

Supporting Information for

Self-Sacrificial templated-directed synthesis of ultrathin 0D/2D FeNi₃-NC/NiFeO_x Schottky junction as hydrogen evolution reaction electrode for alkaline seawater electrolysis

Zili Xu,^{ab#} Yuankang Bao,^{ab#} Xun Xu,^{ab} Ping Li,^{ab} Hao Zhang,^a Deliang Li,^a Shuwang
Duo,^{ab*}*

^a *Jiangxi Key Laboratory of Surface Engineering, Jiangxi Science and Technology
Normal University, Nanchang, 330013, China*

^b *School of Materials and Energy, Jiangxi Science and Technology Normal University,
Nanchang 330013, China*

**Corresponding author.*

E-mail address: rozen121@163.com (Xun Xu), swduo@126.com (Shuwang Duo)

These authors contributed equally to this work.

1、 Electrochemical measurement details

1.1 Preparation of alkaline seawater

Natural seawater is collected from Beishan Bay Beach in Shantou City, Guangdong Province (116.769°E, 23.315°N). The preparation method for alkaline seawater involves creating 1M KOH by using the supernatant of natural seawater after it has settled as deionized water.

1.2 RepARATION of Pt/C, RuO₂ and Ni(R) electrodes

10 mg 20wt.%Pt/C, 400μl ultra-pure water, 540μl ethanol and 60μl Nafion were mixed together for 0.5 hours to form a homogeneous ink. Then, the ink was dripped onto the IF and allowed to dry naturally at room temperature to obtain Pt/C electrodes. The preparation method for the RuO₂ electrode is the same as described above. 10 mg raney nickel, 400μl ultra-pure water, 540μl ethanol and 60μl Nafion were mixed together for 0.5 hours to form a homogeneous ink. The ink was dripped onto the NF and allowed to dry naturally at room temperature to obtain the raney nickel catalyst electrodes.

1.3 Electrochemical measurements

Electrochemical measurements were performed on an electrochemical workstation (Shanghai Chenhua CHI660e) with an electrolytic cell. A three-electrode system was used, with a mercury/mercury oxide electrode serving as the reference electrode, a stone mill rod as the counter electrode, and the synthesized sample as the working electrode. 1M KOH + natural seawater was used as the electrolyte, and the

pH value of the electrolyte was measured using a pH meter. Before all electrochemical tests were prepared, the working electrode was activated through 50 cycles of cyclic voltammetry (CV) scanning in the range of 0.1 to -0.7 V vs. RHE. Additionally, a linear sweep voltammetry (LSV) curve was obtained at a sweep rate of 5 mV s⁻¹. The double layer capacitance (C_{dl}) is determined by utilizing cyclic voltammetry to measure the disparity in current density. The open circuit potential is ±0.05 V vs. RHE at intervals of 10 mV s⁻¹ from 10 mV s⁻¹ to 50 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) is tested in the frequency range from 0.01 to 100,000 Hz with an amplitude of 5 mV.

1.4 The substrates and FeNi₃, NiFeO_x material complement the details

Iron foam: The thickness is 1.2mm, the purity is 99.9%, from Kunshan Jiayisheng Electronics Co., LTD.

Nickel foam: The thickness is 0.5mm, the purity is 99.9%, from Suzhou Kesheng and metal Materials Co., LTD.

FeNi₃: Customized by Kunshan Jiayisheng Electronics Co., LTD.

NiFeO_x: It is obtained by NiFe LDH in argon at 5°C per minute to 280°C, and then at 5°C per minute to 400°C.

1.5 Details of SEM, TEM, or XPS instruments

Scanning electron microscope(SEM): Sigma SEM produced by the German Carl Zeiss Group, electron gun acceleration voltage is 5kV.

Transmission electron microscope(TEM): JEM-2100F model TEM manufactured by Japan JEOL LTD, electron gun acceleration voltage is 300kV.

X-ray Photoelectron Spectroscopy(XPS): The ESCALAB Xi+ model XPS, manufactured by Thermo Fisher Scientific in the United States, the source gun type used is Al K Alpha.

2、 Additional figures and table

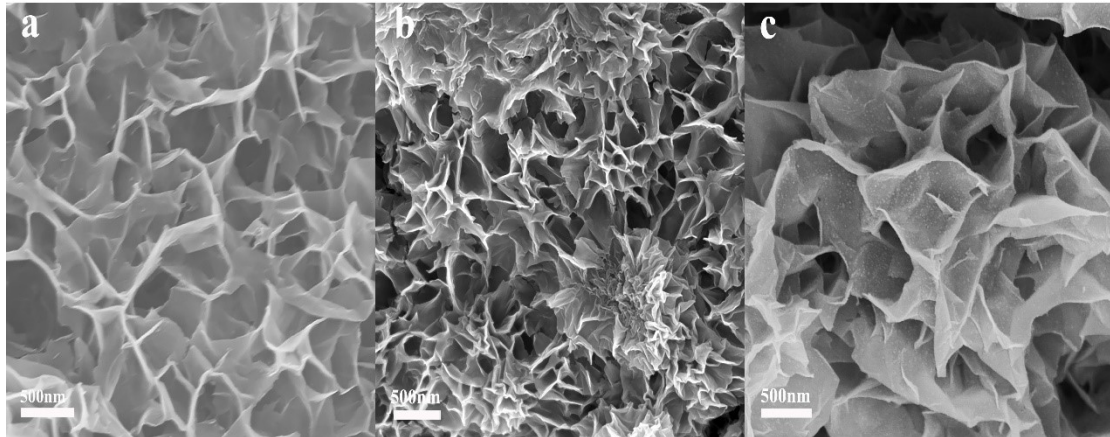


Figure S1. SEM image of NiFe-LDH (a) , MOF/NiFeO_x (b) and FeNi₃-NC/NiFeO_x(c).

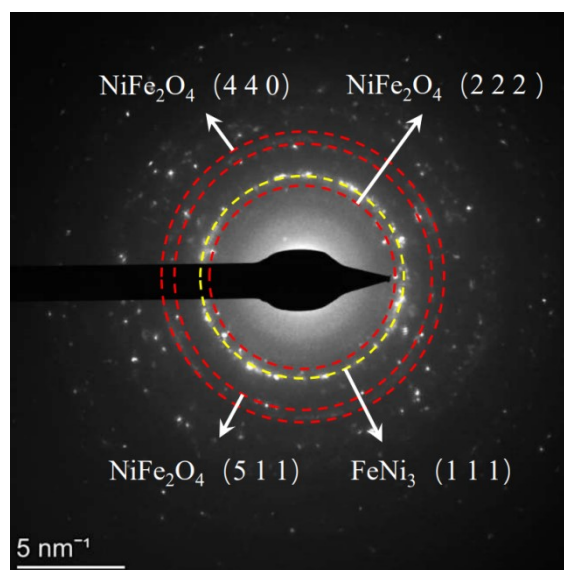


Figure S2. The selected-area electron diffraction (SAED) of FeNi₃-NC/NiFeO_x.

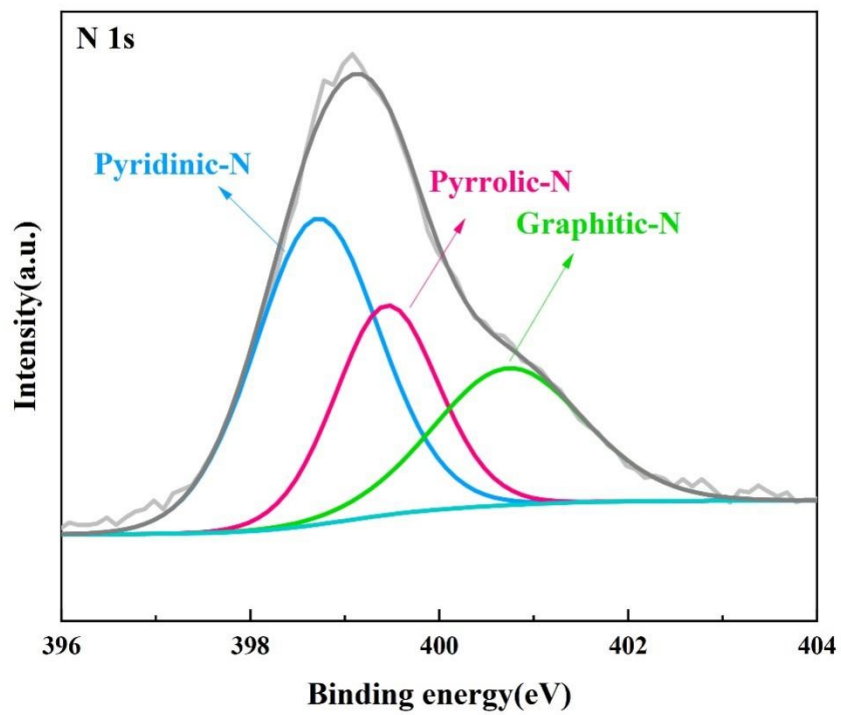


Figure S3. XPS spectra of N 1s in FeNi₃-NC/NiFeO_x.

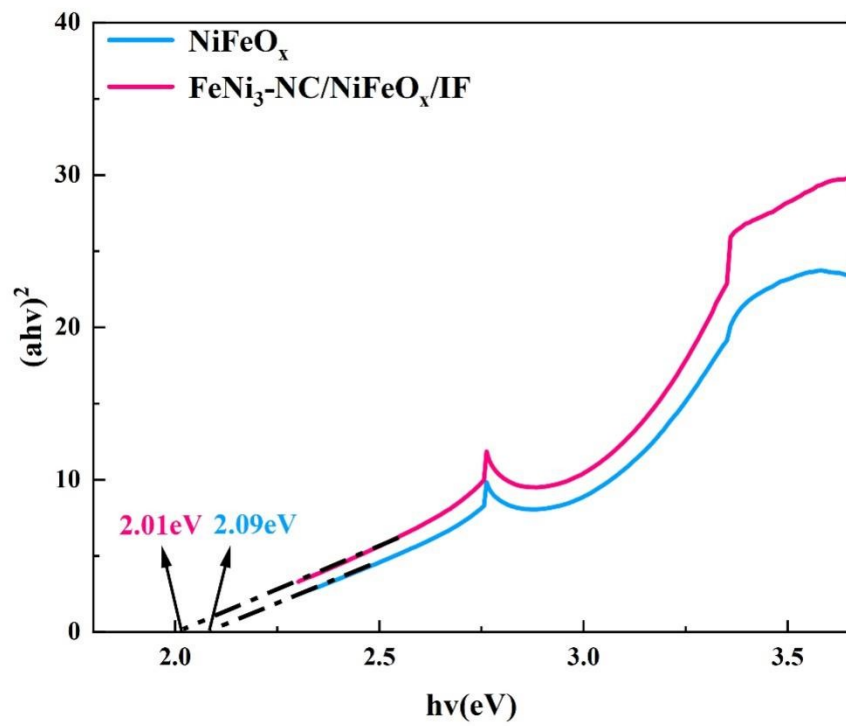


Figure S4. Tauc plot of NiFeO_x $\text{FeNi}_3\text{-NC/NiFeO}_x$.

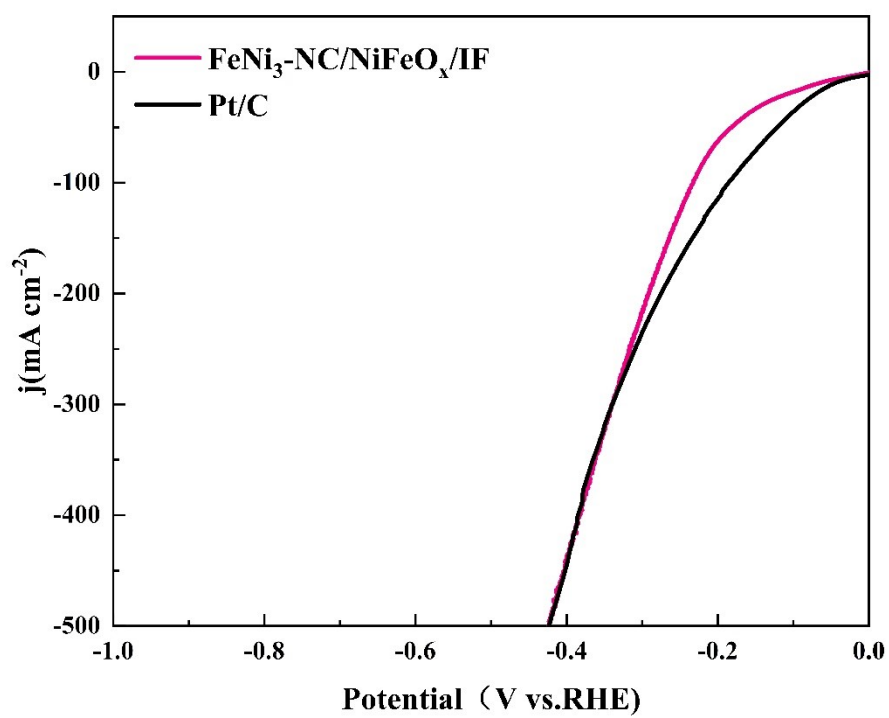


Figure S5. LSV curves of $\text{FeNi}_3\text{-NC/NiFeO}_x$ and Pt/C.

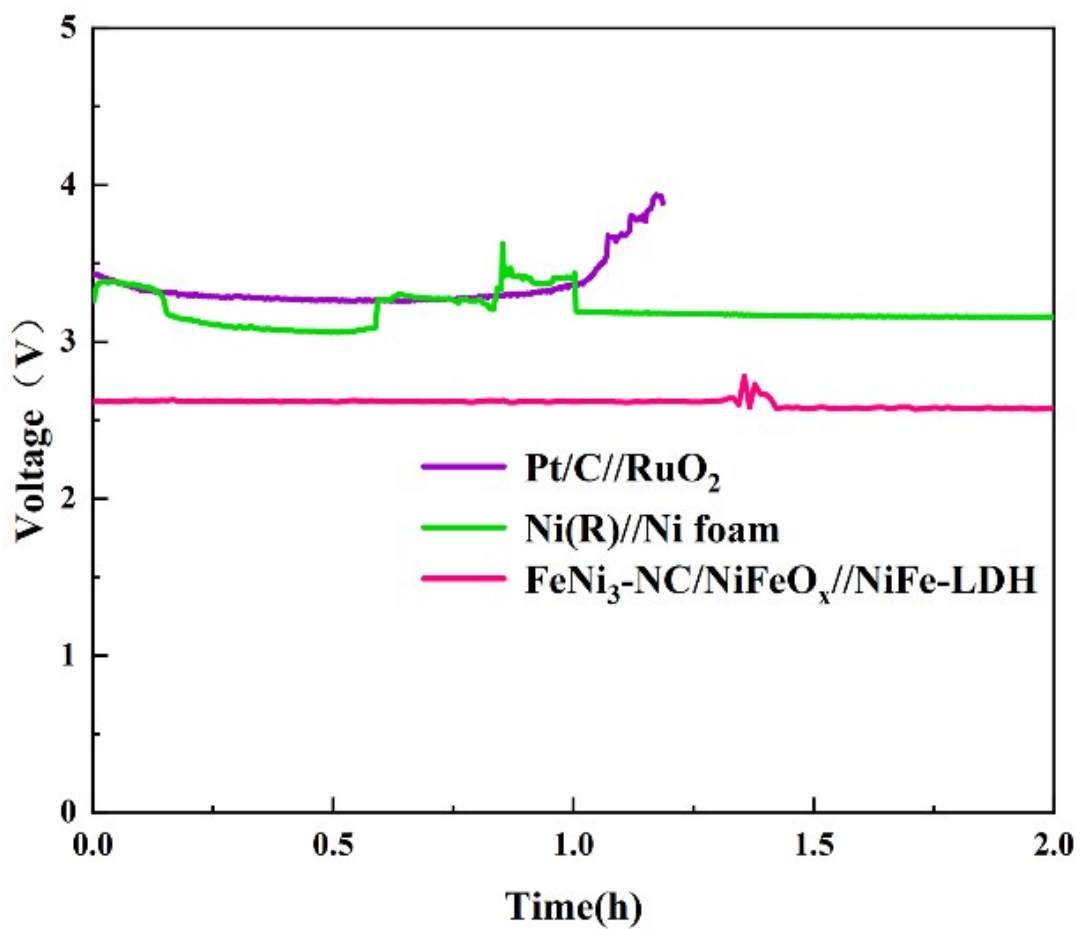


Figure S6. Stability comparison of locally enlarged FeNi₃-NC/NiFeO_x || NiFe-LDH, Pt/C || RuO₂ and Ni (R) || Ni foam at 500mA cm⁻².

Table S1. This work compares the performance of various HER catalysts in an alkaline solution.

Catalyst	η (mV) @ j (mA cm ⁻²)	Stability (h) @ j (mA cm ⁻²)	Electrolyte	Ref.
FeNi ₃ -NC/NiFeO _x	65@10 232@100	500@500	Alkaline seawater	This work
Ni-SA/NC	139@10		Alkaline seawater	[1]
NiFeP-NS-HER	83@10	500@100	alkaline simulated seawater	[2]
NiCo@C/MXene	49@10	140@500	Alkaline seawater	[3]
Ni ₂ P-Fe ₂ P	252@100	36@100	Alkaline seawater	[4]
CoP _x @FeOOH	117@10	80@500	Alkaline seawater	[5]
NiCoP/NiCo-LDH	213@50	50@15	alkaline simulated seawater	[6]
Co-Fe ₂ P	221@100	22@100	alkaline simulated seawater	[7]
NiFe-LDH/(NiFe)S _x	169@10	15@10	1M KOH	[8]
CoNiN@NiFe-LDH	150@10	50@20	1M KOH	[9]
S-NiFeOOH	176@10	70@500	1M KOH	[10]
NiFe-LDH@Mo-NiS ₂ -NiS	120@10	20@10	1M KOH	[11]
NiFeNb-0.25/NF	207@10	40@10	1M KOH	[12]

Reference:

- [1] Zang W, Sun T, Yang T, et al. Efficient Hydrogen Evolution of Oxidized Ni-N3 Defective Sites for Alkaline Freshwater and Seawater Electrolysis. *Advanced Materials*. 2021;33:2003846.
- [2] Liu J, Liu X, Shi H, et al. Breaking the scaling relations of oxygen evolution reaction on amorphous NiFeP nanostructures with enhanced activity for overall seawater splitting. *Applied Catalysis B: Environmental*. 2022;302:120862.
- [3] Sun F, Qin J, Wang Z, et al. Energy-saving hydrogen production by chlorine-free hybrid seawater splitting coupling hydrazine degradation. *Nature Communications*. 2021;12:4182.
- [4] Wu L, Yu L, Zhang F, et al. Heterogeneous Bimetallic Phosphide Ni₂P-Fe₂P as an Efficient Bifunctional Catalyst for Water/Seawater Splitting. *Advanced Functional Materials*. 2020;31:2006484.
- [5] Wu LB, Yu L, McElhenny B, et al. Rational design of core-shell-structured CoP_x@FeOOH for efficient seawater electrolysis. *Applied Catalysis B-Environmental*. 2021;294:120256.
- [6] Wu Y, Tian Z, Yuan S, et al. Solar-driven self-powered alkaline seawater electrolysis via multifunctional earth-abundant heterostructures. *Chemical Engineering Journal*. 2021;411:128538.
- [7] Wang S, Yang P, Sun X, et al. Synthesis of 3D heterostructure Co-doped Fe₂P electrocatalyst for overall seawater electrolysis. *Applied Catalysis B: Environmental*. 2021;297:120386.
- [8] Zou Y, Xiao B, Shi J-W, et al. 3D hierarchical heterostructure assembled by NiFe LDH/(NiFe)_{Sx} on biomass-derived hollow carbon microtubes as bifunctional electrocatalysts for overall water splitting. *Electrochimica Acta*. 2020;348:136339.
- [9] Wang J, Lv G, Wang C. A highly efficient and robust hybrid structure of CoNiN@NiFe LDH for overall water splitting by accelerating hydrogen evolution kinetics on NiFe LDH. *Applied Surface Science*. 2021;570:151182.
- [10] Kim C, Kim SH, Lee S, et al. Boosting overall water splitting by incorporating sulfur into NiFe (oxy)hydroxide. *Journal of Energy Chemistry*. 2022;64:364-371.
- [11] Li Y, Dai T, Wu Q, et al. Design heterostructure of NiS–NiS₂ on NiFe layered double hydroxide with Mo doping for efficient overall water splitting. *Materials Today Energy*. 2022;23:100906.
- [12] Jiang K, Li Q, Lei S, et al. Nb-doped NiFe LDH nanosheet with superhydrophilicity and superaerophobicity surface for solar cell-driven electrocatalytic water splitting. *Electrochimica Acta*. 2022;429:140947.