Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Self-supported MoP nanocrystals embedded in N,P-codoped carbon nanofibers via a polymer-confinement route for electrocatalytic hydrogen production

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1. Supplementary figures

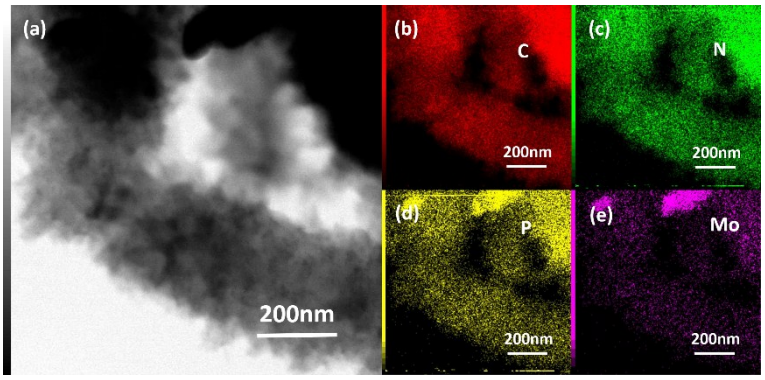

Fig. S1 (a-e) Energy-dispersive X-ray spectroscopy (EDS) elemental mapping images of the PANI-HEDP-$Mo_7O_{24}^{6-}$/CC.

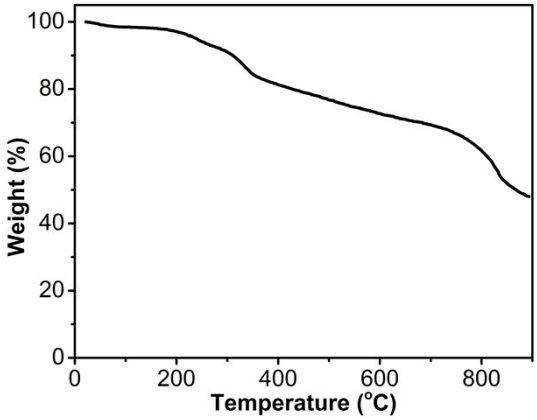

Fig. S2 TGA curves of the PANI-HEDP-$Mo_7O_{24}^{6-}$/CC.

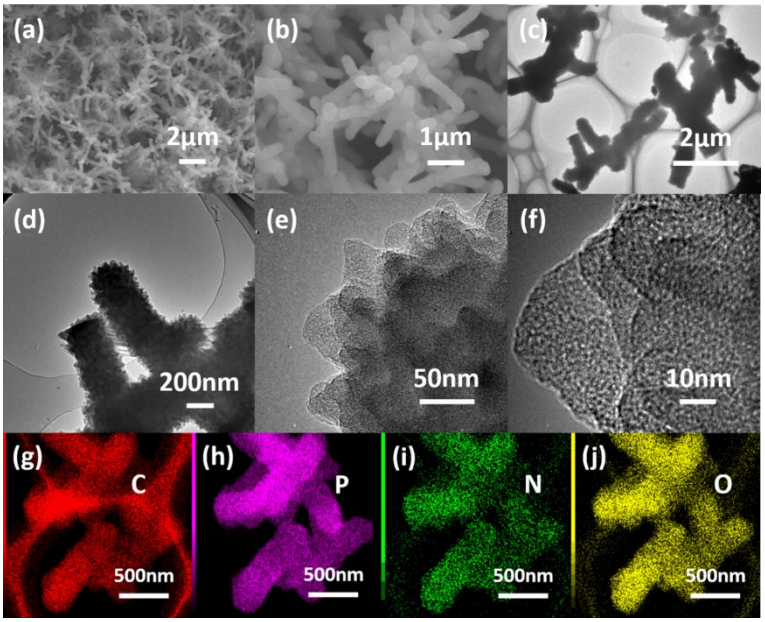

Fig. S3 (a-c) SEM images, (d-f) TEM images of NPCF/CC. (g) EDS mapping images of NPCF/CC.

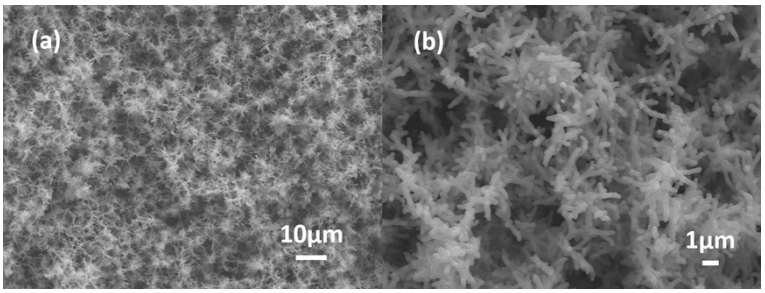

Fig. S4 (a-b) SEM images of NCF/CC.

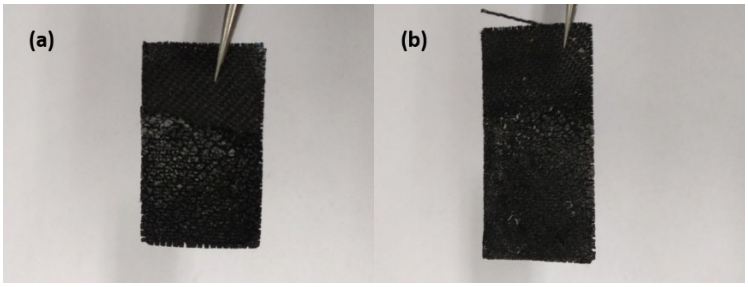

Fig. S5 Optical image of the fabricated NPCF/CC (a) and MoP@NPCF/CC (b).

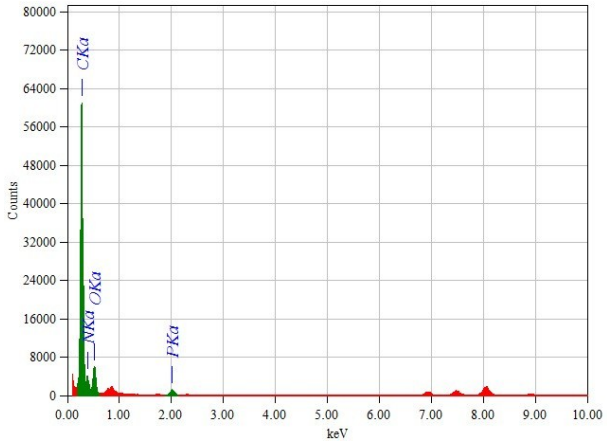

Fig. S6 EDS spectrum of NPCF/CC.

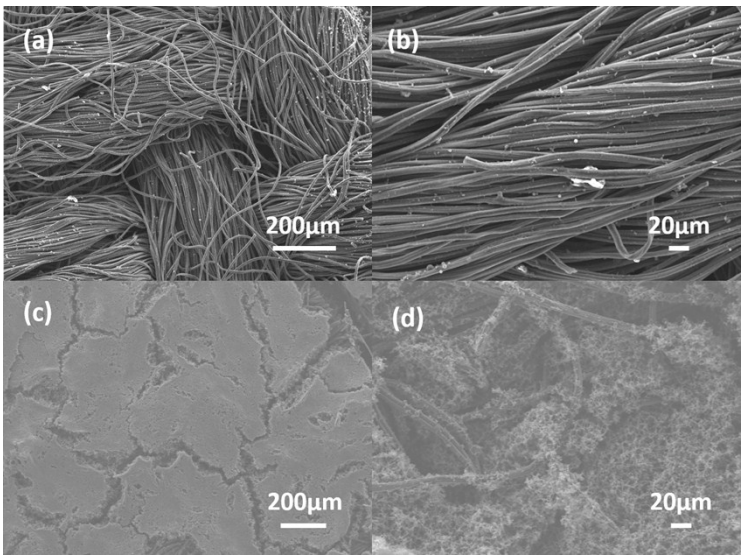

Fig. S7 Low-magnification SEM images of pristine carbon cloth (a-b), and MoP@NPCF/CC (c-d).

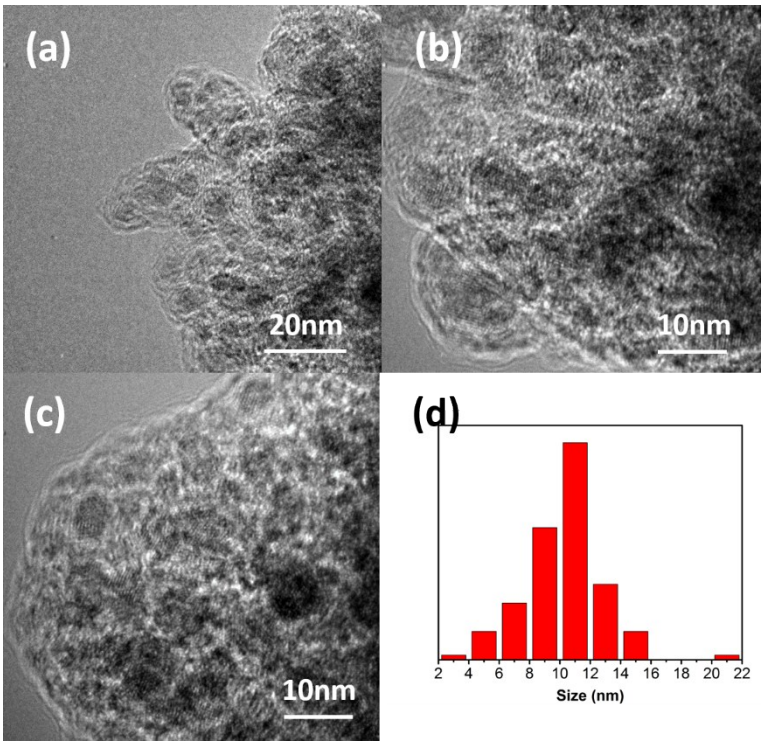

Fig. S8 (a-c) TEM images, and (d) the corresponding particle size distribution of MoP@NPCF/CC.

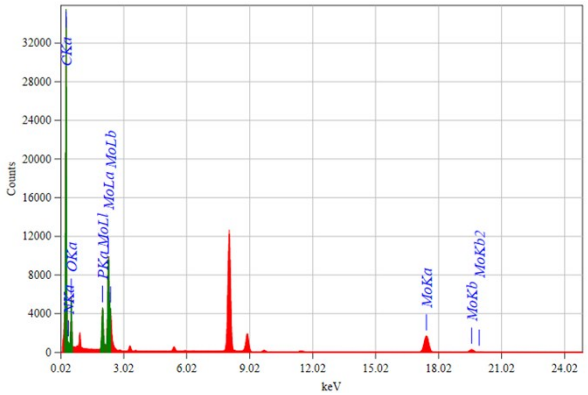

Fig. S9 EDX spectrum of MoP@NPCF/CC.

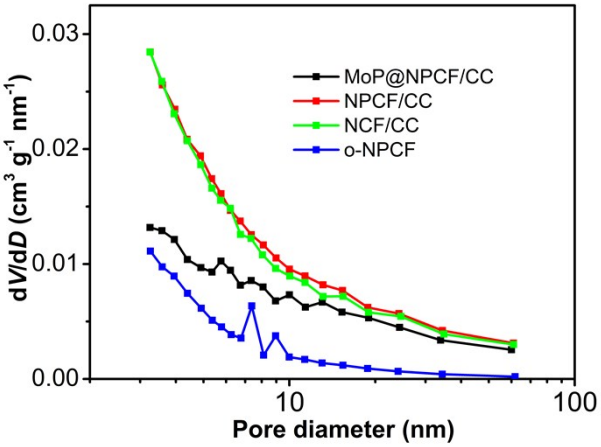

Fig. S10 Pore distribution curves of the developed samples.

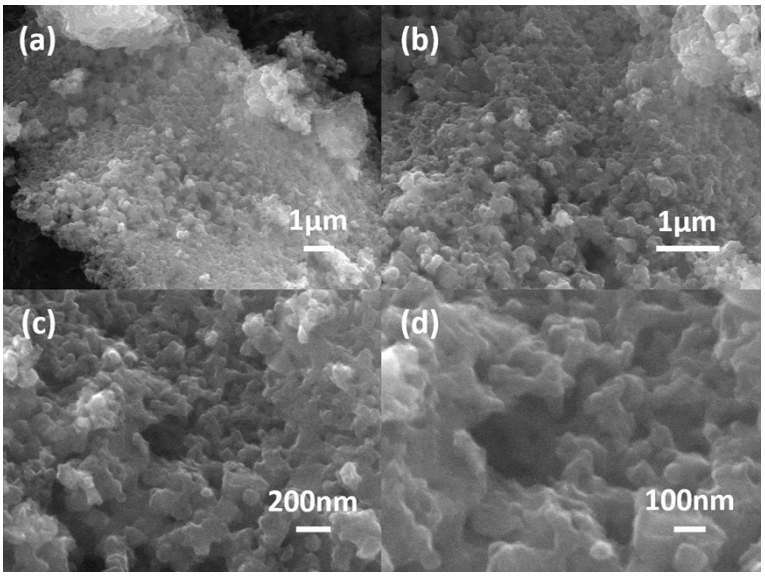

Fig. S11 SEM images of the o-NPCF prepared by oxidation-polymerization method.

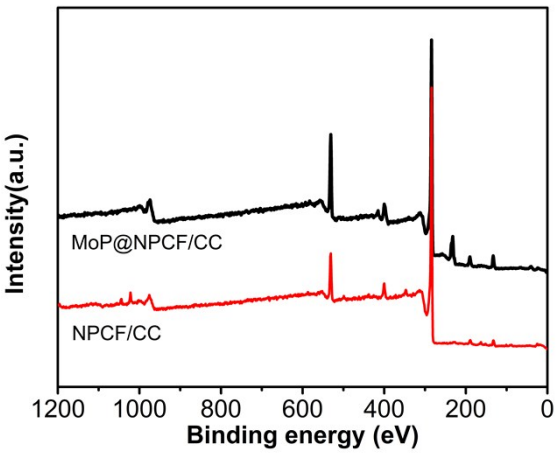

Fig. S12 XPS survey spectrum of MoP@NPCF/CC and NPCF/CC**.**

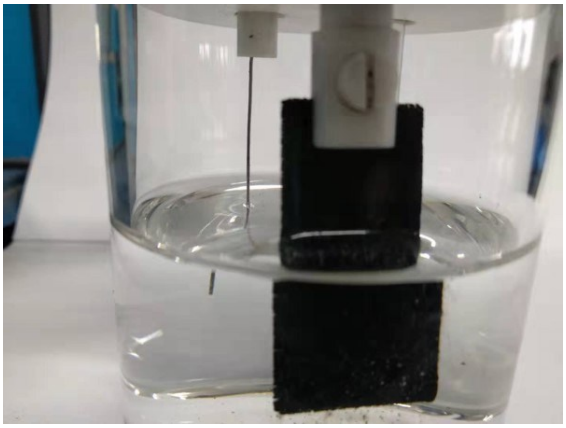

Fig. S13 A typical three-electrode configuration with the use of MoP@NPCF/CC as the self-supported electrode for electrochemical tests.

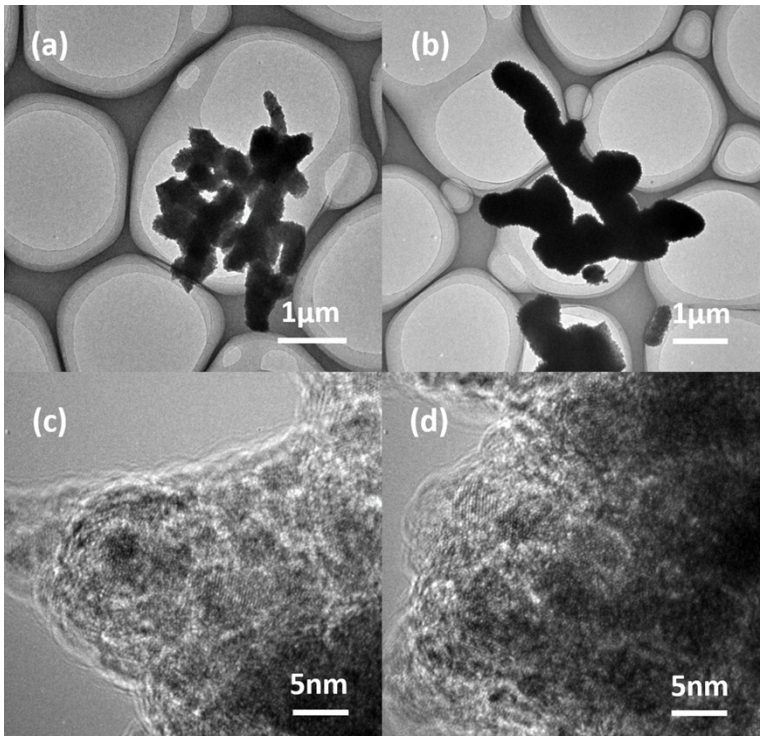

Fig. S14 (a-d) TEM images of MoP@NPCF/CC after long-term HER stability tests.

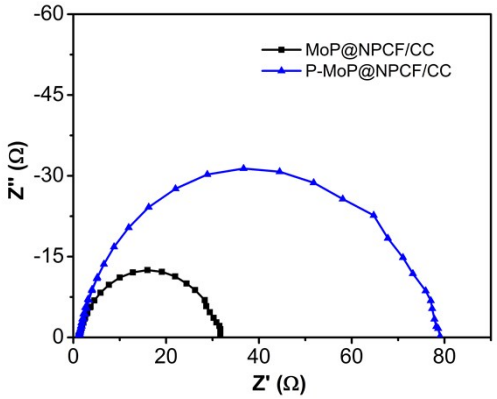

Fig. S15 Nyquist plots of MoP@NPCF/CC and P-MoP@NPCF/CC at an overpotential of 200 mV (*vs.* RHE).

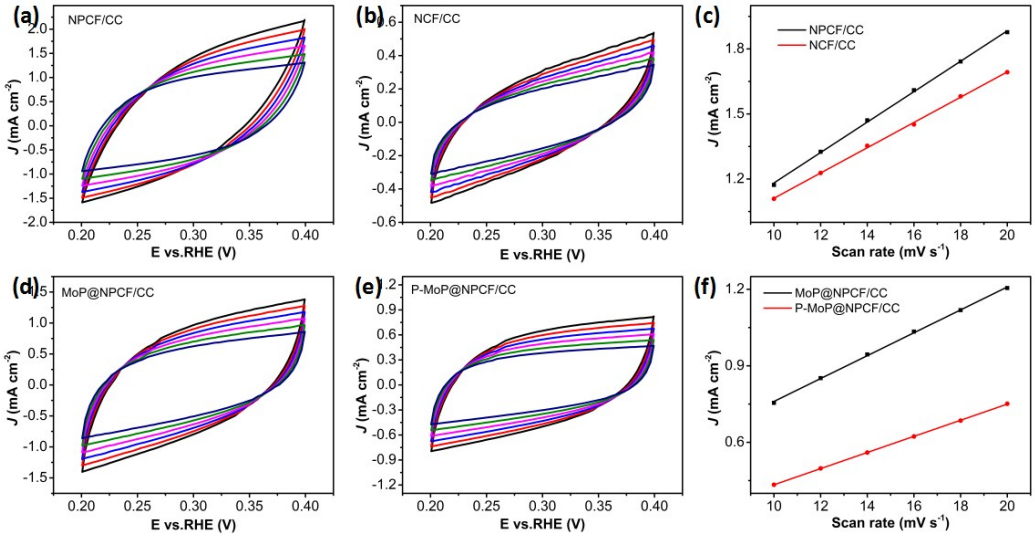

Fig. S16 (a-d) Cyclic voltammograms (CVs) of the fabricated materials measured at different scan rates from 10 to 20 mV s^{-1}. (e-f) Plots of the current densities at 0.35 V (*vs.* RHE) against the scan rates for the fabricated materials.

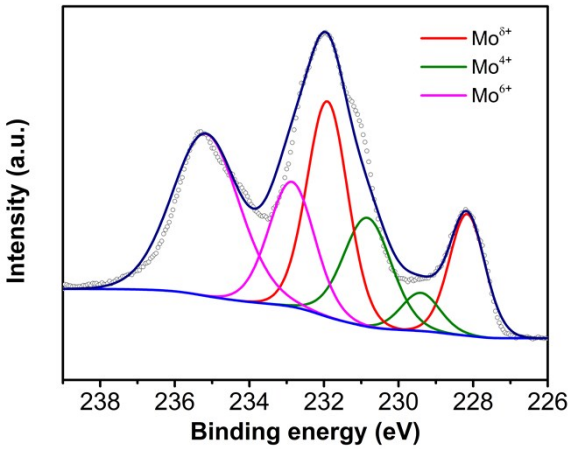

Fig. S17 High resolution XPS spectrum of Mo 3d of com-MoP.

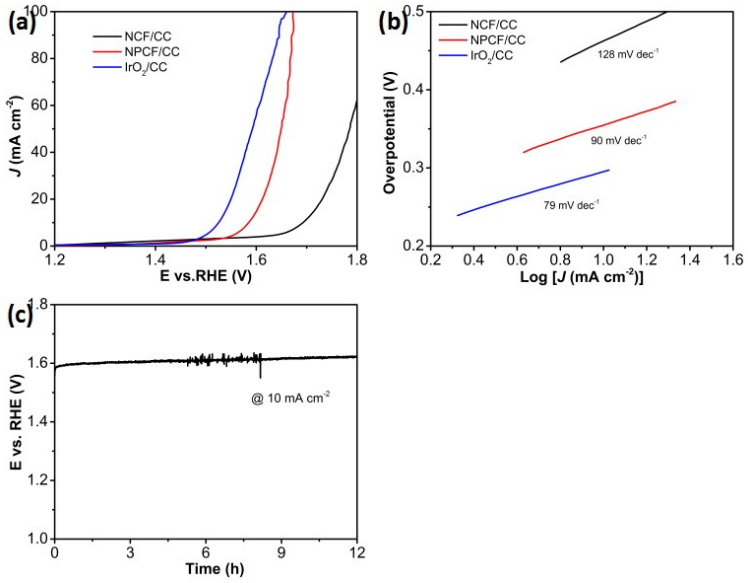

Fig. S18 (a) OER polarization curves and (b) corresponding Tafel plots of fabricated materials in 1.0 M KOH. (c) Chronoamperometry curve of NPCF/CC.

2. Supplementary tables

Table S1. HER electrocatalytic performance of the fabricated catalysts and some recently reported active catalysts based on non-precious metal.

Catalyst	Electrolyte	$E_{J=10}$ (mV vs. RHE)	Tafel slope (mV dec^{-1})	Ref.
MoP@NPCF/CC	0.5 M H_2SO_4	115	37	This work.
MoC@NCS	0.5 M H_2SO_4	81	43	[1]
$MoS_{0.86}P_{0.57}$/CB	0.5 M H_2SO_4	120	57	[2]
PDAP-MoCN-CO_2	0.5 M H_2SO_4	140	46	[3]
NS-doped Mo_2C	0.5 M H_2SO_4	86	60	[4]
$CoMoS_3$	0.5 M H_2SO_4	171	56.9	[5]
Mo_xSo_y (Mo_2C)	0.1 M $HClO_4$	177	54	[6]
Mo_2C/CNT	0.1 M $HClO_4$	152	-	[7]
M-MoS_2	0.5 M H_2SO_4	175	41	[8]
Mo_xC-Ni@NCV	0.5 M H_2SO_4	75	45	[9]
MoC–Mo_2C	0.5 M H_2SO_4	126	43	[10]
MoC_x nanooctahedrons	0.5 M H_2SO_4	142	53	[11]
MoP_2 NS/CC	0.5 M H_2SO_4	58	63.6	[12]
MoP_2 NPs/Mo	0.5 M H_2SO_4	143	57	[13]
MoP	0.5 M H_2SO_4	150	50	[14]
MoP	0.5 M H_2SO_4	180	54	[15]
N,P-doped Mo_2C@C	0.5 M H_2SO_4	141	56	[16]
MoO_2@PC-RGO	0.5 M H_2SO_4	64	41	[17]
Mo_2C@NC	0.5 M H_2SO_4	124	60	[18]
Mo_2C nanowires	0.5 M H_2SO_4	130	53	[19]
$Mo_{0.06}W_{1.94}C$/CB	0.5 M H_2SO_4	220	-	[20]
$Co_{0.6}Mo_{1.4}N_2$	0.5 M H_2SO_4	190	-	[21]
MoP@NPCF/CC	1.0 M KOH	182	46	This work.

MoC@NCS	1.0 M KOH	89	51	[1]
Mo_xC-Ni@NCV	1.0 M KOH	126	93	[9]
MoC-Mo_2C	1.0 M KOH	120	42	[10]
MoC_x	1.0 M KOH	151	59	[11]
MoP_2 NS/CC	1.0 M KOH	67	70	[12]
MoP_2 NPs/Mo	1.0 M KOH	194	80	[13]
MoP	1.0 M KOH	190	-	[14]
MoP	1.0 M KOH	130	48	[15]
MoP@NPCS	1.0 M KOH	107	51	[22]
β-Mo_2C	0.1 M KOH	112	55	[23]
Mo_2C@NC	1.0 M KOH	60	-	[24]
N, P-doped Mo_2C@C	1.0 M KOH	47	71	[25]

Table S2. OER electrocatalytic performance of the fabricated catalysts and some recently reported active catalysts based on metal-free carbon materials.

Catalyst	Electrolyte	Onset potential (V vs. RHE)	$E_{J=10}$ (V vs. RHE)	Tafel slope (mV dec^{-1})	Ref.
NPCF/CC	1.0 M KOH	1.54	1.58	90	This work.
NPCS	1.0 M KOH	1.49	1.62	78	[22]
NPC-CP	1.0 M KOH	1.51	1.54	87	[26]
ONPPGC/OCC	1.0 M KOH	N.A.	1.64	84	[27]
N-doped graphene-carbon nanotubes	0.1 M KOH	1.54	1.70	141	[28]
N-doped carbon microtube sponge	0.1 M KOH	N.A.	1.52	246	[29]
P-doped graphene	1.0 M KOH	1.48	1.56	62	[30]
Defective graphene	1.0 M KOH	N.A.	1.57	97	[31]
N,P,F tri-doped graphene	0.1 M KOH	1.62	N.A.	136	[32]
N, O-VAGNs/CC	0.1 M KOH	1.574	1.62	45	[33]
N, F-doped graphene	1.0 M KOH	1.45	1.57	78	[34]
Porous carbon cloth	1.0 M KOH	-	1.59	98	[35]
O-doped graphene	1.0 M KOH	-	1.68	-	[36]
Nanoporous carbon nanofiber films	0.1 M KOH	1.43	about 1.85	274	[37]

Table S3. Two-electrode overall water splitting based on non-precious metal materials in alkaline electrolyte.

Catalyst	Substrate	Electrolyte	$E_{J=10}$(V)	$E_{J=20}$(V)	Reference
NPCF/CC // MoP@NPCF/CC	Carbon cloth	1.0 M KOH	1.64	1.68	This work.
NPCS // MoP@NPCS	Carbonfiber cloth	1.0 M KOH	1.70	1.76	[22]
NiS // NiS	Ni foam	1.0 M KOH	1.61	1.67	[38]
CoP // CoP	Ni foam	1.0 M KOH	1.62	1.66	[39]
NiCoP // NiCoP	Ti film	1.0 M KOH	1.65	N.A.	[40]
$NiCo_2S_4$ // $NiCo_2S_4$	Ni foam	1.0 M KOH	1.63	N.A.	[41]
NiFe/$NiCo_2O_4$ // NiFe/$NiCo_2O_4$	Ni foam	1.0 M KOH	1.67	N.A.	[42]
Co-P film // Co-P film	Copper film	1.0 M KOH	> 1.62	N.A.	[43]
NiSe // NiSe	Ni foam	1.0 M KOH	1.63	1.75	[44]
Ni_2P // Ni_2P	Ni foam	1.0 M KOH	1.63	N.A.	[45]
NiP/NF // NiP/NF	Ni foam	1.0 M KOH	1.63	1.70	[46]
NiS_X/Ni // NiS_X/Ni	Ni foam	1.0 M KOH	1.47	1.53	[47]
Ni_8P_3/Ni // Ni_8P_3/Ni	Ni foam	1.0 M KOH	1.61	N.A.	[48]
Ni_2P/Ni // Ni_2P/Ni	Ni foam	1.0 M KOH	1.49	N.A.	[49]
Ni_5P_4/Ni foil // Ni_5P_4/Ni foil	Ni foil	1.0 M KOH	about 1.68	N.A.	[50]
Ni_3S_2/Ni foam // Ni_3S_2/Ni foam	Ni foam	1.0 M KOH	about 1.70	N.A.	[51]
CoO-CNF // CoO-CNF	Stainless steel	1.0 M KOH	1.63	N.A.	[52]
CoOx@CN // CoOx@CN	Ni foam	1.0 M KOH	N.A.	1.55	[53]

3. Supplementary references

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