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Electronic Supplementary Information

Ni-Mo nitride synthesized via mild plasma for efficient alkaline hydrogen evolution electrocatalysis

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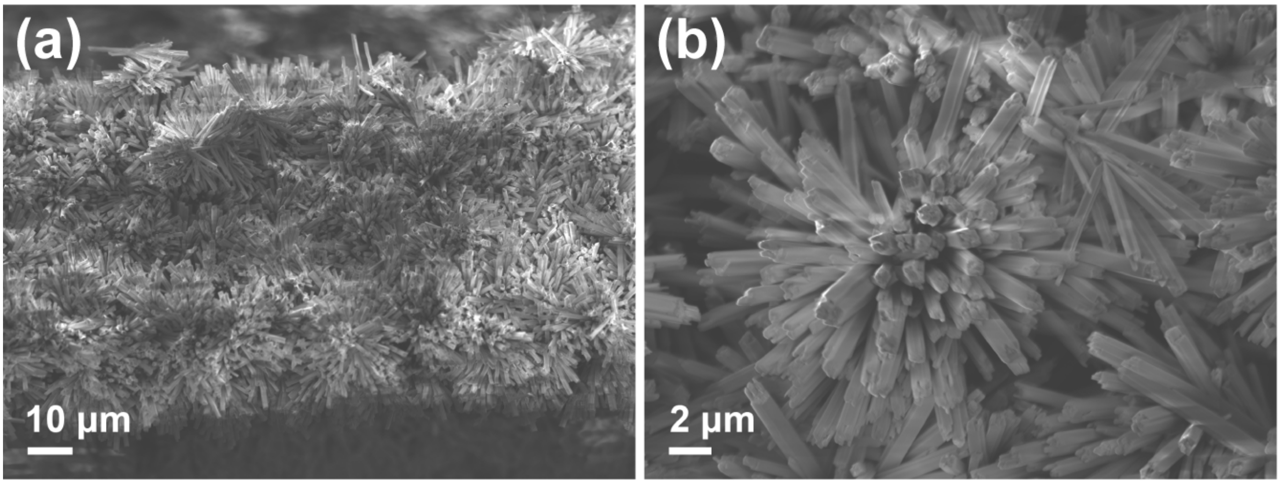

Fig. S1. SEM images of NMO/NF. Due to the poor conductivity of this crystalline oxide hydrate precursor, the SEM images show bright stripes due to local electron accumulation.

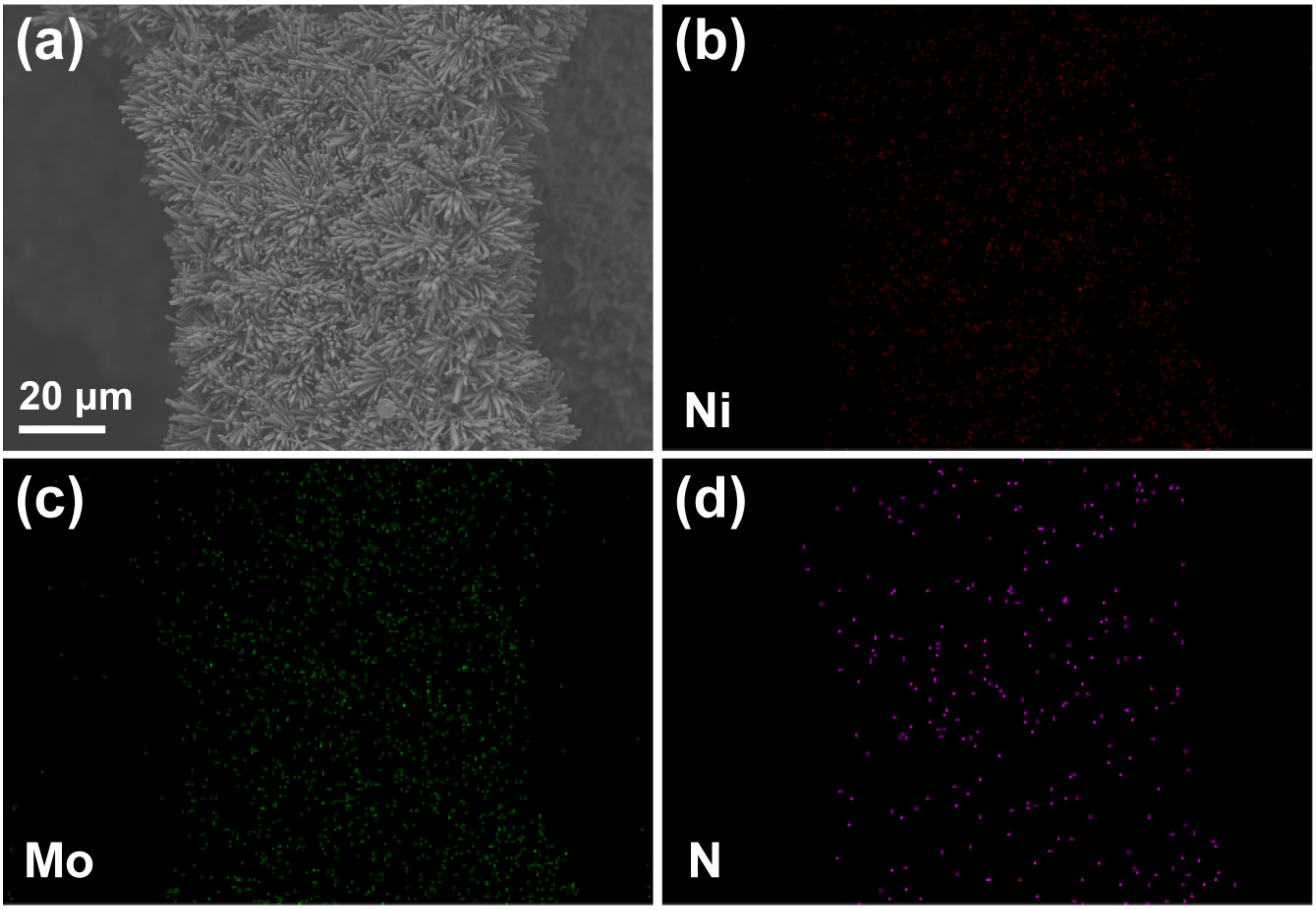

Fig. S2. (a) SEM image of NMN/NF and corresponding EDS elemental mappings of Ni (b), Mo (c) and N (d).

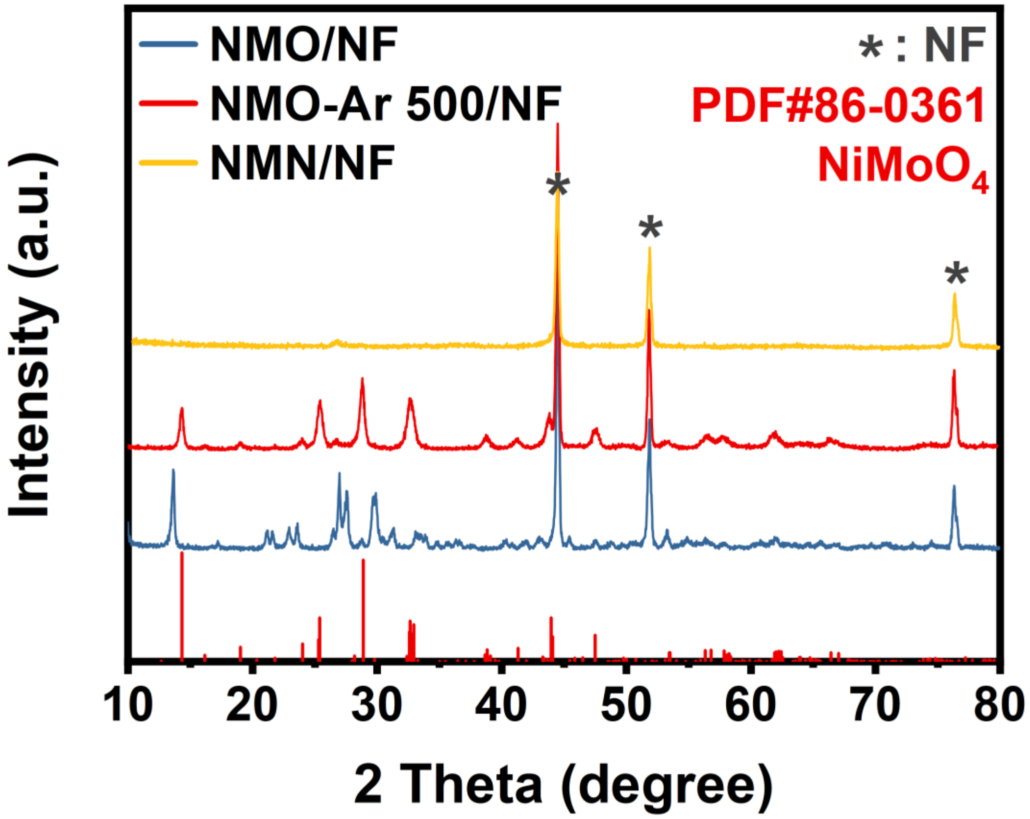

Fig. S3. XRD patterns of NMO/NF, NMO/NF annealed at 500 °C and NMN/NF. The Ni-Mo oxide hydrate phase ($NiMoO_4{\cdot}xH_2O$, PDF no. 13-0128) in NMO/NF was converted to NiMoO4/NF (PDF no. 86-0361) after annealing at 500 °C.

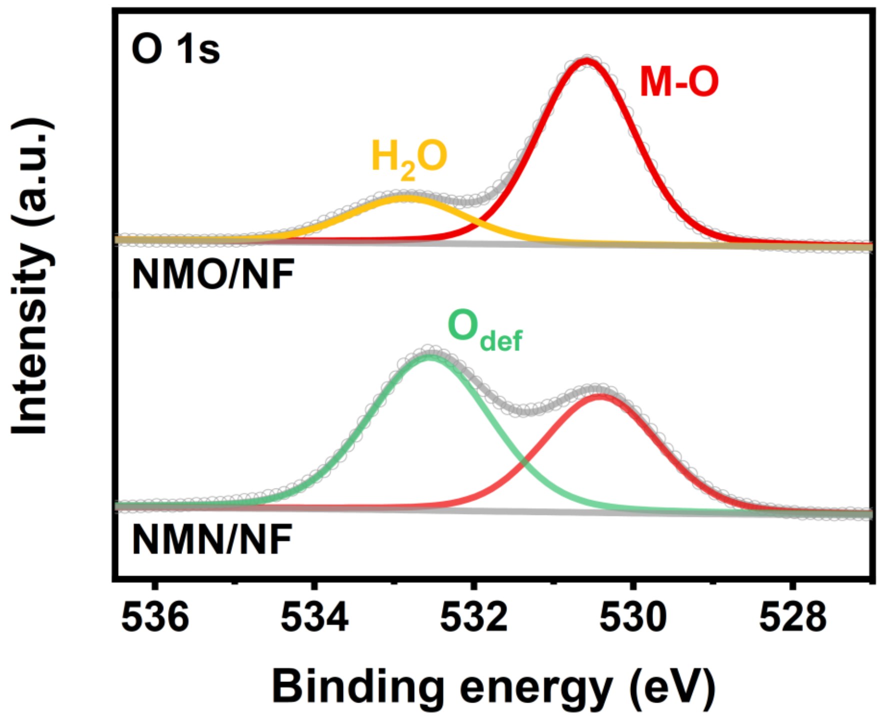

Fig. S4. O 1s XPS spectra of NMO/NF and NMN/NF.

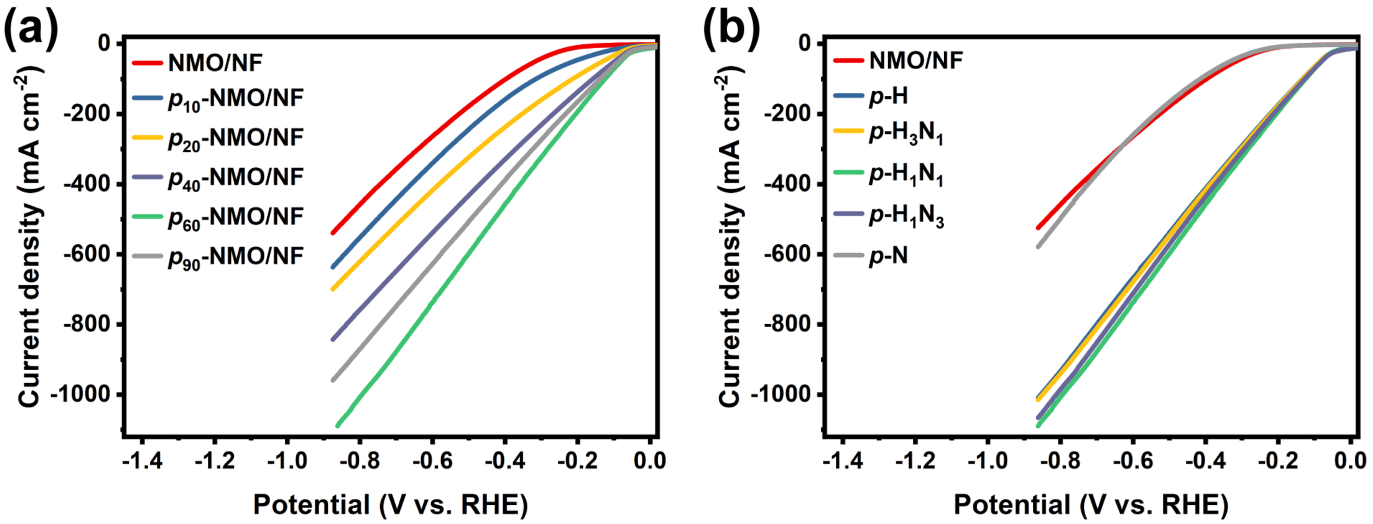

Fig. S5. Optimization of H_2/N_2 plasma duration and H_2/N_2 ratio in terms of HER activity (Without iR correction). (a) LSV curves of NMN/NF with different plasma processing time. (b) LSV curves of NMN/NF with different ratio of H_2 and N_2. *p*-H and *p*-N sample are obtained with pure H_2 and N_2 plasma, respectively. For *p*-H_3N_1, *p*-H_1N_1, and *p*-H_1N_3, the H_2 /N_2 ratios are 3:1, 1:1 and 1:3, respectively. The whole pressure remains 30 Pa for all samples.

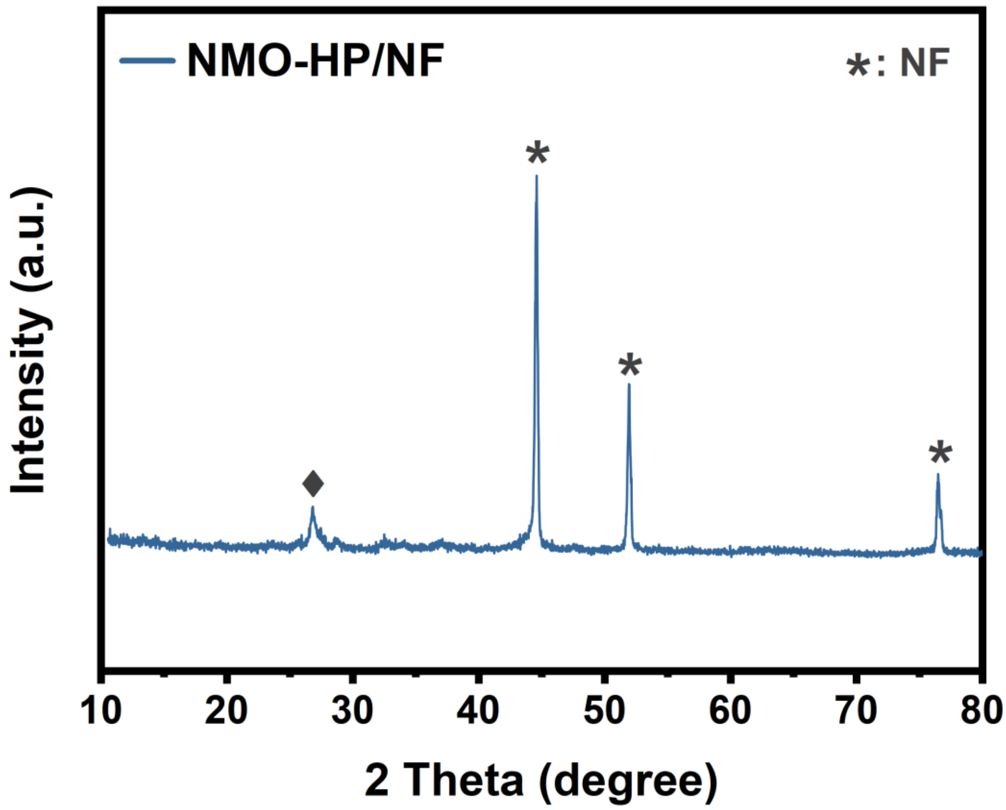

Fig. S6. XRD pattern of NMO/NF after processed in H_2 plasma.

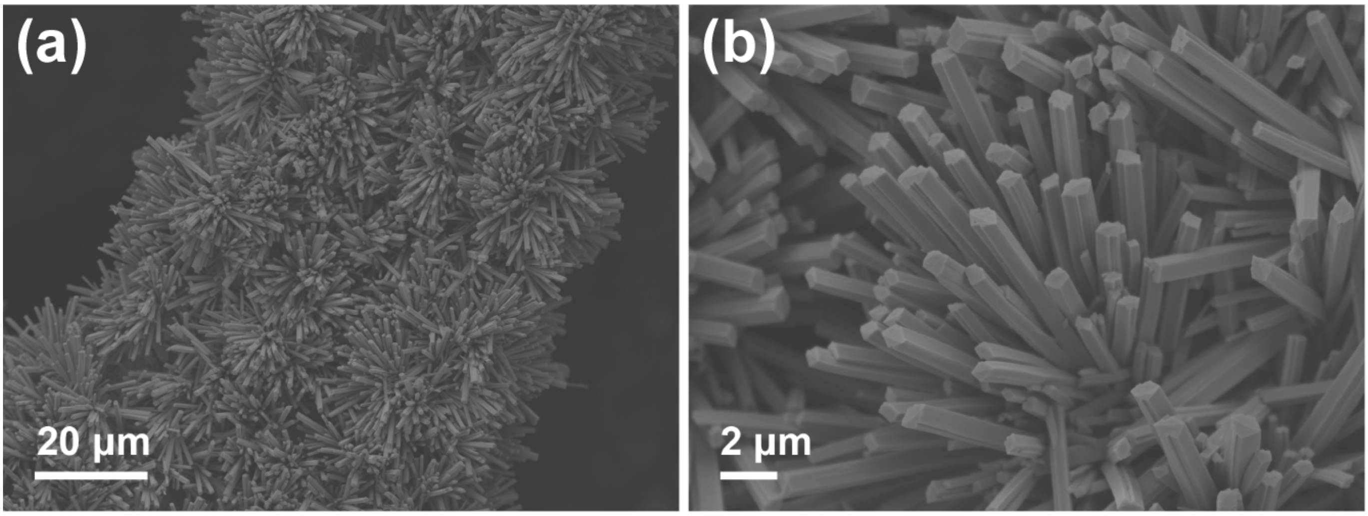

Fig. S7. Low-resolution (a) and high-resolution (b) SEM images of NMO/NF after processed in H_2 plasma.

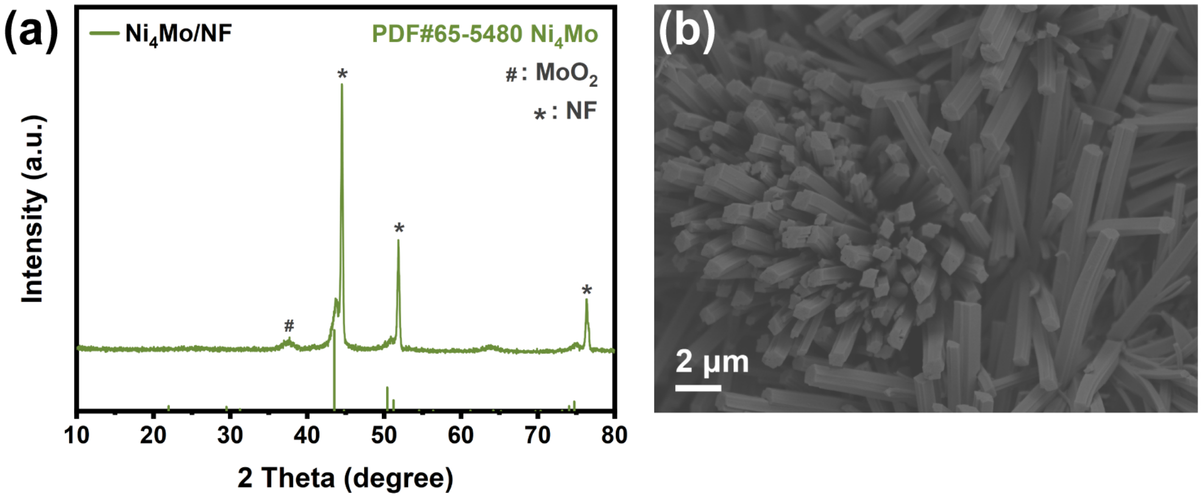

Fig. S8. (a) XRD pattern and (b) SEM image of Ni_4Mo/NF. XRD pattern suggests that NMO precursor was transformed into Ni_4Mo alloy (PDF#65-5480) and a small amount of MoO_2 remains after annealing in H_2/Ar atmosphere at 600℃. SEM image shows that Ni_4Mo/NF retains the nanorod morphology of NMO/NF precursor.

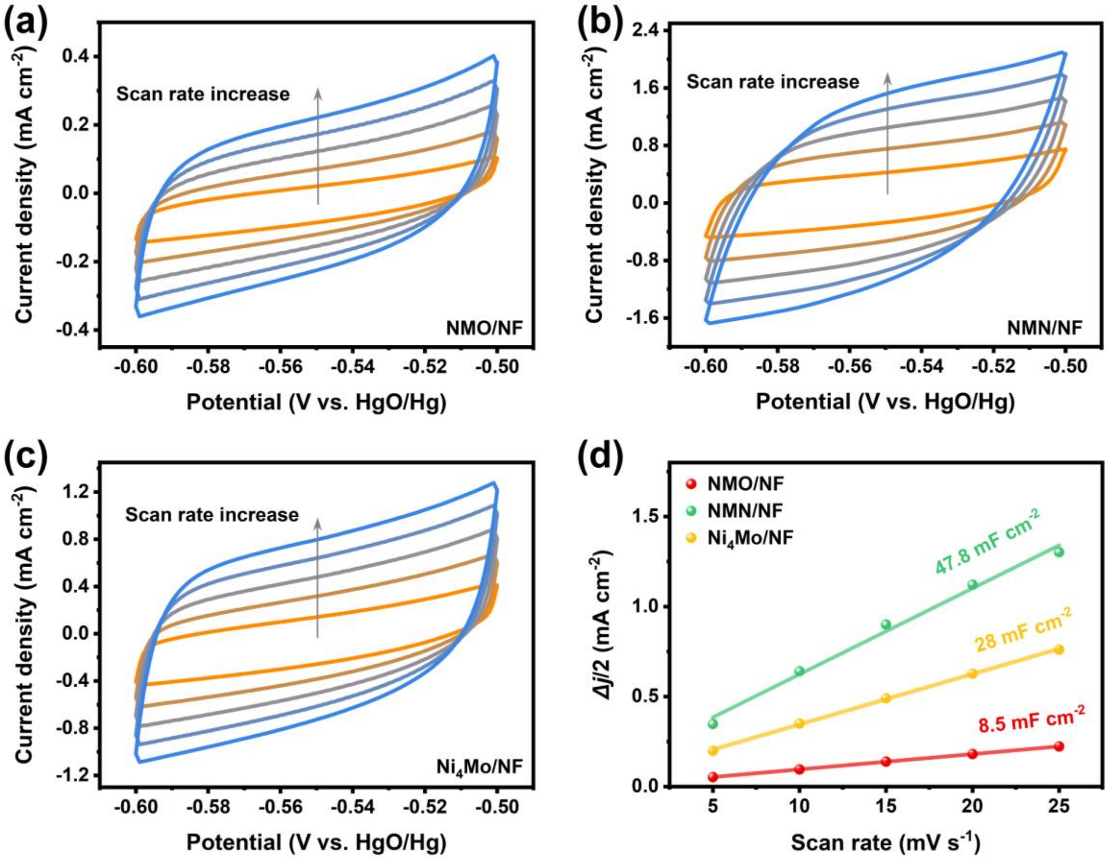

Fig. S9. (a-c) CV curves of NMO/NF (a), NMN/NF (b) and Ni_4Mo/NF (c) with different scan rates at non-Faradaic potential range; (d) corresponding double-layer capacitance (C_{dl}).

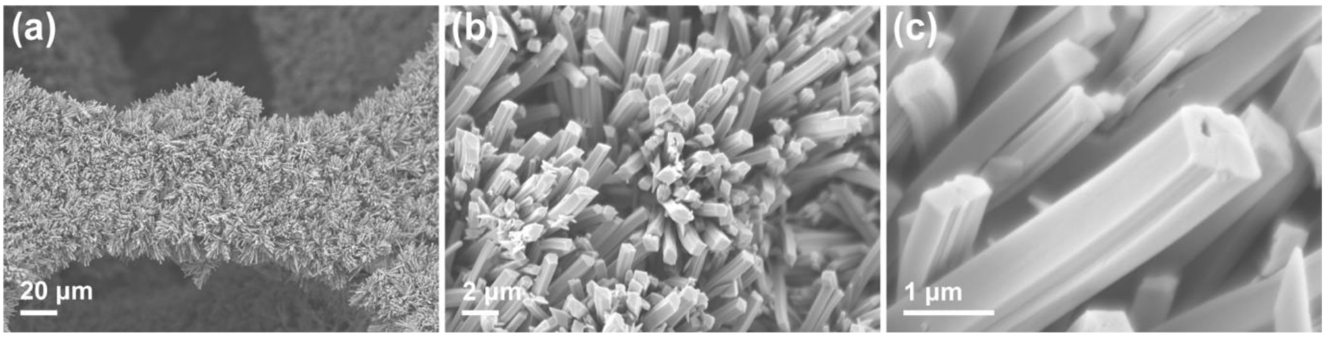

Fig. S10. SEM images of NMN/NF after HER stability test (50 h at 100 mA cm^{-2}).

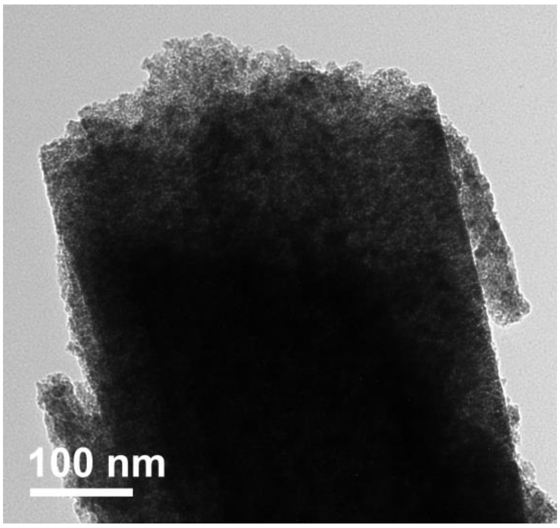

Fig. S11. TEM image of NMN/NF after HER stability test (50 h at 100 mA cm^{-2}).

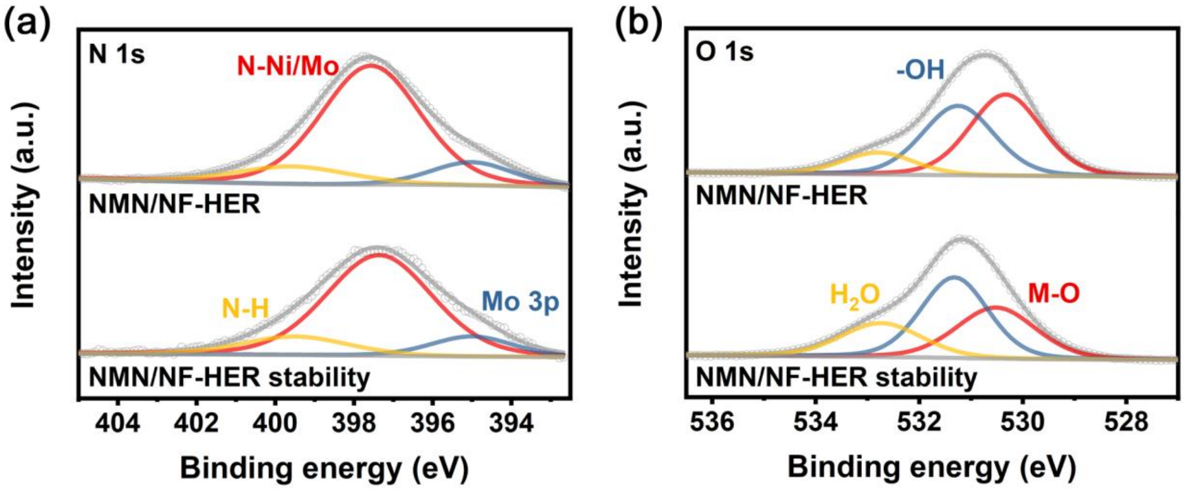

Fig. S12. XPS spectra of NMN/NF after HER and long-term HER stability test: (a) N 1s and (b) O 1s.

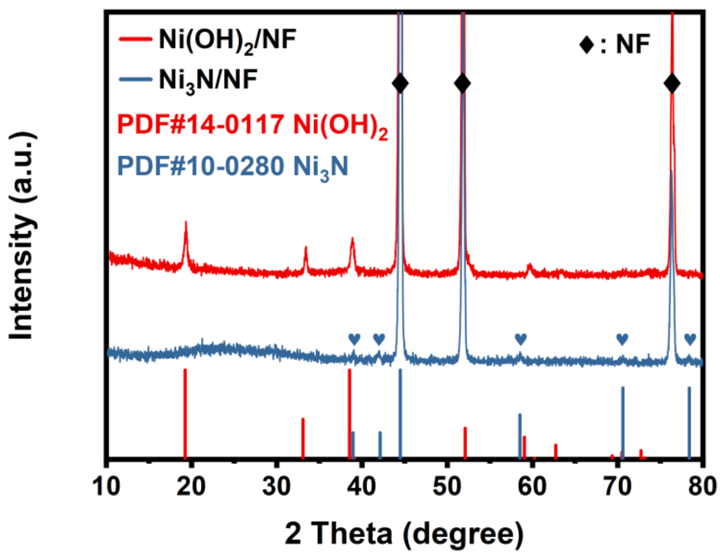

Fig. S13. XRD pattern of $Ni(OH)_2$/NF before and after H_2 /N_2 plasma treatment (denoted as Ni_3N/NF).

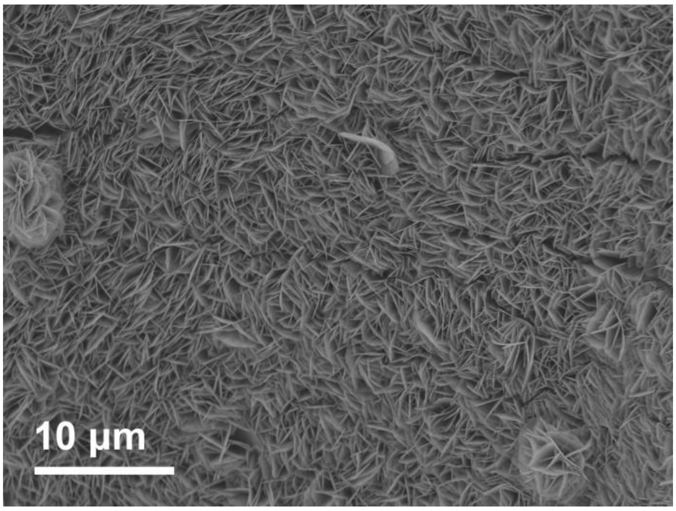

Fig. S14. SEM image of $Ni(OH)_2$/NF.

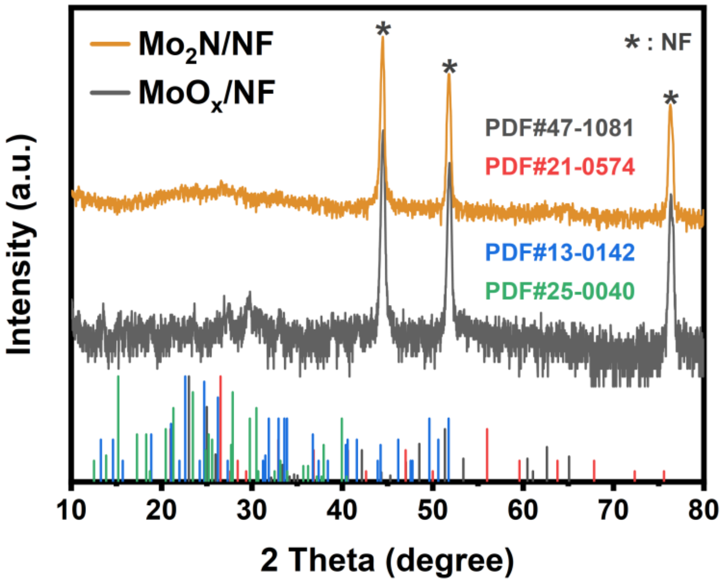

Fig. S15. XRD pattern of MoO_x/NF before and after H_2 /N_2 plasma treatment (denoted as Mo_2N/NF).

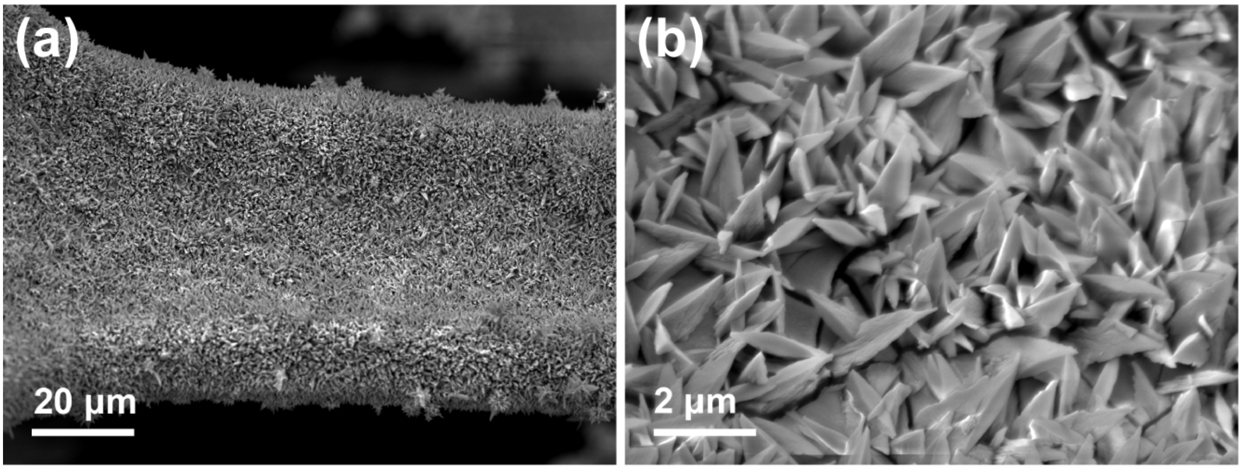

Fig. S16. Low-(a) and high-(b) resolution SEM images of MoO_x/NF.

Table S1. Comparison of the catalytic HER performance between our *p*-NMO/NF and non-noble metal nitride-based electrocatalysts reported in alkaline condition.

Catalyst	Substrate	η_{100} (mV)	Tafel slope (mV dec^{-1})	Electrolyte	Ref.
NMN/NF	NF [a]	66	38	1.0 M KOH	This work
Ni_4Mo/NF	NF	99	66.8	1.0 M KOH	This work
Ni-MoN	CF [b]	61	35.5	1.0 M KOH	[1]
Ni_3N-NiMoN/CC	CC [c]	74	40	1.0 M KOH	[2]
Ni_3N@NiMoN_x/NF	NF	78	55	1.0 M KOH	[3]
NiMoN/Ni_3N-12	NF	93	49	1.0 M KOH	[4]
Ni_3N@C/NF	NF	95	60	1.0 M KOH	[5]
Ni_3N@2M-MoS_2	NF	97	43.2	1.0 M KOH	[6]
P-Mo-$Ni(OH)_2$ NSAs	NF	98	80	1.0 M KOH	[7]
$(Fe_{0.74}Co_{0.26})_2P/Ni_3N$	NF	113	31.8	1.0 M KOH	[8]
Co/MoN	NF	132	77.5	1.0 M KOH	[9]
NiMoN/NiN	NF	136	70	1.0 M KOH	[10]
P-MoP/Mo_2N	NF	137	78	1.0 M KOH	[11]
Ni_3N NCs	GC [d]	142	49	1.0 M KOH	[12]
2D meso-Mo_2C/Mo_2N	GC	164	44.1	1.0 M KOH	[13]
V–Ni_3N/NF	NF	172	45	1.0 M KOH	[14]
cp-Ni_3N	Ni plate	183	64	1.0 M NaOH	[15]
NiPN/Ni/CC-CNT[2]	CC	186	50	1.0 M KOH	[16]
Ni_3N-VN/NF	NF	218	37	1.0 M KOH	[17]
N10V7M3	NF	253	94	1.0 M KOH	[18]

Notes: η_{100} means the overpotentials at current density of 100 mA cm^{-2}; [a] NF: nickel foam, [b] CF: copper foam, [c] CC: carbon cloth, [d] GC: glassy carbon.

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