Electronic Supplementary information:

Surface Engineering-modulated Porous N-doped Rod-like Molybdenum Phosphide Catalysts: towards High Activity and Stability for Hydrogen Evolution Reaction over a Wide pH Range

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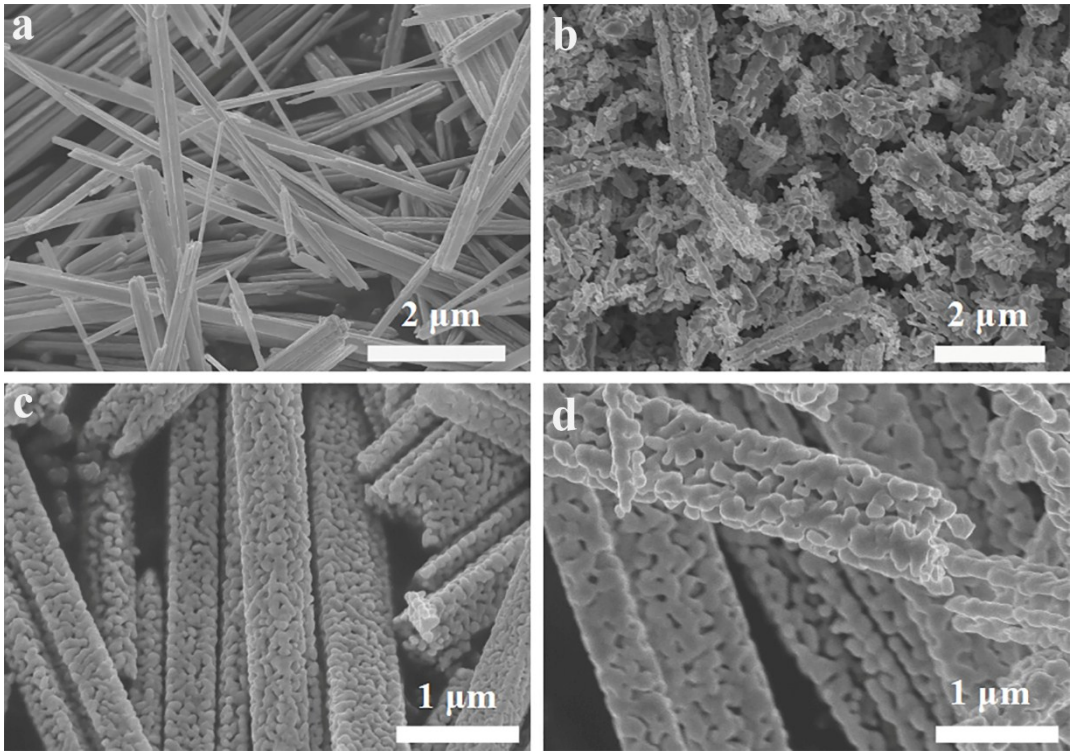

Figure S1. FESEM images of (a) Mo_3O_{10}/EDA, (b) MoP, (c) N-MoP-750 and (d) N-MoP-850.

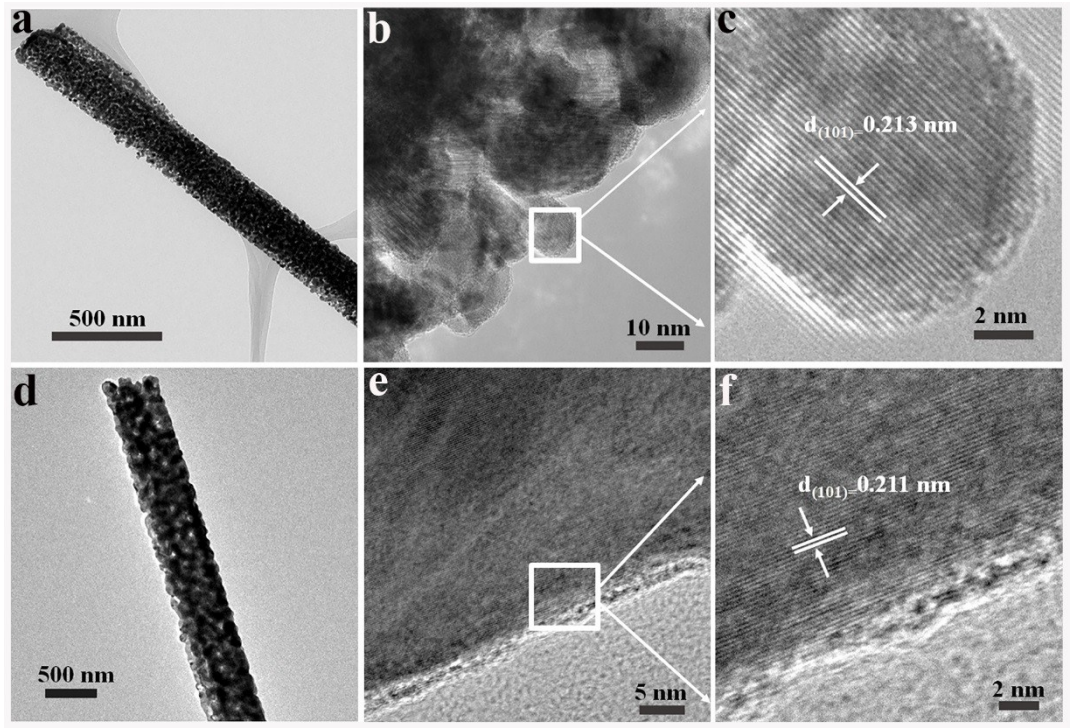

Figure S2. (a, b) TEM images of N-MoP-750; (d, e) TEM images of N-MoP-850; (c) and (f) are HRTEM images of a part of N-MoP-750 in (b) and N-MoP-850 in (f),

respectively.

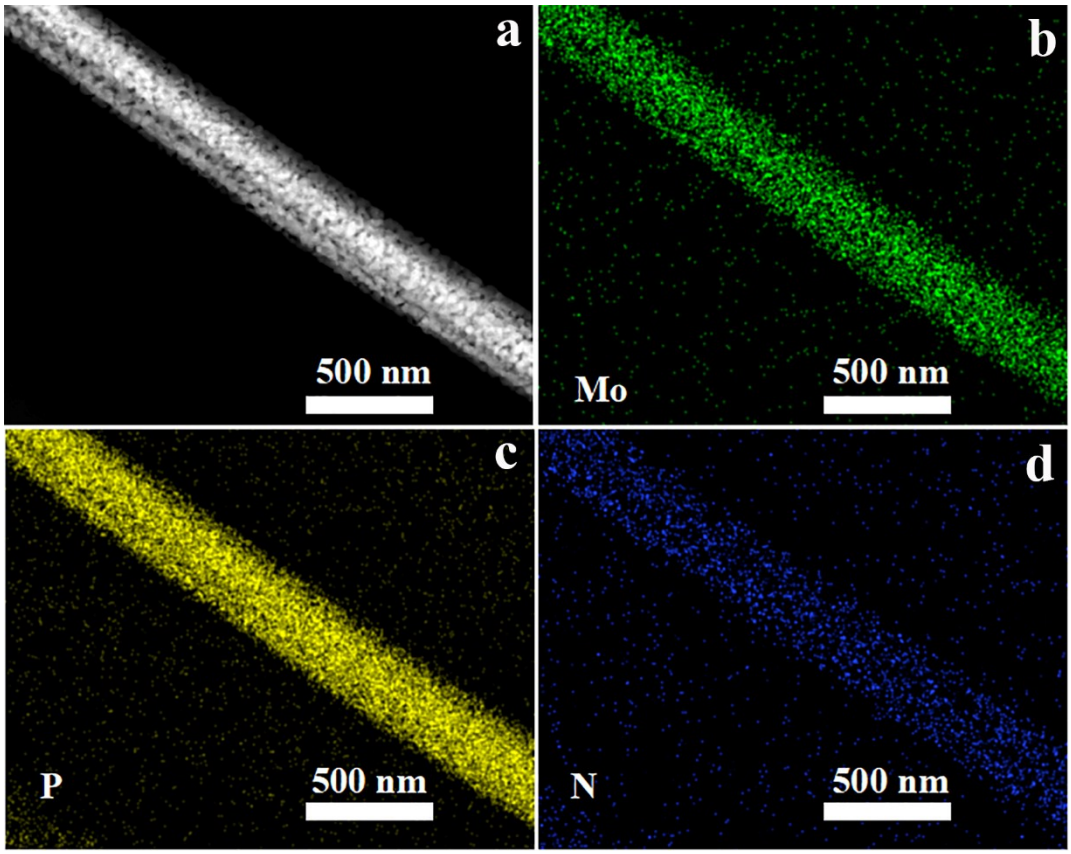

Figure S3. Element mapping analysis for N-MoP-750 sample, a) HADDF image; b) mapping image of Mo element; c) mapping image of P element; d) mapping image of N element.

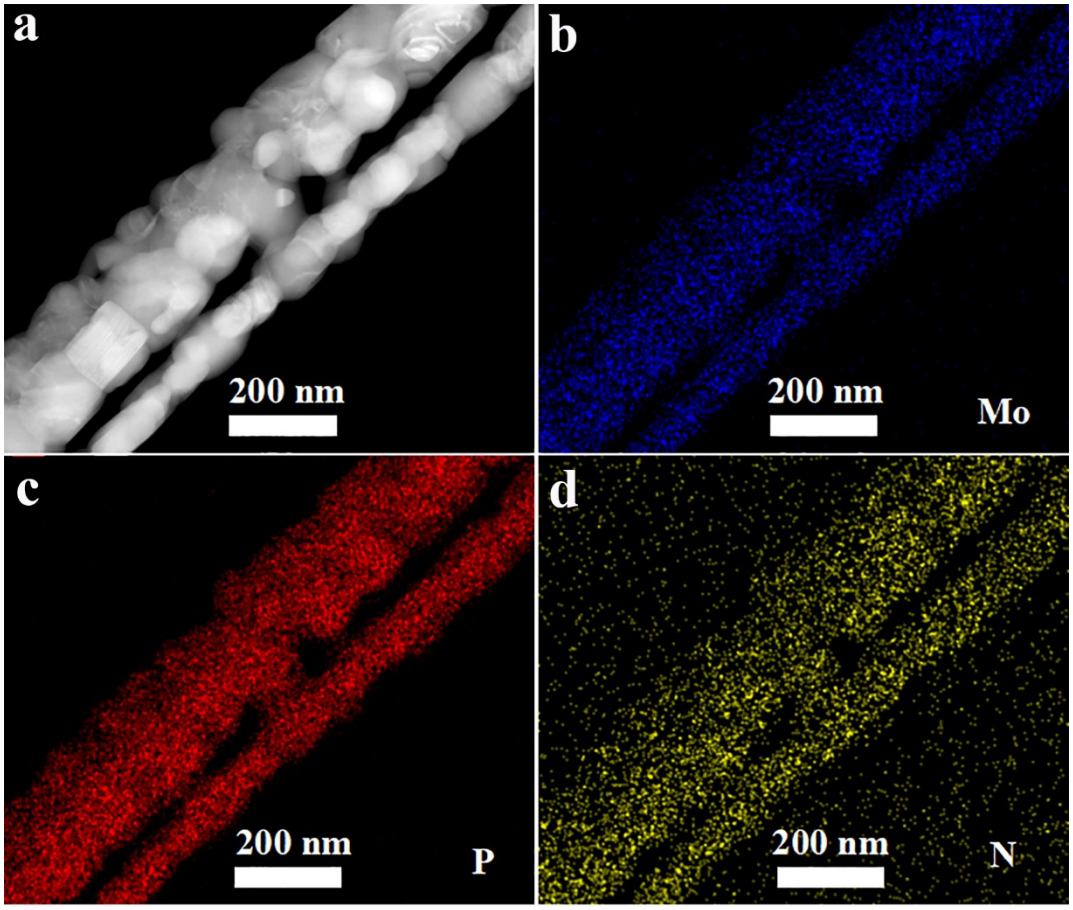

Figure S4. Element mapping analysis for N-MoP-850 sample, a) HADDF image; b) mapping image of Mo element; c) mapping image of P element; d) mapping image of N element.

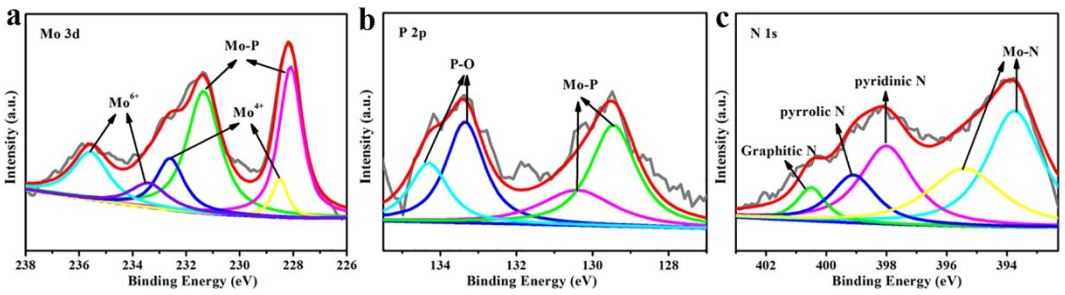

Figure S5. High resolution XPS spectra of (a) Mo 3d, (b) P 2p and (c) N 1s for N-MoP-750 sample.

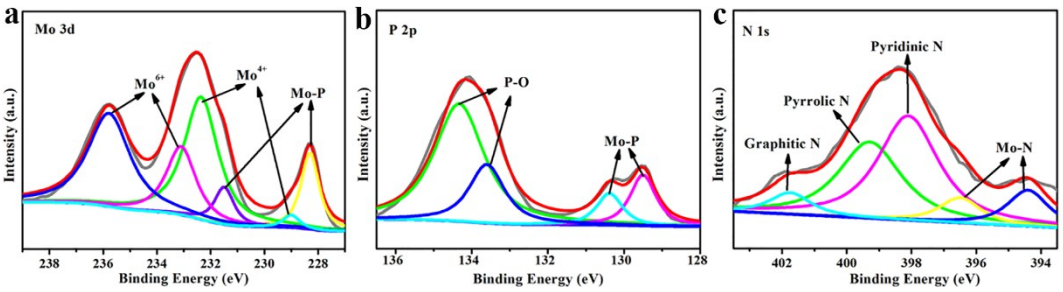

Figure S6. High resolution XPS spectra of (a) Mo 3d, (b) P 2p and (c) N 1s for N-MoP-850 sample.

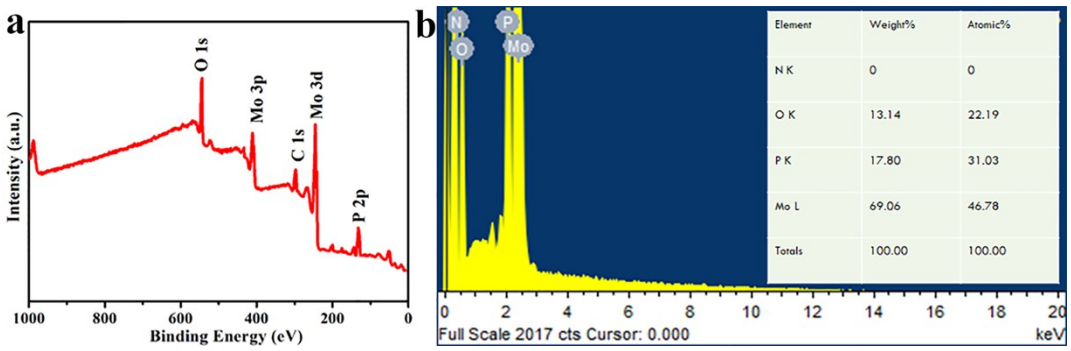

Figure S7. (a) XPS survey spectrum of MoP. (b) EDS pattern of MoP.

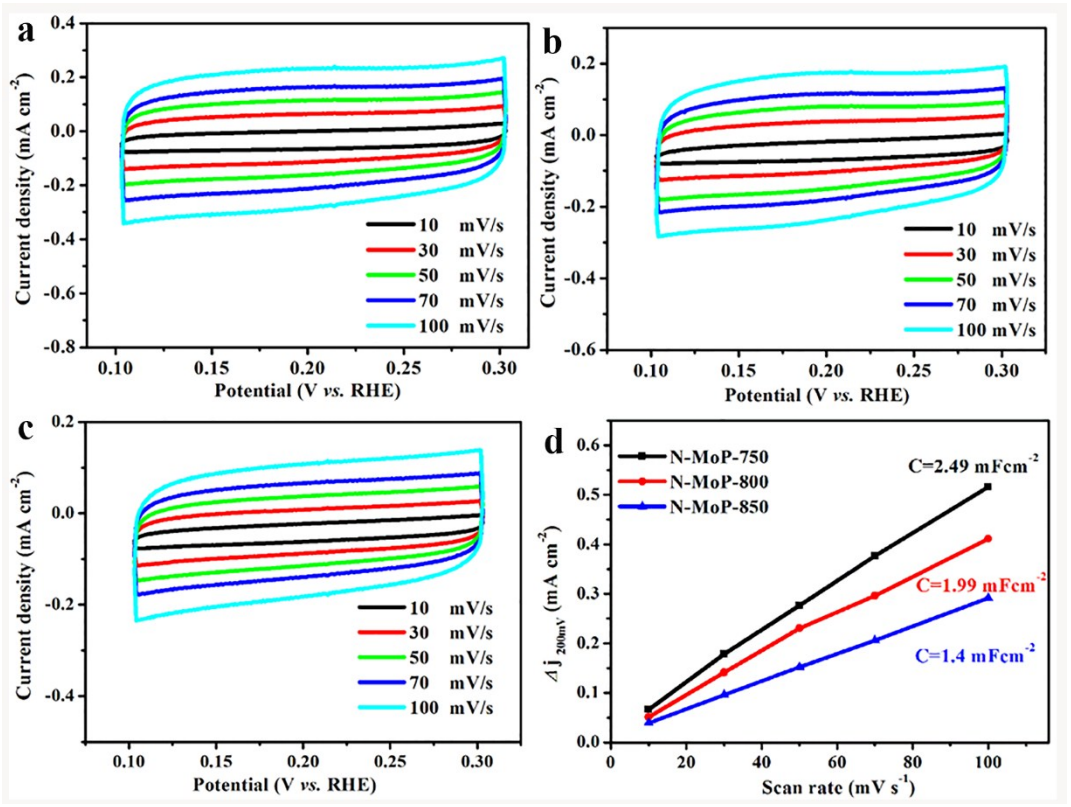

Figure S8. CV curves for (a) N-MoP-750; (b) N-MoP-800 and (c) N-MoP-850 at different rates from 10 to 100 mV s^{-1} in 1 M KOH; (d) the relationship curve between capacitive current and scan rate for N-MoP-750, N-MoP-800 and N-MoP-850 at 0.2 V ($\Delta j = j_a - j_c$).

Table S1. Comparison of HER performance of N-MoP with previously reported MoP based electrocatalysts in acid and basic media

Catalyst	Onset η (mV)	η (mV) (at 10 mA/cm^{-2})	Tafer Slope (mV/dec)	Electrolyte solution	Ref.
N-doped MoP nanorod	65	136 (10)	58.66	0.5 M H_2SO_4	This work
	68	145 (10)	71.15	1M KOH	
MoP@NC	80	135 (10)	57	0.5 M H_2SO_4	1
MoP NPs	—	225(10)	65	0.5 M H_2SO_4	2
	—	276(10)	105	1.0 M KOH	
P-MoP	60	191 (10)	56	0.5 M H_2SO_4	3
MoP-graphite nanosheets	320 (VS Ag/AgCl)	460 (10) (VS Ag/AgCl)	63	0.5 M H_2SO_4	4
Electrochemically activated MoP	80	150 (10)	50	0.5 M H_2SO_4	5
	—	190 (10)	—	1.0 M KOH	
MoP	100	246 (10)	60	0.5 M H_2SO_4	6
$MoS_{2(1-x)}P_x$	—	150 (10)	57	0.5 M H_2SO_4	7
TPC–MoPs	65	126(10)	68.5	0.5 M H_2SO_4	8
CoMoP	85	215	50	0.5 M H_2SO_4	9
rGO-A-MoP	82	152(10)	88	0.5 M H_2SO_4	10
	94	162(10)	57	1.0 M KOH	
MoP/SN	44	104(10)	45.49	0.5 M H_2SO_4	11
	10	94(10)	59.7	1.0 M KOH	
MoP/CC	—	148(10)	55	0.5 M H_2SO_4	12
MoP NPs	—	110(10)	45	0.5 M H_2SO_4	13
MoP-CA2	40	125(10)	54	0.5 M H_2SO_4	14
MoP@PC	48	47(10)	45	0.5 M H_2SO_4	15

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