Supporting Information

Heterostructured CoP/MoO_2 on Mo Foil as High-Efficiency Electrocatalysts for Hydrogen Evolution Reaction in both Acidic and Alkaline Media

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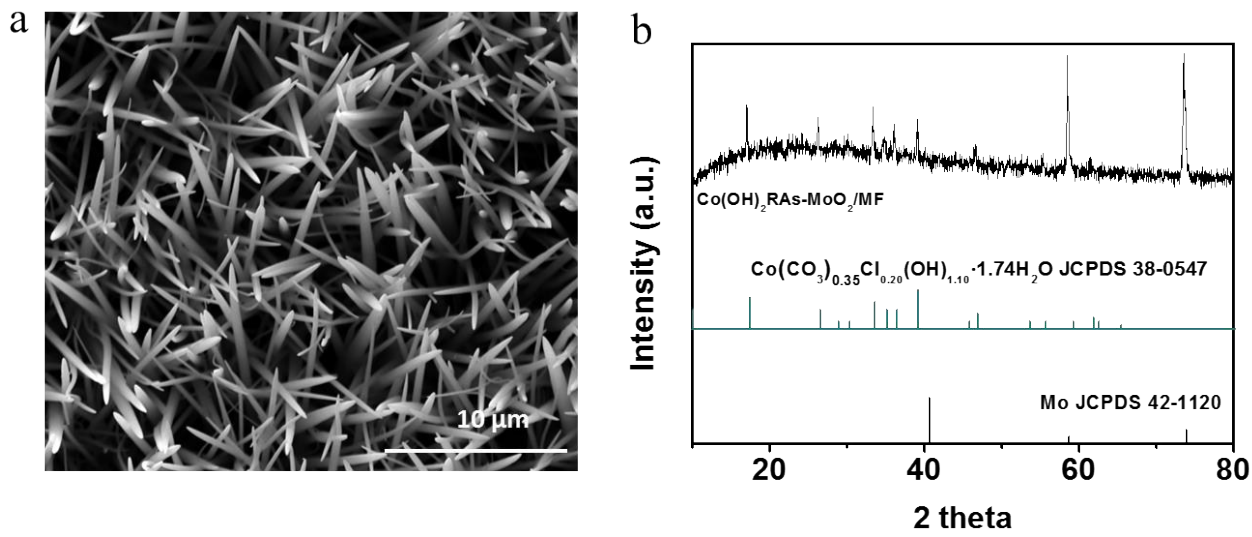

Fig. S1. (a) SEM image of Co precursor-MoO_2/MF, (b) XRD pattern of Co precursor-MoO_2/MF.

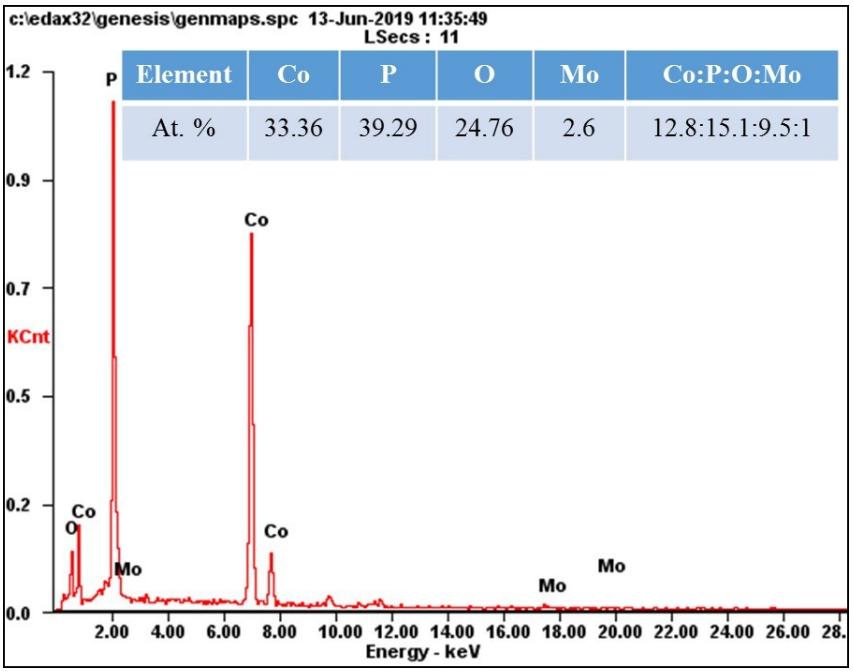

Fig. S2. EDS of CoP-MoO_2/MF

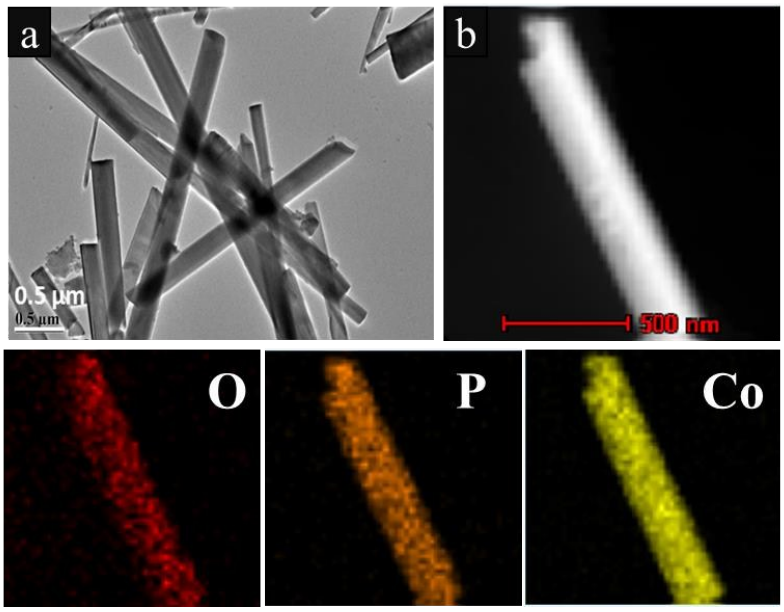

Fig. S3. (a) TEM image of CoP-MoO_2/MF peeling off from the CoP-MoO_2/MF, (b) Elemental mapping of O, P and Co for CoP nanoneedles.

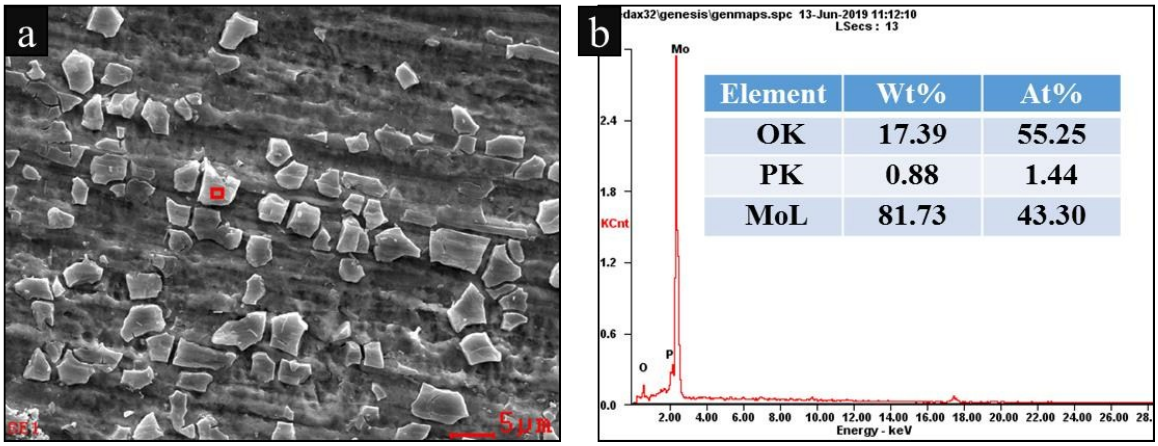

Fig. S4. (a) SEM image of residual CoP-MoO_2/MF after ultrasound treatment and (b) the corresponding EDS.

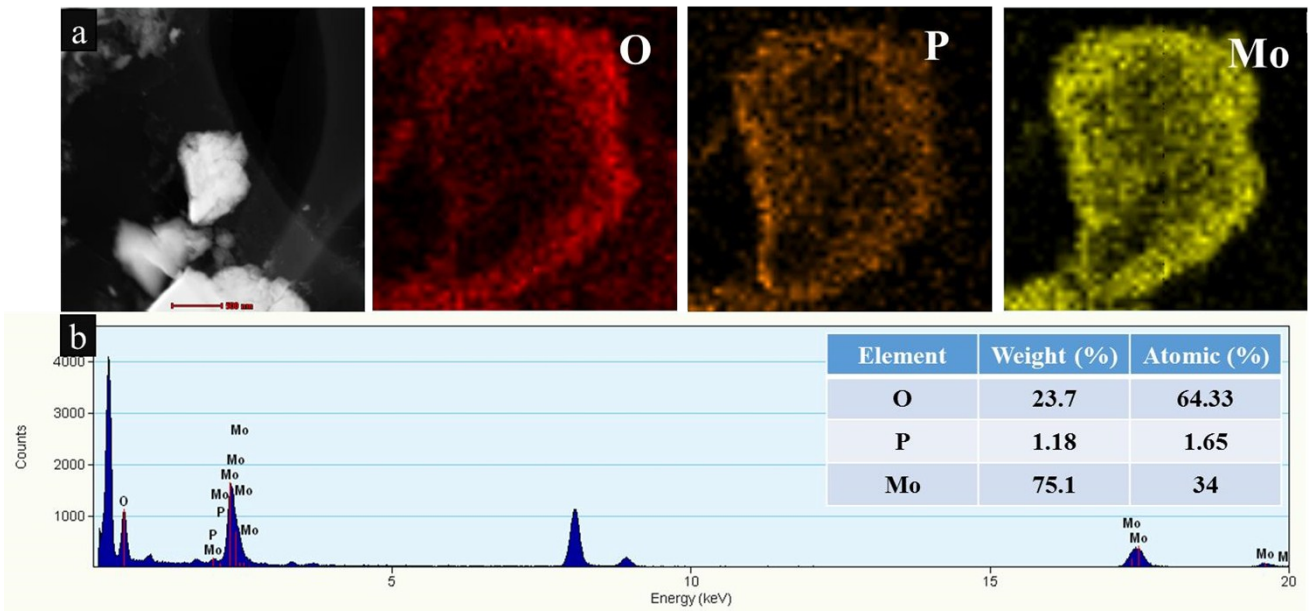

Fig. S5. Elemental mapping of O, P and Mo for P-MoO_2/MF and (b) the corresponding EDS.

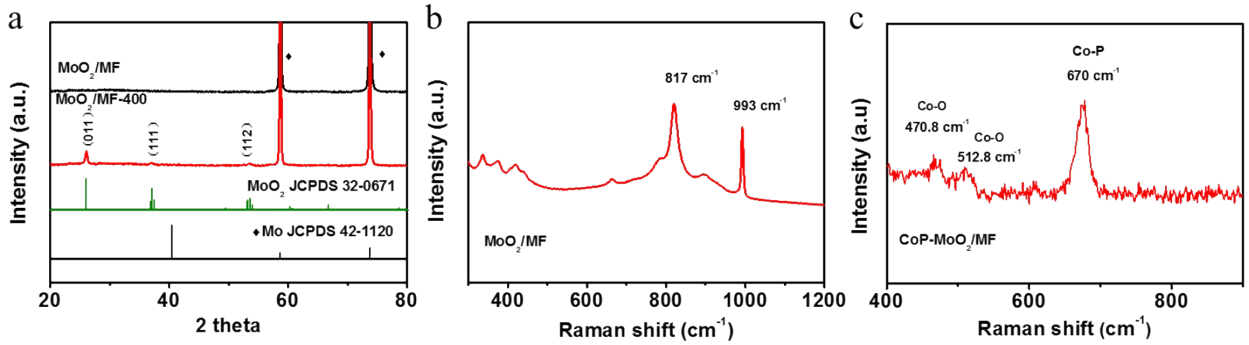

Fig. S6. (a) XRD patterns of MoO2/MF and MoO_2/MF-400. The Raman spectra of (b) MoO_2/MF and (c) CoP-MoO_2/MF.

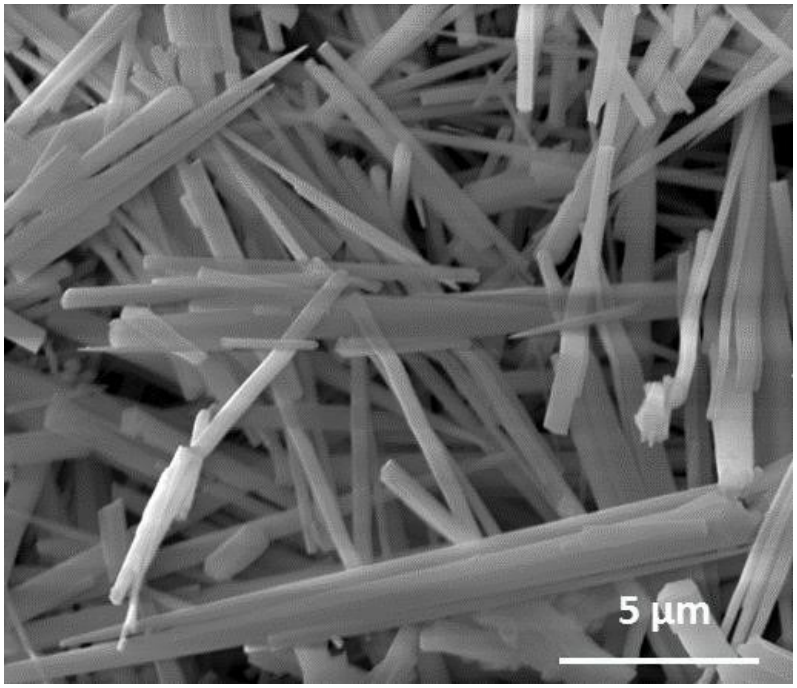

Fig. S7. SEM image of CoP/MF.

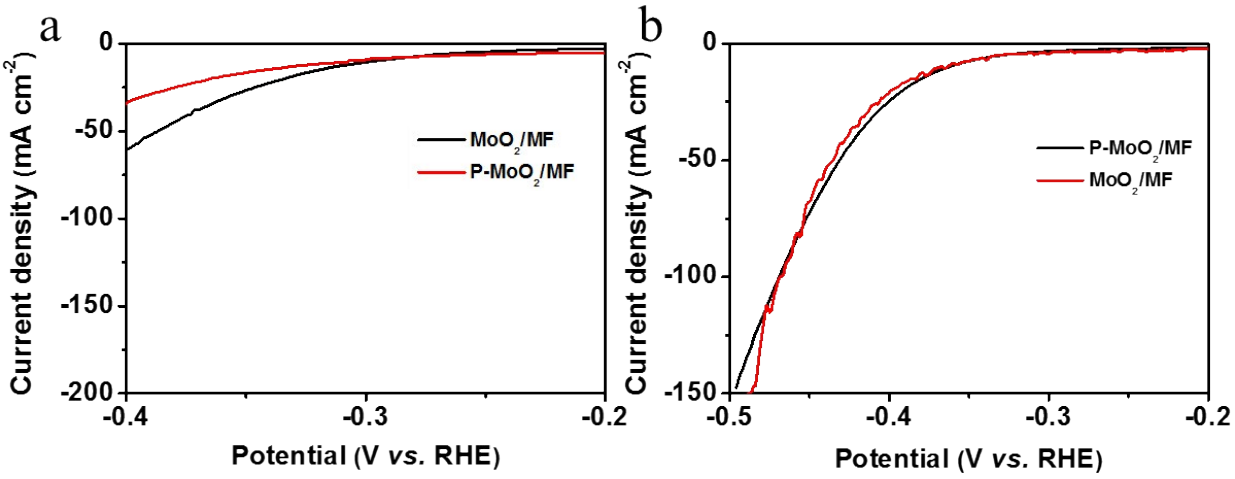

Fig. S8. LSV curves of MoO_2/MF and P-MoO_2/MF in (a) 1.0 M KOH and (b) 0.5 M H_2SO_4 media.

Table S1. HER performance of CoP-MoO_2/MF and several reported representative non-noble metal based electrocatalysts in alkaline solution (1.0 M KOH).

Electrocatalysts	Substrate	Overpotential at 10 mA cm^{-2} (mV)	Ref.
CoP-MoO_2/MF	Mo Foil	42	This work
$(CoP)_{0.54}$-$(FeP)_{0.46}$-NRs/G	Graphene	97	[1]
HNDCM-Co/CoP	Porous Carbon Membrane	135	[2]
$Ni_{0.33}Co_{0.67}Se_2$	Carbon Fiber Paper	106	[3]
CoP/Co-MOF	Carbon Fiber	34	[4]
NiCoP-CoP/NF	Ni Foam	73	[5]
CoP-400-E15	Ti Plate	86	[6]
CoP-CeO_2/Ti	Ti Mesh	43	[7]
CoPS/CP	Carbon Paper	107	[8]
CoNP@C	Carbon Cloth	58	[9]
Mo-doped $Cu_{2.5}CoO_x$	Ni Foam	88	[10]

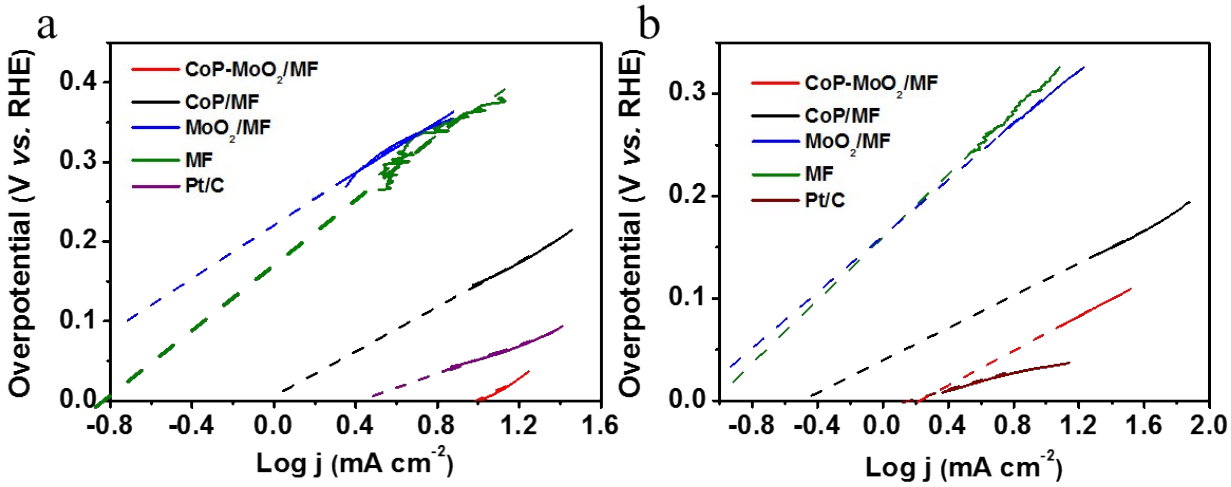

Fig. S9. Calculated exchange current densities by extrapolating the Tafel plots in (a) 1.0 M KOH media and (b) 0.5 M H_2SO_4.

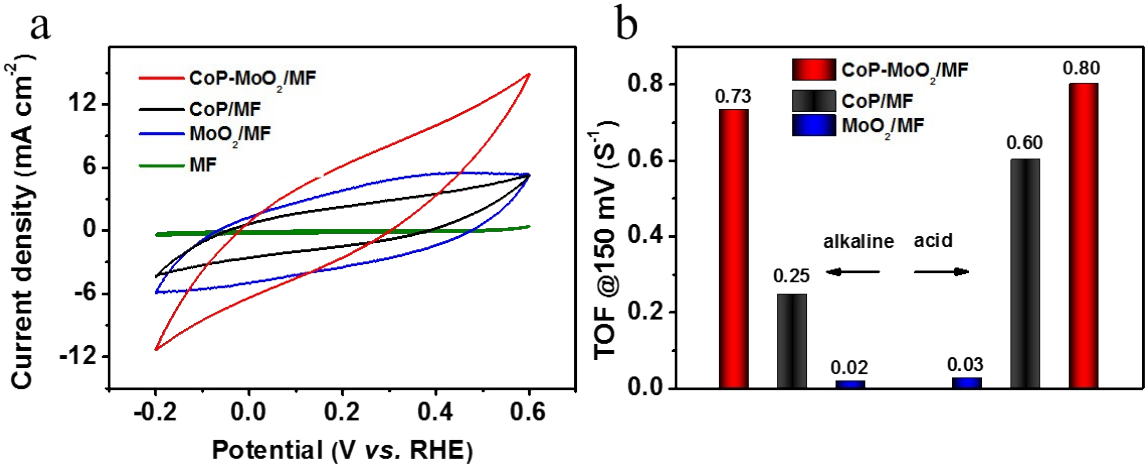

Fig. S10. (a) CV curves recorded between -0.2 V and 0.6 V *vs.* RHE in 1.0 PBS (pH=7) with a scan rate of 50 mV s^{-1}. (b) Calculated turnover frequencies for CoP-MoO_2/MF, CoP/MF, and MoO_2/MF in 1.0 M KOH and 0.5 M H_2SO_4.

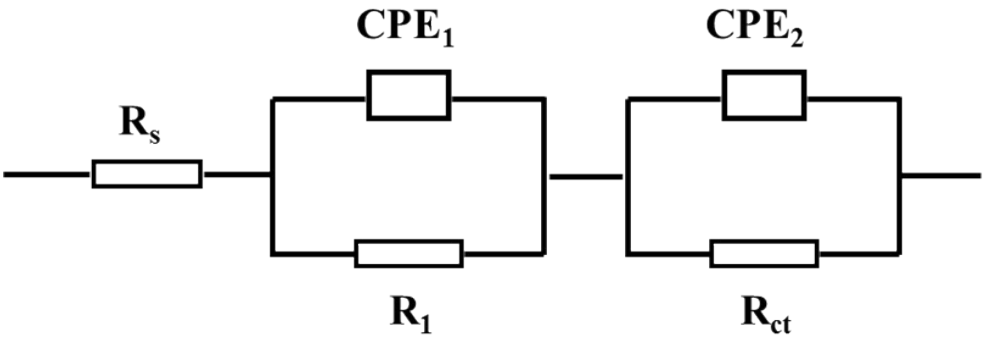

Fig. S11. Electrical equivalent circuit model used for fitting of EIS.

Table S2. Values of elements in equivalent circuit model resulted from fitting the EIS.

Catalysts	Electrolyte	Potential (mV *vs.* RHE)	R_s (Ω)	R_1 (Ω)	R_{ct} (Ω)
$CoP\text{-}MoO_2$/MF	1.0 M KOH	-100	1.42	1.84	2.57
	0.5 M H_2SO_4		1.25	0.11	1.47
CoP/MF	1.0 M KOH	-100	1.68	1.90	23.54
	0.5 M H_2SO_4		1.43	0.20	6.90
MoO_2/MF	1.0 M KOH	-100	1.76	55.45	521.50
	0.5 M H_2SO_4		1.46	0.67	414.30

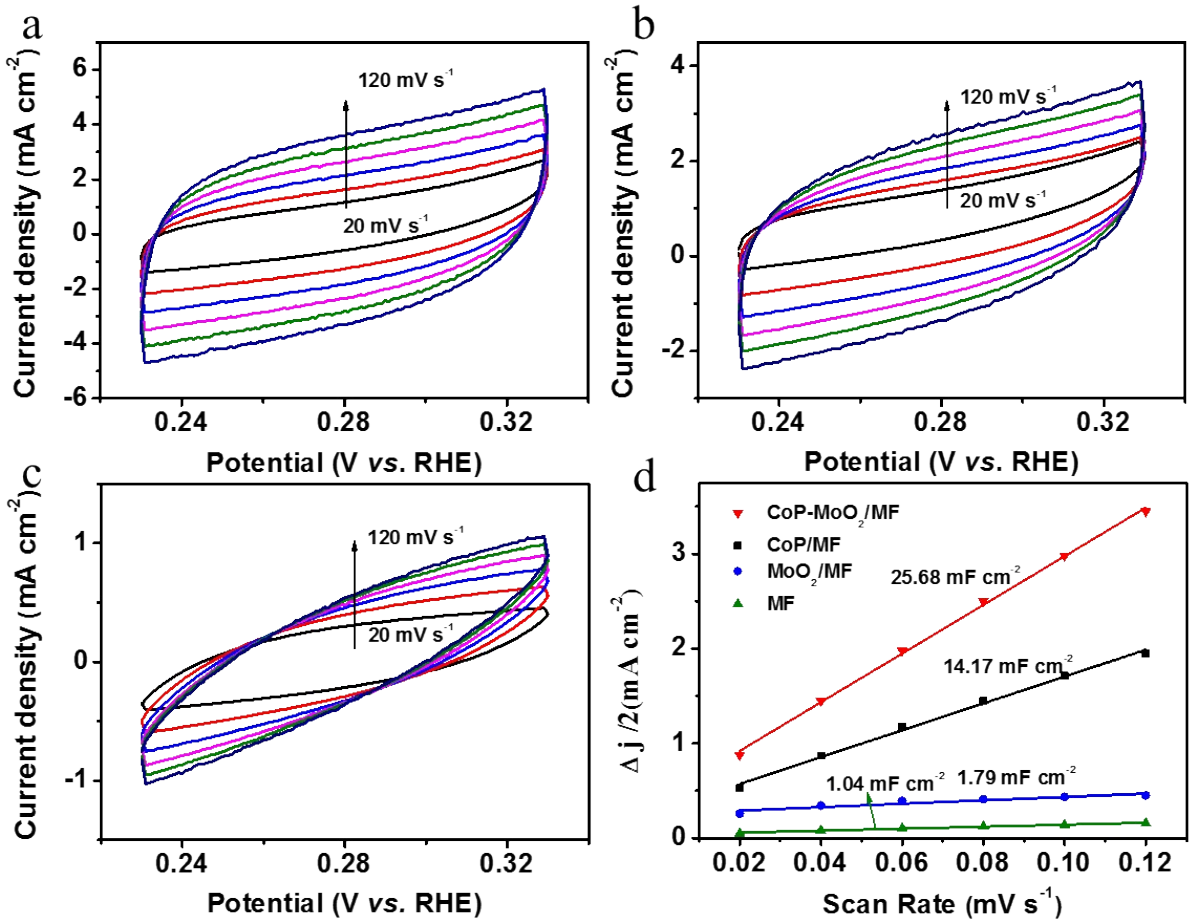

Fig. S12. CVs (0.23-0.33 V *vs.* RHE) of (a) CoP-MoO_2/MF, (b) CoP/MF, (c) MoO_2/MF, (d) The current density at 0.28 V (*vs*. RHE) as a function of scan rate fitted to a linear regression allows for the estimation of C_{dl} in 1.0 M KOH media.

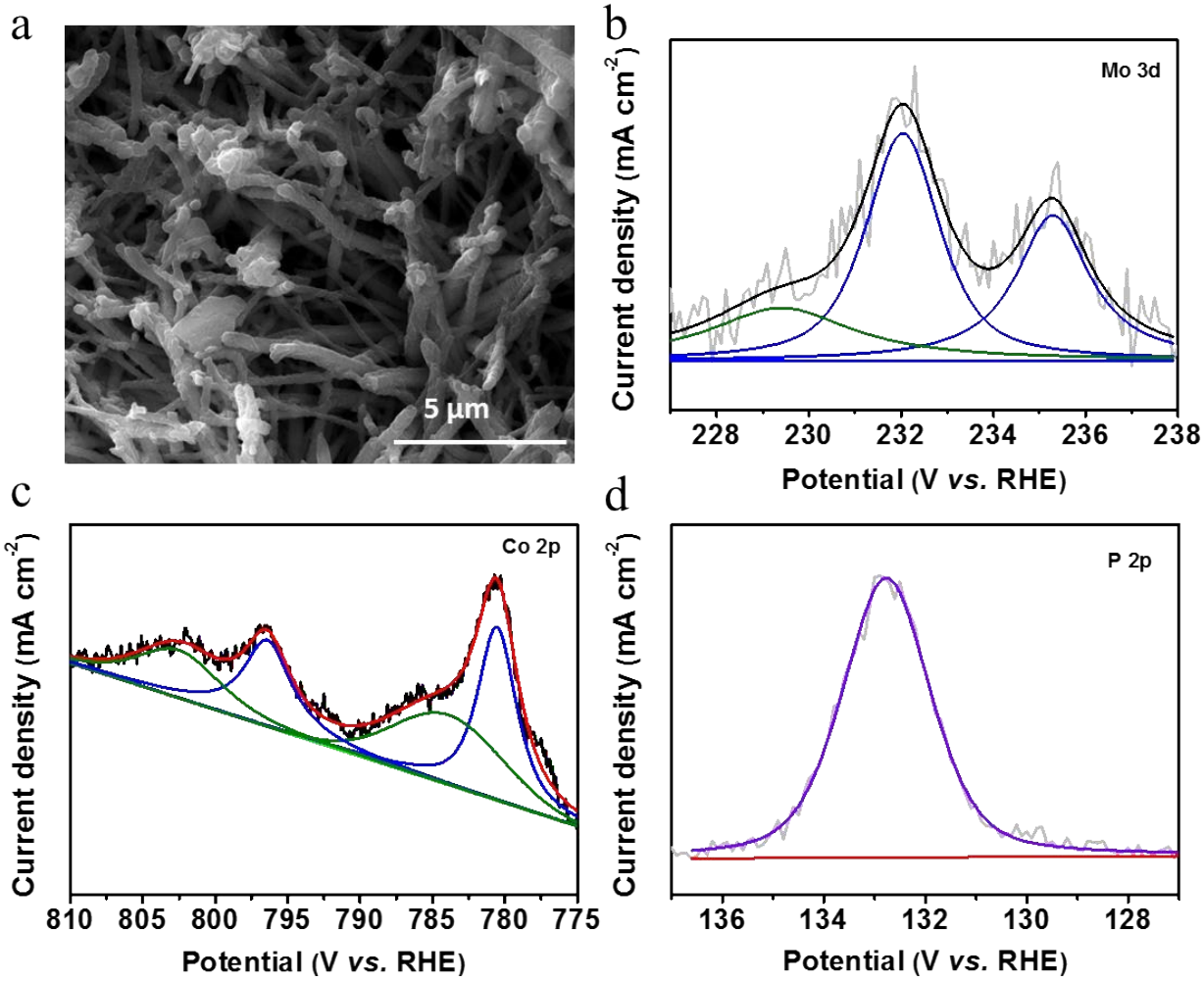

Fig. S13. (a) SEM images, XPS survey spectra of (b) Mo 3d, (c) Co 2p, and (d) P 2p after stability test in 1.0 M KOH.

Table S3. HER performance of CoP-MoO_2/MF and several reported representative non-noble metal based electrocatalysts in 0.5 M H_2SO_4.

Electrocatalysts	Substrate	Overpotential at 10 mA cm^{-2} (mV)	Ref.
CoP-MoO_2/MF	Mo Foil	65	Our work
CoP/CC	Carbon Cloth	67	11
CoP/NPC/TF	Ti Foil	91	12
CoP/CNT	Carbon Nanotubes	122	13
HNDCM-Co/CoP	Porous Carbon Membrane	138	2
$Ni_{0.33}Co_{0.67}Se_2$	Carbon Fiber Paper	65	3
CC@N-CoP	Carbon Cloth	42	14
Co_9S_8-30@MoS_{2x}/CC	Carbon Fiber Paper	98	15
Fe_2P@rGO	Ti Plate	101	16
CoS/Ni/P	Ni Foam	41	17
Ni_2P/MoS_2/N:CNT	Carbon	57.8	18

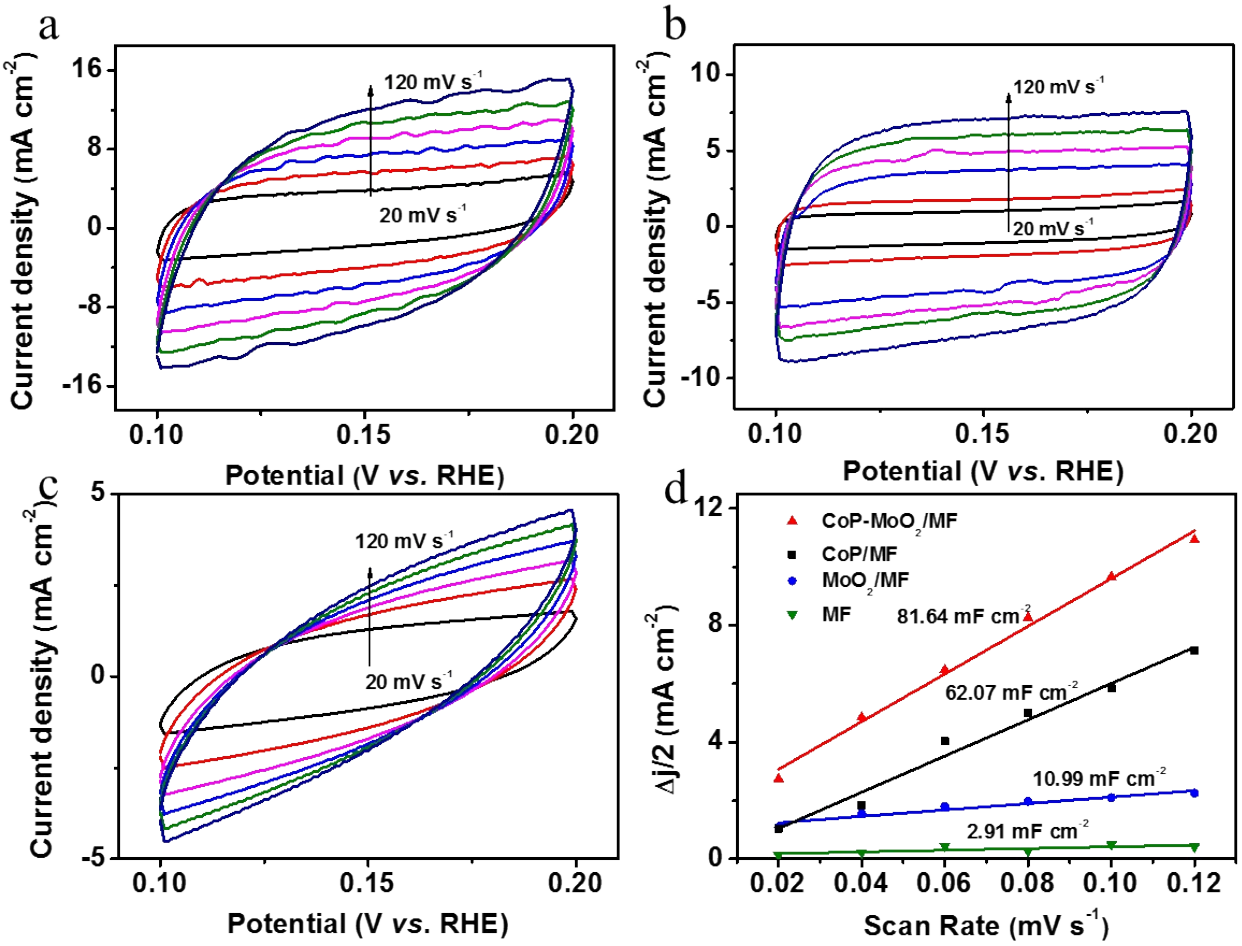

Fig. S14. CVs (0.1-0.2 V *vs.* RHE) of (a) CoP-MoO_2/MF, (b) CoP/MF, (c) MoO_2/MF, (d) The current density at 0.15 V (*vs*. RHE) as a function of scan rate fitted to a linear regression allows for the estimation of C_{dl} in 0.5 M H_2SO_4.

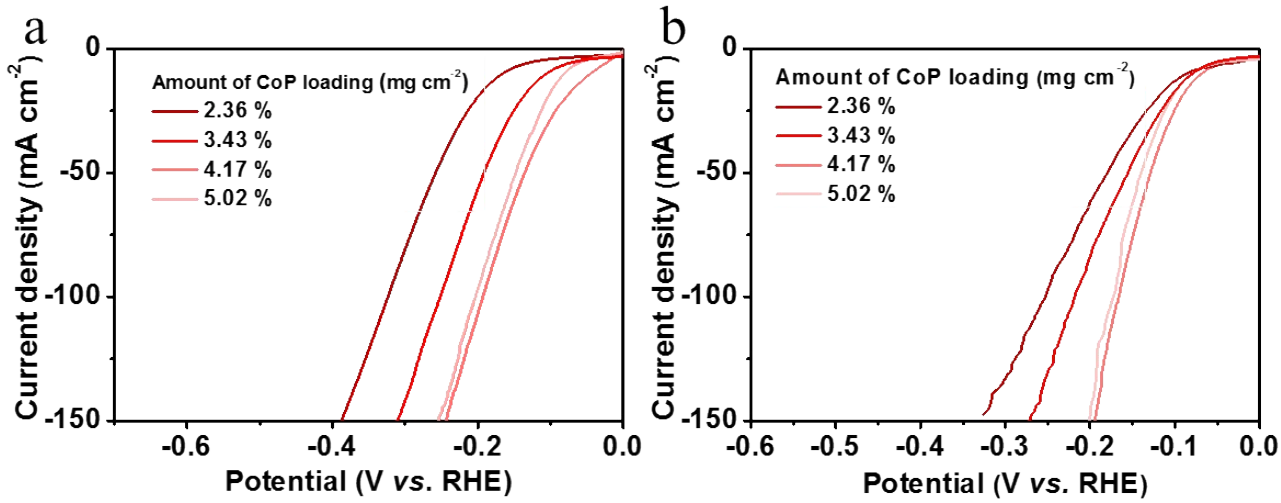

Fig. S15. LSV curves of CoP-MoO_2/MF in (a) 1.0 M KOH and (b) 0.5 M H_2SO_4 with the 2.36, 3.43, 4.17, 5.02 % CoP loading.

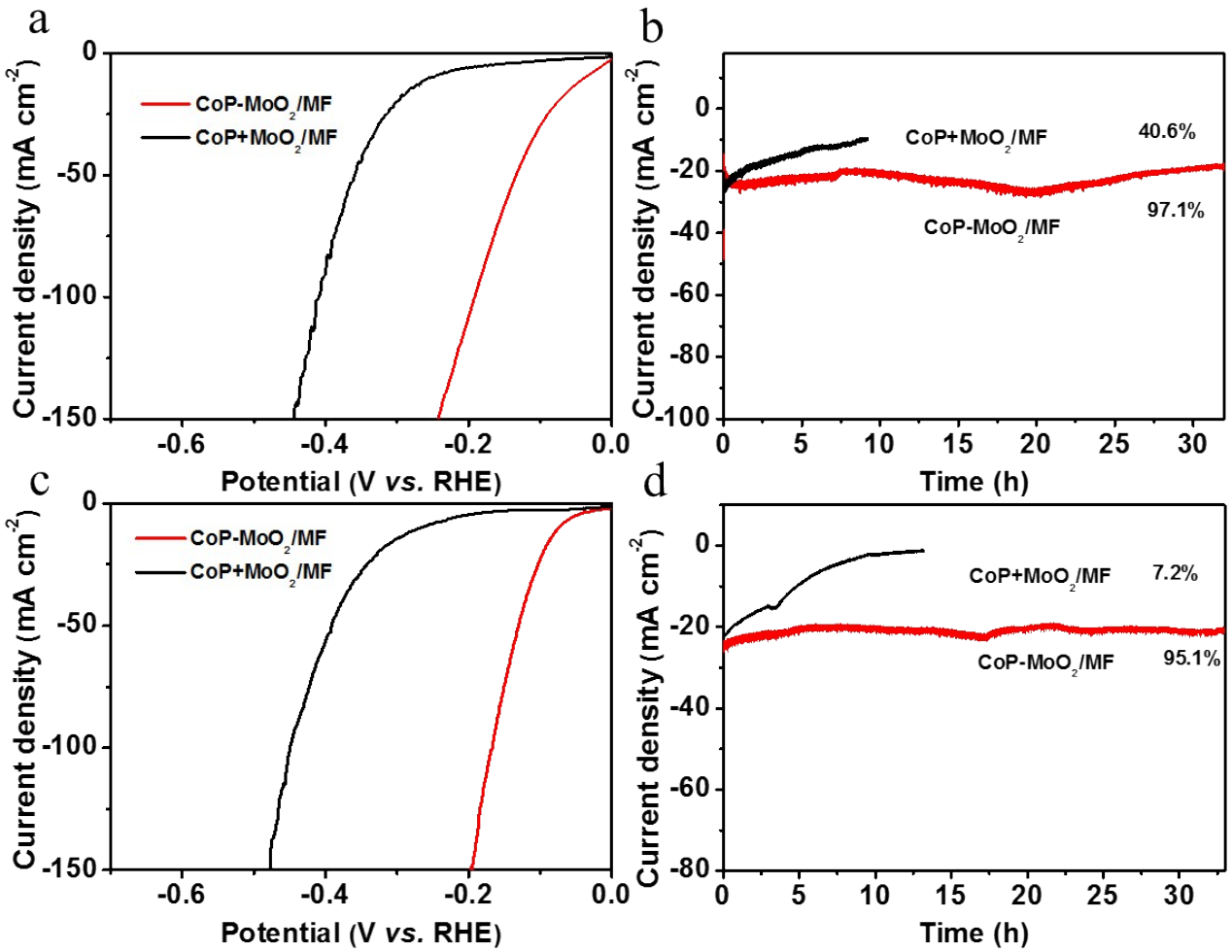

Fig. S16. LSV curves (a, c) and durability tests (b, d) for CoP-MoO_2/MF and CoP+MoO_2/MF in 1.0 M KOH and 0.5 M H_2SO_4, respectively.

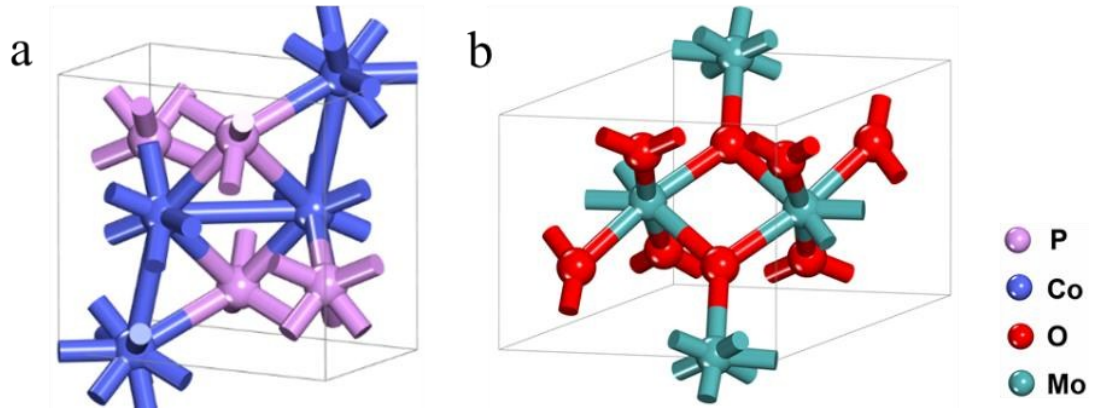

Fig. S17. Primitive cell crystal structures of (a) CoP (a=5.064Å, b=3.283Å, c=5.513Å; α=γ=β=90˚) and (b) MoO_2 (a=5.614Å, b=4.925Å, c=5.686Å; α=β=90˚, γ=120˚).

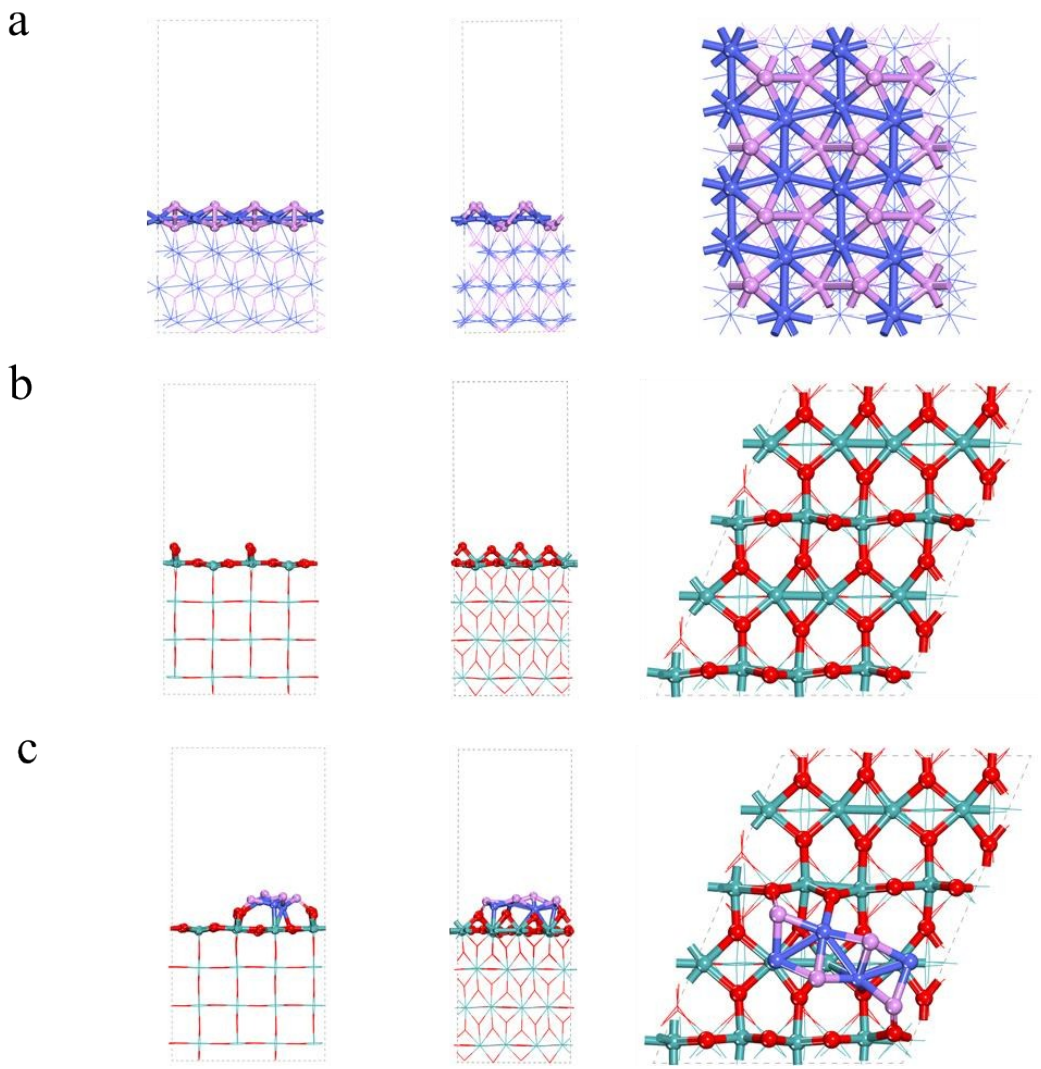

Fig. S18. Optimized surface slab structure models for (a) CoP (011), (b) MoO_2 (011), and (c) CoP-MoO_2 (011).

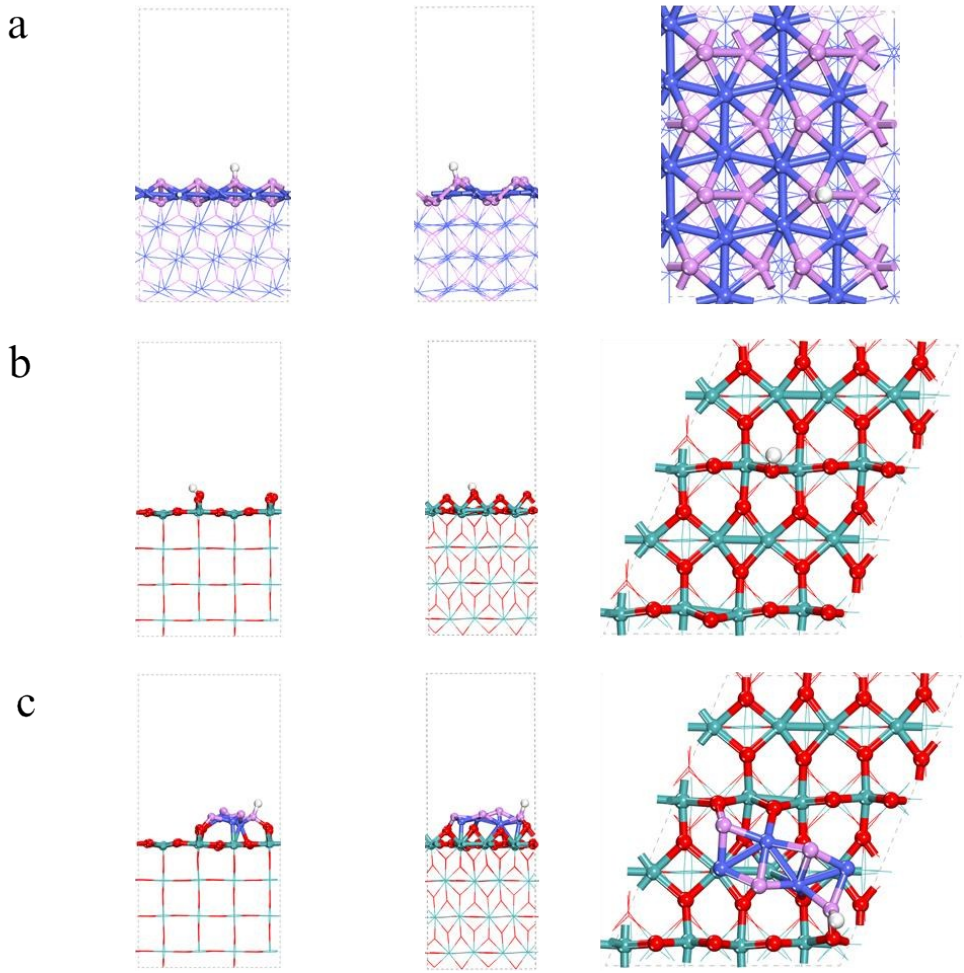

Fig. S19. Hydrogen absorbed position on the surface for (a) CoP (011), (b) MoO_2 (011) and (c) CoP-MoO_2 (011).

Table S4. Bader charge analysis of the CoP cluster and CoP-MoO_2.

Numbers of atoms	CoP cluster	CoP-MoO_2
Co1	-0.223	-0.049
Co2	-0.248	-0.333
Co3	-0.114	-0.126
Co4	-0.232	-0.044
P1	0.249	-0.777
P2	0.152	0.080
P3	0.227	0.032
P4	0.188	-0.721
total	0	-1.938

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