled down to room temperature, the as-prepared sample was cleaned with distilled water and further dried at 80 ºC.

1.4. Synthesis of MoNi$_4$/MoO$_{3-x}$/NiCo@NF

The obtained precursor NiMoO$_4$/NiCo$_2$O$_4$@NF was placed at in the tube furnace. Subsequently, the sample was heated to 350 °C at a heating rate of 2 °C min^{-1} for 2 h under a H$_2$/N$_2$ (v/v, 5/95) atmosphere.

1.5. Characterizations

Powder X-Ray diffraction (PXRD) data were acquired with a Rigaku D/max-II B X-ray diffractometer using Cu-Ka radiation (λ = 1.5418 Å). X-ray photoelectron spectroscopy (XPS) was carried out using an ESCALABMKII spectrometer and the X-ray source was achromatic Al-Ka (1486.6 eV). The transmission electron microscope JEOL-2100F was used to acquire the electron transmission microscopy (TEM) and HRTEM images. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were performed with a JEOL JSM 4800F scanning electron microscope. The evolved gases during HER were detected by gas chromatograph (Shimadzu, GC-2014C with a thermal conductivity detector).

1.6. Electrochemical measurements

CHI 760E electrochemical workstation (Shanghai Chenhua, China) was used to test the electrochemical performance of catalysts in a typical three-electrode system. The electrolyte was 1 M KOH (pH = 14). MoNi$_4$/MoO$_{3-x}$/NiCo@NF works directly as a working electrode. Carbon rod and silver chloride electrode as the counter electrode and the reference electrode, respectively. The working surface area of the electrode maintained 0.1 cm^2, with the rest of the electrode sealed with a modified acrylate adhesive. The fabrication of Pt/C working electrode as follows: 5 mg powdered 20% Pt/C was dispersed into 50 µL of 0.5 % Nafion solution and a homogeneous ink was obtained. Then this Pt/C-Nafion solution (5 µL) was drop-casted on NF and the working electrode surface area (0.1 cm^2) is the same as those of MoNi$_4$/MoO$_{3-x}$/NiCo@NF. The tested potentials vs.Ag/AgCl are converted to the reversible hydrogen electrode (RHE) based on E$_{vs.RHE}$ = E$_{Ag/AgCl}$ + 0.0592 pH+ 0.197 V (E$_{Ag/AgCl}$ = 0.197 V). The linear sweep voltammetry (LSV) curves were obtained at the scan rate of 0.1 mV s^{-1}. The i-t curves were tested to study the stability of catalysts. Unless otherwise stated, all potentials refer to RHE and all test results have not been corrected by IR.

1.7. Estimation of effective electrode surface area

The ECSA (electrochemical surface area) was evaluated with cyclic voltammograms (CV) measurement at non-faradaic overpotentials. The CV measurements were performed at various scan rates (5, 7, 9, 11,and 13 mV/s) in 0.15-0.25 V vs. RHE. A linear trend was observed by plotting the difference of current

density between the anodic and cathodic at 0.2 V vs. RHE against the scan rate. The double layer capacitance (C_{dl}) is equal to half of the slope of the fitting line. The slope is proportional to the electrode surface area of catalysts. Therefore, the electrochemical surface areas of different samples can be compared based on their C_{dl} values.

1.8. Measurements of electrochemical impedance spectroscopy (EIS)

The operated overpotential was 0.2 V vs. RHE. The electrochemical impedance spectroscopy (EIS) was conducted from at certain potential with frequency from 0.1 Hz to 100000 Hz. A sinusoidal voltage with an amplitude of 5 mV were applied to carry out the measurements.

1.9. Determination of Faradaic yield

The faradaic efficiency of electrocatalyst toward HER was carried out. A gas chromatograph was combined with an electrochemical workstation to test the Faraday efficiency in situ during the hydrogen production process. The electrolytic cell was continuously saturated with N_2 at a steady flow rate of 100.00 sccm and injected directly into the gas-sampling loop of a gas chromato-graph to quantitatively analyze the amount of hydrogen produced.
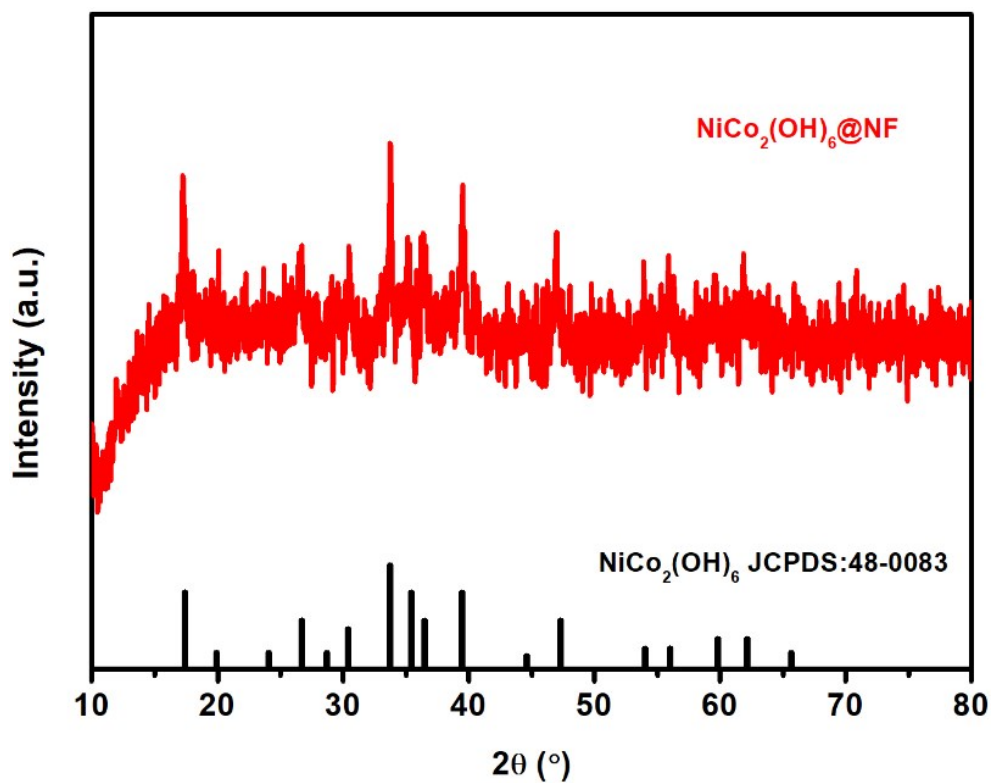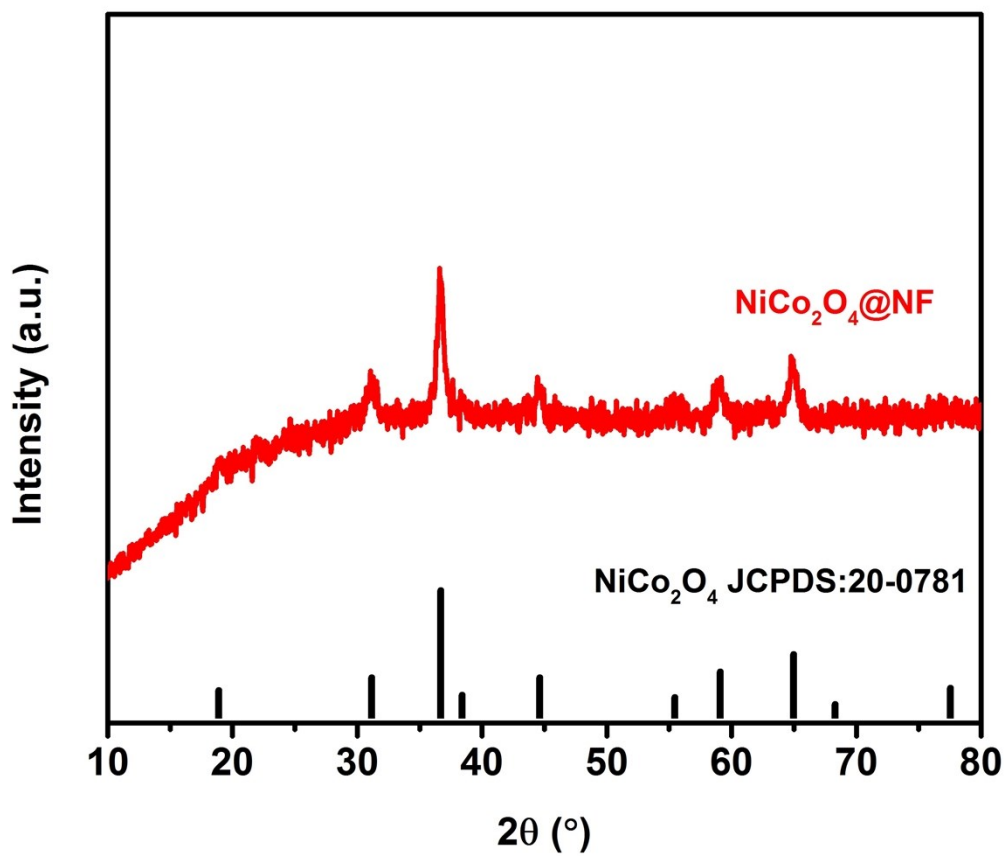
Fig. S1 XRD pattern of $NiCo_2(OH)_6$@NF

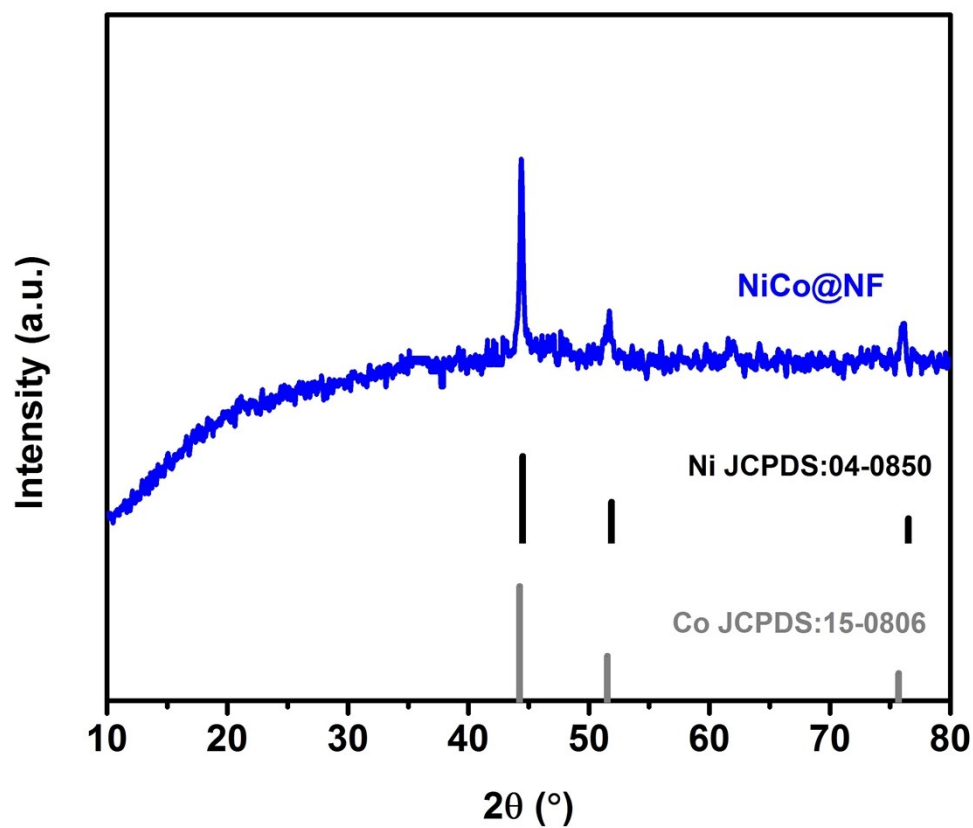**Fig. S2** XRD pattern of $NiCo_2O_4$@NF

Fig. S3 XRD pattern of NiCo@NF
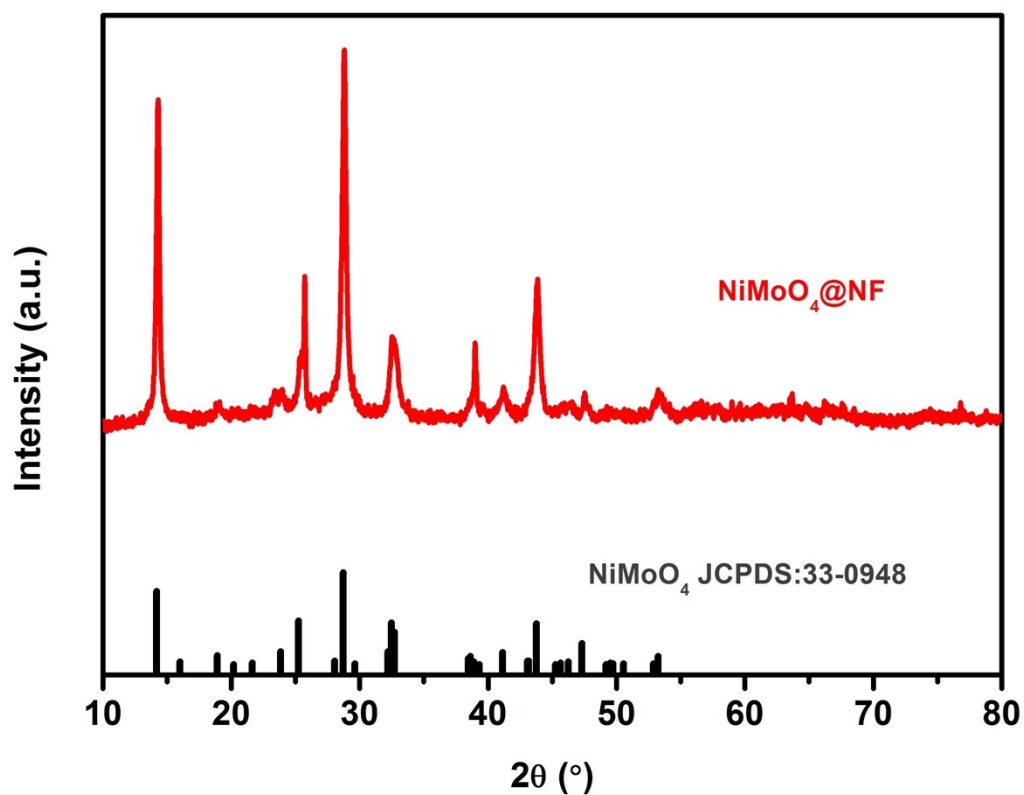
Fig. S4 XRD pattern of NiMoO$_4$@NF
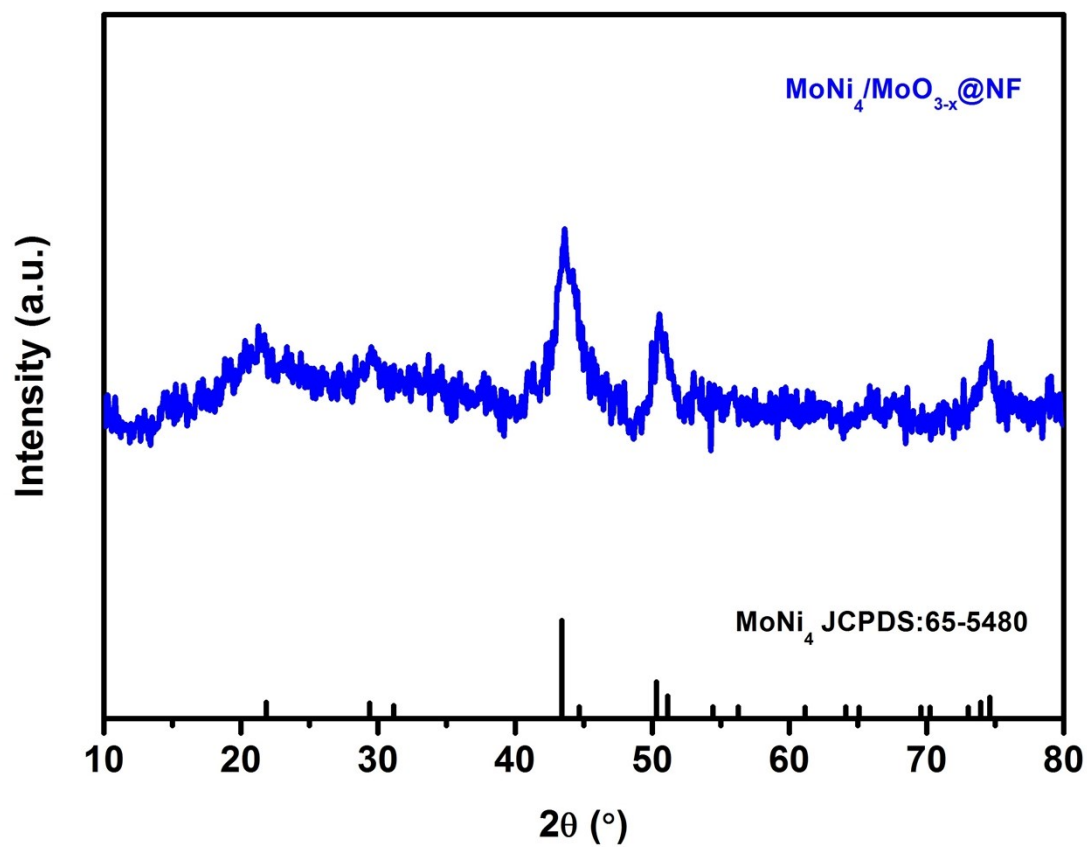
Fig. S5 XRD pattern of $MoNi_4/MoO_{3-x}@NF$
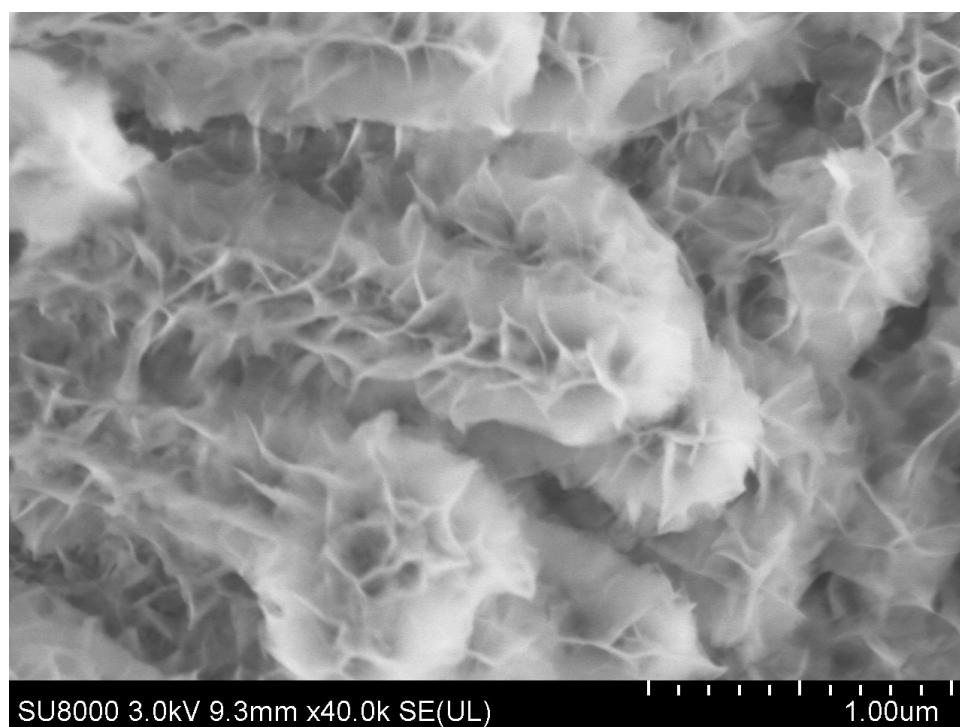
Fig. S6 SEM image of the $NiMoO_4/NiCo_2O_4@NF$

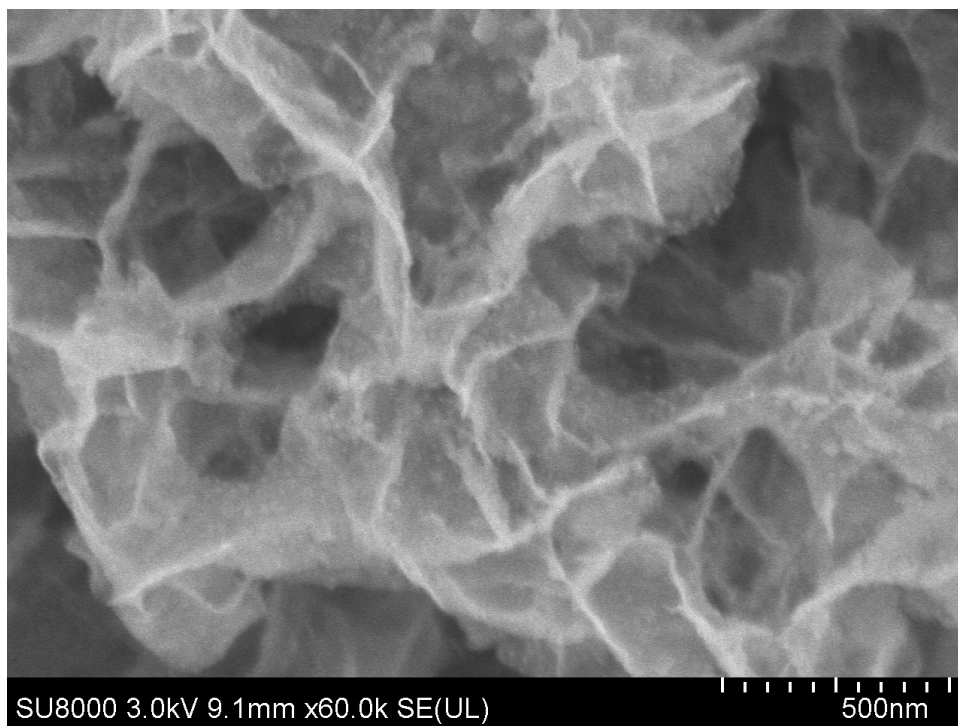SU8000 3.0kV 9.1mm x60.0k SE(UL)   500nm

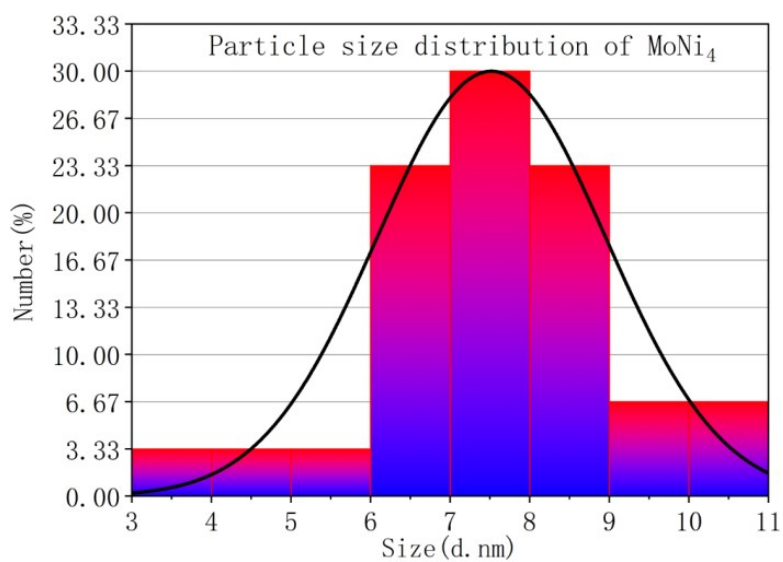**Fig. S7** SEM images of the MoNi$_4$/MoO$_{3-x}$/NiCo@NF

Fig. S8 TEM image and particle size distribution map of the MoNi$_4$/MoO$_{3-x}$/NiCo@NF.
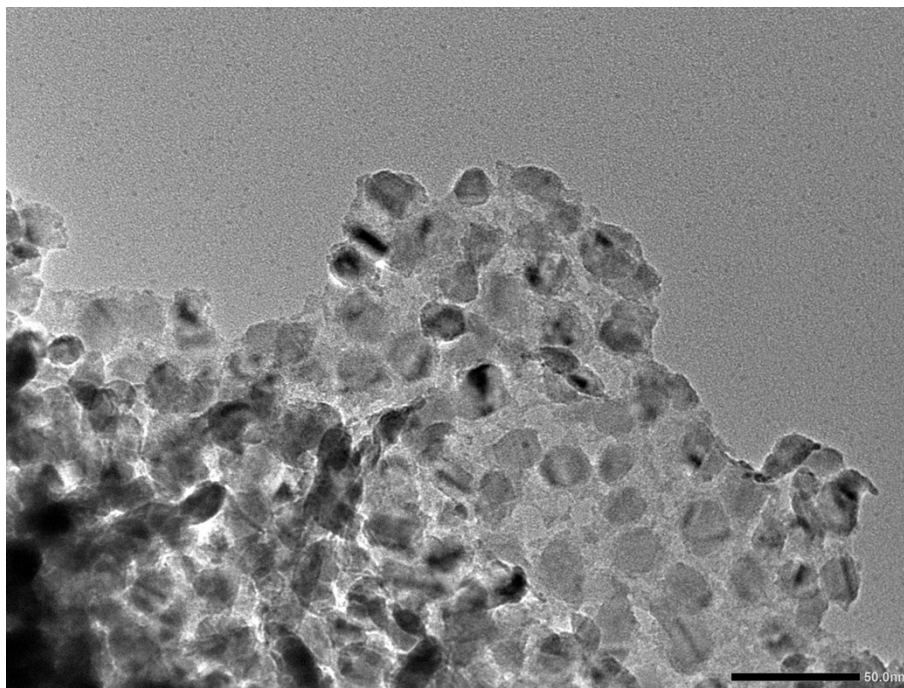
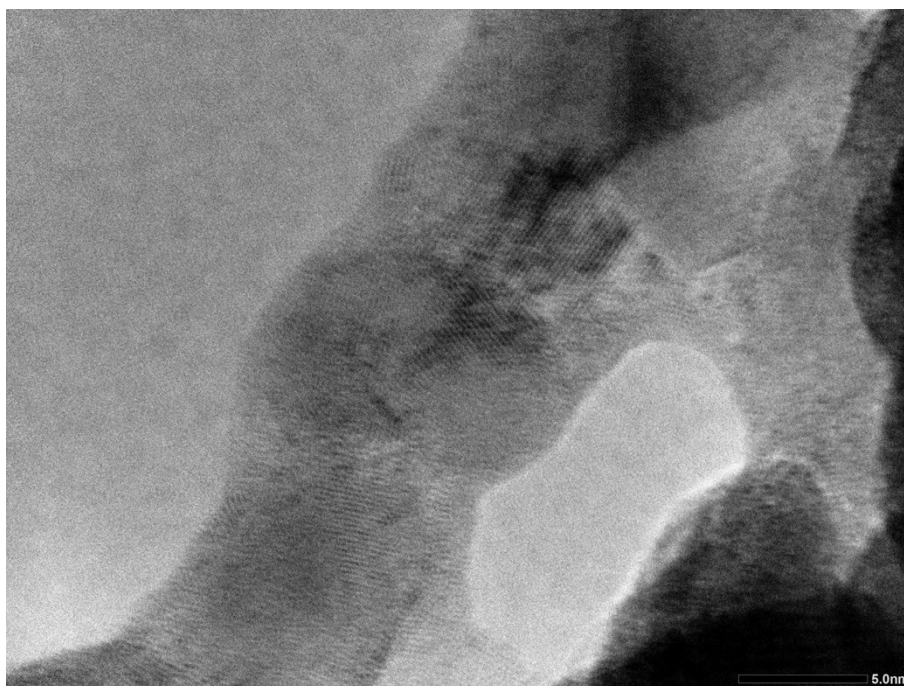**Fig. S9** TEM image of MoNi$_4$/MoO$_{3-x}$/NiCo@NF

Fig. S10 The holes on the nanosheets of MoNi$_4$/MoO$_{3-x}$/NiCo@NF
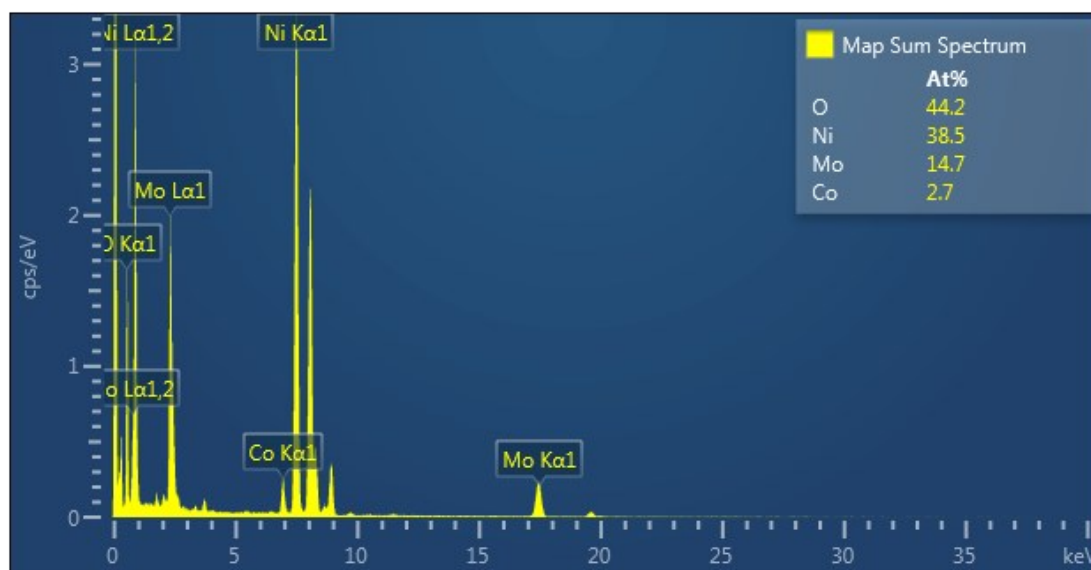

Fig. S11 EDX analysis of the MoNi$_4$/MoO$_{3-x}$/NiCo@NF

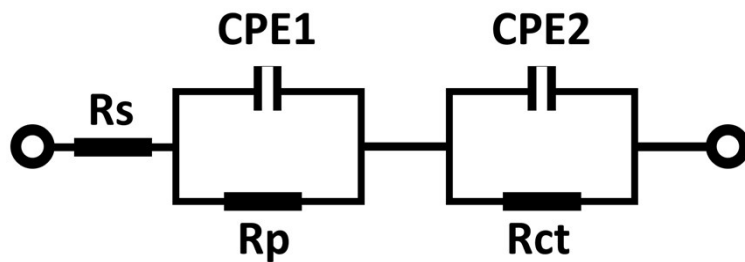**Fig. S12** two-time-constant model equivalent circuit
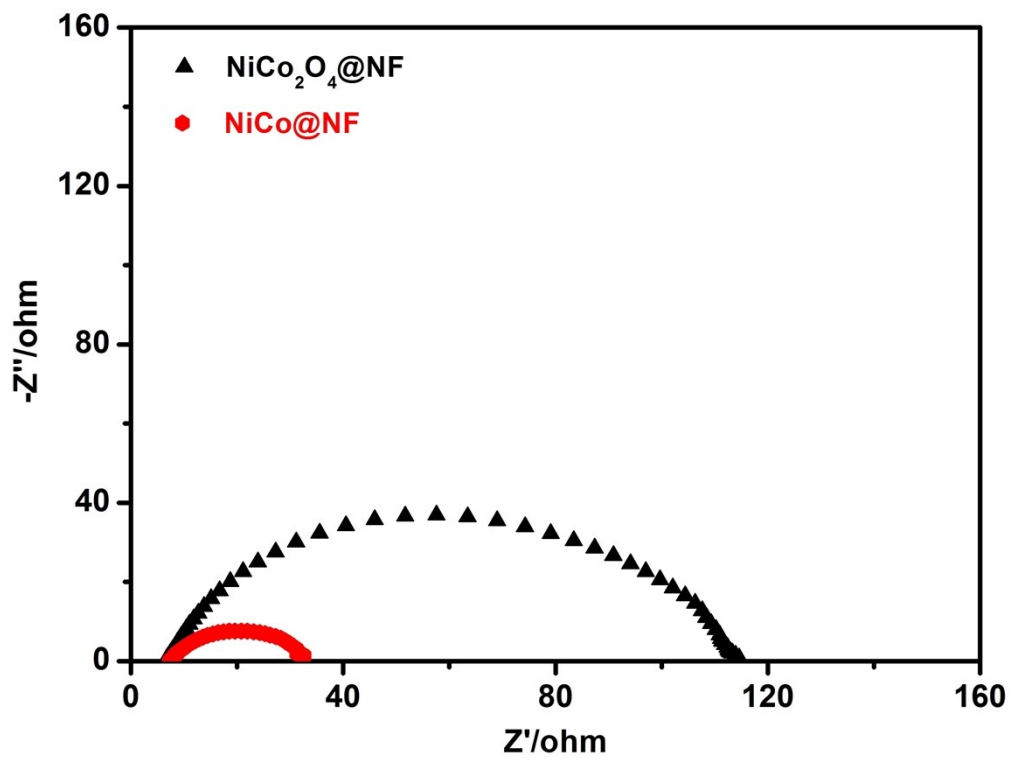
Fig. S13 Electrochemical impedance spectra (EIS) of NiCo$_2$O$_4$@NF and NiCo@NF measured with overpotentials from 200 mV in 1 M KOH.
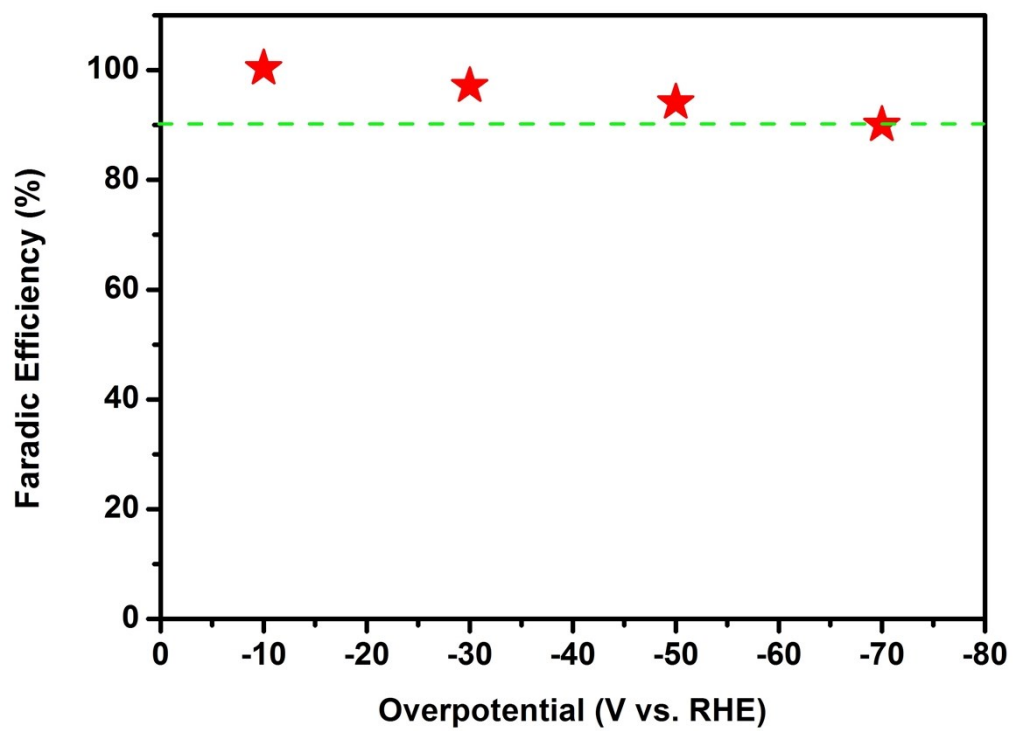
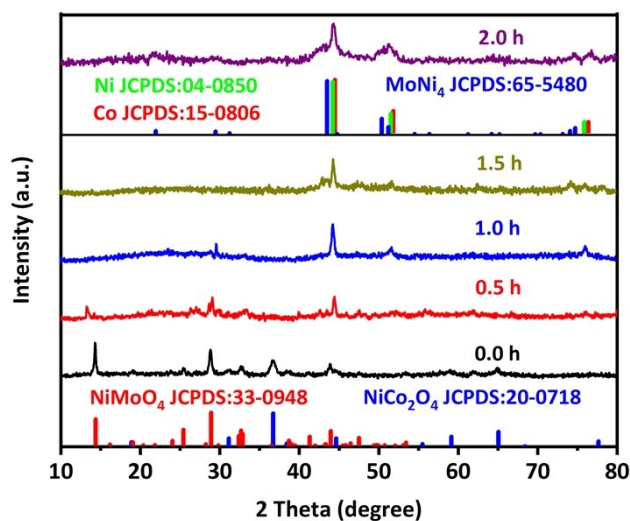**Fig. S14** The Faradaicefficiency of MoNi$_4$/MoO$_{3-x}$/NiCo@NF at different overpotentials in simulated seawater

Fig. S15 XRD of the precursor $NiCo_2O_4/NiMoO_4$@NF calcined at different reduction times
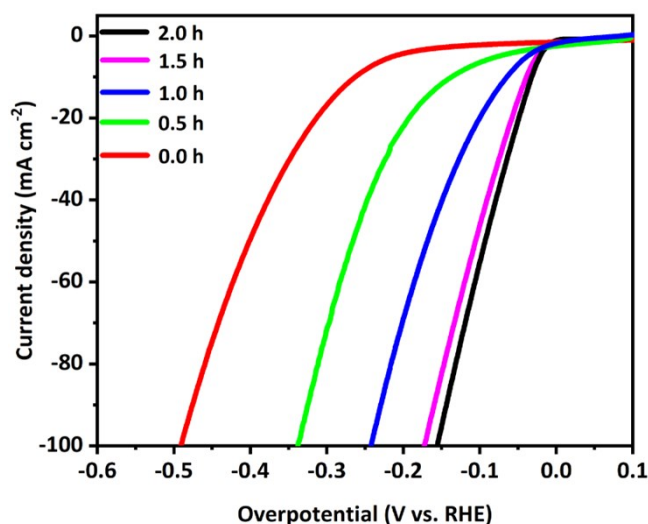
Fig. S16 LSV curves of precursor $NiCo_2O_4/NiMoO_4$@NF calcined at different reduction time

To study the effect of the reduction time on HER, the samples with different reduction time are prepared. The reduction time was 0, 0.5, 1, 1.5, and 2 h, respectively. The XRD diffraction patterns of these samples shows that with the increase of reduction time, the diffraction peak of metal oxide gradually disappears, and only the diffraction peak of $MoNi_4$ can be observed after 2 h of reaction (Fig. R4). The LSV curves of these samples are shown in Fig. R5. To reach current density of 10 mA cm^{-2}, the overpotentials required for samples prepared at 0, 0.5, 1, 1.5, and 2 h are 264 mV, 138 mV, 67 mV, 39 mV and 32 mV. It is obviously that the sample prepared at 2 h has the best HER performance.

Tab. S1 Comparison of the electrocatalytic performance of $MoNi_4/MoO_{3-x}/NiCo@NF$ with the most efficient non-noble metal HER catalysts reported recently in 1 M KOH solution.

Electrocatalysts	η_{10} (mV)	Tafel slope (mV/decade)	C_{dl}(mF cm^{-2})	Reference
$MoNi_4/MoO_{3-x}/NiCo@NF$	**33**	**34**	**405.1**	**This work**
Fe–CoP HTPAs	98	69	127.9	Small 2018, 14, 1704233
Fe-doped Ni2P	33	26	297	ACS Catal. 2019, 9, 8882−8892
Cu@NiFe LDH	30	34.3	59.8	Energy Environ. Sci., 2017, 10, 1820
$Fe_{0.29}Co_{0.71}P$/Ni-foam	74	53.56	52.5	Nano Energy, 2020, 67, 104174
$Mo_2N/CeO_2@NF$	26	37.8	80	ACS Appl. Mater. Interfaces 2020, 12, 29153−29161
$CoWO_{4-x}@C$	46.8	50.1	1.58	Appl Catal B-Environ, 2019, 259, 118090
CoP@NiFe–OH/SPNF	118[a]	71.7	29.75	Nano Energy 2019 63 103821
Ni_3N-NiMoN	31	46	241	Nano Energy, 2018, 44, 353–363
$MoNi_4/MoO_{3-x}$	17	36	128	Adv. Mater. 2017, 29, 1703311
U−Fe-β-$Ni(OH)_2$/NF	121	30.1	3.96	ACS Appl. Mater. Interfaces 2020, 12, 36208−36219
$NiCoO_x/NiCoP$	35	56	5.91	J Alloy Compd, 2020, 835, 155364
$Ni(OH)_2–NiMoO_x$	36	38	168.6	Adv. Energy Mater. 2019, 9, 1902703
$Ni(OH)_2−NiS_2$/TM	90	89	-----	Inorg. Chem. 2017, 22, 13651–13654
Ni/V_2O_3	22[b]	-----	133.9	Nano Research, 2020, 13, 2407–2412

a,b: at 20 mA·cm^{-2}

Tab. S2 Comparison of the electrocatalytic performance of $MoNi_4/MoO_{3-x}/NiCo@NF$ with the most efficient HER catalysts reported recently in natural or simulated seawater.

Electrocatalysts	Overpotential (mV) at 10 mA/cm^2	Reference
$MoNi_4/MoO_{3-x}/NiCo@NF$	**101**	**This work**
Pt@mh-3D MXene	280	Adv. Funct. Mater. 2020, 1910028
Fe-doped Co$_2$P	771[c]	J Energy Chem, 2021, 55, 92–101
Pt–Ru–Mo	196	J. Mater. Chem. A, 2016, 4,6513–6520
Mn–NiO–Ni/Ni-F	170	Energy Environ. Sci., 2018, 11, 1898
Mo$_2$C-MoP NPC/CFP-800	346	ELECTROCHIM ACTA 2018, 281, 710-716
NiCoP (PF-NiCoP/NF)	287	ACS Appl.Energy Mater., 2019, 2, 3910–3917

c: at 300 mA·cm^{-2}