

Supplementary Information

Bimetallic Carbide as A Stable Hydrogen Evolution Catalyst in Harsh Acidic Water

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Experimental Section

Chemicals. Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), ammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), ammonium fluoride (NH_4F), urea ($\text{CO}(\text{NH}_2)_2$), selenium (Se) powder, sodium hydroxide (NaOH), hydrazine ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$), and N, N-dimethylformamide (DMF) were purchased from Shanghai Chemical Reagent Co. Ltd. Pt/C (5 wt% Pt on Vulcan carbon black) was purchased from Alfa Aesar. Nafion (5 wt%) and glucose were obtained from Sigma-Aldrich. All chemicals were of analytical grade and used without any further purification. Ni foam was cleaned ultrasonically with acetone, ethanol, HCl solution (3.0 mol L^{-1}) and DI water for 15 min respectively, to remove the oxide layers on the surface before use.

Synthesis of $\text{Mo}_6\text{Ni}_6\text{C/NF}$. The $\text{Mo}_6\text{Ni}_6\text{C/NF}$ sample was fabricated by a hydrothermal method. First, 0.1000 g glucose, 0.5191 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and 0.4362 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 30 mL DI water, following by sonicated at room temperature for approximately 30 min until a homogeneous solution was achieved. Then, the pre-treated Ni foam (1.6-mm thick, 110 p.p.i., geometric area of 1 cm^2) was placed against the wall of a 50 mL Teflon-lined stainless steel autoclave at a certain angle. The autoclave was sealed and heated at 150°C for 6 h. After the hydrothermal reaction, the samples were completely washed with DI water and dried in a vacuum oven of 60°C . Finally, the samples were annealed to obtain $\text{Mo}_6\text{Ni}_6\text{C/NF}$ at 700°C for 2 h under the mixture gas of 15% H_2/Ar in a tube furnace. The mass loading of $\text{Mo}_6\text{Ni}_6\text{C/NF}$ is about 17.8 mg cm^{-2} by measuring the weight difference between $\text{Mo}_6\text{Ni}_6\text{C/NF}$ and the pristine NF. For comparison, different Ni:Mo ratios and different annealed temperatures were applied.

Synthesis of NiMo alloy. MoNi_4 was prepared by a modified method.¹ Firstly, 0.5191 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and 0.4362 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in DI water, and 1.0 M NaOH was dripped into the solution so as to control the pH of the solution to be ~ 9 . Then, the obtained solid mixture was washed with water and ethanol, respectively, then drying at 60°C in the vacuum oven. The sample was finally annealed at 400°C under 20% H_2/Ar for 2 h in a tube furnace.

Synthesis of Mo₂C. Mo₂C powder was prepared by a modified method.² Firstly, 1.0 g (NH₄)₆Mo₇O₂₄·4H₂O and 0.25 g glucose were dissolved into 30 mL DI water in a 50 mL Teflon-lined stainless steel autoclave, following by sonicated at room temperature for approximately 30 min and then sealed and heated at 200 °C for 12 h in the oven. Then, after the hydrothermal reaction, the samples were completely washed with DI water and dried in a vacuum oven of 60 °C. Finally, the samples were annealed at 750 °C for 4 h under the mixture gas of 5% H₂/Ar in a tube furnace.

Synthesis of Ni_xFe_{1-x}Se₂/NF. Ni_xFe_{1-x}Se₂/NF was prepared by imitating the work conducted by Hu *et. al*³ through two steps: (i) metal hydroxide precursors were grown on nickel foam via a hydrothermal method; and (ii) hydroxide precursors were converted into diselenides via a solvothermal selenization treatment. ‘x’ represents the Ni ratio in the total metal elements of the starting solution. Typically, for Ni_xFe_{1-x}Se₂ (x=0.8), 0.582 g Ni(NO₃)₂·6H₂O, 0.139 g FeSO₄·7H₂O, 0.370 g NH₄F, and 1.501 g urea were dissolved in 40 mL H₂O. The as-obtained solution together with one piece of nickel foam (3 cm×1 cm) were then sealed in a 50 mL Teflon-lined stainless steel autoclave and heated at 120 °C an electric oven for 16 h. After being washed thoroughly with distilled water and absolute ethanol, the as-prepared nickel foam coated with NiFe hydroxides was submerged into another 50 mL autoclave containing 0.296 g Se, 0.300 g NaOH, 0.14 mL hydrazine and 25 mL DMF. After keeping at 180 °C for 1 h, Ni_xFe_{1-x}Se₂/NF was obtained.

Electrochemical measurements. The Mo₆Ni₆C/NF was directly used as the working electrode for electrochemical tests. For powders, 30 mg of catalyst and 80 μL Nafion solution (5 wt%) were dispersed in 1 mL of 4:1 v/v water/ethanol by at least 30 min sonication to form a homogeneous ink. The pretreated Ni foam was immersed into the ink for 30 s, and repeated for several times to obtain a mass loading of about 18 mg cm⁻², noted as Pt/C/NF, NiMo/NF and Mo₂C/NF, as the working electrodes to test linear sweep voltammetry (LSV). All electrochemical studies were performed using an electrochemical station (CHI 660E) in a three-electrode setup with modified Ni foam electrodes as the working electrode, Ag/AgCl/KCl (3.5 M) electrodes as a reference electrode, graphite rod as a counter electrode, and were de-aerated with argon before use. The electrocatalytic activities of the catalysts towards HER were examined by polarization curves with a scan rate of 5 mV s⁻¹ in 0.5 M H₂SO₄ or in 1.0 M KOH at room temperature. All potentials were referenced to reversible hydrogen

electrode (RHE) by following calculations: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.205$. AC impedance measurements were carried out in the same configuration when the working electrode was biased at a certain overpotential from 10^5 Hz to 0.1 Hz with an AC voltage of 5 mV. Noteworthy, all LSV curves and chronopotentiometric curves for stability test conducted at the constant j of 10 mA cm^{-2} were corrected with iR -compensation (90%), and the equivalent series resistance (R_s) can be obtained from the EIS Nyquist plots as the first intercept of the main arc with the real axis.

Gas measurements. Product gas quantification was carried out by gas chromatography. The electrochemical measurements were performed in a home-made H-type electrochemical cell separated by a cation exchange membrane (Nafion®, 115). The electrochemical cell was vigorously stirred and argon (99.99%, GB/T4842-2006) was continuously supplied to the cell at a constant rate of 15 mL min^{-1} using a mass flow controller (Alicat, MCS-Series). A galvanostatic current of -10 mA cm^{-2} was applied to the catalyst samples using a CHI 660E electrochemical analyzer. The outflowing gas was collected and passed into the sampling loop of a gas chromatography apparatus (GC 2060 system) equipped with a 5A column and a TCD detector. Gas samples were periodically (6 min) injected into the column. The Faradaic efficiency (FE) for formation of H_2 was calculated as below:

$$FE = 2FvGP / RTi \times 100\%$$

v (vol%) is the volume concentration of H_2 in the exhaust gas from the electrochemical cell (GC data). G (mL min^{-1} at room temperature and ambient pressure) is the gas flow rate. i (mA) is the steady-state cell current. $P = 1.01 \times 10^5 \text{ Pa}$, $T = 273.15 \text{ K}$, $F = 96485 \text{ C mol}^{-1}$, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.

DFT calculations. All density functional theory (DFT) computations were performed using the Vienna Ab initio Simulation Package (VASP) based on the projector augmented wave (PAW) method.^{4,5} Electron-ion interactions were described using standard PAW potentials, with valence configurations of $4s^2 4p^6 5s^2 4d^4$ for Mo (Mo_sv_GW), $3s^2 3p^6 4s^2 3d^8$ for Ni (Ni_sv_GW), and $2s^2 2p^2$ for C (C_GW_new). A plane-wave basis set was employed to expand the smooth part of wave functions with a cut-off kinetic energy of 520 eV. For the electron-electron exchange and correlation interactions, the functional parameterized by Perdew-Burke-Ernzerhof (PBE),⁶ a form of the general gradient approximation (GGA), was used throughout. The

Mo₆Ni₆C crystal was modelled with the primary unit cell including 12 Ni atoms, 12 Mo atoms and 2 C atoms. The theoretical lattice constant is 7.685 Å, which is almost identical to the experimental value (7.701 Å).⁷ Before the analysis of the electronic properties, the geometry was optimized. All the atoms were allowed to relax until the Hellmann-Feynman forces were smaller than 0.01eV/Å. The convergence criterion for the electronic self-consistent loop was set to 1×10^{-5} eV. We performed Brillouin-zone integrations using a gamma-centered ($4 \times 4 \times 4$) k-point grid for the structural optimization.

The (442) surface was modelled by a slab with the (1×1) surface cell comprising a 26 atomic layers separated by a vacuum region of 10 Å. A gamma-centered ($2 \times 4 \times 1$) k-point mesh was used. All Ni, Mo and C atoms can be found in the topmost layers of the (442) surface, which can adsorb H atoms. The Gibbs Free Energy was calculated by the formula:

$$\Delta G_{H^*} = \Delta E_{H^*} + \Delta ZPE - T\Delta S$$

where ΔE_{H^*} , ΔZPE and ΔS are the binding energy, zero point energy change and entropy change of H* adsorption, respectively. Herein, the $T\Delta S$ and ΔZPE are obtained by following the scheme proposed by Nørskov *et al.*⁸

Characterizations. The crystal structure was determined using X-ray diffraction (Bruker D8 Advanced Diffractometer with Cu K α radiation). The morphologies of the catalysts were examined by scanning electron microscope (Hitachi S4800) and transmission electron microscope (JEM 2100, 200 kV). Furthermore, the chemical states of the elements in catalysts were studied by X-ray photoelectron spectroscopy (Kratos Axis Ultra DLD), and the binding energy of the C 1s peak at 284.8 eV was taken as an internal reference. Mo K-edge and Ni K-edge X-ray absorption fine structure were performed on the 1W1B beamline of the Beijing Synchrotron Radiation Facility, China, operated at ~200 mA and ~2.5 GeV. Mo foil, Ni foil, MoO₃ and NiO powder were used as reference samples.

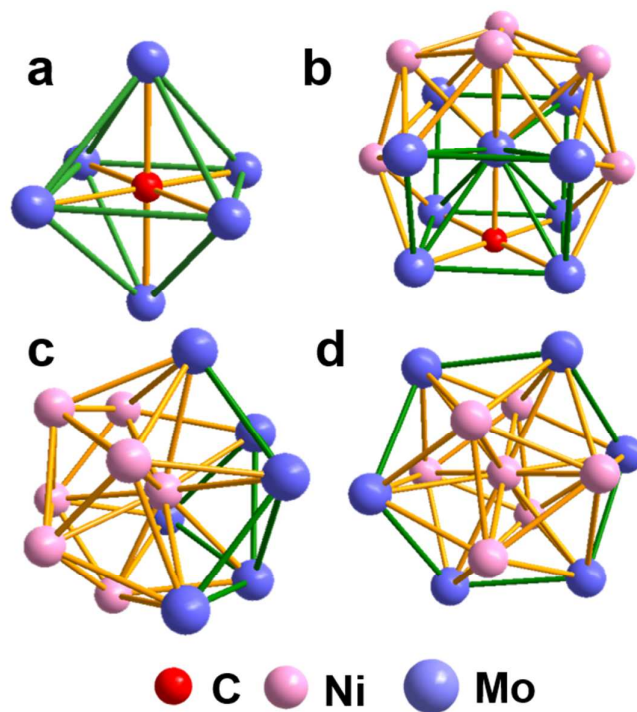


Figure S1. Schematic representations of the consisting figurations of (a) C, (b) Mo, (c) Ni1 and (d) Ni2 in the unit cell of $\text{Mo}_6\text{Ni}_6\text{C}$ (Ni1 and Ni2 are two different figurations for Ni atoms, and all Mo-Mo bonds are emphasized in green color).

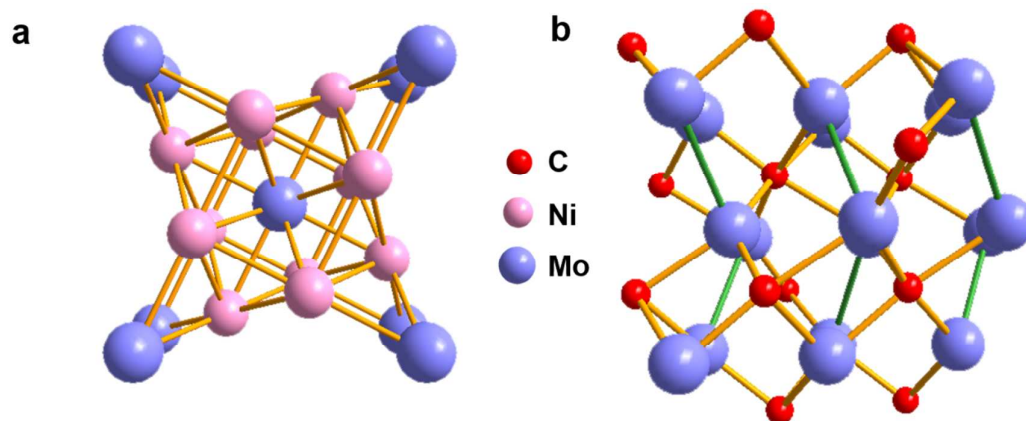


Figure S2. Schematic representations of unit structure for (a) MoNi_4 and (b) Mo_2C , indicating that Mo-Mo bonds only exist in Mo_2C units (Mo-Mo bonds are emphasized in green color).

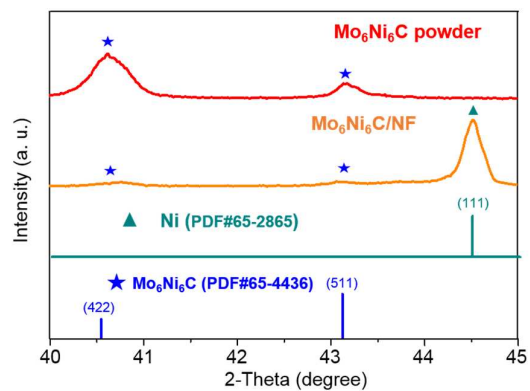


Figure S3. The enlarged XRD patterns of $\text{Mo}_6\text{Ni}_6\text{C}/\text{NF}$ and $\text{Mo}_6\text{Ni}_6\text{C}$ powder from 40 to 45 degree, revealing pure phase of $\text{Mo}_6\text{Ni}_6\text{C}$.

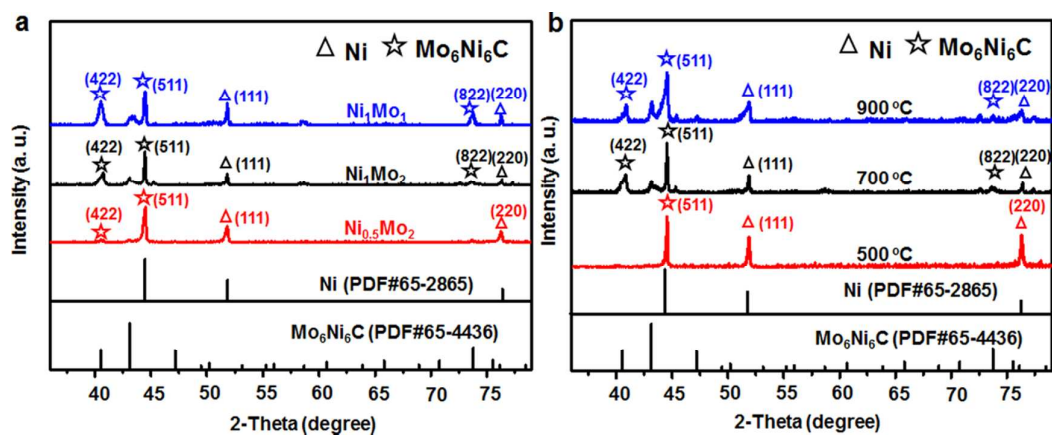


Figure S4. XRD patterns of samples of different (a) Ni:Mo ratios and (b) synthesis temperatures.

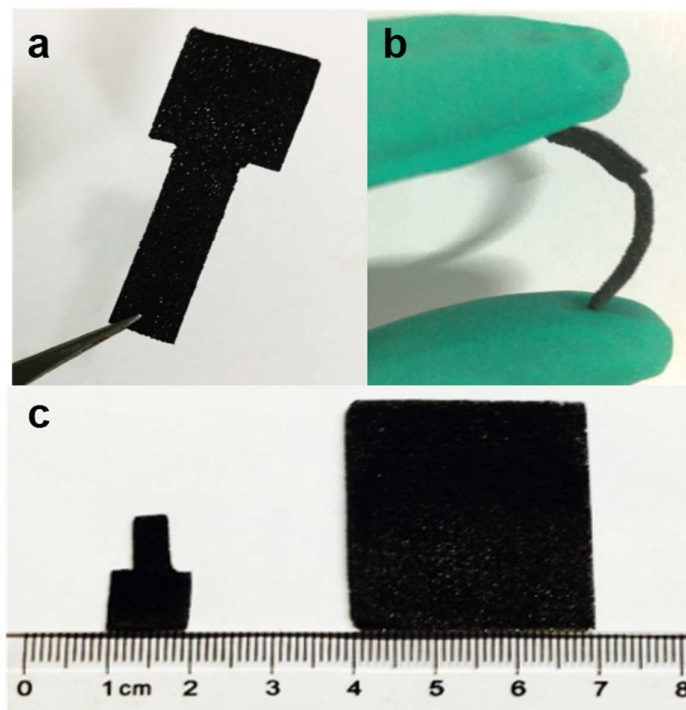


Figure S5. Digital images of $\text{Mo}_6\text{Ni}_6\text{C}/\text{NF}$: (a,b) show photographs of $\text{Mo}_6\text{Ni}_6\text{C}/\text{NF}$ before and after being stretched, indicating the material can be flexed well without undergoing structural damage; (c) shows the enlarged Ni foam with $\text{Mo}_6\text{Ni}_6\text{C}$, and it is obvious that the surface of the Ni foam was still well-proportioned as the pristine samples.

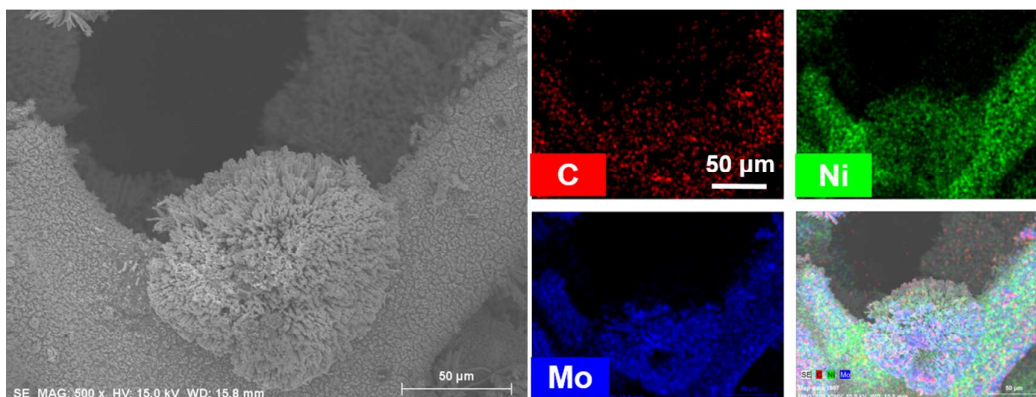


Figure S6. SEM images and corresponding elemental mappings for the sample of Mo₆Ni₆C/NF.

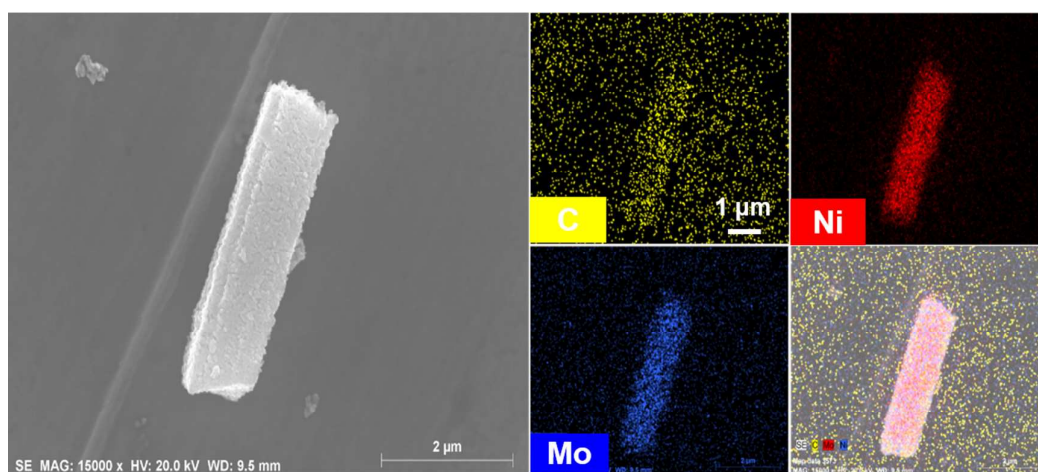


Figure S7. SEM images and corresponding elemental mappings for the sample of $\text{Mo}_6\text{Ni}_6\text{C}$ powder.

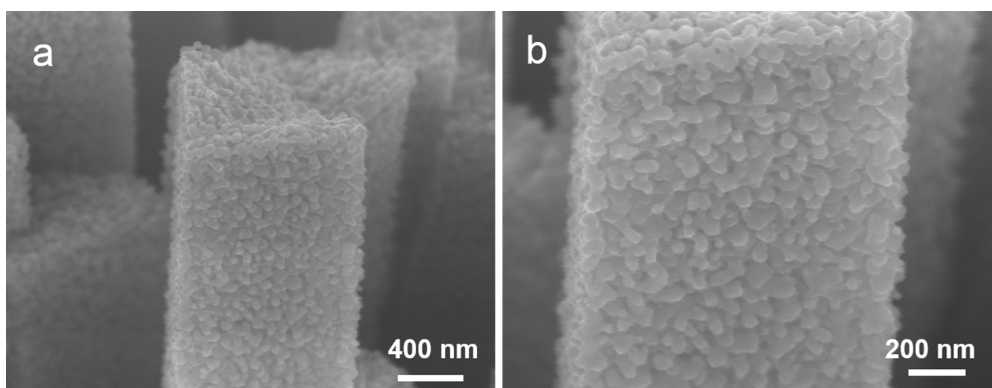


Figure S8. SEM images of $\text{Mo}_6\text{Ni}_6\text{C}/\text{NF}$, which displays the side view of the rods on Ni foam, revealing that the rods are composed of nanoparticles with average size of around 50 nm.

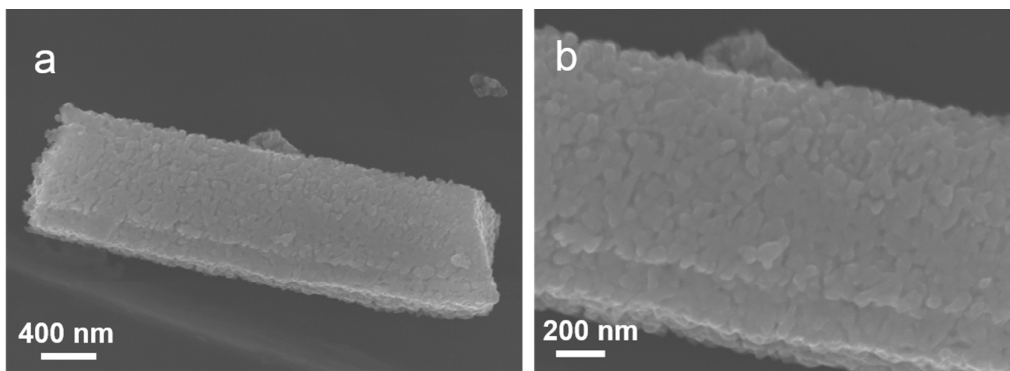


Figure S9. SEM images of the scraped off Mo₆Ni₆C powder, which displays the side view of the rods, revealing that the rods are composed of nanoparticles with average size of around 50 nm.

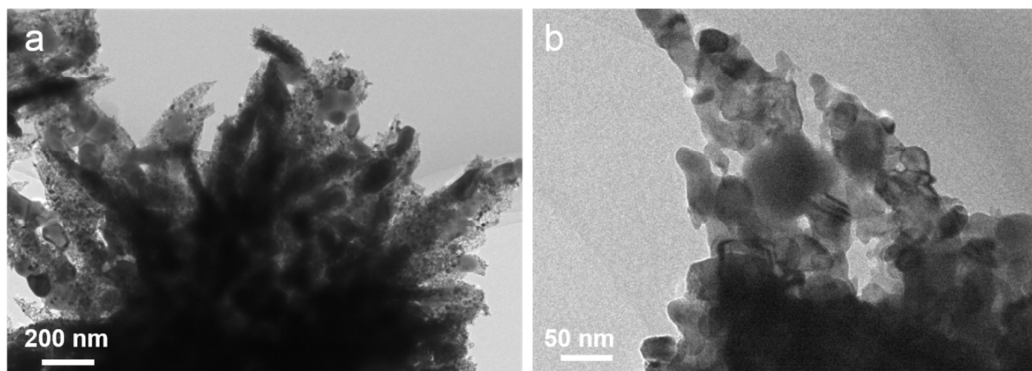


Figure S10. Supplementary TEM images of $\text{Mo}_6\text{Ni}_6\text{C}$, revealing that the other parts of $\text{Mo}_6\text{Ni}_6\text{C}/\text{NF}$ also consist of nanoparticles of around 50 nm in average.

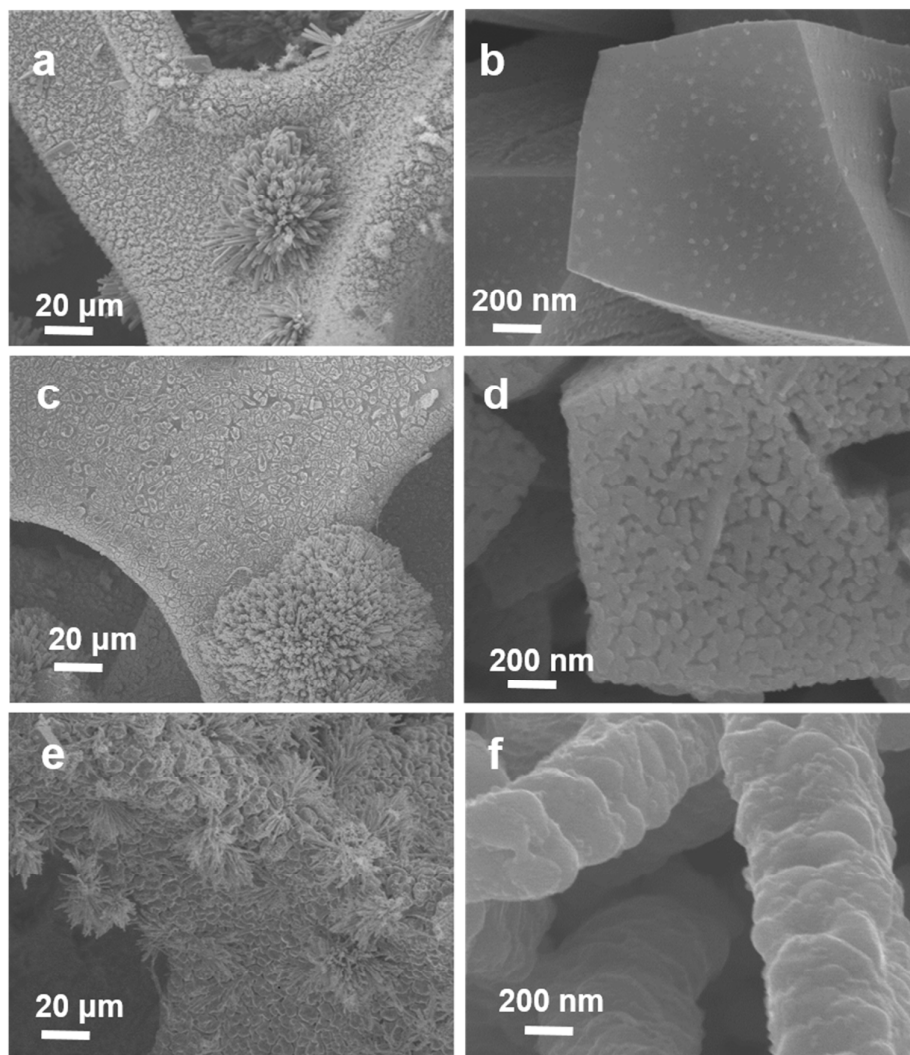


Figure S11. SEM patterns of samples with different synthesis temperatures of (a,b) $\text{Mo}_6\text{Ni}_6\text{C}/\text{NF}/500$, (c,d) $\text{Mo}_6\text{Ni}_6\text{C}/\text{NF}$, and (e,f) $\text{Mo}_6\text{Ni}_6\text{C}/\text{NF}/900$. The temperature influences the particle size of $\text{Mo}_6\text{Ni}_6\text{C}$.

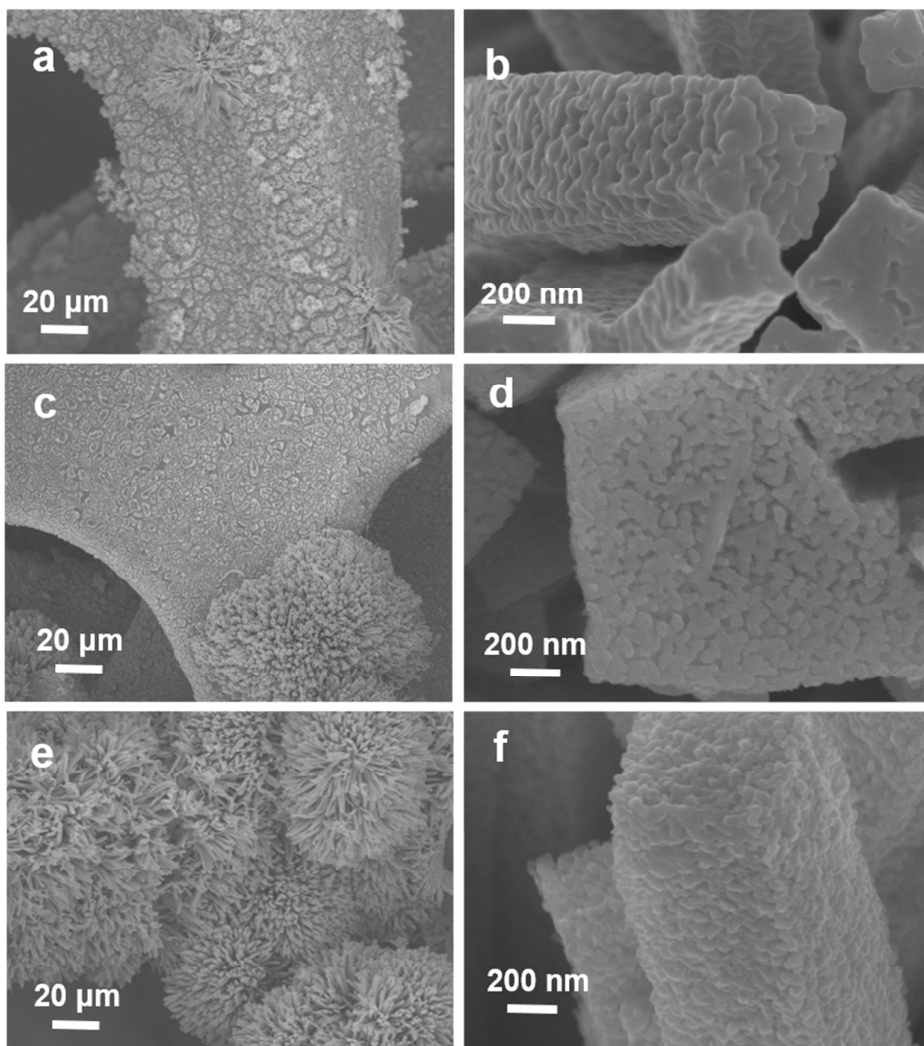


Figure S12. SEM patterns of samples with different Ni:Mo ratios: (a,b) Ni:Mo = 0.5:2; (c,d) Ni:Mo = 1:2; (e,f) Ni:Mo = 1:1. The Ni:Mo ratio affects the density of clusters of rods.

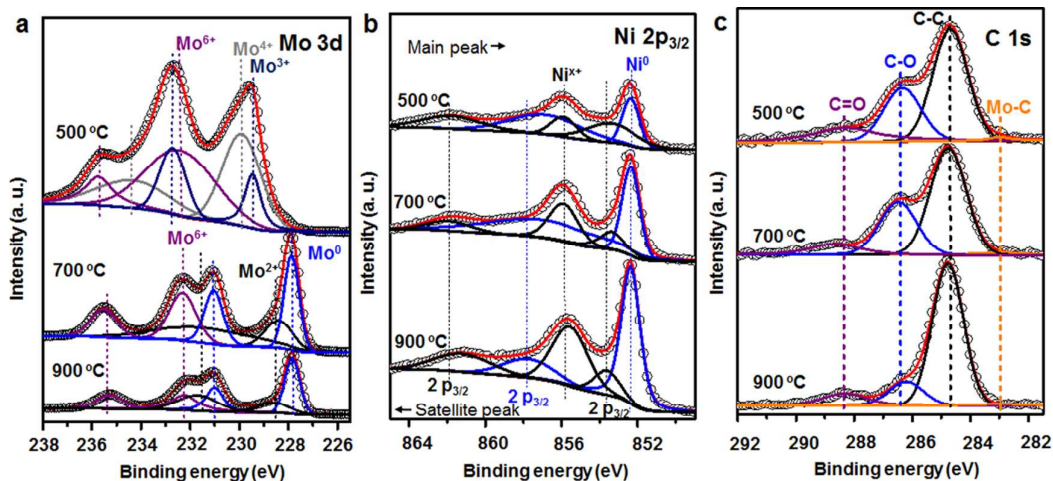


Figure S13. XPS spectra of Mo₆Ni₆C/NF synthesized via different temperatures for (a) Mo 3d, (b) Ni 2p_{3/2} and (c) C 1s. Compositions of the characteristic peaks for Ni 2p_{3/2} and C 1s were similar, while the characteristic peaks for Mo 3d spectrum of Mo₆Ni₆C/NF/500 were quite different from Mo₆Ni₆C/NF and Mo₆Ni₆C/NF/900. The biggest difference was that no Mo⁰ signals at around 227.8 and 231.1 eV were observed, further demonstrating the Mo₆Ni₆C/NF/500 features no Mo-Mo bonds in the crystals.

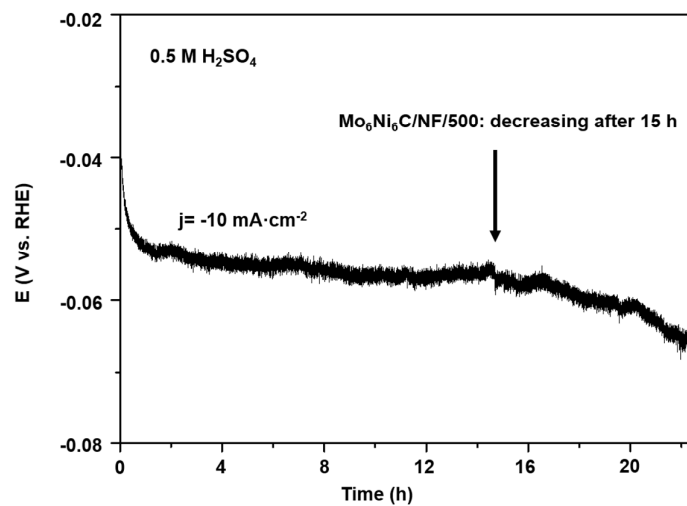


Figure S14. Galvanostatic measurement of Mo₆Ni₆C/NF/500 at the j of -10 mA cm⁻² in 0.5 M H₂SO₄, and the curve decreased apparently after about 15 h, indicating the poor stability of Mo₆Ni₆C/NF/500.

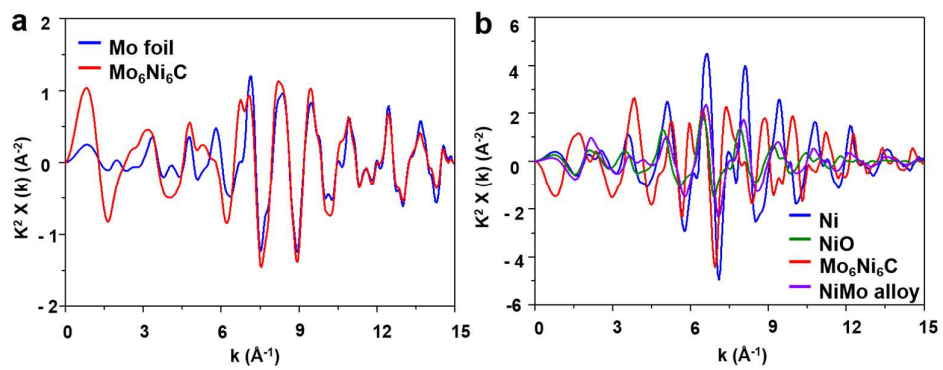


Figure S15. The k^3 -weighted spectra of (a) $\text{Mo}_6\text{Ni}_6\text{C}$, Mo foil and (b) $\text{Mo}_6\text{Ni}_6\text{C}$, NiMo alloy, Ni foil, NiO.

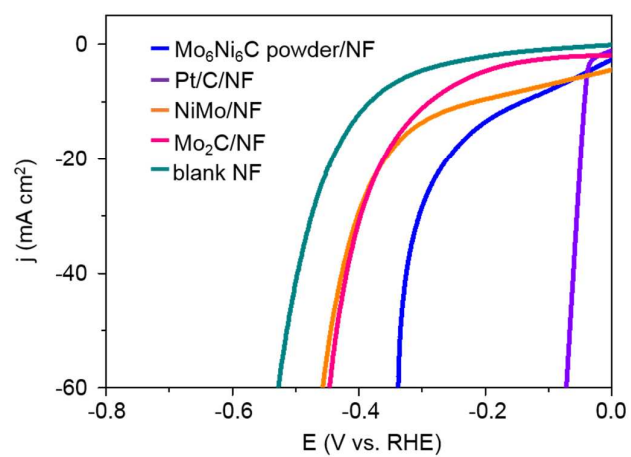


Figure S16. LSV curves for the samples of $\text{Mo}_6\text{Ni}_6\text{C}$ powder/NF, Pt/C/NF, NiMo/NF, Mo_2C /NF and blank Ni foam (the catalyst loading is about 18 mg cm^{-2} for every sample).

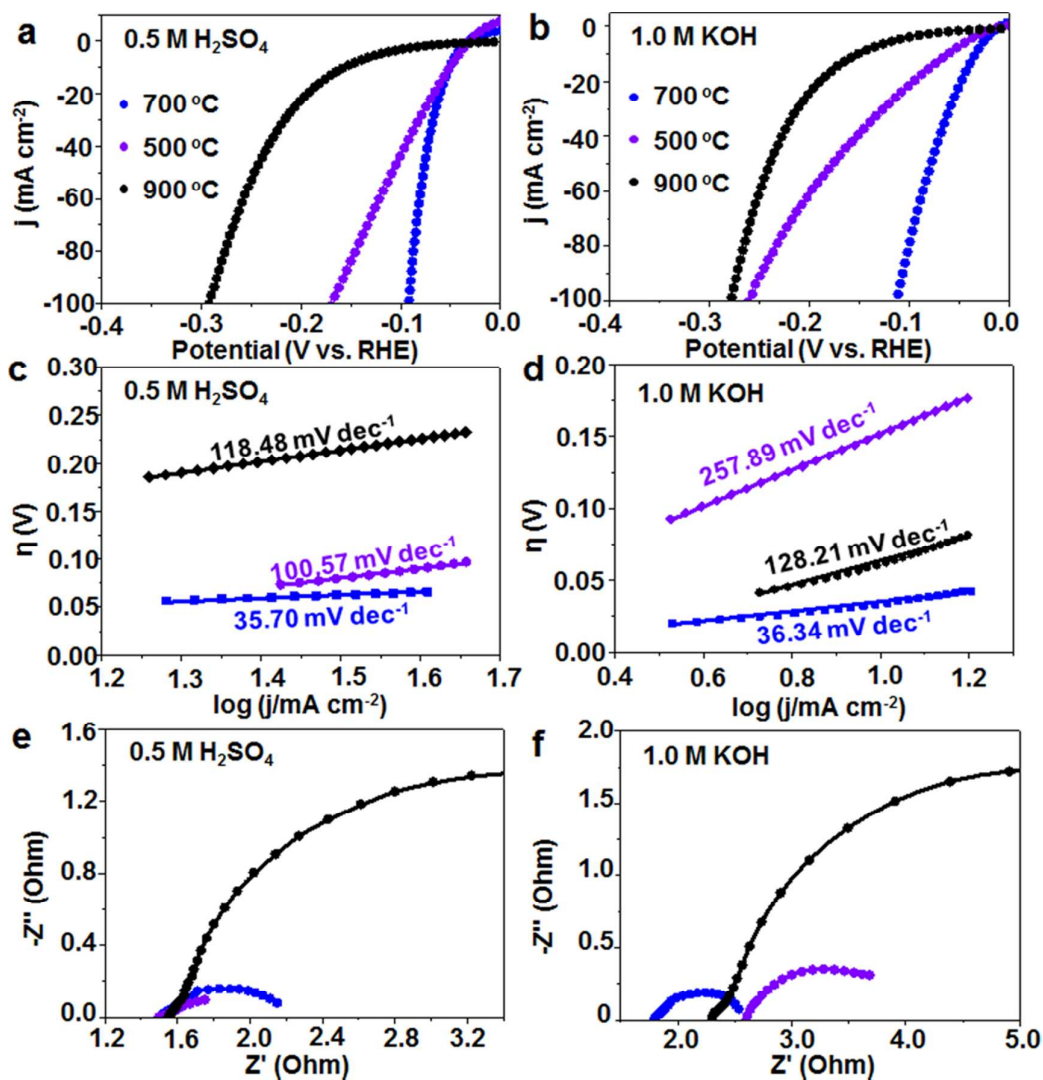


Figure S17. (a,b) LSV curves, (c,d) Tafel and (e,f) Nyquist plots of samples synthesized via different temperatures in 0.5 M H₂SO₄ and 1.0 M KOH, respectively.

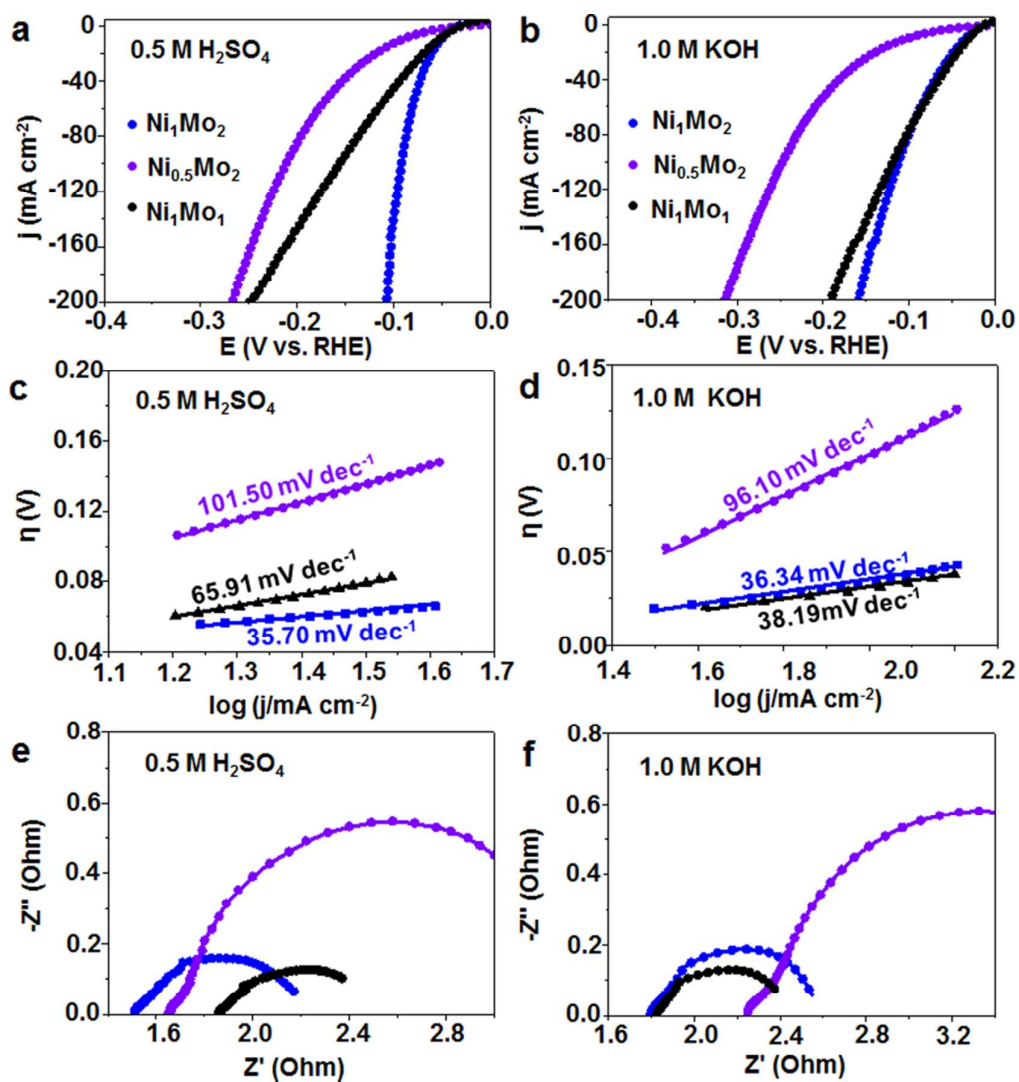


Figure S18. (a,b) LSV curves, (c,d) Tafel and (e,f) Nyquist plots of samples synthesized via different Ni:Mo ratios in 0.5 M H₂SO₄ and 1.0 M KOH, respectively.

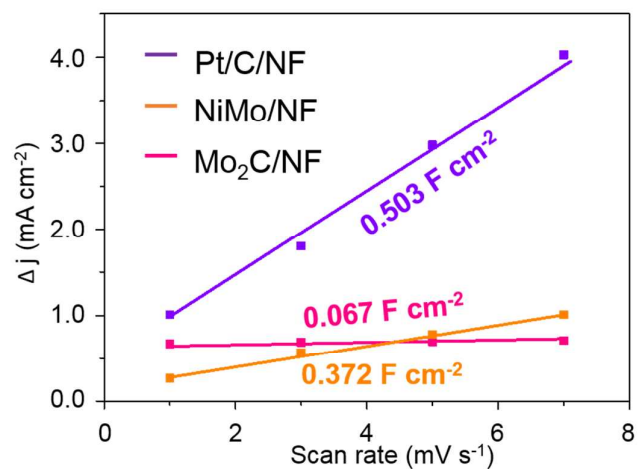


Figure S19. Scan rates dependence of the current densities ($\Delta j = j_a - j_c$) for controlled samples (Pt/C/NF, NiMo/NF and Mo₂C/NF).

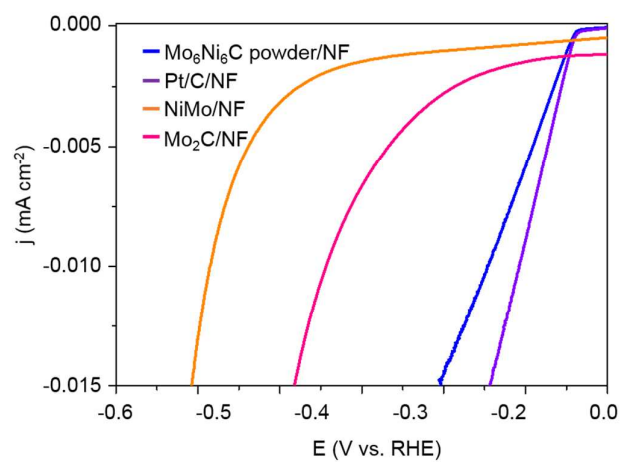


Figure S20. LSV curves normalized by ECSA for Mo₆Ni₆C/NF and controlled samples (Pt/C/NF, NiMo/NF and Mo₂C/NF).

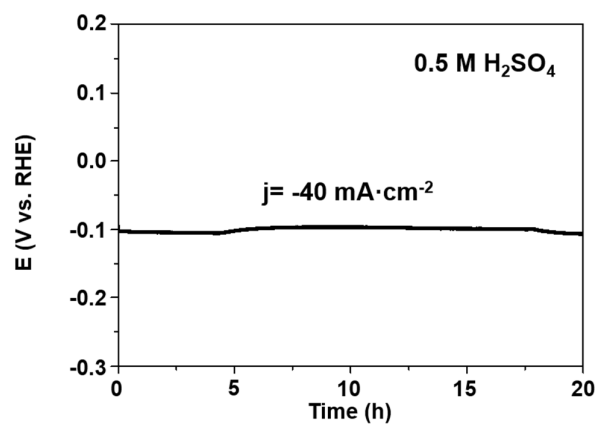


Figure S21. Chronopotentiometric curve of Mo₆Ni₆C/NF at j of -40 mA cm^{-2} for continuous HER process without iR -compensation in 0.5 M H₂SO₄. The geometric area of the electrode used is 0.25 cm^2 ($0.5 \text{ cm} \times 0.5 \text{ cm}$).

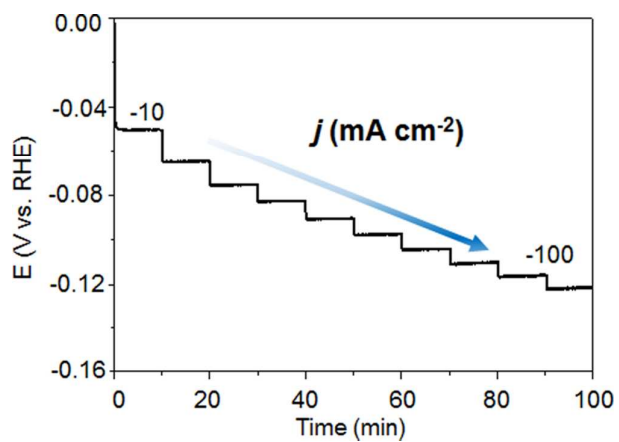


Figure S22. Multi-current curve of Mo₆Ni₆C/NF in 0.5 M H₂SO₄. The j and corresponding η also matched well with those tested in the polarization curves below -100 mA cm⁻², indicating that low capacitance current existed in the HER potential range.

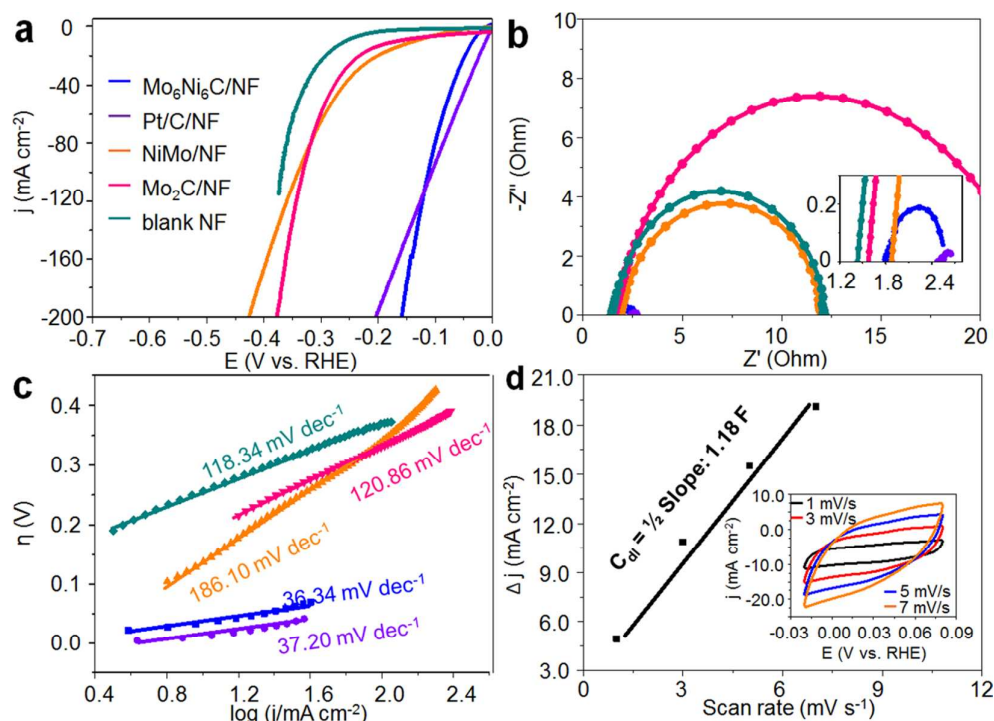


Figure S23. (a) LSV curves, (b) Nyquist and (c) Tafel plots for HER for the samples of Mo₆Ni₆C/NF, Pt/C/NF, NiMo/NF, Mo₂C/NF and blank Ni foam (the catalyst loading is about 18 mg cm⁻² for every sample). Mo₆Ni₆C/NF possesses the fastest charge transport process among all the controlled catalysts. The C_{dl} of Mo₆Ni₆C/NF in 1.0 M KOH was assessed utilizing a series of cyclic voltammetry (CV) cycles at different scan rates. (d) Scan rate dependence of the current densities ($\Delta j = j_a - j_c$) for Mo₆Ni₆C/NF at 0.03 V vs. RHE. Inset of (d): Cyclic voltammograms of Mo₆Ni₆C/NF at different scan rates (from 1 to 7 mV/s with an increment of 2 mV/s).

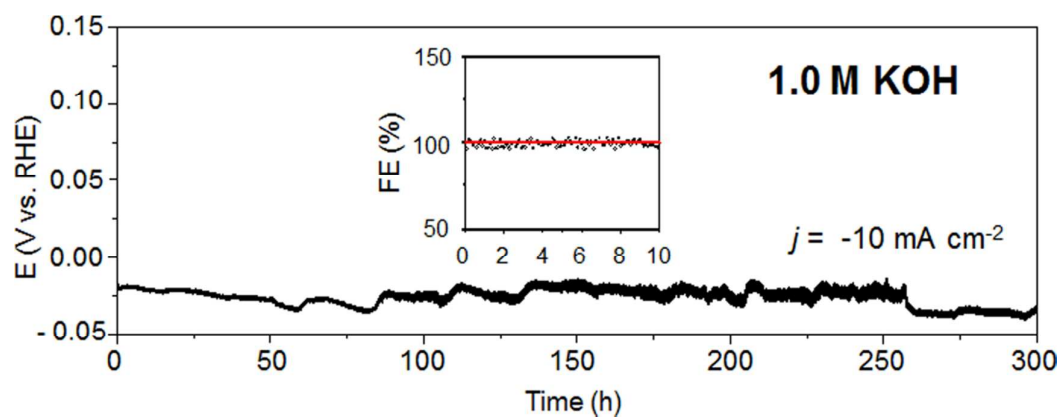


Figure S24. Chronopotentiometric curve of $\text{Mo}_6\text{Ni}_6\text{C/NF}$ at j of -10 mA cm^{-2} for continuous HER process. Inset: the corresponding faradaic efficiency from gas chromatography measurement of evolved H_2 for 10 hours of the chronopotentiometric test.

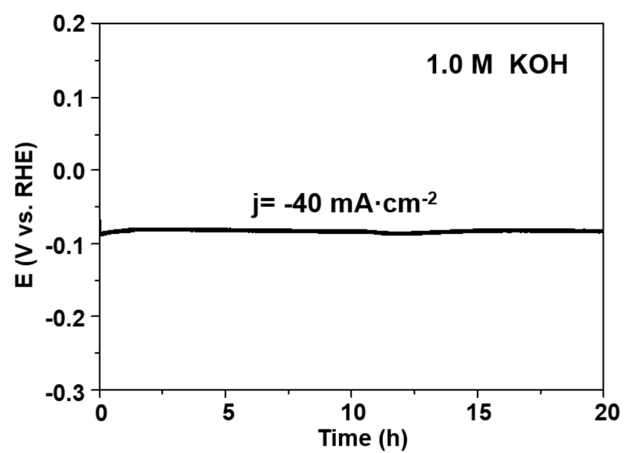


Figure S25. Chronopotentiometric curve of Mo₆Ni₆C/NF at j of -40 mA cm⁻² for continuous HER process without iR -compensation in 1.0 M KOH. The geometric area of the electrode used is 0.25 cm² (0.5 cm×0.5 cm).

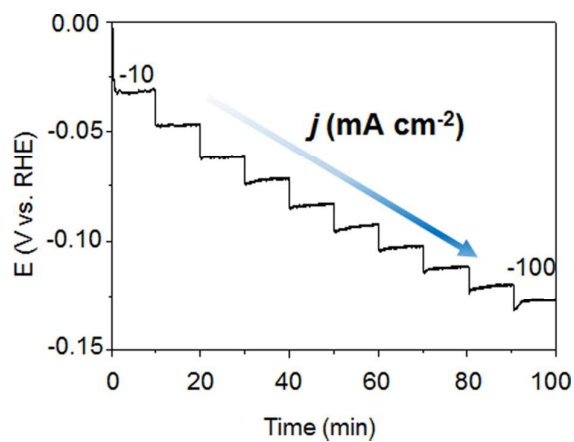


Figure S26. Multi-current curve of Mo₆Ni₆C/NF in 0.5 M H₂SO₄. The j and corresponding η also matched well with those tested in the polarization curves below -100 mA cm⁻², indicating that low capacitance current existed in the HER potential range.

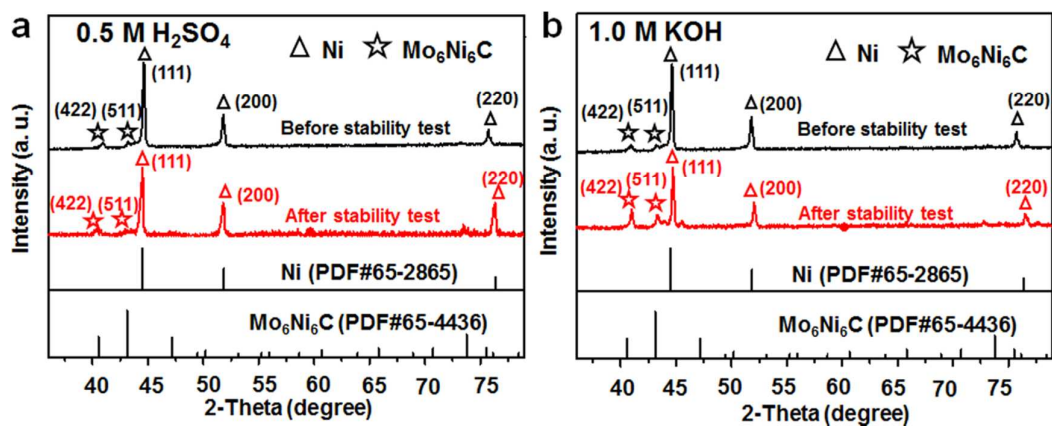


Figure S27. XRD patterns of $\text{Mo}_6\text{Ni}_6\text{C}/\text{NF}$ before and after chronopotentiometric tests in (a) 0.5 M H_2SO_4 and (b) 1.0 M KOH .

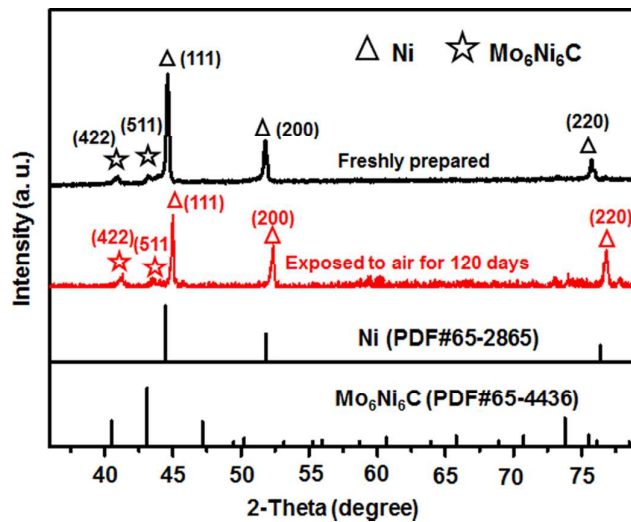


Figure S28. XRD patterns of Mo₆Ni₆C/NF freshly prepared and exposed to air for 120 days. After exposure to air for more than 120 days, the XRD pattern of Mo₆Ni₆C/NF was almost same as the pristine one, demonstrating its extraordinary stability in the air.

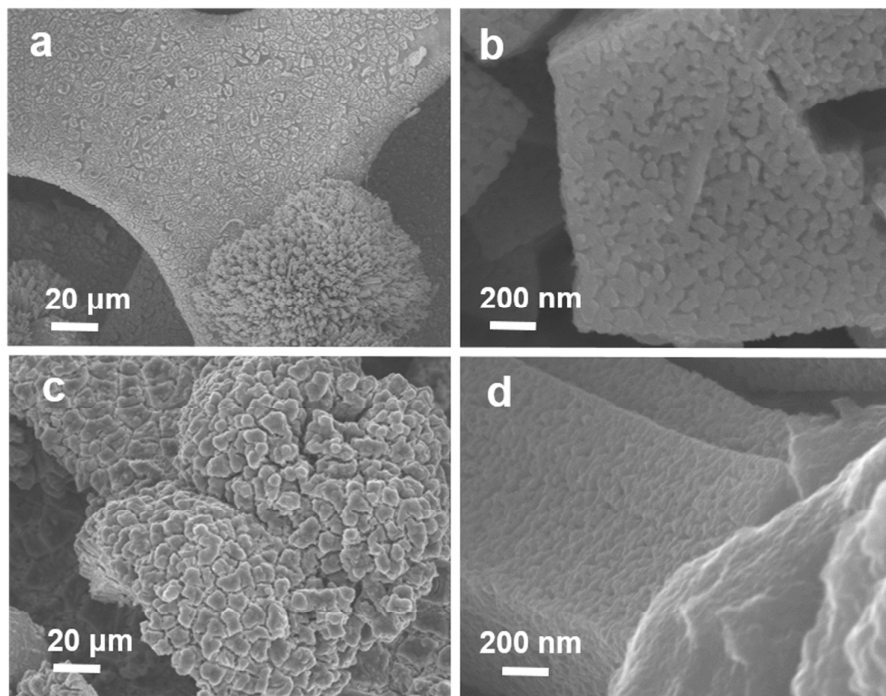


Figure S29. SEM images of $\text{Mo}_6\text{Ni}_6\text{C/NF}$ (a,b) before and (c,d) after chronopotentiometric test in 0.5 M H_2SO_4 . After the stability test, the surface of the material seemed like melting because of the harsh environment of acidic electrolyte. While under the surface, we could clearly see that the material was still constituted with the small particles in nature, which covered the Ni foam uniformly, protecting the substrate from being corroded by the strong acid.

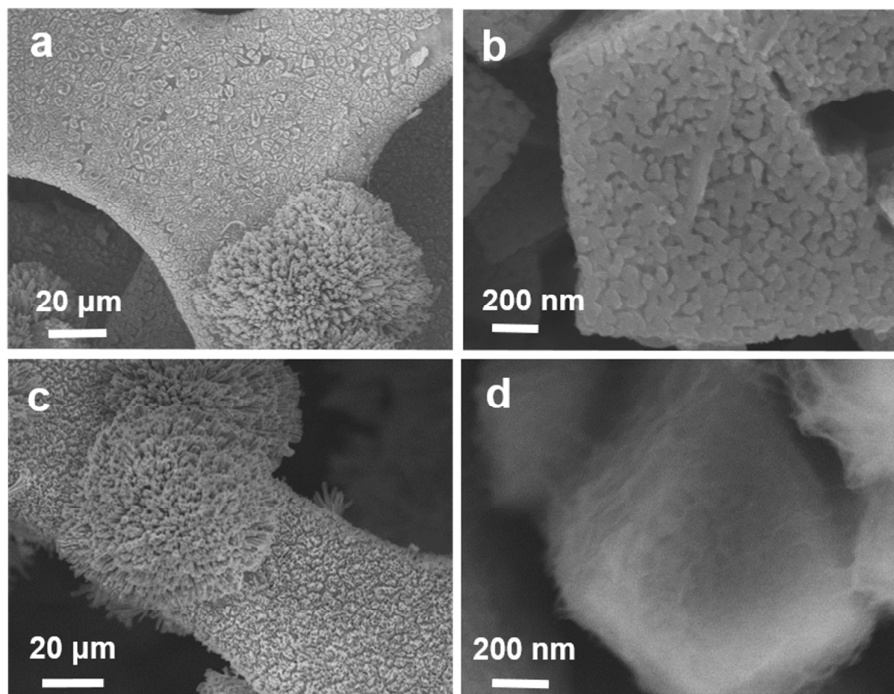


Figure S30. SEM images of $\text{Mo}_6\text{Ni}_6\text{C}/\text{NF}$ (a,b) before and (c,d) after chronopotentiometric test in 1.0 M KOH. After the stability test, it formed lamellar substance on the surface.

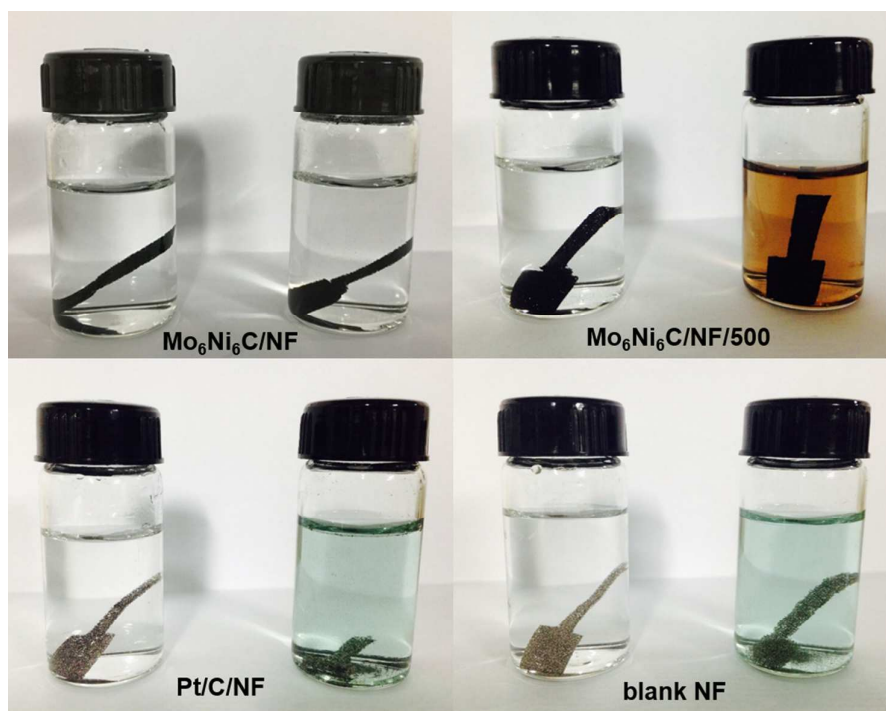


Figure S31. Digital photos of $\text{Mo}_6\text{Ni}_6\text{C}/\text{NF}$, $\text{Mo}_6\text{Ni}_6\text{C}/\text{NF}/500$, $\text{Pt}/\text{C}/\text{NF}$ and blank NF immersed in 0.5 M H_2SO_4 before and after 30 days. $\text{Mo}_6\text{Ni}_6\text{C}/\text{NF}$ did not change significantly, while $\text{Mo}_6\text{Ni}_6\text{C}/\text{NF}/500$ seemed somewhat dissolving into the solution. It was even worse for $\text{Pt}/\text{C}/\text{NF}$ and blank NF, because the color of the solution changed from colorless to green, indicating that Ni leaching took place. These results confirmed the optimum stability for $\text{Mo}_6\text{Ni}_6\text{C}/\text{NF}$ (which was synthesized via 700 °C) in acidic water.

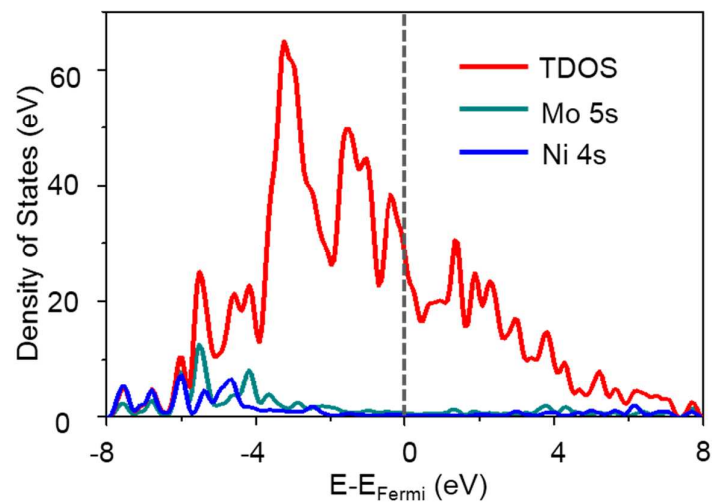


Figure S32. TDOS and PDOS calculated for $\text{Mo}_6\text{Ni}_6\text{C}$, confirming the metallic feature of $\text{Mo}_6\text{Ni}_6\text{C}$. The Fermi level was set at 0 eV.

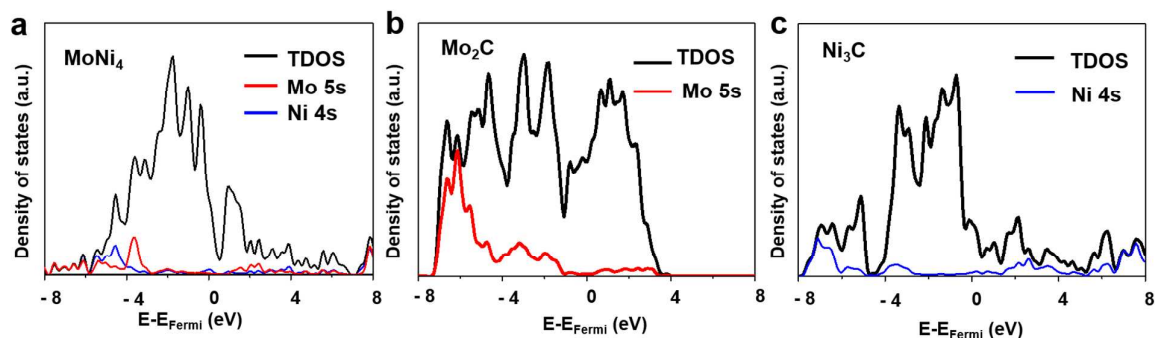


Figure S33. TDOS and PDOS calculated for (a) NiMo alloy, (b) Mo₂C and (c) Ni₃C. The TDOS near the Fermi level are continuous with no obvious gap, which indicates the metallic property of NiMo alloy, Mo₂C and Ni₃C.

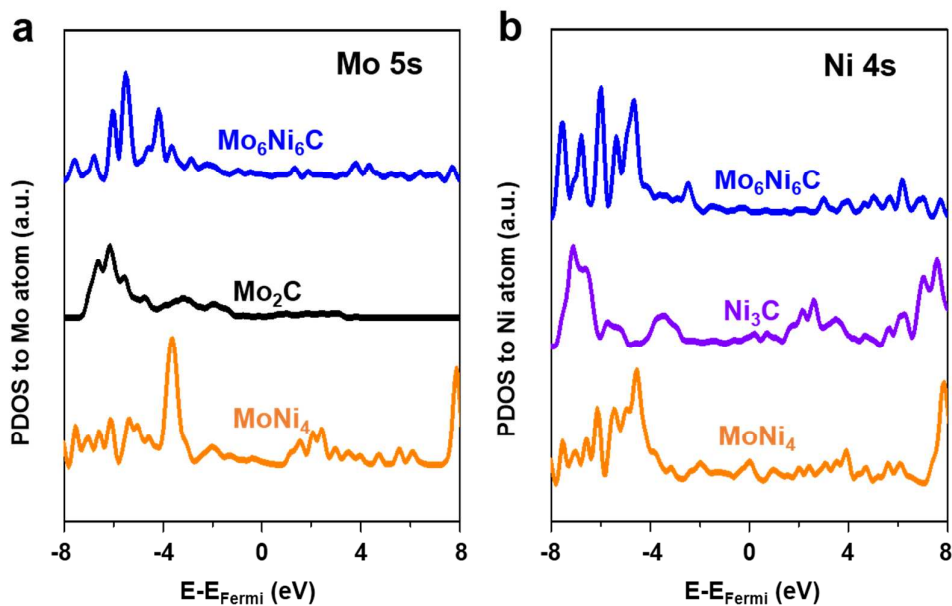


Figure S34. (a) Comparison of PDOS to Mo 5s for $\text{Mo}_6\text{Ni}_6\text{C}$, Mo_2C and MoNi_4 . (b) Comparison of PDOS to Ni 4s for $\text{Mo}_6\text{Ni}_6\text{C}$, Ni_3C and MoNi_4 . It can be found that the peaks of occupied states of $\text{Mo}_6\text{Ni}_6\text{C}$ are higher at the lower energy range ($[-8.0 \text{ eV}, -4.0 \text{ eV}]$) in terms of those of Ni_3C , and Mo_2C , indicating that that $\text{Mo}_6\text{Ni}_6\text{C}$ owns better stability.

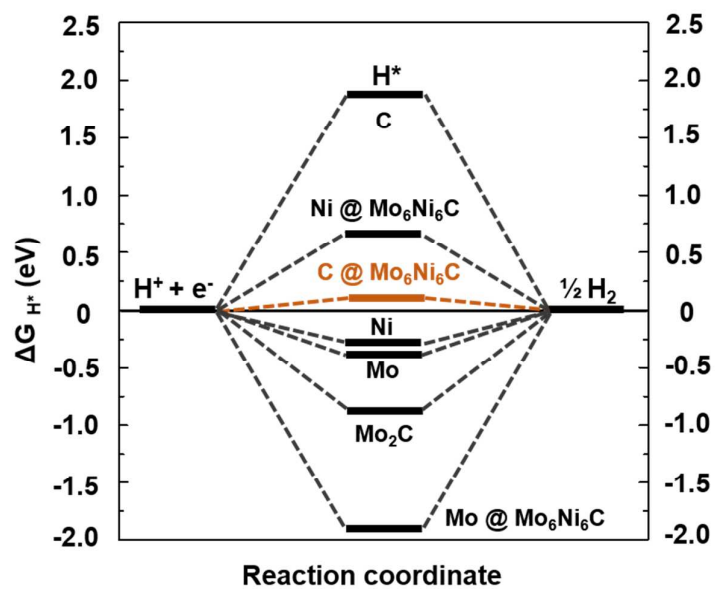


Figure S35. DFT-calculated HER activities. Besides Mo₆Ni₆C, others were cited from previous literatures.^{9,10} For Mo₆Ni₆C, the $\Delta G(H^*)$ of Mo, Ni and C sites were all calculated, among which, C @ Mo₆Ni₆C possess the most optimum $\Delta G(H^*)$, representing the possible active sites on Mo₆Ni₆C.

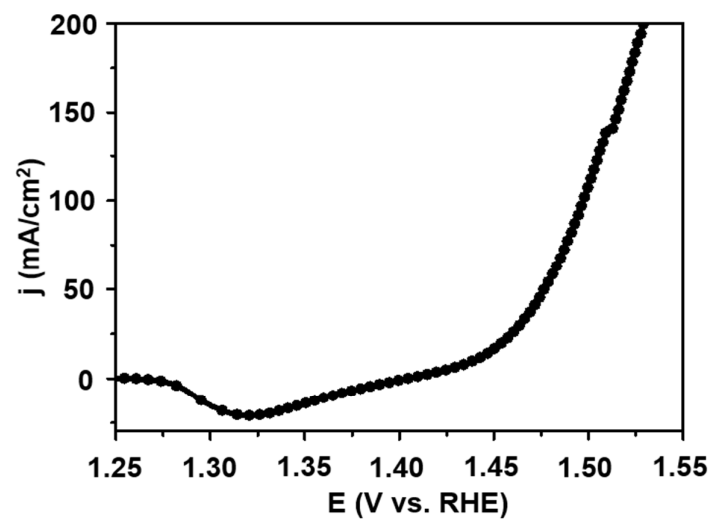


Figure S36. LSV curve of $\text{Ni}_x\text{Fe}_{1-x}\text{Se}_2/\text{NF}$ in 1.0 M KOH.

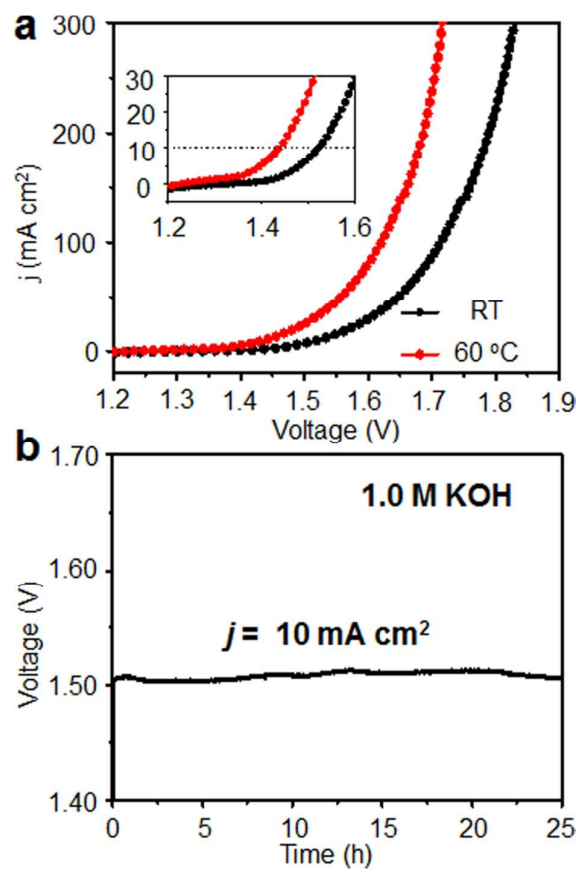


Figure S37. (a) LSV curves for an overall water splitting electrolyzer at room temperature (RT) and 60 °C, which uses $\text{Mo}_6\text{Ni}_6\text{C/NF}$ as cathode and $\text{Ni}_x\text{Fe}_{1-x}\text{Se}_2/\text{NF}$ as anode in 1.0 M KOH. (b) Chronopotentiometric curve of the electrolyzer at j of 10 mA cm^{-2} for continuous water splitting in 1.0 M KOH.

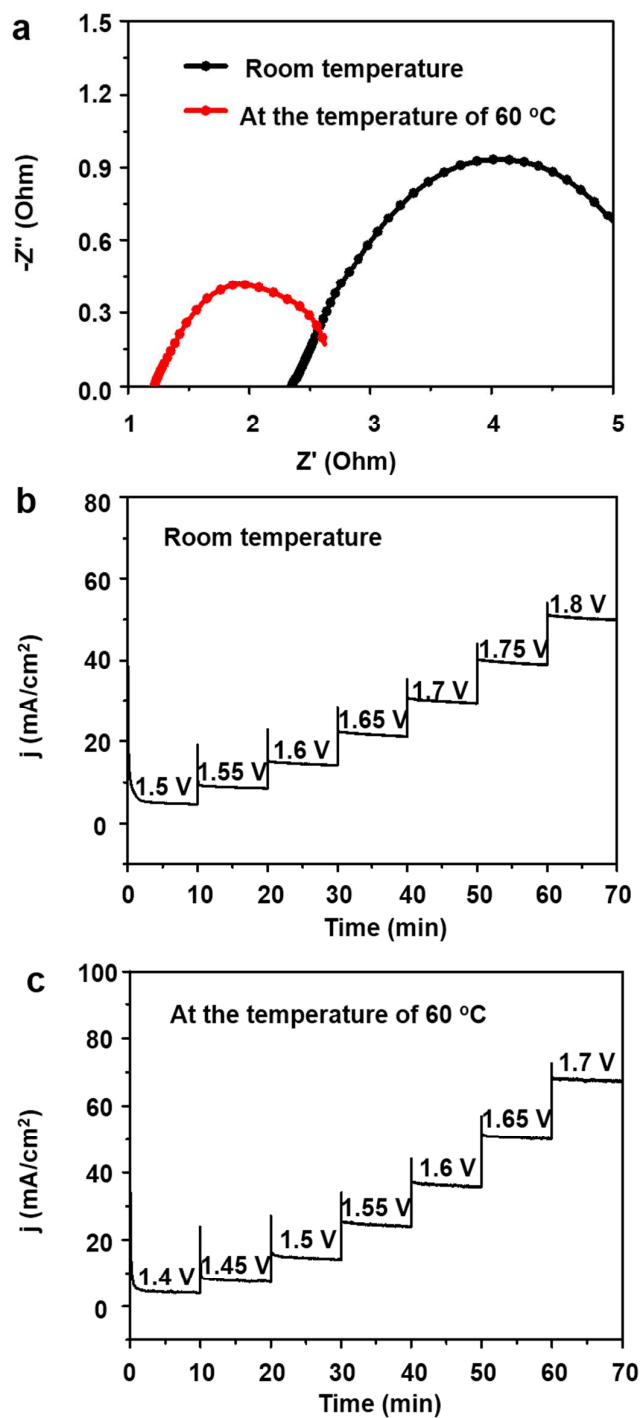


Figure S38. (a) Nyquist plots of the electrolyzer in 1.0 M KOH at room temperature and 60 °C. Multi-potential curves of the electrolyzer in 1.0 M KOH at (b) room temperature and (c) the temperature of 60 °C.

Table S1. Comparison of electrocatalytic performance of Mo₆Ni₆C and other HER electrocatalysts reported recently.

Materials	Electrolyte	η_{10} (mV)	Stability	Reference
Mo ₆ Ni ₆ C	0.5 M H ₂ SO ₄	51	200 h	This work
	1.0 M KOH	34	300 h	
2H-MoS ₂	0.5 M H ₂ SO ₄	170	65 h	11
Mo ₂ C@NPC/NPRGO	0.5 M H ₂ SO ₄	34	10 h	12
MoC ₂ @C	0.5 M H ₂ SO ₄	78	12 h	13
NiMoN _x	0.1 M HClO ₄	> 200	2000 cycles	14
NiMoN	1.0 M KOH	109	36 h	15
β -Mo ₂ C	0.5 M H ₂ SO ₄	172	8 h	16
	1.0 M KOH	112	/	
porous MoC _x	0.5 M H ₂ SO ₄	142	10 h	17
NiFeO _x /carbon	1.0 M KOH	88	100 h	18
NiSe ₂	0.5 M H ₂ SO ₄	117	65 h	19
NiO _x /Pt ₃ Ni	1.0 M KOH	40	3 h	20
MoS ₂ /CoSe ₂	0.5 M H ₂ SO ₄	68	22 h	21

Note: η_{10} represents the overpotential at the current density of -10 mA cm⁻².

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