

Supporting Information

Template-Preparation of Three-Dimensional Molybdenum Phosphide Sponges as High Performance Electrode for Hydrogen Evolution

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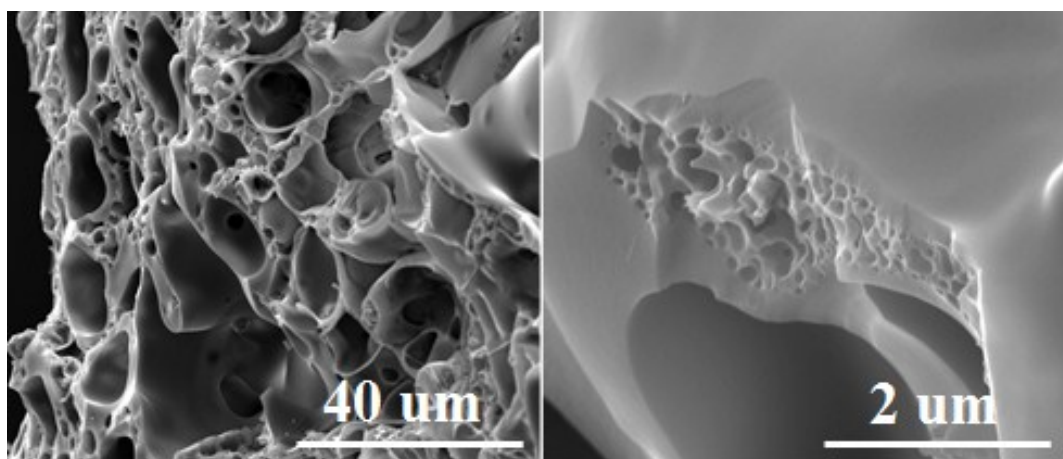


Fig. S1 SEM images of 3D MoP-650 precursor.

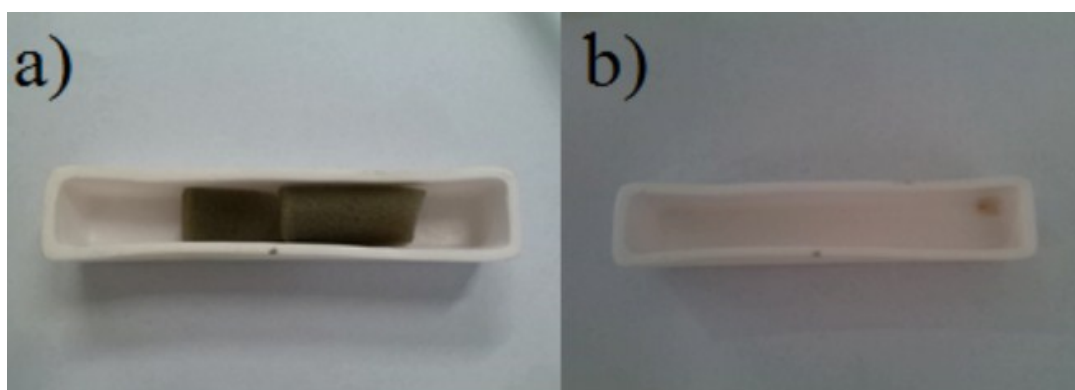


Fig. S2 Optical photos of polyurethane sponge before (a) and after (b) sintering for 3h at a ramping rate of 2 °C per min from room temperature to 500 °C in air.

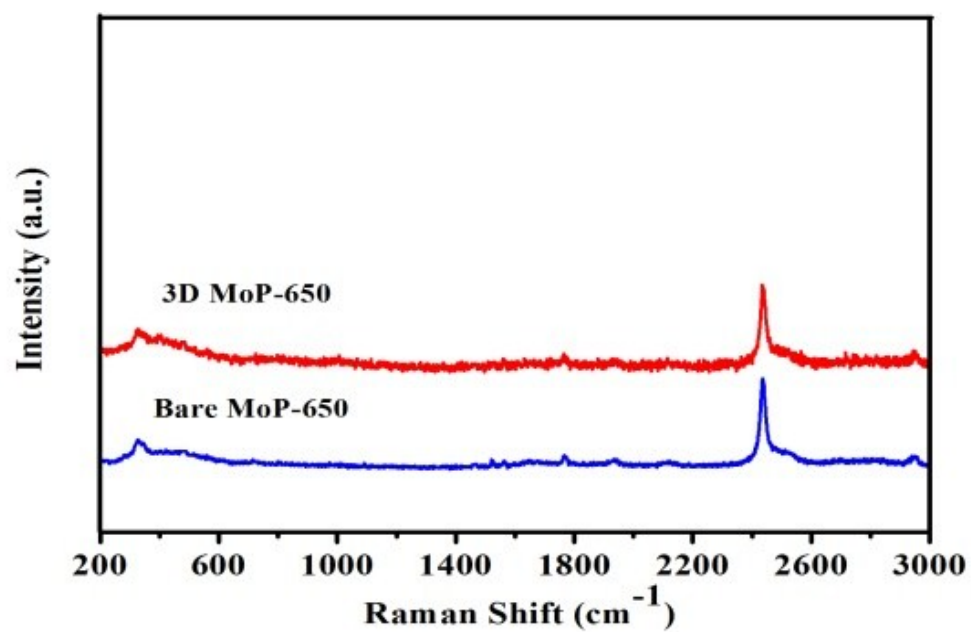


Fig. S3 The Raman spectra of 3D MoP-650 and Bare MoP-650.

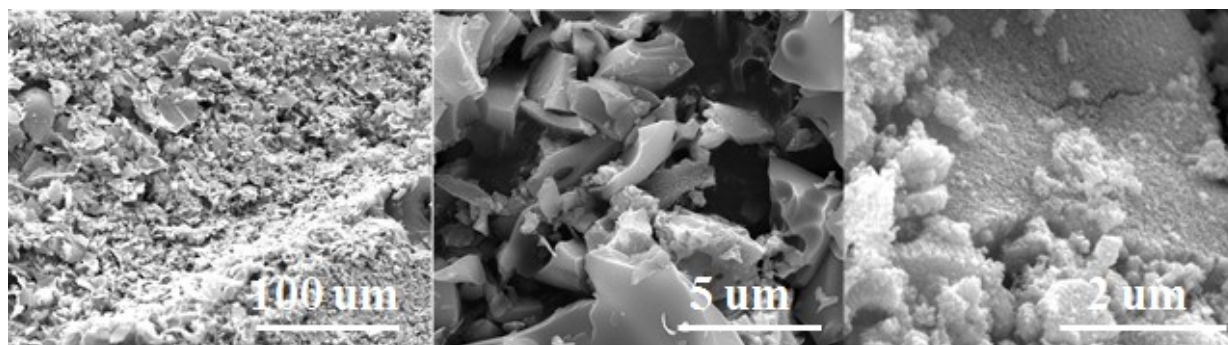


Fig. S4 SEM images of Bare MoP prepared without sponges at 650 °C.

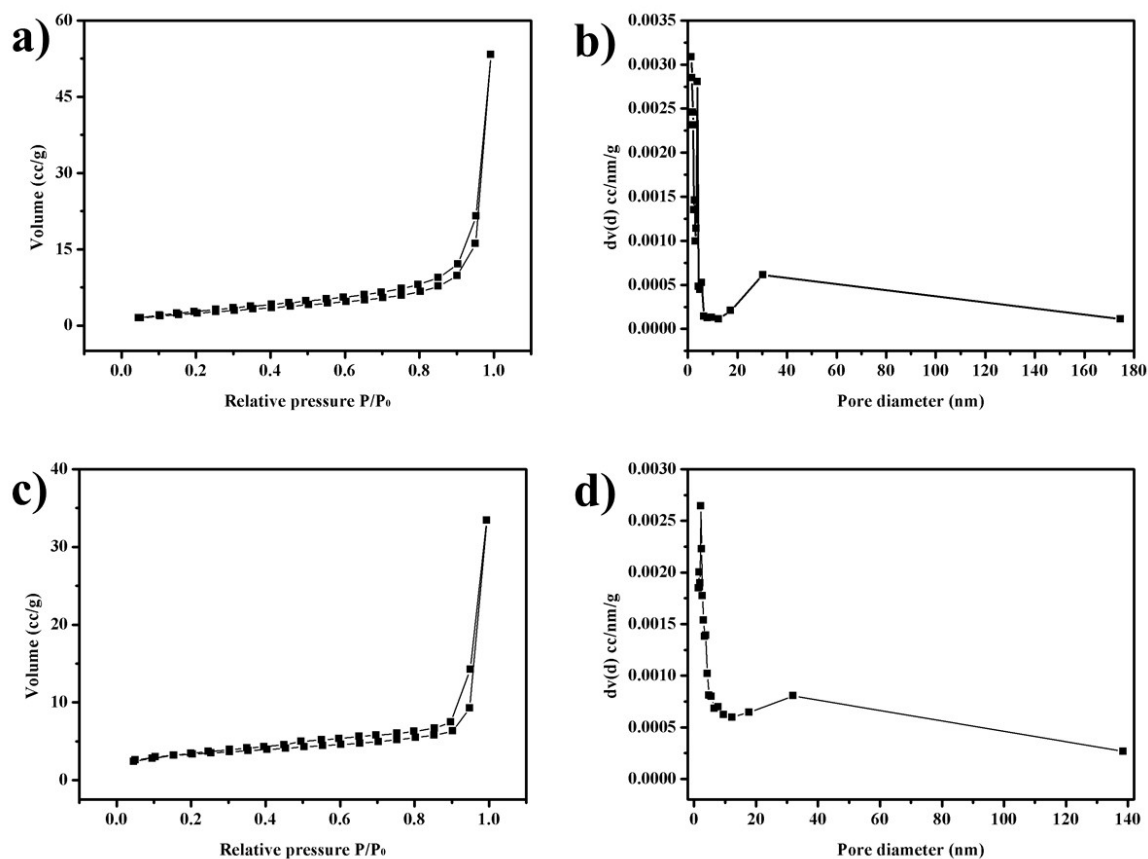


Fig. S5 Nitrogen adsorption/desorption isotherm plots and the BJH pore-size distribution curves of (a) (b) 3D MoP-650, and (c) (d) Bare MoP-650.

Table S1 Summary of BET tests for all 3D MoP samples.

$T/^\circ\text{C}$	Surface areas / m^2	Average pore sizes /nm	Pore volumes / $\text{cm}^3\cdot\text{g}^{-1}$
550	3.291	12.35	0.013
600	6.185	22.20	0.036
650	11.548	33.48	0.085
700	10.930	32.83	0.098
750	5.103	39.03	0.051
650(Bare)	9.851	17.92	0.052

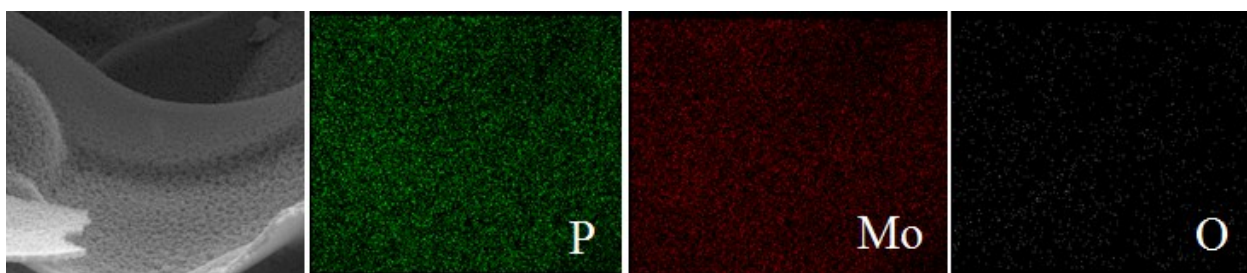


Fig. S6 EDS elemental mappings of Mo, P and O at the surface of 3D MoP-650.

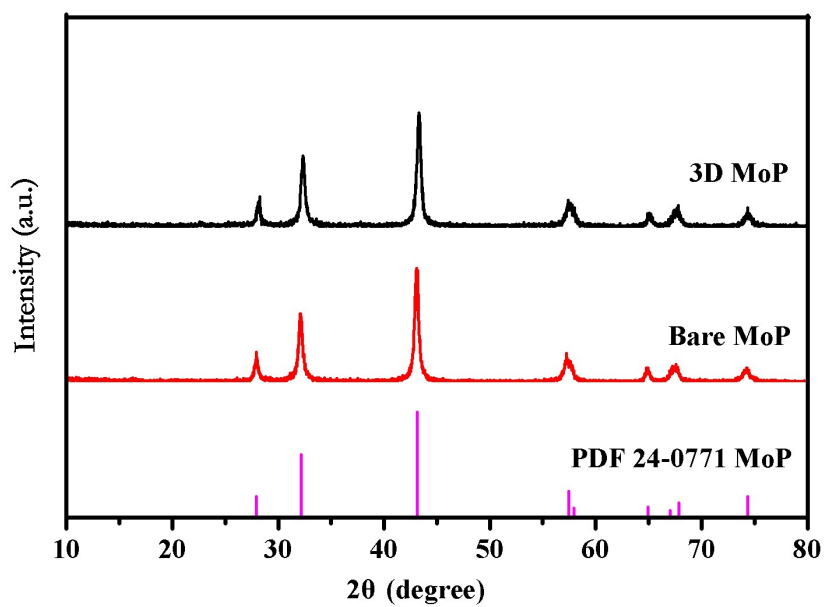


Fig. S7 XRD pattern of Bare MoP-650 and 3D MoP-650.

Table S2 Information of binding energy for 3D MoP prepared at different temperature.

$T/$ $^{\circ}\text{C}$	$n(\text{P}) / n(\text{Mo})$	$\text{Mo}^{\delta+}$	$\text{Mo}^{6+}/$ Mo^{4+}	$\text{Mo}^{\delta+}/\text{Mo}$	$\text{P}^{\delta-}$	P^{5+}	$\text{P}^{\delta-}/\text{P}$
550	-	-	232.3, /	-	-	133.8	-
600	1.26	227.8	232.3, 228.9	33%	129.3	134.0	40%
650	1.23	227.9	232.2, 228.7	50%	129.4	133.8	56%
700	1.22	227.9	232.2, 228.7	51%	129.4	133.8	60%
750	1.19	227.8	232.2, 228.7	59%	129.4	133.8	67%

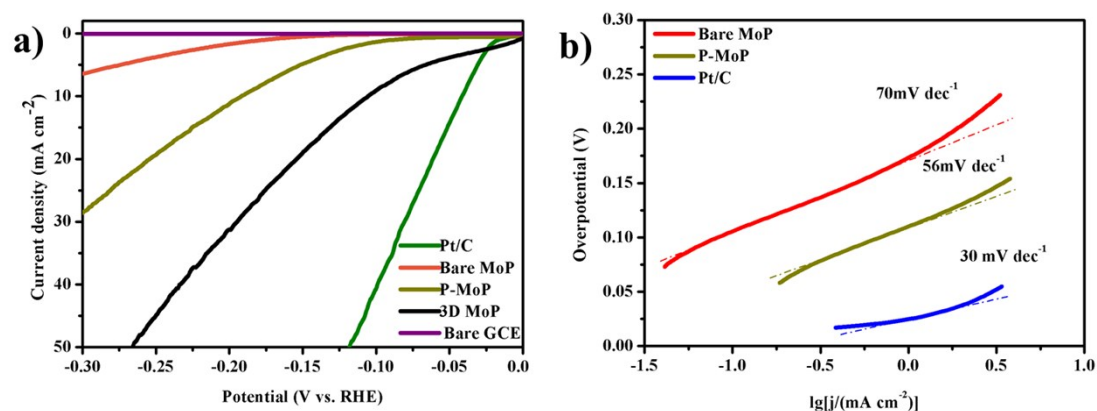


Fig. S8 (a) Linear sweep voltammetry (LSV) curves of Bare GCE, Bare MoP, P-MoP, 3D MoP, and Pt/C in 0.5 M H₂SO₄ at a scan rate of 2 mV s⁻¹. (b) Tafel plots for Bare MoP, P-MoP, and Pt/C.

Table S3 Comparison of HER performance of 3D MoP sponge with other reported Mo-based HER electrocatalysts in acidic media.

Catalyst	Tafel slope (mV/dec)	Current density j (mA cm ⁻²)	η at the corresponding j (mV)	Exchange current density (mA cm ⁻²)	Reference
double-gyriod MoS ₂ /FTO	50	2	190	6.9×10 ⁻⁴	[1]
MoO ₃ -MoS ₂ /FTO	50-60	10	300	8.2×10 ⁻⁵	[2]
metallic MoS ₂ nanosheets	54	10	195	-	[3]
MoS ₂ /graphene/Ni foam	42.8	10	141	-	[4]
MoP	54	30	180	3.4×10 ⁻²	[5]
MoP	60	10	246	4.15×10 ⁻³	[6]
MoP network	54	10	125	8.6×10 ⁻²	[7]
amorphous MoP NPs	45	10	90	1.2×10 ⁻¹	[8]
MoS _x -coated sponge	185	71	200	6.99×10 ⁻³	[9]
bulk Mo ₂ C	-	1	150	1.3×10 ⁻³	[10]
bulk Mo ₂ C	87.6	1	204	6.9×10 ⁻⁴	[11]
Mo ₂ C/CNT	55.2	10	152	1.4×10 ⁻²	[11]
MoN/C	54.5	2	290	3.6×10 ⁻²	[12]
MoS ₂ /CNFs	44	16	230	-	[13]
3D MoP	126	10	105	3.052	This work
		20	155		
P-MoP	56	2	115	1.26×10 ⁻²	This work
		10	191		
MoP-graphite	63	30	300	6.367×10 ⁻²	[14]
MoP nanosheets /CF	56.4	10.1	200	-	[15]

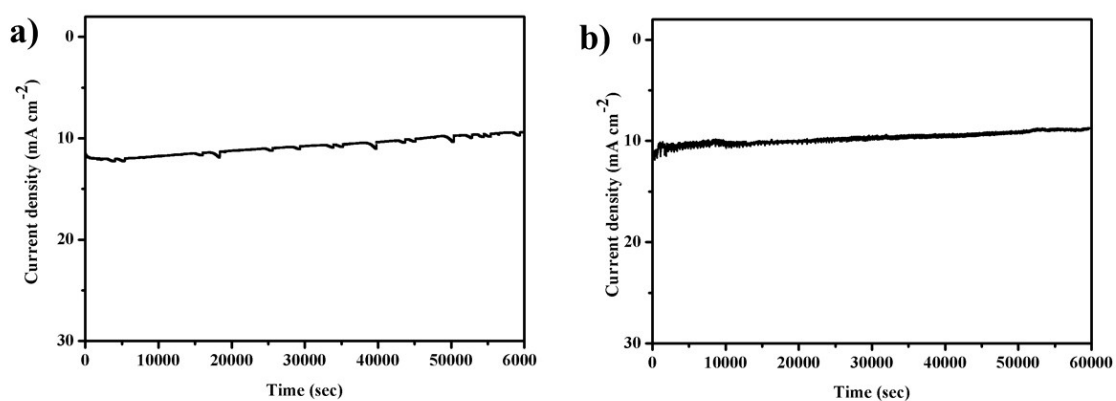


Fig. S9 Time dependence of catalytic current density during electrolysis for (a) P-MoP at an overpotential of 190 mV and (b) Pt/C in 0.5 M H₂SO₄.

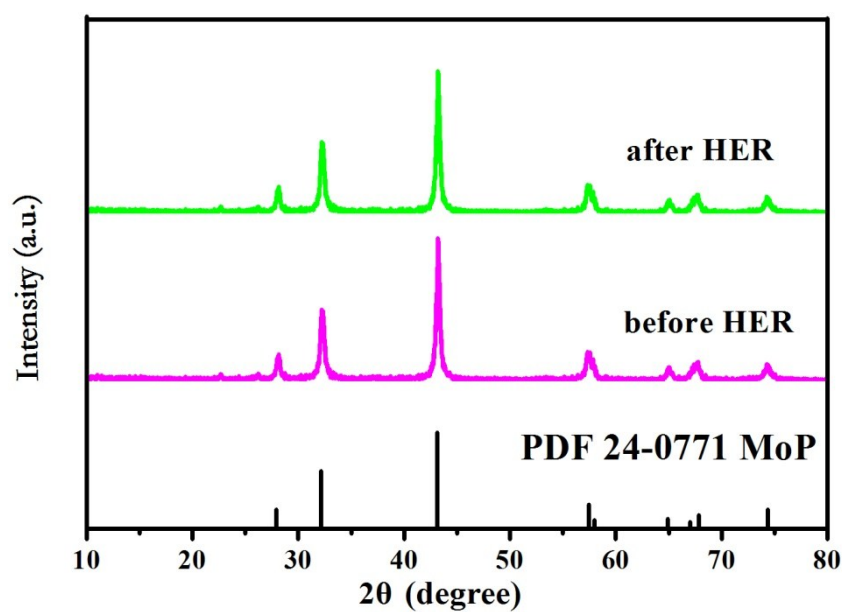


Fig. S10 XRD pattern of 3D MoP-650 before and after long-term stability test.

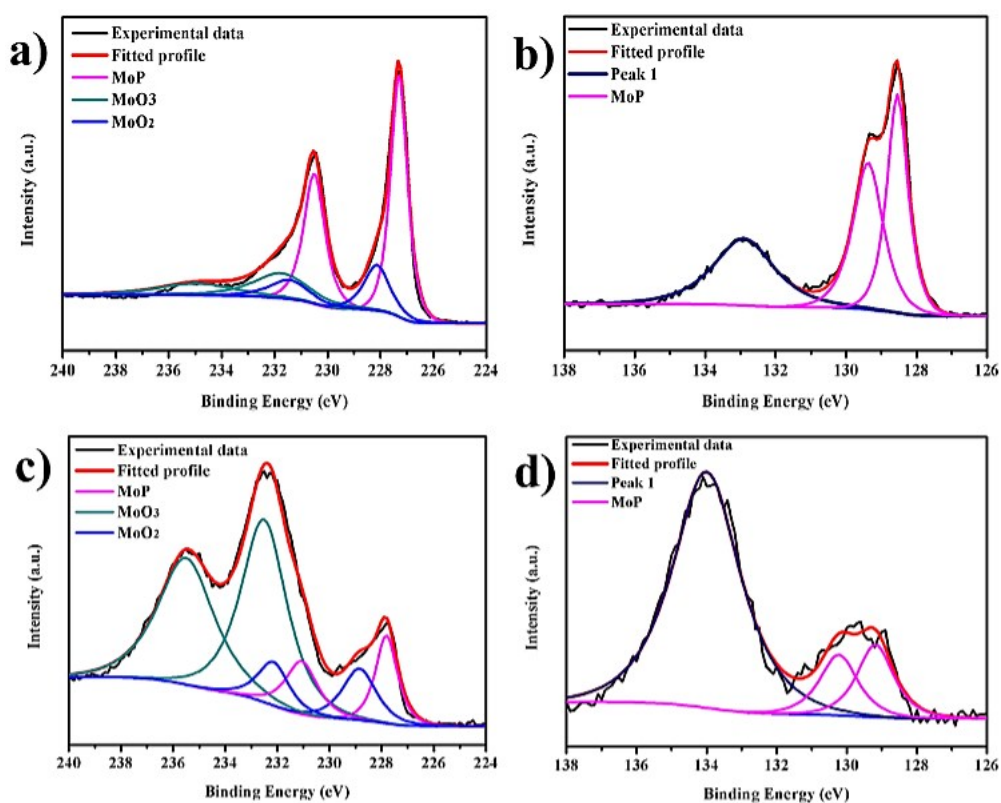


Fig. S11 XPS spectra of Mo 3d and P 2p region for 3D MoP-650 after long-term stability test (a) (b) and 3D MoP-650 after test and long-term storage again (c) (d).

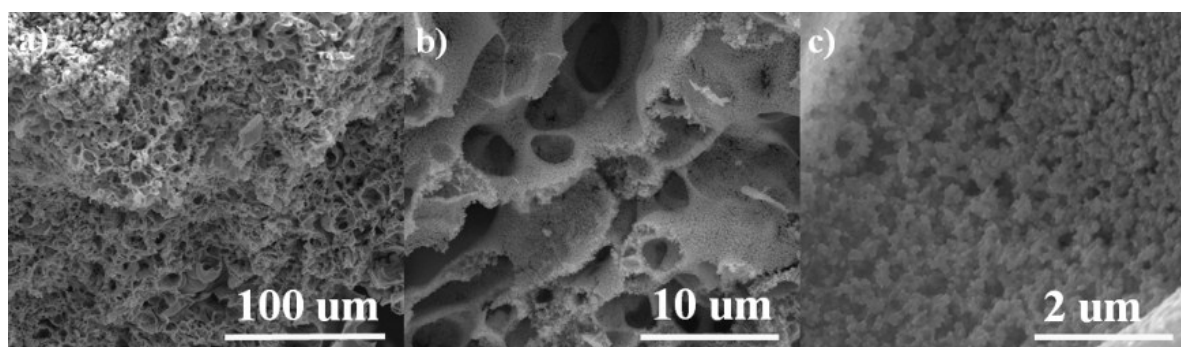


Fig. S12 SEM images of 3D MoP-650 after electrochemical test.

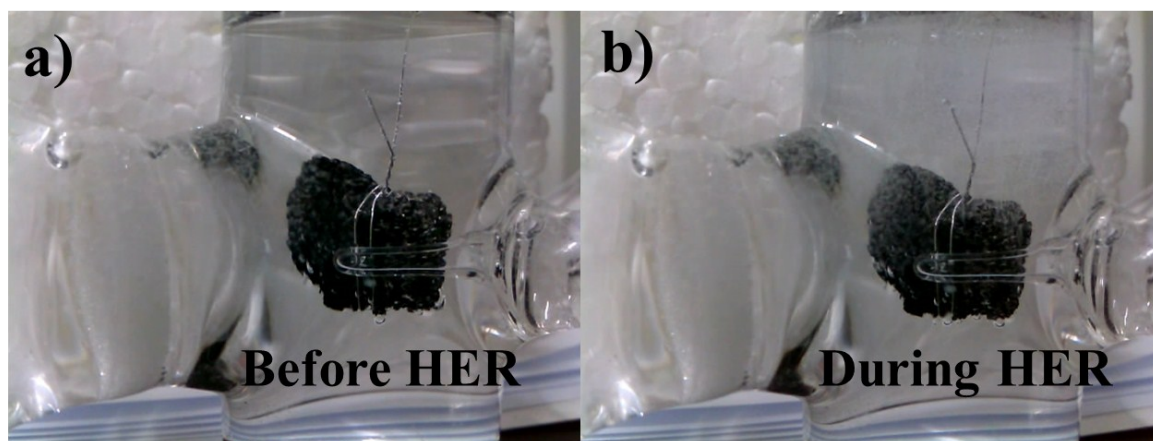


Fig. S13 Optical photos of 3D MoP-650 electrode in the solution (a) before HER (b) during HER.

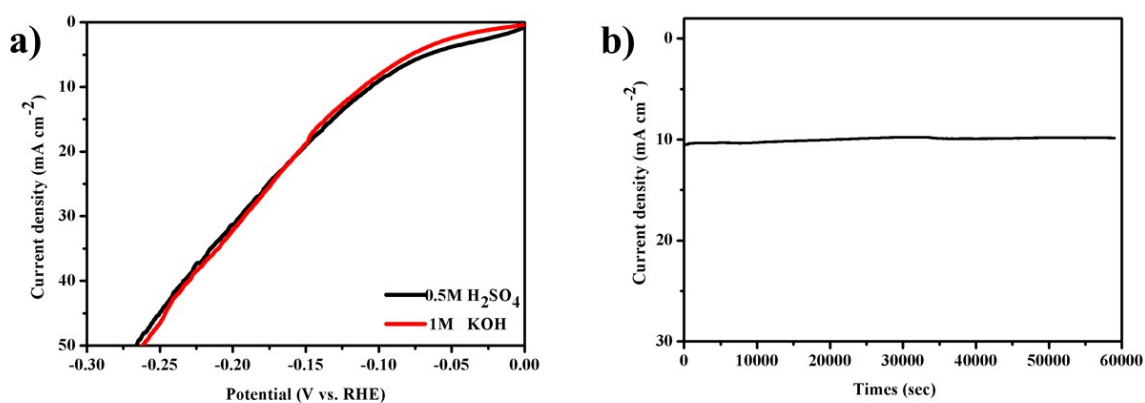


Fig. S14 (a) Linear sweep voltammetry (LSV) curves of 3D MoP-650 in 0.5 H_2SO_4 and in 1 M KOH, respectively, scan rate: 2 mV s^{-1} ; (b) Time dependence of catalytic current density during electrolysis for 3D MoP-650 in 1 M KOH at an overpotential of 110 mV.

Supplementary Movie

Movie S1 This movie shows the dynamic hydrogen production process at 3D MoP-650 operated from +0.05 V to -0.35 V vs. RHE.

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