

Supporting Information

Highly Active Bimetallic Phosphides Electrocatalysts for Hydrogen Evolution

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Chemicals and Regents

All of chemicals and reagents were purchased from commercial sources and used as received without further purification.

Characterization

The phase analysis of the samples was performed by powder X-ray diffraction (PXRD) patterns with the range of 5°-80° via using Siemens D5005 diffractometer with Cu-K α ($\lambda=1.5418$ Å) radiation. Transmission electron microscopy (TEM) images were measured at JEOL-2100F transmission electron microscope to analyze the microstructures of samples. The interrelated energy dispersive X-ray detector (EDX) spectra

were obtained by using a SU8000 ESEM FEG microscope. X-ray photoelectron spectroscopy (XPS) measurement was collected by the KRATOS Axis ultra with a Mg K α X-ray source. N₂ absorption-desorption isotherms were measured on an ASAP 2020 (Micromeritics, USA). Raman spectra was achieved by JY Labram HR 800.

Electrochemical measurements

All electrochemical measurements were conducted with a conventional three-electrode system through a CHI 760D instrument (shanghai, China) in H₂SO₄ (0.5 M) and KOH (1.0 M) solution at room temperature. Herin, the glassy carbon electrode (GCE) with diameter of 3 mm was used as working electrode. A carbon rod was used as the counter electrode and Ag/AgCl was used as the reference electrode. Among them, the working electrode preparation process details are as follows: a certain amount of catalyst was dispersed into a mixture which contained 100 μ L ethanol, 300 μ L water and 30 μ L Nafion (5 wt%). Then, the above solution was sonicated for 30 min to form a homogeneous ink. At last, the prepared ink of 5 μ L was covered by a pipette on the GCE surface and dried naturally at room temperature.

In this work, the catalytic performance of the catalyst was evaluated by linear sweep voltammetry (LSV) with a scan rate of 5 mV s⁻¹. Significantly, all overpotential calculations were based on the Nernst equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.059 * \text{pH}$. And the Cyclic voltammetry was test

between -0.1V and 0.1V with the scan rate of 100 mV s⁻¹. Tafel plots was obtained via the equation of $\eta = a + \text{blog } |j|$ according to the LSV curves. Electrochemical impedance spectroscopy (EIS) was conducted on the PARSTAT 2273 electrochemical system (Princeton Applied Research Instrumentation, USA) with frequencies from 0.1 to 100000 Hz and an amplitude of 5 mV. The stability was measured by chronoamperometry with *i-t* curves under controlled overpotential for 24 h

Experiment section

Synthesis of PPy

Polypyrrole (PPy) was synthesized according to previous literature [S1]. Pyrrole monomer (Py, 0.16 M) was added to 40 mL of 1 M hydrochloric acid solution, and the above solution was vigorously stirred for 30 min to obtain a uniformly mixed solution. Then 20 mL of ammonium persulfate (APS, 0.04 M) solution was added dropwise to the above mixed solution, followed by static polymerization for 24 h. The obtained product was washed several times with deionized water and ethanol, dried at 60°C and the product was collected.

Synthesis of (NH₄)₁₂Na₁₂[Mo₄₀O₁₂₈]·ca. 70H₂O

The polyoxometalate Mo₄₀ was synthesized by the literature [S2]. 3.00 g of ammonium molybdate (2.4 mmol) was dissolved in 25 mL of water. Then, 0.8 mL of glacial acetic acid (100%) was added to acidify. After that, 0.20 g of sodium dithionite (1.1 mmol) was added, the color of the solution

changes to dark green. 3.00 g of sodium chloride was dispersed in the above solution after stirring 5 min. The resulting solution was aged and crystallized for 4.5 h. Finally, the obtained solution was washed with amounts of 50% (v/v) acetone solution and filtered to obtain a red rhombohedral crystal precipitate, which was dried in air and the product was collected.

Synthesis of MoP/MoNiP@NC

In a typical procedure, 25 mg of Mo₄₀, 25 mg of nickel acetate and 100 mg of PPy were dissolved in 25 mL of deionized water and stirred for 10 h to obtain a homogeneous mixed solution. Then, the above solution was heated to boiling until the solvent was evaporated to dryness. Finally, the obtained black powder solid with 0.8 g of sodium hypophosphite in front were calcined at 900 °C under an Ar flow for 2 hours at a heating rate of 5 °C min⁻¹. Then, the temperature was naturally cooled to obtain the black electrocatalyst material.

Furthermore, the control samples of MoP@NC, Ni₁₂P₅@NC, and NC were synthesized by the same experimental process without the polyoxometalate Mo₄₀ and the metal salt nickel acetate.

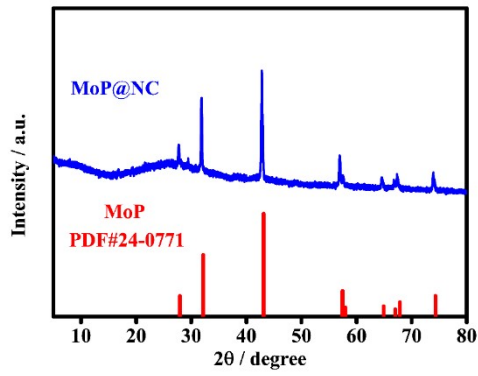


Figure S1. PXRD pattern of MoP@NC.

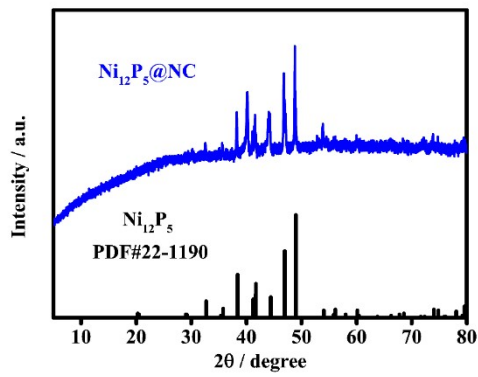


Figure S2. PXRD pattern of Ni₁₂P₅@NC.

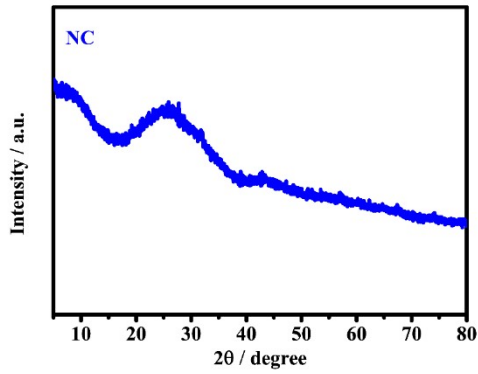


Figure S3. PXRD pattern of NC.

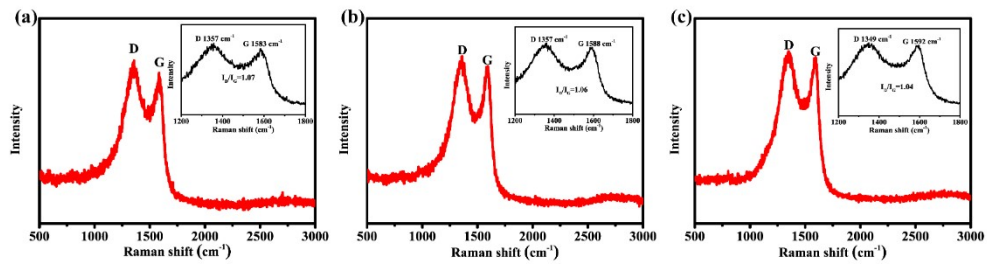


Figure S4. Raman spectrum of (a) MoP/MoNiP@NC, (b) MoNiP@NC and (c) Ni₁₂P₅@NC.

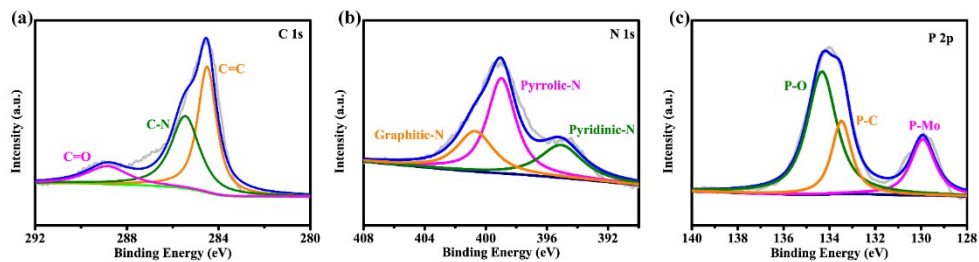


Figure S5. XPS spectra of (a) C 1s, (b) N 1s and (c) P 2p of MoP/MoNiP@NC.

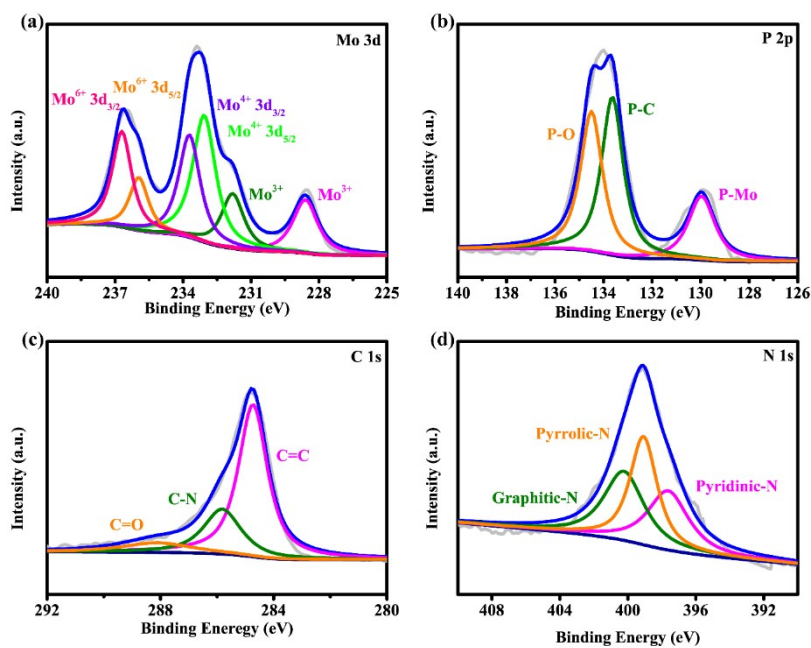


Figure S6. XPS spectra of (a) Mo 3d, (b) P 2p, (c) C 1s and (d) N 1s of MoP@NC.

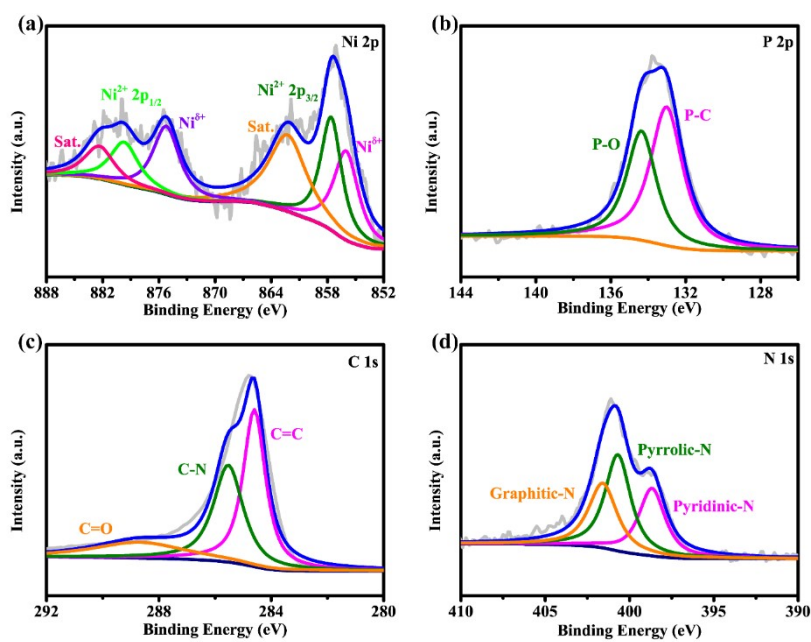


Figure S7. XPS spectra of (a) Ni 2p, (b) P 2p, (c) C 1s and (d) N 1s of Ni₁₂P₅@NC.

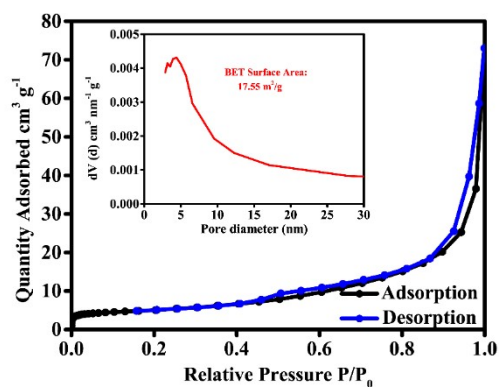


Figure S8. N₂ adsorption-desorption isotherms of MoP/MoNiP@NC (Inset: pore diameter distribution diagram).

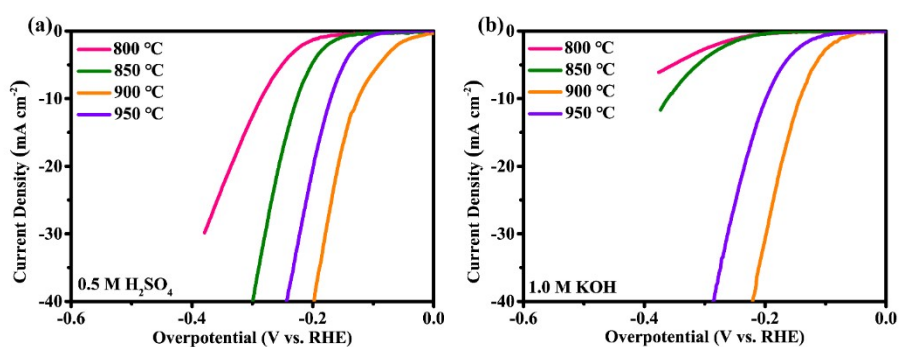


Figure S9. HER polarization curves for catalyst with different calcination temperatures (800, 850, 900 and 950 °C) in (a) 0.5 M H₂SO₄ and (b) 1.0 M KOH.

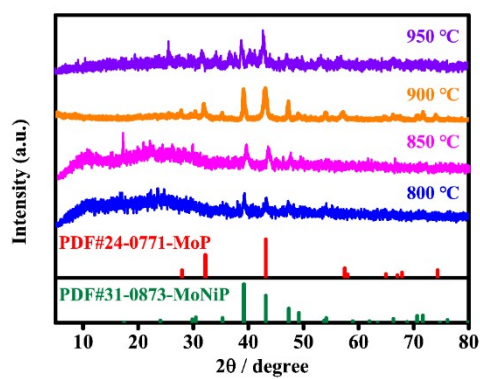


Figure S10. PXRD pattern of MoP/MoNiP@NC with different temperatures (800, 850, 900 and 950 °C).

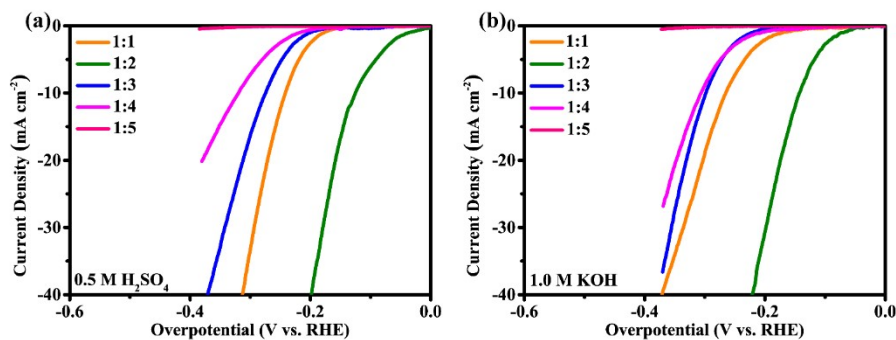


Figure S11. HER polarization curves for catalyst with different content of Mo₄₀ in (a) 0.5 M H₂SO₄ and (b) 1.0 M KOH. (Note: Calcination temperature: 900 °C, M_{Mo40}:M_{Ni²⁺}=1:1).

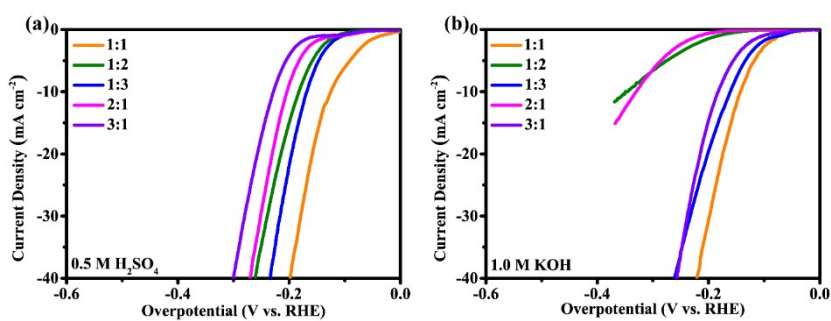


Figure S12. HER polarization curves for catalyst with different ratio of nickel ions (a) 0.5 M H₂SO₄ and (b) 1.0 M KOH. (Note: Calcination temperature: 900 °C, M_{metal}:M_{ppy}=1:2).

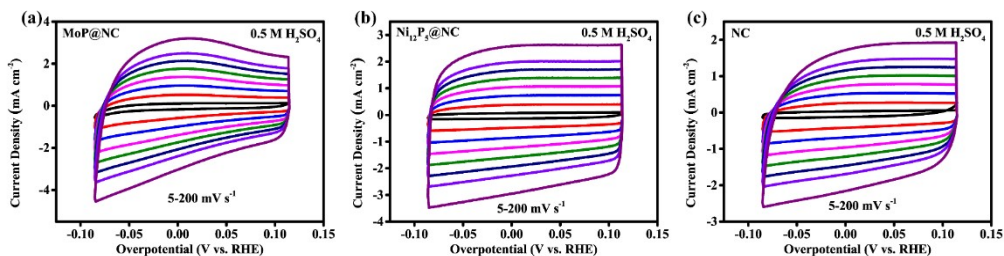


Figure S13. CVs of (a) MoP@NC, (b) Ni₁₂P₅@NC, (c) NC with the scan rate ranging from 5 to 200 mV s⁻¹ in 0.5 M H₂SO₄.

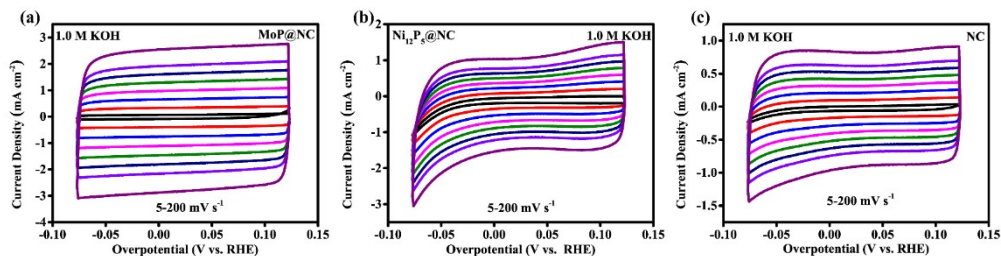


Figure S14. CVs of (a) MoP@NC, (b) Ni₁₂P₅@NC, (c) NC with the scan rate ranging from 5 to 200 mV s⁻¹ in 1.0 M KOH.

Table S1. The contents of Mo, Ni and MoP from the inductively coupled plasma (ICP) measurement.

	Mo	Ni	MoP
Content (wt%)	15.26	3.42	11.84

Table S2. HER performance of transitional metal phosphide.

Catalyst	Electrolyte	Overpotential	Tafel slope	Stability	Ref.
		(mV) η_{10}	(mV dec ⁻¹)		
MoP/MoNiP@NC	0.5 M H₂SO₄	125	115	24 h	This work
	1.0 M KOH	144	85	24 h	
MoP/NPG	0.5 M H ₂ SO ₄	148	49	3000 cycles 60 h	S3
	1.0 M KOH	126	56	3000 cycles 60 h	
	1.0 M PBS	150	102	3000 cycles 60 h	
MoP@NC	0.5 M H ₂ SO ₄	96	49.2	5000 cycles	S4
	1.0 M KOH	149	61.7	5000 cycles	
C/NiP-C	1.0 M PBS	191	95.0	5000 cycles	S5
	1.0 M KOH	176	100	1000 cycles 36000 s	
MoNiP NWs	0.5 M H ₂ SO ₄	179	60	1000 cycles	S6
MoO ₂ /MoS ₂ /MoP-800	0.5 M H ₂ SO ₄	135	67	1000 cycles 30 h	S7
	0.5 M H ₂ SO ₄	158	58	5000 cycles 24 h	
MoC-MoP/BCNC NFs	1.0 M KOH	137	65	5000 cycles 24 h	S8
	0.5 M H ₂ SO ₄	156	51	1000 cycles	
MoP/Fe ₂ P/RGO	0.5 M H ₂ SO ₄	156	51	1000 cycles	S9

N/C/MoP	1.0 M KOH	169	51.3	1000 cycles	S10
MoP@C@rGO	1.0 M H ₂ SO ₄	168.9	79	17 h	S11
Mo ₂ C-MoP	0.5 M H ₂ SO ₄	85	66	5000 cycles 16 h	S12
NPC/CFP-800	1.0 M KOH	146	71	5000 cycles 16	

Reference

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