Enhanced electrocatalytic activity of *in-situ* carbon encapsulated Molybdenum Phosphide derived from hybrid POM for HER over a wide pH range

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Synthesis of POM-MoP

100 mg of commercial phosphomolybdic acid and 500 mg of sodium hypophosphite were mixed together and followed by calcined at 700 °C for 2h with a heating rate of 5 °C min^{-1} under N_2 atmosphere. The black solid was washed with DI water and ethanol then vacuum dried at 60 °C for overnight

Synthesis of MoP

100 mg of sodium molybdate dihydrate and 500 mg of sodium hypophosphite were mixed together to form a homogeneous mixture. The obtained mixture was calcined at 700 °C for 2h with ramping range of 5 °C min^{-1} under N_2 atmosphere. The final product was washed with DI water and ethanol then vacuum dried at 60 °C for overnight.

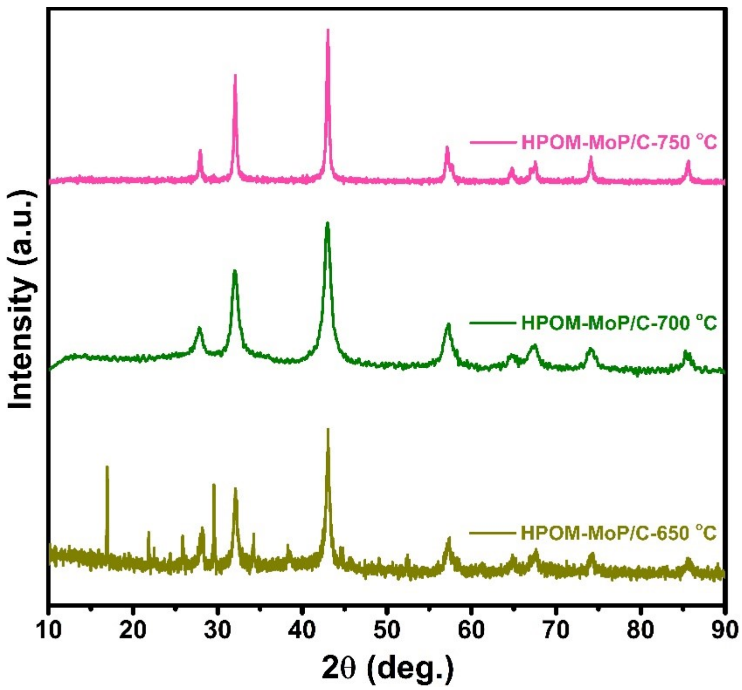

Fig. S1 Powder XRD profiles of HPOM-MOP/C-650 °C, HPOM-MOP/C-700 °C, and HPOM-MOP/C-750 °C.

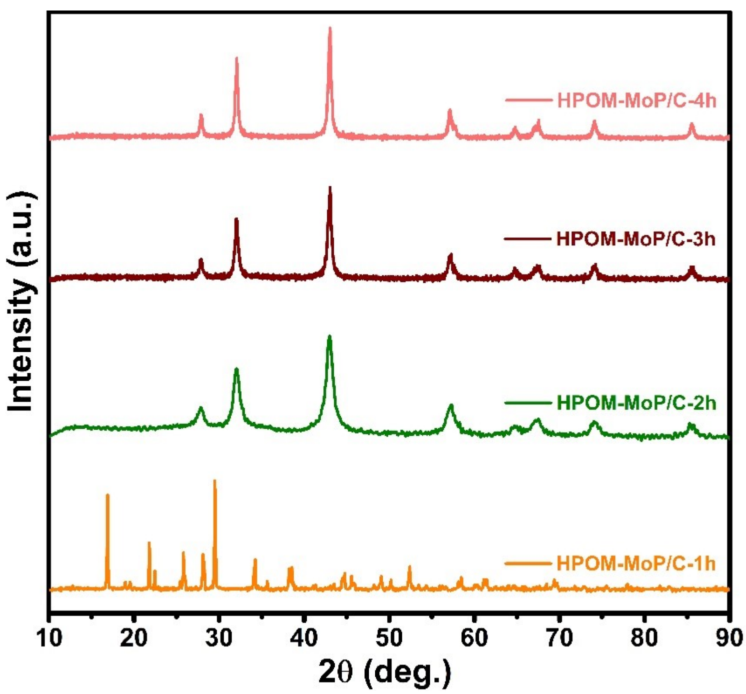

Fig. S2 Powder XRD profiles of HPOM-MOP/C-1 h, HPOM-MOP/C-2 h, HPOM-MOP/C-3 h and HPOM-MOP/C-4 h.

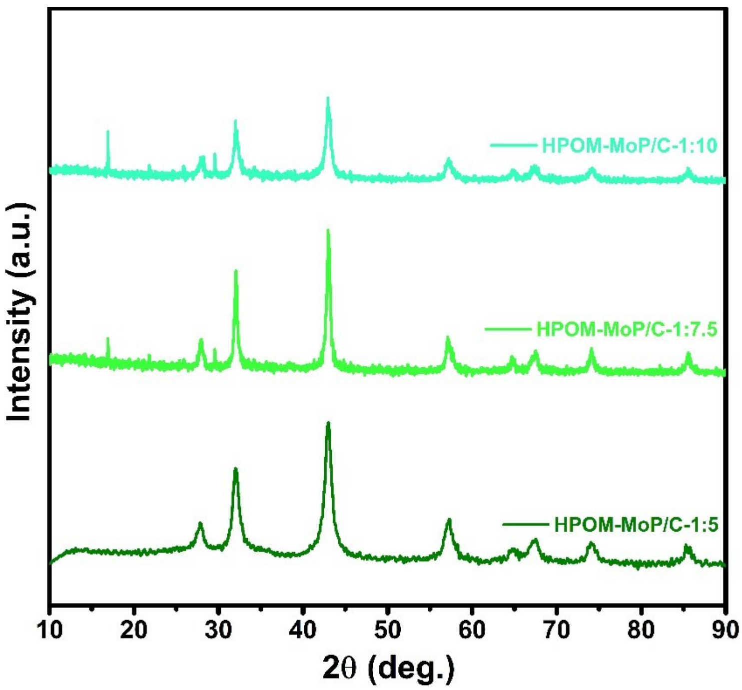

Fig. S3 Powder XRD profiles of HPOM-MOP/C-1:5, HPOM-MOP/C-1:7.5, and HPOM-MOP/C-1:10.

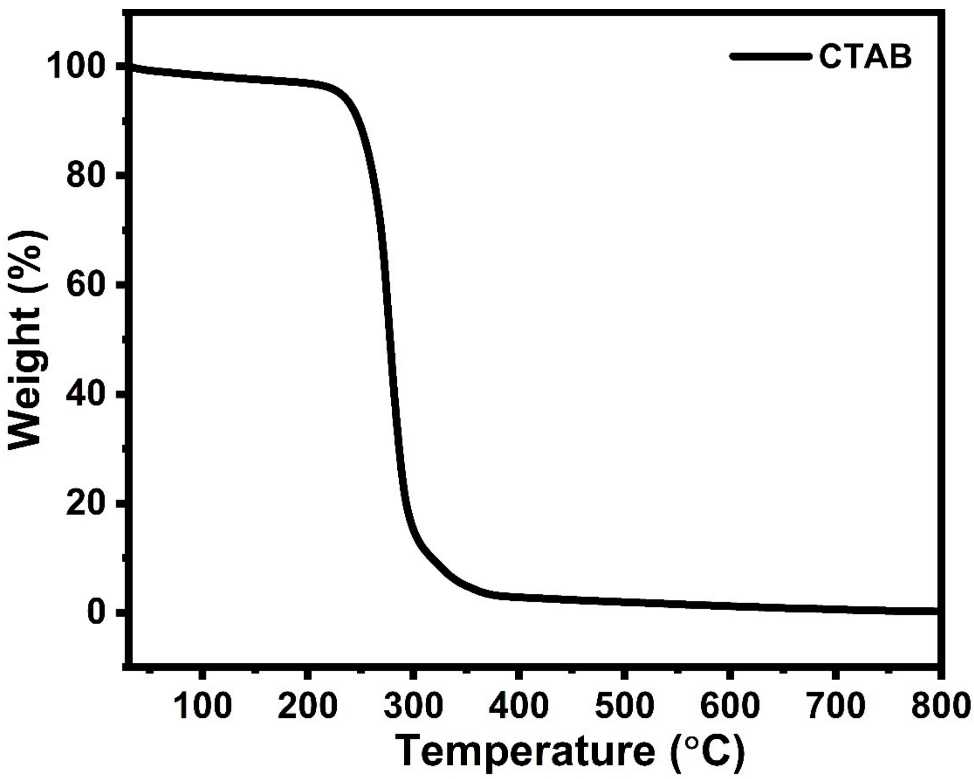

Fig. S4 TGA curve of cetyltrimethylammonium bromide (CTAB).

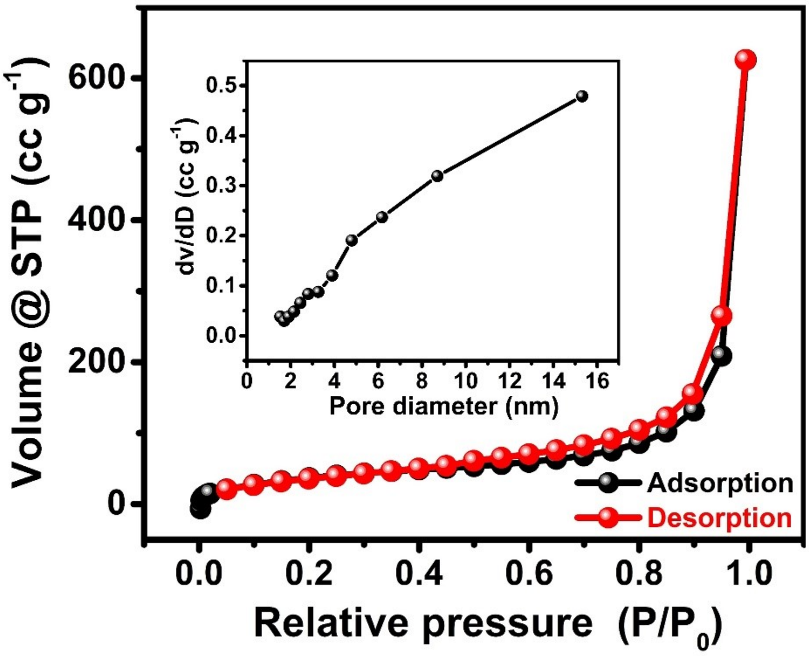

Fig. S5 BET N_2 adsorption and desorption isotherm curves of HPOM-MoP/C with inset image showing the pore size distribution curves.

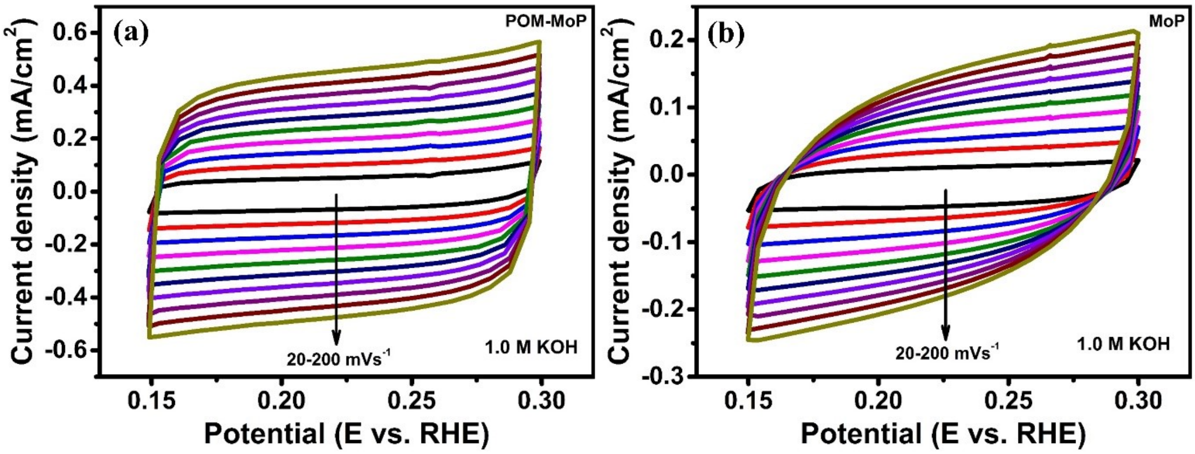

Fig. S6 Cyclic voltammetry graphs for **(a)** POM-MoP and **(b)** MoP in the HER region of 0.15 to 0.30 V vs. RHE in 1.0 M KOH.

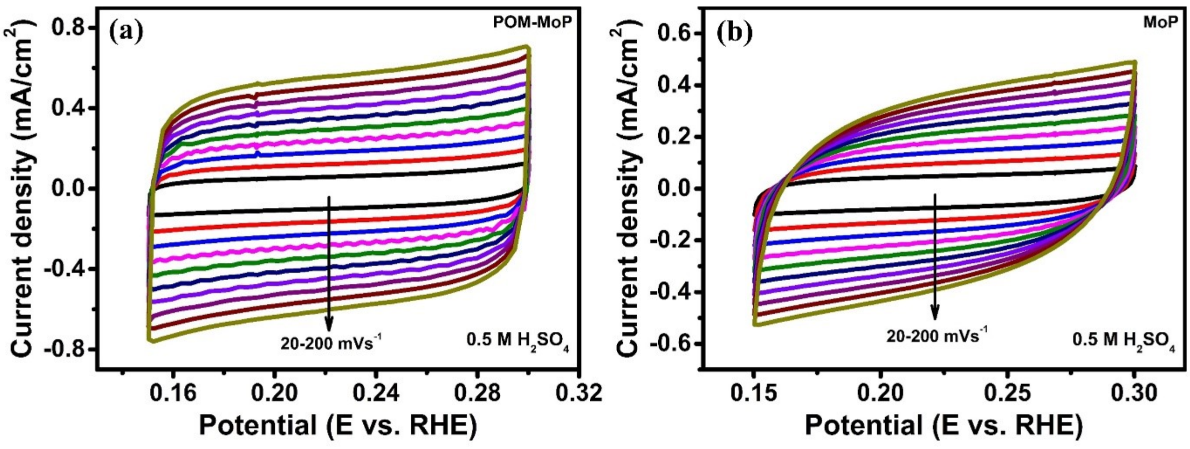

Fig. S7 Cyclic voltammetry graphs for **(a)** POM-MoP and **(b)** MoP in the HER region of 0.15 to 0.30 V vs. RHE in 0.5 M H_2SO_4.

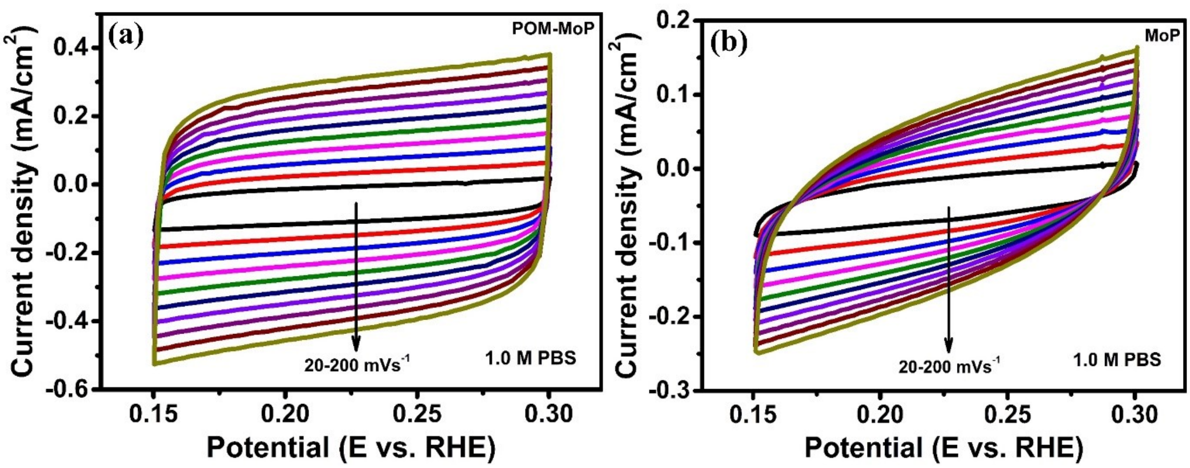

Fig. S8 Cyclic voltammetry graphs for **(a)** POM-MoP and **(b)** MoP in the HER region of 0.15 to 0.30 V vs. RHE in 1.0 M PBS.

Calculation of TOF

The HER Turn over frequency (TOF) of the HPOM-MoP/C electrocatalyst were determined by the following equations.

$$n = \frac{m_{mass}}{M}$$

Where, n is the number of moles of active sites on the working electrode, m_{mass} is the mass loading of the active materials and M is the molar mass of the active materials.

Then we can calculate the TOF using the following equation,

$$TOF = \frac{JA}{2Fn}$$

Where, J is the current density at the overpotential of 200 mV in A/cm^2, A is the area of the working electrode (0.196 cm^2), 2 represents the stoichiometric number of electrons consumed in the electrode HER reaction and F is the Faraday constant (96485 C mol^{-1}).

Table S1. Comparison of HER performance with existing POM based MoP catalysts in acidic, alkaline and neutral medium

Catalyst	Particle diameters	Morphology	Over potential (mV) @ 10 mA cm^{-2}			Reference
			Acid (0.5 M H_2SO_4)	Alkaline (1.0 M KOH)	Neutral (1.0 M PBS)	
MoP@NPC/rGO	~ 500 nm	Rod-like	218	NA	NA	1
MoP@PC-CNTs	~ 200 nm	Nano spherical	220	NA	NA	2
CQDs/MoP	20 nm	Irregular Particles	NA	210 @ η_{20}	NA	3
MoP - 700	8-30 nm	Nanoparticles	NA	NA	196	4
MoP@PC	~ 200 nm	Polyhedral	258	NA	NA	5
MoP/rGO	3 nm	Cluster-like	119	140	NA	6
MoP/NC	1.5–3 µm	Microflower	120	170	NA	7
MoP@NC	50 to 65 nm	Hollow Quasi-Spherical	52	106	171	8
α-MoC_{1-x}-MoP/C	2 nm to 5 nm	Ultrafine Nanoparticles	173	NA	NA	9
HPOM-MoP/C	15-20 nm	Spherical	163	135	166	This work

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