

Supporting Information

Self-supported bifunctional MoNi₄ framework by iron doping for ultra-efficient water splitting

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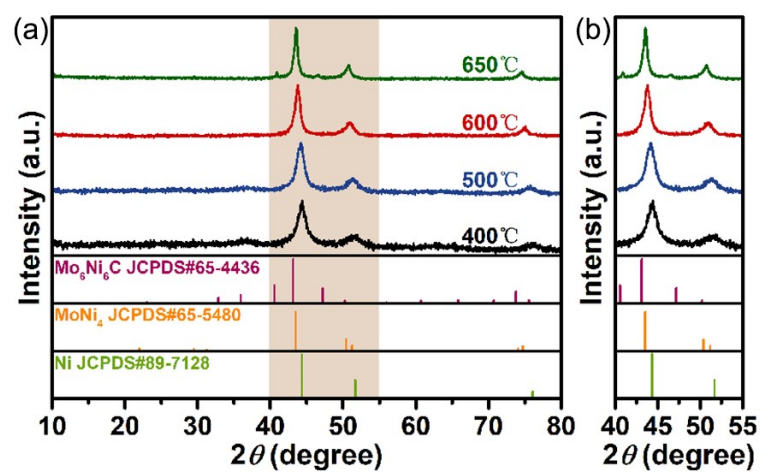


Fig. S1 The XRD pattern of the MNF_{2.5} CFs samples treated under different temperature from 400 °C to 650 °C. (a) XRD patterns, (b) magnified XRD patterns in the 2θ range from 40° to 55°.

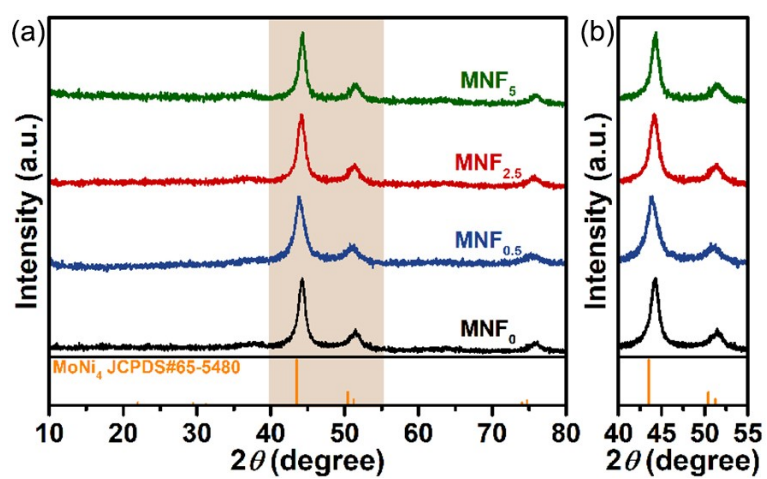


Fig. S2 The XRD patterns of MNF_n CFs samples with various Fe addition treated under 500 °C. (a) XRD patterns, (b) magnified XRD patterns in the 2θ range from 40° to 55°.

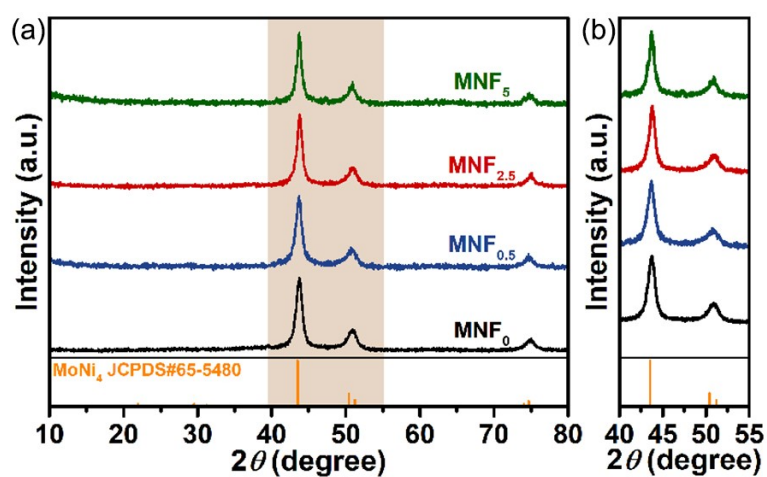


Fig. S3 The XRD patterns of MNF_n CFs samples with different Fe addition, which were treated at 600 °C. (a) XRD patterns, (b) magnified XRD patterns in the 2θ range from 40° to 55°.

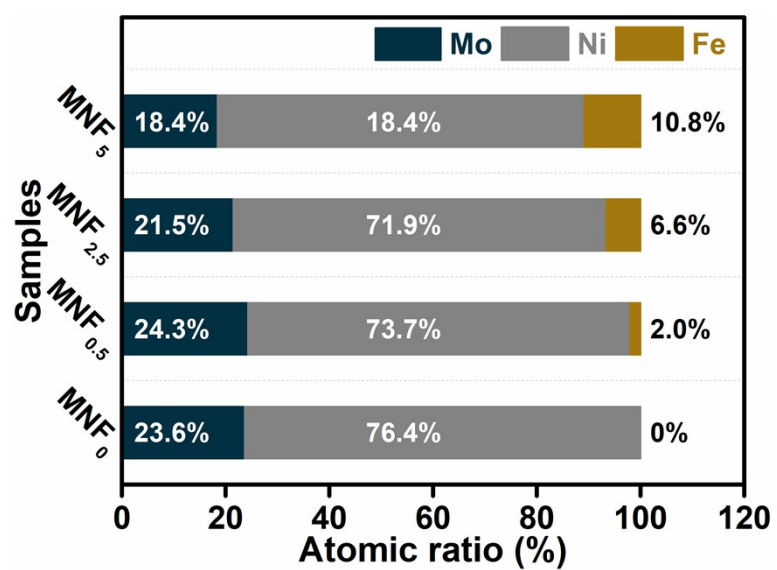


Fig. S4 The elemental ratios of Mo, Ni, and Fe in the series of MNF_n CFs samples by ICP-OES.

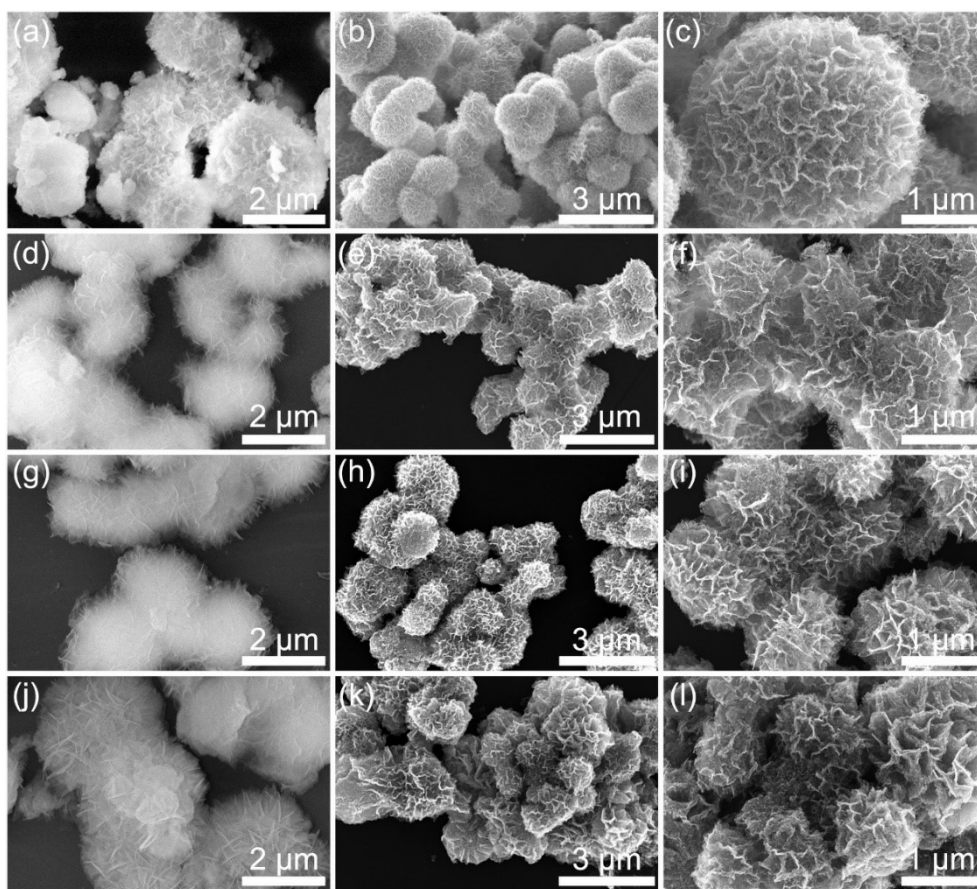


Fig. S5 The SEM images of MNF_n CFs samples with different Fe addition, which were treated at 500 °C. (a) MNF_0 precursor and (b-c) MNF_0 , (d) $\text{MNF}_{0.5}$ precursor and (e-f) $\text{MNF}_{0.5}$, (g) $\text{MNF}_{2.5}$ precursor and (h-i) $\text{MNF}_{2.5}$, and (j) MNF_5 precursor and (k-l) MNF_5 CFs.

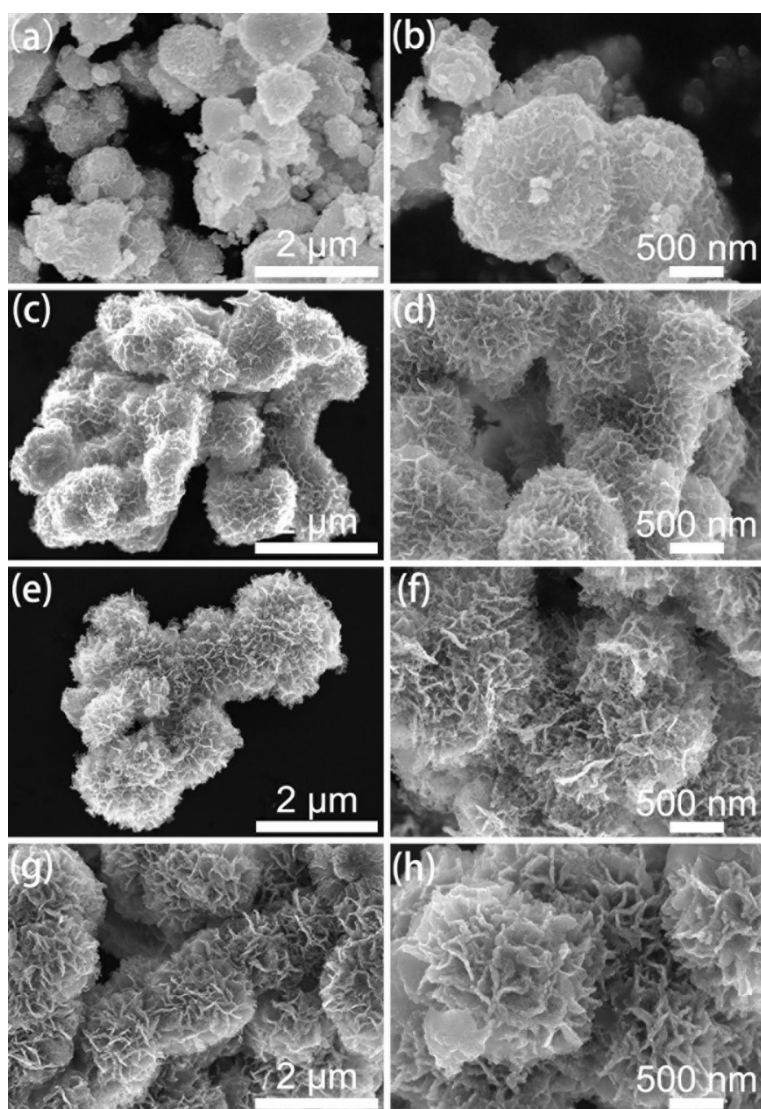


Fig. S6 The SEM images of MNF_n CFs samples with different Fe addition, which were treated at 600 °C. (a-b) MNF_0 , (c-d) $\text{MNF}_{0.5}$, (e-f) $\text{MNF}_{2.5}$, and (g-h) MNF_5 CFs.

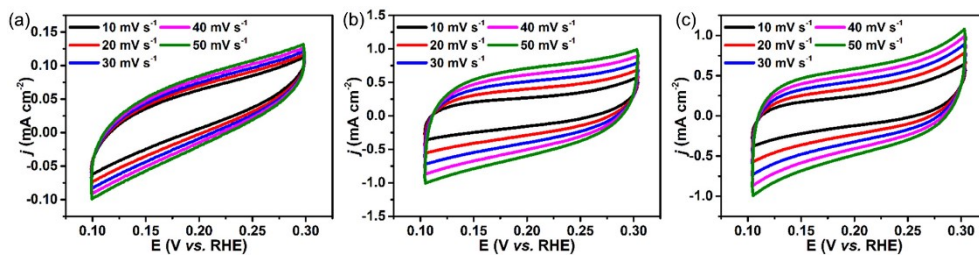


Fig. S7 Cyclic voltammograms (CV) curves of the $\text{MNF}_{2.5}$ CFs samples treated at (a) 400 °C, 500 °C, and (b) 600 °C, which were measured at various scan rates of 10, 20, 30, 40, and 50 mV s^{-1} in 1 M KOH solution.

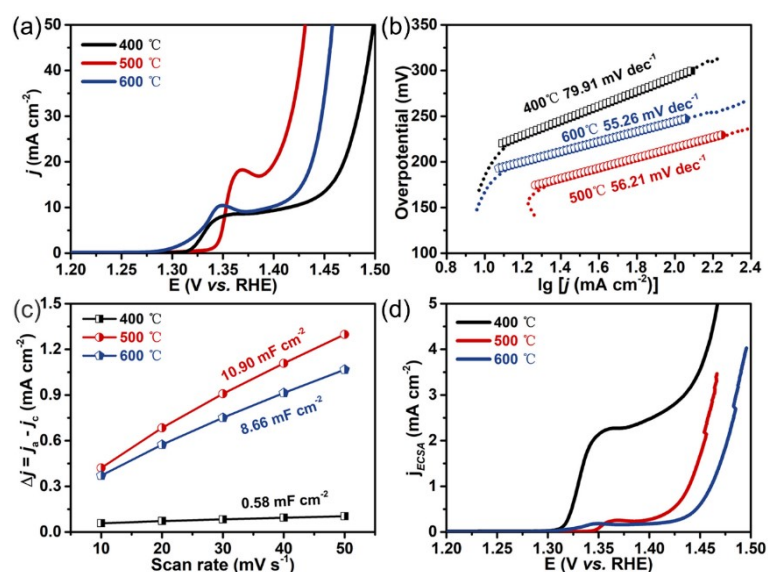


Fig. S8 (a) LSV curves of MNF_{2.5} CFs samples treated at the temperature range from 400 °C to 600 °C in 1M KOH at a scan rate of 1 mV s⁻¹, (b) corresponding Tafel plots of the series of MNF_{2.5} CFs samples, (c) C_{dl} values of the different MNF_{2.5} CFs samples, (d) normalized LSV curves by ECSA.

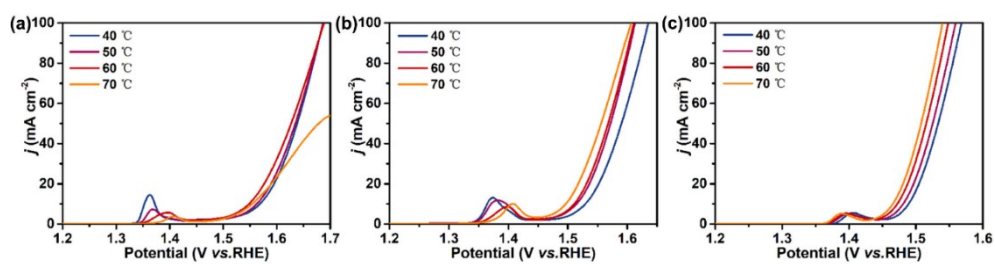


Fig. S9 OER polarization curves of the (a) MNF_0 , (b) $\text{MNF}_{0.5}$, and (c) MNF_5 CFs samples in the 1 M KOH aqueous electrolyte at different temperatures from 40 °C to 70 °C.

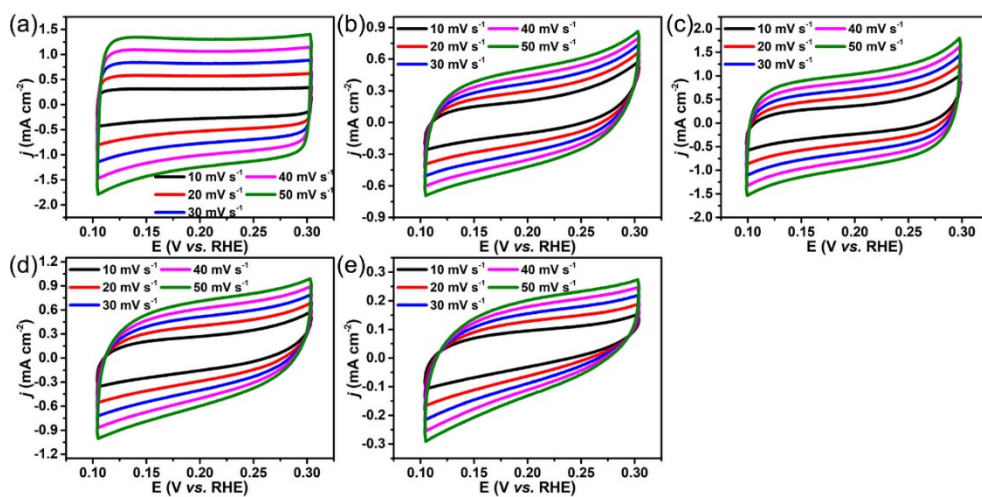


Fig. S10 Cyclic voltammograms (CV) curves of (a) IrO_2 catalyst, (b-e) the MNF_0 , $\text{MNF}_{0.5}$, $\text{MNF}_{2.5}$, and MNF_5 CFs samples treated at 500°C , which were measured at various scan rates of 10, 20, 30, 40, and 50 mV s^{-1} in 1 M KOH solution.

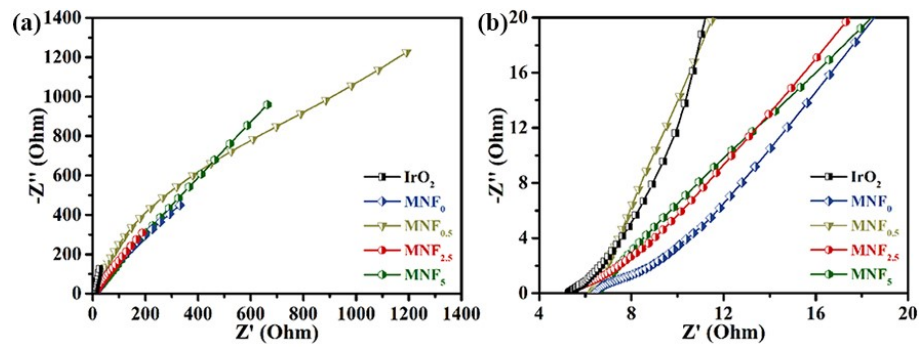


Fig. S11 The EIS spectra (a) and enlarged spectra (b) of IrO_2 and $\text{MNF}_{2.5}$ CFs in 1M KOH.

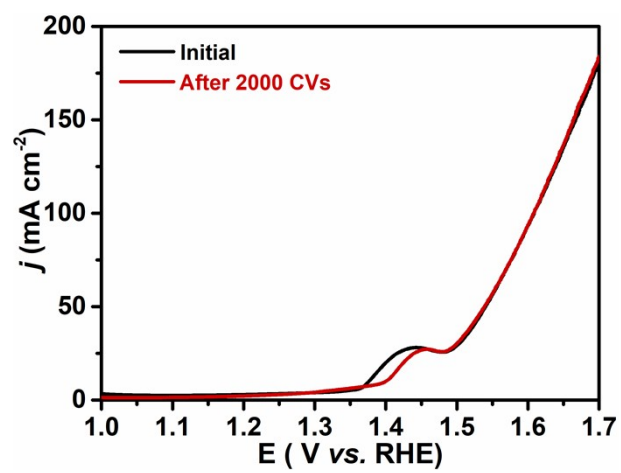


Fig. S12 Polarization curves of MNF_{2.5} CFs sample before and after 2000 CV cycles.

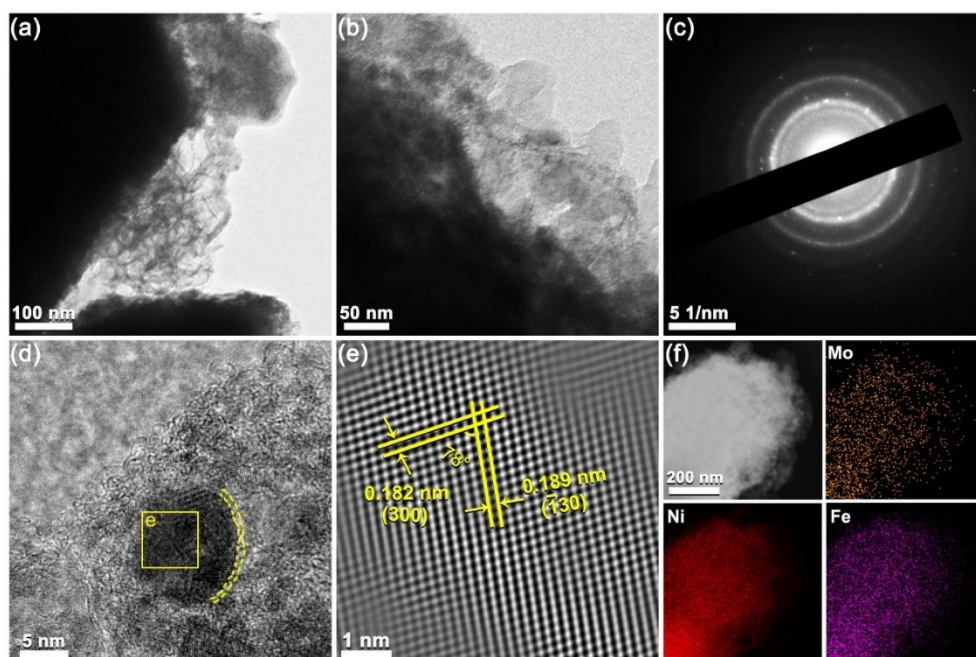


Fig. S13 The TEM images of $\text{MNF}_{2.5}$ CFs catalyst treated at 500°C after OER stability test process. (a) and (b) TEM, (c) SAED pattern, (d) HRTEM, (e) the inverse-FFT image of highlighted block in (d), and (f) the EDX elemental mapping.

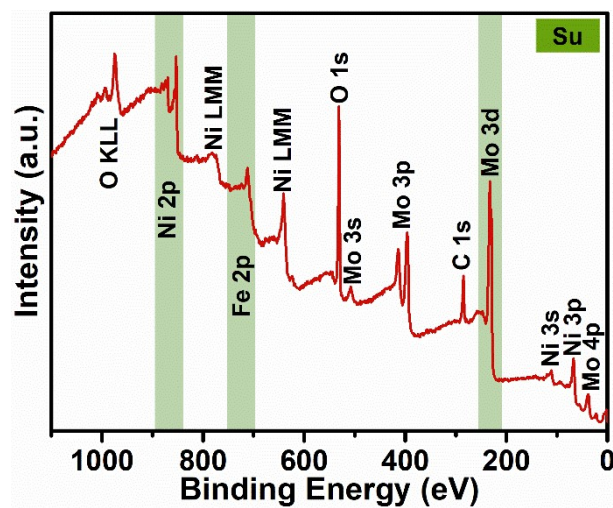


Fig. S14 The Survey XPS spectrum of the $\text{MNF}_{2.5}$ CFs sample treated at 500 °C.

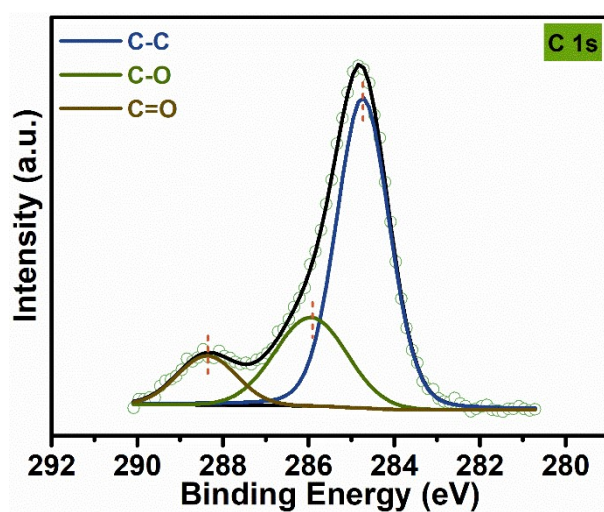


Fig. S15 High-resolution XPS spectrum of C 1s of MNF_{2.5} CFs sample treated at 500 °C.

The peaks at 284.75, 285.45, and 288.46 eV can be recognized to C-C, C-O, and C=O bonds, respectively.¹

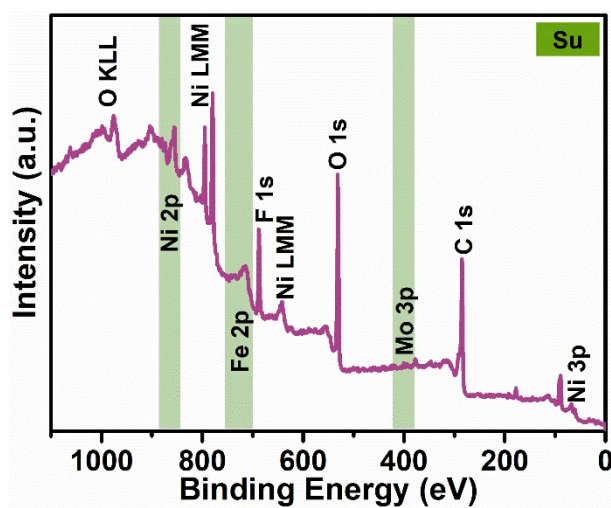


Fig. S16 The Survey XPS spectrum of the $\text{MNF}_{2.5}$ CFs sample after OER measurement.

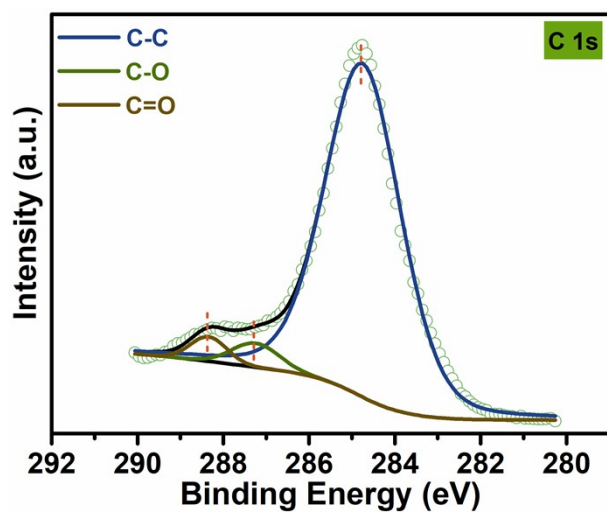


Fig. S17 High-resolution XPS spectrum of C 1s of MNF_{2.5} CFs sample after OER measurement.

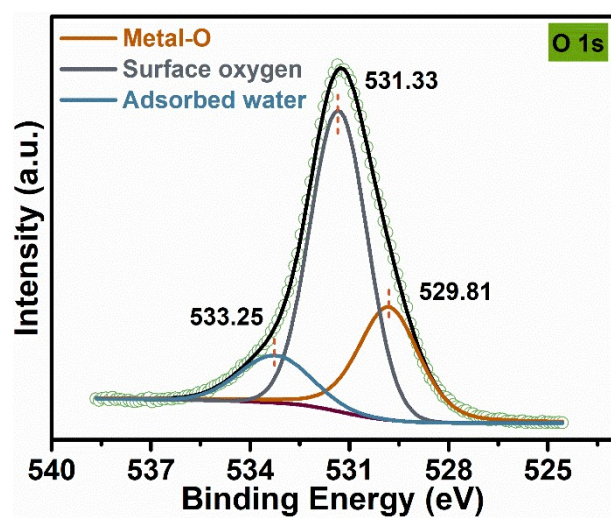


Fig. S18 High-resolution XPS spectrum of O 1s of MNF_{2.5} CFs sample after OER measurement.

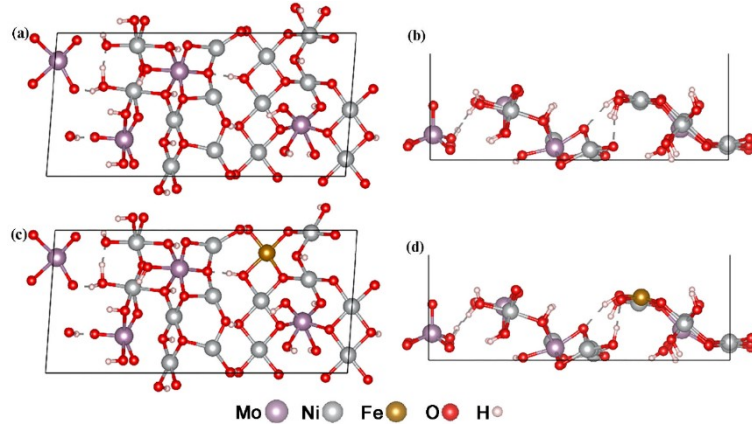
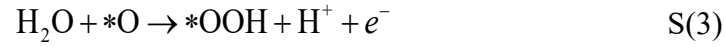


Fig. S19 Top (a) and side (b) view of MoNiOOH, top (c) and side (d) view of MoNiFeOOH.

Eq. S(1) - S(4) were adopted to express the mechanism of OER, as the four-electron transfer reaction pathway in the calculation.



Here, the * represents the catalytic active sites on the surface of the samples, and the oxygen-containing groups (*OH, *O, and *OOH) express the adsorbed intermediates on the active sites.

The free energy of the adsorbed intermediates was calculated based on the standard hydrogen electrode, defined as Eq. S(5), where E , ZPE , ΔH_t , T , and S represented the total energy, zero-point energy, the change in the heat capacity, thermal correction energy (298.15 K), and entropy, respectively. The Gibbs free energy in the OER process were obtained according to the formulas Eq. S(5) – S(12).

$$G = E + ZPE + \Delta H_t - T \cdot S \quad \text{S(5)}$$

$$ZPE = \frac{h}{2} \sum_{i=1}^{3N} \nu_i \quad \text{S(6)}$$

$$\Delta H_t = \sum_{i=1}^{3N} \frac{h\nu_i}{e^{\frac{h\nu_i}{k_B T}} - 1} \quad S(7)$$

$$T \cdot S = \sum_{i=1}^{3N} \left[\frac{h\nu_i}{e^{\frac{h\nu_i}{k_B T}} - 1} - k_B T \ln \left(1 - e^{-\frac{h\nu_i}{k_B T}} \right) \right] \quad S(8)$$

$$\Delta G_1 = G(*OH) + \frac{1}{2}G(H_2) - G(H_2O) - G(*) - eU - k_B T \ln(10) \times pH \quad S(9)$$

$$\Delta G_2 = G(*O) + \frac{1}{2}G(H_2) - G(*OH) - eU - k_B T \ln(10) \times pH \quad S(10)$$

$$\Delta G_3 = G(*OOH) + \frac{1}{2}G(H_2) - G(H_2O) - G(*O) - eU - k_B T \ln(10) \times pH \quad S(11)$$

$$\Delta G_4 = 4.92 \text{ eV} - \sum_{i=1}^3 \Delta G_i(0,0) - eU - k_B T \ln(10) \times pH \quad S(12)$$

Where U , e , and k_B is the applied electrode potential, the charge transferred, the Boltzmann constant, respectively.

The overpotential (η) was defined as below:

$$\eta = \max \{ \Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4 \} / e - 1.23 \text{ V} \quad S(13)$$

Here, 1.23 V represents the balanced potential.²

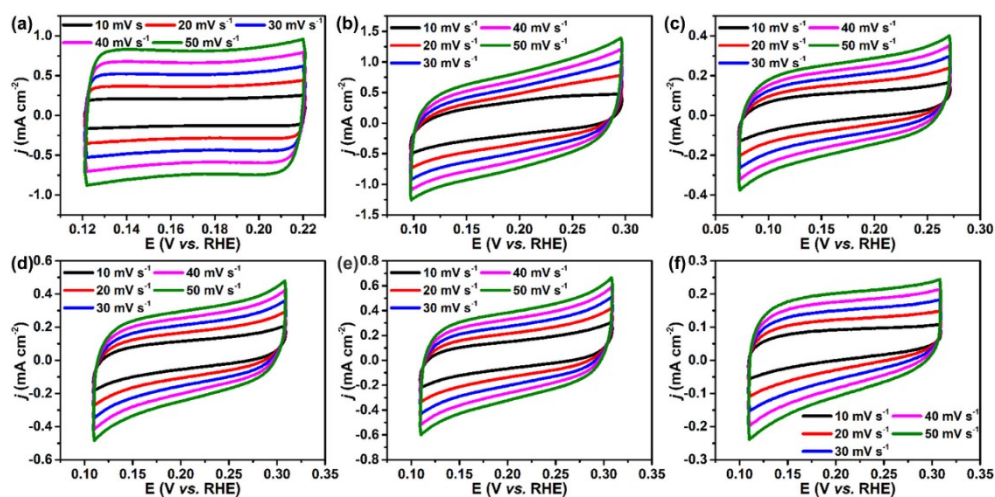


Fig. S20 Cyclic voltammograms (CV) curves of (a) 10 wt.% Pt/C catalyst, (b) MNF_{2.5} CFs annealed at 500 °C, (c-f) MNF₀, MNF_{0.5}, MNF_{2.5}, and MNF₅ CFs treated at 600 °C, which were measured at various scan rates of 10, 20, 30, 40, and 50 mV s⁻¹ in 1 M KOH solution before HER.

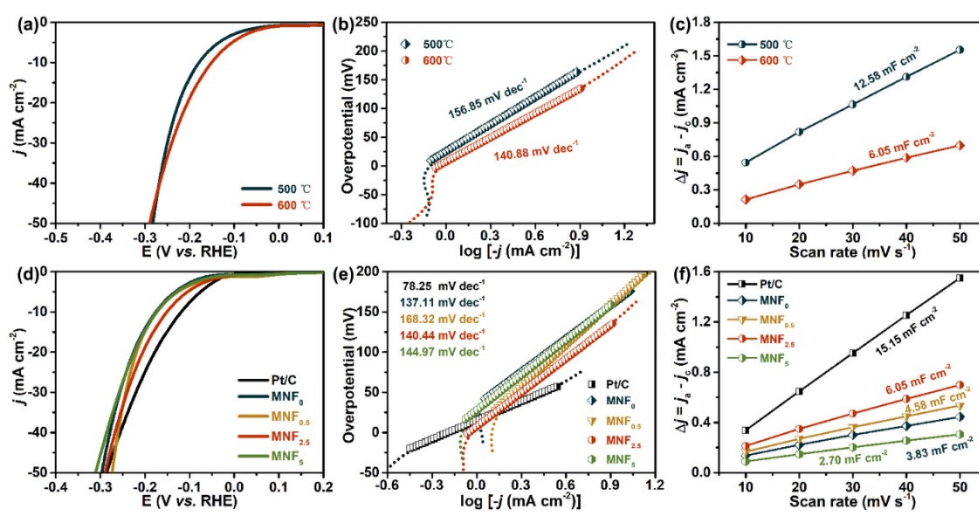


Fig. S21 (a) LSV curves, (b) Tafel plots, and (c) C_{dl} values of MNF_{2.5}-500 CFs and MNF_{2.5}-600 CFs. (d) LSV curves, (e) Tafel plots, and (f) C_{dl} values of the MNF_{*n*} CFs samples treated at the temperature of 600 °C.

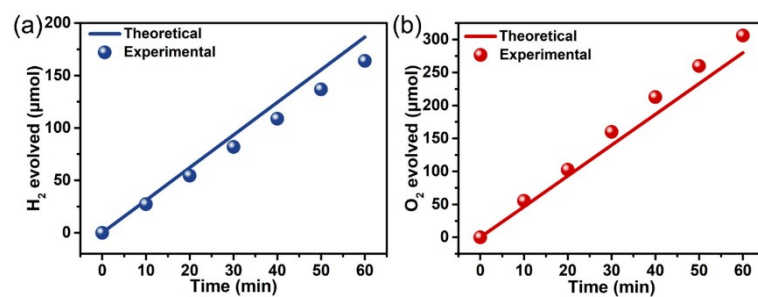


Fig. S22 The amounts of (a) H_2 and (b) O_2 theoretically calculated and experimentally measured versus time.

Table S1. Comparison of the OER performance of MNF_{2.5} CFs treated at 500 °C with other reported OER electrocatalysts in 1 M KOH electrolyte.

Electrocatalysts	Electrolyte	Overpotential (mV) at 30 mA cm ⁻²	Tafel slope (mV dec ⁻¹)	References
MNF _{2.5} -500 CFs	1M KOH	188	56.5	This work
N-WS ₂ /Ni ₃ FeN	1M KOH	220	55	3
TiO ₂ @Co ₉ S ₈	1M KOH	270	55	4
Ni _{0.83} Fe _{0.17} (OH) ₂	1M KOH	290	61	5
B,N:Mo ₂ C@BCN	1M KOH	320	61	6
Co-Ni/Ni ₃ N	1M KOH	350	63	7
NiMo-FG	1M KOH	370	67	8
Co@N-CS/N-HCP@CC	1M KOH	290	68	9
CoTeNR/NF	1M KOH	330	75	10
Ni-Co-P HNBs	1M KOH	310	76	11
FeCo-LDH/MXene	1M KOH	315	85	12
TTL	1M KOH	420	98.4	13
Ni ₁₁ (HPO ₃) ₈ (OH) ₆ /NF	1M KOH	290	102	14
NiCo ₂ O ₄ @CoMoO ₄ /NF-7	1M KOH	340	102	15
Co@HMNC	1M KOH	370	110	16
NiMoN/NF-450	1M KOH	310	116	17

Table S2. Comparison of the electrocatalytic activity of MNF_{2.5} CFs for overall water splitting with other recently reported bifunctional catalysts.

Electrode pair	Electrolyte	Overall voltage (V) at 20 mA cm ⁻²	References
MNF _{2.5} CFs	1M KOH	1.57	This work
RuCoO _x	1M KOH	1.58	18
Ni ₂ P-Ru ₂ P/NF	1M KOH	1.58	19
Ni ₂ P@NSG	1M KOH	1.60	20
Ti ₃ C ₂ @mNiCoP	1M KOH	1.61	21
Co-NiMoN-400	1M KOH	1.62	22
CoP-HS	1M KOH	1.63	23
Co-Ni/Ni ₃ N	1M KOH	1.65	7
O-NiMoP/NF	1M KOH	1.68	24
Mo _{0.6} Ni _{0.4}	1M KOH	1.72	25
NiCo ₂ S ₄ /CC	1M KOH	1.73	26
Co/Ni-CW	1M KOH	1.79	27

Reference

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