Supporting Information

W-Doped MoP Nanospheres as Electrocatalysts for pH-Universal Hydrogen Evolution Reaction

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1. Chemicals

Ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$), AR), tungsten hexachloride (WCl_6, AR), sulfuric acid (H_2SO_4, AR) and potassium hydroxide (KOH, AR) were purchased from Beijing Chemical Works. 2-methylimidazole ($CH_3C_3H_2N_2H$,), dimethylformamide (C_3H_7NO, AR) and ethanol (C_2H_6O, AR) were obtained from Aladdin. Commercial Pt/C (20 wt%) was received from Alfa Aesar. Deionized water was supplied by a Nanopure water system (18.25 MΩ cm). All chemicals were used as received without further purification.

2. Materials characterizations

SEM images were measured using scanning electron microscopy (SEM, XL30) operated at an accelerating voltage of 20 kV. Power X-ray diffraction (XRD, Bruker Corporation, Germany) was performed at D8 ADVANCE with Cu Kα radiation (λ = 0.154 nm). High resolution transmission electron microscopy (HRTEM) and STEM (JEM-2010 HR), equipped with energy-dispersive X-ray spectroscopy (EDS) were operated at 200 kV. X-ray photoelectron spectroscopy (XPS, VG Thermo ESCALAB 250) spectra were obtained at 120 W.

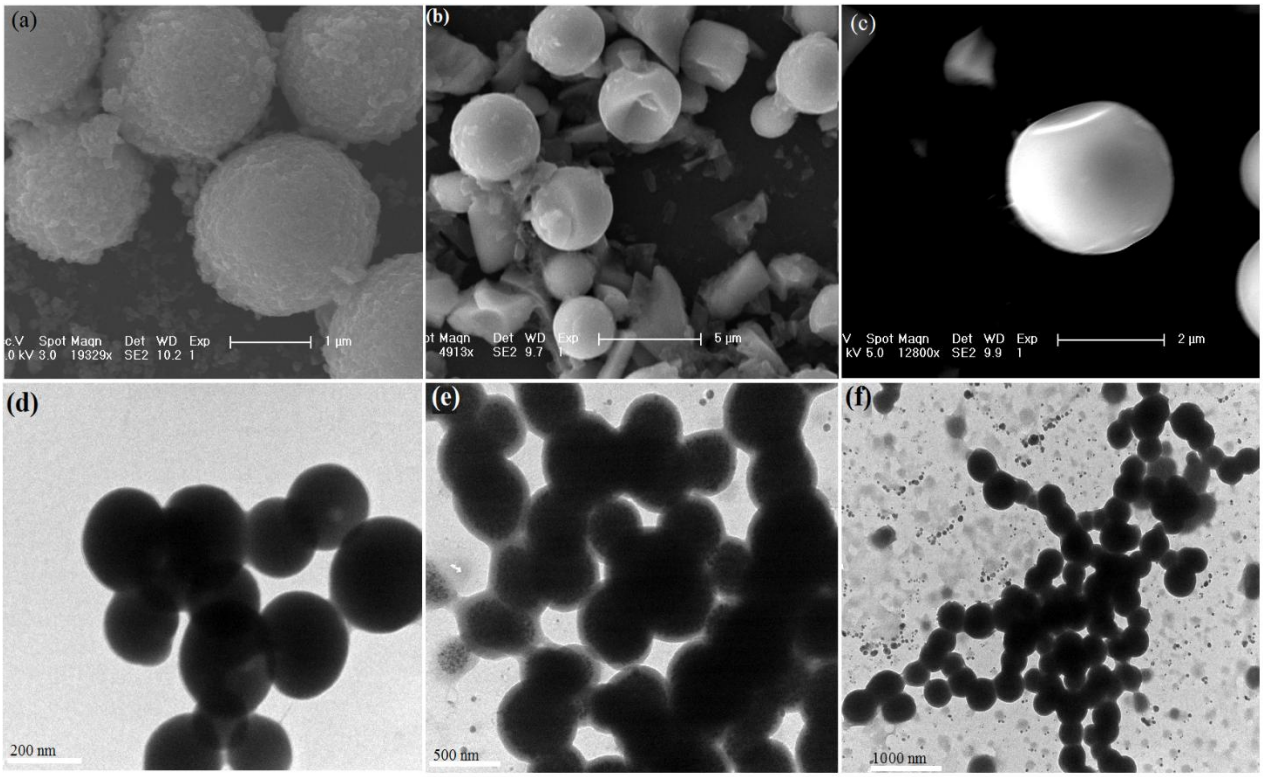

Figure S1. (a, b and c) SEM images of W-MoP, W_4MoO_3 and Mo-MOF, respectively. (d, e, f) TEM images of, W-MoP, W_4MoO_3 and Mo-MOF respectively.

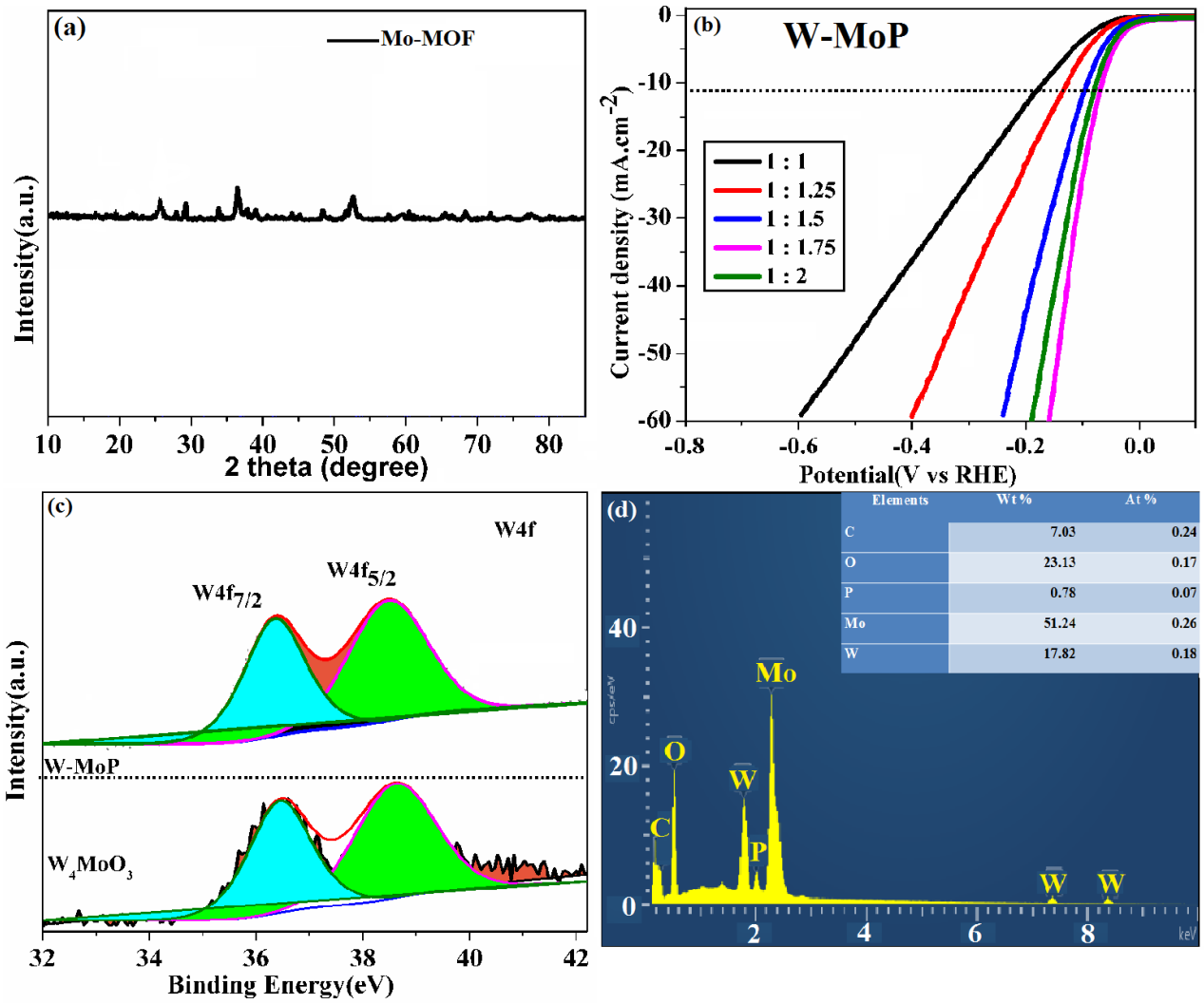

Figure S2. (a) XRD pattern of Mo-MOF. (b) Polarization curves of W-MoP at different W: Mo atomic ratios. (c) The W 4f XPS spectra of W-MoP and W_4Mo_3. (d) EDS of W-MoP.

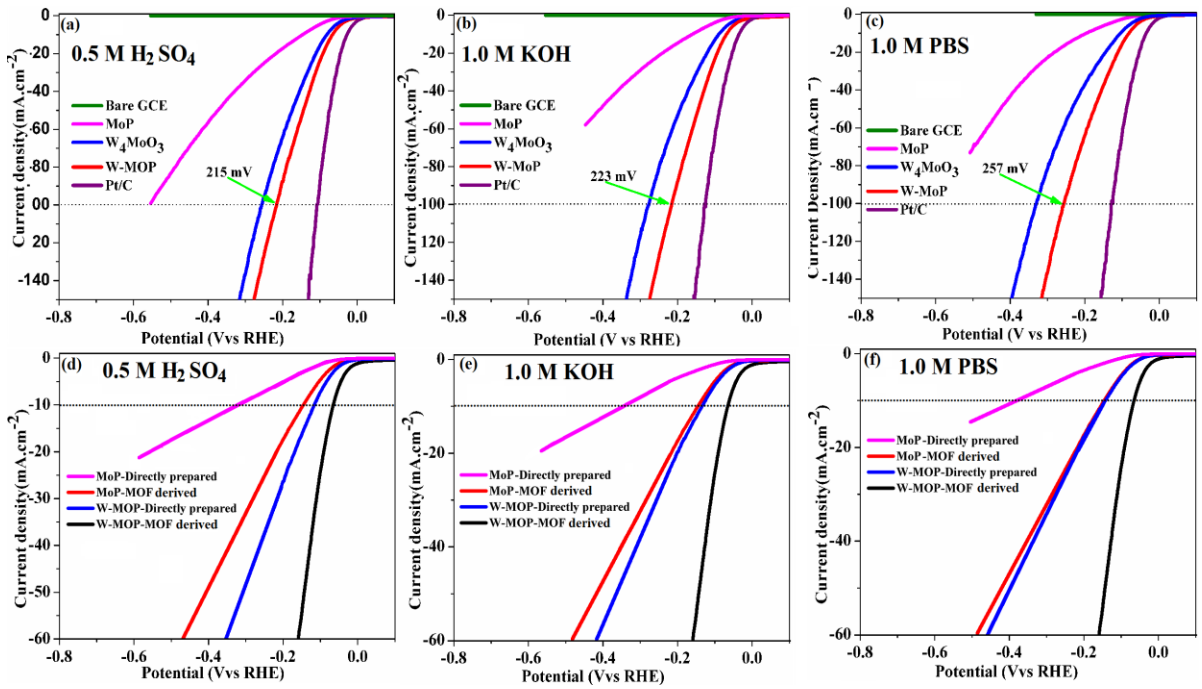

Figure S3. (a-c) Polarization curves of Pt/C, W-MoP, W_4MoO_3, MoP and bare GC electrodes in 0.5 M H_2SO_4 (a), 1.0 M KOH (b) and 1.0 M PBS (c), respectively. (d-f) Polarization curves of W-MoP and MoP prepared from MOF and directly from W_4MoO_3, in 0.5 M H_2SO_4 (d), 1.0 M KOH (e) and 1.0 M PBS (f), respectively.

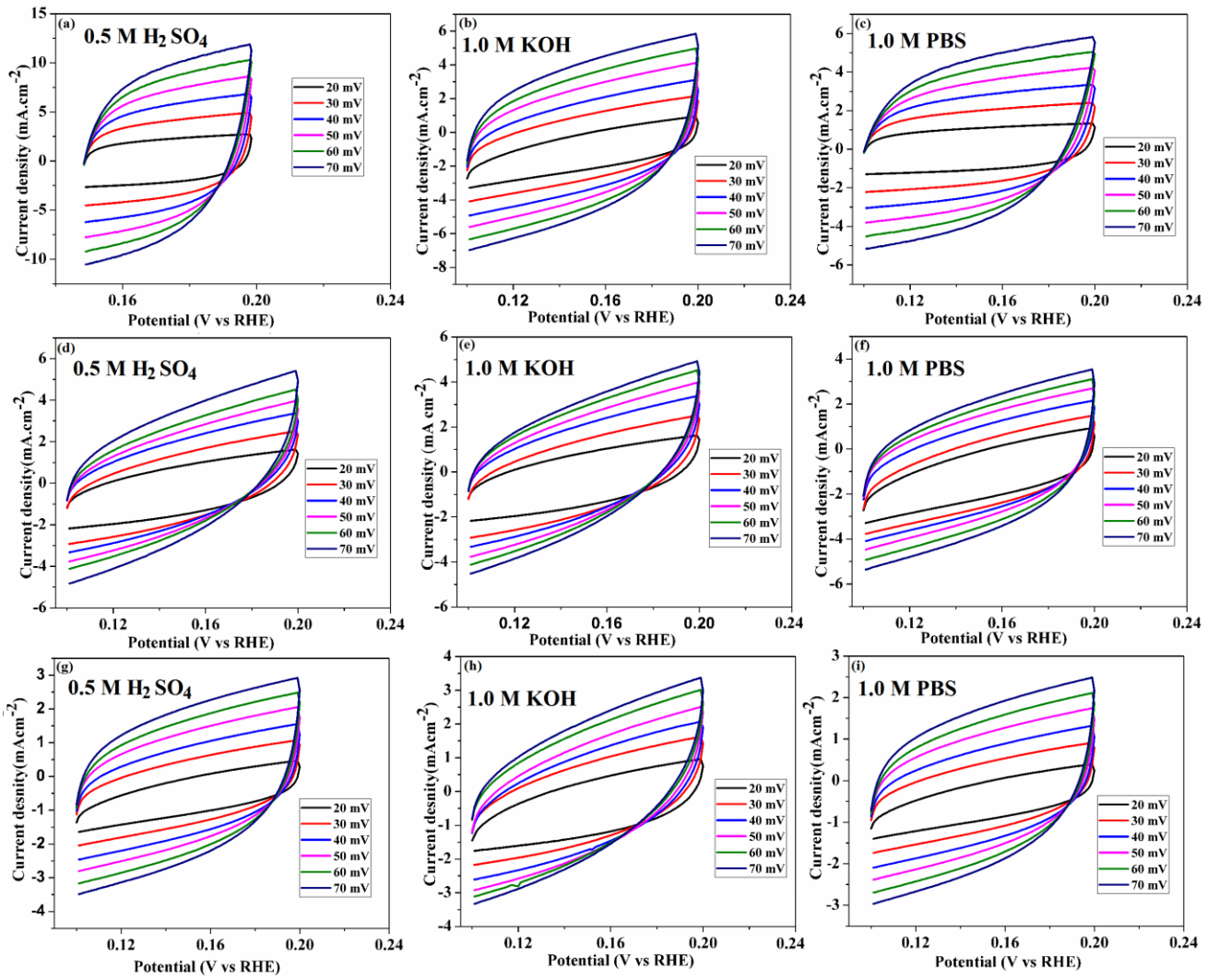

Figure S4. (a, b and c) CV curves of W-MoP electrode, (d, e and f) CV curves of W_4MoO_3 electrode, (g, h and i) CV curves of MoP electrode in 0.5 M H_2SO_4, 1.0 M KOH and 1.0 M PBS, respectively.

Table S1. Comparison of the electrocatalytic performances of W-MoP and other reported HER electrocatalysts in 0.5 M H_2SO_4 electrolyte.

Catalyst	Overpotential @ 10 mA/cm^2 (mV)	Tafel slope (mV/dec)	Reference
W-MoP	**63**	**53**	**This study**
Co-P@PC	72	49	[1]
MoP@PC	69	55	[2]
MoP@NPSC	71	75	[3]
Ce-CoP	54	54	[4]
Mn-CoP	49	55	[5]
$Ni_{1.5}Co_{1.4}P$@Ru	49	49	[6]
Co-Co_2P@NPC/Rgo	61	50	[7]
S-MoP NPL	86	34	[8]
Ni_2P–CoP	105	64	[9]
MoP/MoS_2	69	61	[10]
Ni–Co–P	92	50	[11]
Co–P	160	56	[12]
CoP_3@Cu/Cu	101	44	[13]
m-CoP–NiCoP/CC	82	57	[14]
Cu–Co–P	262	59	[15]
CoMoNiS-NF-31	103	55	[16]

Table S2. Comparison of the electrocatalytic performances of W-MoP and other reported HER electrocatalysts in 1.0 M KOH electrolyte.

Catalyst	Overpotential @ 10 mA/cm^2 (mV)	Tafel slope (mV/dec)	Reference
W-MoP	**71**	**68**	**This study**
CoP/NiCoP	75	64	[17]
S-MoP NPL	104	56	[8]
CoP	100	76	[18]
Ni–Co–P	83	47	[11]
$Ni_{1.5}Co_{1.4}P$@Ru	52	50	[6]
CoP	54	51	[19]
CoP-Co_2P@PC/PG	39	59	[20]
$NiCo_xP_y$-P/CC	42	66	[21]
Co–P	175	84	[12]
Mn–Co–P/Ti	76	52	[5]
Ni-Co-P/NF	85	46	[22]
CoP_3@Cu/Cu	92	82	[13]
$CoFeN_x$HNAs/NF	200	60	[23]
Co, Mo_2C-CNF	128	60	[24]
CoMoNiS-NF-31	113	85	[16]
MoS_2–Ni_3S_2 HNRs/NF	98	61	[25]
Fe-Ni_3S_2/NF	142	95	[26]
Ni_2V-MOFs@NF	89	97	[27]

Table S3. Comparison of the electrocatalytic performances of W-MoP and other reported HER electrocatalysts in 1.0 M PBS electrolyte.

Catalyst	Overpotential @ 10 mA/cm^2 (mV)	Tafel slope (mV/dec)	Reference
W-MoP	**82**	**74**	**This study**
Co-P@PC	91	58	[1]
S-MoP NPL	142	98	[8]
Mn–Co–P/Ti	86	56	[5]
CoMoNiS-NF-31	117	56	[16]
Co–Mo–S	213	94	[28]
Ni_3N@Ni–Bi	265	190	[29]
SiO_2/PPy NTs–CFs	192	100.2	[30]
$Ni(S_{0.5}Se_{0.5})_2$	124	81	[31]
$Cu_{0.08}Co_{0.92}P$ NAs/CP	81	83.5	[32]
MoP NWAs/CFP	84	63	[33]
Ni -CrO_x / Cu	48	-	[34]

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