

Electronic Supplementary Information (ESI)

Highly Active and Stable Nickel-Molybdenum Nitride ($\text{Ni}_2\text{Mo}_3\text{N}$)

Electrocatalyst for Hydrogen Evolution

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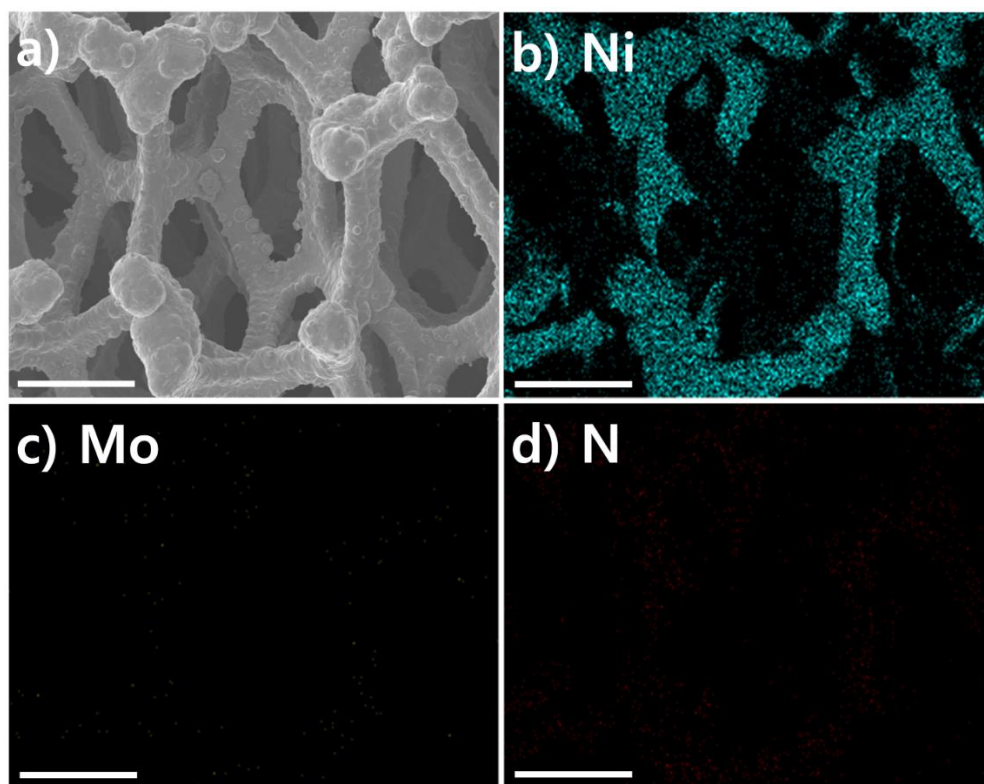


Fig. S1. SEM-EDS elemental mapping images for pristine Ni foam (scale bar = 300 μm).

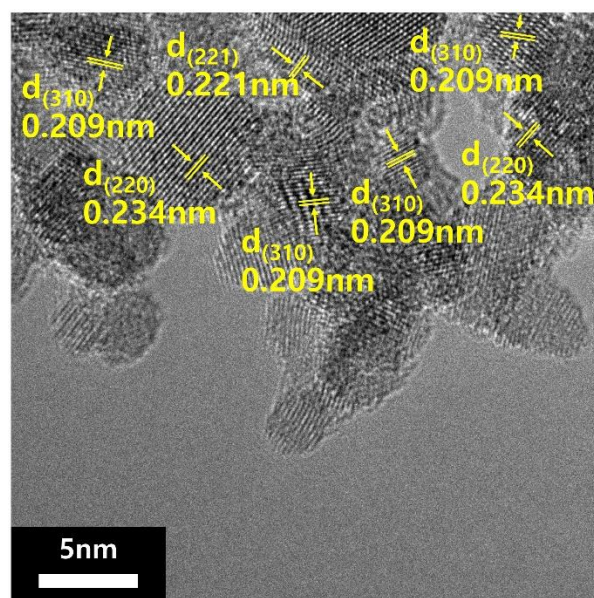


Fig. S2. HRTEM image of $\text{Ni}_2\text{Mo}_3\text{N}/\text{NF}$.

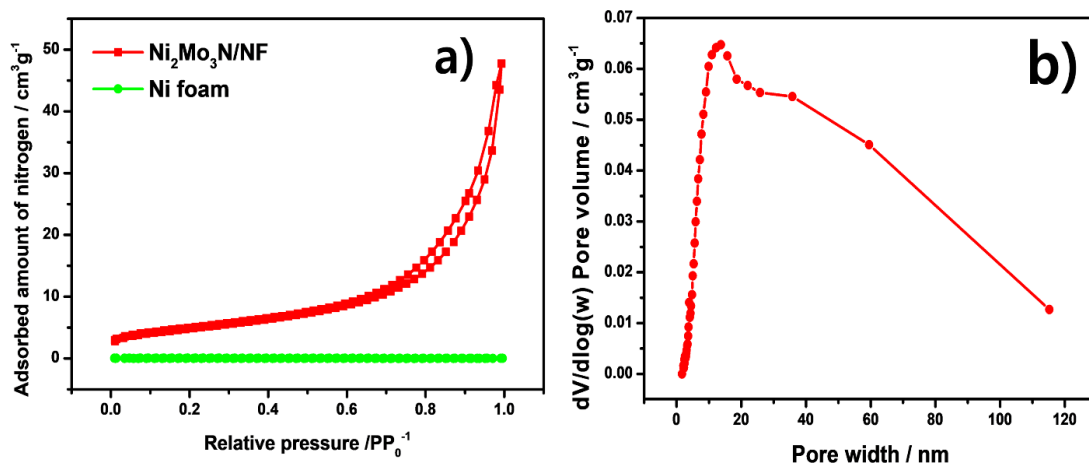


Fig. S3. a) N_2 adsorption-desorption isotherms and b) pore size distribution plot of $\text{Ni}_2\text{Mo}_3\text{N/NF}$.

N_2 isotherm of pristine Ni foam was added in a) for comparison.

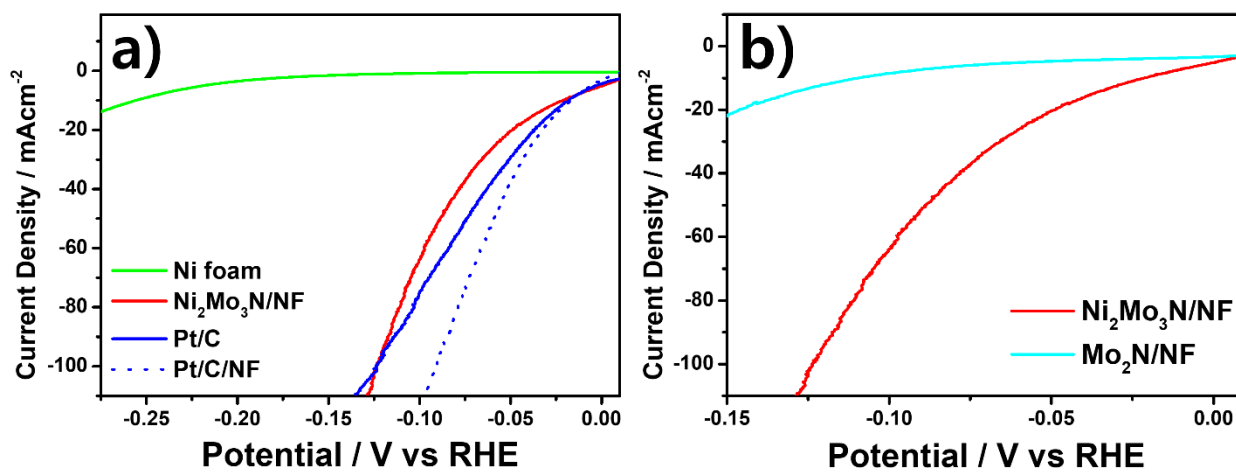


Fig. S4. Electrochemical polarization curves for the prepared catalysts a) including Pt/C/NF and b) including $\text{Mo}_2\text{N/NF}$.

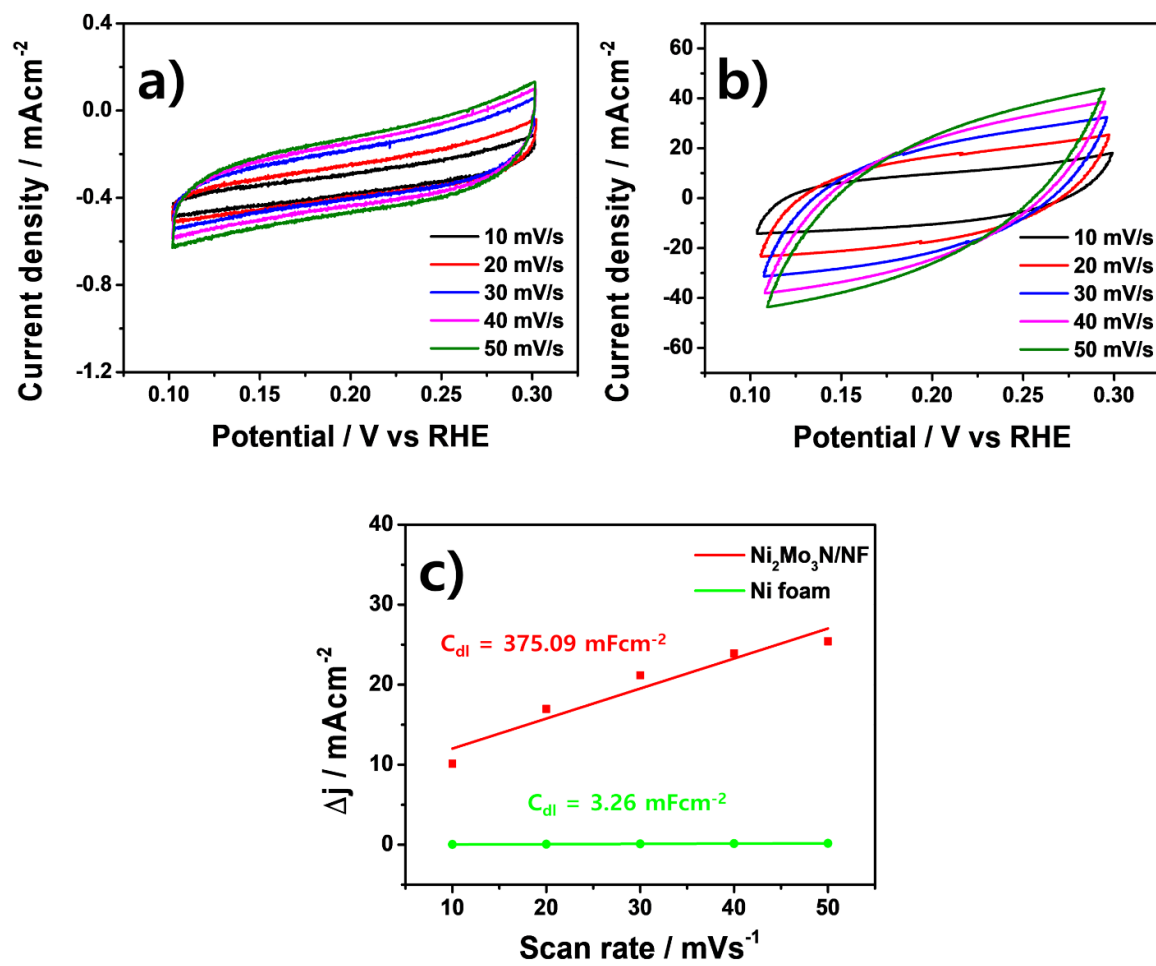


Fig. S5. Cyclic voltammograms of a) pristine Ni foam and b) Ni₂Mo₃N/NF at different scan rates in 1 M KOH solution. c) The corresponding current density versus scan rate plots showing C_{dl} values for pristine Ni foam and Ni₂Mo₃N/NF.

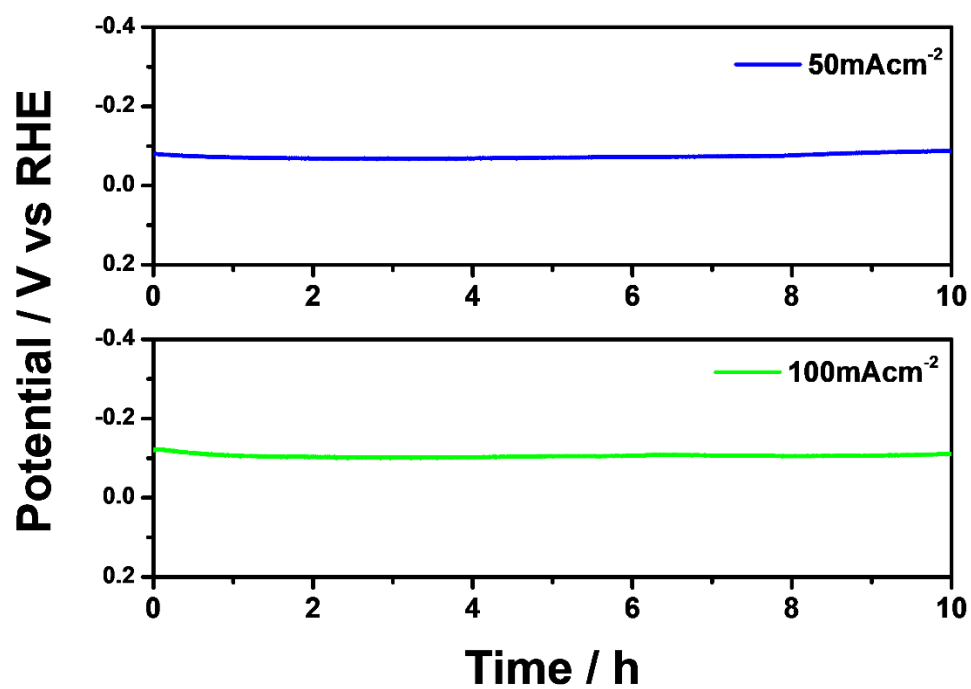


Fig. S6. Chronopotentiometry curves of Ni₂Mo₃N/NF at 50 and 100 mA cm⁻² for 10 h.

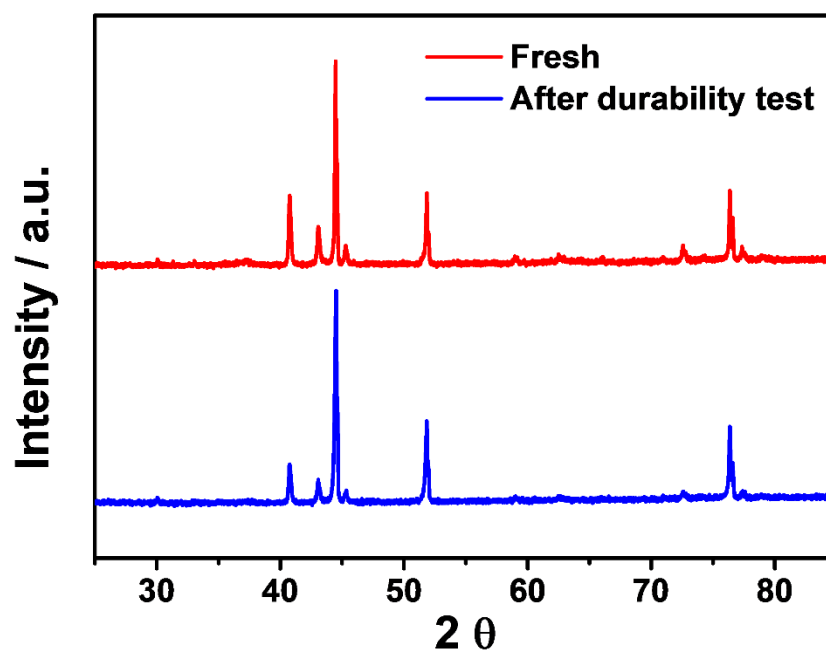


Fig. S7. XRD patterns of Ni₂Mo₃N/NF fresh and after durability tests.

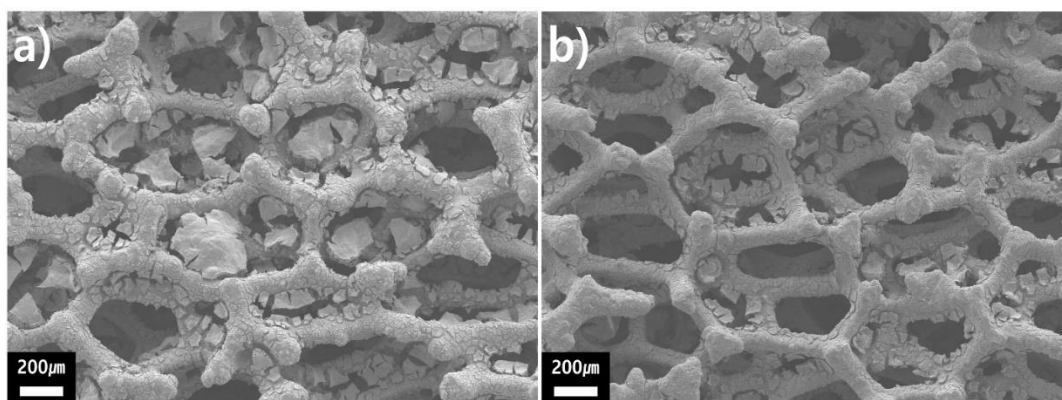


Fig. S8. SEM images of $\text{Ni}_2\text{Mo}_3\text{N}/\text{NF}$ a) before and b) after durability tests.

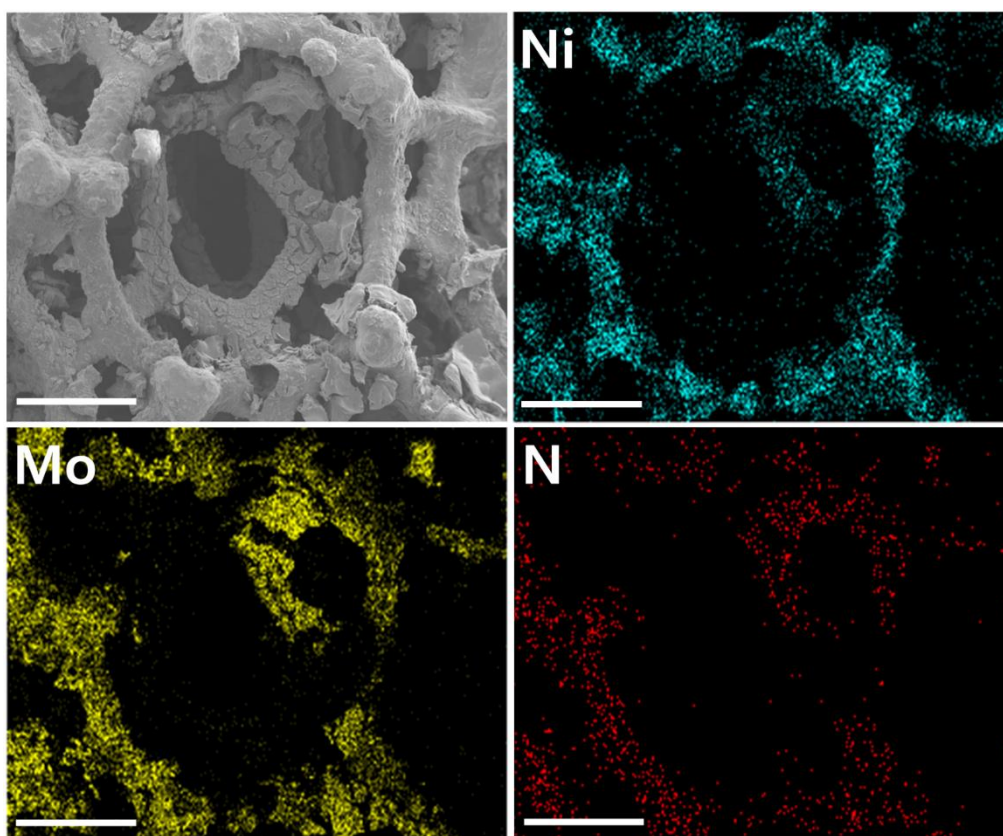


Fig. S9. EDS elemental mapping images of $\text{Ni}_2\text{Mo}_3\text{N}/\text{NF}$ after durability tests (scale bar = 300 μm).

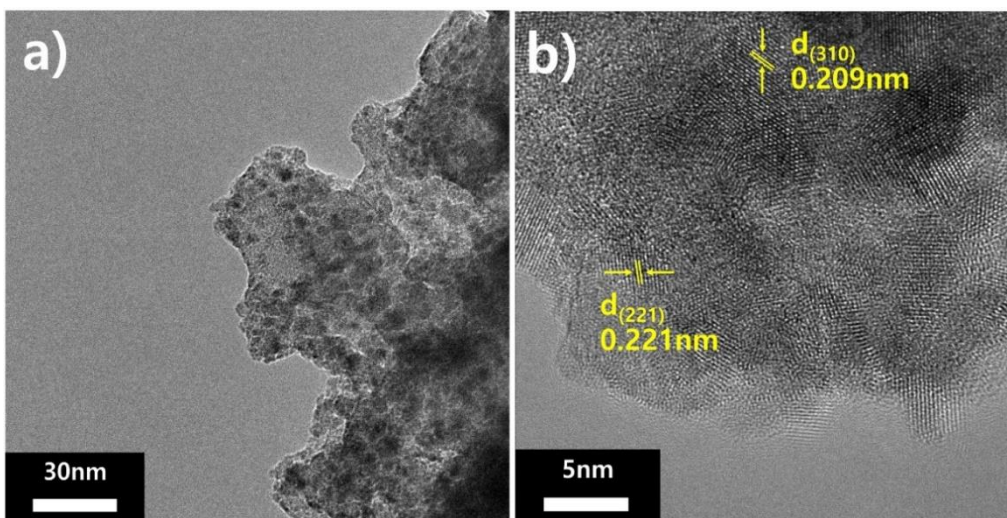


Fig. S10. TEM images of $\text{Ni}_2\text{Mo}_3\text{N}/\text{NF}$ after durability tests.

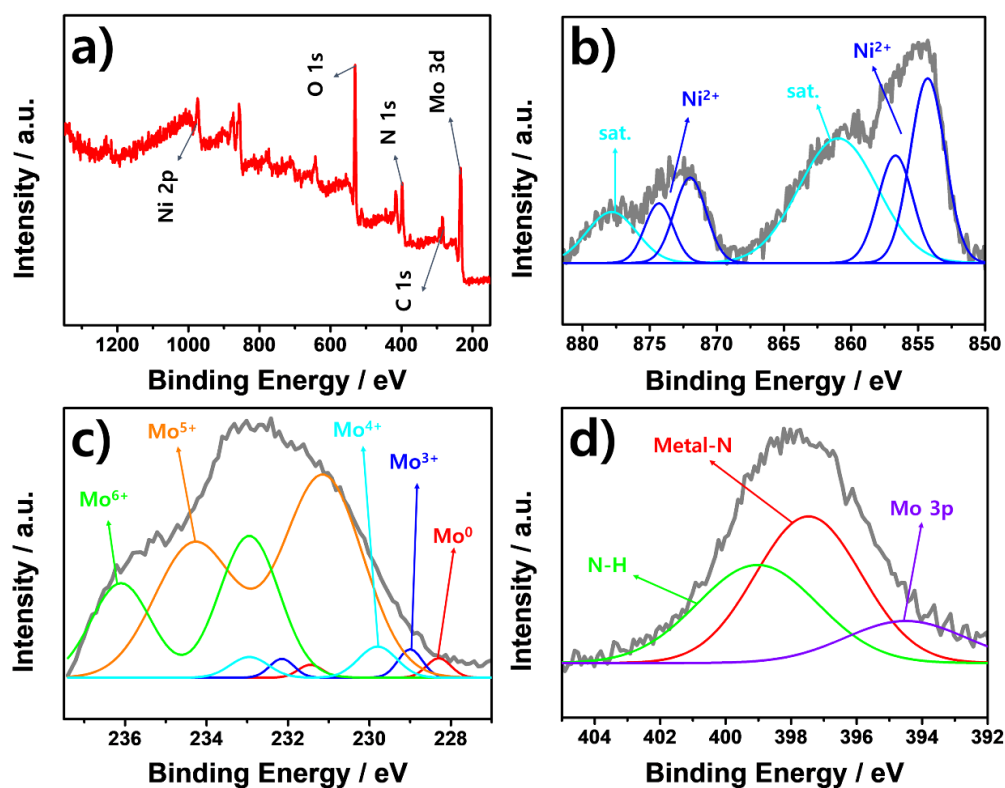


Fig. S11. XPS spectra of $\text{Ni}_2\text{Mo}_3\text{N}/\text{NF}$ after durability tests for a) survey, b) Ni 2p, c) Mo 3d, and d)

N 1s.

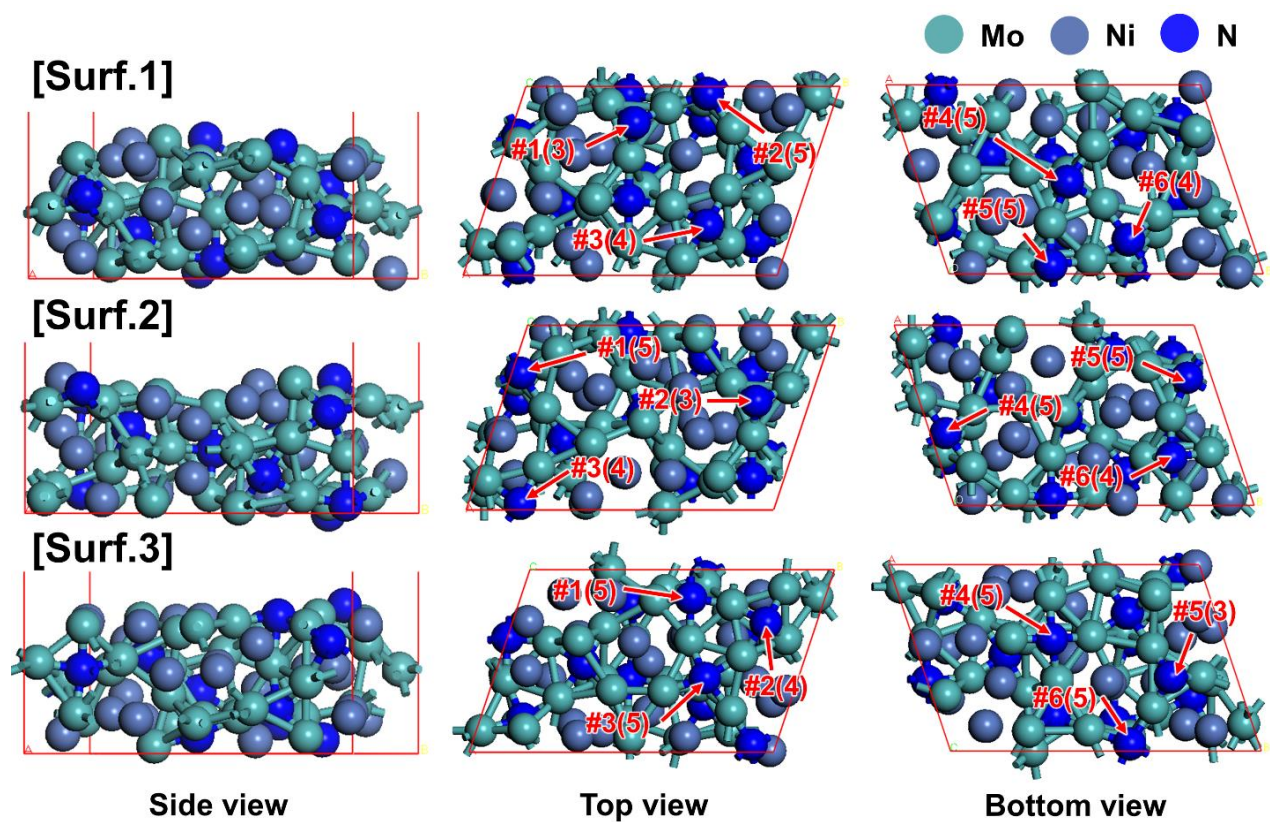


Fig. S12. The atomic structure of stoichiometric surface models which parallel to the (221) surface. Possible nitrogen active sites are indicated with a red arrow, and the numbers in parenthesis denote coordination number counting the N-Mo bonding.

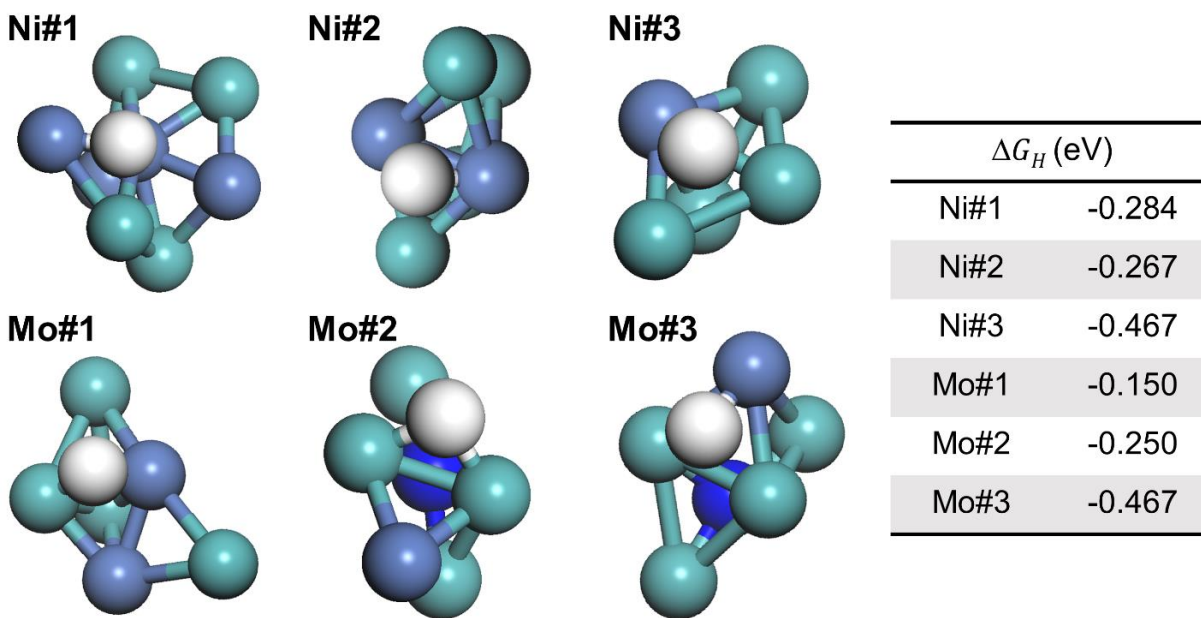


Fig. S13. H-adsorption structures and energies for Ni and Mo sites on the surface of Surf.1 in Figure S12. Light blue, turquoise, blue, and white spheres represent Ni, Mo, N, and H atoms, respectively.

Table S1. Comparison of the HER performance in alkaline media with reported state-of-the-art TMN-based catalysts.

| Catalyst | η_{10} (mV) | η_{100} (mV) | Tafel slope (mV dec ⁻¹) | Reference |
|---|---------------------------------|-----------------------------------|-------------------------------------|-----------|
| Ni ₂ Mo ₃ N/NF | 21.3 | 123.8 | 62 | This work |
| V-Ni ₂ Mo ₃ N | 54 | 117 | 42.8 | 1 |
| V-Ni _{0.2} Mo _{0.8} N | 39 | 178 (200 mA cm ⁻²) | 37.7 | 2 |
| NiMoN-NF700 | 38 | 118 (50 mA cm ⁻²) | 46 | 3 |
| FeNi ₃ N/NG | 98 (20 mA cm ⁻²) | 186 | 83.1 | 4 |
| Co-NiMoN-400 NRs | 45 | | 72.2 | 5 |
| Ni@NCNT/NiMoN-8 | 15 | 156 (50 mA cm ⁻²) | 68 | 6 |
| Ni-Mo-N/NG | 46.6 | 159.8 | 45 | 7 |
| Ni-Fe-MoN NTs | 55 | 199 | 109 | 8 |
| NiMoN-550 | 89 | ≈260 | 79 | 9 |
| NiMoN | 109 | ≈180 | 95 | 10 |
| MoVN | 108 | ≈175 | 60 | 11 |
| NiSP-Co ₃ FeN _x | 23 | 147 | 94 | 12 |
| Co ₂ Ni ₁ N | 102.6 | ≈200 (50 mA cm ⁻²) | 60.2 | 13 |
| Mo ₂ (CN) _{0.5} | 80 | 202 | 40 | 14 |
| Co-Mo ₂ N@NC | 47 | 170 | 43 | 15 |
| Mo ₂ N/NC-2 | 217 | ≈410 | 115.7 | 16 |
| <i>h</i> -MoN@BNCNT | 78 | | 46 | 17 |
| CoN-400/CC | 97 | ≈200 | 93.9 | 18 |
| Mo-600 | 85 | | 54 | 19 |
| S-2-T5 | 76 | 240 | 47 | 20 |

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