Supplementary Information

$Ni_xFe_yN@C$ microsheet arrays on Ni foam as an efficient and durable electrocatalyst for electrolytic splitting of alkaline seawater

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Supplementary Methods

Calibration of reference electrode (RE)

Briefly, two Pt electrodes were first polished and cycled in 0.5 M H_2SO_4 (about ±2 V for 2 h) for cleaning purpose, and then employed as working electrode (WE) and counter electrode (CE) in 1 M KOH electrolyte. The electrolyte was saturated by H_2 before use, and continuous H_2 was bubbled over the WE during the calibration. To perform the calibration, CV measurement was carried out to determine the zero current potential (the interconversion between the hydrogen oxidation and hydrogen evolution reaction). The scan rate of the CV measurement was set as low as 0.2 mV s^{-1}, and the average of the two potentials at which the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode reactions. The result (Fig. S12) showed that the potential of zero net current can be estimated to be -0.927 V versus the Hg/HgO electrode, and the relation between the Hg/HgO reference and reversible hydrogen electrode (RHE) in 1 M KOH solution can be estimated by using formula: $E_{\mathrm{RHE}} = E_{\mathrm{Hg/HgO}} + 0.927$ V.

Turnover frequency calculations

According to the references (Nat. Commun., 2018, **9**, 5309; Nano Energy, 2018, **53**, 492-500), we have carried out the TOF calculation using the following formula (1)

$$TOF_{per\ site} = \frac{\#\ Total\ Hydrogen\ Turn\ Overs/cm^2 geometric\ area}{\#\ Surface\ Sites\ /cm^2\ geometric\ area}$$

(1)

The number of total hydrogen or oxygen turn overs was calculated from the current density by the following equation (2-1 or 2-2):

$$\#_{H_2} = \left(j\frac{mA}{cm^2}\right)\left(\frac{1C\ s^{-1}}{1000\ mA}\right)\left(\frac{1\ mol\ e^-}{96485.3\ C}\right)\left(\frac{1\ mol\ H_2}{2\ mol\ e^-}\right)\left(\frac{6.022\ \times 10^{23}\ H_2\ molecules}{1\ mol\ H_2}\right) = \times 10^{15}\frac{H_2/s}{cm^2} per \frac{mA}{cm^2}$$

(2-1)

$$\#_{O_2} = \left(j\frac{mA}{cm^2}\right)\left(\frac{1C\ s^{-1}}{1000\ mA}\right)\left(\frac{1\ mol\ e^-}{96485.3\ C}\right)\left(\frac{1\ mol\ O_2}{4\ mol\ e^-}\right)\left(\frac{6.022\ \times 10^{23}\ O_2\ molecules}{1\ mol\ O_2}\right) = \times 10^{15}\frac{O_2/s}{cm^2} per \frac{mA}{cm^2}$$

(2-2)

The total number of effective surface sites was calculated based on the following equation (3):

$$\frac{\#\,Surface\ sites}{cm^2\ geometric\ area} = \frac{\#\,Surface\ sites\ (flat\ standard)}{cm^2\ geometric\ area} \times Roughness\ factor$$

(3)

In the equation (3), the roughness factor (R_f) can be determined by the double-layer capacitance (C_{dl}) from Fig. 5e of the main text. The specific capacitance can be converted into an electrochemical active surface area using the specific capacitance value for a flat standard with 1 cm^2 of real surface area. According to the reference (Energy Environ. Sci., 2015, **8**, 3022-3029), we assumed 60 μF cm^{-2} for a flat electrode and the surface sites of 2×10^{15} for the flat standard electrode. Thus, the number of surface active sites for Ni_3N@C/NF catalyst was estimated to be:

$$\frac{25.02 \times 10^3}{60} \times 2 \times 10^{15}\ \text{surface sites/cm}^2 = 0.834 \times 10^{18}\ \text{surface sites/cm}^2.$$

Therefore, the TOF_{HER} per site for the Ni_3N@C/NF catalyst at different overpotentials (η) was calculated as follows:

$$TOF_{HER} = \frac{3.12 \times 10^{15}}{0.834 \times 10^{18}} \times j = 0.00374 \times j \qquad (4)$$

j corresponds to the current density at different overpotentials.

For HER, at the overpotentials of 250 mV, the current density for Ni_3N@C/NF is 620.25 mA cm^{-2}. Thus, we can get the corresponding TOF value to be 2.32 H_2 s^{-1} per surface site.

According to this method, we can get the corresponding TOF values for other samples. And by using the same calculation method, the TOF values of OER for different samples were also obtained.

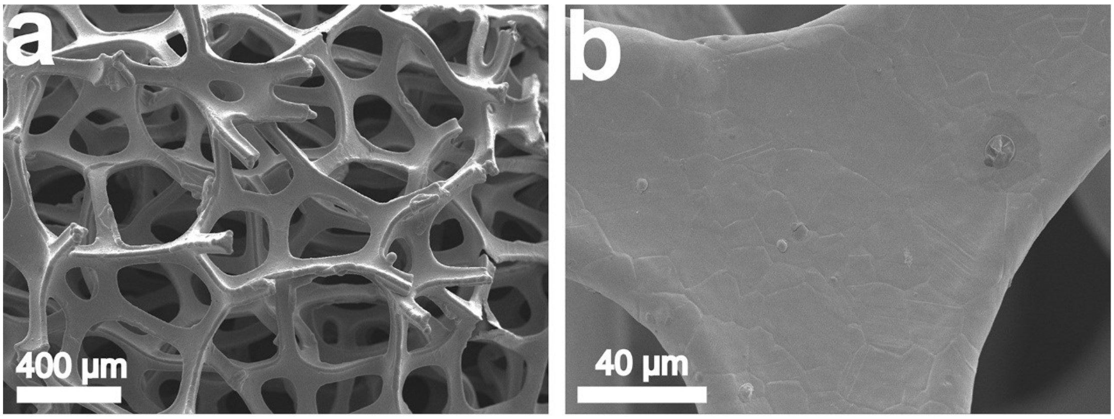

Fig. S1 SEM images of blank Ni foam.

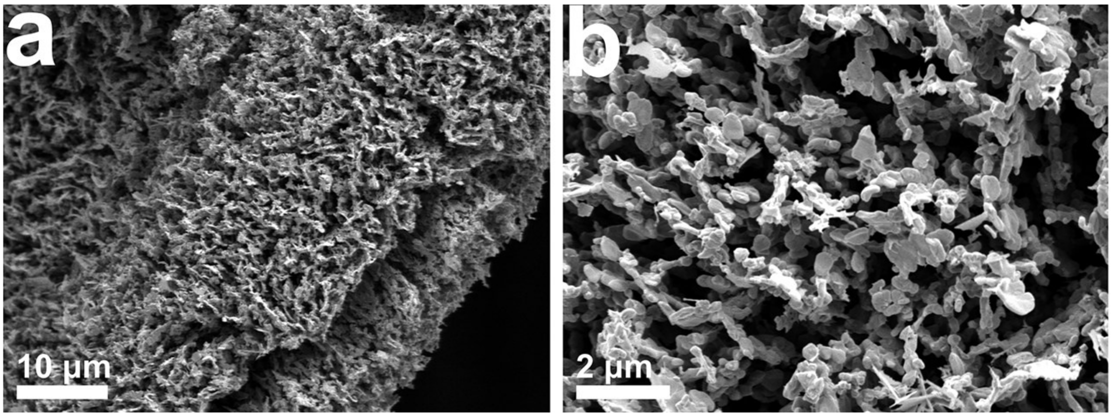

Fig. S2 SEM images of Ni_3FeN/NF.

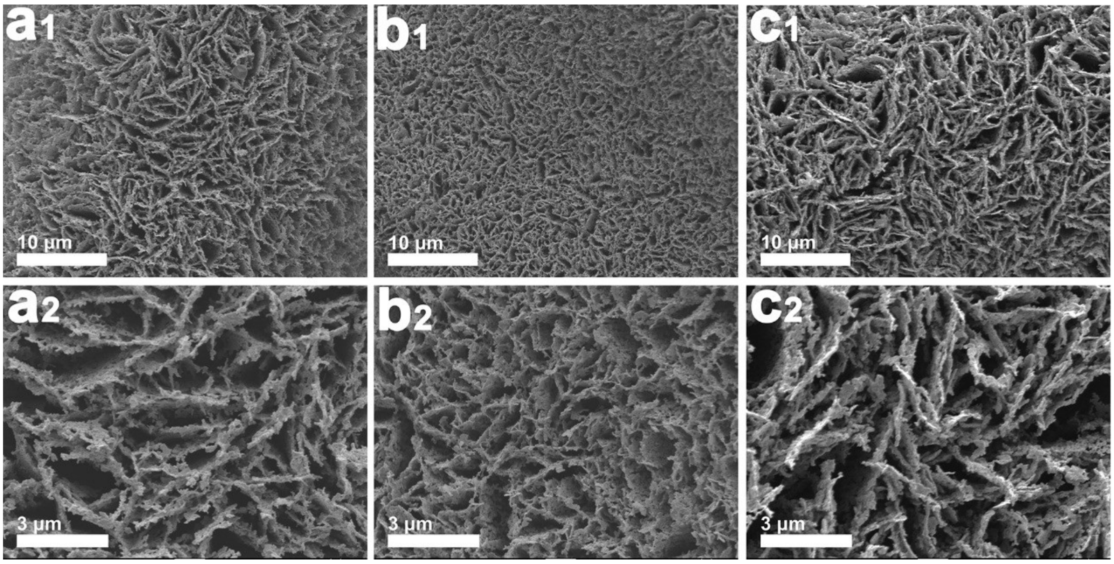

Fig. S3 SEM images of Ni_xFe_yN@C/NF with different Ni/Fe ratio: (a_1, a_2) x=5, y=1; (b_1, b_2) x=1, y=1 and (c_1, c_2) x=1, y=3.

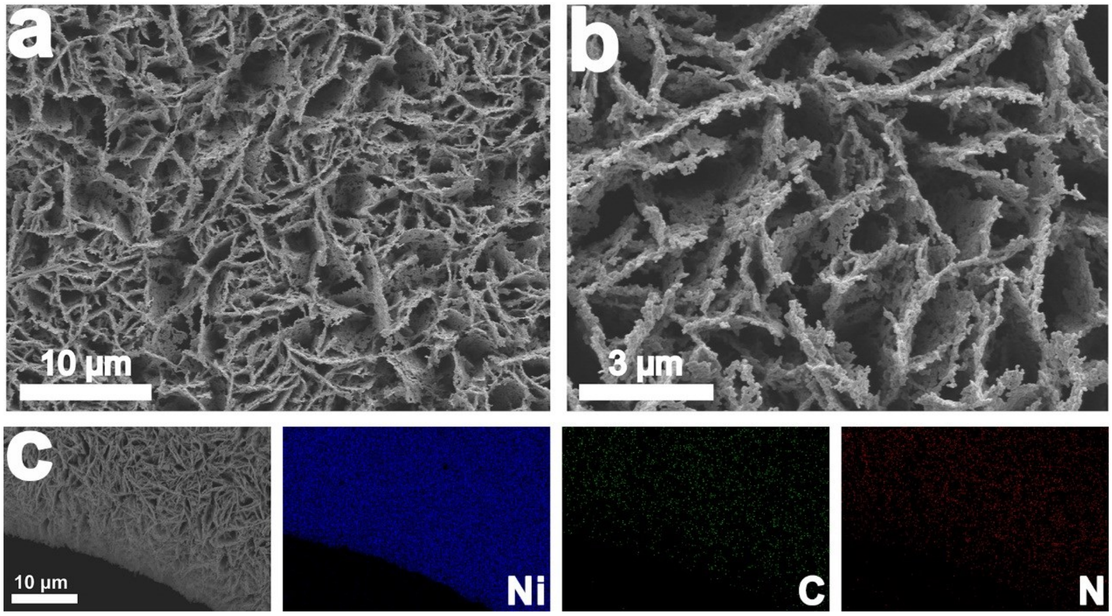

Fig. S4 (a, b) SEM images and (c) corresponding elemental mappings of Ni_3N@C/NF.

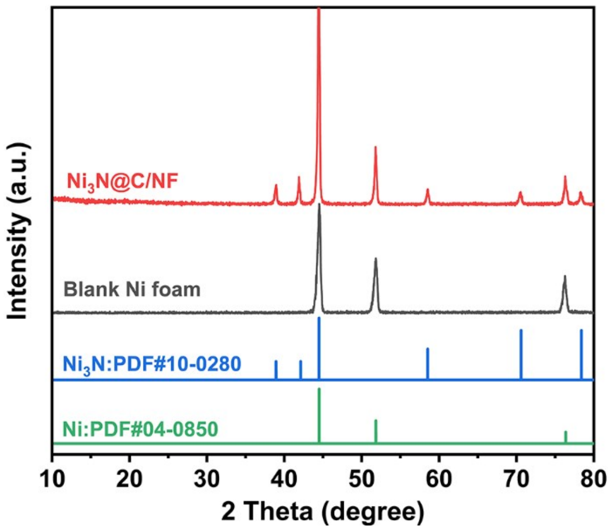

Fig. S5 XRD patterns of Ni_3N@C/NF and blank Ni foam.

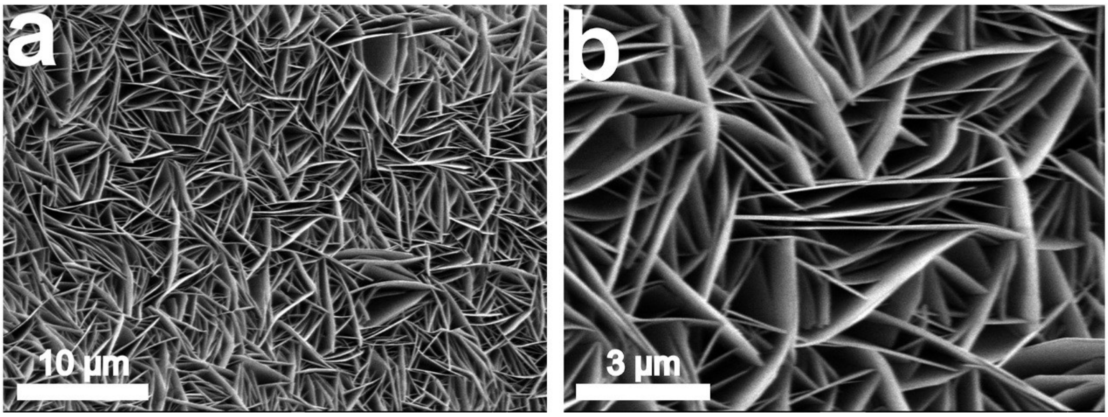

Fig. S6 SEM images of Ni-OH/NF.

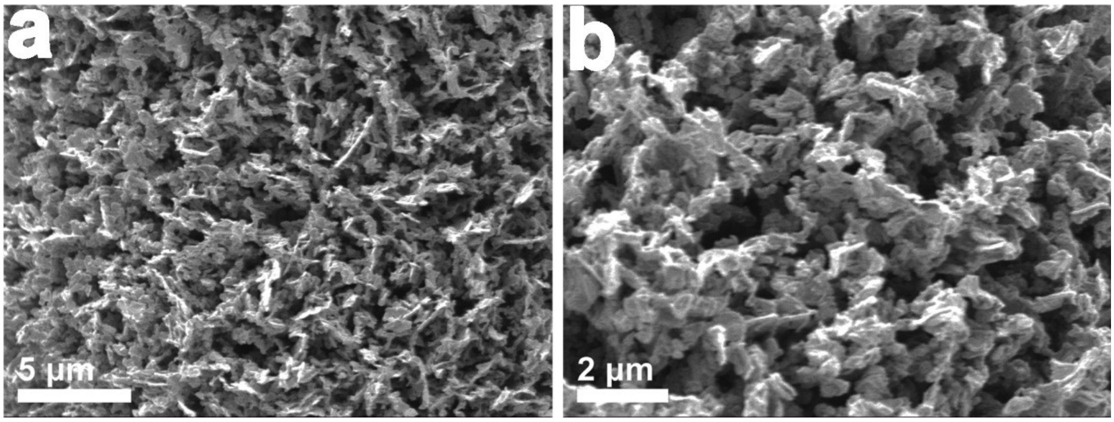

Fig. S7 SEM images of Ni_3N/NF.

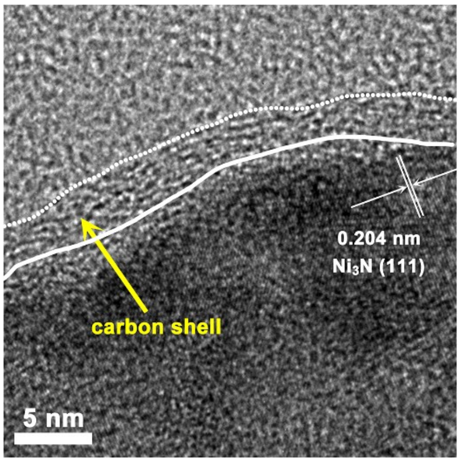

Fig. S8 HRTEM image of Ni_3N@C microsheets.

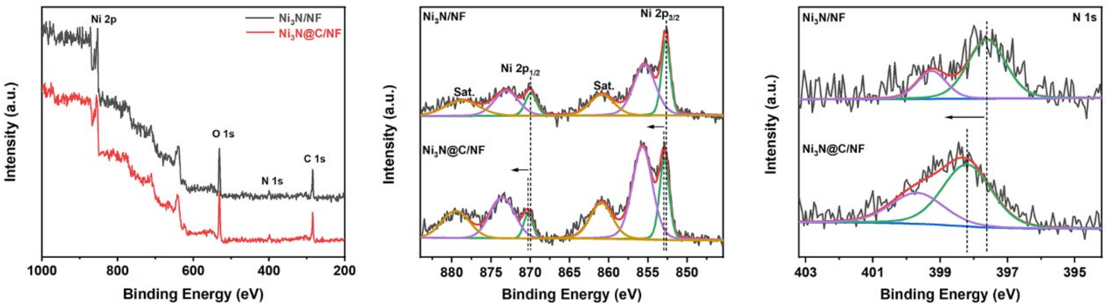

Fig. S9 XPS spectra of Ni_3N@C/NF and Ni_3N/NF, (a) survey scan; (b) Ni 2p and (c) N 1s.

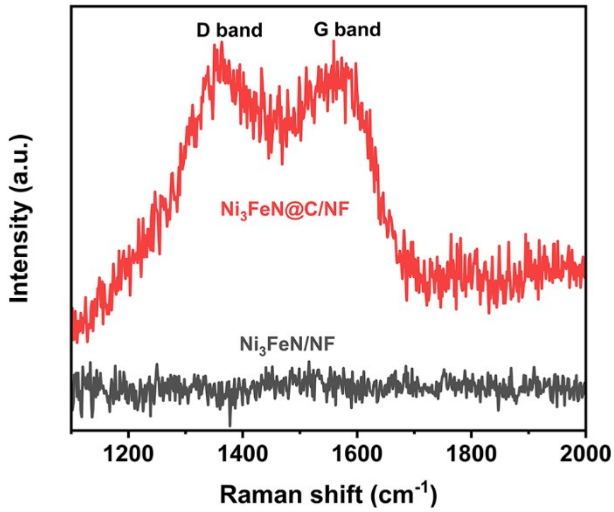

Fig. S10 Raman spectra of Ni_3FeN@C/NF and Ni_3FeN/NF.

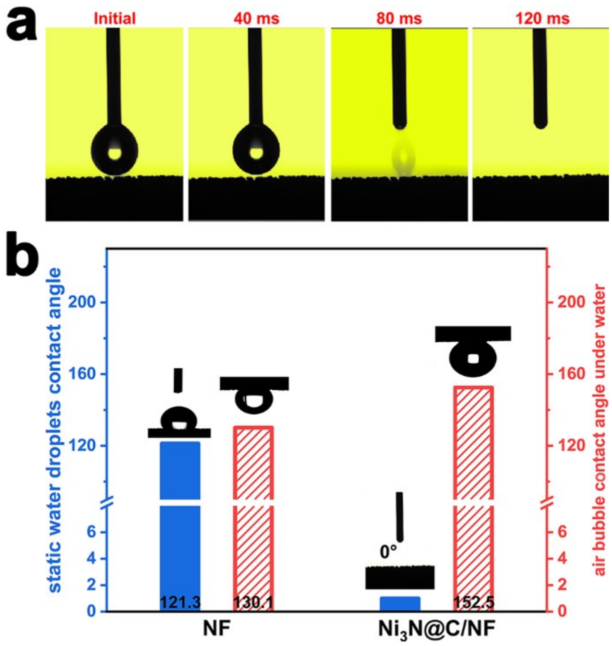

Fig. S11 (a) Penetration process of water droplet on the Ni_3N@C/NF; (b) static water droplets contact angles (blue) and air bubble contact angles under water (red) on the Ni_3N@C/NF and Ni foam, respectively.

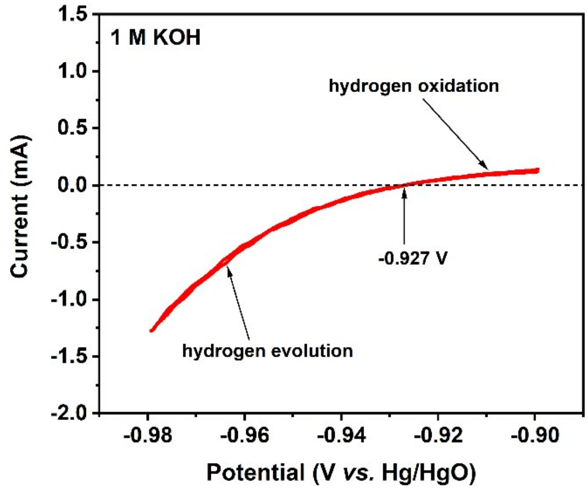

Fig. S12 Calibration of Hg/HgO reference electrode with respect to RHE.

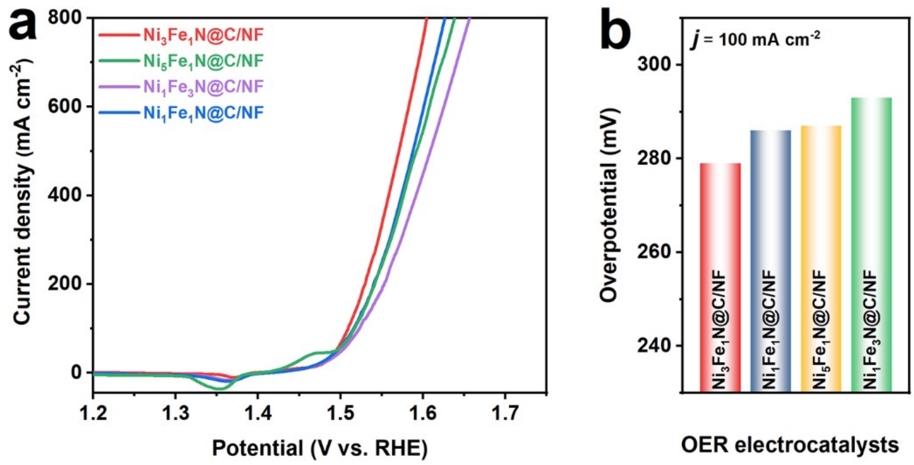

Fig. S13 (a) Polarization curves of Ni_3FeN@C/NF, Ni_5Fe_1N@C/NF, Ni_1Fe_3N@C/NF and Ni_1Fe_1N@C/NF in 1 M KOH electrolyte; (b) comparison of the overpotentials required for these electrocatalysts to achieve a current density of 100 mA cm^{-2} for OER.

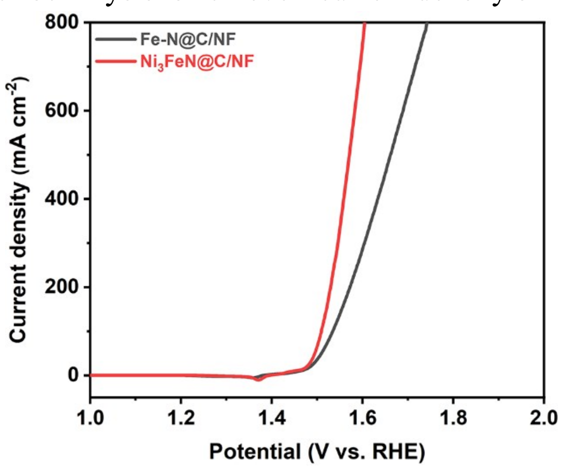

Fig. S14 Polarization curves of Fe-N@C/NF and Ni_3FeN@C/NF in 1 M KOH electrolyte for OER electrocatalysis.

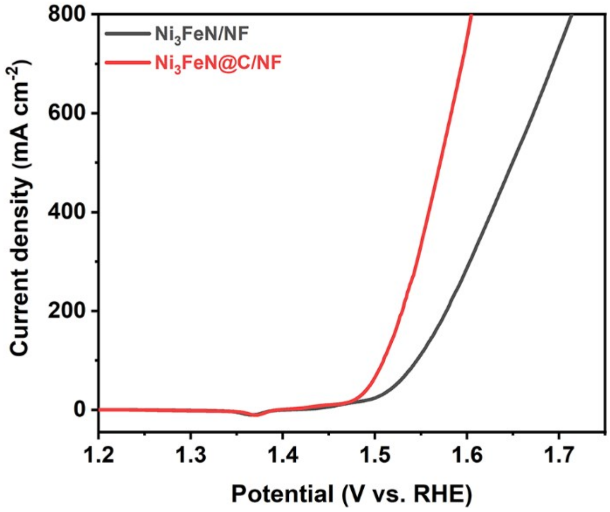

Fig. S15 Polarization curves of Ni_3FeN@C/NF and Ni_3FeN/NF in 1 M KOH electrolyte for OER electrocatalysis.

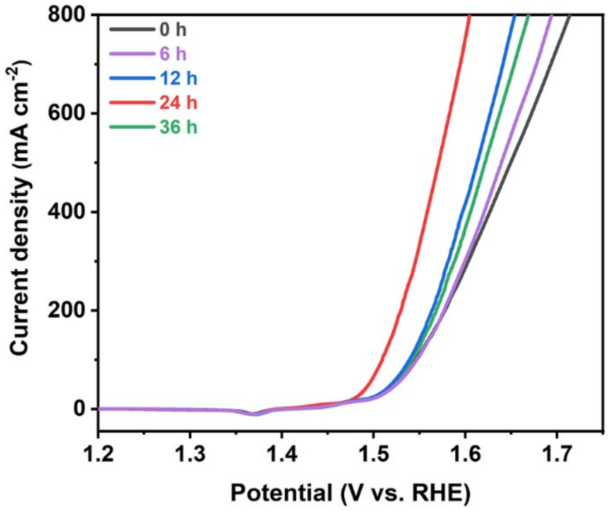

Fig. S16 Polarization curves of Ni_3FeN@C/NF samples with only varying the coating time of glucose in 1 M KOH electrolyte for OER electrocatalysis.

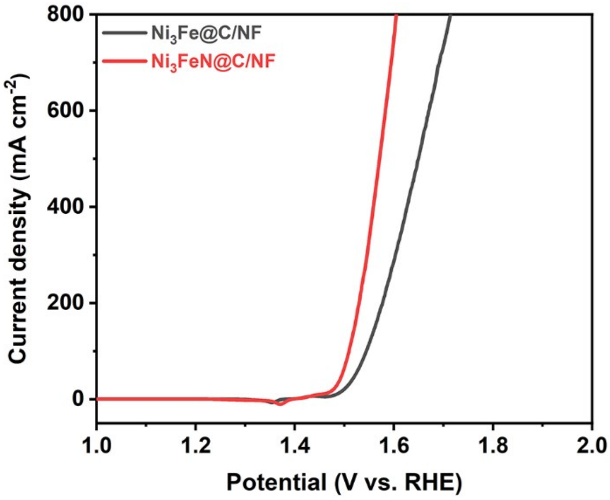

Fig. S17 Polarization curves of $Ni_3Fe@C/NF$ and $Ni_3FeN@C/NF$ in 1 M KOH electrolyte for OER electrocatalysis.

For comparison, one sample, namely, $Ni_3Fe@C/NF$, was obtained under a H_2 atmosphere with the same procedure as that of $Ni_3FeN@C/NF$.

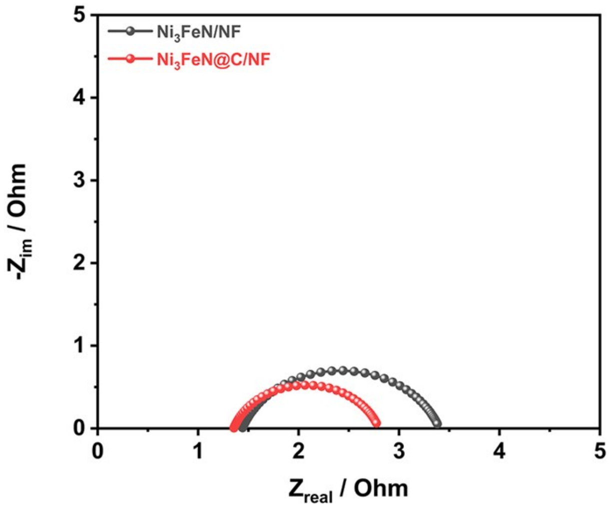

Fig. S18 Nyquist plots (overpotential = 250 mV) of $Ni_3FeN@C/NF$ and Ni_3FeN/NF in 1 M KOH electrolyte for OER electrocatalysis.

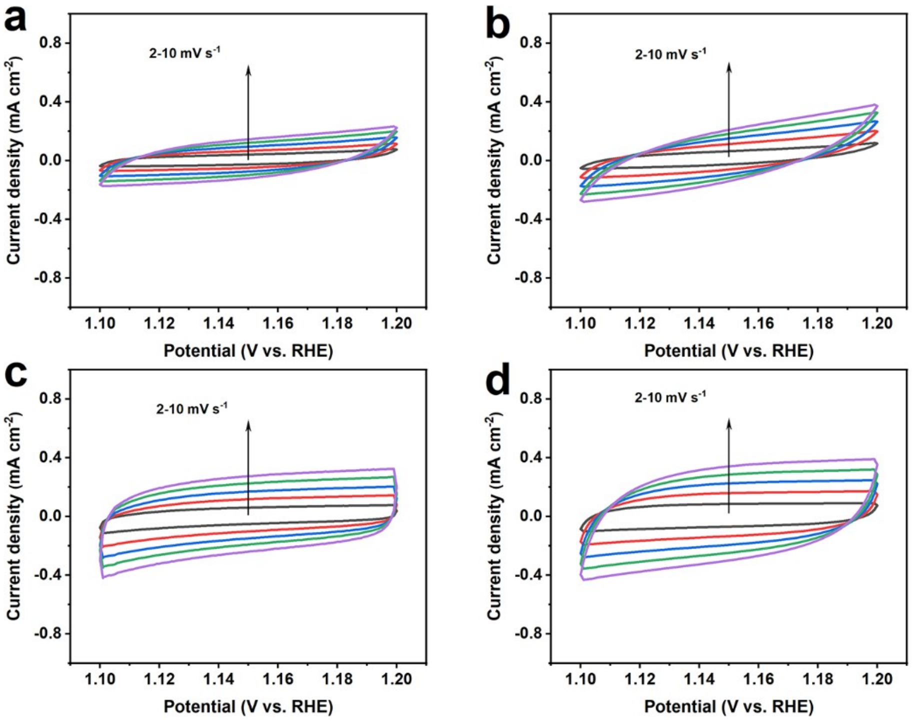

Fig. S19 CV curves of (a) Ni-OH/NF; (b) Ni_3Fe-OH/NF; (c) Ni_3N@C/NF and (d) Ni_3FeN@C/NF measured at different scan rates in 1 M KOH electrolyte.

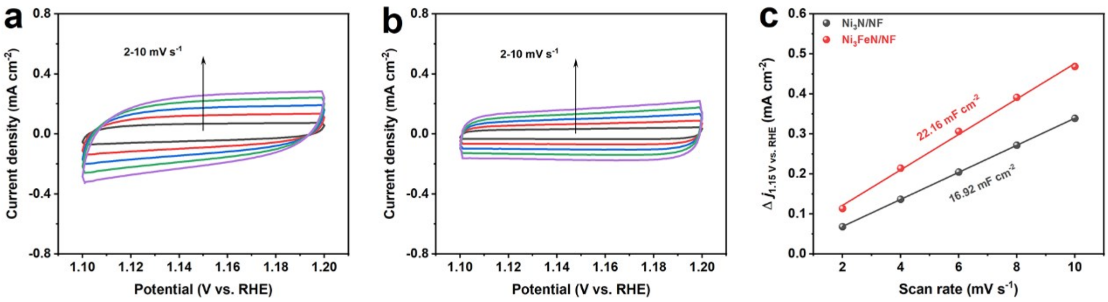

Fig. S20 CV curves of (a) Ni_3FeN/NF and (b) Ni_3N/NF measured at different scan rates in 1 M KOH electrolyte; and (c) C_{dl} plots of Ni_3FeN/NF and Ni_3N/NF.

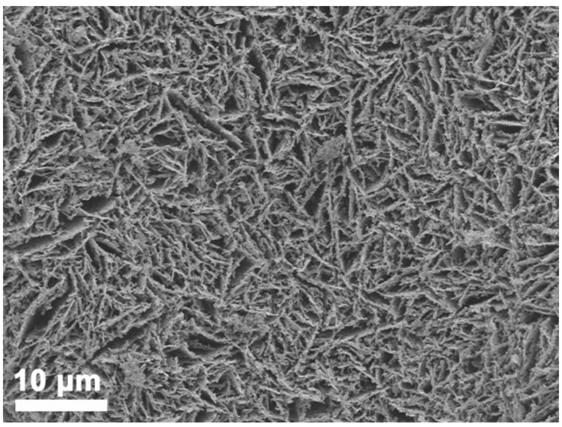

Fig. S21 SEM image of $Ni_3FeN@C/NF$ after 3,000 CV scans for OER electrocatalysis.

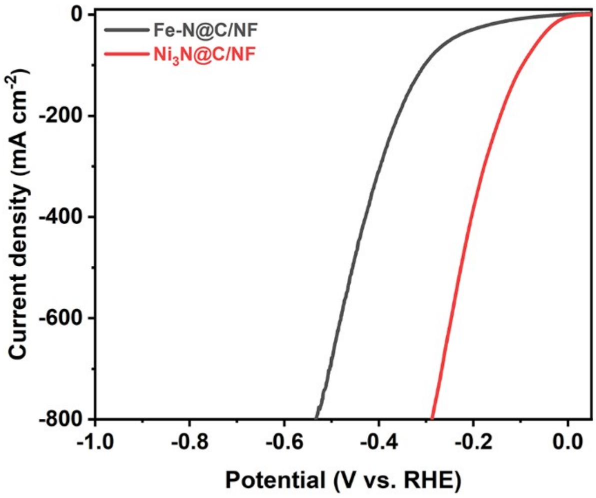

Fig. S22 Polarization curves of Fe-N@C/NF and $Ni_3N@C/NF$ in 1 M KOH electrolyte for HER electrocatalysis.

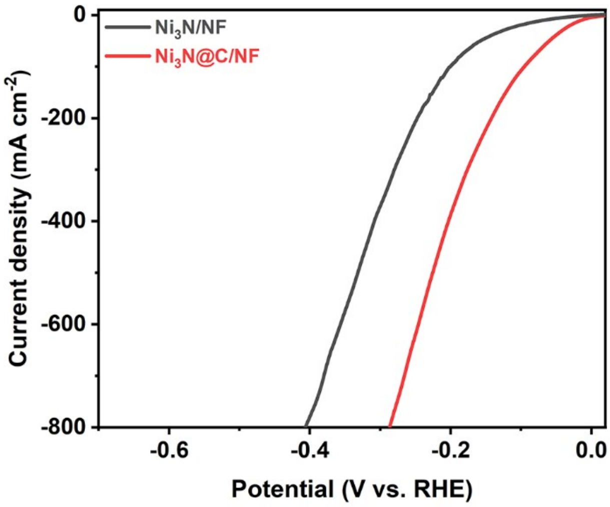

Fig. S23 Polarization curves of $Ni_3N@C/NF$ and Ni_3N/NF in 1 M KOH electrolyte for HER electrocatalysis.

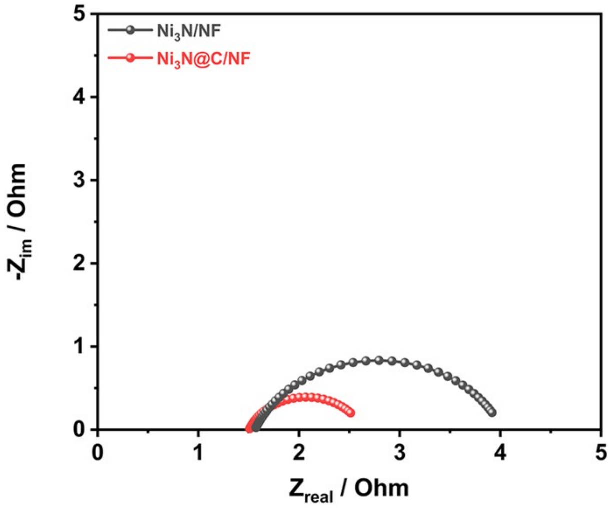

Fig. S24 Nyquist plots (overpotential = 100 mV) of Ni_3N@C/NF and Ni_3N/NF in 1 M KOH electrolyte for HER electrocatalysis.

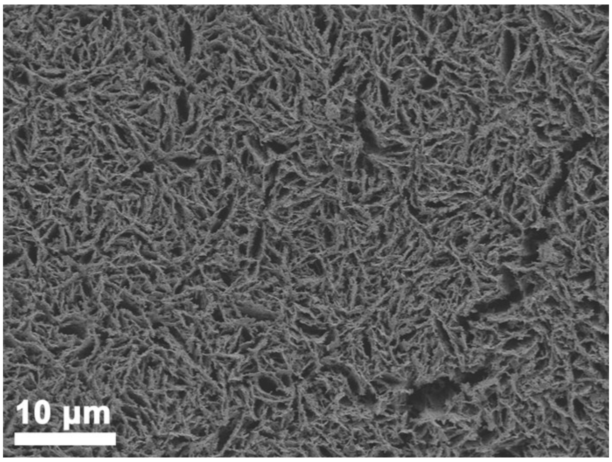

Fig. S25 SEM image of Ni_3N@C/NF after 3,000 CV scans for HER electrocatalysis.

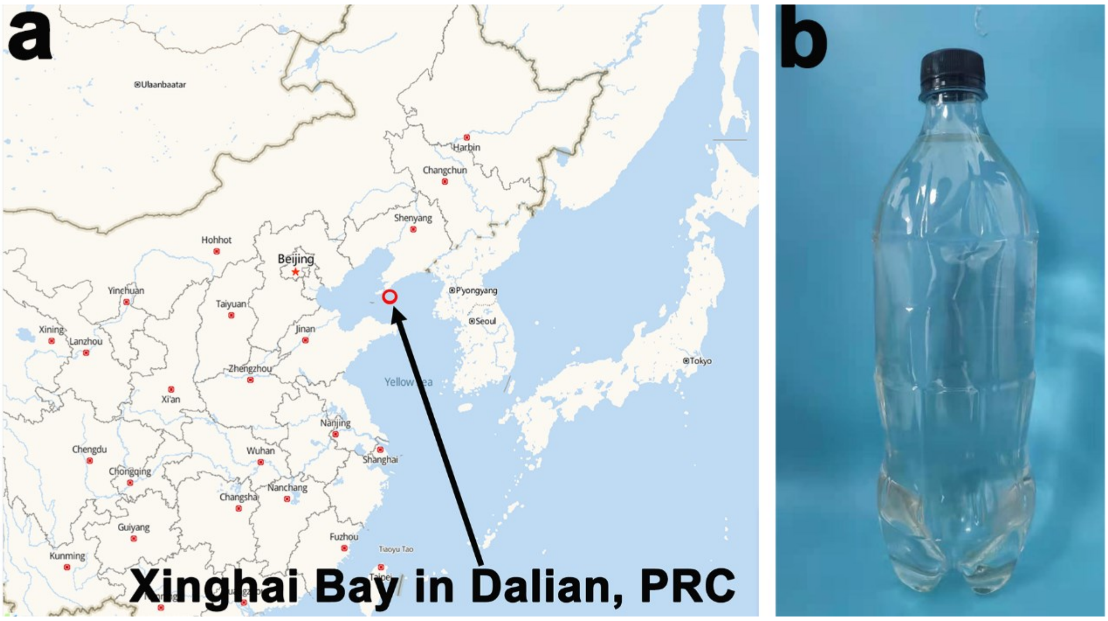

Fig. S26 Collection of seawater. (a) Photograph of Xinghai Bay in Dalian, Liaoning, PRC; (b) photograph of the collected seawater.

The seawater stood for about 10 days before using its supernatant to prepare the alkaline seawater electrolyte.

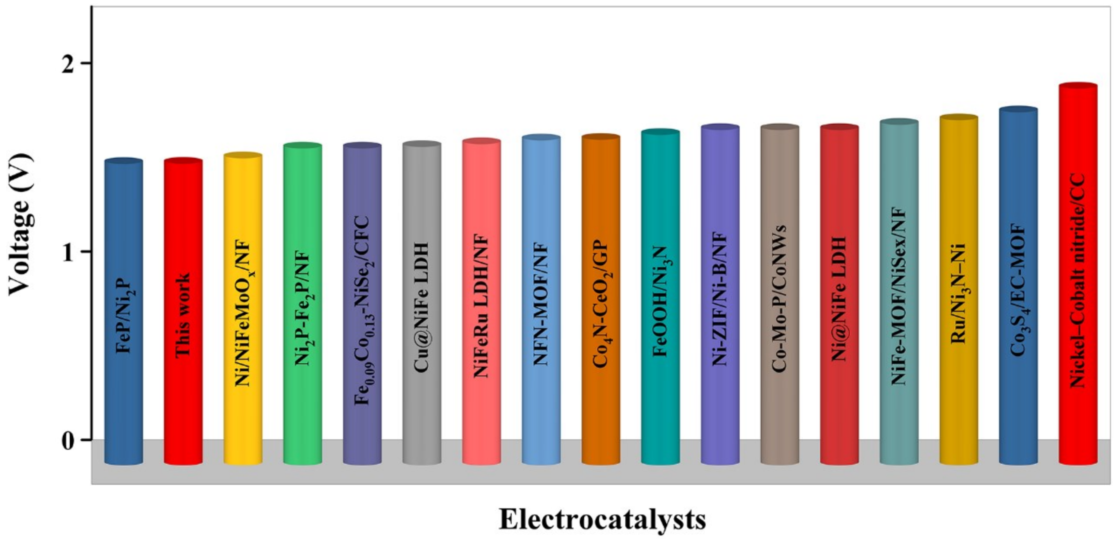

Fig. S27 Comparison of the voltages required to achieve a current density of 100 mA cm^{-2} for overall water splitting between the eletrolyzer of $Ni_3FeN@C/NF$ // $Ni_3N@C/NF$ and some recently reported electrolyzer fabricated with bifunctional electrocatalysts in 1 M KOH electrolyte.

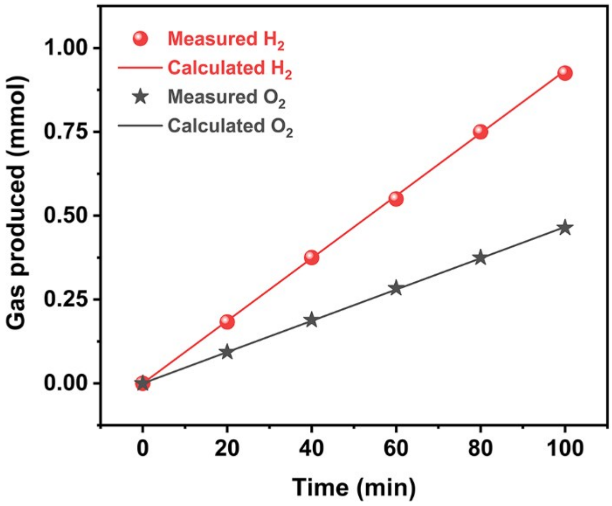

Fig. S28 Experimental and theoretical amounts of H_2 and O_2 production by the Ni_3FeN@C/NF // Ni_3N@C/NF electrolyzer for overall seawater splitting.

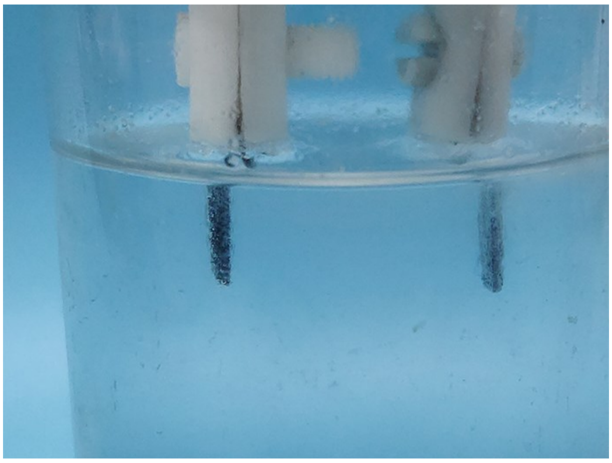

Fig. S29 Photograph of the two-electrode electrolyzer for overall seawater splitting at a current density of 100 mA cm^{-2}.

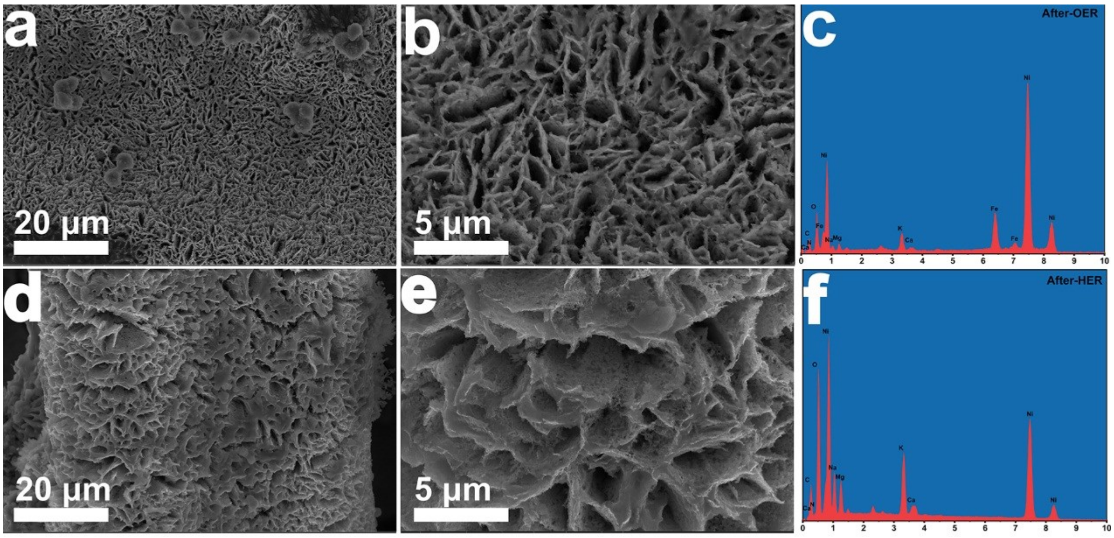

Fig. S30 (a, b) SEM images and (c) EDS spectrum of $Ni_3FeN@C/NF$ electrode after 100 h continuous test at a current density of 100 mA cm^{-2}; (d, e) SEM images and (f) EDS spectrum of $Ni_3N@C/NF$ electrode after 100 h continuous test at a current density of 100 mA cm^{-2}.

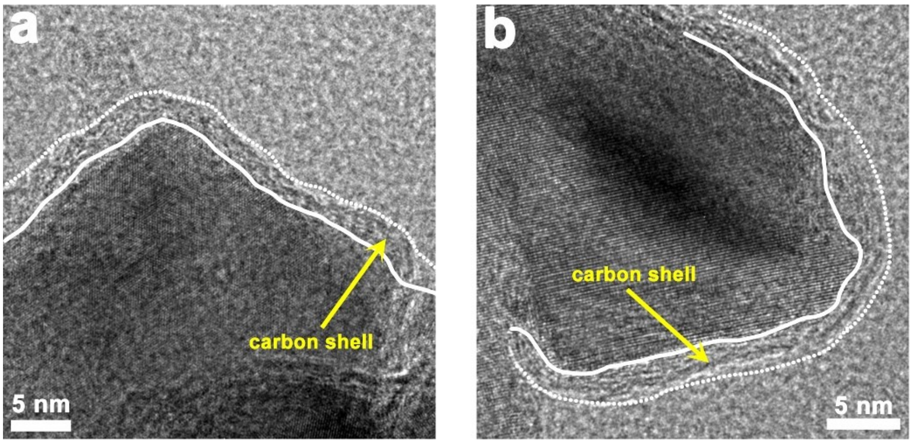

Fig. S31 HRTEM images of (a) $Ni_3FeN@C/NF$ and (b) $Ni_3N@C/NF$ electrodes after 100 h continuous test at a current density of 100 mA cm^{-2}.

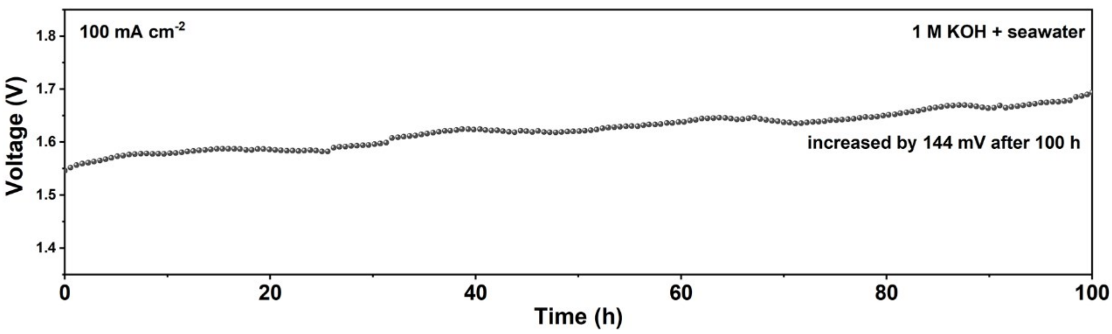

Fig. S32 OER stability of Ni_3FeN/NF tested at a current density of 100 mA cm^{-2} in the alkaline seawater electrolyte.

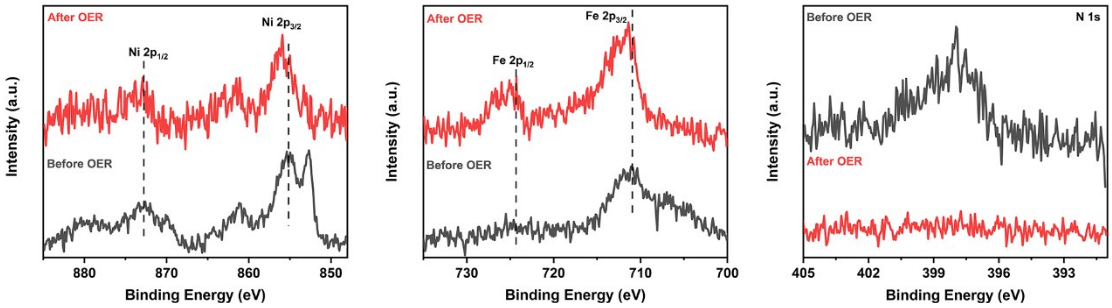

Fig. S33 High-resolution XPS spectra of the initial Ni_3FeN@C/NF electrode and Ni_3FeN@C/NF electrode after 100 h continuous test at a current density of 100 mA cm^{-2}, (a) Ni 2p, (b) Fe 2p and (c) N 1s.

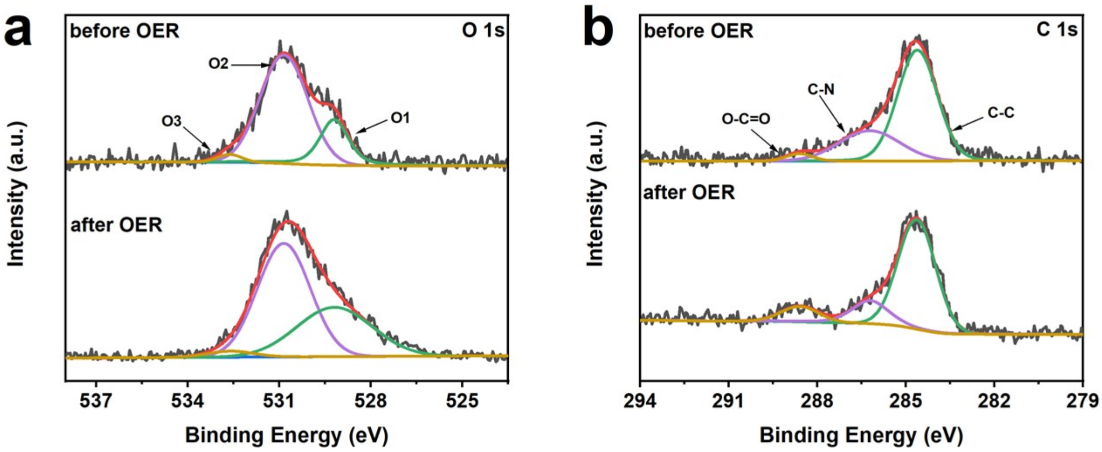

Fig. S34 High-resolution XPS spectra of the initial Ni_3FeN@C/NF electrode and Ni_3FeN@C/NF electrode after 100 h continuous test at a current density of 100 mA cm^{-2}, (a) O 1s and (b) C 1s.

In the O 1s spectrum (Fig. S34a), the binding energy of 529.8 eV is assigned to the typical metal−oxygen species, the binding energy of 531.3 eV can be ascribed to defects, contaminants, and surface species including hydroxyls, chemisorbed oxygen, and under-coordinated lattice oxygen, and the binding energy of 532.4 eV is associated with the unavoidable adsorbed water. (ACS Appl. Mater. Interfaces, 2013, **5**, 981-988; Microporous Mesoporous Mater., 2014, **200**, 92-100) It is evident that the metal−oxygen species increased after OER stability test. The C 1s spectrum in Figure S34b shows C−C species (284.8 eV), C−N species (286.2 eV), and O−C=O species (288.9 eV). (Appl. Surf. Sci., 2017, **400**, 245-253) The C−N species decreased and the O−C=O species increased after OER stability test, which confirms an electron-transfer interaction between the carbon coating and Ni_3FeN. (Angew. Chem., 2019, **131**, 16042-16050)

Table S1. Some recently reported electrocatalysts and $Ni_3FeN@C/NF$ in this work to achieve a current density of 100 mA cm^{-2} for OER in 1 M KOH electrolyte.

Electrocatalysts	Support	η (mV)	References
$Ni_3FeN@C/NF$	Ni foam	279	This work
CoNi-MOFNA	CoNi alloy foam	250	Nano Energy, 2020, 68 104296
CoVFeN@NF	Ni foam	264	Adv. Energy Mater., 2020, 10, 2002464
NiMoN@NiFeN	Ni foam	277	Nat. Commun., 2019, 10, 5106
NiFe-LDH/NF	Ni foam	281*	Small Methods, 2020, 4, 1900796
S-(Ni,Fe)OOH	Ni foam	281	Energy Environ. Sci., 2020, 13, 3439-3446
NiV-LDH@FeOOH	Ni foam	297	Chem. Commun., 2020, 56, 9360-9363
Co_4N-CeO_2/GP	Graphite plate	310*	Adv. Funct. Mater., 2020, 30, 1910596
Nickel–Cobalt nitride	carbon cloth	311*	J. Mater. Chem. A, 2018, 6, 4466-4476
$FeOOH/Ni_3N$	carbon fiber	333*	Appl. Catal., B, 2020, 269, 118600
$NiCo-nitrides/NiCo_2O_4/GF$	graphite fibers	431	Adv. Sci., 2019, 6, 1801829
$Ni_3N-NiMoN-5$	carbon cloth	509*	Nano Energy, 2018, 44, 353-363

* The value is calculated from the curves shown in the literatures.

Table S2. OER turnover frequency values for different samples at the overpotential of 300 mV.

Electrocatalysts	TOF (s^{-1})
Ni-OH/NF	0.010
Ni_3Fe-OH/NF	0.28
$Ni_3FeN@C/NF$	0.31
$Ni_3N@C/NF$	0.017

Table S3. HER turnover frequency values for different samples at the overpotential of 250 mV.

Electrocatalysts	TOF (s^{-1})
Ni-OH/NF	0.11
Ni_3Fe-OH/NF	0.08
$Ni_3FeN@C/NF$	0.18
$Ni_3N@C/NF$	2.32

Table S4. Comparison of the voltages required to achieve a current density of 100 mA cm^{-2} for overall water splitting between the eletrolyzer of $Ni_3FeN@C/NF$ // $Ni_3N@C/NF$ and some recently reported electrolyzer fabricated with bifunctional electrocatalysts in 1 M KOH electrolyte.

Water alkaline electrolyzer	Support	Cell voltage (V) at 100 mA cm^{-2}	Reference
FeP/Ni_2P	Ni foam	1.6	Nat. Commun., 2018, 9, 2551
$Ni_3FeN@C/NF$ // $Ni_3N@C/NF$	Ni foam	1.61	This work
$Ni/NiFeMoO_x/NF$	Ni foam	1.63	Adv. Sci., 2020, 7, 1902034
$Ni_2P\text{-}Fe_2P/NF$	Ni foam	1.682	Adv. Funct. Mater., 2020, 2006484
$Fe_{0.09}Co_{0.13}\text{-}NiSe_2/CFC$	Carbon fiber cloth	1.682*	Adv. Mater., 2018, 30, 1802121
Cu@NiFe LDH	Cu foam	1.69	Energy Environ. Sci., 2017, 10, 1820-1827
NiFeRu LDH/NF	Ni foam	1.705	Adv. Mater., 2018, 30, 1706279
NFN-MOF/NF	Ni foam	1.725*	Adv. Energy Mater. 2018, 8, 1801065
$Co_4N\text{-}CeO_2/GP$	Graphite plate	1.728	Adv. Funct. Mater., 2020, 30, 1910596
$FeOOH/N_3N$	carbon fiber	1.754*	Appl. Catal., B, 2020, 269, 118600
Ni-ZIF/Ni-B/NF	Ni foam	1.78	Adv. Energy Mater., 2020, 10, 1902714
Co-Mo-P/CoNWs	Ni foam	1.78	Adv. Funct. Mater., 2020, 30, 2002533
Ni@NiFe LDH	Ni foam	1.78	J. Mater. Chem. A, 2019, 7, 21722-21729
$NiFe\text{-}MOF/NiSe_x/NF$	Ni foam	1.808*	J. Mater. Chem. A, 2020, 8, 16908-16912
$Ru/Ni_3N\text{-}Ni$	glassy carbon	1.832*	Chem. Commun., 2020, 56, 2352-2355
$Co_3S_4/EC\text{-}MOF$	carbon cloth	1.874*	Adv. Mater., 2019, 31, 1806672
Nickel-Cobalt nitride/CC	carbon cloth	2*	J. Mater. Chem. A, 2018, 6, 4466-4476

* The value is calculated from the curves shown in the literatures.