

Supporting Information

Mo-doped FeP nanoparticles encapsulated in N, P doped carbon matrix with optimized d-band center for highly efficient and stable hydrogen evolution reaction

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2. Materials and Methods

2.1. Sample preparation

2.1.1 Synthesis of Mo-FeP nanoparticles encapsulated in N, P doped carbon matrix

FeOOH particles are synthesized by the hydrolysis process of FeCl₃ as reported in the previous research ¹. To be specific, 2 mmol FeCl₃ was melted in 30 mL DI water, after stirring for 30 mins, the prepared solution was transferred to the 100 mL autoclave and heated under 150 °C for 3 h. After cooled to the room temperature, 3 mmol Na₂MoO₄ was dissolved in the prepared solution and after stirring for 60 min, 10 mmol 2-methylimidazole dissolved in the solution followed with 30 min stirring. After centrifugation the prepared precursor was washed by DI water and ethanol for several times, then was put in the vacuum oven under 60 °C for 24 h. The obtained powder was annealed in the tube furnace with NaH₂PO₂ placed in the upstream of the crucible under 400 °C, 450 °C, and 500 °C for 2 h in an Ar atmosphere, separately.

2.1.2 Synthesis of FeP nanoparticles encapsulated in N, P doped carbon matrix

FeOOH particles are synthesized by the hydrolysis process of FeCl₃ as reported in the previous research ¹. To be specific, 2 mmol FeCl₃ was melted in 30 mL DI water, after stirring for 30 mins, the prepared solution was transferred to the 100 mL autoclave and heated under 150 °C for 3 h. After cooled to the room temperature, 10 mmol 2-methylimidazole dissolved in the solution followed with 30 min stirring. After centrifugation the prepared precursor was washed by DI water and ethanol for several times, then was put in the vacuum oven under 60 °C for 24 h. The obtained powder

was annealed in the tube furnace with NaH_2PO_2 placed in the upstream of the crucible under $450\text{ }^\circ\text{C}$ for 2 h in an Ar atmosphere.

2.1.3 Synthesis of Mo-Fe₂O₃ nanoparticles encapsulated in N doped carbon matrix

FeOOH particles are synthesized by the hydrolysis process of FeCl_3 as reported in the previous research 1. To be specific, 2 mmol FeCl_3 was melted in 30 mL DI water, after stirring for 30 mins, the prepared solution was transferred to the 100 mL autoclave and heated under $150\text{ }^\circ\text{C}$ for 3 h. After cooled to the room temperature, 3 mmol Na_2MoO was dissolved in the prepared solution and after stirring for 60 min, 10 mmol 2-methylimidazole dissolved in the solution followed with 30 min stirring. After centrifugation the prepared precursor was washed by DI water and ethanol for several times, then was put in the vacancy oven under $60\text{ }^\circ\text{C}$ for 24 h. The obtained powder was annealed in the tube furnace under $450\text{ }^\circ\text{C}$ for 2 h in an Ar atmosphere, separately.

2.1.4 Synthesis of Mo-FeP nanoparticles

Mo-FeP without the protection of N, P doped carbon matrix was prepared by putting 2 mmol FeCl_3 and 2 mmol NaOH in 30 mL DI water and stirring for 15 min. The prepared solution was transferred to an autoclave and heated in the oven under $150\text{ }^\circ\text{C}$ for 3 h. After cooling down to room temperature, 3 mmol Na_2MoO_4 was added and stirred for 60 mins. The prepared precursor was centrifuged and washed three times by DI water and ethanol, separately. Then it was dried in the vacuum oven under $60\text{ }^\circ\text{C}$ for 24 h. The obtained powder was annealed in the tube furnace with NaH_2PO_2 placed upstream of the crucible under $450\text{ }^\circ\text{C}$ for 2 h in an Ar atmosphere.

2.2. Material Characterization

Powder X-ray diffraction (XRD, Smartlab, 9 kw) spectrum was collected with Cu K α radiation to analyze the crystal structure of the catalyst with a scanning rate of 2°/min between 2 θ ranging 20°-80°. The microstructure of the catalysts was characterized through SEM (FEI XL30 S-FEG) under a voltage of 20 kV and TEM (FEI Tecnai G2 F20) operating at a voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was applied to observe the chemical valence states of different catalyst elements.

2.3. Electrochemical measurements

The electrochemical properties of the catalyst were analyzed using a three-electrode system with a CHI 650E electrochemical workstation. Mo-FeP@NPC-400, Mo-FeP@NPC, Mo-FeP@NPC-500, FeP@NPC, Fe₂O₃-MoC@NPC and Pt sheet were tested in both 0.5 M H₂SO₄ and 1.0 M KOH electrocatalyst. The working electrode was prepared by adding 5 mg prepared catalyst and 1.5 mg carbon black in 250 μ L DI water, 250 μ L ethanol, and 50 μ L of Nafion 117 solution (5 wt.%). The prepared slurry was ultrasonic treated for 10 min in iced water and then prepared as the working electrode. The Pt sheet was applied as the counter reference, and saturated calomel electrode (SCE) was prepared as the reference electrode.

Potentials tested were iR-compensated from the equation: $E_{\text{RHE}} = E_{\text{SCE}} + 0.059 \text{ pH} + 0.245 \text{ V}$. Linear sweep voltammetry (LSV) was tested with the rate of 5 mV s⁻¹. The Electrochemical impedance spectroscopy (EIS) was measured at 63 mV (H₂SO₄) and 116 mV (KOH) with a frequency range of 100 KHz to 10 MHz. The electrochemical

active surface area was tested through the electrochemical double layer capacitance (Cdl) spectrum through the scan rate from 20 mV s⁻¹ to 100 mV s⁻¹. The stability of the catalyst was analyzed through the chronopotentiometry spectrum under the overpotential of 86 mV and 134 mV in acid and alkaline electrolytes, separately.

2.4. Theoretical calculations

Perdew-Burke-Ernzerhof (PBE) exchange-correlation function was applied in Density function theory calculation by the module of CASTEP in Materials Studio. The cutoff energy was set up as 381 eV for the valence electrons cell, and the parameters were optimized until the force on each atom was less than 0.05 eV Å⁻¹. FeP space group 33 was used in the calculation, with lattice constants of $a = 5.191 \text{ \AA}$, $b = 3.108 \text{ \AA}$, and $c = 5.794 \text{ \AA}$.

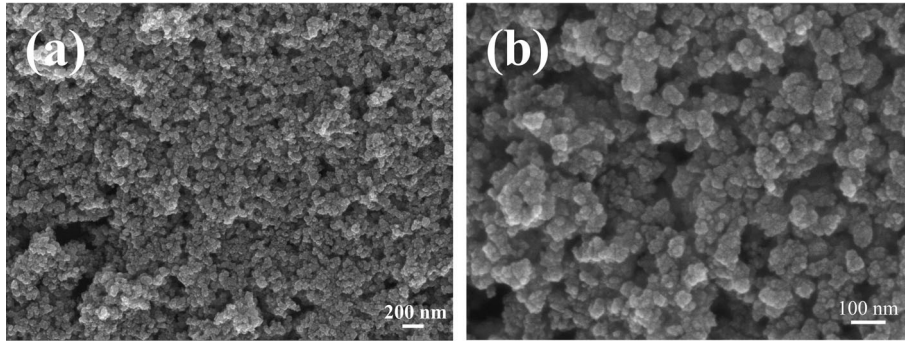


Figure S1 SEM images of Mo-FeP@NPC-400.

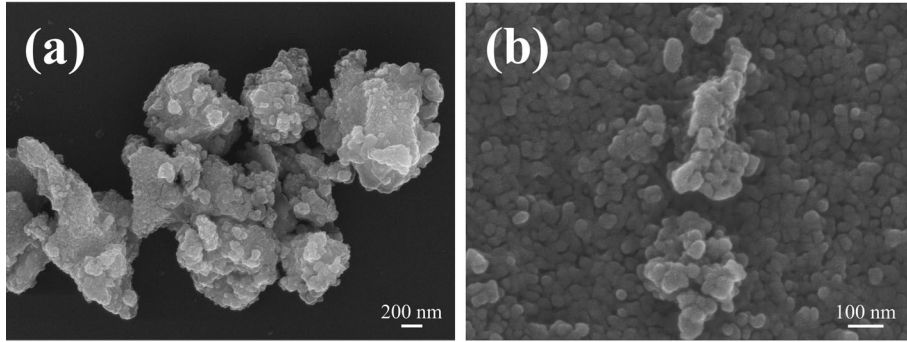


Figure S2 SEM images of Mo-FeP@NPC-450.

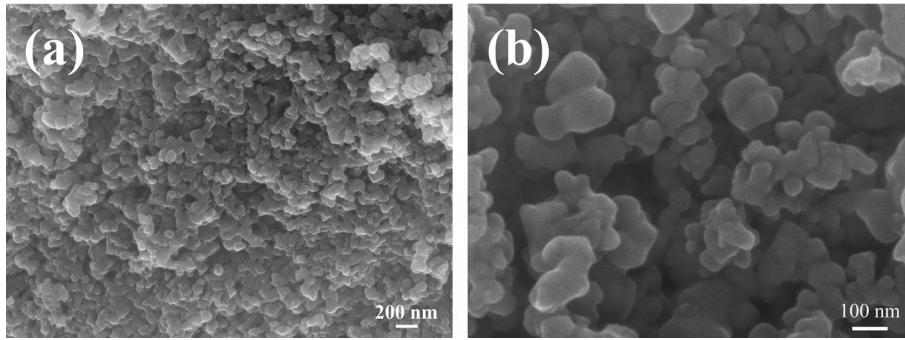


Figure S3 SEM images of Mo-FeP@NPC-500.

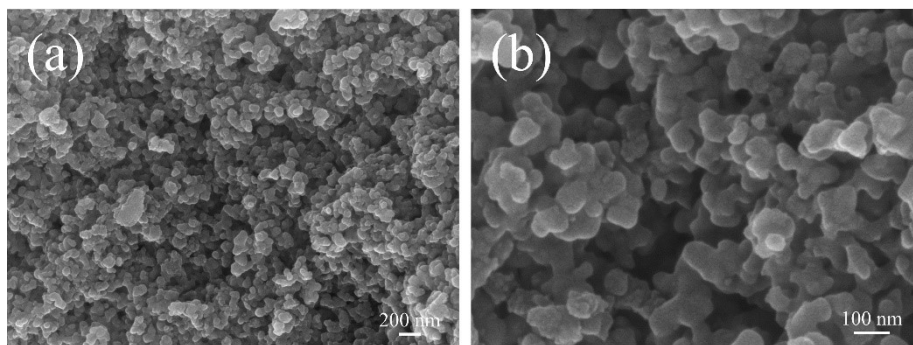


Figure S4 SEM images of FeP@NPC-450.

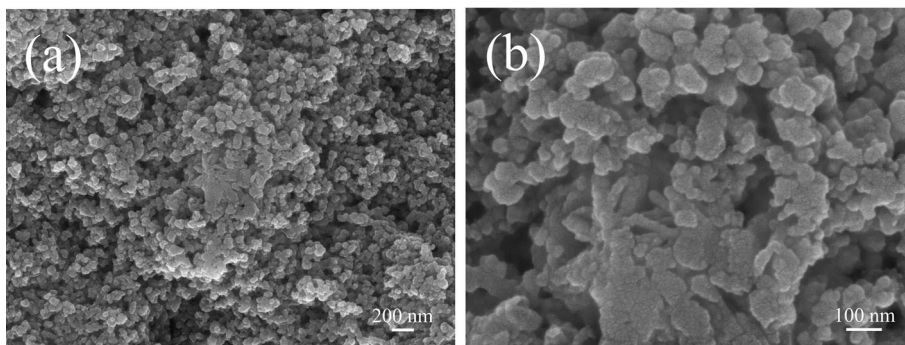


Figure S5 SEM images of Mo-Fe₂O₃@NC-450

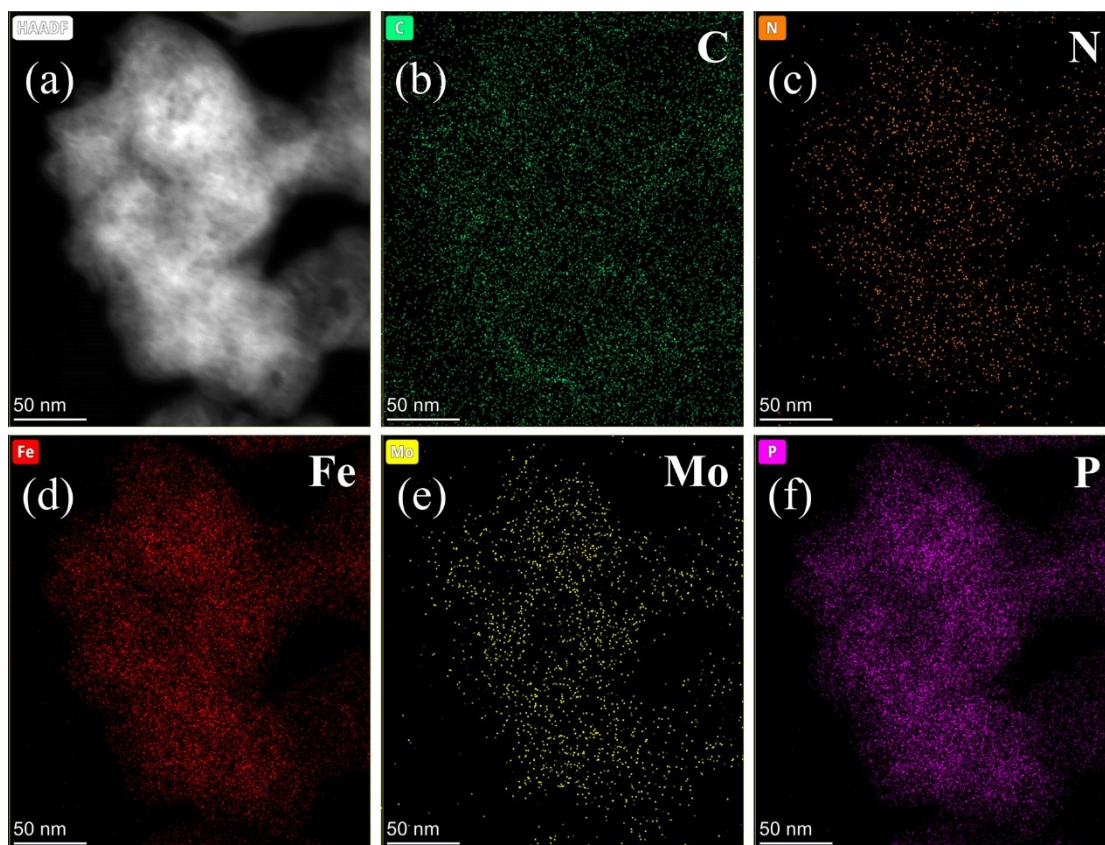


Figure S6 EDS elemental mapping images of Mo-FeP@NPC

Table S1. Comparison of the catalytic performances involving FeP.

Catalyst	Overpotential @10 mA cm ⁻² [mV]	Tafel slope [mV dec ⁻¹]	Stabilization	Electrolyte	Ref
Co-Doped FeP	126	63.6	60 min	0.5 M H ₂ SO ₄	²
Ni-doped FeP/carbon hollow nanorods	72	54	12 h	0.5 M H ₂ SO ₄	³
Sm-Doped FeP	71	85.9	40 h	1.0 M KOH	⁴
V-Doped FeP	149	40.97	24 h	1.0 M KOH	⁵
MoO ₂ -FeP	103	61.92	24 h	1.0 M KOH	⁶
Ni-FeP/TiN/CC	75	96	10 h	1.0 M KOH	⁷
N-FeP	226	84.8	/	1.0 M KOH	⁸
3F-FeP	191	56.12	100 h	1.0 M KOH	⁹
Mo-FeP@NPC	63/116	57.9/63.8	40 h	0.5 M H ₂ SO ₄ /1.0M KOH	This work

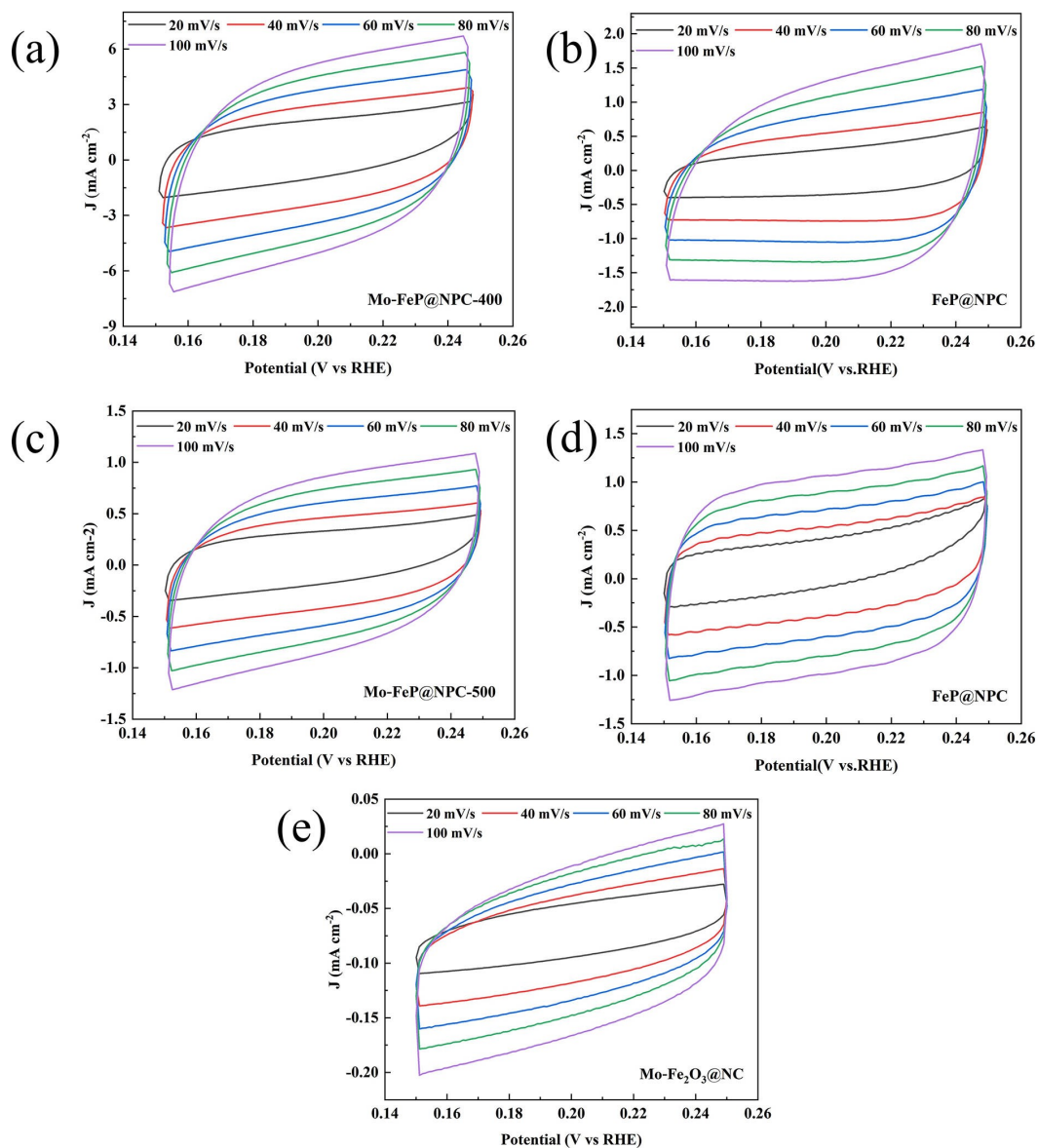


Figure S7 Cyclic voltammograms (CV) in the region of 0.15-0.25 V vs. RHE for (a) Mo-FeP@NPC-400; (b) Mo-FeP@NPC; (c) Mo-FeP@NPC-500; (d) FeP@NPC and (e) Mo-Fe₂O₃@NC in 0.5 M H₂SO₄.

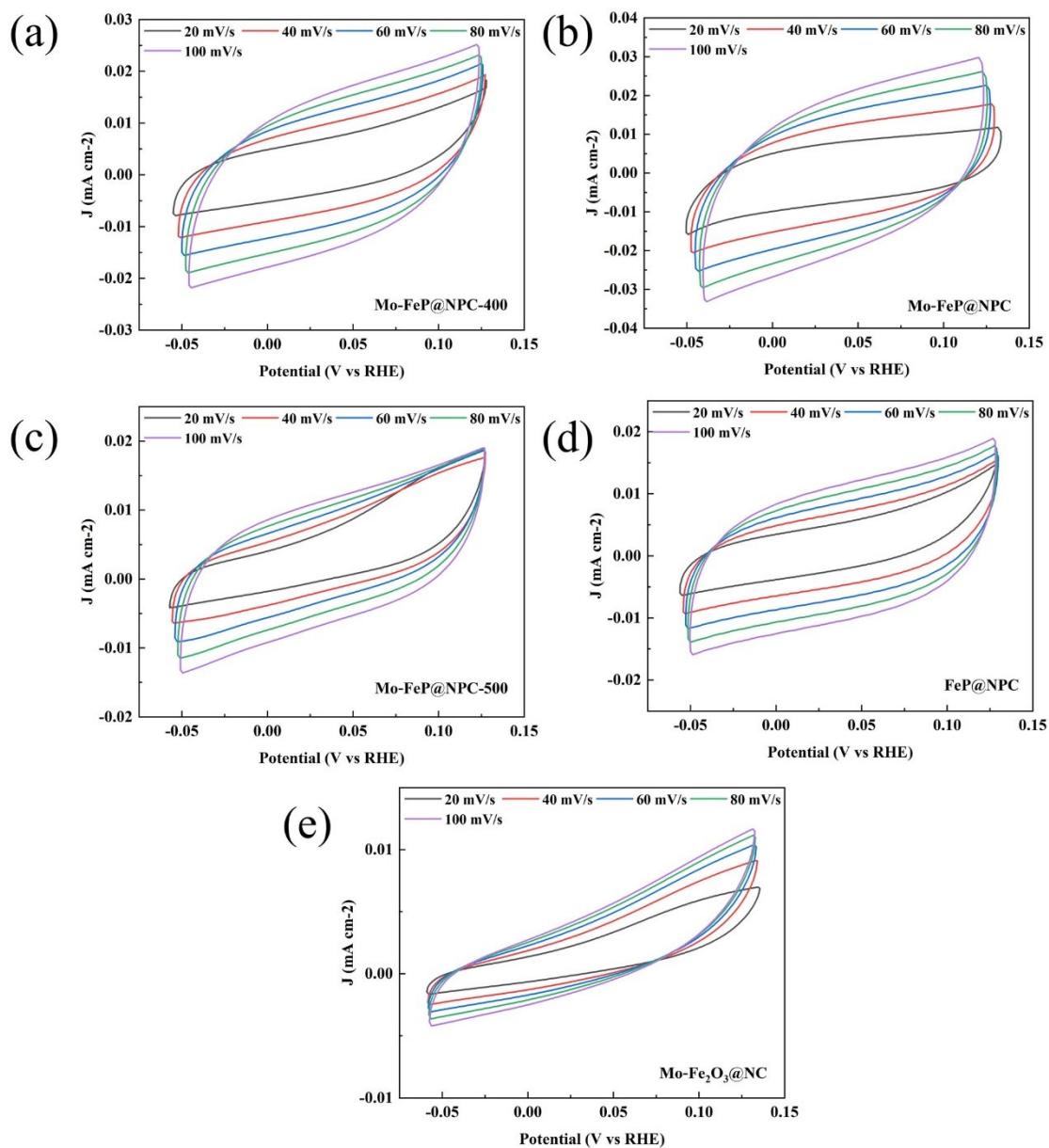


Figure S8 Cyclic voltammograms (CV) in the region of 0.15-0.25 V vs. RHE for (a) Mo-FeP@NPC-400; (b) Mo-FeP@NPC; (c) Mo-FeP@NPC-500; (d) FeP@NPC and (e) Mo-Fe₂O₃@NC in 1.0 M KOH.

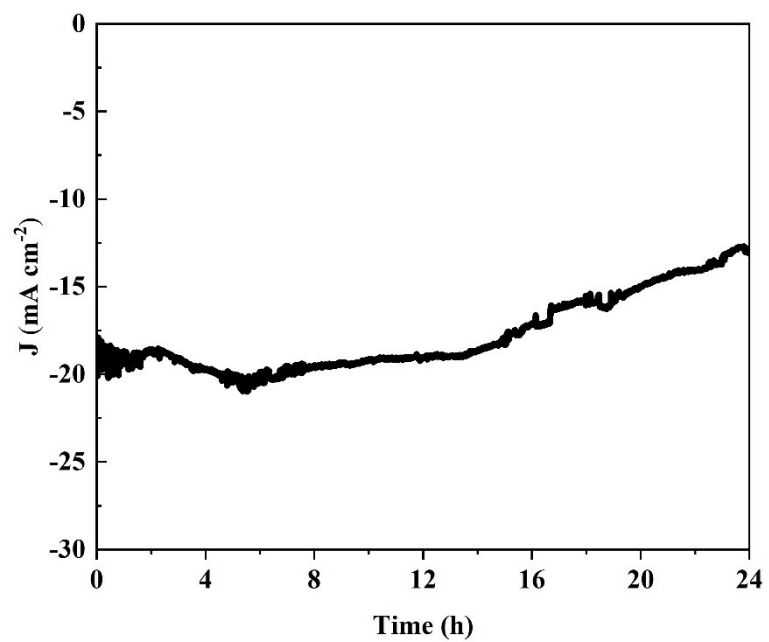


Figure S9 Chronoamperometry of Mo-FeP@NPC under 86 mV for 24 h in 0.5 M H_2SO_4 .

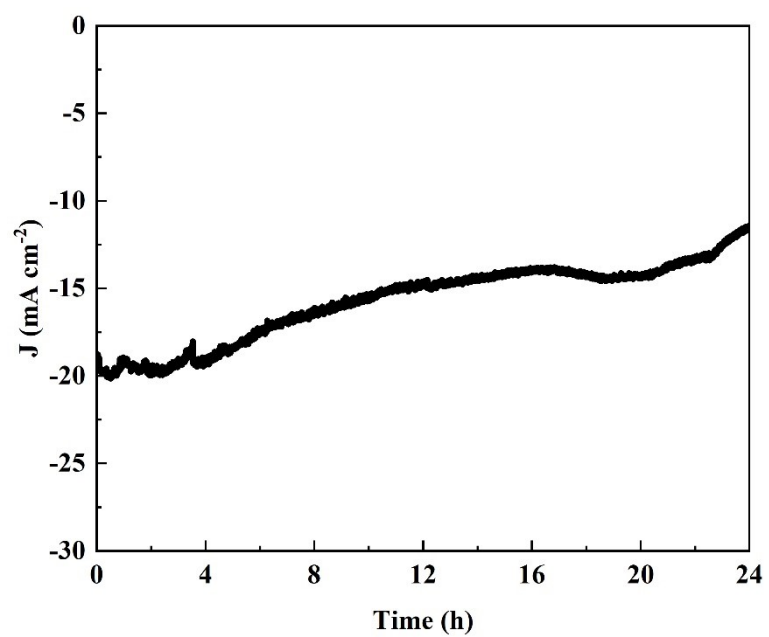


Figure S10 Chronoamperometry of Mo-FeP@NPC under 134 mV for 24 h in 1.0 M KOH.

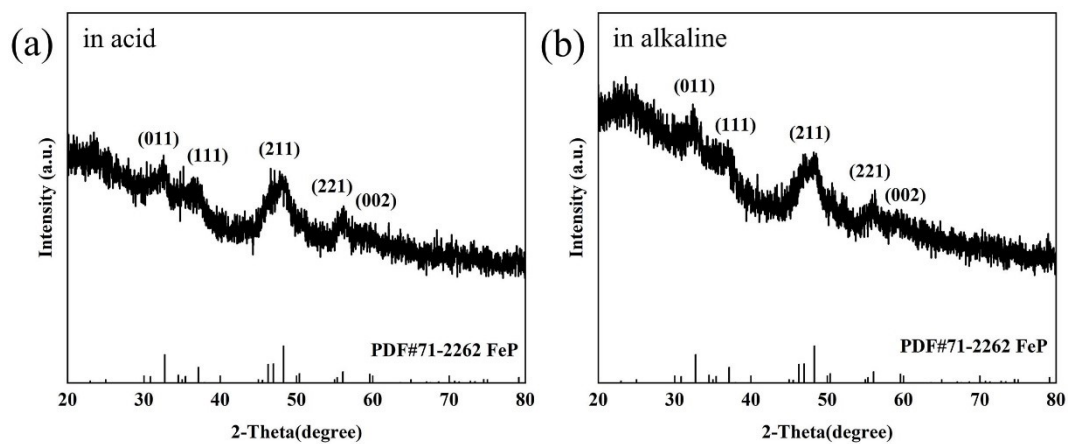


Figure. S11. XRD images of Mo-FeP@NPC after 40 h chronoamperometry test in (a) 0.5 M H₂SO₄ and (b) 1.0 M KOH.

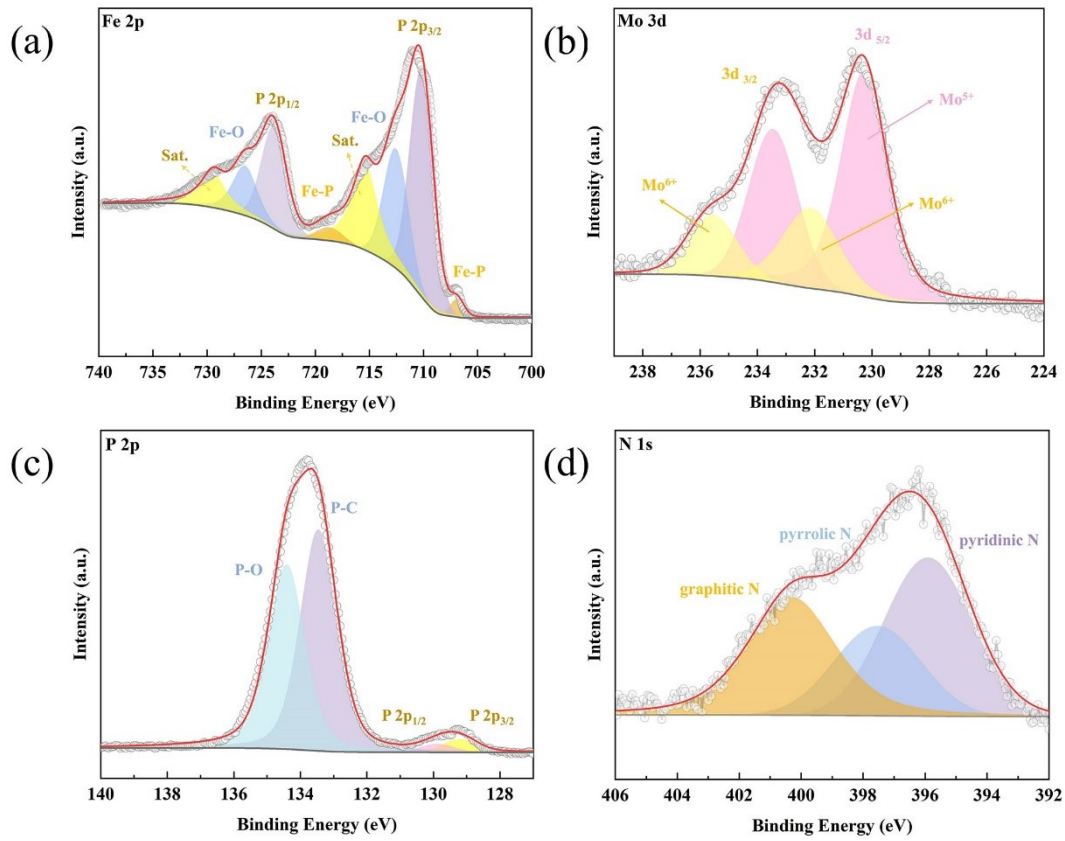


Figure. S12. XPS images of Mo-FeP@NPC after 40 h chronoamperometry test in 0.5 M H₂SO₄.

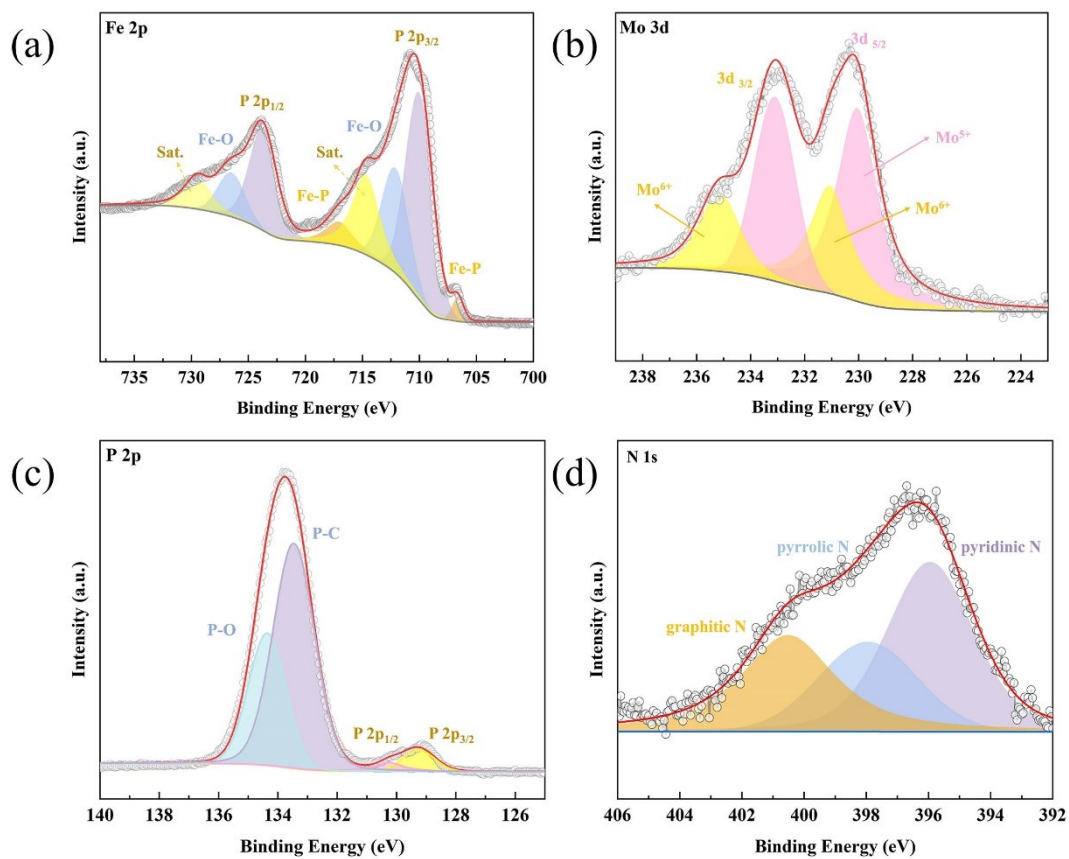


Figure. S13. XPS images of Mo-FeP@NPC after 40 h chronoamperometry test in 1.0 M KOH.

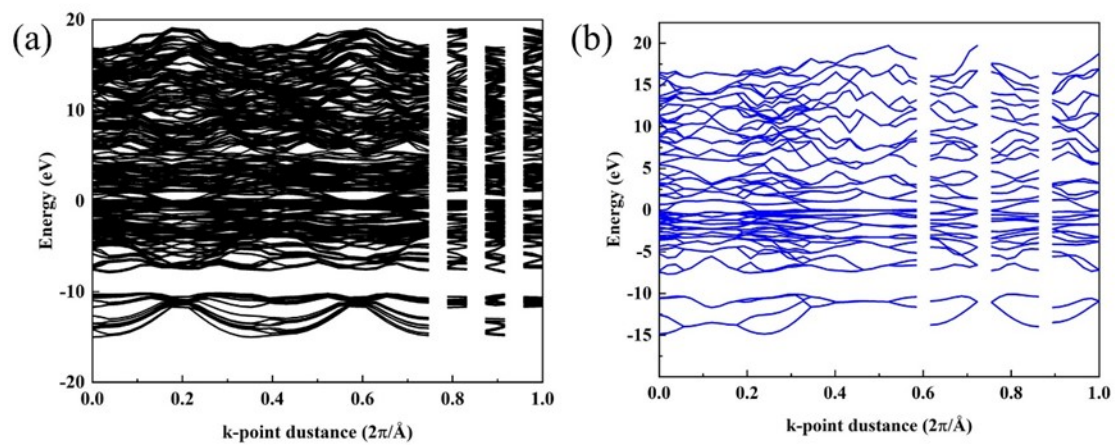


Figure S14 Calculated electronic band structure for configurations of (a) Mo-FeP and (b) FeP.

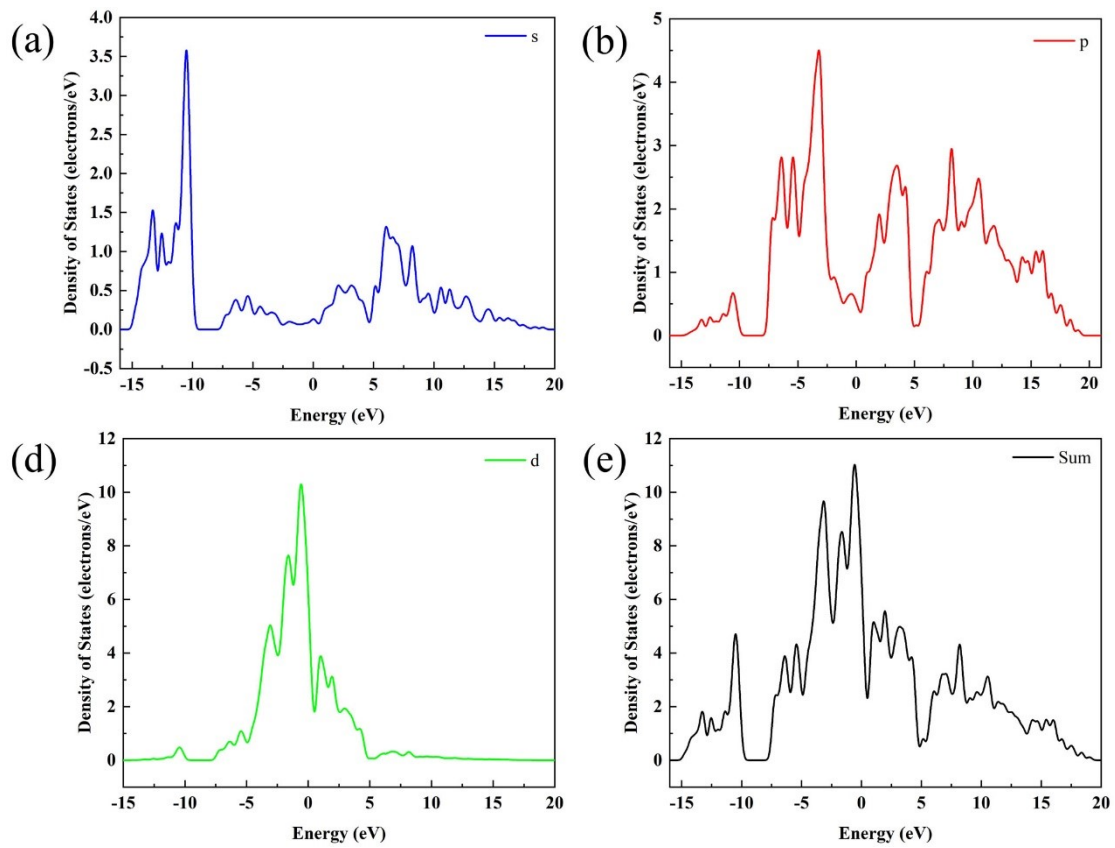


Figure S15 Partial electronic density of state (PDOS) calculated of Mo-FeP for (a) s, (b) p, (c) d, (c) sum.

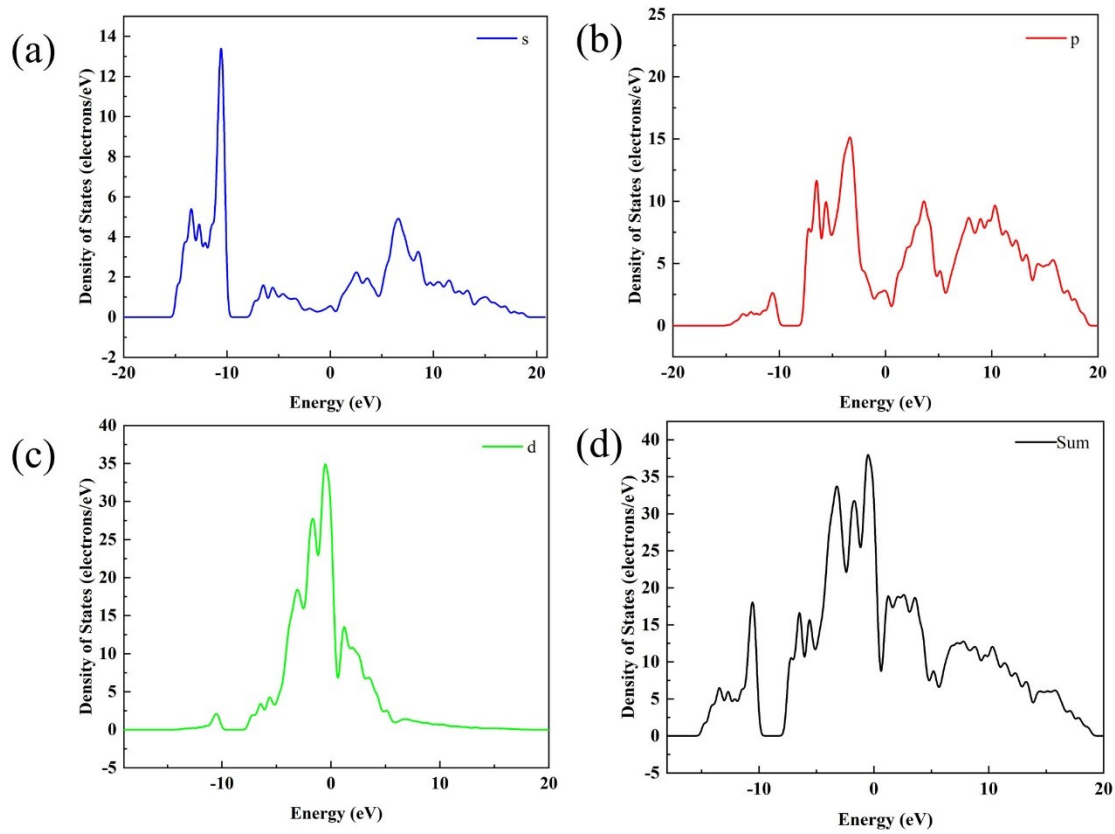


Figure S16 Partial electronic density of state (PDOS) calculated of FeP for (a) s, (b) p, (c) d, (c) sum.

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