Supporting Information

Multi-interfacial engineering of interlinked Ni₂P-MoP heterojunction to modulate the electronic structure for efficient overall water splitting

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Experimental section

Chemicals and Reagents

Phosphomolybdic acid hydrate (H₃PMo₁₂O₄₀·nH₂O) was purchased from Sinopharm Chemical Reagent Co., Ltd. Histidine (C₆H₉N₃O₂), polyvinylpyrrolidone (PVP) and sodium hypophosphite (NaH₂PO₂·H₂O) were purchased from Aladdin Chemical Reagent Co., Nickel acetate (Ni(CH₃COO)₂·4H₂O) was purchased from Tianjin Kermel Chemical Reagent Co., Ltd. Commercial 20 wt% Pt/C catalyst and Nafion solution (5% (w/w) in low aliphatic alcohols and water) were bought from Johnson Matthey and Sigma-Aldrich, respectively. Ethanol was obtained from Tianjin Kermel Chemical Reagent Co., Ltd. The deionized water (DI water, 18.2 Ω M·cm) was applied throughout the whole experimental process. All other reagents were of analytical grade, and were used as received.

Synthesis of Ni₂P-MoP@NC

Typically, histidine (0.140 g, 0.9 mmol) was dissolved in DI water (25 mL) and stirred to form a homogeneous dispersion. PVP (0.1 g) was poured into the above aqueous histidine solution. Next, H₃PMo₁₂O₄₀·nH₂O (0.548 g, 0.3 mmol) was dispersed in ethanol (25 mL) and poured into the above mixed solution. Afterward, the yellow mixture was stirred at room temperature for 24 h. The as-prepared precipitate (Mo precursor) was centrifuged, washed with DI water and ethanol several times, and then dried at 60 °C for 12 h. Then, the Mo precursor (0.2 g) was uniformly dispersed in 30 mL of mixed solution ($V_{ethanol}/V_{water} = 1:1$), and Ni(CH₃COO)₂·4H₂O (0.1 g) was added to the above solution and stirred for 2 h to obtain the Ni-Mo precursor. The resulting suspension was washed several times by centrifugation with deionized DI water and ethanol, and then dried at 60 °C overnight.

Subsequently, the as-obtained Ni-Mo precursor (0.1 g) and NaH₂PO₂ (0.5 g) were placed on the downstream and upstream of the quartz tube, respectively. Before phosphorization, N₂ was purged for 30 min to remove the air. The Ni-Mo precursor was heated to 700 °C with a ramp rate of 5 °C min⁻¹ and maintained at 700 °C for 3h. After natural cooling, the targeted sample (Ni₂P-MoP@NC) was obtained. To investigate the effects of calcination temperature and Ni(CH₃COO)₂·4H₂O addition on the catalytic activity, Ni₂P-MoP@NC-650 and Ni₂P-MoP@NC-750 were obtained by varying the phosphorylation temperature to 650 and 750 °C under identical conditions. Ni₂P-MoP@NC-50 and Ni₂P-MoP@NC-150 were obtained by varying the addition amount of Ni(CH₃COO)₂·4H₂O. In addition, for comparative analysis, MoP@NC was obtained by similar conditions without adding Ni(CH₃COO)₂·4H₂O, while Ni₂P@NC was obtained by grinding the mixture of histidine and Ni(CH₃COO)₂·4H₂O followed by phosphorylation treatment.

Material Characterizations

The scanning electron microscopy (SEM) test was conducted on a Hitachi S-4800 instrument at an accelerating voltage at 5KV. Transmission electron microscopy (TEM) was carried out on a JEM-2100 at an accelerating voltage of 200 kV to characterize the structure and morphology of the as-synthesized samples. Powder X-ray diffraction (XRD) measurement was recorded radiation on a Bruker D8 diffractometer using Cu K α (λ =1.5406 Å) radiation with an acceleration voltage of 40 kV. The specific 6 surface area was identified by Brunauer–Emmett–Teller (BET) method using a Tristar II 3020 surface area and porosity analyzer (Micromeritics). X-ray photoelectron spectroscopy (XPS) characterization was conducted on a VG ESCALAB MK II with the excitation source of Mg K α (1253.6 eV) achromatic X-ray radiation. Scanning Kelvin Probe (SKP) measurement (SKP5050 system, Scotland) was performed in ambient atmosphere with the use of a gold electrode as the reference electrode.

Electrochemical Measurements

All electrochemical measurements were performed on a CHI 760E electrochemical workstation in a typical three-electrode configuration at room temperature. The catalyst inks were prepared by dispersing the samples (2.5 mg) and carbon black (0.5 mg) into 200 μ L of water/ethanol mixture (V_{water} /V_{ethanol} = 1) containing 25 μ L of 5% Nafion solution. Then, the catalyst ink was coated onto the Ni foam current collector (NF, 1.0 × 1.0 cm⁻²) for alkaline HER and OER tests. A standard Hg/HgO electrode and a graphite rod were used as the reference electrode and the

counter electrode. All potentials in this work are referenced to reversible hydrogen electrode (RHE) according to $E_{RHE} = E_{Hg/HgO} + 0.059 \times pH + E_{Hg/HgO}^{0}$. The linear sweep voltammograms (LSV) tests were collected to obtain polarization curves at a scan rate of 5 mV s⁻¹ and performed after 20 cycles of cyclic voltammetry (CV) tests to stabilize the current. Cyclic voltammetry was tested at different scan rates in the non-Faradaic potential range to calculate the electrochemical double layer capacitance (C_{dl}). Tafel plots were obtained from the polarization curves. Electrochemical impedance spectroscopy (EIS) data were acquired in the frequency range of 0.01-100,000 Hz. Long-term stability was evaluated by performing 2000 cycles of CV at a scan rate of 100 mV s⁻¹ over selected potential ranges. In addition, the chronoamperometry current density-time (i-t) curves were performed for a total of 30 h at the control potential. All electrochemical measurements were performed with 95% iR compensation.

Computational details

All the density functional theory (DFT) calculation was performed using the CASTEP program as implemented in the Materials Studios package. The projector augmented-wave (PAW) technique with the set planewave energy cutoff of 400 eV was conducted. The Perdew–Burke–Ernzerhof (PBE) functional of generalized gradient approximation was selected as the electron exchange-correlation potential. The sampling over Brillouin zone was treated by a $3 \times 3 \times 1$ Monkhorst-Pack grid, and a vacuum slab with the length of 15 Å was placed along z axis on each slab to avoid the pseudo interactions between periodic images. Geometry optimization was repeated until the total energy tolerance was converged to 2×10^{-5} eV and the changes of the force on the atoms are less than 0.05 eV/Å. The surface energies of Ni₂P (1 1 1) surface, Ni₂P (2 0 1) surface, Ni₂P (2 1 0) surface and Ni₂P (0 0 2) surface were calculated to compare the stability of various surface of the model system. Different surfaces of MoP were also calculated, including (1 0 1), (1 0 0), (1 1 0), and (0 0 1). The surface energy (BE) was calculated as follow:

$$E_{surf} = (E_{slab} - E_{bulk})/2S \times 16.02$$

 Ni_2P (1 1 1) surface shows the lowest E_{surf} among the different surfaces of Ni_2P .

For MoP, MoP (1 0 1) surface and MoP (1 0 0) surface has the lower E_{surf} . Considering the lattice match, the hetero junction was modeled based on the (1 0 0) crystal plane of MoP and (1 1 1) crystal plane of Ni₂P, which are mainly exposed in experiment. The planes of MoP and Ni₂P were further adjusted so that the lattice mis-match was less than 5%. The slab models are cleaved along the (1 1 1) of Ni₂P, (1 0 0) of MoP, and (1 0 0) of MoP.Ni₂P heterojunction.

The formation energy of the heterojunction catalyst Ni₂P-MoP was calculated as

$$E = [E_{bulk(Ni^2P-MoP)} - E_{(Ni^2P)} - E_{(MoP)}]/A \times 16.02$$

where $E_{\text{bulk}(\text{Ni}:P-\text{MoP})}$ is the total energy of bulk Ni₂P-MoP, $E_{(\text{Ni}:P)}$ is calculated after cutting the MoP part from Ni₂P-MoP to leave Ni₂P unit. Cut the Ni₂P part from the Ni₂P-MoP to separate the MoP part for calculating $E_{(\text{MoP})}$. The cross-sectional area A is 92.31775 Å². $E_{\text{bulk}(\text{Ni}:P-\text{MoP})} = -74491.5606$ eV; $E_{(\text{Ni}:P)} = -35653.7592$ eV; $E_{(\text{MoP})} = -38803.7922$ eV. Accordingly, E is -5.90165 J/m².

The HER catalytic activity of materials can be evaluated by ΔG_H , which is defined as

$$\Delta G_{\rm H} = \Delta E_{\rm H} + \Delta E_{\rm ZPE} - T\Delta S,$$

where $\Delta E_{\rm H}$ is the hydrogen adsorption energy defined as

 $\Delta E_{\rm H} = E_{\rm (total)} - E_{\rm (surface)} - 1/2 E_{\rm H2},$

in which $E_{(total)}$ and $E_{(surface)}$ are the energies of all research systems with and without H adsorption, respectively. ΔE_{ZPE} is the amount of change of zero-point energy in the total system, and T is 300 K. ΔS is the entropy change of the H atom after it transits from gaseous to adsorbed state. Herein, ΔE_{ZPE} –T ΔS is approximated to 0.24^[1].

On this basis, the adsorption behaviors of *O, *OH, and *OOH intermediates for each catalyst were simulated, and each model was optimized to convergence. ΔG for each OER step was calculated through the model of computational hydrogen electrode along with the equation as following: $\Delta G = \Delta E_{ZPE} + \Delta E - T\Delta S$, where ΔE refers to DFT energy difference; ΔS and ΔE_{ZPE} refer to corrections with entropy through vibrational analysis and zero-point energy at 300 K, respectively.

[1] J. Nørskov, T. Bligaard, A. Logadottir, J. Kitchin, J. Chen, S. Pandelovc, U. Stimming, J. Electrochem. Soc., 2005, 152, 23.



Fig. S1. Photographs of the synthesis process for Ni-Mo precursor: (a) The mixture aqueous solution of PVP and histidine, (b) The ethanol solution of PMo_{12} , (c) Adding PMo_{12} solution to the mixture of PVP and histidine (Mo precursor), (d) Adding $Ni(CH_3COO)_2$ aqueous solution into the dispersion of Mo precursor (Ni-Mo precursor).



Fig. S2. IR spectra for Ni-Mo precursor, Mo precursor, Ni(CH₃COO)₂·4H₂O and PMo₁₂.



Fig. S3. SEM images of Mo precursor.



Fig. S4. SEM images of Ni-Mo precursor.



Fig. S5. XRD patterns of Ni₂P-MoP@NC with different amounts of Ni.



Fig. S6. XRD patterns of MoP@NC and Ni₂P@NC.



Fig. S7. SEM image of Ni₂P@NC.



Fig. S8. (a) SEM and (b) TEM images of MoP@NC.



Fig. S9. SEM image of Ni₂P-MoP@NC.



Fig. S10. HRTEM images of Ni₂P-MoP@NC.

The high-resolution TEM (HRTEM) image (Fig. S10a) shows an obvious interface between Ni₂P (111) (0.221 nm) and MoP (100) (0.279 nm), implying the formation of Ni₂P-MoP heterojunction. Moreover, a clear interface according to the lattice fringes of Ni₂P (002) (0.169 nm) and MoP (101) (0.210 nm) was also observed (Fig. S10b), supporting the intimate contact between Ni₂P and MoP.



Fig. S11. BJH pore size distribution curves of Ni₂P@NC, MoP@NC and Ni₂P-MoP@NC.



Fig. S12. LSV curves of Ni₂P-MoP@NC with different calcination treatment temperatures in 1.0 M KOH.



Fig. S13. LSV curves of Ni₂P-MoP@NC with different amounts of Ni in 1.0 M KOH.



Fig. S14. (a) LSV curves of Ni₂P-MoP@NC with different catalyst loading, (b) LSV curves of Ni₂P-MoP@NC, MoP@NC, Ni₂P@NC, Pt/C on CC with the catalyst loading of 2.5 mg.

Fig. S14a shows the LSV curves of Ni₂P-MoP@NC with different catalyst loading on CC, confirming the catalyst loading can influence the catalytic performance. When the catalyst loading is 0.5 mg, the catalytic activity is not actually competing with that with the catalyst loading of 1.5 and 2.5 mg. After using CC as the substrate, Ni₂P-MoP@NC catalyst (Fig. S14b) also shows enhanced HER activity with the overpotential of 75 mV at the current density of 10 mA cm⁻², which is lower than that of MoP@NC (115 mV) and Ni₂P@NC (189 mV), indicating the superiority of heterojunctions.



Fig. S15. Exchange current density of the Ni₂P@NC, MoP@NC, Ni₂P-MoP@NC and Pt/C in 1 M KOH.



Fig. S16. CVs of (a) Ni₂P-MoP@NC, (b) MoP@NC, (c) Ni₂P@NC with different rates for HER in the region of 0.15–0.25 V in 1 M KOH.



Fig. S17. LSV curves of Ni₂P@NC, MoP@NC and Ni₂P-MoP@NC in 1 M KOH normalized by ECSA for HER.



Fig. S18. XRD pattern of Ni₂P-MoP@NC after HER cyclic test.



Fig. S19. XPS of Ni₂P-MoP@NC after HER cyclic test: the XPS high-resolution spectra of (a) Mo 3d, (b) Ni 2p and (c) P 2p for Ni₂P-MoP@NC.



Fig. S20. (a) LSV curves of Ni₂P-MoP@NC with different catalyst loading, (b) LSV curves of Ni₂P-MoP@NC, MoP@NC, Ni₂P@NC, RuO₂ on CC with the catalyst loading of 2.5 mg.

Fig. S20a suggests the best catalyst loading is 2.5 mg. Then, the electrochemical tests were performed by using the catalyst loading of 2.5 mg. As shown in Fig. S20b, Ni₂P-MoP@NC requires a lower overpotential of 276 mV at the current density of 10 mA cm⁻² than that of MoP@NC (341 mV) and Ni₂P@NC (355 mV), which implies the important role of the heterostructure in enhancing the activity of the catalyst.



Fig. S21. CVs of (a) Ni₂P-MoP@NC, (b) MoP@NC, (c) Ni₂P@NC with different rates for OER in the region of 1.15–1.25 V in 1 M KOH.



Fig. S22. LSV curves of Ni₂P@NC, MoP@NC and Ni₂P-MoP@NC in 1 M KOH normalized by ECSA for OER.



Fig. S23. XRD pattern of Ni₂P-MoP@NC after OER cyclic test.





TEM and HRTEM images (Fig. S24a) show that the entire morphology of Ni₂P-MoP@NC was still well preserved, with a new phase of Ni₂O₃ observed. The lattice fringes with an interplanar distance of 0.279, 0.221 and 0.162 nm, which can be corresponded to the (100) lattice plane of MoP, (111) lattice plane of Ni₂P, and (002) lattice plane of Ni₂O₃ respectively.



Fig. S25. The XPS high-resolution spectra of (a) Mo 3d, (b) Ni 2p, (c) P 2p and (d) O 1s for Ni₂P-MoP@NC after OER cyclic test.

As seen in Fig. S25, all the elements in the Ni₂P-MoP@NC after the OER have obvious change. The peaks belonged to the high valences of the Ni, Mo and P elements increased. As shown in the Ni XPS spectrum (**Fig. S25b**), the peaks attributed to Ni-O show increased intensity clearly after OER, manifesting the valence change of Ni element and the formation of Ni-oxides. With respect to the P XPS spectrum (**Fig. S25c**), the peaks related to P-O bond are strengthened, validating the surface oxidation after OER. In the high-revolution O spectrum, there are three peaks for O–M (531.7 eV), –OH (533.1 eV) and adsorbed water (535.5 eV), further indicating the surface reconstruction induces the formation of metal oxides.



Fig. S26. Geometric models of (a) MoP, (b) Ni_2P and (c) Ni_2P -MoP heterojunction.



Fig. S27. Geometric models of H^* adsorption on (a) MoP, (b) Ni_2P and (c) Ni_2P -MoP surfaces.



Fig. S28. Geometric models for the adsorption of (a) OH*, (b) O*and (c) *OOH on the MoP surface.



Fig. S29. Geometric models for the adsorption of (a) OH^* , (b) O^* and (c) *OOH on the Ni_2P surface.



Fig. S30. Geometric models for the adsorption of (a) OH^* , (b) O^* and (c) *OOH on the Ni_2P -MoP surface.

Table S1. Comparison of HER activity of Ni₂P-MoP@NC, MoP@NC and Ni₂P@NC in 1.0 M KOH.

Catalysts	η (mV)		Tafel slopes	jo	C _{dl}
	η_{10}	η_{100}	(mV dec ⁻¹)	(mA cm ⁻²)	(mF cm ⁻²)
Ni ₂ P-MoP@NC	69	161	56	0.703	70.0
MoP@NC	101	202	78	0.592	37.0
Ni ₂ P@NC	191	304	121	0.450	8.2

Table S2. Comparison of HER performance of Ni_2P -MoP@NC with other Mo-based and Ni-based electrocatalyst in 1 M KOH.

Catalysts	η_{10}	Tafel slopes	Reference
	(mV)	(mV dec ⁻¹)	
Ni ₂ P-MoP@NC	69	56	This work
Ni ₂ P@C	148	83.5	Adv. Mater., 2022, 9, 2200673
Mo-Ni ₃ S ₂ /Ni _x P _y	109	68.4	Adv. Energy Mater., 2020, 10, 1903891
H-MoS ₂ /MoP	92	59.8	Small, 2020, 16, e2002482
Ni ₂ P@NSG	110	43	Chem. Mater., 2021, 33, 234–245
NiS ₂ /MoS ₂	204	65	ACS Catal., 2017, 7, 6179–6187
MoS ₂ /Ni ₃ S ₂ @CA	96	61	Small, 2023, 19, 2205431
Mo ₃ P/Mo	78	43	Angew. Chem. Int. Ed., 2018, 57, 14139-14143.
MoP/Mo ₂ N	89	78	Angew. Chem. Int. Ed., 2021, 60, 6673-6681.
MoS ₂ /Ni ₃ S ₂	89	62	Small, 2021, 17, 2006730
Ni _{2(1-x)} Mo _{2x} P	72	46.4	Nano Energy, 2018, 53,492–500
Ni/NiO/N	180	121	Carbon, 2020,157, 515e524

MoP/NF	114	54.6	Small, 2018, 2, 1700369
Ni/Ni(OH) ₂	77	53	Adv. Mater., 2020, 32, 1906915
MoS ₂ /Ni ₃ S ₂	110	83	Angew. Chem. Int. Ed., 2016, 128 , 6814-6819.
NP-Mo ₂ C	210	64	Carbon, 2018,139 845e852
Mo/MoS _{1.15} P _{0.30} @PNC	131	82	Small, 2020, 2004973
Ni-Mo ₂ C@NPC	183	64	Appl. Catal. B: Environ., 2021,296 120336
Mo-doped Ni ₂ P	81	53.4	J. Mater. Chem. A, 2019, 7, 7636–7643
MoP/MoNiP@NC	94	70	Chem. Eng. J., 2022, 431 ,133696
M0S2/C09S8/Ni3S2/Ni	113	85	J. Am. Chem. Soc., 2019, 141, 26, 10417-10430
MoS ₂ /MoP/NC	208	62	J. Mater. Chem. A, 2018, 6, 24783–24792
NiS/MoS ₂	174	70.2	J. Mater. Chem. A, 2019,7, 21514-21522
MoS ₂ /NiCoS	189	75	J. Mater. Chem. A, 2019, 7, 27594–27602
NiMoN	109	95	Adv. Energy Mater., 2016, 6,1600221-1600227.
Mo ₂ C/CNTs	135	55.3	J. Mater. Chem. A, 2020,8, 18180-18187

Ru/Mo ₂ CT _x	73	57	Adv. Funct. Mater., 2023, 2214375
Ni/a-Ni(OH) ₂	110	99	Energy Environ. Sci., 2020, 13, 174-182
Ni ₃ S ₂ -MoS ₂ @TiO ₂	115	67	Small, 2022, 18, 2201896
MoP ₂ -MoP	196	79	ACS Catal., 2019, 9, 8712-8718
Co–Mo ₂ N	76	47	J. Mater. Chem. A, 2018, 6, 20100-20109

Table S3. Comparison of OER activity of Ni₂P-MoP@NC, MoP@NC, Ni₂P@NC and RuO₂ in 1.0 M KOH.

Catalysts	η (mV)		Tafel slopes	C _{dl}
	η_{10}	η_{100}	(mV dec ⁻¹)	(mF cm ⁻²)
RuO ₂	319	461	85	/
Ni ₂ P-MoP@NC	249	315	53	48.0
MoP@NC	319	431	74	16.5
Ni ₂ P@NC	327	500	114	13.5

Table S4. Comparison of OER performance of Ni_2P -MoP@NC with other Mo-basedand Ni-based electrocatalyst in 1 M KOH.

Catalysts	η_{10}	Tafel slopes	Reference
	(mV)	(mV dec ⁻¹)	
Ni ₂ P-MoP@NC	249	53	This work
Ru SAs–Ni ₂ P	260	-	Nano Energy, 2021, 80,
			105467
Ni ₂ P@C	326	93.5	Adv. Mater., 2022, 9,
			2200673

MoP/NF	265	56.6	Small, 2018, 2, 1700369
NiMoFeP	286	28	Small, 2019, 15, 1905501
Ni/NiO/N	346	70	Carbon, 2020, 157, 515e524
Ni/Ni(OH) ₂	270	70	Adv. Mater., 2020, 32, 1906915
P-Mo-Co ₃ O ₄ @CC	276	53.9	Carbon Energy, 2022, 1– 14
NiFeB-P MNs	252	35.2	Small., 2022, 18, 2203411
Ni-Fe-O-S	272	70	J. Mater. Chem. A, 2018, 6, 7062–7069
NiFeP–WO _x	270	66	J. Mater. Chem. A, 2021, 9, 10909–10920
Ni _{1.75} Rh _{0.25} P	273.1	30	Chem. Mater., 2022, 34, 4414-4427
HP Ni–P	286	39.5	J. Mater. Chem. A, 2020, 8, 12069–12079
Ni-CoP	290	66	Nano Lett., 2021, 21, 823–832
Co–Mo ₂ N	296	90	J. Mater. Chem. A, 2018, 6, 20100-20109
Ni ₃ N-NiMoN	277	118	Nano Energy, 2018, 44, 353-363
Ni/NiFeMoO _x /NF	255	35	Adv. Sci., 2020, 7, 1902034.

MoS ₂ /NiS ₂	278	91.7	Adv. Sci., 2019, 6,
			1900246.
Co/β-Mo ₂ C@N-CNTs	356	67	Angew. Chem. Int. Ed.,
			2019, 58, 4923-4928.
N-NiMoO ₄ /NiS ₂	283	44.3	Adv. Funct. Mater., 29,
			1805298.
Ni/Ni ₂ P/Mo ₂ C@C	368	75	J. Mater. Chem. A, 2018,
			6, 5789
C02P/M03C03C/M02C@C	362	82	J. Mater. Chem. A, 2018,
			6, 5789
Ni/Mo ₂ C-NCNFs	288	78.4	Adv. Funct. Mater., 2019,
			9, 1803185.
Co-MoS ₂ /BCCF-21	260	85	Adv. Motor 2018 20 1 7
			Auv. Mater.,2018, 50, 1-7.
NiMoP ₂	330	90.6	J. Mater. Chem. A,
			2017, 5, 7191.

Table S5. The energy, surface area (S), and surface energy (γ) of each low-index facet for MoP and Ni₂P.

Sample	Model	Energy (eV)	S/Å ²	γ/J·m ⁻²
	bulk	-17837.5331	/	/
	(111)	-17831.4529	45.6420	1.0671
Ni ₂ P	(201)	-17830.0579	49.7844	1.2027
	(210)	-17826.6382	52.6023	1.6590
	(002)	-17832.5597	29.9556	1.3299
	bulk	-6471.4347	/	/
	(101)	-6468.0625	13.8018	1.9571
MoP	(100)	-6468.5201	10.3713	2.2510
	(110)	-6466.3747	17.9637	2.2562
	(001)	-6468.1841	9.1064	2.8592

Models	$\Delta G_1 = \Delta G_{HO^*}$	$\Delta G_2 = \Delta G_{O^*}$	$\Delta G_3 = \Delta G_{HOO} $	$\Delta G_4 = \Delta G_{O_2}$ -
	ΔG_{H^2O} (eV)	ΔG_{OH^*} (eV)	ΔG_{0^*} (eV)	ΔG _{HOO*} (eV)
Ni ₂ P-MoP	1.08	1.33	1.68	0.84
MoP	1.10	0.57	1.75	1.50
Ni ₂ P	0.80	0.71	2.62	0.78

Table S6. The free energy of different models for OER at U = 0 V.

Table S7. Comparison of overall water splitting performance of Ni₂P-MoP@NC with recently reported nonprecious metal-based bifunctional electrocatalyst in 1 M KOH.

Catalysts	Cell voltage at 10 mA	Reference
	cm ⁻² (V)	
Ni ₂ P-MoP@NC	1.54	This work
Ni ₂ P@NSG	1.572	Chem. Mater., 2021, 33, 234–245
Ni/NiO/N	1.688	Carbon, 2020, 157, 515e524
$(Co_{1-x}Ni_x)$	1.65	Adv. Energy Mater., 2018,
$(S_{1-y}P_y)_2/G$		8, 1802319
Ni/Ni ₈ P ₃	1.61	Adv. Funct. Mater., 2016, 26, 3314-3323
NCP	1.56	J. Am. Chem. Soc., 2018, 140, 5241–5247
MoS ₂ /Ni ₃ S ₂	1.56	Angew. Chem. Int. Ed., 2016, 128 23, 6814-6819.
MoP/NF	1.62	Small, 2018, 2, 1700369
Ni/Ni(OH) ₂	1.59	Adv. Mater., 2020, 32, 1906915

Co–Mo ₂ N	1.576	J. Mater. Chem. A, 2018, 6, 20100-20109
MoS ₂ /NiS ₂	1.59	Adv. Sci., 2019, 6, 1900246.
Co/β-Mo ₂ C@N-CNTs	1.64	Angew. Chem. Int. Ed., 2019, 58, 4923-4928.
N-NiMoO4/NiS2	1.60	Adv. Funct. Mater., 29, 1805298.
Ni/Ni ₂ P/Mo ₂ C@C	1.78	J. Mater. Chem. A, 2018, 6, 5789
C02P/M03C03C/M02C@C	1.74	J. Mater. Chem. A, 2018, 6, 5789
Ni/Mo ₂ C-NCNFs	1.64	Adv. Funct. Mater., 2019, 9, 1803185.
CoMoP@Co ₃ O _{4-x}	1.614	ACS Appl. Mater. Interfaces, 2021, 13, 46, 55263–55271
PMo/ZIF-67-6-6/7N	1.61	Chem. Sci., 2018, 9, 4746–4755
a-CoMoP _x /CF	1.581	Adv. Funct. Mater., 2020, 30, 2003889
Mo-NiCoP	1.61	Nano-Micro Lett., 11, 55 (2019).
NiCo ₂ P ₂	1.61	Nano Energy, 2018, 48, 284
Ni/Mo ₂ C	1.66	Chem. Sci., 2017, 8, 968.
NiMoP ₂	1.67	J. Mater. Chem. A, 2017, 5, 7191.