Electronic Supplementary Information

MoP nanocrystals encapsulated in N-doped three-dimensional carbon networks for efficient hydrogen evolution electrocatalysis

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Characterization

The as-fabricated hybrids were characterized by a Bruker D8 Discover X-ray diffractometer, Cu Kα radiation (λ = 1.5418 Å), scanning electron microscopy (SEM: FEI, Nova 154 NanoSEM 450) and transmission electron microscopy (TEM: Talos-155 f200s)). The specific surface area and pore-size distribution were tested by nitrogen adsorption-desorption measurement (TriStar II 3020 analyzer) at 77 K. The X-ray photoelectron spectra (XPS) were conducted on an AXIS-ULTRA DLD-600W instrument (Shimadzu- Kratos Co. Ltd.). Raman shifts were recorded on a VERTEX 70 spectrometry instrument (Bruker). ICP-AES (Perkin-Elmer Optima 4300DV) and elemental analysis (Vario EL Cube CHNSO Elemental Analyzer) were used to determine the composition and elemental ratio for the obtained materials.

Electrochemical Measurements

The electrochemical properties of all samples were measured by using a CHI 760E electrochemical workstation (Chenhua, Shanghai) in a typical three-electrode system at room temperature. The GCE modified with different samples, a saturated calomel electrode (SCE, in 0.5 M H_2SO_4) and a graphite rod were used as the working electrode, reference electrode, and auxiliary electrode, respectively.

To prepare the working electrode, 5 mg of the catalyst was dispersed in a solution of 980 μL of ethanol mixed with 20 μL of 5 wt % Nafion solution and then sonicated for 1h to form the homogeneous dispersion. Then, 6 μL of the catalyst ink was dropwise casted on the surface of the glass carbon electrode (GCE, 3 mm) with a mass loading of 0.38 mg cm^{-1}.

Cyclic voltammetry (CV), linear sweep voltammetry (LSV), and amperometric i−t curve were carried out to investigate the electrochemical performances of the working electrode. All the measured potentials were iR-corrected and calibrated to RHE ($E_{(RHE)} = E_{(SCE)} + 0.241\ V + 0.059\ pH$). Electrochemical impedance spectroscopy (EIS) for HER was carried out in the frequency range of 100 kHz-0.1 Hz with an AC amplitude of 10 mV using an Autolab Potentiostat Galvanostat (PGSTAT302N). In addition, cyclic voltammetry (CV) was conducted at a non-Faradaic region (0.10-0.25 V vs. RHE) to evaluate the electrochemical double-layer capacitance (Cdl) for the as-synhesized electrocatalysts.

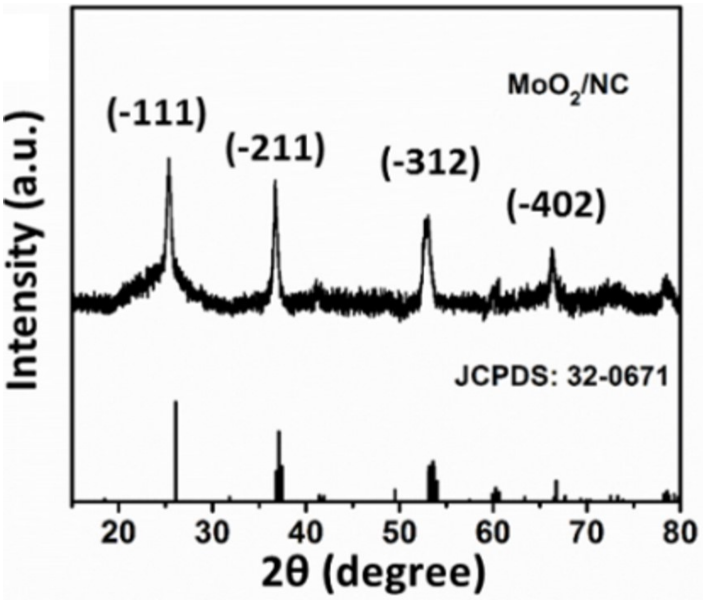

Figure S1. XRD pattern of the MoO_2/NC.

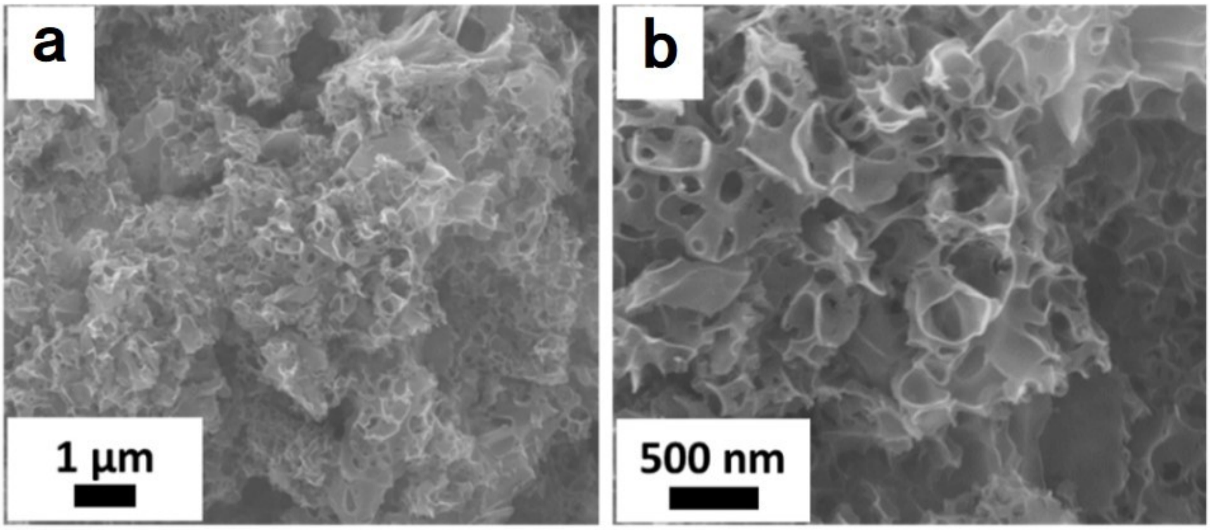

Figure S2. SEM images of the MoO_2/NC.

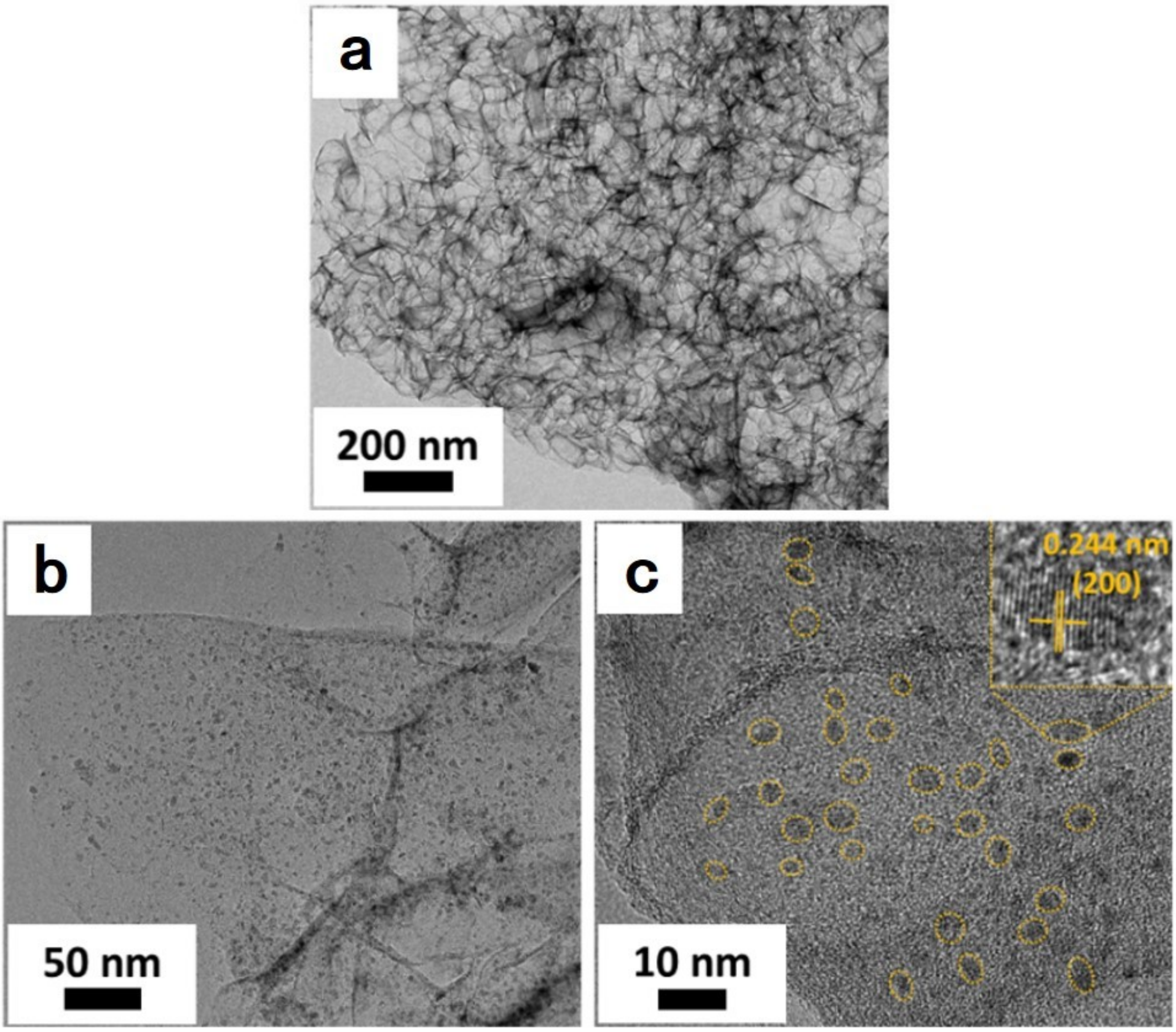

Figure S3. TEM images of the MoO_2/NC.

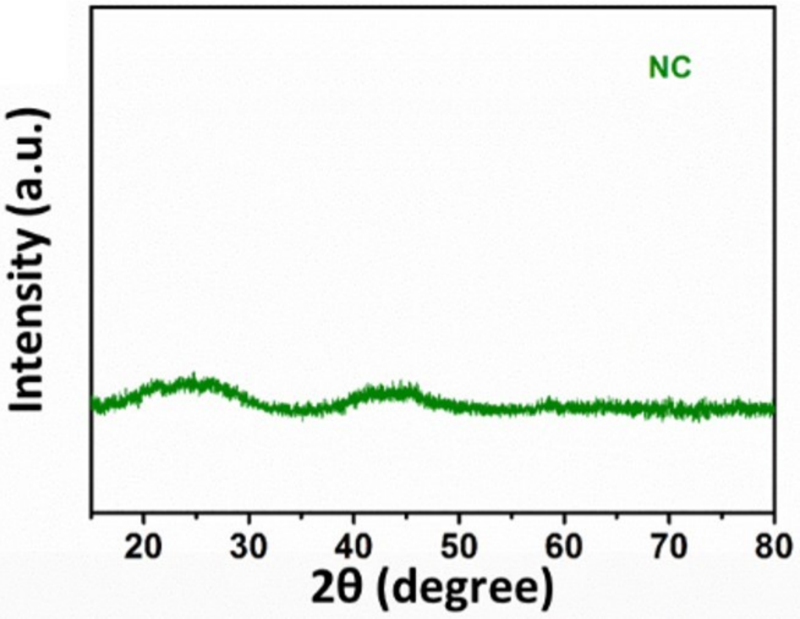

Figure S4. XRD pattern of the NC.

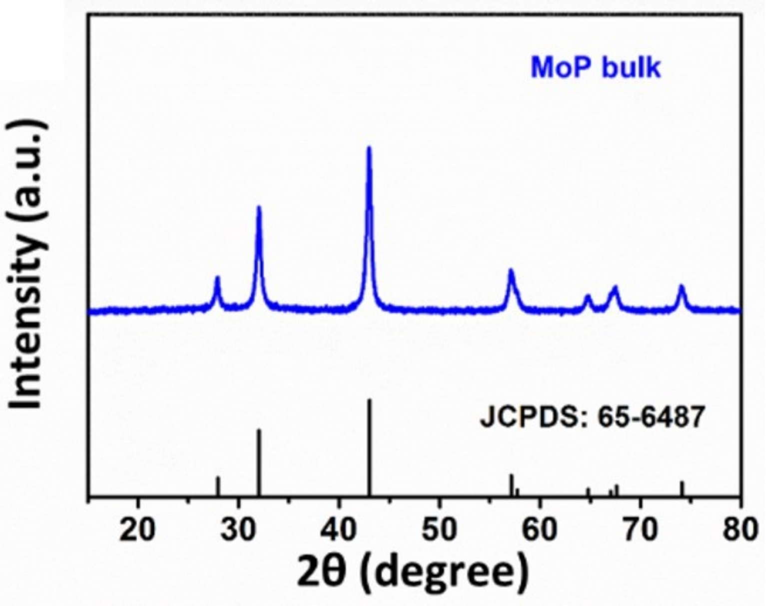

Figure S5. XRD pattern of the MoP bulk.

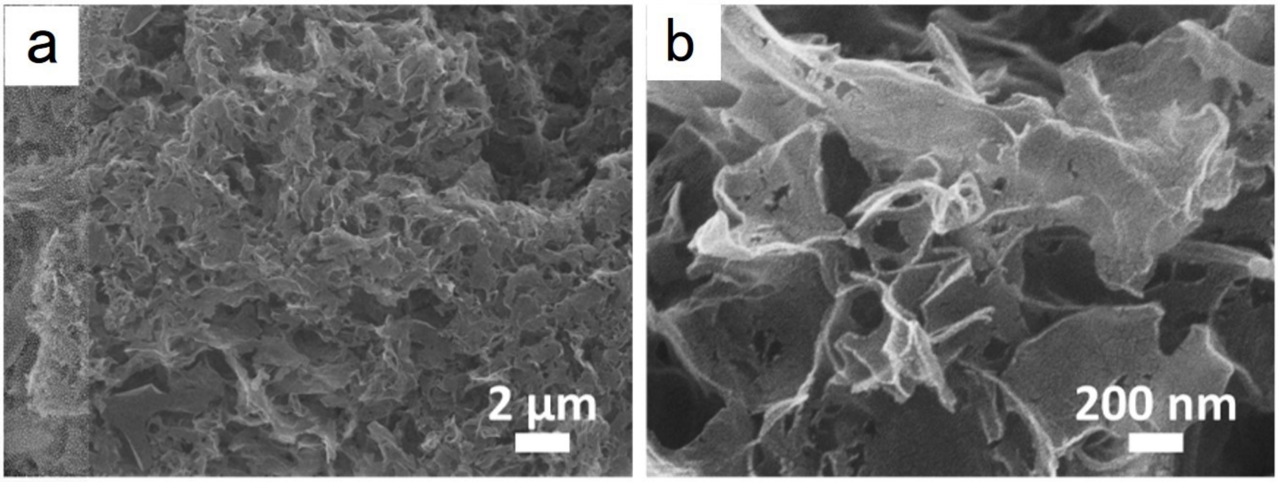

Figure S6. SEM images of the NC.

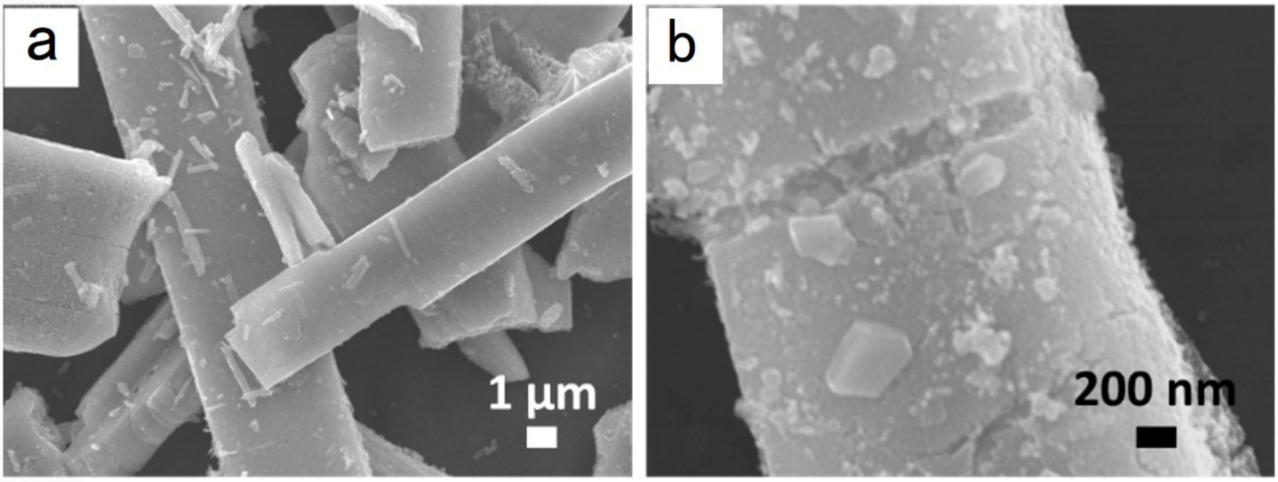

Figure S7. SEM images of the MoP bulk.

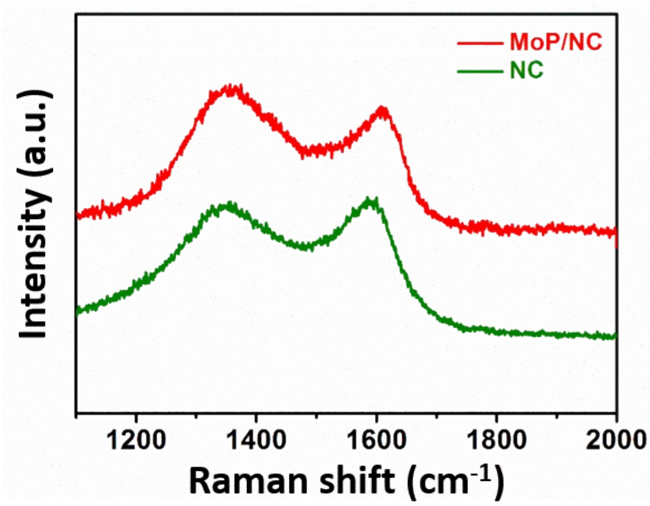

Figure S8. Raman spectra of the MoP/NC and NC.

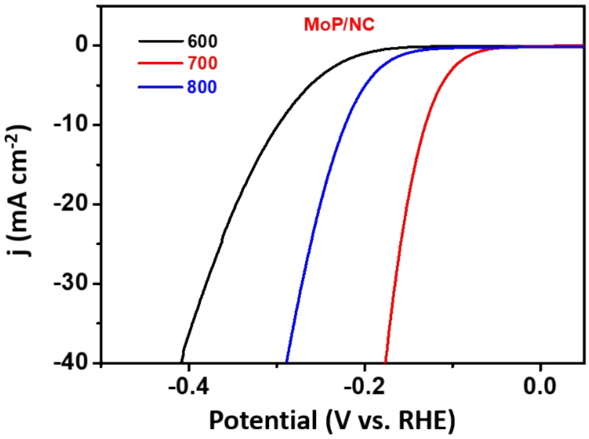

Figure S9. LSVs of the MoP/NC obtained at different phosphorization temperatures in 0.5 M H_2SO_4.

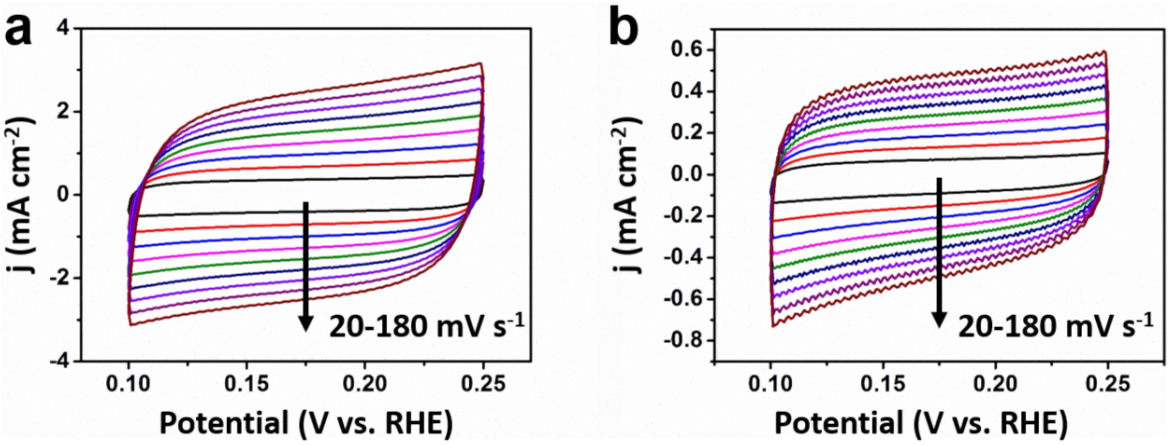

Figure S10. CVs of the MoP/NC and MoP bulk with different scanning rates from 20 to 180 mV s^{-1} at a potential range of 0.1-0.25 V in 0.5 M H_2SO_4.

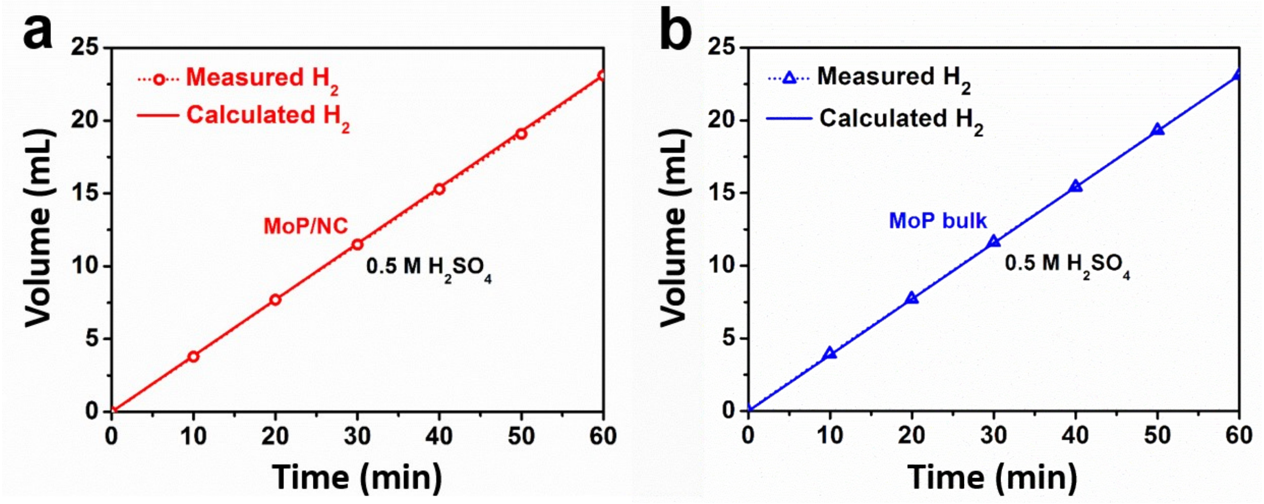

Figure S11. The theoretically calculated and experimentally measured amount of H_2 during the electrochemical test with the drainage gas-collecting method in 0.5 M H_2SO_4 for the (a) MoP/NC and (b) MoP bulk.

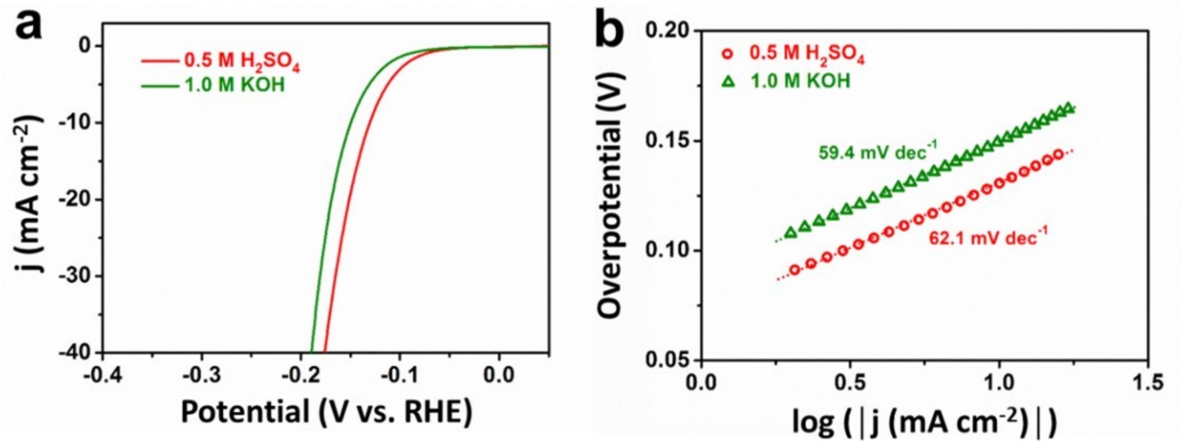

Figure S12. (a) LSVs and (b) Tafel plots of the MoP/NC in 0.5 M H_2SO_4 and 1 M KOH.

Table S1. Elemental analysis result of MoP/NC.

Sample mass (mg)	N (wt. %)	C (wt. %)	H (wt. %)	S (wt. %)
1.975	1.16	31.31	0.00	0.00

Table S2. Mass fraction and atomic ratio of Mo and P in MoP/NC obtained by ICP-AES.

Sample	Mo (wt. %)	P (wt. %)	Ratio of Mo to P
MoP/NC	43.19	14.03	0.99

Table 3. Comparison of the HER activity between MoP/NC and other reported MoP-based carbonaceous hybrid under acidic and alkaline condition.

Catalyst	Media	η_{10} (mV)	Tafel slope (mV dec^{-1})	Reference
MoP/NC	**0.5 M H_2SO_4**	**130**	**62.1**	**this work**
MoP-QDs@PC	0.5 M H_2SO_4	118.8	59	[S1]
MoP@NPC/CNT	0.5 M H_2SO_4	155	76	[S2]
MoP NPs@NC	0.5 M H_2SO_4	115	65	[S3]
MoP/rGO	0.5 M H_2SO_4	117	62	[S4]
MoP/MWCNTs	0.5 M H_2SO_4	109	56.5	[S5]
MoP@NPCS	0.5 M H_2SO_4	113	58	[S6]
MoP/NC	**1.0 M KOH**	**150**	**59.4**	**this work**
MoP-QDs@PC	1.0 M KOH	98.8	66	[S1]
MoP@NPC/CNT	1.0 M KOH	131	73	[S2]
N/C/MoP	1.0 M KOH	169	51.3	[S7]
MoP/rGO	1.0 M KOH	150	66	[S4]
MoP/MWCNTs	1.0 M KOH	155	56.8	[S5]
MoP@NC	1.0 M KOH	149	55.9	[S8]

References

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