

Supporting Information

Constructing interface structure of $\text{Mo}_5\text{N}_6/\text{Ni}_3\text{N}/\text{Ni}/\text{NF}$ for efficient and stable electrocatalytic hydrogen evolution under alkaline conditions

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Chemicals and materials

Nickel chloride anhydrous (NiCl_2 , Ni > 42.0%), ammonium chloride (NH_4Cl , 99.0%), sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, 99.0%+), potassium hydroxide (KOH, $\geq 90.0\%$) purchased from Shanghai Titan Scientific Co. LTD (www.tansoole.com). Ethanol absolute ($\text{C}_2\text{H}_6\text{O}$, $\geq 99.7\%$) and acetone ($\text{C}_3\text{H}_6\text{O}$, $\geq 99.5\%$) purchased from Shanghai Lingfeng Chemical Reagent Co. LTD (www.yonghuachem.com). Hydrochloric acid (HCl , 36.0~38.0%) purchased from www.reagent.com.cn. All of the reagents were used as received without further purification. Deionized water was used throughout the experiments.

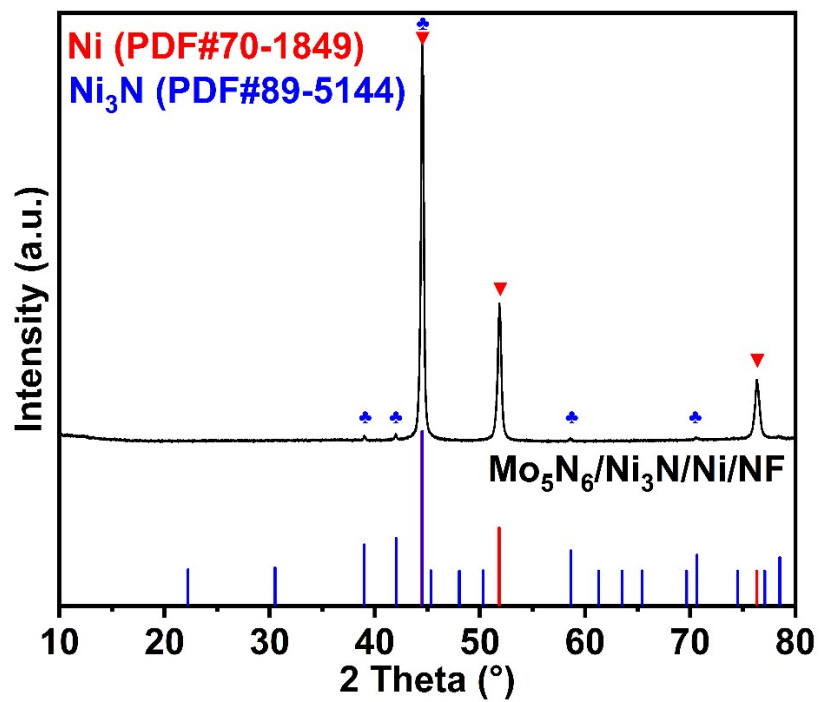


Fig. S1. XRD pattern of the $\text{Mo}_5\text{N}_6/\text{Ni}_3\text{N}/\text{Ni}/\text{NF}$.

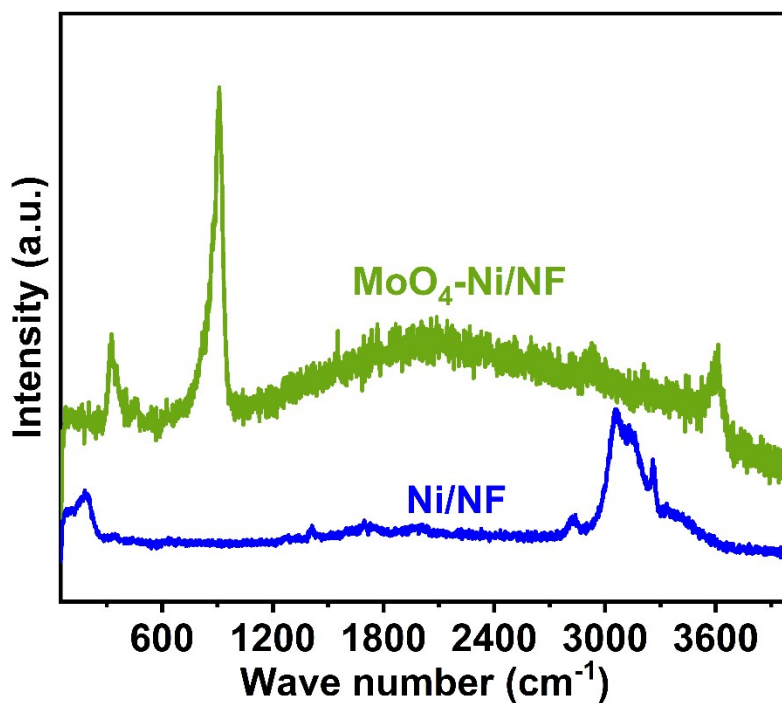


Fig. S2 Raman spectra of Ni/NF and $\text{MoO}_4\text{-Ni}/\text{NF}$.

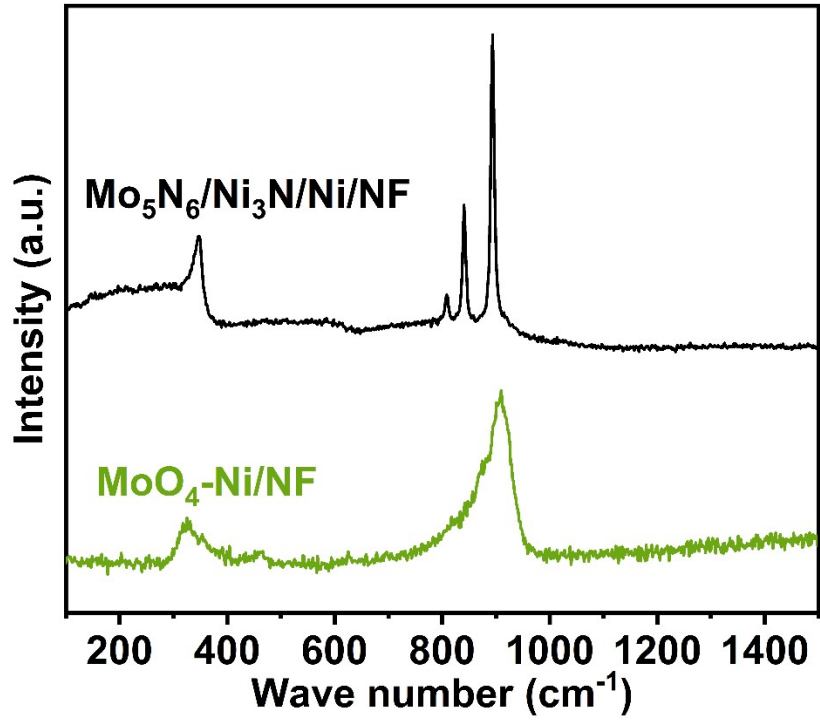


Fig. S3 Raman spectra of MoO₄-Ni/NF and Mo₅N₆/Ni₃N/Ni/NF.

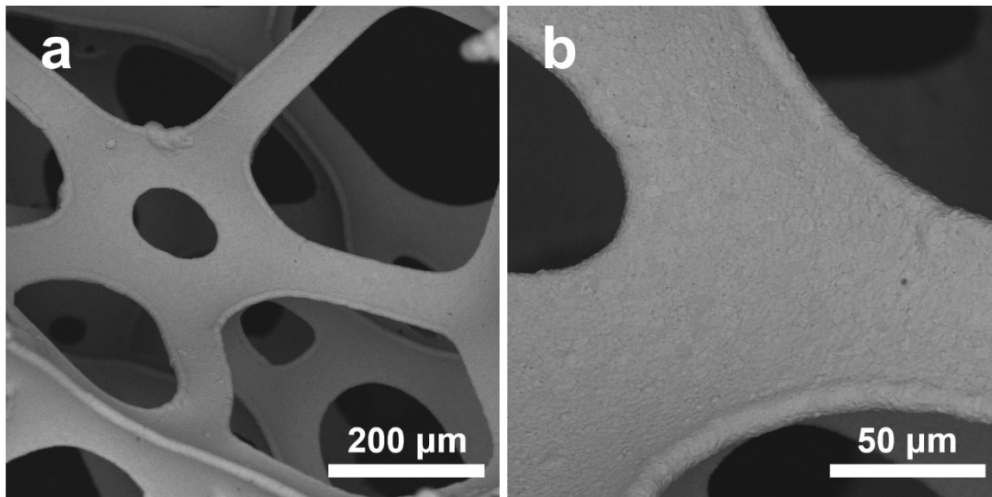


Fig. S4. SEM images of the commercial Ni foam.

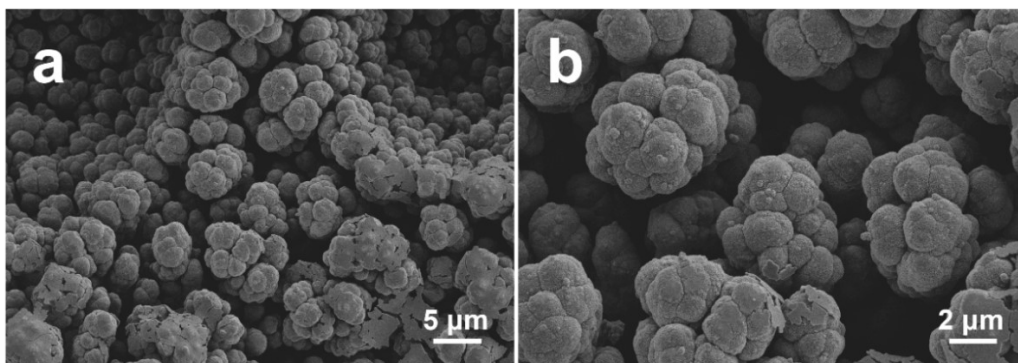


Fig. S5. Low-magnification SEM images of Ni/NF.

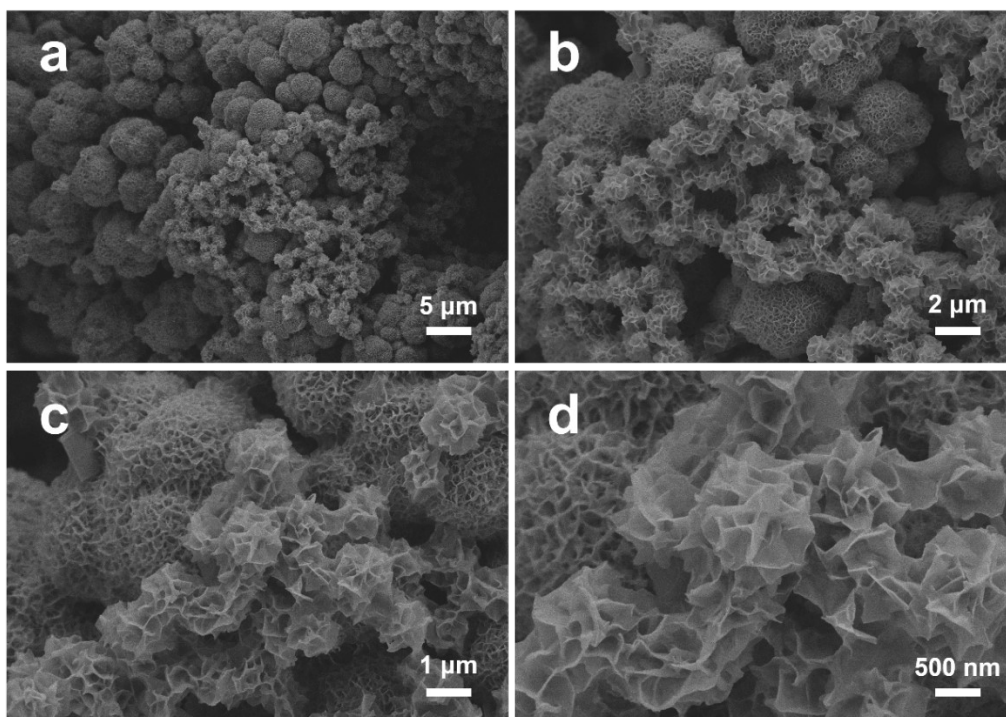


Fig. S6. Low-magnification SEM images of MoO₄-Ni/NF.

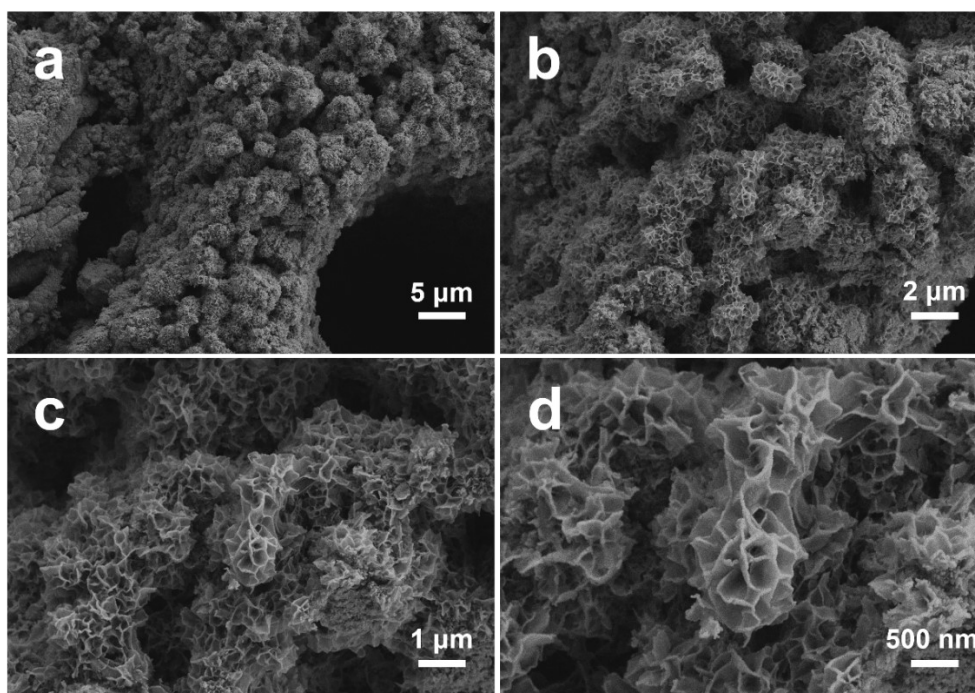


Fig. S7. Low-magnification SEM images of $\text{Mo}_5\text{N}_6/\text{Ni}_3\text{N}/\text{Ni}/\text{NF}$.

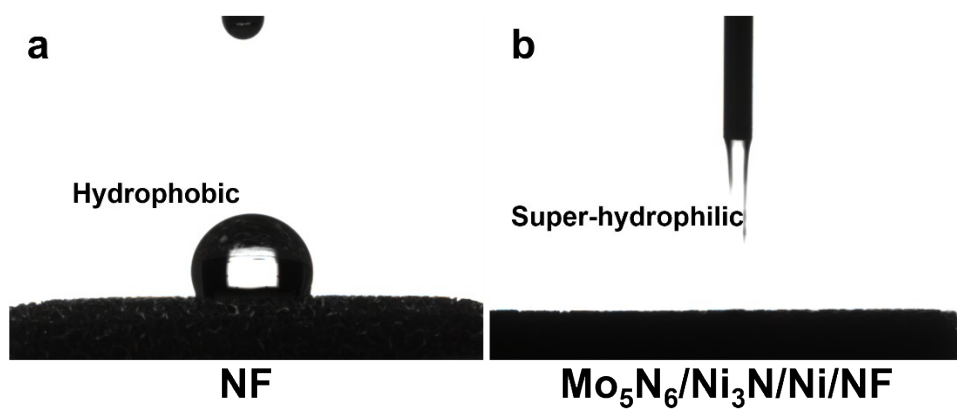


Fig. S8. Photographs of contact angle of the (a) NF and (b) $\text{Mo}_5\text{N}_6/\text{Ni}_3\text{N}/\text{Ni}/\text{NF}$.

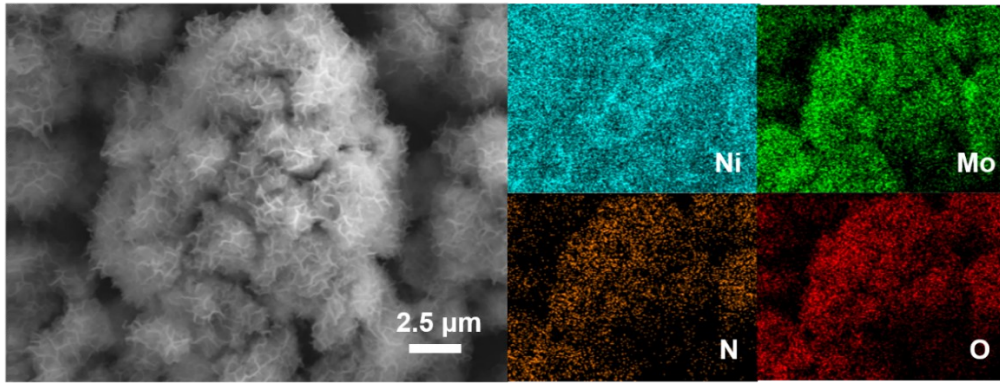


Fig. S9. The scanning electron microscopy image and the corresponding elemental mappings of Ni, Mo, N, and O in the $\text{Mo}_5\text{N}_6/\text{Ni}_3\text{N}/\text{Ni}/\text{NF}$.

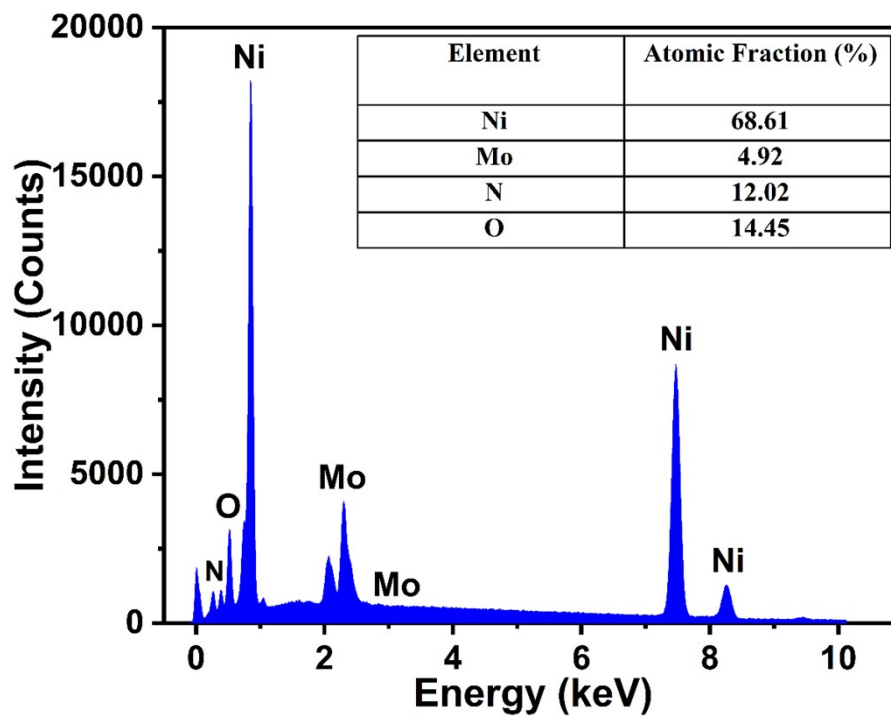


Fig. S10. EDS spectrum of $\text{Mo}_5\text{N}_6/\text{Ni}_3\text{N}/\text{Ni}/\text{NF}$ sample (inset is the ratio of Ni, Mo, N, O).

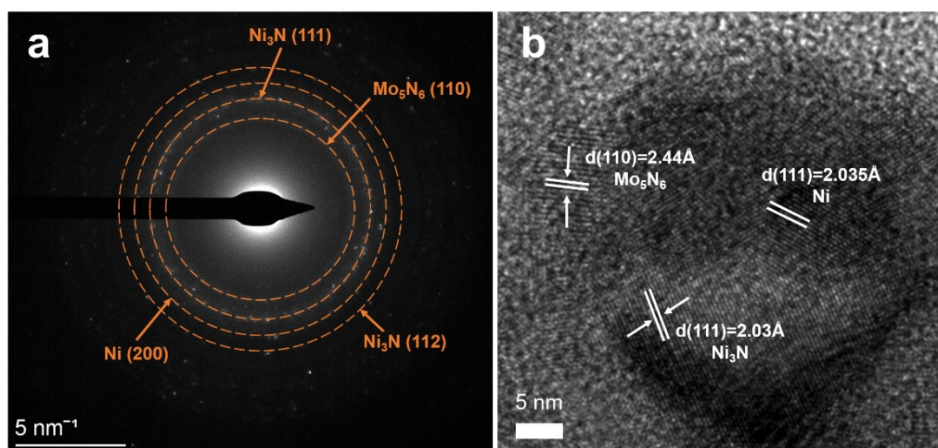


Fig. S11. (a, b) More detailed SAED pattern information of $\text{Mo}_5\text{N}_6/\text{Ni}_3\text{N}/\text{Ni}/\text{NF}$ and HRTEM image.

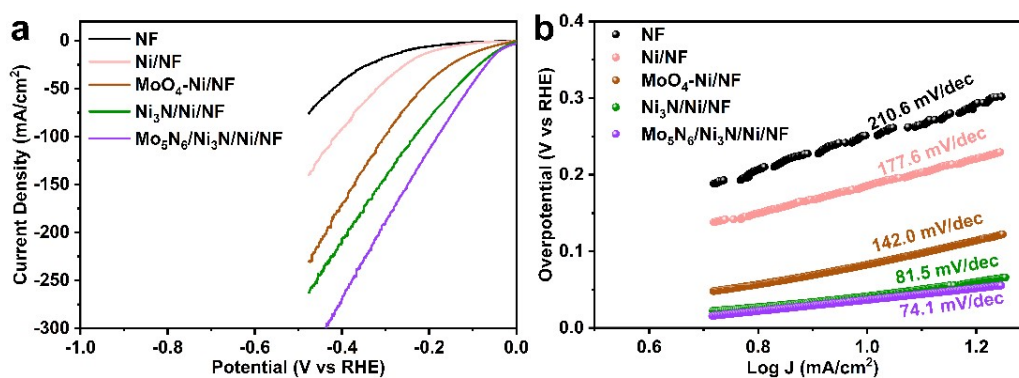


Fig. S12. (a) LSV polarization curves and (b) the corresponding Tafel plots of the as-prepared catalysts without IR-correction.

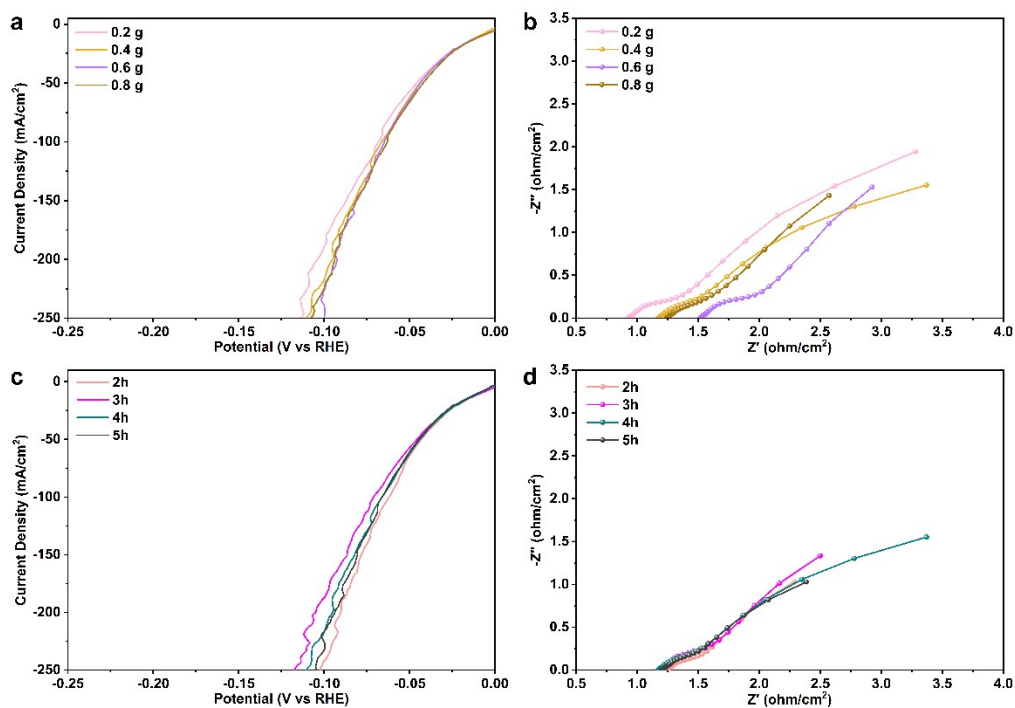


Fig. S13. (a, b) LSV polarization curves and the corresponding Nyquist plots of the $\text{Mo}_5\text{N}_6/\text{Ni}_3\text{N}/\text{Ni}/\text{NF}$ which prepared by different concentrations of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ in hydrothermal reaction. (c, d) LSV polarization curves and the corresponding Nyquist plots of the $\text{Mo}_5\text{N}_6/\text{Ni}_3\text{N}/\text{Ni}/\text{NF}$ which prepared by different nitridation time.

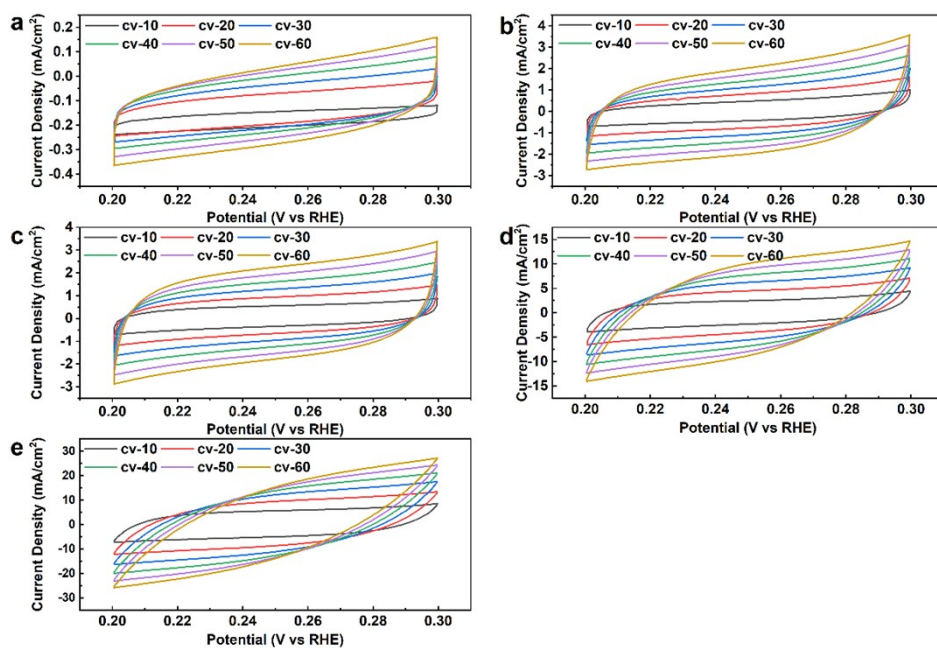


Fig. S14. CV curves of the (a) blank Ni foam; (b) Ni/NF; (c) MoO₄-Ni/NF; (d) Ni₃N/Ni/NF; (e) Mo₅N₆/Ni₃N/Ni/NF tested at different scan rates.

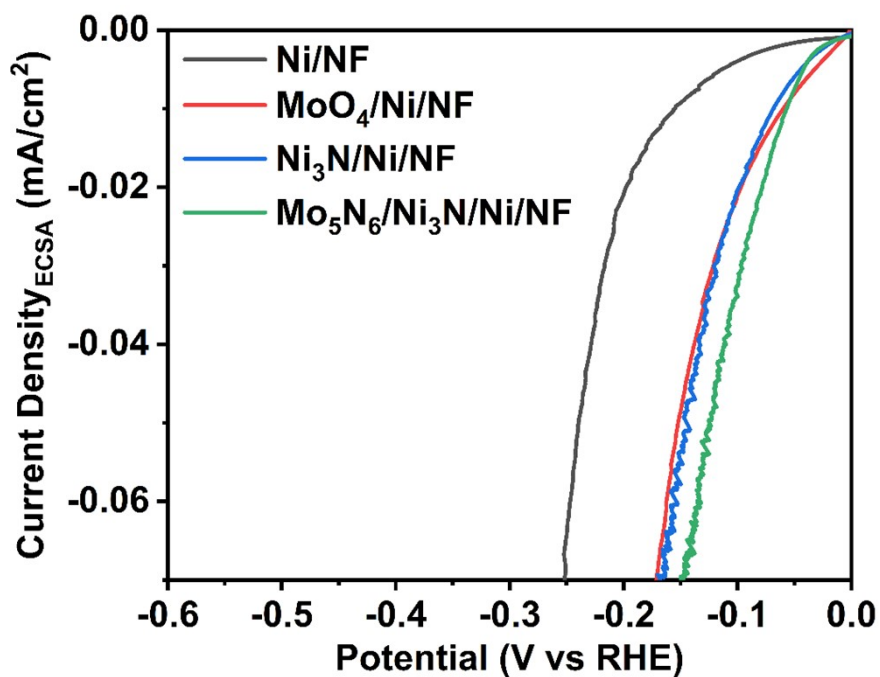


Fig. S15. The LSV curves of Mo₅N₆/Ni₃N/Ni/NF, MoO₄-Ni/NF, Ni₃N/Ni/NF and Ni/NF normalized to ECSA.

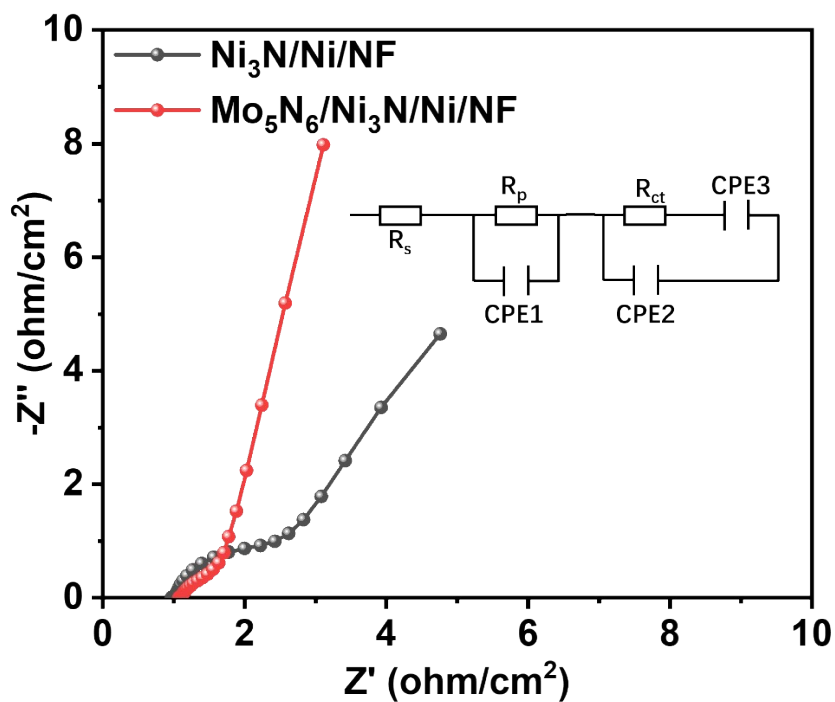


Fig. S16. The Nyquist plots of $\text{Ni}_3\text{N}/\text{Ni}/\text{NF}$ and $\text{Mo}_5\text{N}_6/\text{Ni}_3\text{N}/\text{Ni}/\text{NF}$ which performed at OCV. Inset: equivalent circuit model.

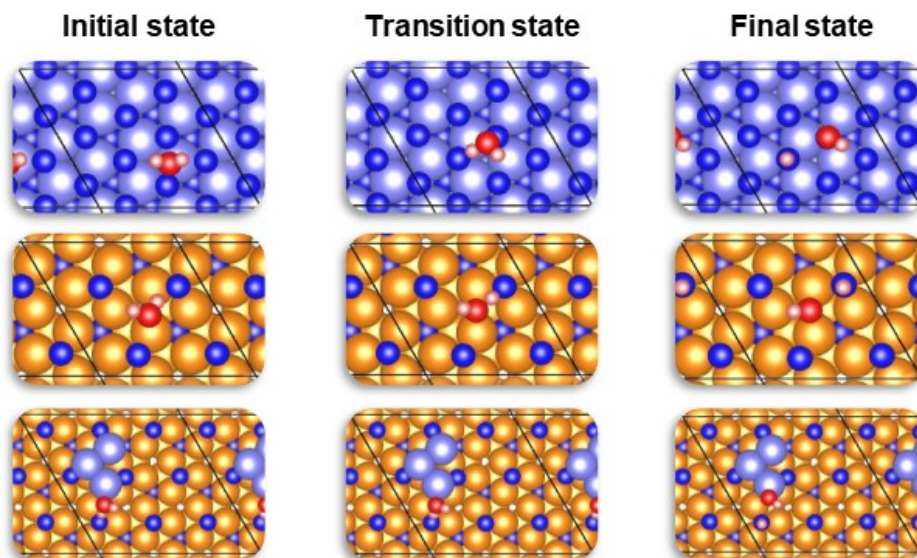


Fig. S17. Initial, transition and final states for water decomposition. Orange, pink, blue, and purple atoms represent Ni, H, N, and Mo atoms, respectively.

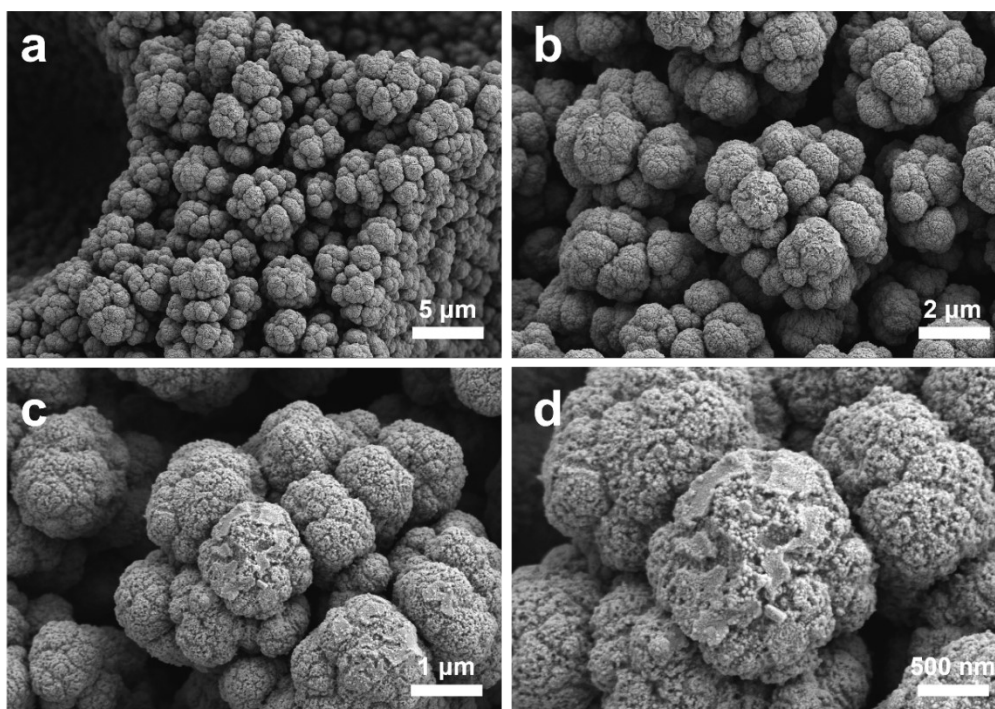


Fig. S18. The SEM images of the $\text{Mo}_5\text{N}_6/\text{Ni}_3\text{N}/\text{Ni}/\text{NF}$ after chronopotentiometry measurement ($-100 \text{ mA}/\text{cm}^2@100\text{h}$).

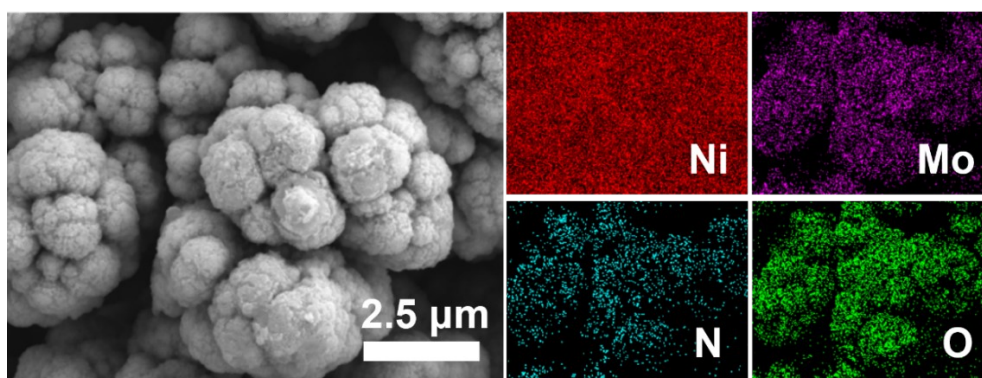


Fig. S19. The scanning electron microscopy image and the corresponding elemental mappings of Ni, Mo, N, and O in the $\text{Mo}_5\text{N}_6/\text{Ni}_3\text{N}/\text{Ni}/\text{NF}$ after chronopotentiometry measurement ($-100 \text{ mA}/\text{cm}^2@100\text{h}$).

Table S1. Elemental composition of Mo₅N₆/Ni₃N/Ni/CF (CF is copper foam) by ICP-OES tests.

Element	Mass fraction (%)
Ni	74.78
Mo	0.71

Table S2. The atomic percentages of Ni and Mo in MoO₄-Ni/NF and Mo₅N₆/Ni₃N/Ni/NF in XPS spectra.

MoO ₄ -Ni/NF				
Name	Ni 2p	Mo 3d	N 1s	C 1s
Atomic %	27.1	7.48	25.65	39.76
Mo ₅ N ₆ /Ni ₃ N/Ni/NF				
Name	Ni 2p	Mo 3d	N 1s	C 1s
Atomic %	8.89	13.72	52.97	24.42

Table S3. Comparison of HER catalytic activity, stability and Tafel slope between Mo₅N₆/Ni₃N/Ni/NF and recently reported self-supporting transition metal nitride catalysts under alkaline condition.

Catalyst	η_{10} (mV)	Tafel slope (mV/dec)	Stability (mA/cm ² or mV for h)	Reference
Mo ₅ N ₆ /Ni ₃ N/Ni/NF	27	46.8	-100 mA/cm ² for 100 h	This work
NiMoN/CC	109	95.0	-50 mA/cm ² for 12 h	1
Nb ₂ O ₅ -Ni ₃ N/NF	80	100.4	-100 mA/cm ² and -200 mA/cm ² for 12 h	2
NiCo ₂ N/NF	180	79.0	-10 mA/cm ² for 50 h	3
NiMoN/Ni ₃ N/NF	28	49.0	-10 mA/cm ² for 24 h	4
Ni ₃ N-V ₂ O ₃ /NF	57	50.0	-100 mV for 24 h	5
Ni-Mo-N/CFC	40	70.0	-10 mA/cm ² for 12 h	6
Ni ₃ N-Mo ₂ N/NF	66	67.4	-10 mA/cm ² for 48 h	7
Ni ₃ N/Ni _{0.2} Mo _{0.8} N/NF	55	54.0	-10 mA/cm ² for 50 h	8
Co-Ni ₃ N/NF	30	41.6	-50 mA/cm ² for 24 h	9
Ni ₃ N/W ₅ N ₄ /NF	31	34.0	-100 mA/cm ² for 150 h	10
Co ₂ NiN/CC	123	98.0	-100 mA/cm ² for 6 h	11
FeOOH/Ni ₃ N/CC	67	82.0	-10 mA/cm ² for 50 h	12
Co/MoN/NF	52	77.5	-40 mA/cm ² for 70 h	13
Ni ₂ Mo ₃ N/NF	21	62.0	-10 mA/cm ² for 24 h	14

NF: nickel foam; CC: carbon cloth; CFC: conductive carbon fiber cloth.

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