

Supporting Information

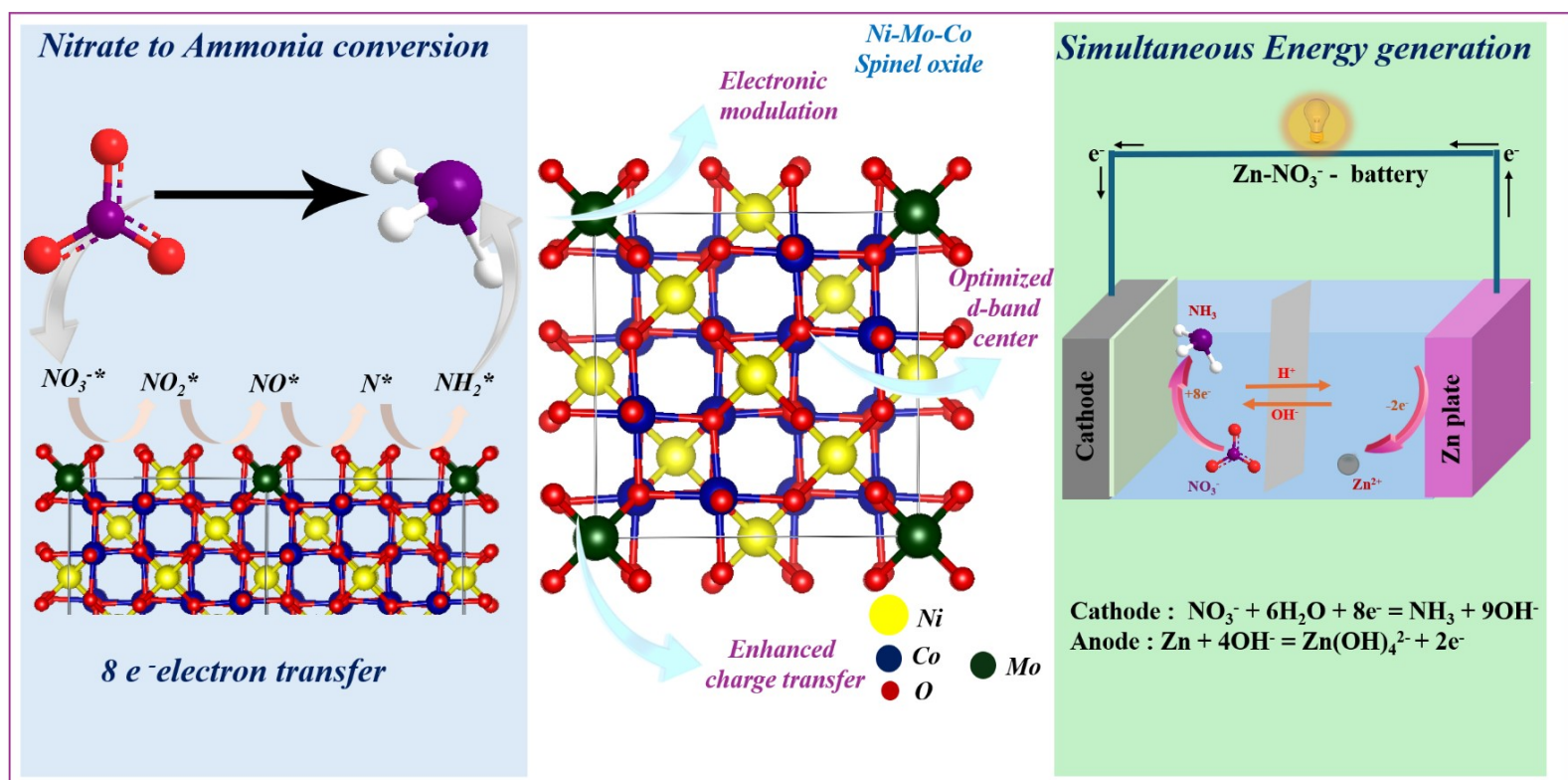
Mo-doped spinel NiCo₂O₄ as a bifunctional electrocatalyst for highly efficient nitrate reduction to ammonia and oxygen evolution

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Graphical Abstract



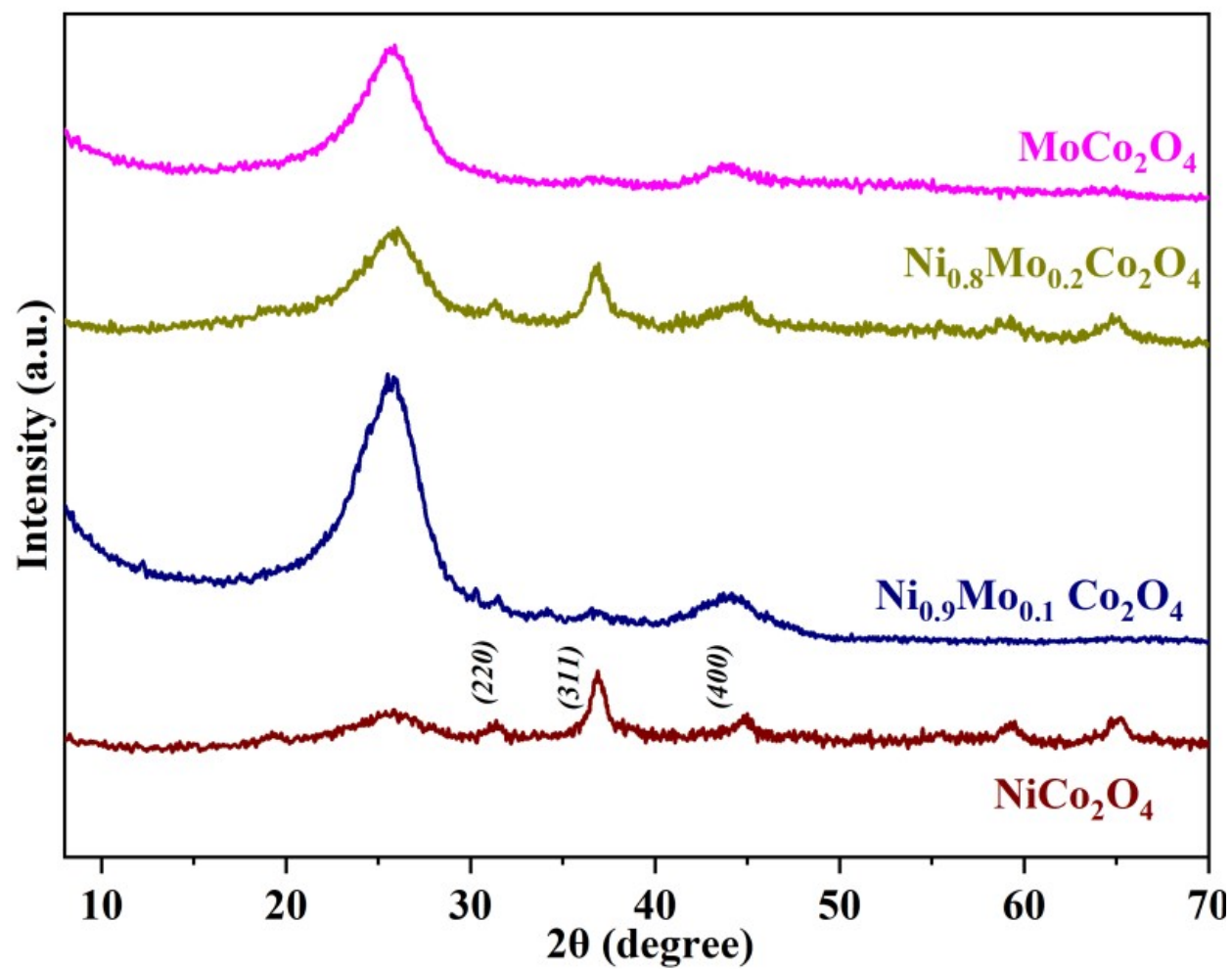


Figure S1. XRD pattern of the material growth of carbon cloth.

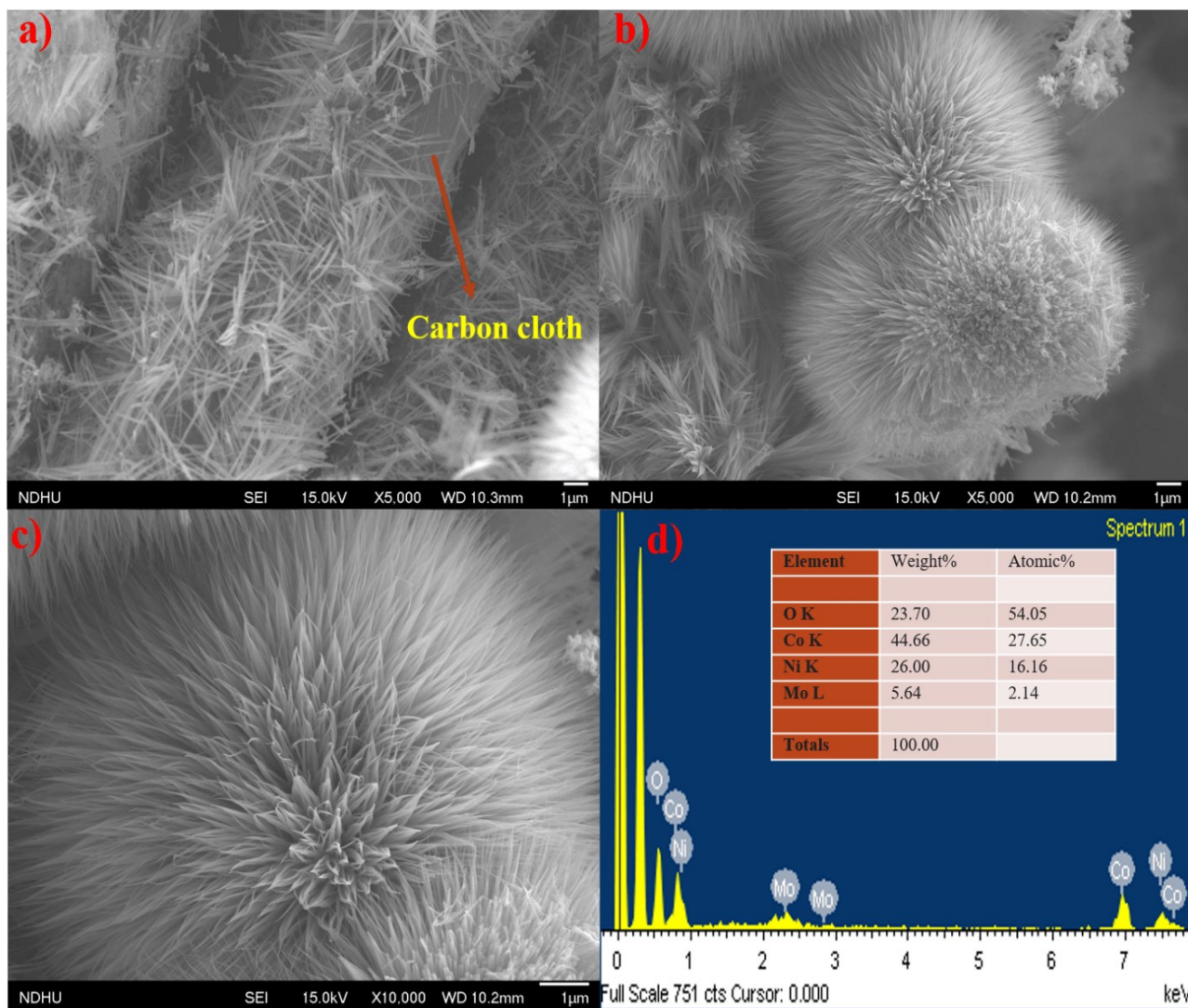


Figure S2. a-c) FESEM Image of NiCo_2O_4 , d) EDS for $\text{Ni}_{0.9}\text{Mo}_{0.1}\text{Co}_2\text{O}_4$.

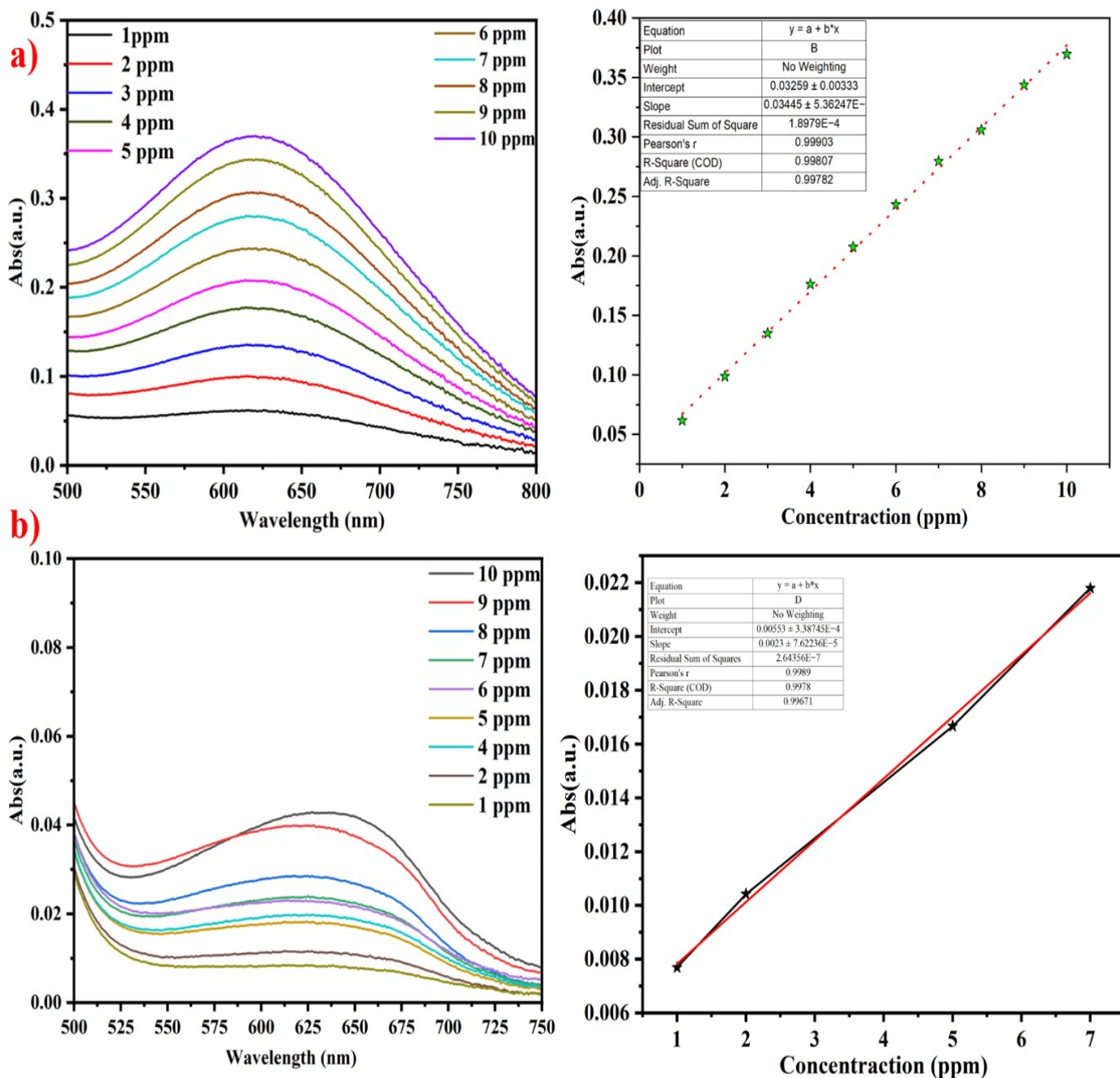


Figure S3. UV-Visible curves and concentration-absorbance calibration curves of NH_4Cl . **a)** UV-Visible absorption graph and calibration curve of $\text{NH}_4\text{Cl} + \text{Na}_2\text{SO}_4$, **b)** UV absorption graph and calibration curve of $\text{NH}_4\text{Cl} + \text{KOH}$.

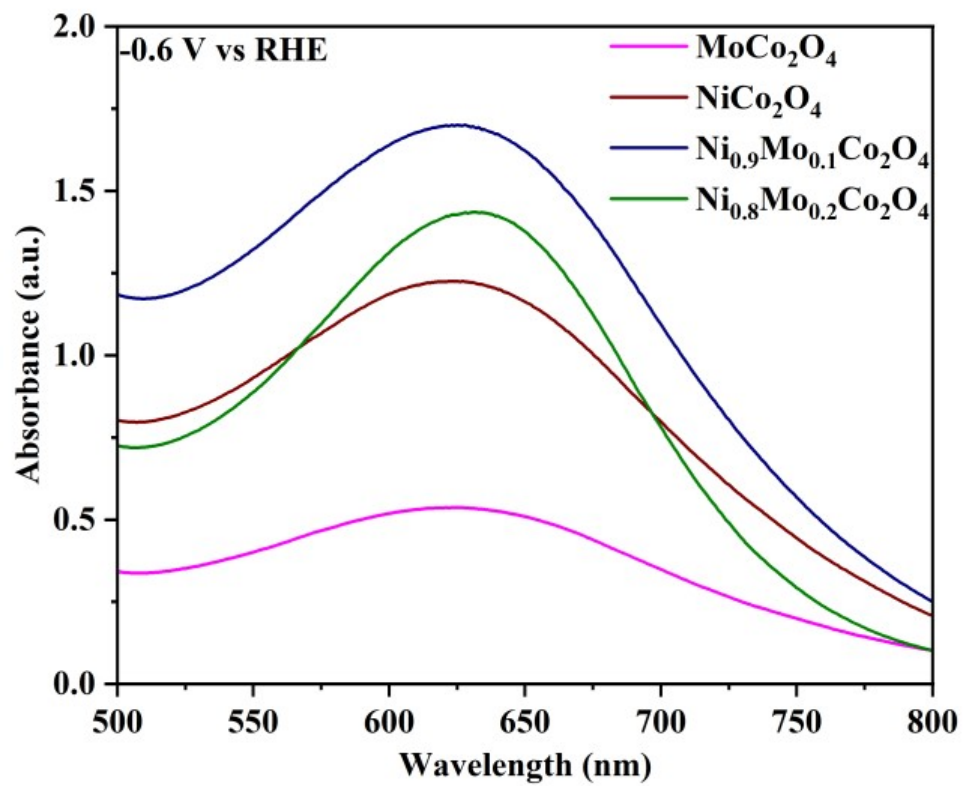


Figure S4. UV-Visible absorption graph of the electrocatalyst with the Indophenol method.

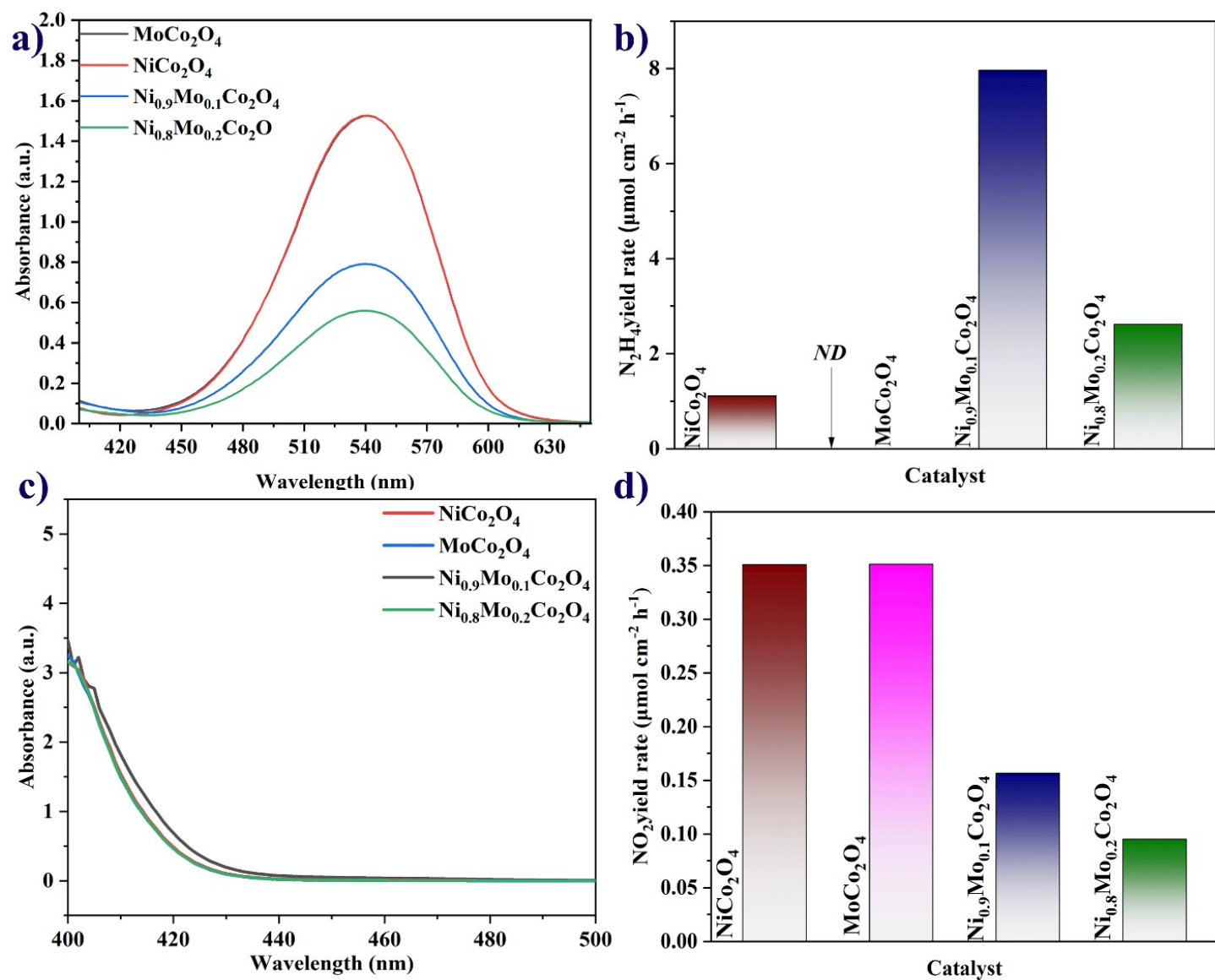


Figure S5. Intermediate formation during EnitRR: **a)** UV-Visible absorbance for NO_2 , **b)** Yield rate of NO_2 , **c)** UV-Visible absorbance for N_2H_4 , **d)** Yield rate of N_2H_4 .

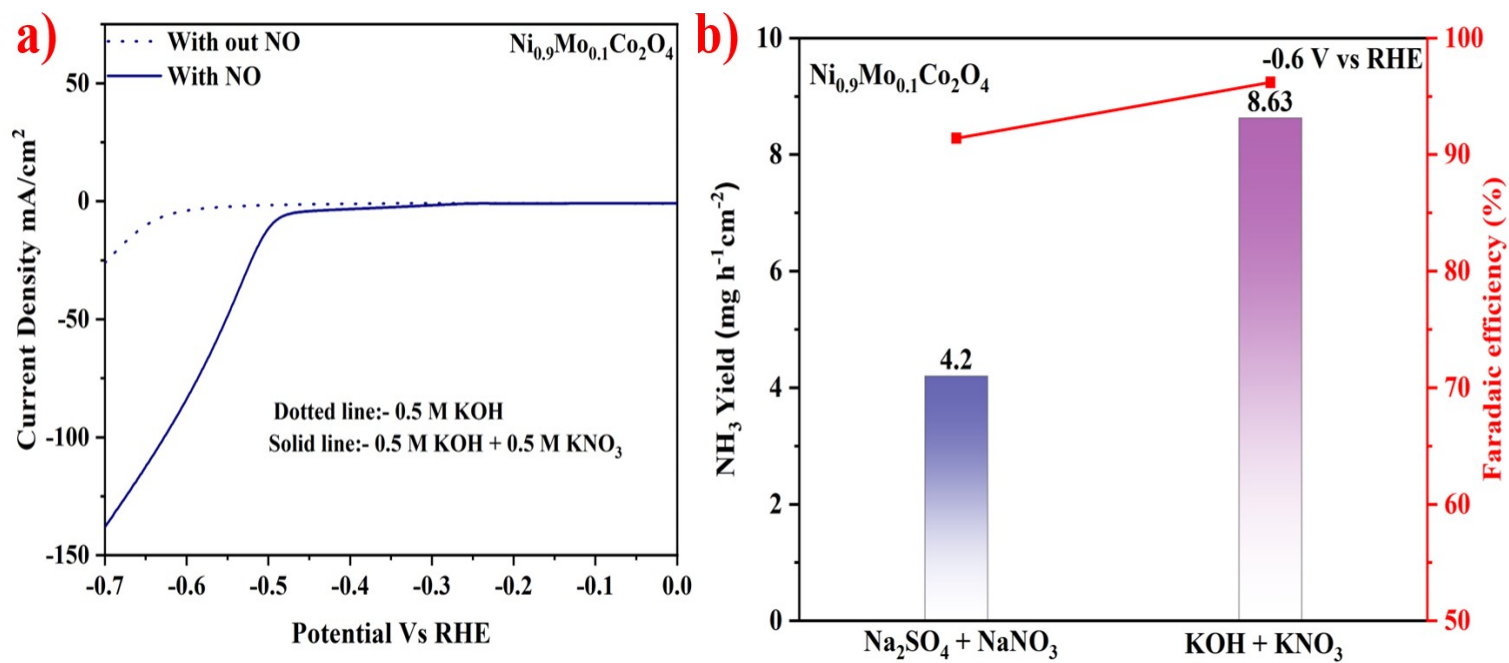


Figure S6. a) LSV curve of $\text{Ni}_{0.9}\text{Mo}_{0.1}\text{Co}_2\text{O}_4$ under the alkaline environment, **b)** NH_3 yield rate of $\text{Ni}_{0.9}\text{Mo}_{0.1}\text{Co}_2\text{O}_4$ under the different environments.

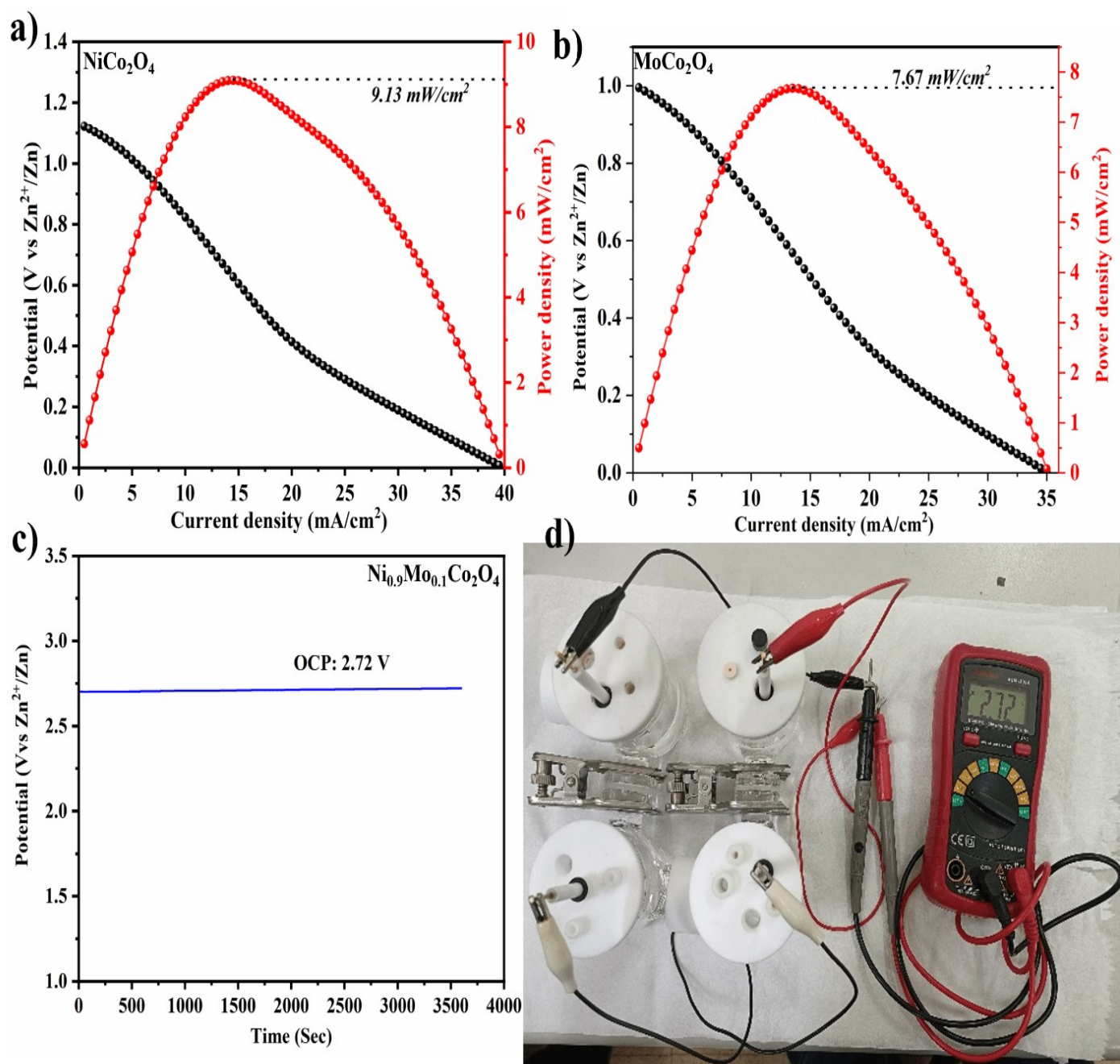


Figure S7. The polarization and power density curves: **a)** NiCo_2O_4 , **b)** MoCo_2O_4 , **c)** $\text{Ni}_{0.9}\text{Mo}_{0.1}\text{Co}_2\text{O}_4$ open circuit potentials under the series connection, **d)** Digital picture of the series connection.

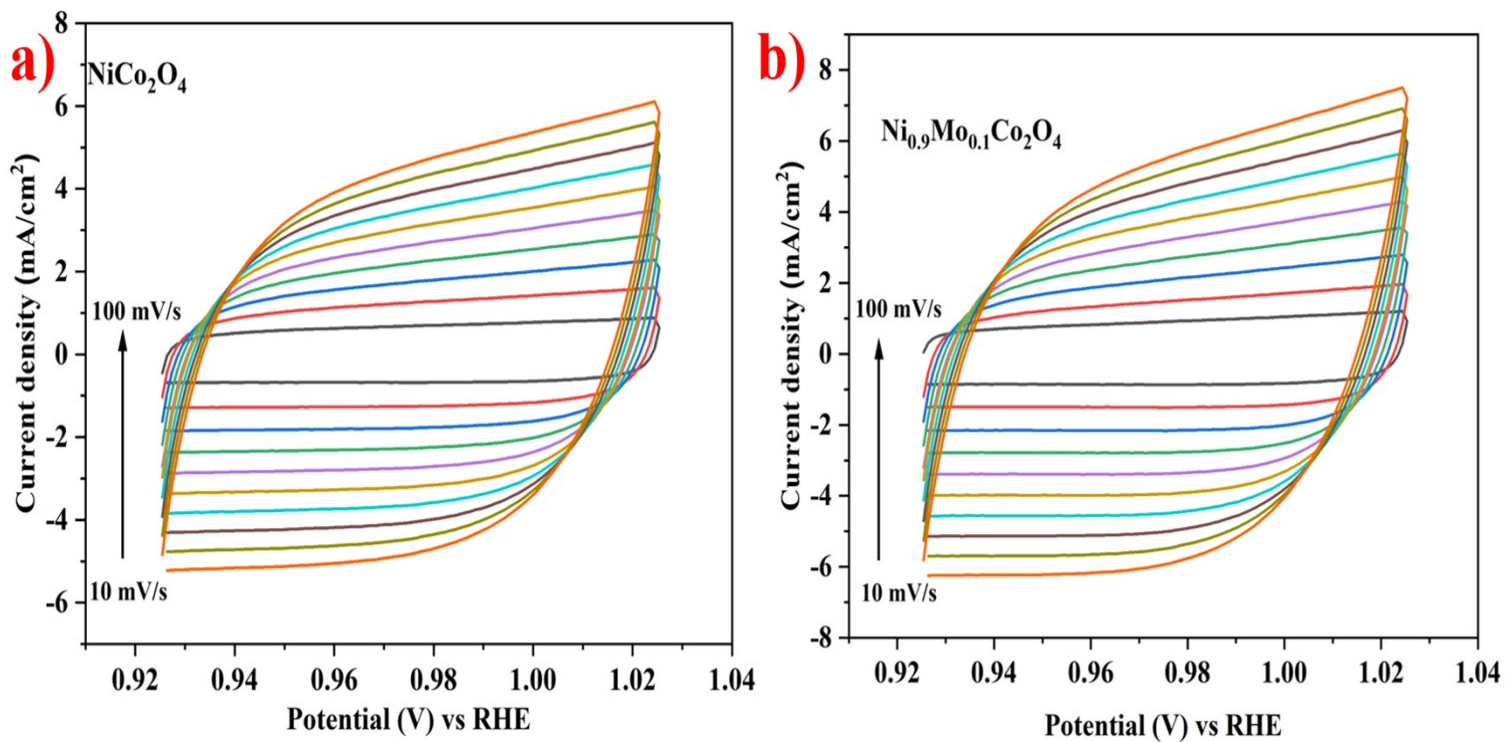


Figure S8. CV Curve during the OER: **a)** NiCo_2O_4 , **b)** $\text{Ni}_{0.9}\text{Mo}_{0.1}\text{Co}_2\text{O}_4$.

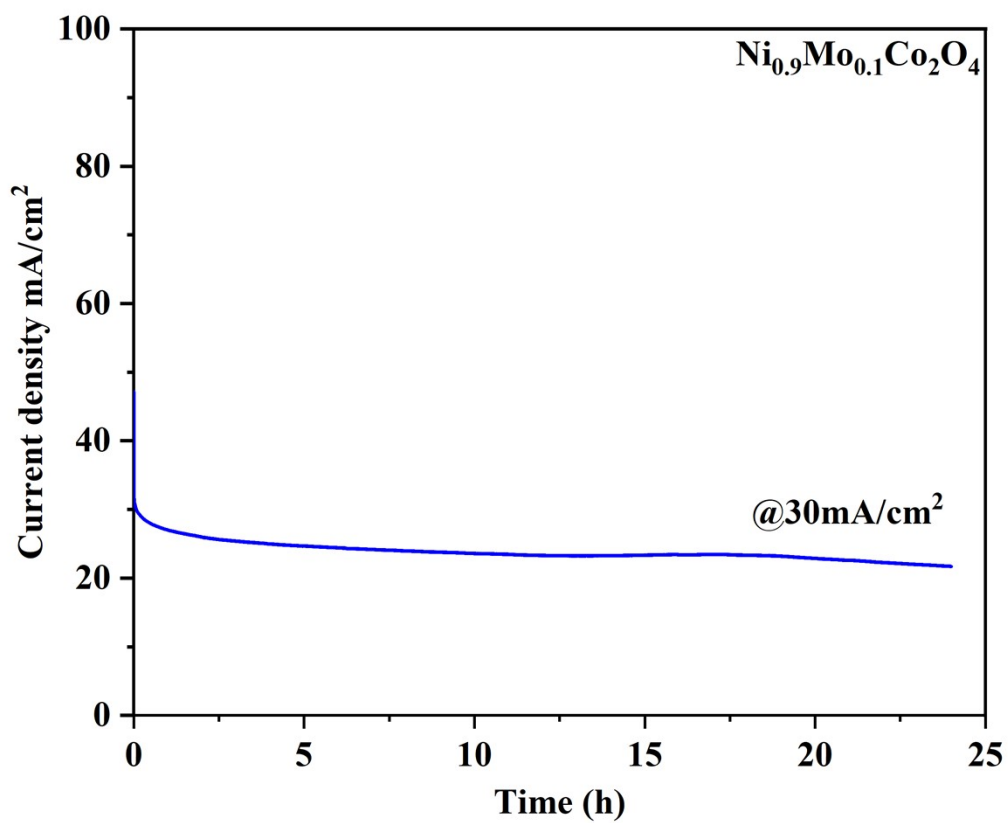


Figure S9. Stability test of $\text{Ni}_{0.9}\text{Mo}_{0.1}\text{Co}_2\text{O}_4$ at a constant current density @ 30 mA/cm² over 24 h.

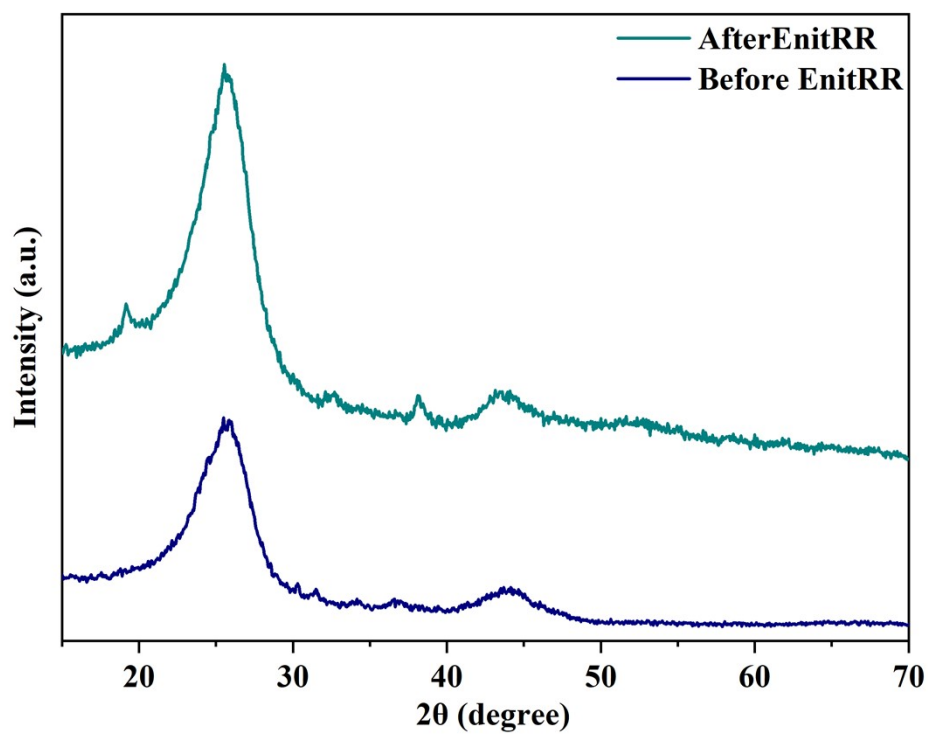


Figure S10. XRD pattern for $\text{Ni}_{0.9}\text{Mo}_{0.1}\text{Co}_2\text{O}_4$ before and after EnitRR.

Table S1. Comparison of recently reported top-performing electrocatalyst for NO₃⁻ reduction to NH₃

Electrocatalyst	NH₃ yield (mgh⁻¹cm⁻²)	FE (%)	Potential (V vs RHE)	Electrolyte	Ref
Fe-MoS₂	0.144 mgh ⁻¹ cm ⁻²	80	-0.53	0.01 M PBS 500 ppm of NO ₃ ⁻	1
V_{Zn}-ZnCo₂O₄	4.21 mg h ⁻¹ cm ⁻²	94	-0.5	1.0 M KOH + 0.1 M NO ₃ ⁻	2
ZnMn_{0.5}Co_{1.5}O₄	3.87 mg h ⁻¹ cm ⁻²	96	-0.5	1.0 M KOH + 0.1 M NO ₃	3
HEAOs are composed of Mn, Fe, Co, Ni, and Cu.	5.35 mgh ⁻¹ cm ⁻²	84	-0.6	1.0 M KOH + 0.1 M NO ₃	4
Co/CoO NSAs	3.3 mgh ⁻¹ cm ⁻²	94	-0.65	0.1 M Na ₂ SO ₄ + 200 ppm NO ₃ ⁻	5
Fe₁/Cu₂-Co₃O₄	2.98 mgh ⁻¹ cm ⁻²	98	-0.78	0.2 M Na ₂ SO ₄ + 100 ppm of NO ₃ ⁻	6
Au-Cu NWs/CF	0.1592 mgh ⁻¹ cm ⁻²	84	-1.05	0.1 M Na ₂ SO ₄ + 10.0 mM KNO ₃	7
Ni_{0.9}Mo_{0.1}Co₂O₄	4.20 mgh ⁻¹ cm ⁻²	91	-0.6	0.5 M Na ₂ SO ₄ + 0.5 M NaNO ₃ ⁻	This work
Ni_{0.9}Mo_{0.1}Co₂O₄	8.63 mgh ⁻¹ cm ⁻²	96	-0.6	0.5 M KOH + 0.5 M KNO ₃	This work

Table S2. The full normalized activity for all prepared catalysts.

Catalyst	Mass loading (mg cm ⁻²)	Yield rate (mg h ⁻¹ cm ⁻²)	Yield mass (mgh ⁻¹ mg ⁻¹)	C _{dl} (mF cm ⁻²)	ECSA (cm ²)	Yield ECSA (mg h ⁻¹ cm ⁻²)
NiCo ₂ O ₄	2.3	2.46	1.07	3.17	79.3	0.031
MoCo ₂ O ₄	2.5	1.20	0.48	-	N/A	N/A
Ni _{0.95} Mo _{0.05} Co ₂ O ₄	2.1	3.11	1.48	-	N/A	N/A
Ni _{0.9} Mo _{0.1} Co ₂ O ₄	2.3	4.20	1.83	4.67	116.8	0.036
Ni _{0.8} Mo _{0.2} Co ₂ O ₄	2.6	3.50	1.35	-	N/A	N/A

Table S3. Comparison of Mo engineering and Ni/Co spinel OER catalysts.

Catalyst	Tafel Slope (mV/dec)	Overpotential (mV)	Electrolyte	Ref
CuO/NiCo ₂ O ₄	94	230 @10mA/cm ²	1 M KOH	8
V _O -Mo _x Co _{3-x} O ₄	102.5	490 @ 100mA/cm ²	acidic	9
NiCo ₂ O ₄ @CeO ₂	108	228 @ 10mA/cm ²	1 M KOH	10
Mo-Doped α-MnO ₂	86	440 @ 10mA/cm ²	1 M KOH	11
Fe ₂ O ₃ @Mo	80	359	1 M KOH	12
Ni _{0.9} Mo _{0.1} Co ₂ O ₄	99.74	239	1 M KOH	This work

Table S4. The detailed deconvolution parameters for the Ni 2p spectra, including peak positions and FWHM values, are summarized in Table S1.

Sample	Region	Peak assignment	Binding energy (eV)	FWHM (eV)	Area (%)
NiCo ₂ O ₄	Ni 2p _{3/2}	Ni ²⁺	854.46	2.57	3817.87
NiCo ₂ O ₄	Ni 2p _{3/2}	Ni ³⁺	856.42	2.70	6168.20
NiCo ₂ O ₄	Ni 2p _{3/2}	Satellite			
NiCo ₂ O ₄	Ni 2p _{1/2}	Ni ²⁺	872.13	2.70	1465.17
NiCo ₂ O ₄	Ni 2p _{1/2}	Ni ³⁺	874.46	1.91	6168.20
NiCo ₂ O ₄	Ni 2p _{1/2}	Satellite			
Ni _{0.9} Mo _{0.1} Co ₂ O ₄	Ni 2p _{3/2}	Ni ²⁺	854.64	2.09	5234.19
Ni _{0.9} Mo _{0.1} Co ₂ O ₄	Ni 2p _{3/2}	Ni ³⁺	856.21	2.87	2787.11
Ni _{0.9} Mo _{0.1} Co ₂ O ₄	Ni 2p _{3/2}	Satellite			
Ni _{0.9} Mo _{0.1} Co ₂ O ₄	Ni 2p _{1/2}	Ni ²⁺	872.71	2.50	1338.66
Ni _{0.9} Mo _{0.1} Co ₂ O ₄	Ni 2p _{1/2}	Ni ³⁺	874.96	1.78	1924.70
Ni _{0.9} Mo _{0.1} Co ₂ O ₄	Ni 2p _{1/2}	Satellite			

Table S5. ICP-MS elemental composition of Ni_{0.9}Mo_{0.1}Co₂O₄.

Element	Atomic Weight (g/mol)	Measured Content (wt%)	Moles (mol)	Normalized Ratio
Ni	58.69	3.63	0.0619	0.86
Mo	95.95	0.35	0.0036	0.05
Co	58.93	8.46	0.1436	2.00

Reference

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