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Supporting Information

Ultrafine molybdenum phosphide nanocrystals on highly porous N,P-codoped carbon matrix as efficient catalyst for hydrogen evolution reaction

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1. Supplementary Figures

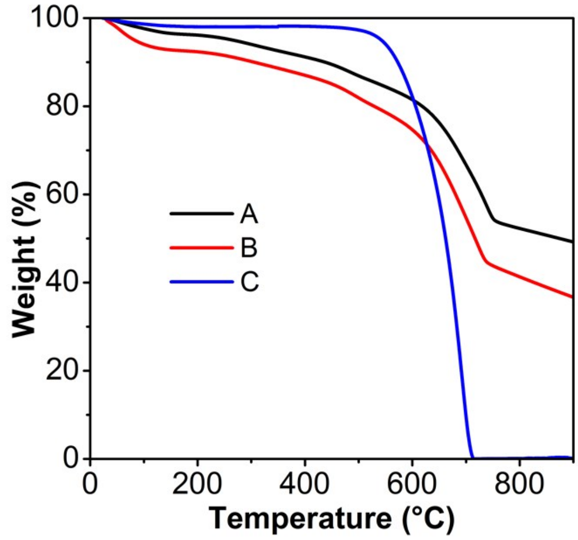

Fig. S1 Thermal gravimetric curves of polymeric precursor of MoP@NPCF (A), polymeric precursor of MoP@NPCS (B), and g-C_3N_4 monolith (C).

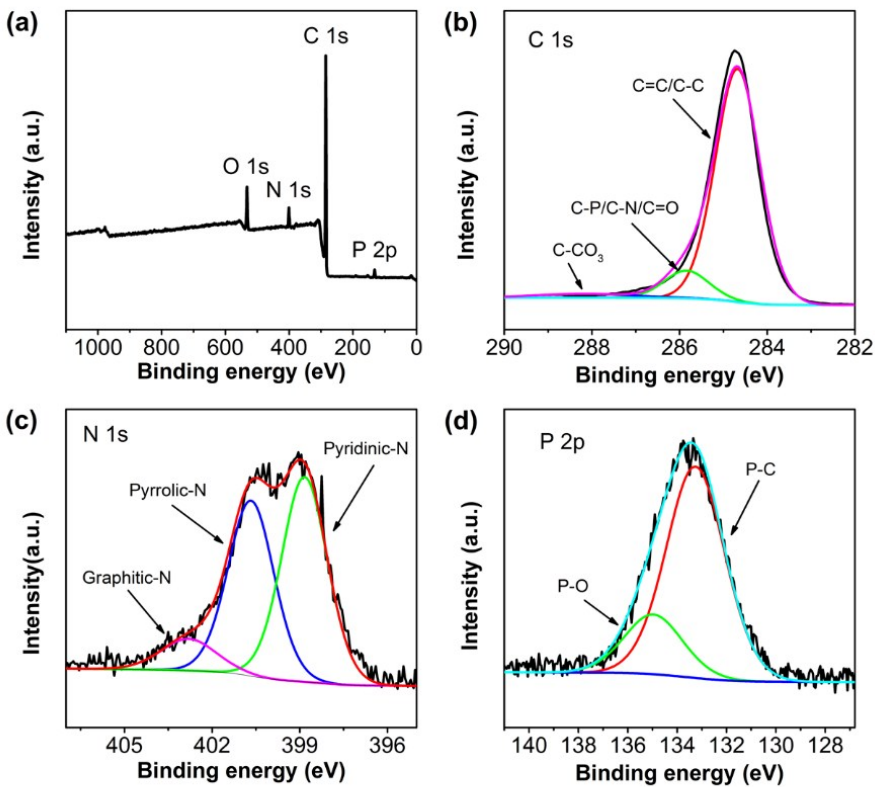

Fig. S2 (a) XPS survey spectra of NPCS; high-resolution (b) C 1s, (c) N 1s and (d) P 2p XPS spectra of NPCS.

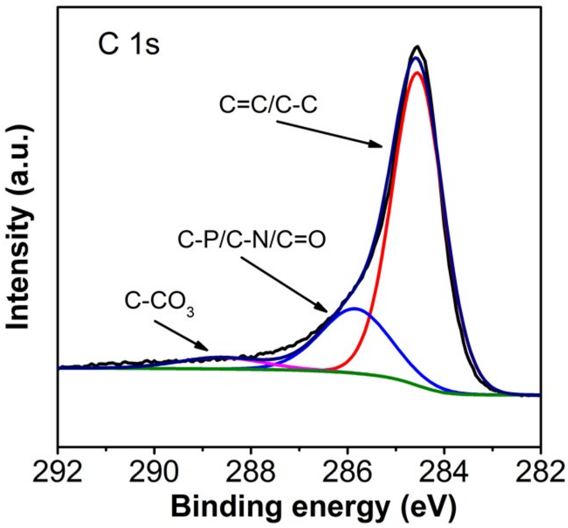

Fig. S3 High-resolution XPS C 1s spectrum of MoP@NPCS.

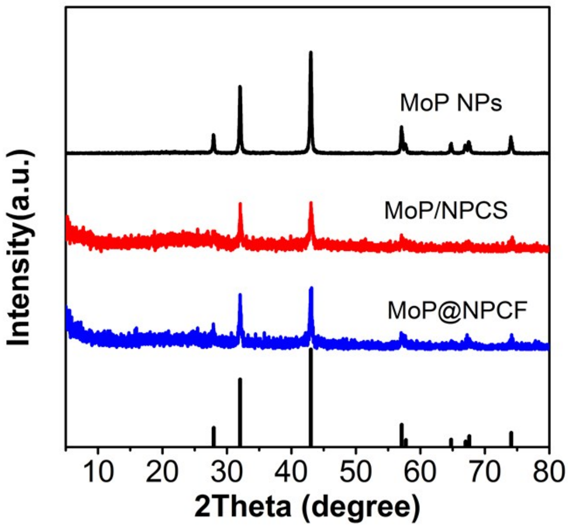

Fig. S4 Wide-angle XRD patterns of MoP@NPCF, MoP/NPCS and MoP NPs. XRD analysis indicates that the prepared MoP NPs, MoP/NPCF and MoP@NPCF all exhibit hexagonal MoP phase (JCPDS No. 65-6487).

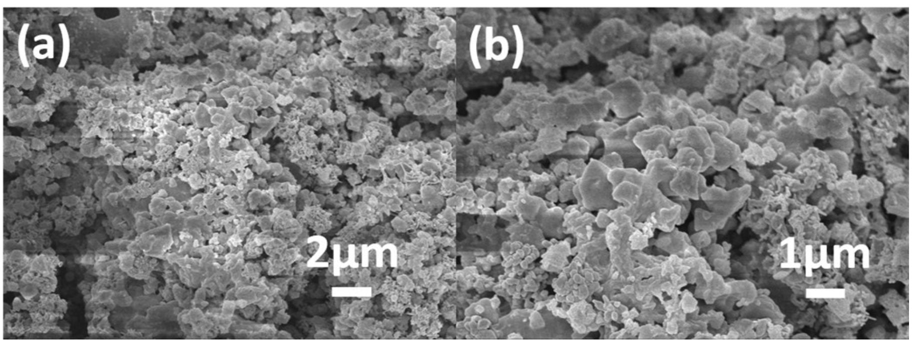

Fig. S5 SEM images of MoP@NPCF.

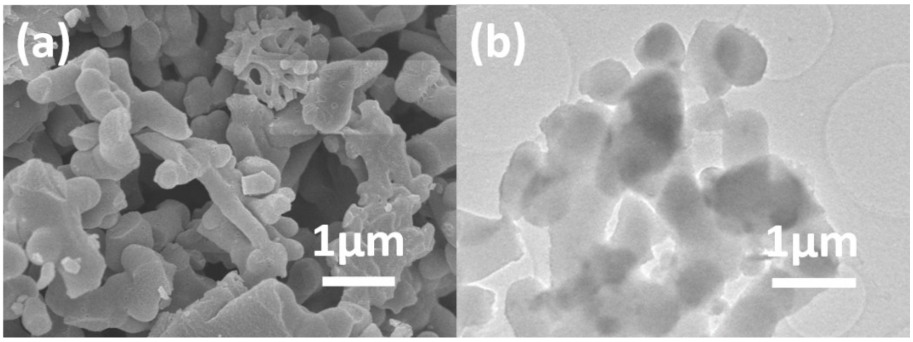

Fig. S6 SEM (a) and TEM (b) images of NPCF.

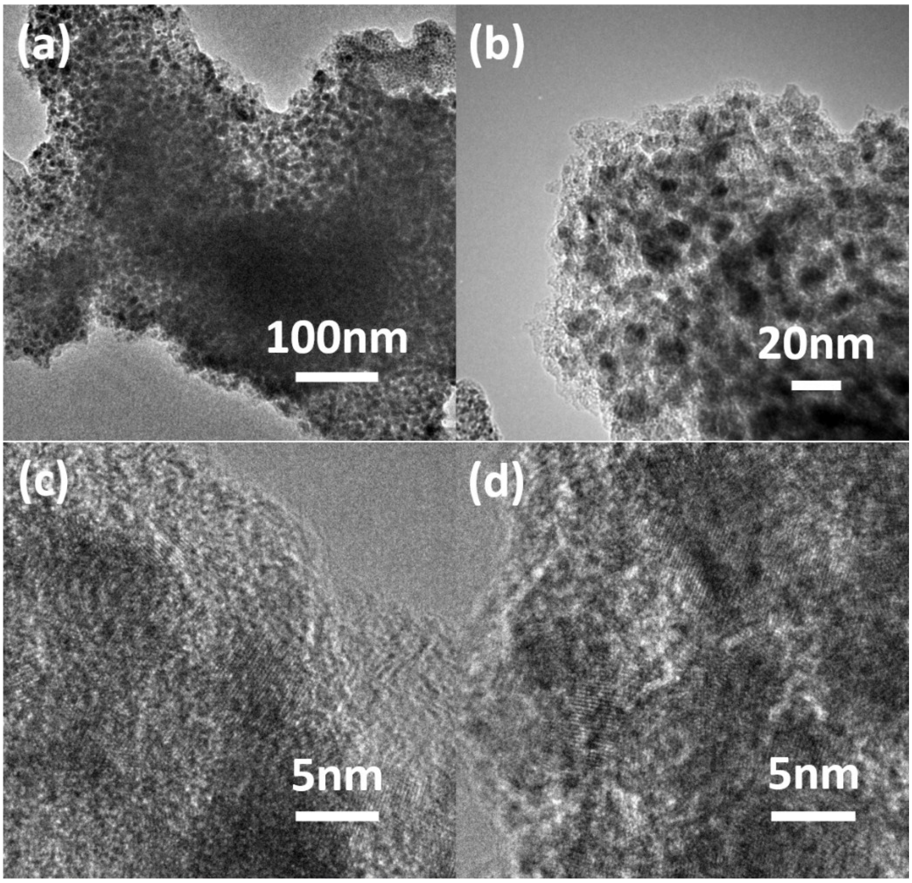

Fig. S7 TEM images of MoP@NPCF.

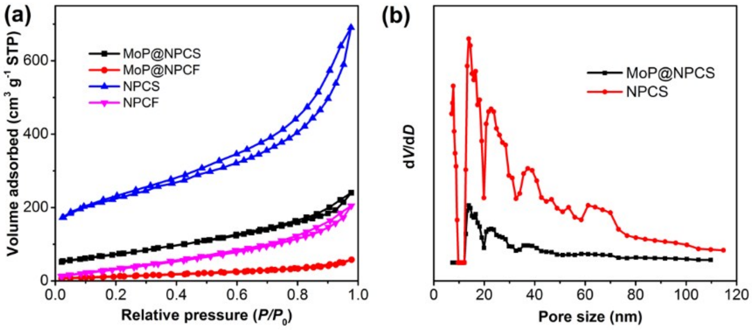

Fig. S8 (a) N_2 sorption isotherms of NPCS, MoP@NPCS, NPCF and MoP@NPCF, and (b) the corresponding pore size distribution curves of NPCS, MoP@NPCS.

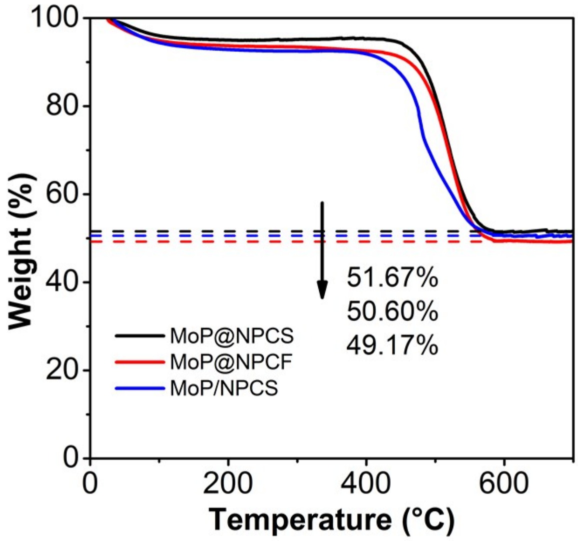

Fig. S9 Thermal gravimetric curves of MoP@NPCS, MoP@NPCF and MoP/NPCS under the air flow.

As exhibited in TGA curves, the initial weight loss below 200 ℃ can be attributed to the evaporation of adsorbed water. Following, the obviously weight loss should be ascribed to the combustion of carbonaceous materials, and the gradual oxidation of MoP and transformation to MoO_3. The remaining weights after heating over 600 ℃ are about 51.67 wt.%, 50.60 wt.% and 49.17 wt.% for MoP@NPCS, MoP@NPCF and MoP/NPCS, respectively.

Specially, the MoP content of these fabricated composites is calculated from the following equation:

m%(MoP) = residual mass * M(MoP)/M(MoO_3)

Therefore, the MoP contents in the MoP@NPCS, MoP@NPCF and MoP/NPCS are 45.55 wt.%, 44.63 wt.%, and 43.37 wt.%, respectively.

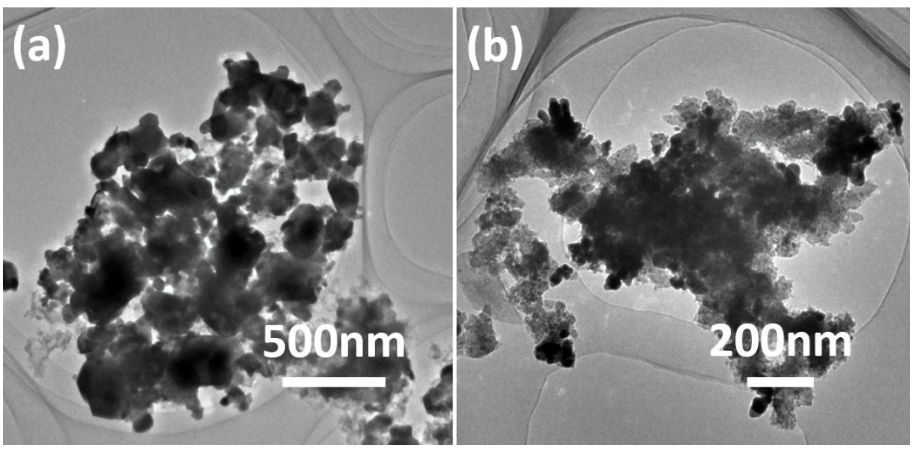

Fig. S10 TEM images of MoP/NPCS.

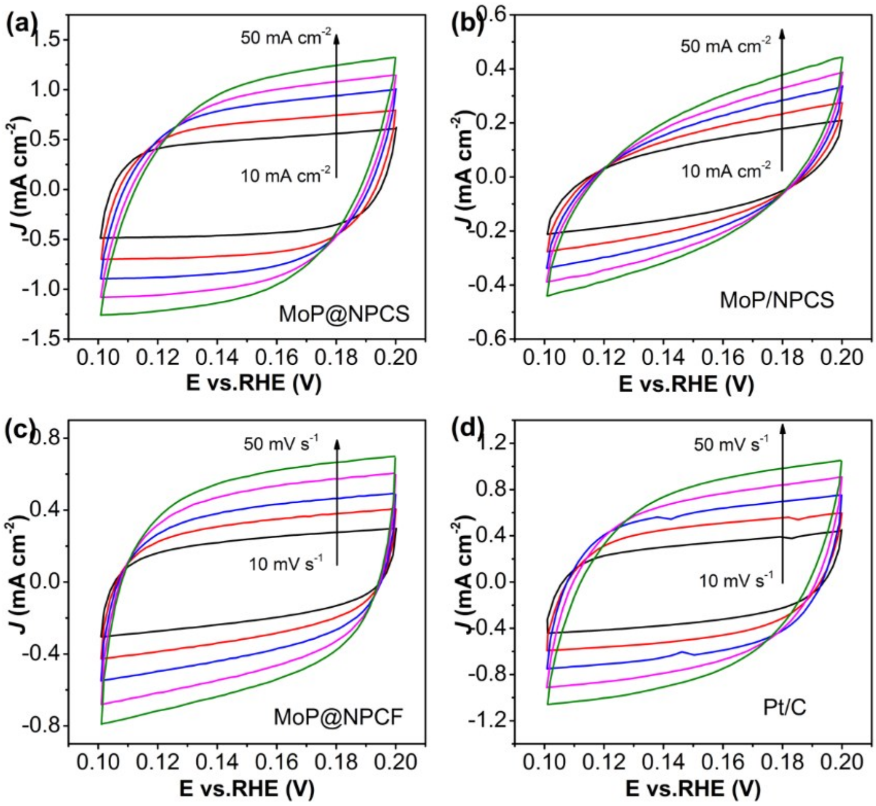

Fig. S11 Cyclic voltammograms of (a) MoP@NPCS, (b) MoP/NPCF, (c) MoP@NPCF and (d) Pt/C measured at different scan rates from 10 to 50 mV s^{-1}.

ECSA calculation:

The electrochemically active surface area (ECSA) can be determined using the capacitance (C_{dl}). The specific capacitance for a flat surface is generally found to be in the range of 20~60 μF cm^{-2}. In there, 40 μF cm^{-2} was used in the following calculations of the ECSA as literatures generally did.

The following formula was used to calculate ECSA:[1, 2]

$$\mathrm{ECSA} = \frac{\mathrm{C}}{40\ \mu\mathrm{F\ cm^{-2}\ per\ cm^{-2}}}$$

Therefore, the ECSA for MoP@NPCF, MoP@NPCS, MoP/NPCS and Pt/C were calculated to be 242.5, 422.4, 122.5 and 367.5 cm^2, respectively.

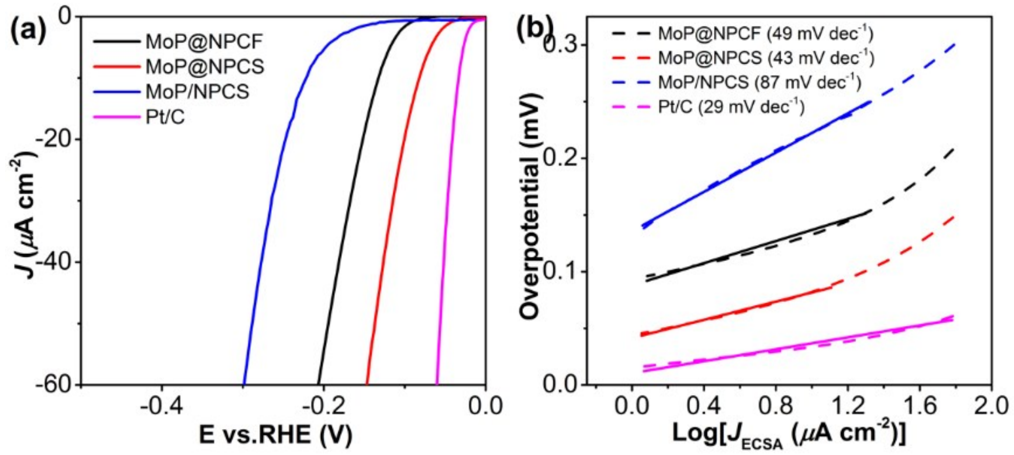

Fig. S12 (a) Polarization curves and (b) Tafel plots normalized by ECSA for MoP@NPCF, MoP@NPCS, MoP/NPCS and reference Pt/C.

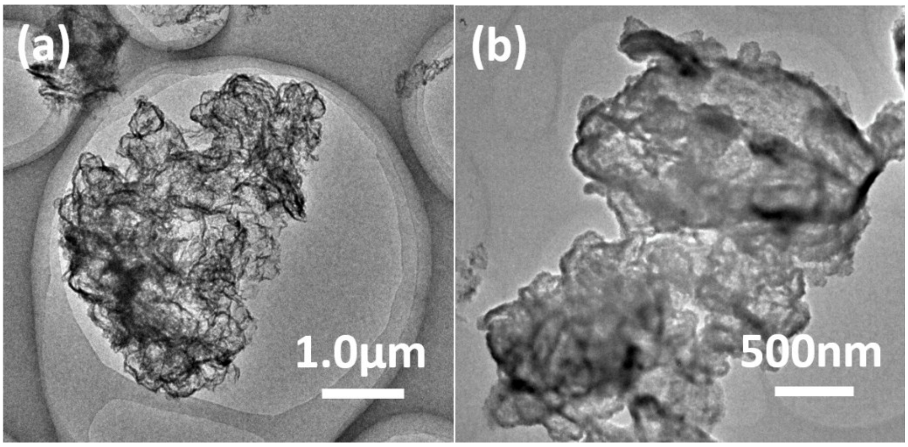

Fig. S13 TEM images of NCS. The TEM images exhibits the sponge-like architecture of the prepared NCS, which is similar to that of NPCS.

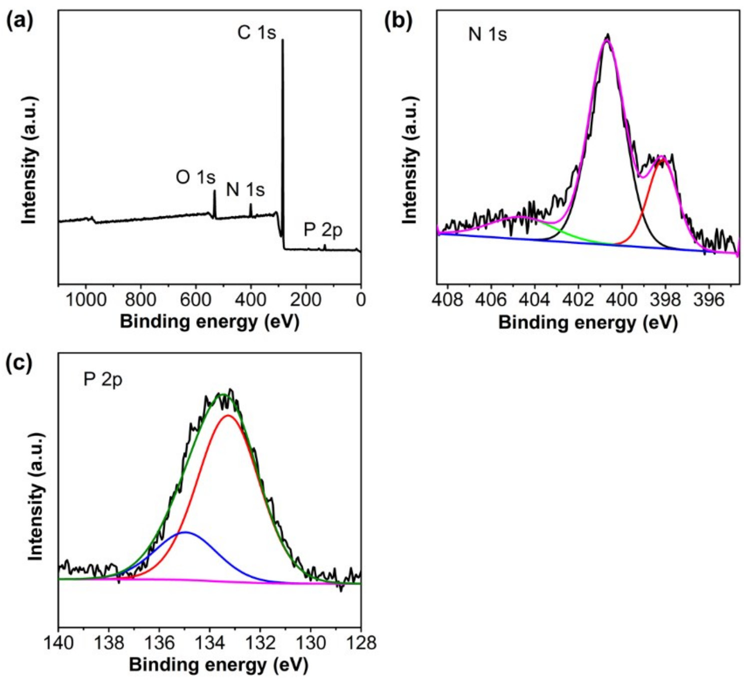

Fig. S14 (a) XPS survey spectra of NPCF, and high-resolution (b) N 1s and (c) P 2p XPS spectra. There are 5.56 at% N, and 3.34 at% P in NPCF depending on the XPS analysis.

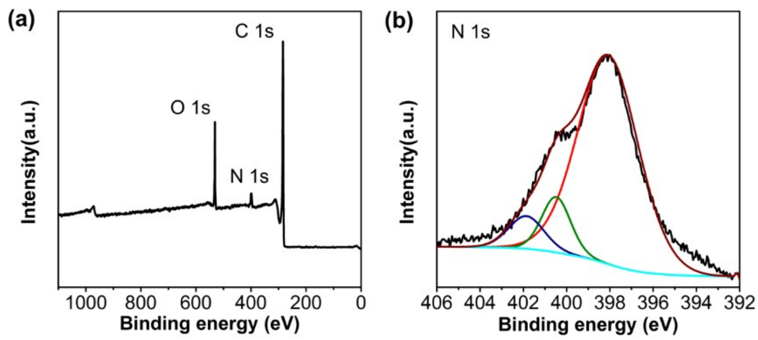

Fig. S15 (a) XPS survey spectrum of NCS. (b) High-resolution XPS N 1s spectrum. There are 7.72 at% N in NCS depending on the XPS analysis.

2. Supplementary Tables

Table S1. Summary of the HER performance of Mo-based electrocatalysts in alkaline electrolyte.

Catalyst	Electrolyte	$E_{J=10}$ (mV vs. RHE)	J_0 (mA cm^{-2})	Tafel slope (mV dec^{-1})	Ref.
MoP@NPCS	1.0 M KOH	107	0.127	51	This work
N, P-doped Mo_2C@C	1.0 M KOH	47	2.042	71	S3
N@MoPCx	1.0 M KOH	139	0.3023	86.6	S4
Mo_2C@NC	1.0 M KOH	60	N.A.	N.A.	S5
β-Mo_2C	0.1 M KOH	112	N.A.	55	S6
MoP_2 NPs/Mo	1.0 M KOH	194	N.A.	80	S7
Mo_xC-Ni@NCV	1.0 M KOH	126	N.A.	93	S8
MoP	1.0 M KOH	190	N.A.	N.A.	S9
MoC_x	1.0 M KOH	151	0.029	59	S10
MoP	1.0 M KOH	130	0.046	48	S11

Table S2. Summary of heteroatoms doped carbonaceous materials for OER in alkaline electrolyte.

Catalyst	Electrolyte	Onset potential (V vs. RHE)	$E_{J=10}$ (V vs. RHE)	Tafel slope (mV dec^{-1})	Ref.
NPCS	1.0 M KOH	1.49	1.62	78	This work
Porous carbon cloth	1.0 M KOH	N.A.	1.59	98	S12
N-doped graphene-carbon nanotubes	0.1 M KOH	1.54	1.70	141	S13
Defective graphene	1.0 M KOH	N.A.	1.57	97	S14
ONPPGC/OCC	1.0 M KOH	N.A.	1.64	84	S15
N, O-VAGNs/CC	0.1 M KOH	1.574	1.62	45	S16
N-doped carbon microtube sponge	0.1 M KOH	N.A.	1.52	246	S17
Nanoporous carbon nanofiber films	0.1 M KOH	1.43	about 1.85	274	S18
O-doped graphene	1.0 M KOH	N.A.	1.68	N.A.	S19
P-doped graphene	1.0 M KOH	1.48	1.56	62	S20
N, F-doped graphene	1.0 M KOH	1.45	1.57	78	S21
N,P,F tri-doped graphene	0.1 M KOH	1.62	N.A.	136	S22
NPC-CP	1.0 M KOH	1.51	1.54	87	S23

Table S3. Summary of recently active bifunctional nonprecious electrocatalysts used for overall water splitting in alkaline electrolyte.

Catalyst	Substrate	Electrolyte	$E_{J=10}$ (V)	$E_{J=20}$ (V)	Reference
NPCS // MoP@NPCS	Carbonfiber cloth	1.0 M KOH	1.70	1.76	This work
Ni_8P_3/Ni // Ni_8P_3/Ni	Ni foam	1.0 M KOH	1.61	N.A.	S24
Ni_3S_2/Ni foam // Ni_3S_2/Ni foam	Ni foam	1.0 M KOH	about 1.70	N.A.	S25
Co-P film // Co-P film	Copper film	1.0 M KOH	> 1.62	N.A.	S26
CoOx@CN // CoOx@CN	Ni foam	1.0 M KOH	N.A.	1.55	S27
Ni_5P_4/Ni foil // Ni_5P_4/Ni foil	Ni foil	1.0 M KOH	about 1.68	N.A.	S28
NiS // NiS	Ni foam	1.0 M KOH	1.61	1.67	S29
NiP/NF // NiP/NF	Ni foam	1.0 M KOH	1.63	1.70	S30
$NiCo_2S_4$ // $NiCo_2S_4$	Ni foam	1.0 M KOH	1.63	N.A.	S31
Ni_2P // Ni_2P	Ni foam	1.0 M KOH	1.63	N.A.	S32
NiSe // NiSe	Ni foam	1.0 M KOH	1.63	1.75	S33
NiCoP // NiCoP	Ti film	1.0 M KOH	1.65	N.A.	S34
CoO-CNF // CoO-CNF	Stainless steel	1.0 M KOH	1.63	N.A.	S35
NiFe/$NiCo_2O_4$ // NiFe/$NiCo_2O_4$	Ni foam	1.0 M KOH	1.67	N.A.	S36
Ni_2P/Ni // Ni_2P/Ni	Ni foam	1.0 M KOH	1.49	N.A.	S37
NiS_X/Ni // NiS_X/Ni	Ni foam	1.0 M KOH	1.47	1.53	S38
CoP // CoP	Ni foam	1.0 M KOH	1.62	1.66	S39

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