

Polyoxometalates Combined Polypyrrole Induced Bimetallic Phosphide for Electrocatalytic Hydrogen Evolution

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Experimental Section

All chemicals were purchased from commercial sources and used as received without further purification. Nafion solution (5 wt.%) was purchased from Alfa Aesar. The water used throughout all experiments was purified through a Millipore system.

Synthesis of PPy

Polypyrrole (PPy) was synthesized by literature S1. Firstly, Pyrrole monomer was the pyrrole monomer was dissolved in 40ml 1M hydrochloric acid solution. Then 20 mL ammonium sulfate (APS, 0.04 M) was mixed with pyrrole monomer and polymerized for 24 h. Finally, it was washed with deionized water and ethanol for several times and dried for collection.

Synthesis of MoP/MoNiP@C

100 mg of polypyrrole, 25 mg of molybdate phosphate and 25 mg of nickel acetate were dissolved in deionized water, mixed evenly and then heated until the solvent evaporated completely. Sodium hypophosphite as the phosphorus source was placed in the upstream of the tube furnace, heated to 900 °C at the rate of 5 °C min⁻¹ under argon atmosphere for 2 h, and then lowered to room temperature.

In addition, the control samples of MoNiP@C, MoP@C, Ni₂P@C and PC were synthesized by the same experimental procedure expect for the different content of polyoxometalate PMo₁₂ and the metal salt nickel acetate.

Characterization

Powder X-ray diffraction (PXRD) patterns was collected by using Siemens D5005 diffractometer with Cu-K α ($\lambda=1.5418$ Å) radiation at the range of 5°-80°. Transmission electron microscopy (TEM) images were gathered at JEOL-2100F transmission electron microscope. Interrelated energy dispersive X-ray detector (EDX) spectra were collected via using a SU8000 ESEM FEG microscope. X-ray photoelectron spectroscopy (XPS) measurements were proceeded on the PHI Quantera SXM (ULVAC-PHI). N₂ adsorption test was conducted on an automatic volume adsorption device. Raman spectra was carried out by JY Labram HR 800.

Electrochemical measurements

All electrochemical tests were performed using a conventional three-electrode system (CHI 760D instrument (Shanghai, China)) with electrolytes at H₂SO₄ (0.5 M) and KOH (1.0 M), respectively. The 3 mm glass carbon electrode was chosen as the working electrode, the carbon rod as the opposing electrode, and Ag/AgCl as the reference electrode. Preparation of the ink: A certain amount of catalyst is uniformly dispersed in a mixture containing 200 μL ethanol, 200 μL water, and 40 μL Nafion (5 wt%). Then, the ultrasonic treatment is applied for 30 minutes to form a uniform ink. Finally, 5 μL ink is absorbed and covered on the surface of GCE and dried naturally at room temperature.

The hydrogen evolution performance of the catalyst was evaluated by linear sweep voltammetry (LSV) with a scanning rate of 5 mV s⁻¹. The overpotential was calculated using Nernst equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.059 * \text{pH}$. Cyclic voltammetry is tested between -0.1 V and 0.1 V with a scan rate of 100 mV s⁻¹. The Tafel plot is obtained by $\eta = a + \text{blog } |j|$ according to the LSV curve. Electrochemical impedance spectroscopy (EIS) was performed at a frequency of 0.1 to 100,000 Hz and an amplitude of 5 mV. The 24-hour stability was measured using chronoamperometry method and the *i*-*t* curve under the control of the excess potential.

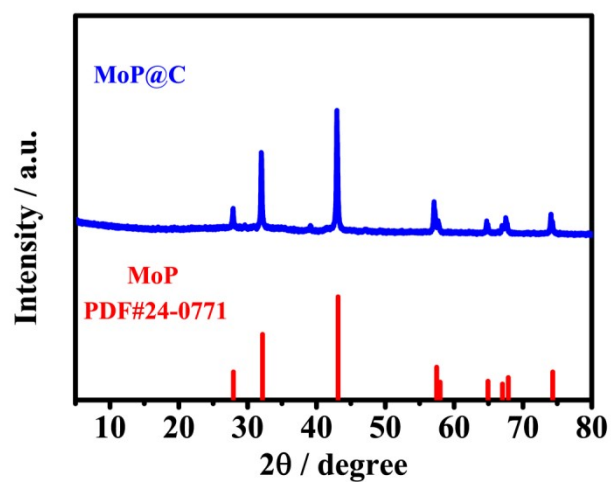


Figure S1. PXRD pattern of MoP@C.

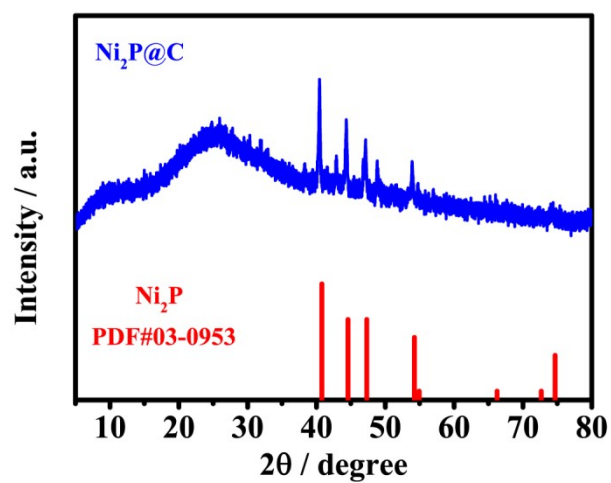


Figure S2. PXRD pattern of Ni₂P@C.

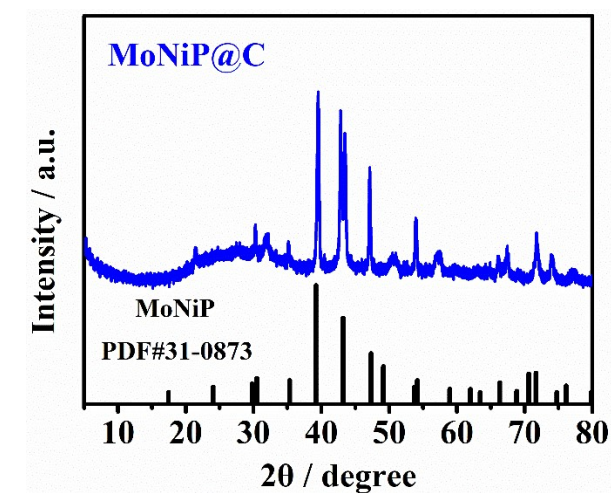


Figure S3. PXRD pattern of MoNiP@C.

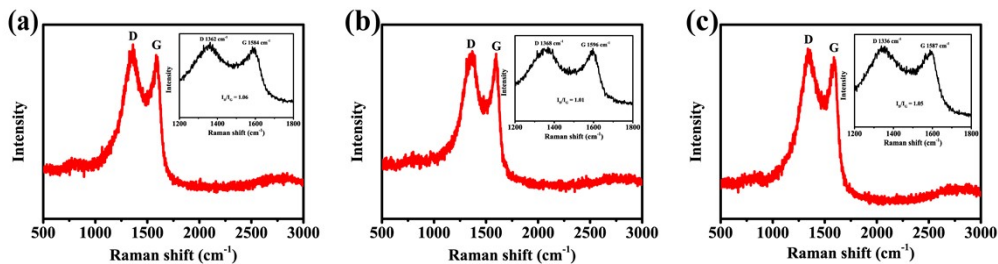


Figure S4. Raman spectrum of (a) MoP/MoNiP@C, (b) MoP@C and (c) Ni₂P@C.

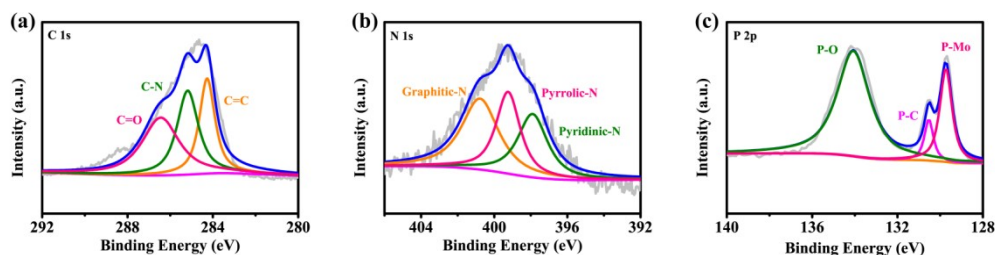


Figure S5. XPS spectra of (a) C 1s, (b) N 1s and (c) P 2p of MoP/MoNiP@C.

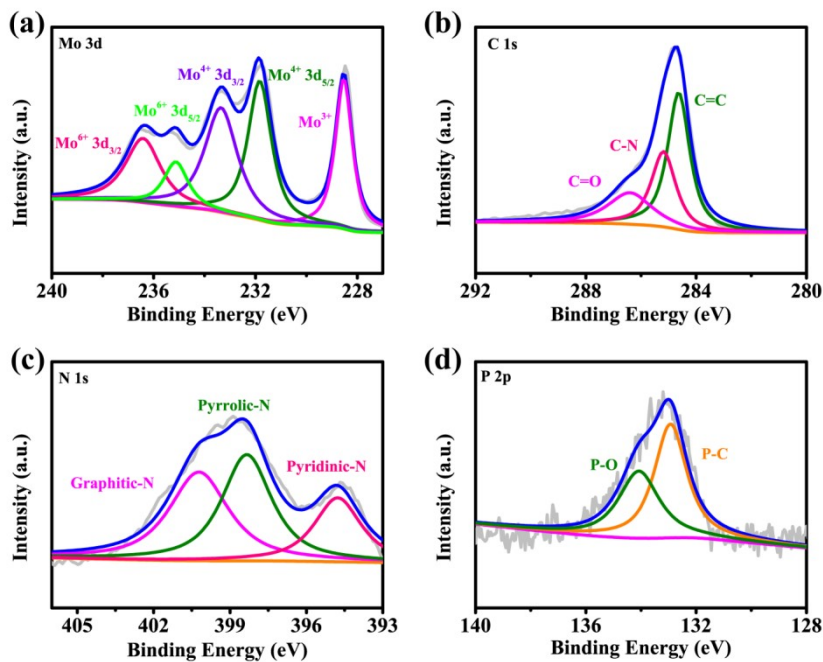


Figure S6. XPS spectra of (a) Mo 3d, (b) C 1s, (c) N 1s and (d) P 2p of MoP@C.

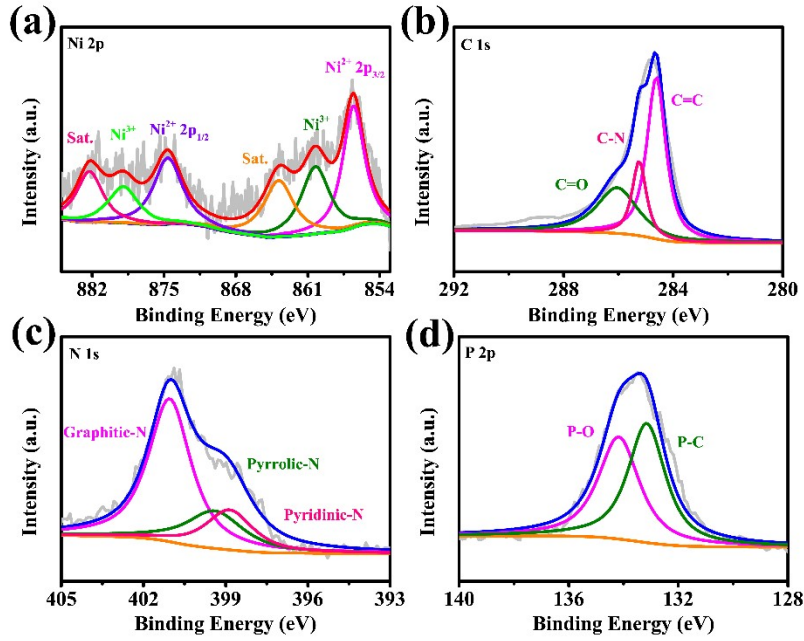


Figure S7. XPS spectra of (a) Ni 2p, (b) C 1s, (c) N 1s and (d) P 2p of Ni₂P@C.

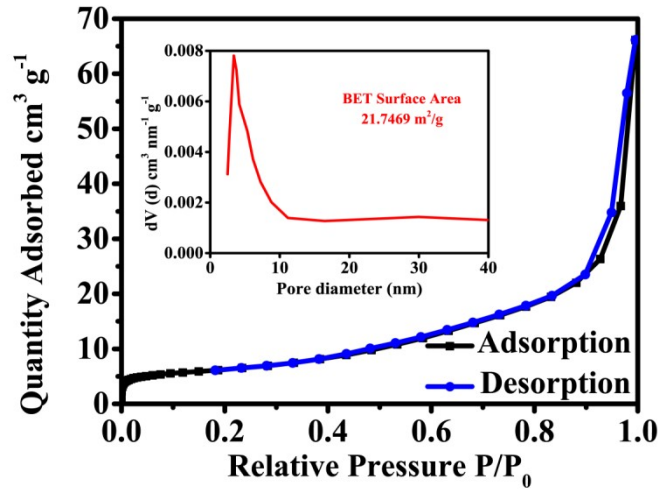


Figure S8. N₂ adsorption-desorption isotherms of MoP/MoNiP@C (Inset: pore diameter distribution diagram).

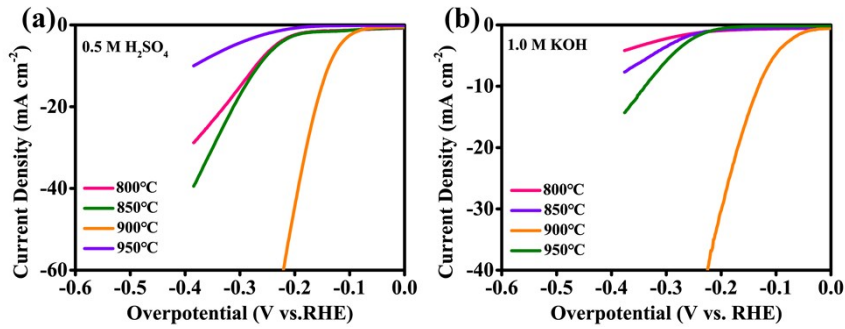


Figure S9. HER polarization curves for catalyst with different calcination temperatures (800, 850, 900 and 950°C) in (a) 0.5 M H₂SO₄ and (b) 1.0 M KOH.

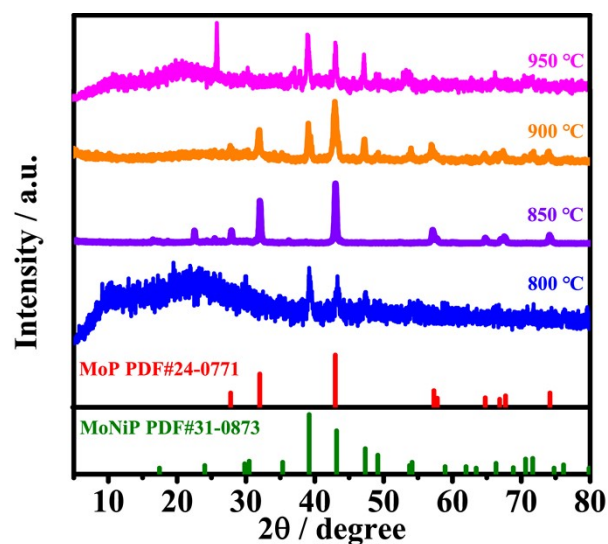


Figure S10. PXRD pattern of MoP/MoNiP@C with different temperatures (800, 850, 900 and 950 °C).

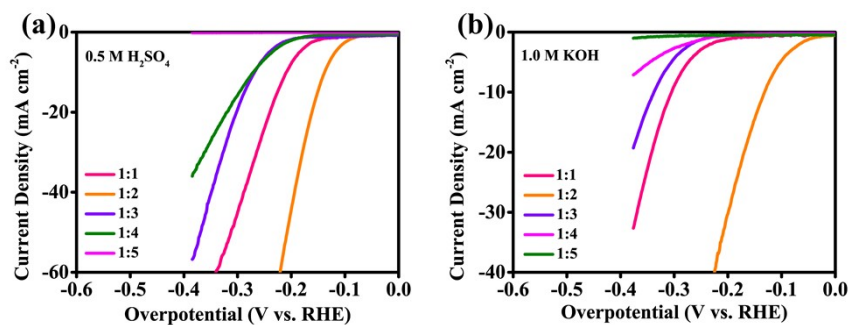


Figure S11. HER polarization curves for catalyst with different content of PMo_{12} in (a) 0.5 M H_2SO_4 and (b) 1.0 M KOH. (Note: Calcination temperature: 900 °C, $M_{\text{PMo}_{12}}:M_{\text{Ni}^{2+}}=1:1$).

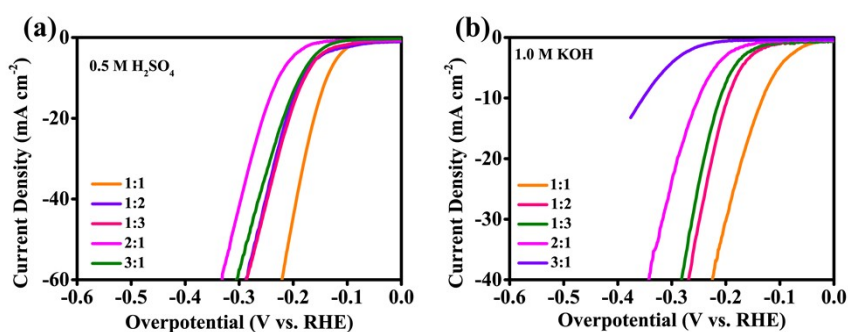


Figure S12. HER polarization curves for catalyst with different ratio of nickel ions (a) 0.5 M H_2SO_4 and (b) 1.0 M KOH. (Note: Calcination temperature: 900 °C, $M_{\text{metal}}:M_{\text{PPy}}=1:2$).

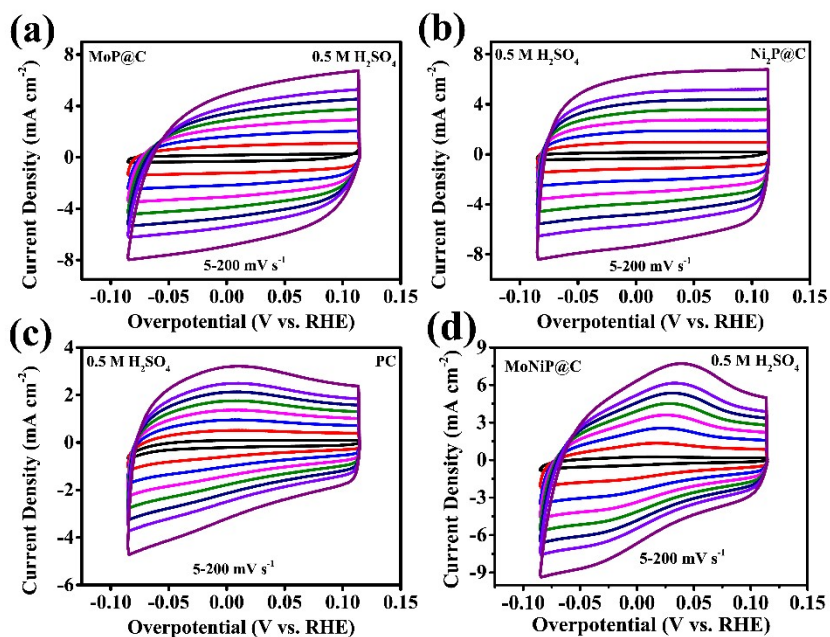


Figure S13. CVs of (a) MoP@C, (b) Ni₂P@C, (c) PC and (d) MoNiP@C with the scan rate ranging from 5 to 200 mV s⁻¹ in 0.5 M H₂SO₄.

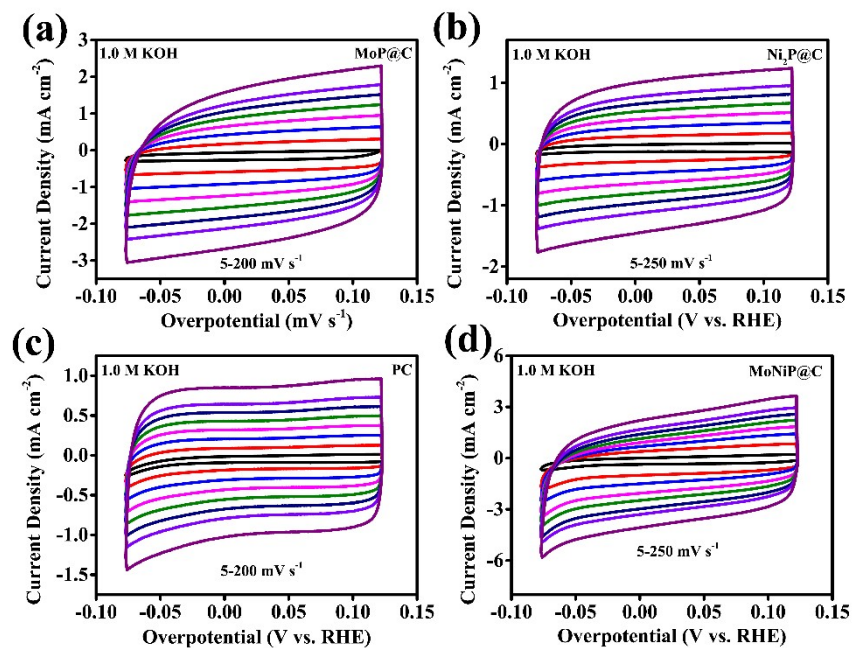


Figure S14. CVs of (a) MoP@C, (b) Ni₂P@C, (c) PC and (d) MoNiP@C with the scan rate ranging from 5 to 200 mV s⁻¹ in 1.0 M KOH.

Table S1. Comparison of HER performance of MoP/MoNiP@C with other PPy-based HER catalysts.

Catalysts	Electrolyte	η_{10} (mV)	Tafel Slope (mV dec ⁻¹)	Stability	Ref.
MoP/MoNiP@C	0.5 M H₂SO₄	138	61	2000 cycles/	This
	1.0 M KOH	135	88	24 h	work
MoP/MoNiP@NC	1.0 M KOH	144	85	2000 cycles	[2]
	0.5 M H ₂ SO ₄	125	115	/24 h	
Mo ₂ C/MoP/MoNiP@C	0.5 M H ₂ SO ₄	154	113	1000 cycles /14 h	[3]
MoP/MoNiP@C	0.5 M H ₂ SO ₄	134	66	2000 cycles /24 h	[4]
MoNiP	0.5 M H ₂ SO ₄	179	60	1000cycles	[5]
MoP-NC	1.0 M KOH	131	66	1000 cycles	[6]
MoP/NPCs	0.5 M H ₂ SO ₄	205	71	19 h at 0.18V	[7]
	0.5 M H ₂ SO ₄	141	59	1000 cycles	
MoP@NPC-H	1.0 M KOH	176	61	1000 cycles	[8]
	0.2 M PBS	198	94	1000 cycles	

Reference

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