

Supporting Information

Tuning the Crystal Facets of MoP₂ in a Phosphide-Nitride Heterostructure via Interface

Engineering for Energy Efficient Ethanol Oxidation Coupled H₂ Production

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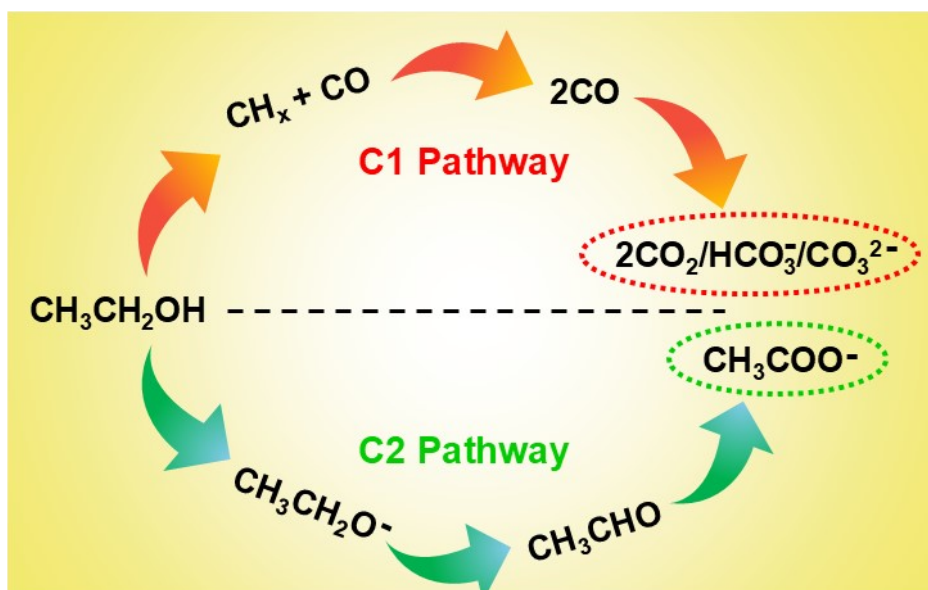


Figure S1: The dual pathway mechanism of EOR.

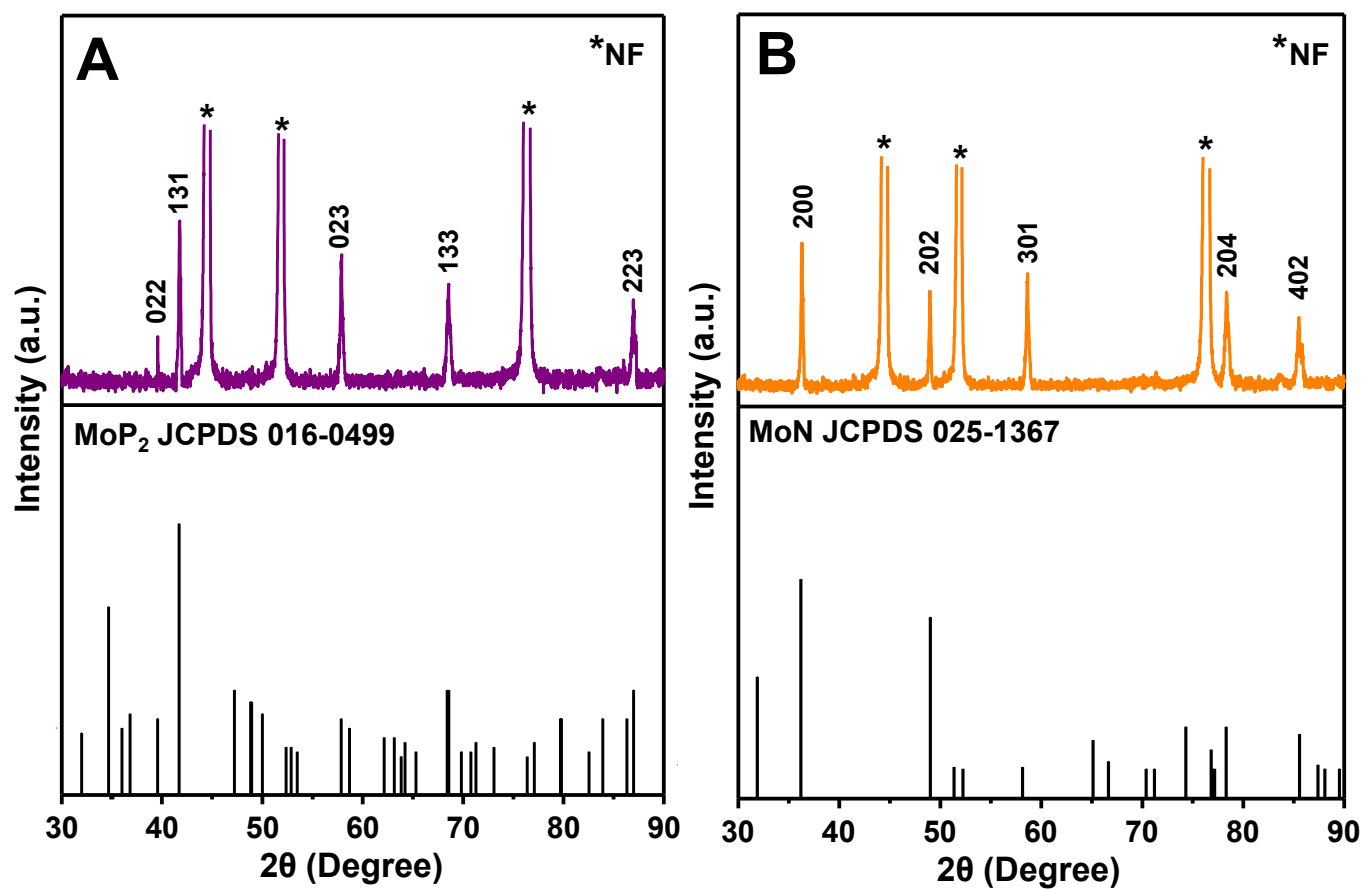


Figure S2: The XRD data of (A) MoP₂, and (B) MoN.

Table S1: The summary of facet TC value for all the catalysts.

Catalysts	Facet Texture Coefficient (TC)									
	(200)	(022)	(131)	(202)	(023)	(202)	(204)	(260)	(402)	(223)
MoP ₂ /MoN-300	0.011	1.5	0.22	0.07	0.25	0.71	0.46	0.67	0.70	0.08
MoP ₂ /MoN-350	0.13	4.1	0.34	0.12	0.95	0.51	0.44	0.12	0.95	0.28
MoP ₂ /MoN-400	0.05	4.86	0.90	0.08	0.90	0.43	0.34	0.38	0.90	0.12

MoP₂/MoN-450	0.39	2.35	4.04	0.16	0.06	0.63	0.59	0.35	0.56	0.07
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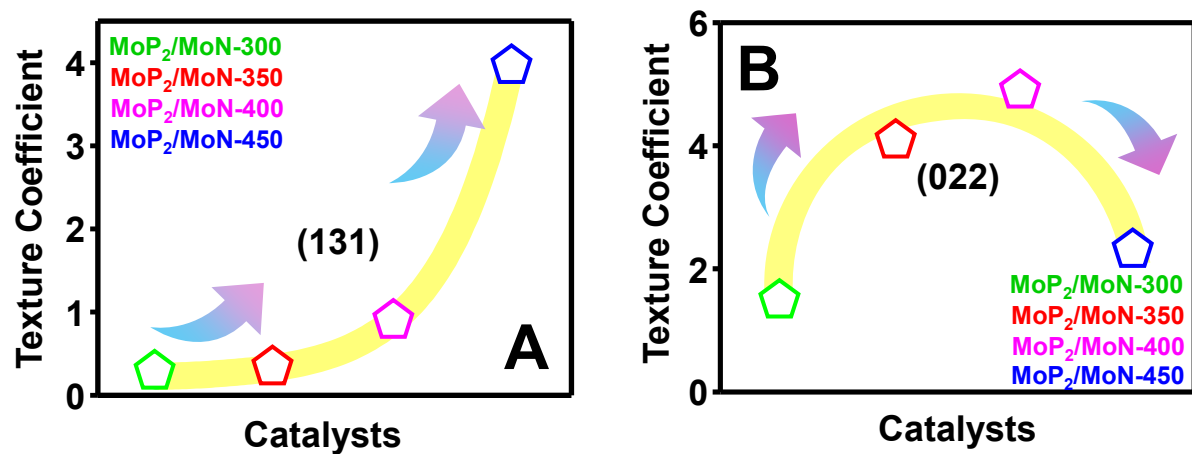


Figure S3: The TC plot for (A) 131, and (B) 022 facet for all the catalysts.

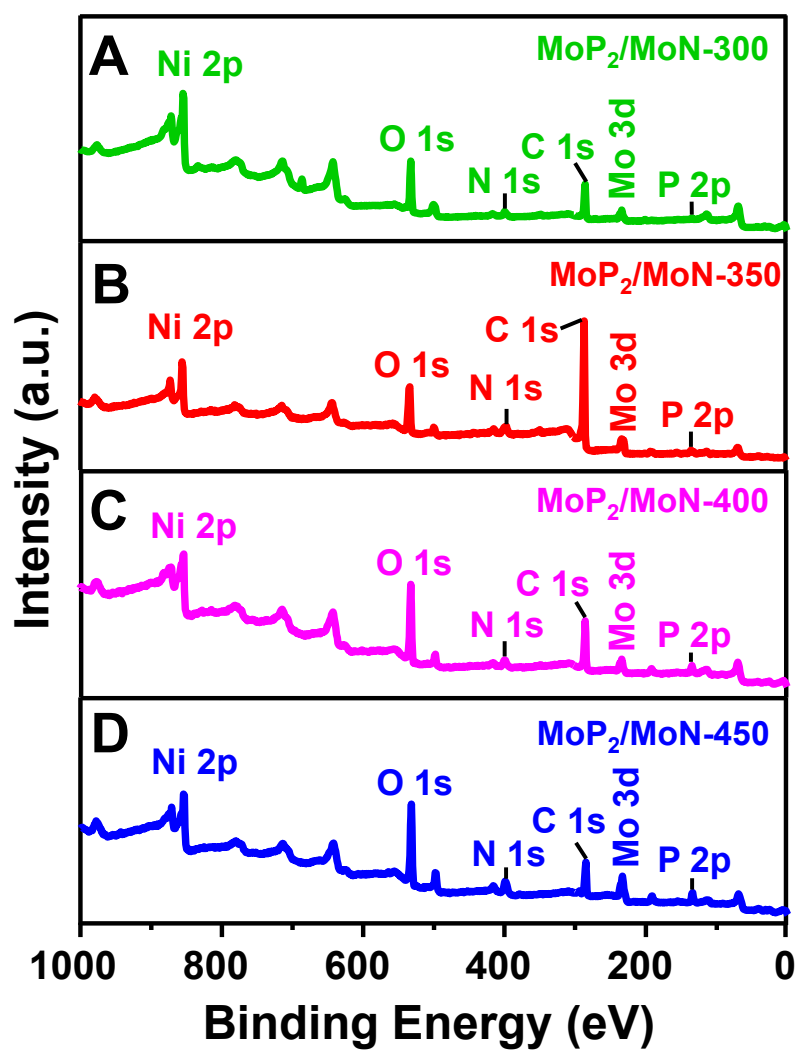


Figure S4: The XPS survey spectra of (A) MoP₂/MoN-300, (B) MoP₂/MoN-350, (C) MoP₂/MoN-400, (D) MoP₂/MoN-450.

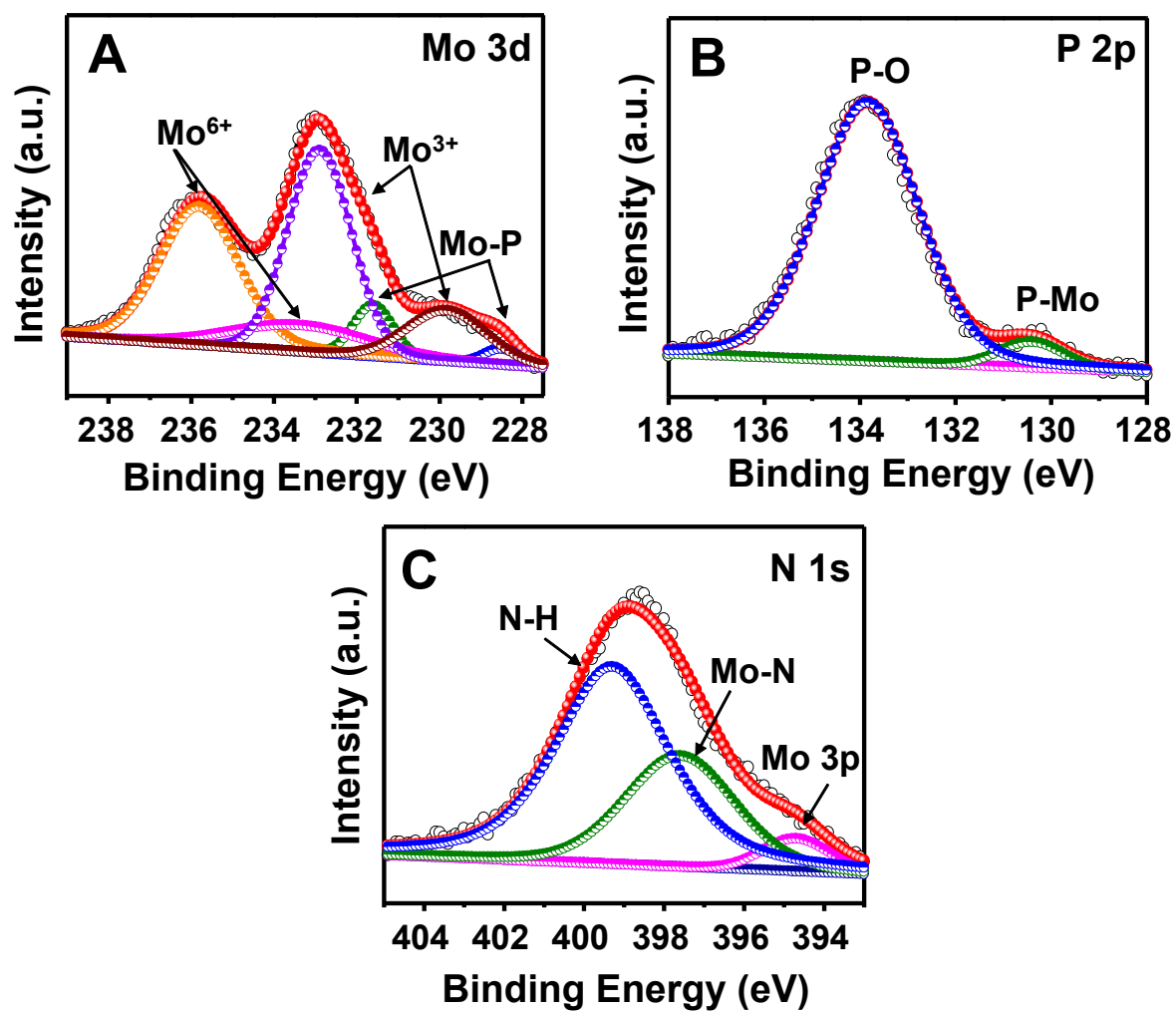


Figure S5: The XPS data of (A) Mo 3d, (B) P 2p, and (C) N 1s of the MoP₂/MoN-300.

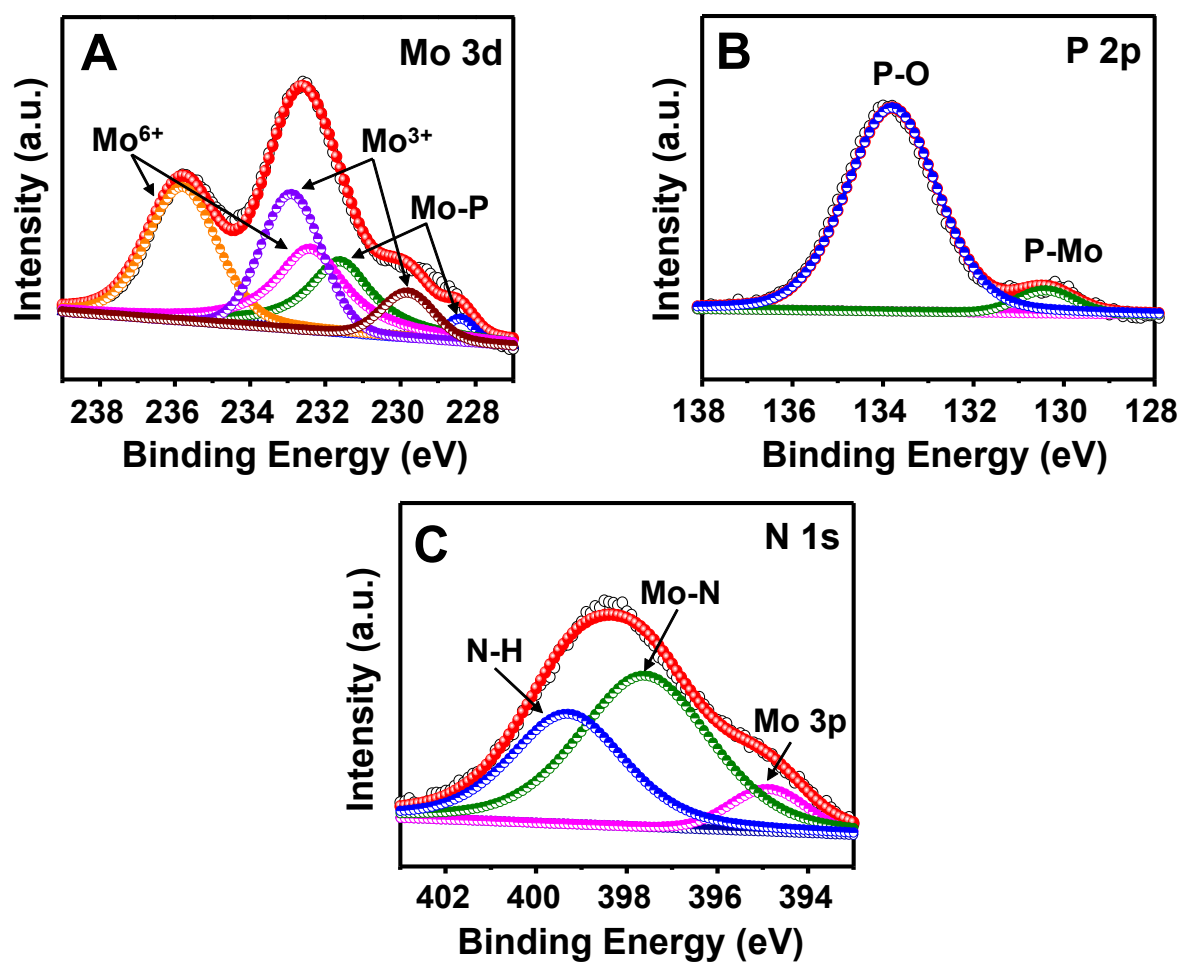


Figure S6: The XPS data of (A) Mo 3d, (B) P 2p, and (C) N 1s of the MoP₂/MoN-350.

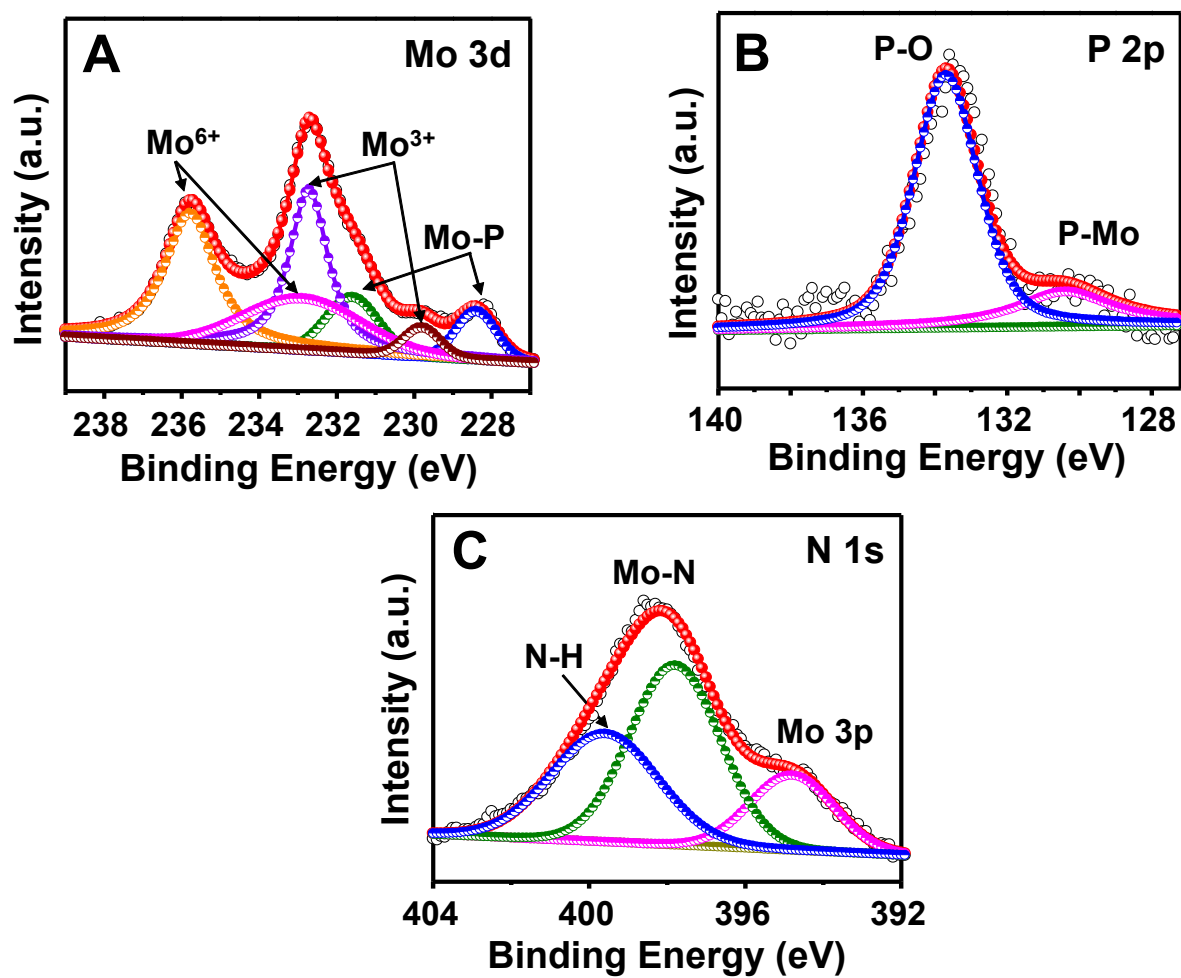


Figure S7: The XPS data of (A) Mo 3d, (B) P 2p, and (C) N 1s of the MoP₂/MoN-400.

Table S2: The summary of FWHM values for MoP₂/MoN-450.

Full width at half maximum (FWHM) (eV)							
Mo 3d			P 2p		N 1s		
Mo-P	Mo ³⁺	Mo ⁶⁺	P-O	P-Mo	N-H	Mo-N	Mo 3p
1.23, 1.39	1.91, 1.65	2.73, 2.75	2.59	2.11	3.74	2.20	2.96

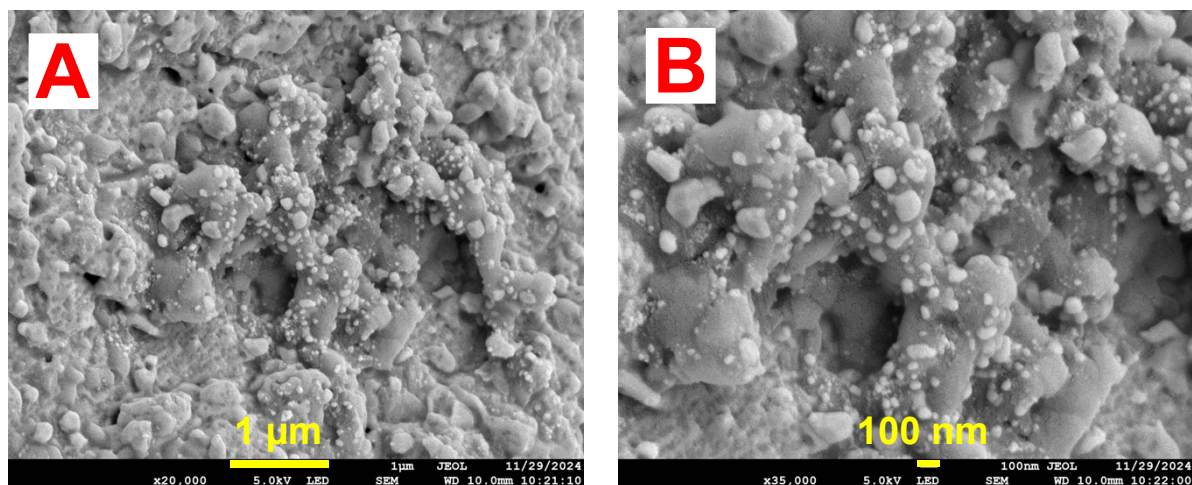


Figure S8: The FESEM images of MoP₂/MoN-300 at (A) 1 μm, and (B) 100 nm.

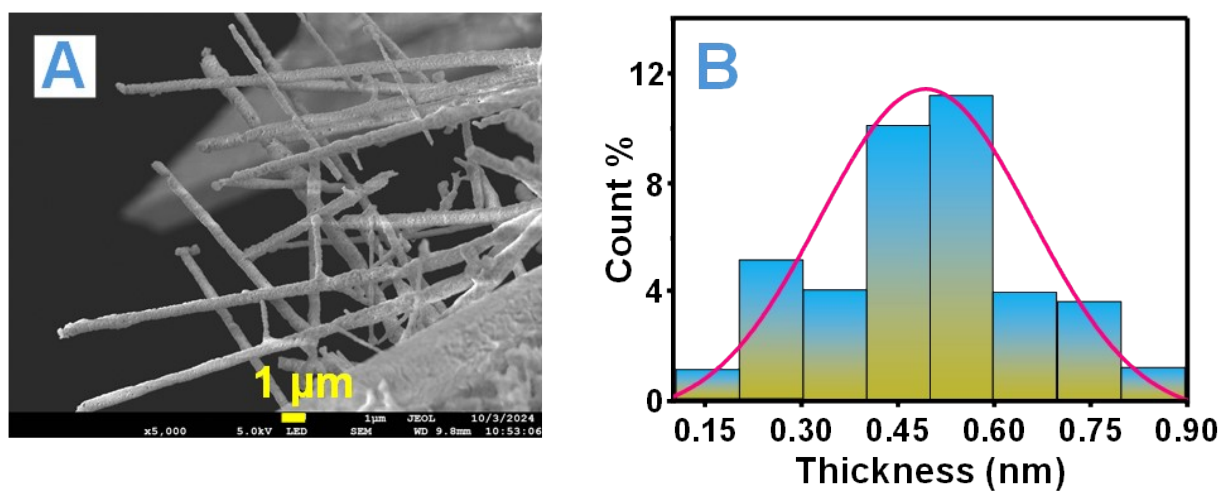


Figure S9: The FESEM image of (A) MoP₂/MoN-450 at 1 μm, and (B) particle size distribution.

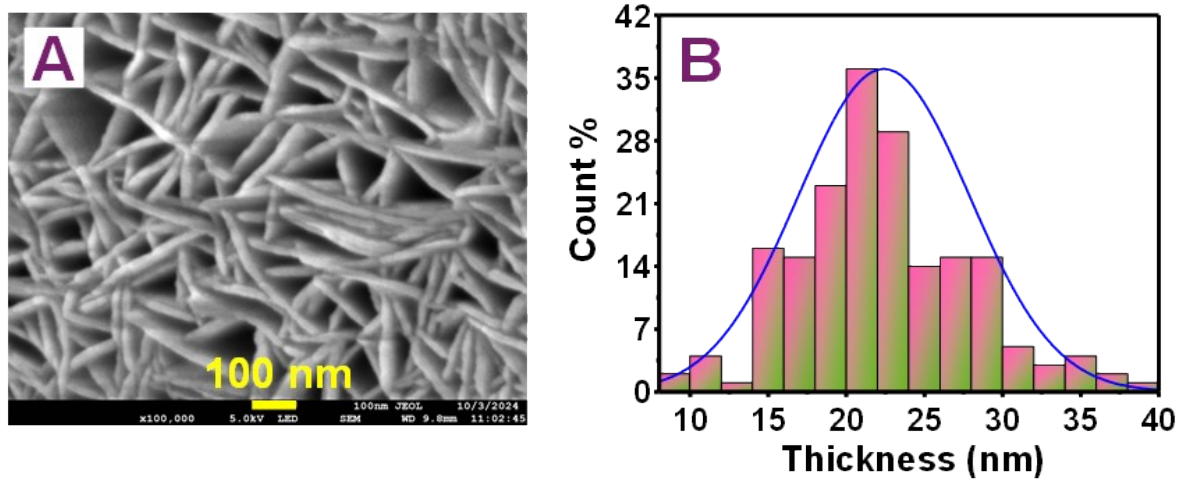


Figure S10: The FESEM image of (A) MoP₂/MoN-450 at 100 nm, and (B) particle size distribution.

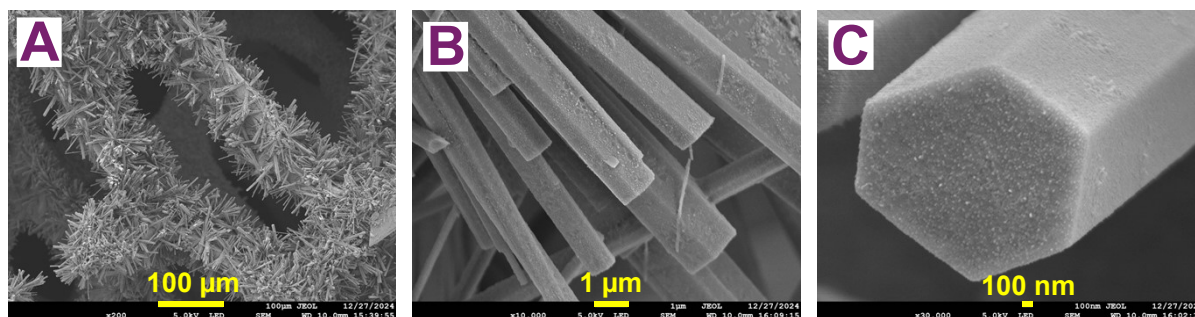


Figure S11: The FESEM images of MoP₂ at (A) 100 μm, (B) 1 μm, and (C) 100 nm.

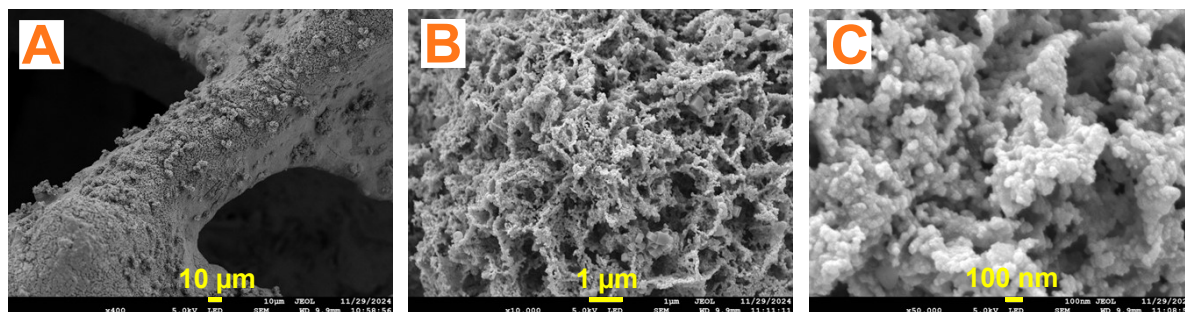


Figure S12: The FESEM images of MoN at (A) 10 μm, (B) 1 μm, and (C) 100 nm.

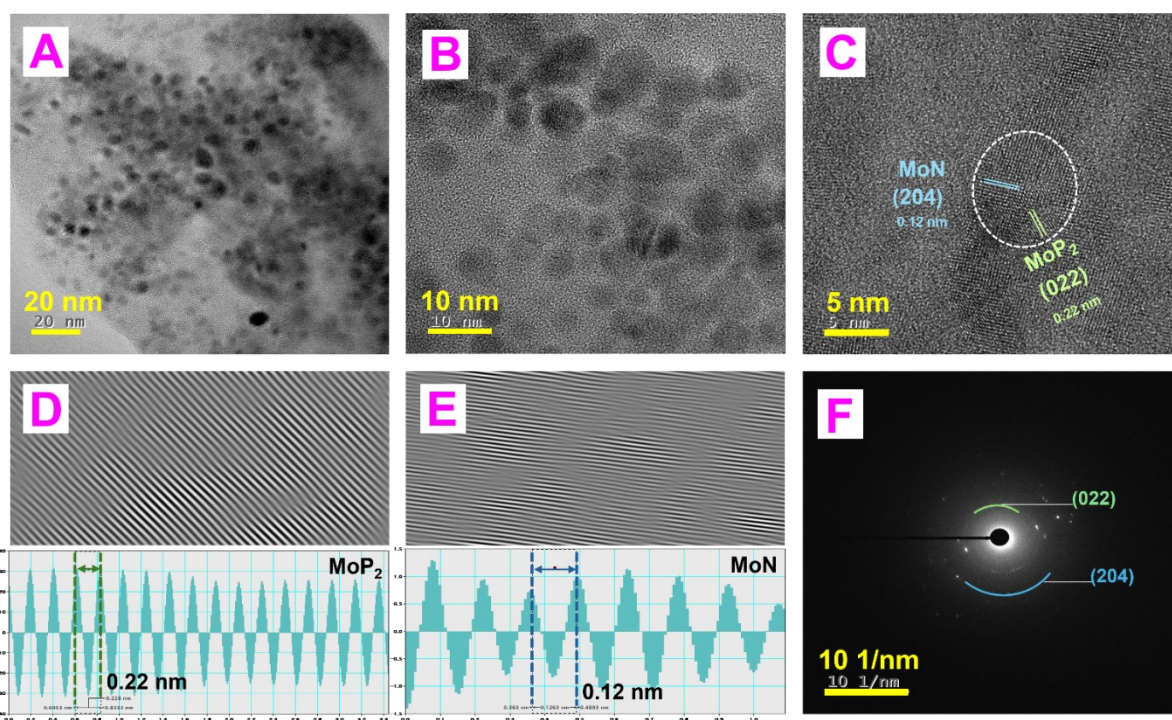


Figure S13: (A-C) HRTEM images at 20 nm, 10 nm and 5 nm, (D-E) IFFT images of MoP₂ and MoN, (F) SAED pattern of MoP₂/MoN-400.

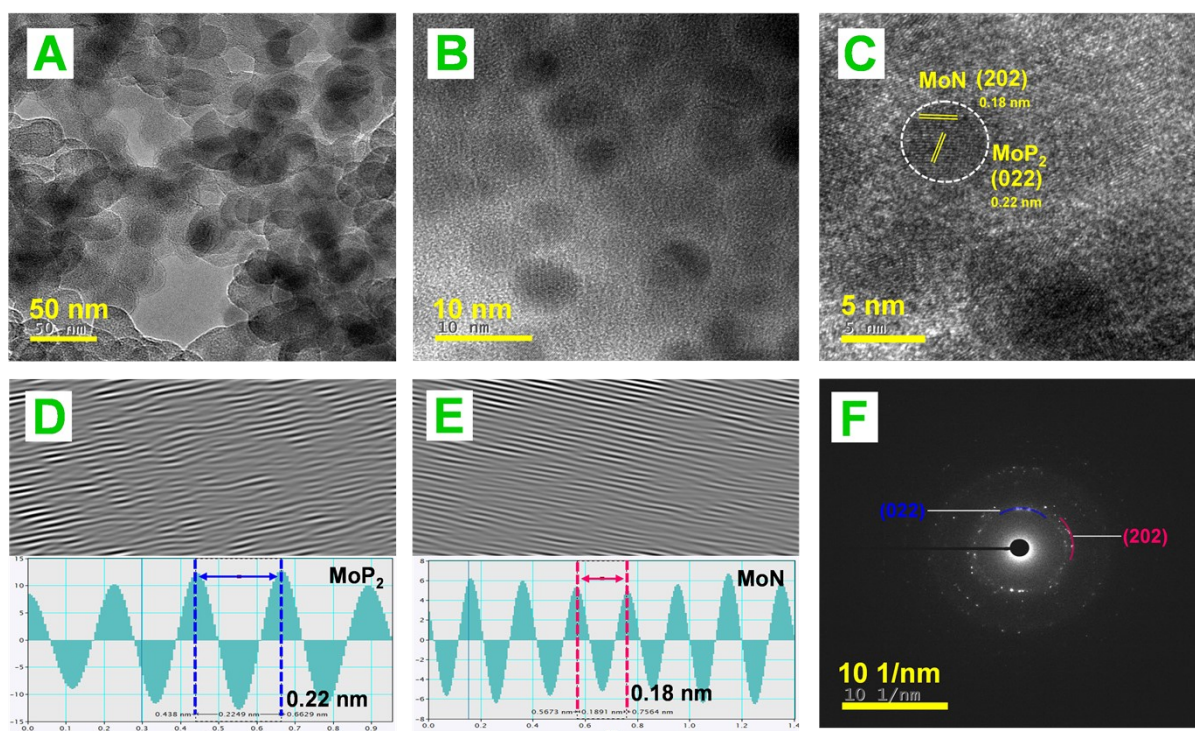


Figure S14: (A-C) HRTEM images at 50 nm, 10 nm and 5 nm, (D-E) IFFT images of MoP₂ and MoN, (F) SAED pattern of MoP₂/MoN-300.

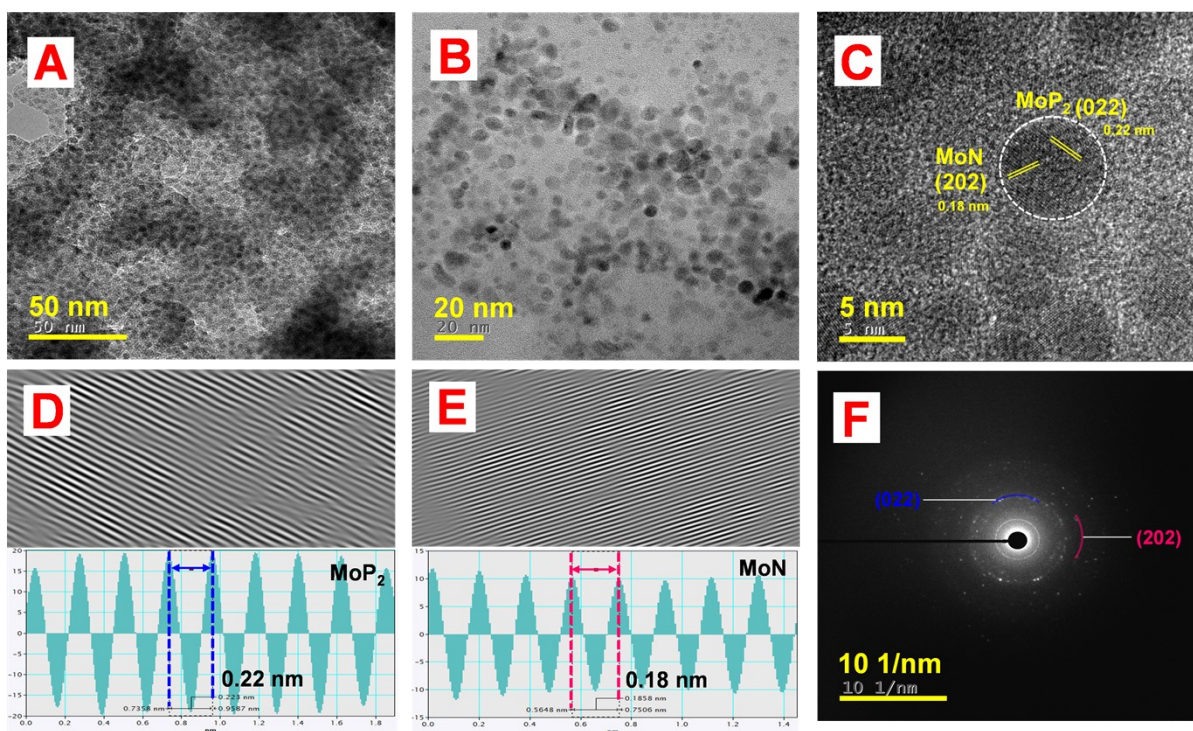


Figure S15: (A-C) HRTEM images at 50 nm, 20 nm and 5 nm, (D-E) IFFT images of MoP₂ and MoN, (F) SAED pattern of MoP₂/MoN-350.

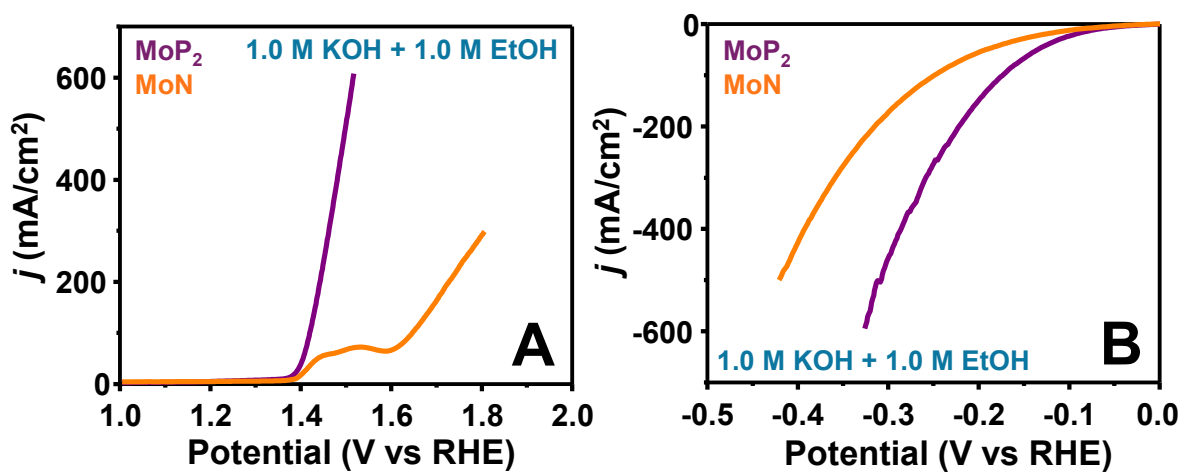


Figure S16: The plot of (A) EOR, and (B) HER in 1.0 M KOH + 1.0 M EtOH of MoP₂ and MoN.

Table S3: Resistance of the following electrodes through Nyquist plot in 1.0 M KOH.

Catalysts	R_s (Ω)	R_{ct} (Ω)
MoP₂/MoN-300	2.19	2.51
MoP₂/MoN-350	1.53	1.59
MoP₂/MoN-400	1.49	1.46
MoP₂/MoN-450	1.45	0.53

Table S4: Resistance of the following electrodes through Nyquist plot in 1.0 M KOH + 1.0 M EtOH.

Catalysts	R_s (Ω)	R_{ct} (Ω)
MoP₂/MoN-300	1.46	1.29
MoP₂/MoN-350	1.42	0.96
MoP₂/MoN-400	1.40	0.72
MoP₂/MoN-450	1.35	0.33

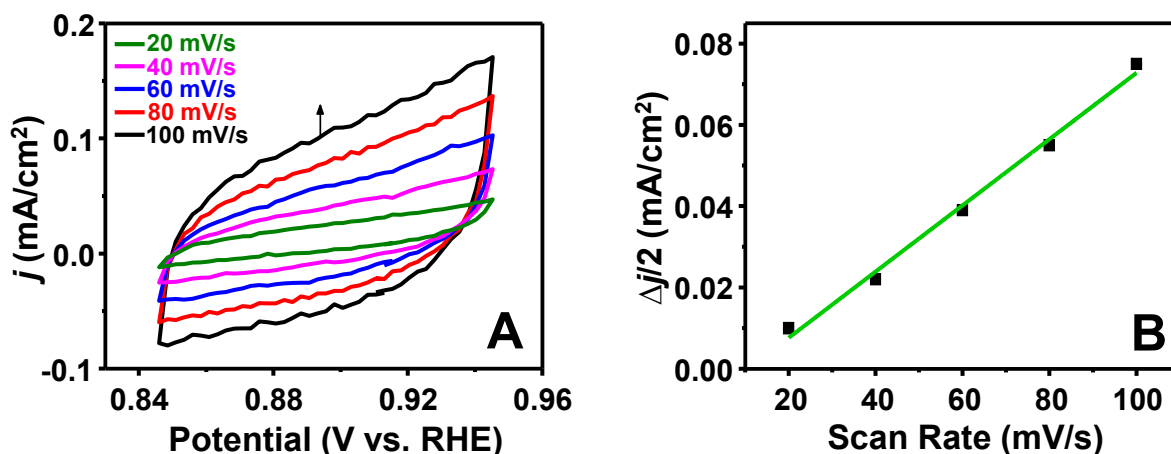


Figure S17: The cyclic voltammograms of (A) MoP₂/MoN-300 electrode at various scan rates in the non-faradaic potential region, and (B) average current density versus scan rate plot.

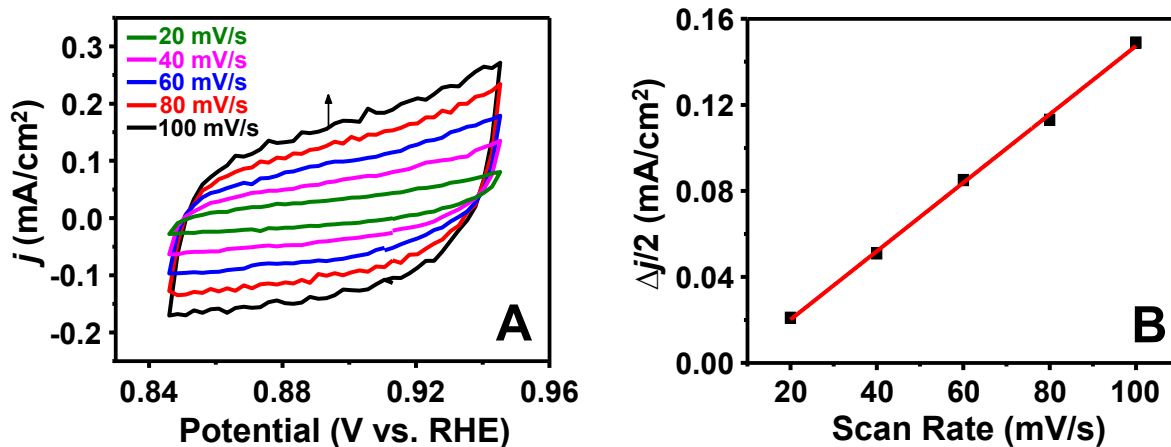


Figure S18: The cyclic voltammograms of (A) MoP₂/MoN-350 electrode at various scan rates in the non-faradaic potential region, and (B) average current density versus scan rate plot.

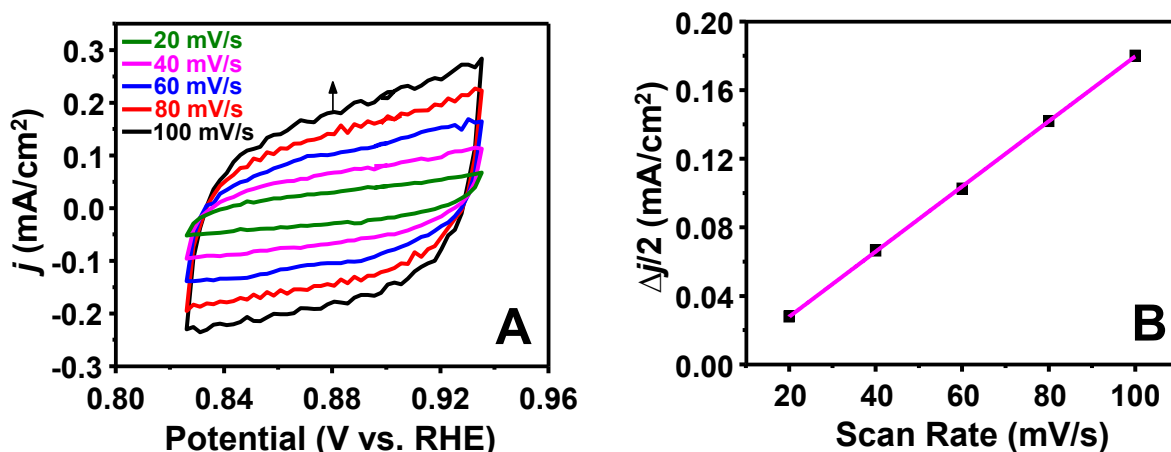


Figure S19: The cyclic voltammograms of (A) MoP₂/MoN-400 electrode at various scan rates in the non-faradaic potential region, and (B) average current density versus scan rate plot.

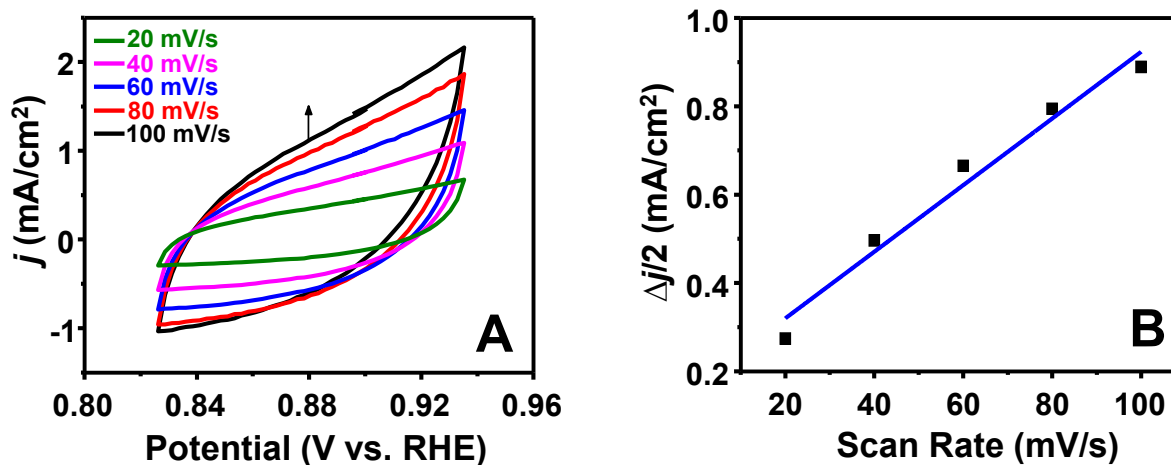


Figure S20: The cyclic voltammograms of (A) MoP₂/MoN-450 electrode at various scan rates in the non-faradaic potential region, and (B) average current density versus scan rate plot.

Table S5: The electrochemical surface area (ECSA) of the following electrodes.

Catalysts	Cdl (mF)	ECSA (cm ²)
MoP₂/MoN-300	0.20	5.09
MoP₂/MoN-350	0.39	9.92
MoP₂/MoN-400	0.47	11.87
MoP₂/MoN-450	1.88	47.12

Table S6: Comparison of the EOR Efficiency of the current electrodes with literature.

Electrodes	Electrolyte	Current Density (mA/cm ²)	Potential (V vs RHE)	Ref.
MoP₂/MoN-450	1.0 M KOH+1.0 M EtOH	100	1.34	This work
Co₃S₄-NSs/Ni-F	1.0 M KOH+0.5 M EtOH	100	1.36	66
Co-S-P/CC	1.0 M KOH+1.0 M EtOH	100	1.53	67
CoS₂/CC	1.0 M KOH+1.0 M EtOH	100	1.64	67
CoNi-PHNs	1.0 M KOH+1.0 M EtOH	10	1.39	68
Co₃O₄ NSs	1.0 M KOH+1.0 M EtOH	100	1.59	69

Co₃O₄ NCs	1.0 M KOH+1.0 M EtOH	100	1.70	69
NiO_x/CN_x	1.0 M KOH+1.0 M EtOH	10	1.354	70
Bare NiO_x	1.0 M KOH+1.0 M EtOH	10	1.396	70
Comm RuO₂	1.0 M KOH+1.0 M EtOH	10	1.55	70
Ni-Fe-P/NF	1.0 M KOH+0.5 M EtOH	100	1.40	71
Ni-Fe LDH/NF	1.0 M KOH+1.0 M EtOH	100	1.50	71

Table S7: Potential of the following electrodes at different current densities in a 3-electrode system.

Catalysts	V_{RHE} (EOR)		V_{RHE} (HER)	
	@j₁₀₀ (mA/cm²)	@j₅₀₀ (mA/cm²)	@j₁₀₀ (mA/cm²)	@j₅₀₀ (mA/cm²)
MoP₂/MoN-300	1.63	1.56	-0.33	-0.51
MoP₂/MoN-350	1.40	1.45	-0.22	-0.41
MoP₂/MoN-400	1.38	1.43	-0.20	-0.31
MoP₂/MoN-450	1.34	1.38	-0.18	-0.25

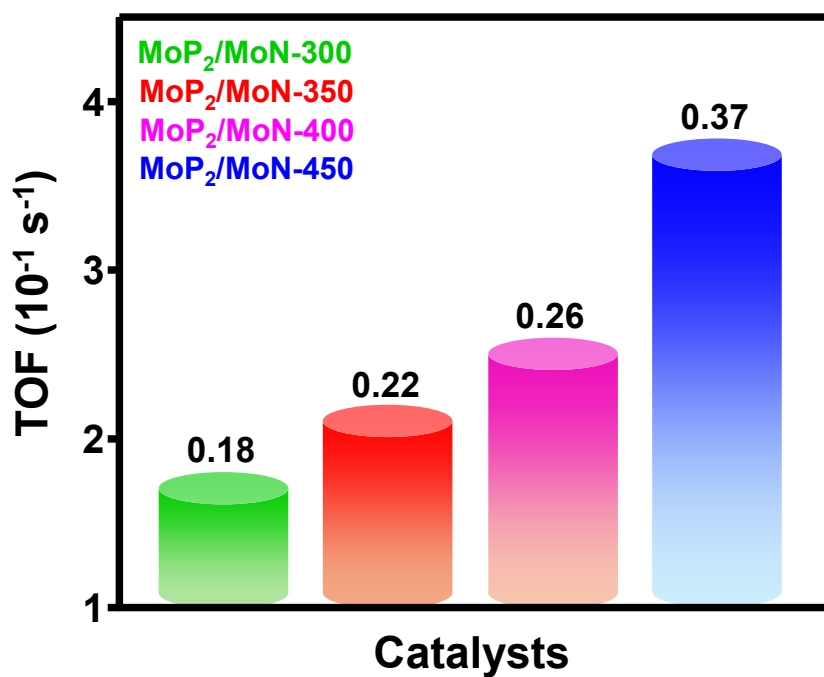


Figure S21: The TOF plot of all the catalysts.

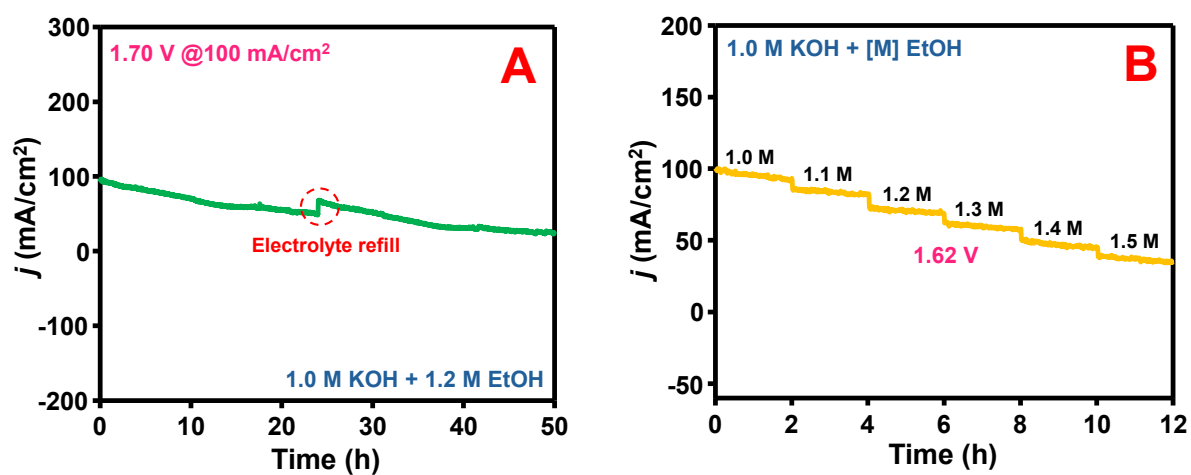


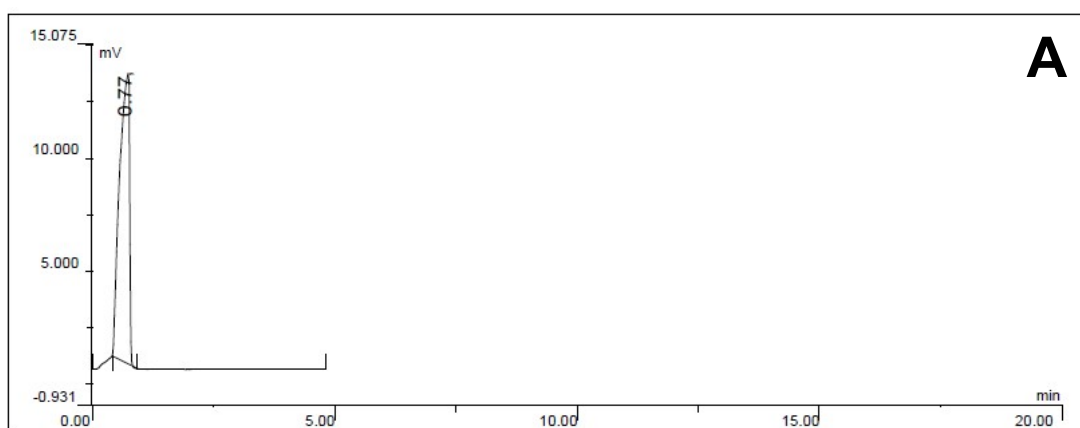
Figure S22: The CA plot of MoP₂/MoN-450 electrode in (A) 1.0 M KOH + 1.2 M EtOH for 50 h at 1.70 V, and (B) 1.0 M KOH + [M] EtOH over 12 h at 1.62 V.

Table S8: Resistance of the MoP₂/MoN-450 through Nyquist plot in different concentrations EtOH.

Catalyst	R _s (Ω)	R _{ct} (Ω)
1.0 M KOH + 0.2 M EtOH	1.45	0.54
1.0 M KOH + 0.5 M EtOH	1.41	0.42
1.0 M KOH + 0.8 M EtOH	1.39	0.41
1.0 M KOH + 1.0 M EtOH	1.35	0.33
1.0 M KOH + 1.2 M EtOH	1.38	0.35

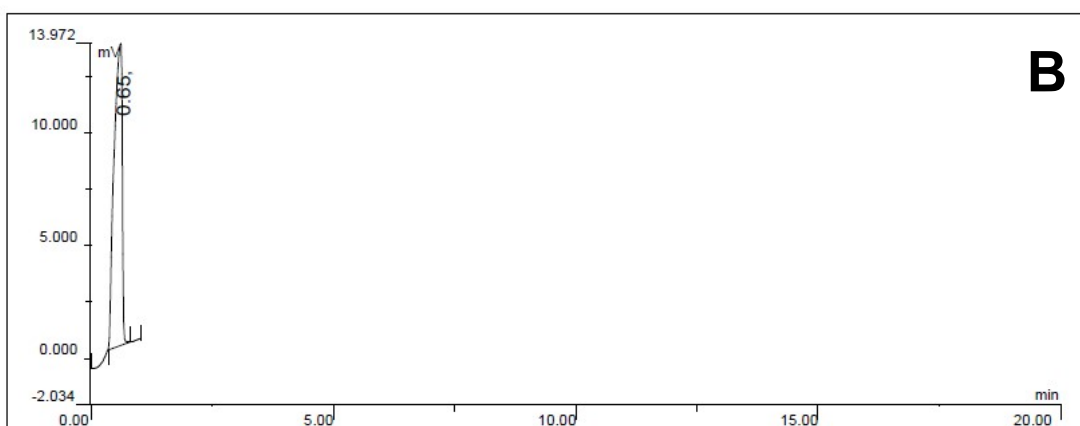
Table S9: Comparison of the EOR + HER Efficiency of the current electrode with literature.

Catalyst System	Anodic Electrolyte	<i>j</i> (mA/cm ²)	Voltage (V)	Ref.
MoP ₂ /MoN-450	1.0 M KOH+1.0 M EtOH	10	1.52	This work
MoP ₂ /MoN-450	1.0 M KOH+0.5 M EtOH	100	1.62	This work
Co ₃ S ₄ -NSs/Ni-F//Co ₃ S ₄ -NSs/Ni-F	1.0 M KOH+1.0 M EtOH	10	1.48	66
Co-S-P/CC//Co-S-P/CC	1.0 M KOH+1.0 M EtOH	10	1.63	67
CoS ₂ -MoS ₂ //CoNi-PHNs	1.0 M KOH+1.0 M EtOH	10	1.57	68
Ni-Fe-P/NF//Ni-Fe-P/NF	1.0 M KOH+1.0 M EtOH	10	1.53	70
NiFe ₂ O ₄ /NF//NiFe ₂ O ₄ /NF	1.0 M KOH+1.0 M EtOH	10	1.70	70
Ni-Fe LDH/NF	1.0 M KOH+1.0 M EtOH	10	1.60	70
VO _x -Ni ₃ N//VO _x -Ni ₃ N	1.0 M KOH + 0.25 M EtOH	50	1.50	74
Se-NiS _x /NF//CoP	1.0 M KOH+1.0 M EtOH	50	1.50	75
NiOOH-CuO/CF//NiOOH-CuO/CF	1.0 M KOH+1.0 M EtOH	50	1.611	76
PtC/NF//RuO ₂ /NF	1.0 M KOH	50	1.76	77



Area % Height %

Sr. No.	Component Name	Ret. Time.	Area μ volt sec	Height μ volt	Area %	Height %	ID Type	Peak Type
1		0.77	177546.11	13068	100.00	100.00	U	BB
			177546.11	13068	100.00	100.00		



Area % Height %

Sr. No.	Component Name	Ret. Time.	Area μ volt sec	Height μ volt	Area %	Height %	ID Type	Peak Type
1		0.65	152734.80	13840	100.00	100.00	U	BB
			152734.80	13840	100.00	100.00		

Figure S23: Gas Chromatograph of (A) Pure H_2 , (B) H_2 produced from our electrolyser system.

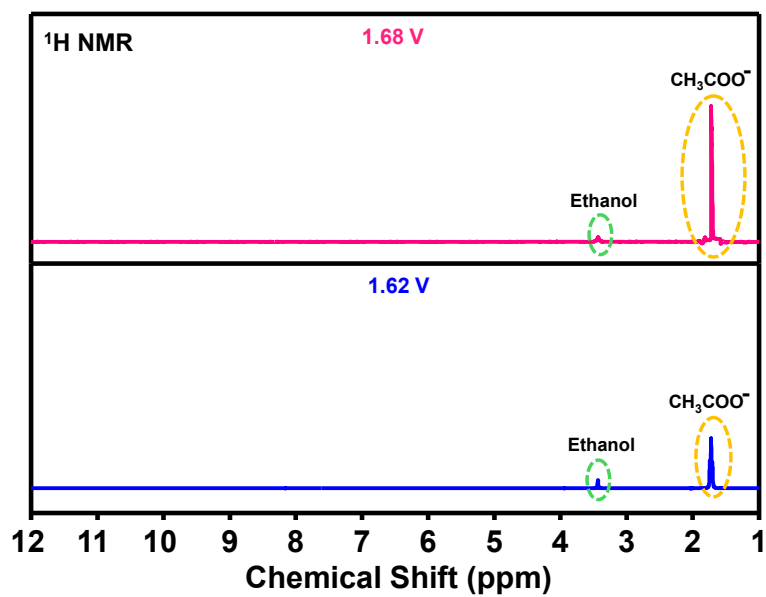


Figure S24: Full ¹H-NMR of the electrolyte after CA measurements at 1.62 and 1.68 V.

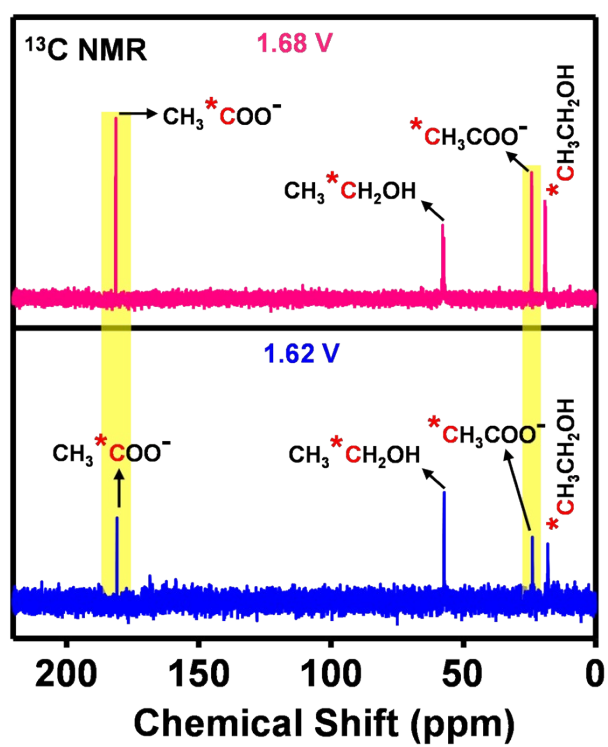


Figure S25: ¹³C-NMR of the electrolyte after CA measurements at 1.62 and 1.68 V.

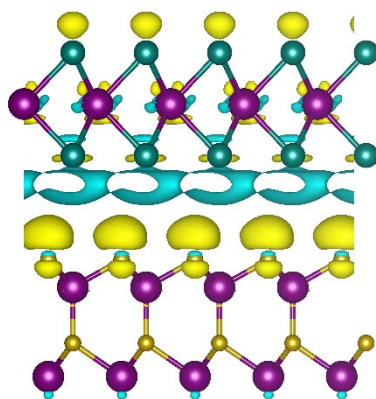


Figure S26: Charge density difference plot of the MoN/MoP₂ heterosystem. (Electron accumulation and depletion regions are represented by yellow and cyan lobes, respectively, with an iso-surface at 0.0001 e/Å³).

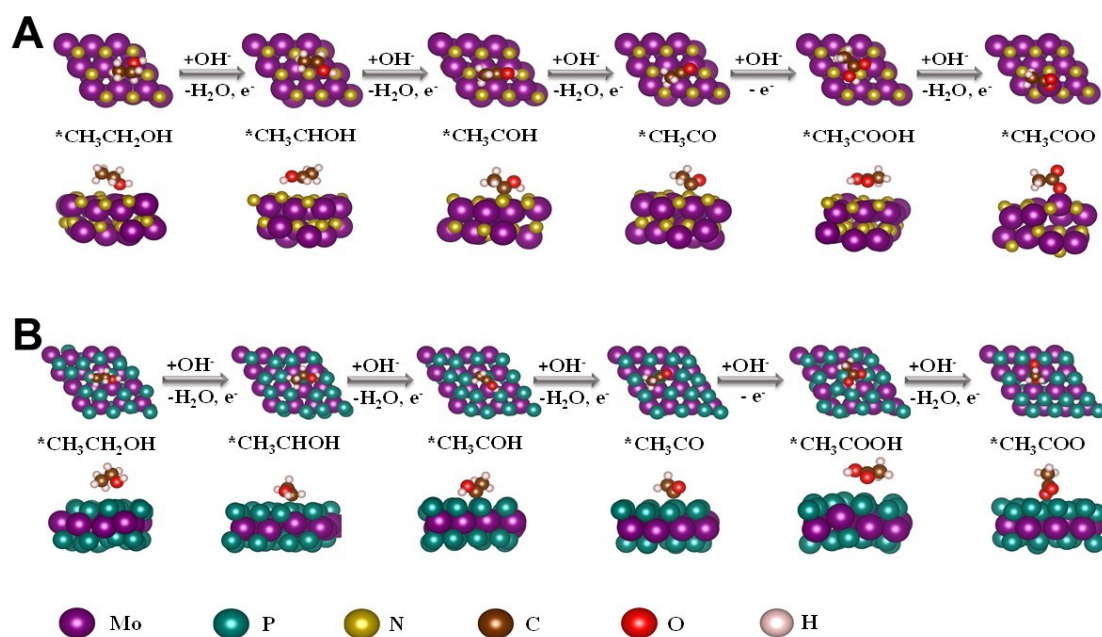


Figure S27: Schematic illustration for the EtOH oxidation pathway for (A) MoN, (B) MoP₂ surfaces (top and side views).

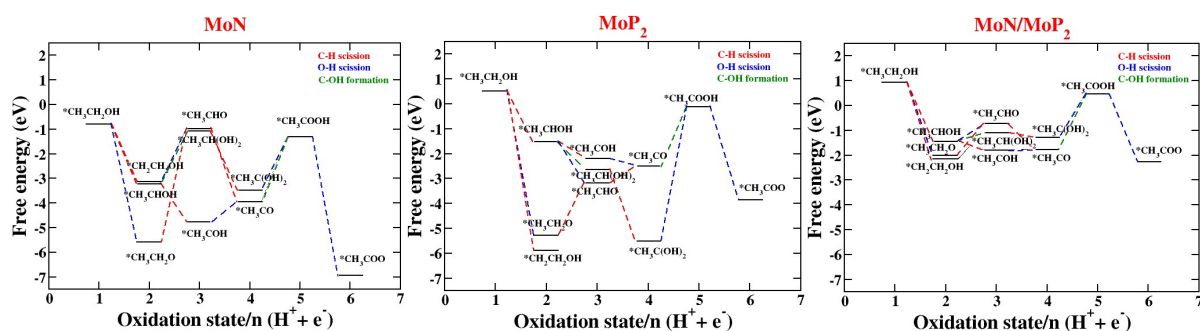


Figure S28: Reaction energy profile for EtOH electro-oxidation on MoN surface, MoP₂ surface, and MoN/ MoP₂ heterosystem. Only the most important (and low-lying) intermediates are shown. The dotted lines connecting the intermediates are color coded, according to the reaction process taking place: red corresponds to C–H bond scission, blue corresponds to O–H bond scission, and green corresponds to C–OH bond formation.