

Supplementary Information

Ultrathin hollow hemisphere-carbon-anchored Ni₃FeN nanoparticles as nanoreactors facilitating the formation of NiC_x with long-term durability for the oxygen evolution reaction

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1. Experimental section

1.1 Prepared Electrodes

Synthesis of SiO₂ Templates: All the chemicals were analytical grade; they were used without further purification. The SiO₂ Templates were prepared as previous reports.¹ 300 mL of ethanol, 6 mL of distilled water, 21 mL of ammonia and 24 mL of tetraethoxysilane (TEOS) were stirring at 35 °C for 8 h. The white precipitate was centrifuged and washed with ethanol and distilled water, and calcinated at 420 °C for 2 h in air.

Synthesis of HC/NF

Nickel Foam (NF) was soaked in ethanol continuous ultrasound for 30 min and repeated 3 times to obtain clean NFs. The as prepared SiO₂ and pitch with a mass ratio of 1:0.09 were added into tetrahydrofuran (THF) under violently stirring for 4 h. Take 240 μL mixed solution and apply it to the blank Ni foam. NF with solution was carbonized under N₂ flow at several temperature (550 °C, 650 °C, 750 °C, 850 °C, 950 °C) for 2 h with a heating rate of 5 °C min⁻¹. After being cooled down to room temperature, the Ni foam (NF) with production (pre-HC) were dipped in NaOH solution 48 h to removed SiO₂ templates. Pre-HC/NF were washed several times (DI water and ethanol) and dried at 60 °C for 2 h. HC/NF was obtained by annealing Ni₃Fe-HC/NF at 400 °C for 2 h under NH₃ (heating rate: 5 °C min⁻¹).

Synthesis of Ni₃FeN-HC/NF

Ni₃FeN-HC/NF was prepared similarly to HC/NF, but nickel nitrate and iron nitrate with a molar ratio of 3:1 are added to the mixture of SiO₂ and pitch. The NF with precursor of Ni₃FeN-HC was calcined under N₂ atmosphere for 2h at 850 °C (heating

rate: 5 °C min⁻¹); then, the SiO₂ in product were removed by immersion in NaOH solution to get pre-Ni₃FeN-HC/NF; finally, the Ni₃FeN-HC/NF was obtained by calcining pre-Ni₃FeN-HC/NF under NH₃ for 2 h at 400 °C (heating rate: 5 °C min⁻¹).

Synthesis of Ni₃FeN-HC/NF(D)

Dropping nickel nitrate and iron nitrate with a molar ratio of 3:1 to the pre-HC/NF, and was subjected to the same nitriding process to obtain Ni₃FeN-HC/NF(D).

Synthesis of Ni₃FeN-C/NF

Ni₃FeN-C/NF was prepared by the same method with Ni₃FeN-HC/NF but without SiO₂.

Synthesis of Ni₃FeN/NF

Iron nitrate and nickel nitrate were dissolved in THF in a ratio of 1:3, and then dropped onto NF nickel. Then it was held at 850 °C in nitrogen atmosphere for 2 h, followed by 400 °C in ammonia atmosphere for 2 h, which was consistent with the high-temperature treatment process of HC/NF to obtain electrode Ni₃FeN/NF.

Commercial RuO₂/C/NF (Pt/C/NF) electrode: for comparison, RuO₂/C/NF (Pt/C/NF) electrode was prepared as follow: 5.0 mg of RuO₂/C (Pt/C) were dispersed in a mixture containing 20 μL Nafion (5 w%), 50 μL ethanol, 50 μL isopropanol, the mixture solution was ultrasonicated for 30 min to obtain ink. 120 μL ink was then loaded on a clean 1 cm *1 cm NF.

1.2 Materials characterization

Thermogravimetric (TG) was carried out with a STA449F5 instrument and the temperature range is 20-1000 °C with a heating rate of 10 °C min⁻¹ under the N₂ atmosphere. The X-ray diffraction (XRD) measurement were carried out on an X-ray diffractometer (Panalytical Aries) with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). Renishaw/inVia Qontor with an excitation laser of 532 nm was used to detect Raman signal. The X-ray photoelectron spectroscopy (XPS; Thermo Fisher, USA) was recorded with a monochromatic Al K α radiation source, and was corrected for surface charging by referencing to the designate hydrocarbon C 1s binding energy at 284.8 eV. Transmission electron microscopy (TEM) images were obtained on JEM-2100 (Japan) transmission electron microscope at an operating voltage of 200 kV. Brunauer-Emmet-Teller analysis was done on a Micromeritics Instrument Corporation sorption analyzer (Micromeritics TriStar II 3020). Total Organic Carbon (TOC) was measured with ELEMENTAR, vario TOC. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was obtained with Agilent 7700s. The contact angle (CA) measurements were performed on a Kino SL250 system at ambient temperature.

1.3 Electrochemical measurements:

Electrochemical experiments were done on a typical three-electrode system by an electrochemical work station (CHI 760E) and with an electrolyte of 1 M O₂-saturated KOH solution for OER test. A prepared electrode, a Hg/HgO electrode, a graphite rod

was used as the working, reference, counter electrodes, respectively. Before the linear sweep voltammetry (LSV) tests for OER, the repeated cyclic voltammogram (CV) cycles were carried out with a scan rate of 100 mV s^{-1} to obtain steady voltammogram curves, and the LSV were tested with a scan rate of 5 mV s^{-1} . The OER polarization curves were 85% iR-corrected. The EIS measurement were performed at 294 mV (vs. RHE) with the scanning frequency values ranging from 100 kHz to 0.01 Hz. The electrochemical double-layer capacitance (C_{dl}) of the catalytic surface was obtained by CV test in a non-faradaic potential range of 0.781~0.881 V (vs. RHE) at various scan rate (v) of 5, 10, 20, 40, 60, 80, 100, 120, 140, 160 180 and 200 mV s^{-1} . By plotting the current density (J) difference between the anodic and cathodic sweeps at the middle potential versus scan rate, C_{dl} is half of the linear slope.² The electrochemically active surface area (ECSA) could be estimated by the C_{dl} ($\text{ECSA} = C_{dl}/C_s$, $C_s = 0.060 \text{ mF cm}^{-2}$)³. All potentials in this work were referenced to the reversible hydrogen electrode (RHE), and the converted equation is $E(\text{RHE}) = E(\text{Hg}/\text{HgO}) + E_{\text{Hg}/\text{HgO}}^0 (0.924 \text{ V})$ in 1 M KOH at pH=14⁴.

2. Figures and tables

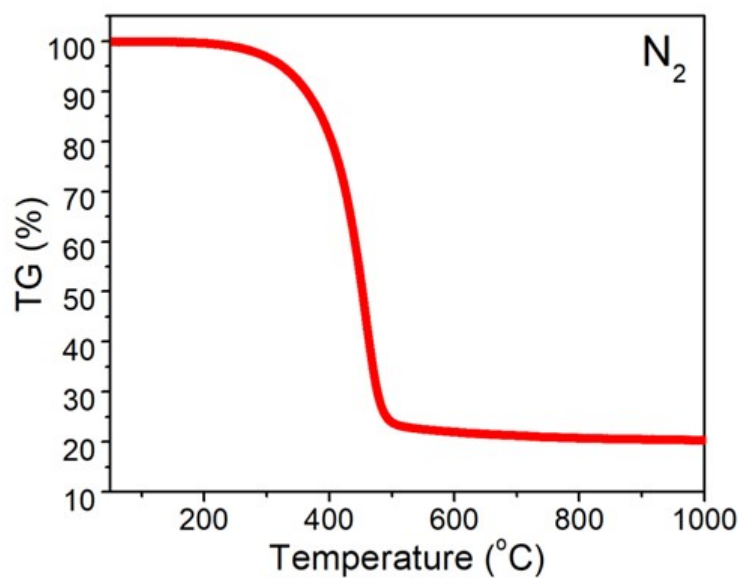


Figure. S1 TG curves of Pitch

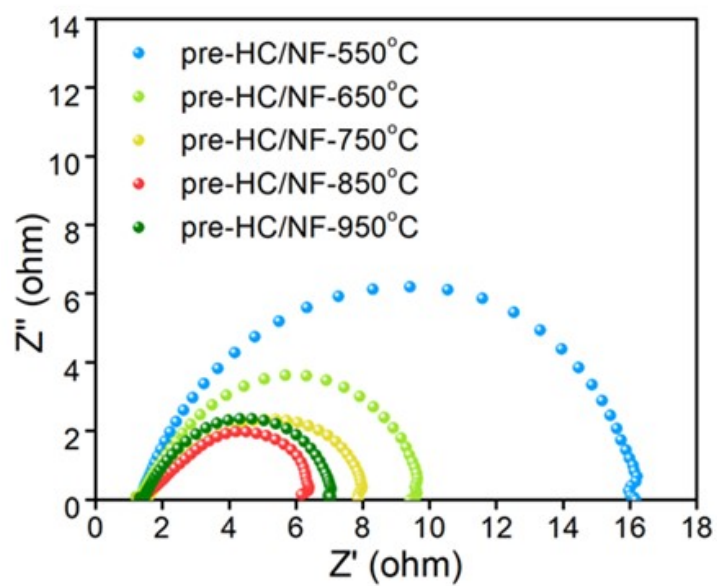


Figure. S2 Nyquist plots of pre-HC/NF in 1 M KOH.

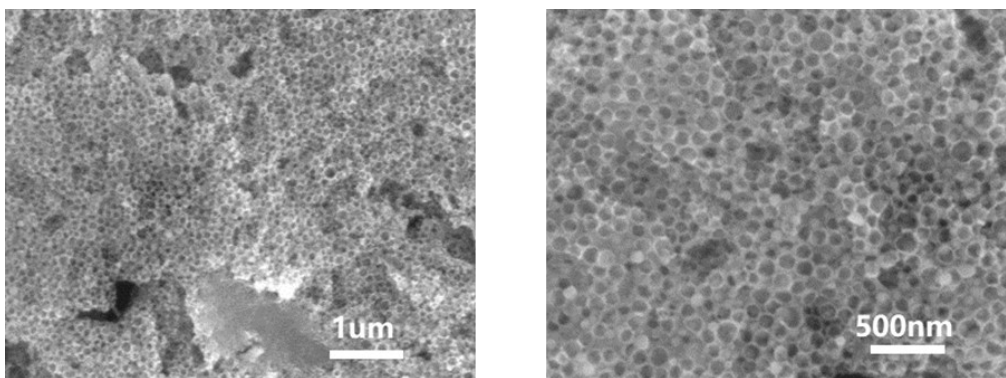


Figure S3. SEM images of pre-HC/NF (850 °C).

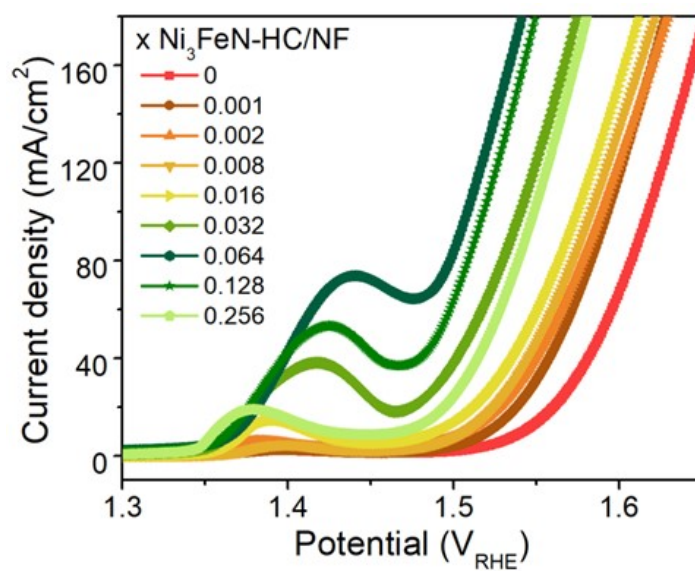


Figure S4. OER linear sweeping voltammetry curves of X Ni₃FeN-HC/NF in 1 M KOH.

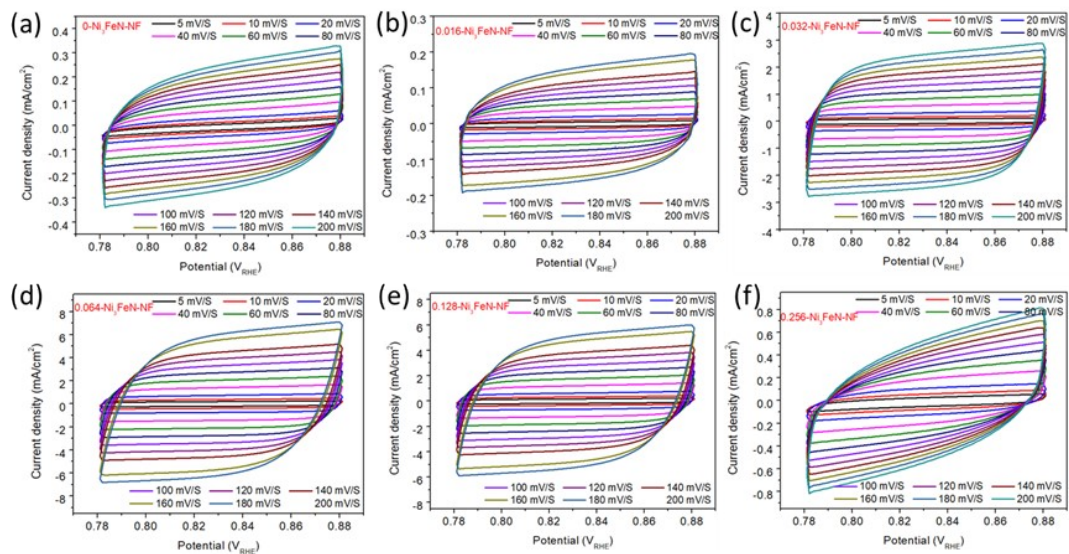


Figure. S5. Cyclic voltammograms at different scan rates in the potential range of 0.781-0.881 V (vs. RHE) for x-Ni₃FeN-HC/NF electrodes.

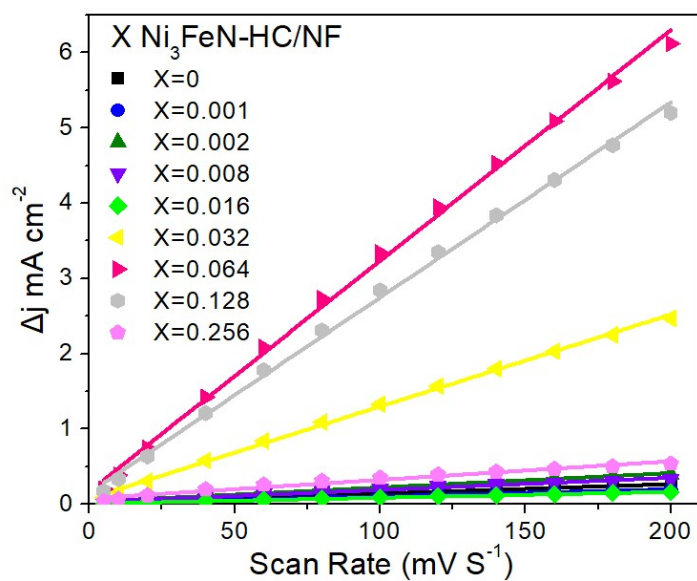


Figure. S6. The double-layer current density difference plotted as a function of scan rate fitted to a linear regression for C_{dl} of x-Ni₃FeN-HC/NF.

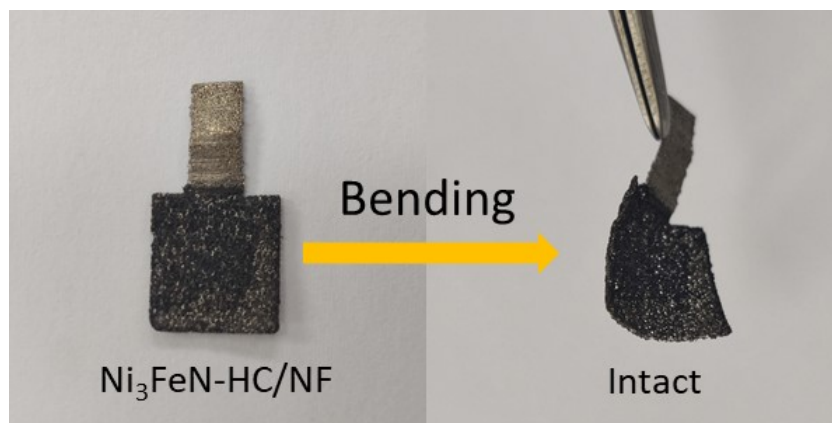


Figure. S7. Photographs of $\text{Ni}_3\text{FeN-HC/NF}$ at original and bending states.

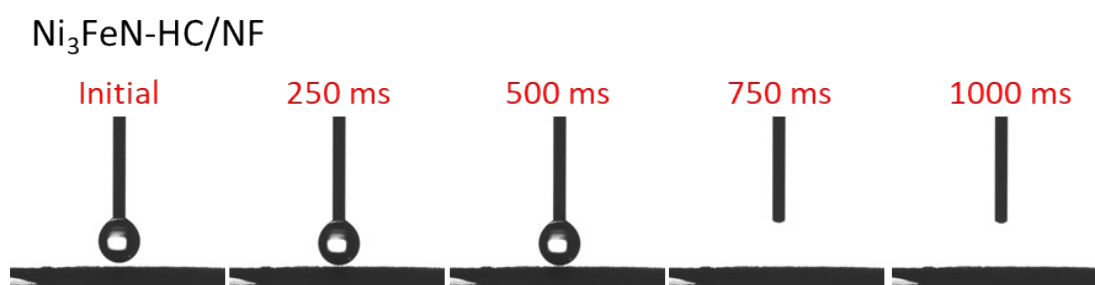


Figure. S8. Penetration process of a water droplet on $\text{Ni}_3\text{FeN-HC/NF}$.

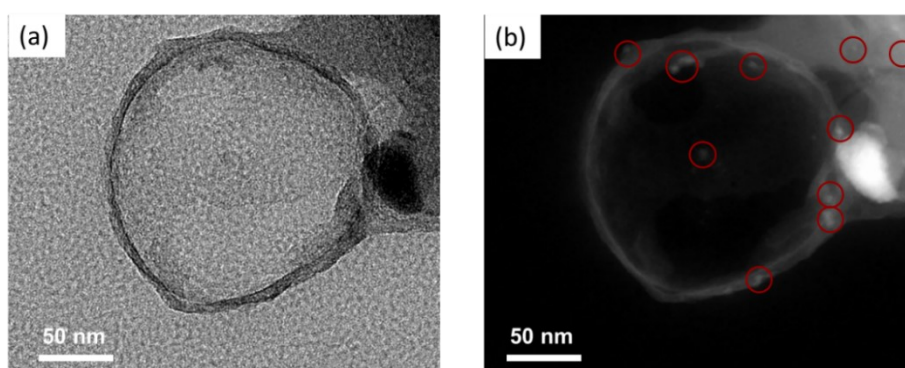


Figure. S9. TEM and HAADF-STEM patterns of $\text{Ni}_3\text{FeN-HC/NF}$.

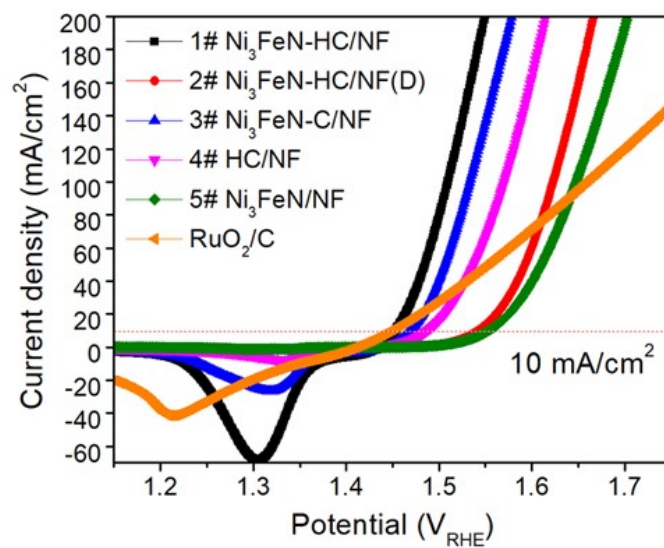


Figure. S10. OER linear sweeping voltammetry curves by negative scanning of different electrodes ($\text{Ni}_3\text{FeN-HC/NF}$, $\text{Ni}_3\text{FeN-HC/NF(D)}$, $\text{Ni}_3\text{FeN-C/NF}$, HC/NF , $\text{Ni}_3\text{FeN/NF}$ and RuO_2/C).

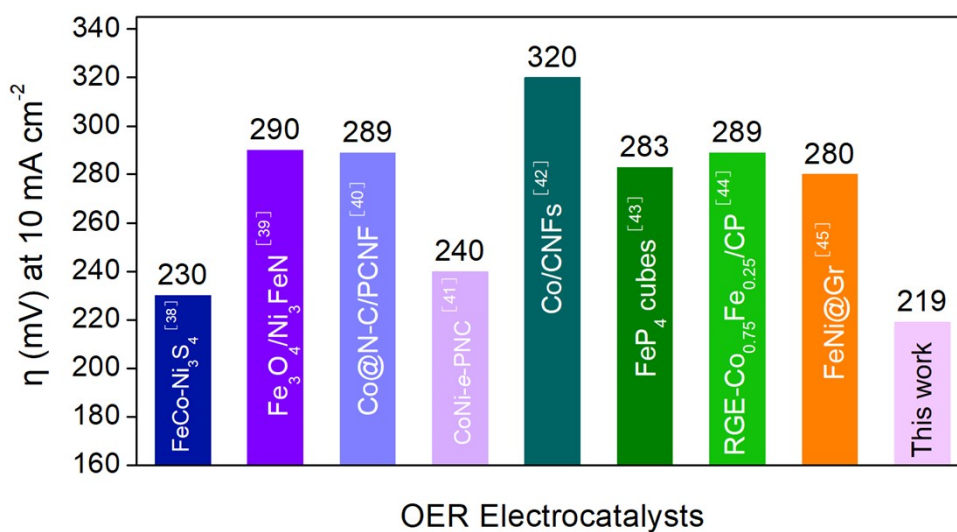


Figure. S11. Comparison of overpotential at 10 mA cm^{-2} for $\text{Ni}_3\text{FeN-HC/NF}$ with currently reported OER electrocatalysts.

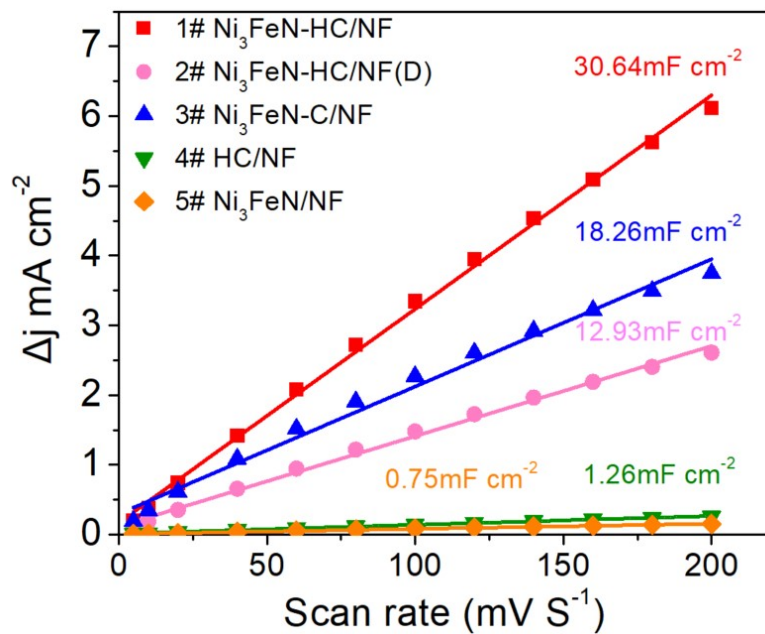


Figure. S12. The double-layer current density difference plotted as a function of scan rate fitted to a linear regression for C_{dl} of $Ni_3FeN-HC/NF$, $Ni_3FeN-HC/NF(D)$, Ni_3FeN-C/NF , HC/NF and Ni_3FeN/NF .

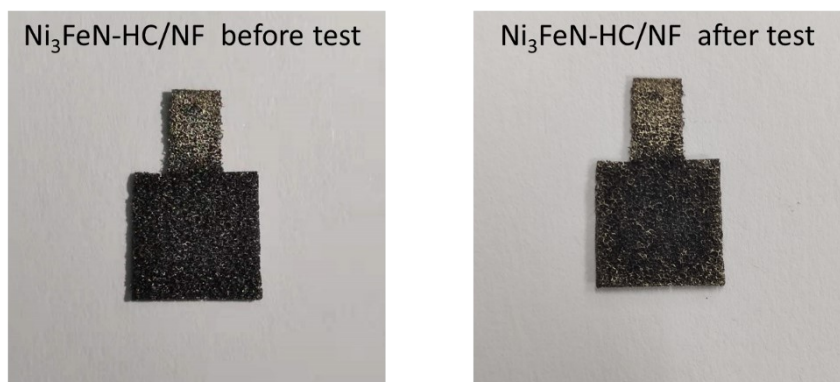


Figure. S13. The photograph of $Ni_3FeN-HC/NF$ electrode and $Ni_3FeN-HC/NF$ electrode after OER.

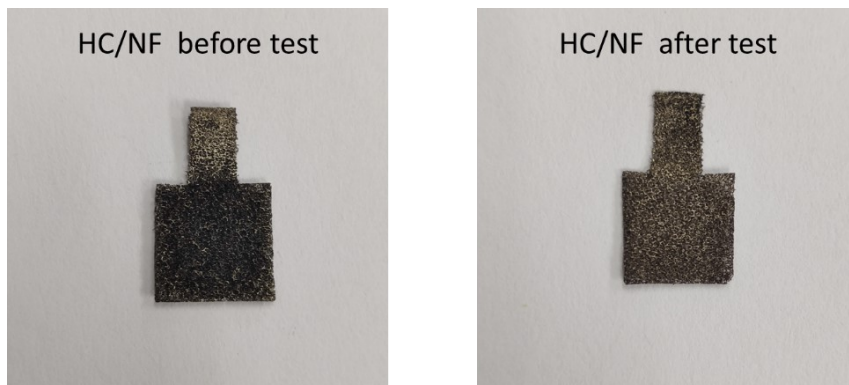


Figure. S14. The photograph of HC/NF electrode and HC/NF electrode after OER.

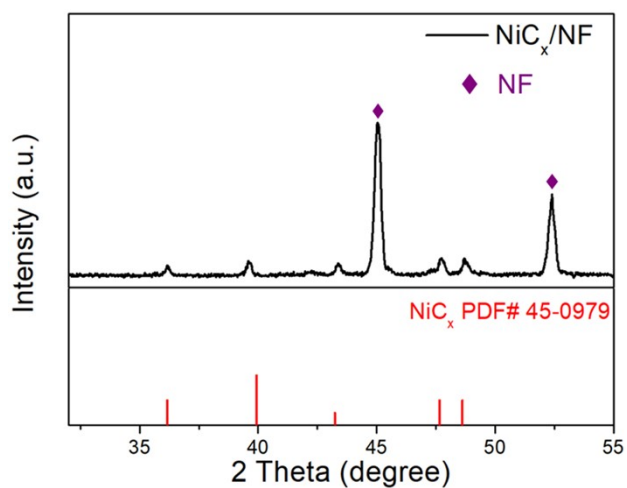


Figure. S15. XRD pattern of NiC_x/NF.

The NiC_x/NF was prepared according to the previous report.⁵ The main peaks at 36.15°, 39.64°, 43.37°, 47.74° and 48.69° are well matched with (114), (204), (205), (123) and (009) of NiC_x (PDF#45-0979); and other peaks belong to NF. This result suggests the NiC_x was synthesized on the surface of NF successfully

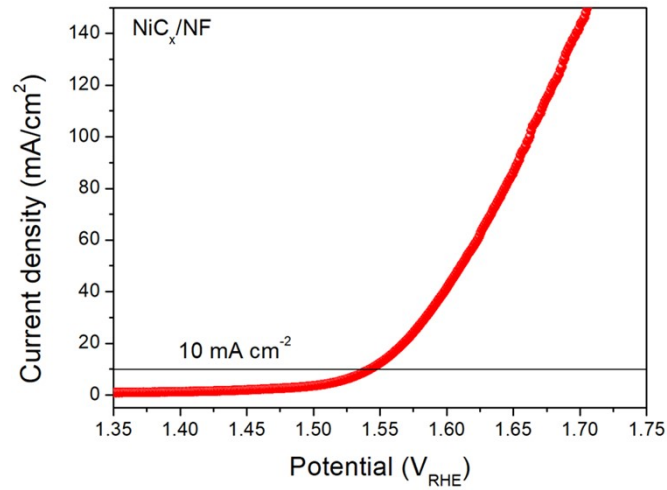


Figure. S16. OER linear sweeping voltammetry curve of NiC_x/NF .

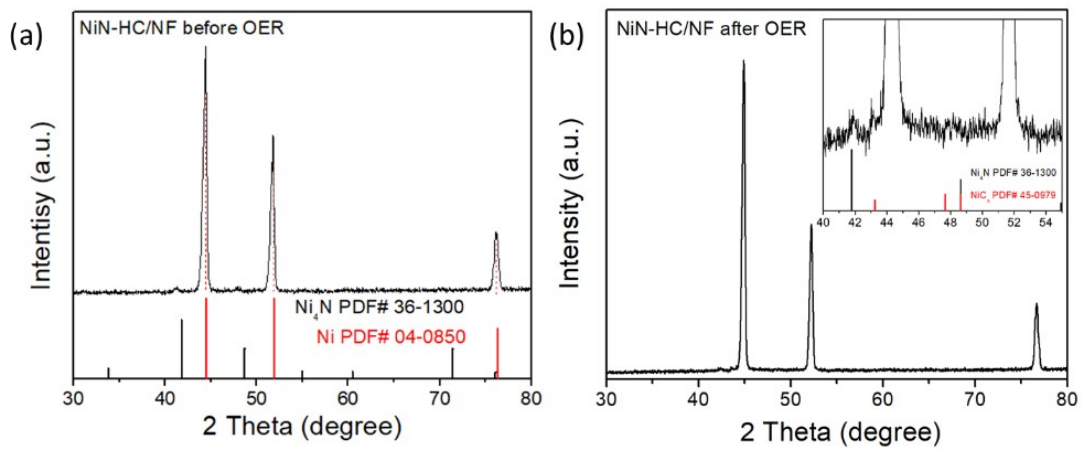


Figure. S17. XRD patterns spectra of NiN-HC/NF before and after 72 hours OER stability testing.

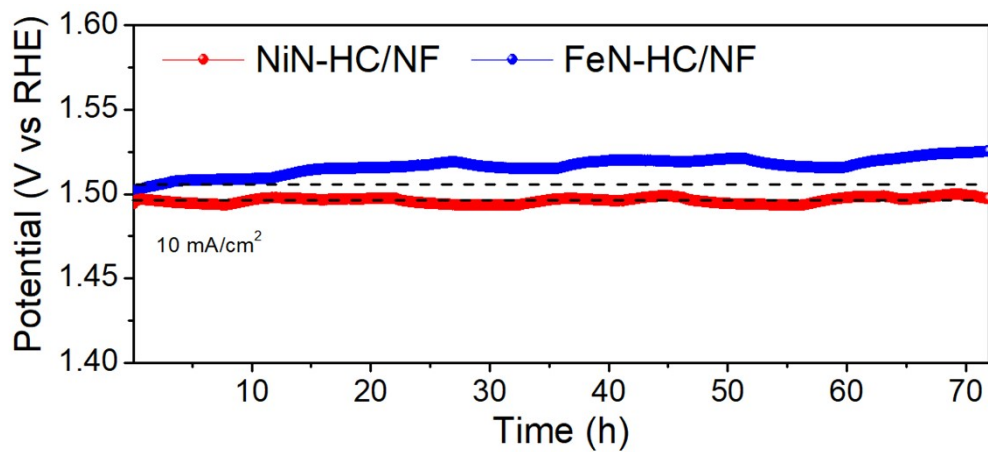


Figure S18. Long-term stability testing of the set of NiN-HC/NF and FeN-HC/NF at 10 mA cm^{-2} .

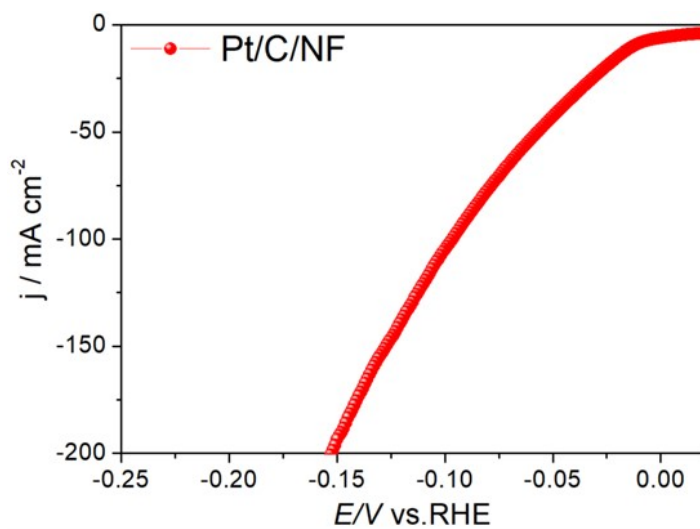


Figure. S19. LSV curve of Pt/C/NF towards HER in 1M KOH.

This Pt/C/NF electrode possesses a relatively smaller overpotential of 12 mV for HER in 1.0 M KOH according to the LSV curves

Table S1. TOC, TIC and ICP-MS result of the concentration of C, Fe and Ni in 1 M KOH electrolyte before and after stability test of 72 hours for Ni₃FeN-HC/NF electrode.

Element concentration		Original electrolyte	Electrolyte after stability testing of 72 h
C (mg/L)	TOC	1.503	2.263
	TIC	1.707	1.696
Fe (mg/L)		0.0013	0.0233
Ni (mg/L)		0.0004	0.0061

Notes and references

1. L. Sheng, L. Jiang, T. Wei, Z. Liu and Z. Fan, *Adv. Energy Mater.*, 2017, **7**, 1700668.
2. J. Zhu, E. Jiang, X. Wang, Z. Pan, X. Xu, S. Ma, P. Kang Shen, L. Pan, M. Eguchi, A. K. Nanjundan, J. Shapter and Y. Yamauchi, *Chem. Eng. J.*, 2022, **427**, 130946.
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5. H. Yang, S. Luo, X. Li, S. Li, J. Jin and J. Ma, *J. Mater. Chem. A*, 2016, **4**, 18499-18508.