

Supplementary Materials

Unveiling proton-regulated Mo=O/Mo-O⁻ centers in reconstructed Ni₂Mo-NiOOH/MoO_x interfaces toward accelerated proton-coupled electron transfer for urea oxidation reaction

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1. Experimental Section

1.1 Material Characterization

X-ray diffraction (XRD) patterns of the catalysts were measured using a bulk X-ray diffractometer (D8 Advance, Cu K α radiation). Scanning electron microscopy (SEM, JSM-IT800) and transmission electron microscopy (TEM, Talos L120C, Thermo Fisher Scientific (formerly FEI), USA) were adopted to characterize the morphology and microstructure of the catalysts. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific, USA) was used to analyze the valence state and crystal structure of the samples. The peak positions and full widths at half maximum (FWHMs) were constrained within physically reasonable ranges. Specifically, the FWHM values of all fitted characteristic peaks were limited in the range of 1.0-2.5 eV, and the binding energy positions of Ni 2p, Mo 3d, and O 1s peaks were restricted within the standard elemental and chemical state reference ranges of ± 0.2 eV. Consistent fitting constraints were applied to ensure reliable and reproducible peak assignments. Conventional Raman tests were performed on a Renishaw inVia spectrometer with an excitation wavelength of 532 nm. Operando electrochemical Raman measurements were carried out on a Renishaw inVia Raman spectrometer equipped with the HORIBA LabSpec 6 software platform. A 532 nm Edge excitation laser was applied, and a 100 $\times$ VIS objective lens was used to focus the laser beam. The operando tests were implemented in a homemade three-electrode electrochemical cell. The catalyst-modified substrate acted as the working electrode, a saturated calomel electrode served as the reference electrode, and a carbon rod was used as the counter electrode. The electrolyte was 1.0 M KOH solution containing 0.33 M urea. Various potentials were applied through an electrochemical workstation, and Raman signals on the catalyst surface were collected synchronously. The dynamic structural evolution and active species transformation of the catalyst during UOR were monitored in real time.

1.2 Electrochemical Measurements

All electrochemical measurements were performed on a CHI 760E electrochemical

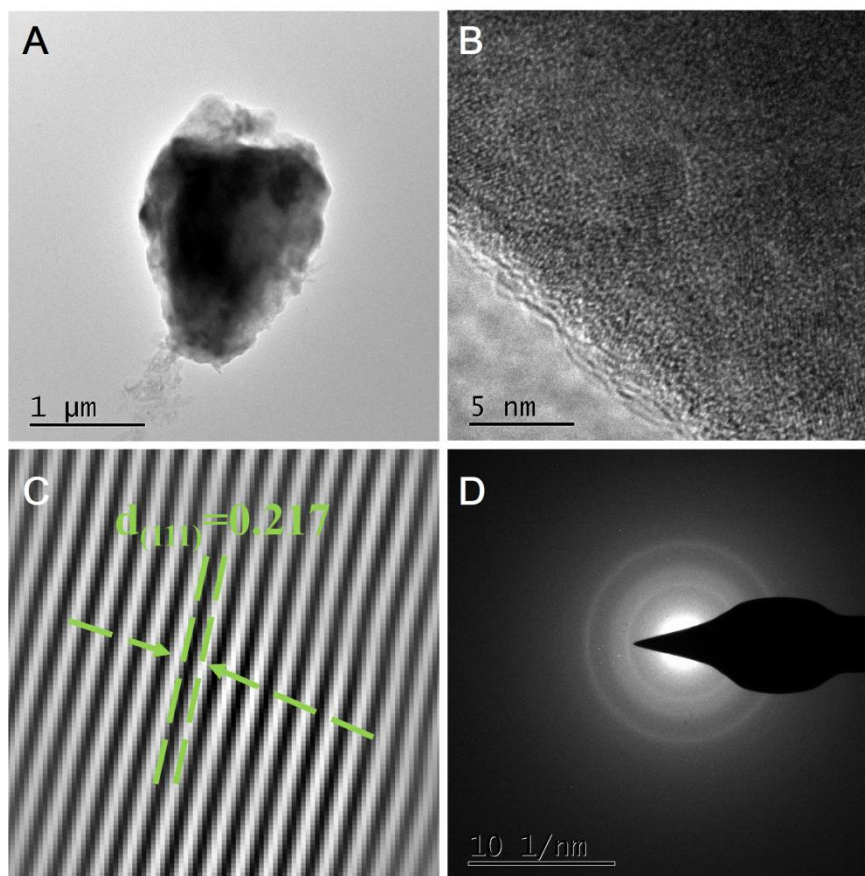
workstation (Chenhua Instrument Co., Ltd., Shanghai) in an electrolyte containing 1.0 M KOH and 0.33 M urea. All electrochemical tests were conducted in a standard three-electrode system. The self-supported electrode with an area of 1 cm² served as the working electrode, a saturated calomel electrode (SCE) was used as the reference electrode, and a carbon rod acted as the counter electrode. The scan rate was set at 5 mV s⁻¹ for cyclic voltammetry (CV) and linear sweep voltammetry (LSV).

Electrochemical impedance spectroscopy (EIS) was measured over a frequency range of 10⁻²-10⁻⁵ Hz at an applied potential of 0.23 V *vs.* SCE with an amplitude of 0.0005 V. All polarization curves were corrected by iR compensation. All measured potentials were converted to the reversible hydrogen electrode (RHE) scale according to the following formula: $E \text{ (vs. RHE)} = E \text{ (vs. SCE)} + 0.241 + 0.059 \text{ pH}$. The Tafel slope was determined by fitting the linear region and calculated according to the equation $\eta = a + b \log j$ represents the overpotential, j is the current density, and b is the Tafel slope. The electrochemically active surface area (ECSA) of the catalyst was calculated by the following formula:

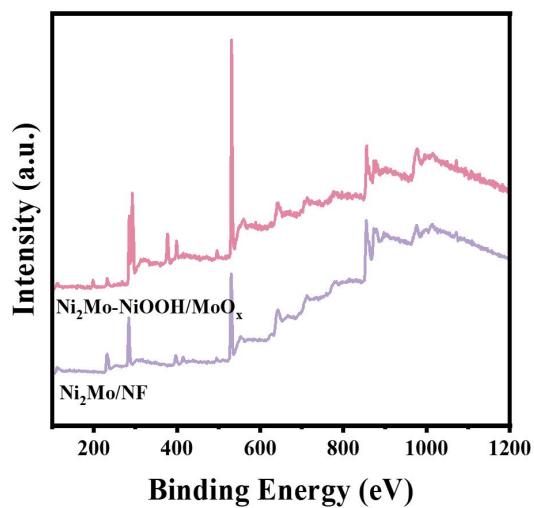
$$\text{ECSA} = \frac{C_{dl}}{40 \mu\text{F cm}^{-2}} \text{ cm}^2$$

The double-layer capacitance (C_{dl}) was acquired from CV curves measured at various scan rates within the non-Faradaic potential range of 1.14-1.24 V *vs.* RHE, and the specific capacitance was set to 40 $\mu\text{F cm}^{-2}$. Operando electrochemical impedance spectroscopy tests were conducted at applied potentials from 0.15-0.65 V *vs.* SCE with a potential increment of 0.05 V for each test. The electrolyte concentration dependence of catalytic electrodes was explored by adjusting the concentrations of KOH (1 M, 0.5 M, 0.1 M) and urea (0.33 M, 0.0825 M, 0.0333 M, 0.0125 M). Furthermore, the influence of different metal ions on catalytic performance was investigated by introducing graded concentrations of Ni²⁺ and Mo⁶⁺ into the baseline electrolyte consisting of 1.0 M KOH and 0.33 M urea.

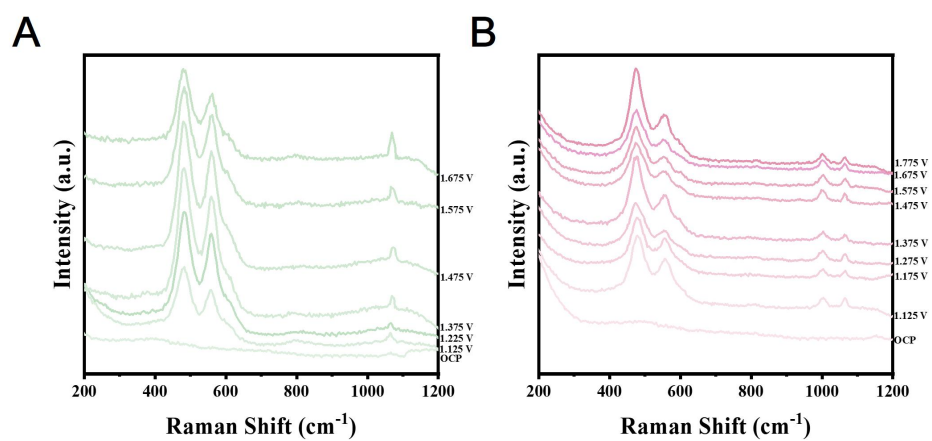
Supplementary Figures:



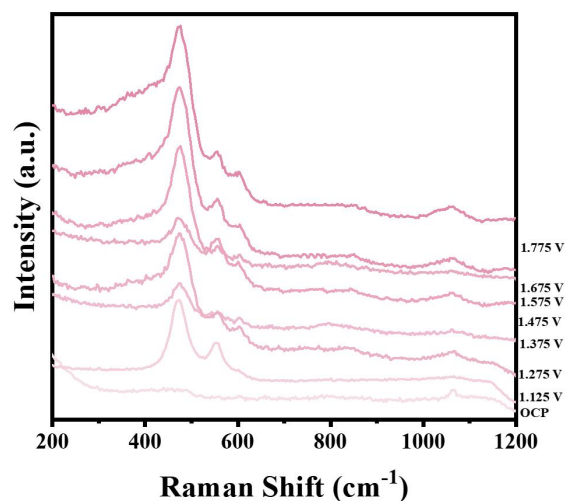
Supplementary Figure 1. Morphology and crystal structure characterization of Ni₂Mo/NF. (A) TEM image; (B) HRTEM image; (C) Fast Fourier transform (FFT) analysis of lattice fringes in (B), where the lattice spacing of the (111) crystal plane for Ni₂Mo/NF is labeled as $d = 0.217$ nm; (D) SAED pattern



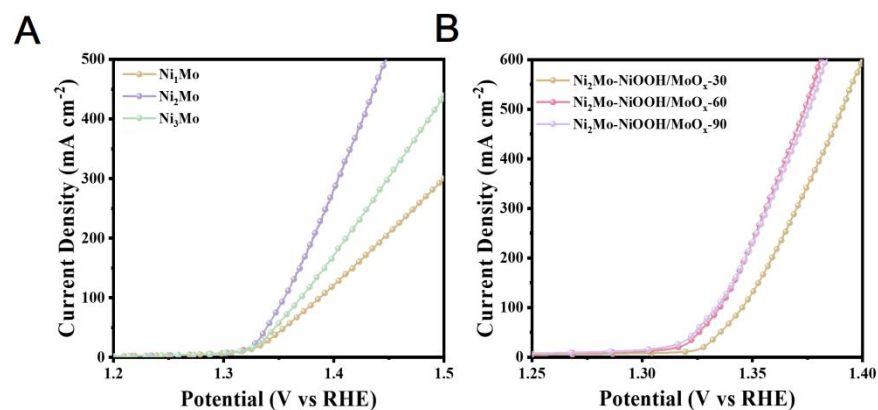
Supplementary Figure 2. XPS survey spectra of $\text{Ni}_2\text{Mo/NF}$ and $\text{Ni}_2\text{Mo-NiOOH/MoO}_x$.



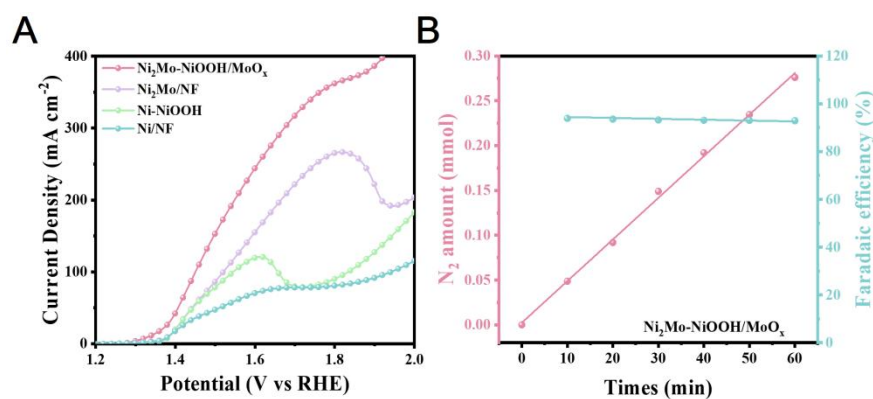
Supplementary Figure 3. Operando stacked Raman spectra of catalytic electrodes under UOR. (A) Operando Raman spectra of Ni-NiOOH ; (B) Operando Raman spectra of $\text{Ni}_2\text{Mo-NiOOH/MoO}_x$.



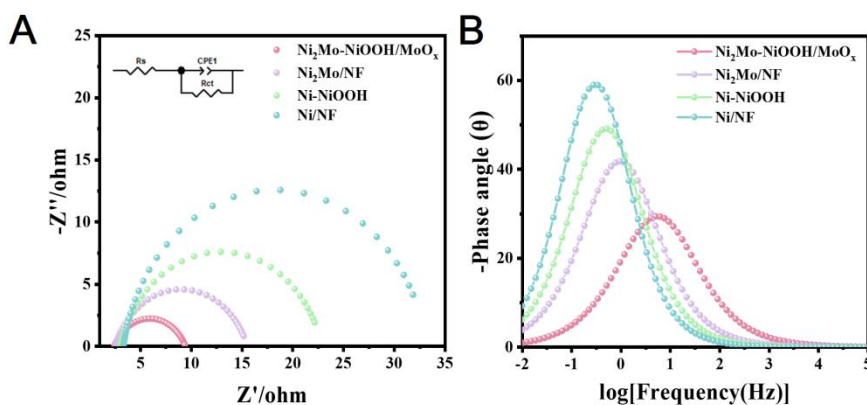
Supplementary Figure 4. Operando stacked Raman spectra of the $\text{Ni}_2\text{Mo-NiOOH/MoO}_x$ catalytic electrode under OER.



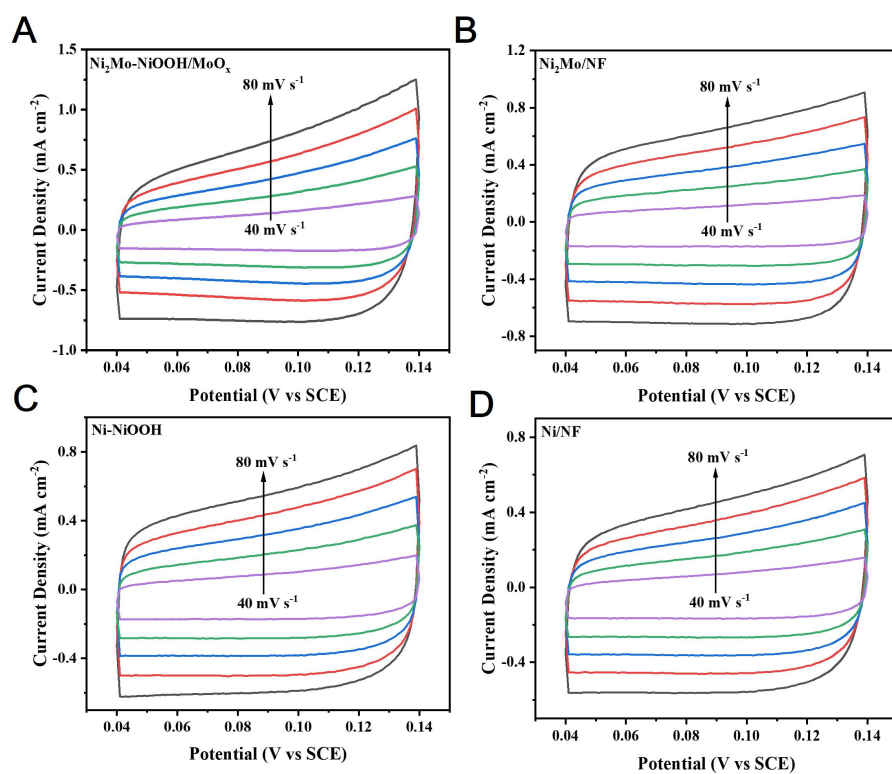
Supplementary Figure 5. UOR electrocatalytic performance characterization of catalysts under optimized preparation conditions. (A) LSV curves of catalysts derived from precursors with different Ni/Mo molar ratios (Ni_1Mo , Ni_2Mo , Ni_3Mo); (B) LSV curves of $\text{Ni}_2\text{Mo-NiOOH/MoO}_x$ catalysts prepared at different anodic reconstruction times.



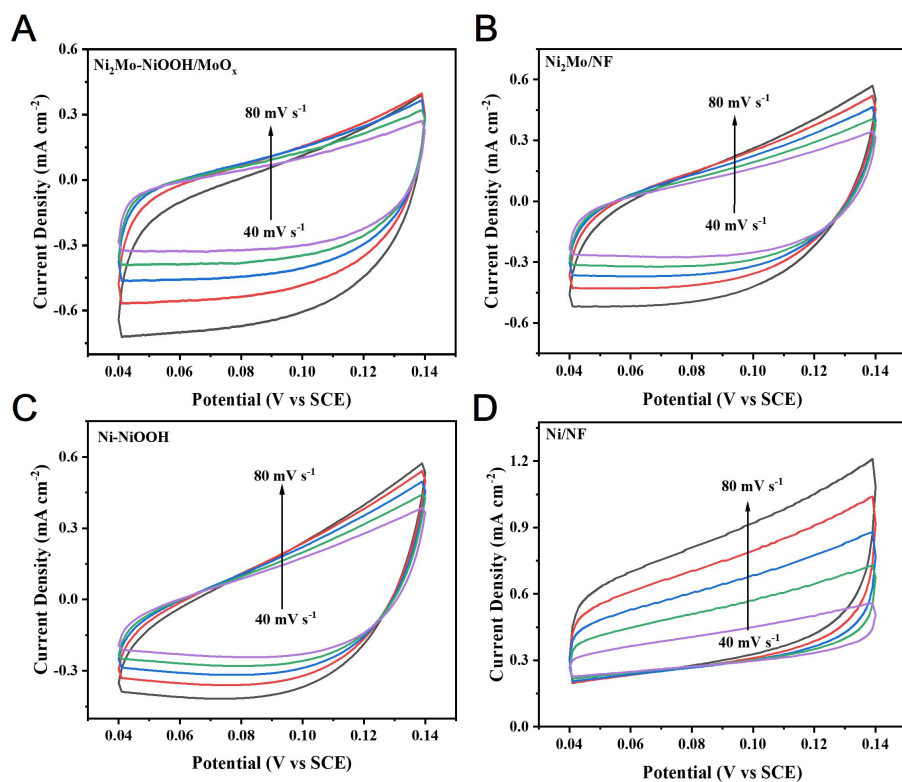
Supplementary Figure 6. (A) LSV curves of Ni₂Mo-NiOOH/MoO_x, Ni₂Mo/NF, Ni-NiOOH and Ni/NF catalytic electrodes toward OER; (B) Ni₂Mo-NiOOH/MoO_x the amount of N₂ produced and FE of urea electrolysis.



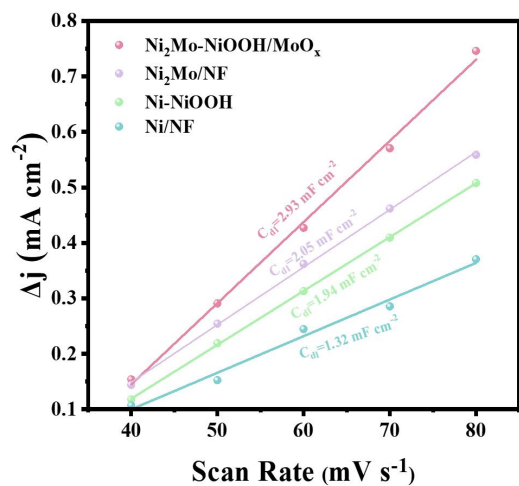
Supplementary Figure 7. Electrochemical impedance characterization of different catalysts under OER. (A) Nyquist impedance plots, the inset shows the corresponding equivalent circuit model; (B) Corresponding Bode phase plots.



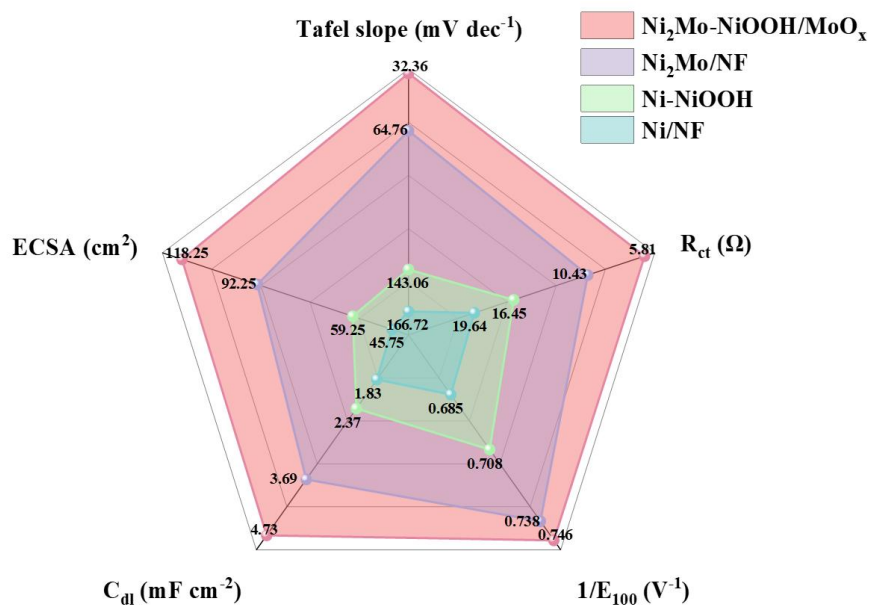
Supplementary Figure 8. CV curves for Cdl calculation of different catalysts under UOR: (A) $\text{Ni}_2\text{Mo-NiOOH/MoO}_x$; (B) $\text{Ni}_2\text{Mo/NF}$; (C) Ni-NiOOH ; (D) Ni/NF . The scan rate ranges from 40-80 mV·s⁻¹.



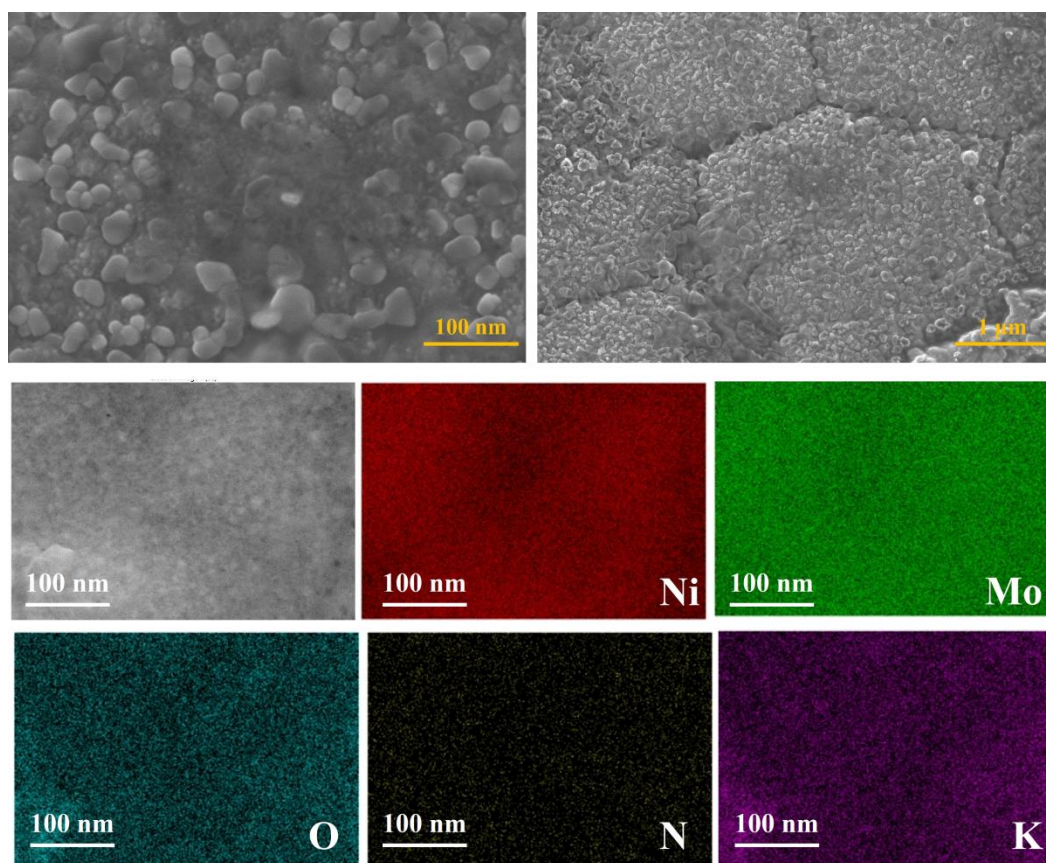
Supplementary Figure 9. CV curves for C_{dl} calculation of different catalysts under OER: (A) $Ni_2Mo-NiOOH/MoO_x$; (B) Ni_2Mo/NF ; (C) $Ni-NiOOH$; (D) Ni/NF . The scan rate ranges from $40-80\text{ mV}\cdot\text{s}^{-1}$.



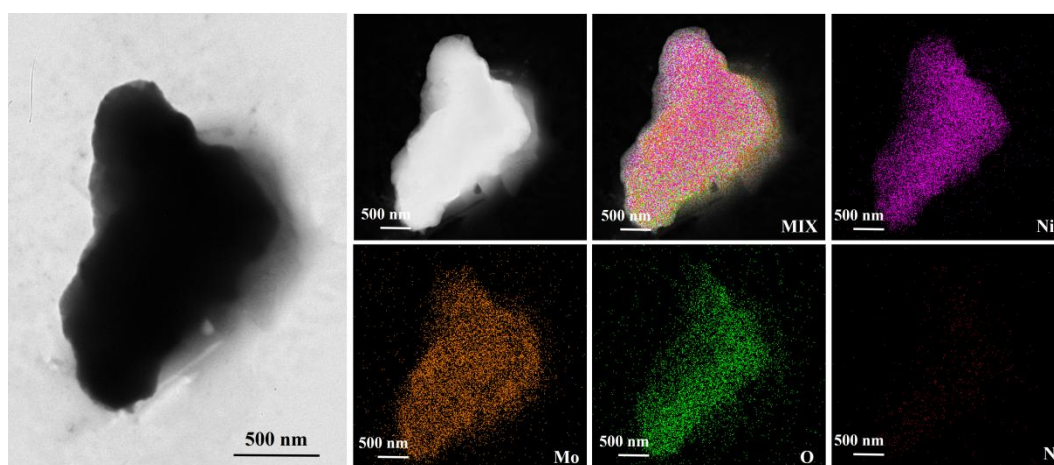
Supplementary Figure 10. C_{dl} curves of $Ni_2Mo-NiOOH/MoO_x$, Ni_2Mo/NF , $Ni-NiOOH$ and Ni/NF catalytic electrodes in OER.



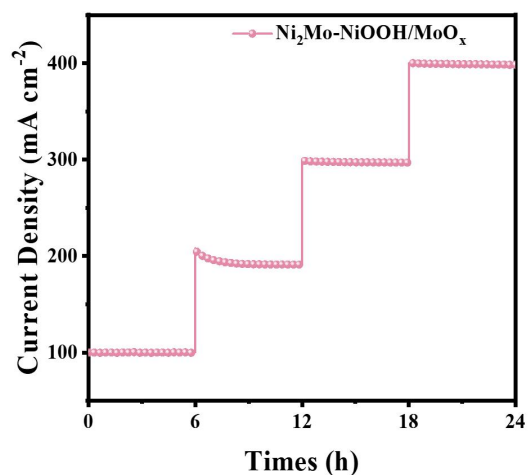
Supplementary Figure 11. Radar plot of key UOR electrocatalytic performance parameters for different catalysts. Comparison indicators include Tafel slope, R_{ct} , reciprocal potential at $100 \text{ mA} \cdot \text{cm}^{-2}$, C_{dl} and ECSA, which intuitively demonstrates the comprehensive performance differences among various catalysts.



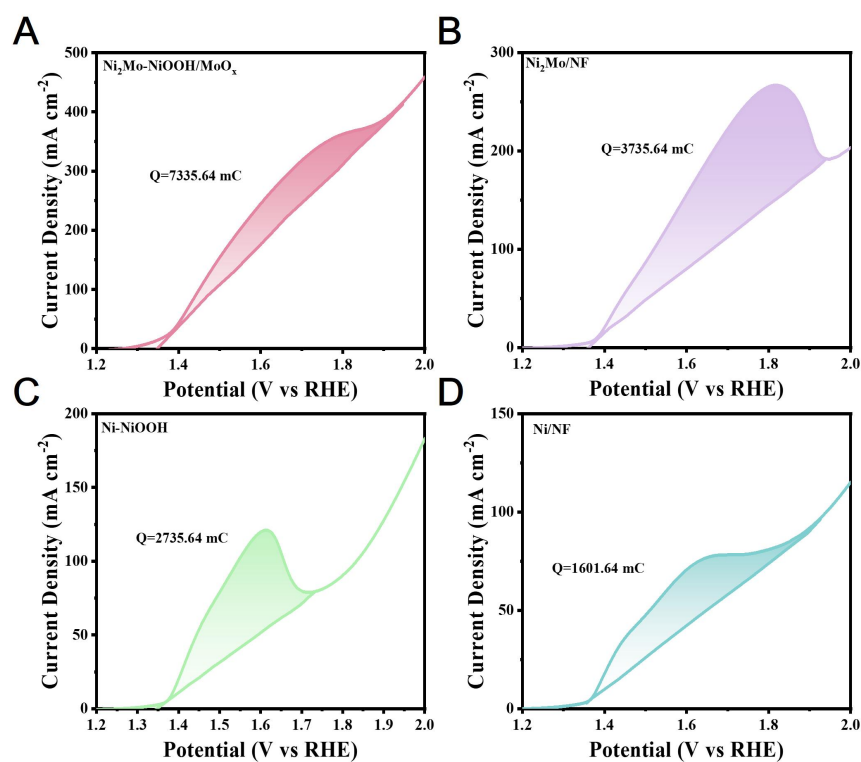
Supplementary Figure 12. SEM morphology and elemental distribution characterization of the $\text{Ni}_2\text{Mo-NiOOH/MoO}_x$ catalytic electrode after 300 h stability test.



Supplementary Figure 13. TEM morphology and elemental distribution characterization of the $\text{Ni}_2\text{Mo-NiOOH/MoO}_x$ catalytic electrode after 300 h stability test.



Supplementary Figure 14. Multi-current step V-t test.



Supplementary Figure 15. Evaluation of the formation of dynamic Ni^{3+} active species. LSV curves and integrated charge of redox peaks (A) $\text{Ni}_2\text{Mo-NiOOH/MoO}_x$ ($Q = 7335.64 \text{ mC}$); (B) $\text{Ni}_2\text{Mo/NF}$ ($Q = 3735.64 \text{ mC}$); (C) Ni-NiOOH ($Q = 2735.64 \text{ mC}$); (D) Ni/NF ($Q = 1601.64 \text{ mC}$). Here, Q is the Faradaic charge transfer amount, which is adopted to evaluate the capability of Ni^{2+} oxidizing to Ni^{3+} . The value is calculated by the equation $Q = S/v$, where v is the scan rate ($5 \text{ mV} \cdot \text{s}^{-1}$) and S represents the mathematical integral area.

Supplementary Tables:

Supplementary Table 1. Relative atomic percentage from XPS Ni 2p spectrum of catalysts

Catalyst	Relative atomic percentage (%)			
	Ni 2p _{3/2}		Ni 2p _{1/2}	
	Ni ³⁺	Ni ²⁺	Ni ³⁺	Ni ²⁺
Ni ₂ Mo-NiOOH/MoO _x	17.76%	48.73%	7.98%	25.53%
Ni ₂ Mo/NF	13.34%	52.33%	7.28%	27.05%

Supplementary Table 2. Relative atomic percentage from XPS Mo 3d spectrum of catalysts

Catalyst	Relative atomic percentage (%)							
	Mo 3d _{5/2}				Mo 3d _{3/2}			
	Mo ⁶⁺	Mo ⁵⁺	Mo ⁴⁺	Mo ⁰	Mo ⁶⁺	Mo ⁵⁺	Mo ⁴⁺	Mo ⁰
Ni ₂ Mo-NiOOH/M	17.68	30.50	8.31	4.43	11.56	19.28	5.23	3.01
oO _x	%	%	%	%	%	%	%	%
Ni ₂ Mo/NF	36.96	16.35	\	6.74	24.77	10.76	\	4.42
	%	%		%	%	%		%

Supplementary Table 3. R_s and R_{ct} values of Ni₂Mo-NiOOH/MoO_x and other catalysts in UOR respectively

Catalysts	R _s (Ω)	R _{ct} (Ω)
Ni ₂ Mo-NiOOH/MoO _x	1.53	5.81
Ni ₂ Mo/NF	1.57	10.43
Ni-NiOOH	1.61	16.45
Ni/NF	1.63	19.64

Supplementary Table 4. C_{dl} and ECSA of $Ni_2Mo-NiOOH/MoO_x$ and other catalysts in UOR respectively

Catalysts	C_{dl} (mF cm^{-2})	ECSA (cm^2)
$Ni_2Mo-NiOOH/MoO_x$	3.81	95.25
Ni_2Mo/NF	2.67	66.75
$Ni-NiOOH$	1.61	40.25
Ni/NF	0.78	19.5

Supplementary Table 5. Comparison of the potential of $Ni_2Mo-NiOOH/MoO_x$ and other UOR catalysts at a current density of 100 $mA \cdot cm^{-2}$.

Catalysts	Electrolyte	Potential at 100 $mA \cdot cm^{-2}$ (V)	Ref.
$Ni_2Mo-NiOOH/MoO_x$	1M KOH+ 0.33 M urea	1.341 V	This work
$NiCoCr-LDH/NF$	1M KOH+ 0.33 M urea	1.38 V	[1]
$NiOOH(LDH/\alpha-FeOOH)$	1M KOH+ 0.33 M urea	1.35 V	[2]
$Ni_{60}Nb_{40}$	1M KOH+ 0.33 M urea	1.41V	[3]
$MoNi_{0.85}Se/CuO$	1M KOH+ 0.33 M urea	1.38 V	[4]
$Ni_3S_2@Ni_3P//Ni_3S_2@Ni_3P$	1M KOH+ 0.33 M urea	1.54V	[5]
$Ir@Mn-NiOOH$	1M KOH+ 0.33 M urea	1.378V	[6]
$NiOOH-SnO_3^{2-}$	1M KOH+ 0.33 M urea	1.4V	[7]
Ni_3N-V_N	1M KOH+	1.35 V	[8]

	0.33 M urea		
Ni ₂ P/WP/W _{0.12}	1M KOH+	1.44V	[9]
	0.33 M urea		
Mn-NiOOH	1M KOH+	1.41 V	[10]
	0.33 M urea		
A/C-Ni@G	1M KOH+	1.358 V	[11]
	0.33 M urea		
N-Ni ₂ P	1M KOH+	1.347 V	[12]
	0.33 M urea		

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