

aSupplementary Information

Mn-Doped Cobalt Phosphide Non-Noble Catalyst: Boosting HER for Stable and High-performance Zn-CO₂ system

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Calculation of the Faradaic Efficiency (FE): The FE value (η) was calculated by the following formulas:

$$n_{measured} = \frac{pV}{RT}$$

$$Q_{measured} = n_{measured} \cdot 2 \cdot F = \frac{pV}{RT} \cdot 2F$$

$$Q_{theoretical} = It$$

$$\eta = \frac{Q_{measured}}{Q_{theoretical}} \times 100\% = \frac{\frac{pV}{RT} \cdot 2F}{It} \times 100\% = \frac{pV \cdot 2F}{RT \cdot It} \times 100\%$$

where $n_{measured}$ is the amount of produced H₂ (mol), Q is the quantity of electric charge (C), p is the hydrogen pressure (atm), V is the volume of produced H₂ (L), F is the Faraday constant (96485 C mol⁻¹), R is the gas constant (0.082057 L·atm·mol⁻¹·K⁻¹), T is the operating temperature (K), I is the applied current (A), t is the duration of the test (s), and 2 represents the number of electrons transferred to produce a hydrogen molecule.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS):

The bulk elemental composition of the Mn-CoP catalyst was determined by inductively coupled plasma mass spectrometry (ICP-MS). Approximately 10.0 mg of catalyst powder, detached from the 2 cm × 2.5 cm (5 cm²) NF substrate via ultrasonication, was accurately weighed and digested in a mixture of 1 mL concentrated HCl (37 wt%) and 3 mL concentrated HNO₃ (65 wt%) using microwave-assisted digestion (80 °C for 20 min). After cooling, the clear solution was diluted to 50 mL with ultrapure water. The mass loading of Mn-CoP on nickel foam was determined to be 2.0 mg cm⁻² (geometric area) by differential weighing. The 10.0 mg of powder used for ICP-MS analysis corresponds to approximately 5 cm² of electrode area. The measured bulk atomic ratio (≈ 9.04: 1.00: 1.43) is in good agreement with the surface EDS result (9.42: 1.00: 1.43).

Table S1. Elemental composition of Mn-CoP determined by ICP-MS (three parallel measurements)

Sample	Co (mg L ⁻¹)	Mn (mg L ⁻¹)	P (mg L ⁻¹)	Atomic ratio (Co:Mn:P)
1	18.92	2.10	4.42	9.01:1.00:1.42
2	18.65	2.05	4.38	9.09:1.00:1.44
3	18.78	2.08	4.40	9.03:1.00:1.43
Average	18.78	2.08	4.40	9.04:1.00:1.43

Table S2. Preliminary techno-economic assessment of the Zn-CO₂ system (1 m² electrode area, 300h), price reference source: <https://markets.businessinsider.com>, <https://www.dailymetalprice.com>, <https://carboncredits.com>, <https://www.eia.gov/outlooks/aeo>.

Item	Quantity	Unit Price (USD)	Revenue/Cost (USD)
Zn metal consumed	366 kg	3.00 kg ⁻¹	-1,098
ZnO recovered (net)	455.6 kg	2.2 kg ⁻¹	+1,002
KOH consumed	628 kg	1.10 kg ⁻¹	-691
KHCO ₃ solid product	1,121 kg	1.25 kg ⁻¹	+1,401
H ₂ produced	11.2 kg	8.00 kg ⁻¹	+89.6
Electricity generated	270 kWh	0.1 kWh ⁻¹	+27
CO ₂ captured (credit)	0.493 ton	5 ton ⁻¹	+2.5
Net result			+733

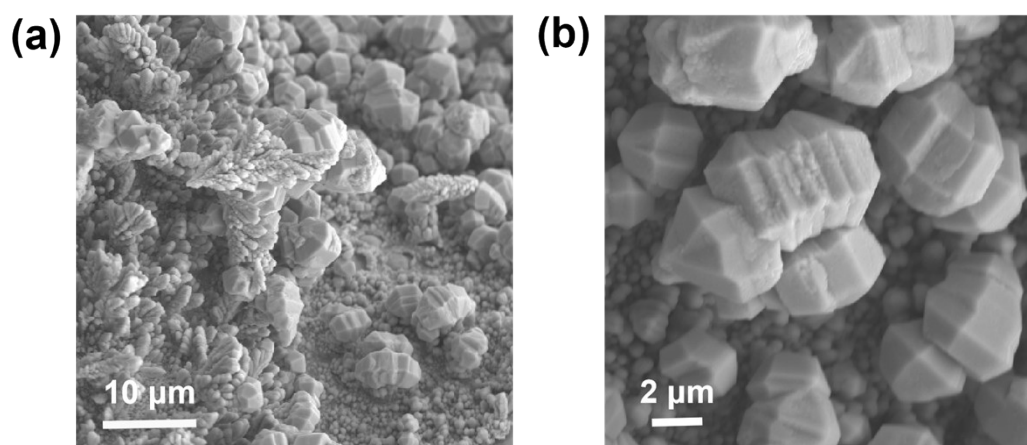


Figure S1. SEM images of CoP/NF at different magnifications of (a) 10 μm, (b) 2 μm.

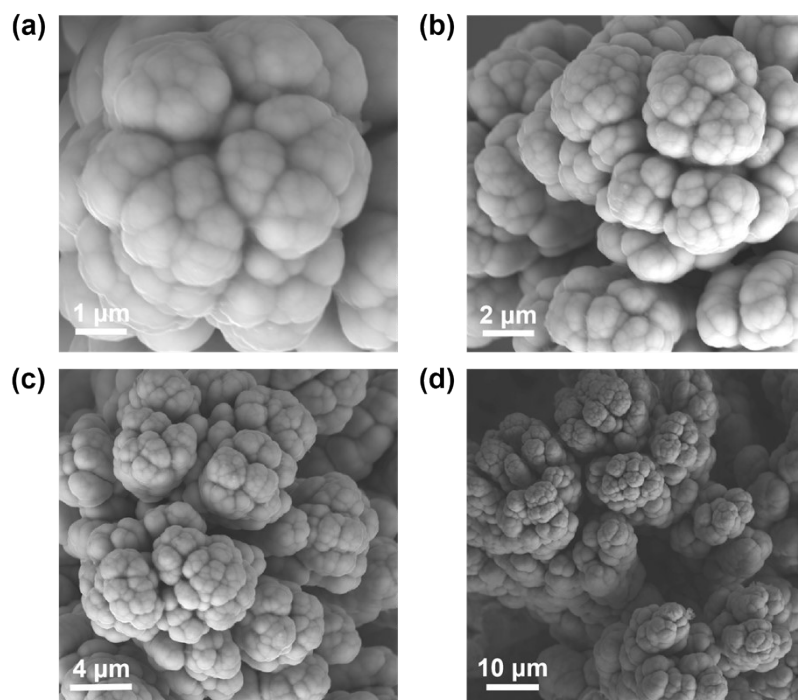


Figure S2. SEM images of Mn-CoP/NF at different magnifications of (a) 1 μm, (b) 2 μm, (c) 4 μm, (d) 10 μm.

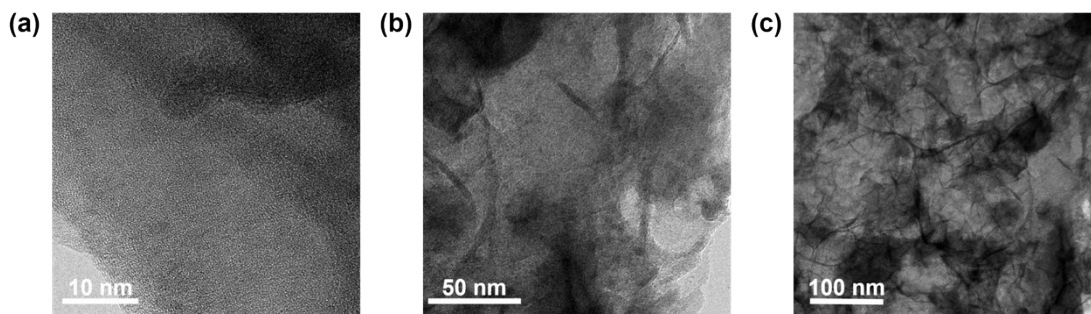


Figure S3. TEM images of Mn-CoP at different magnifications of (a) 10 nm, (b) 50 nm, (c) 100 nm.

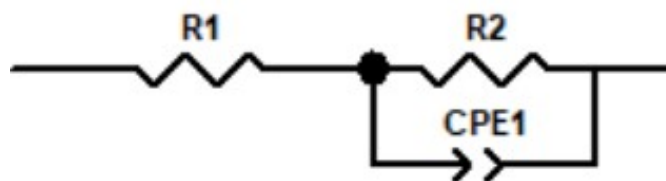


Figure S4. The equivalent circuit for EIS fitting.

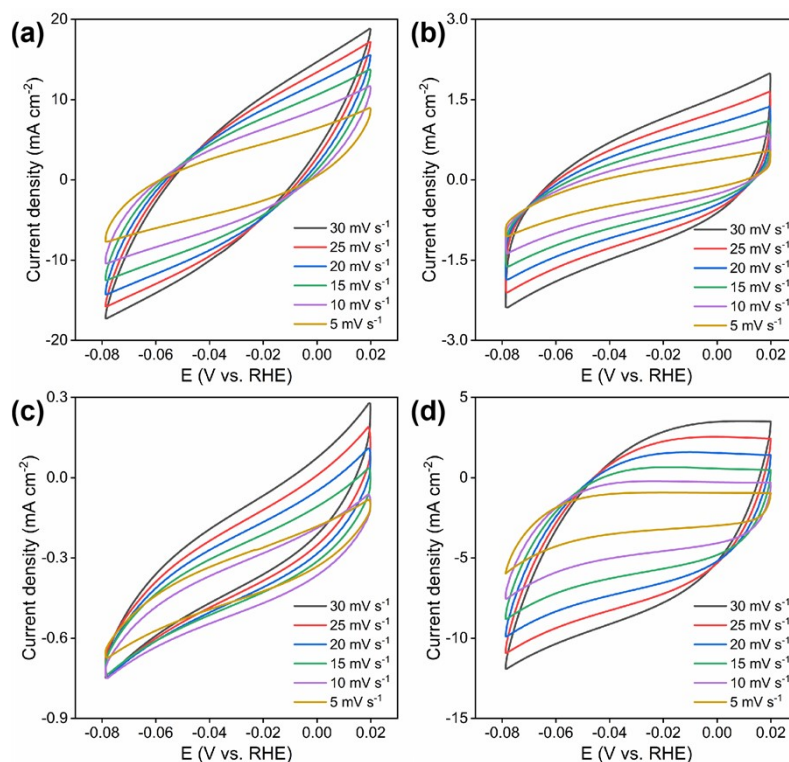


Figure S5. CV curves in the range of -0.08 V to 0.02 V (vs. RHE) at different scan rates in 3.4 M KHCO_3 solution. (a) Mn-CoP/NF, (b) CoP/NF, (c) Co/NF, and (d) Pt/C.

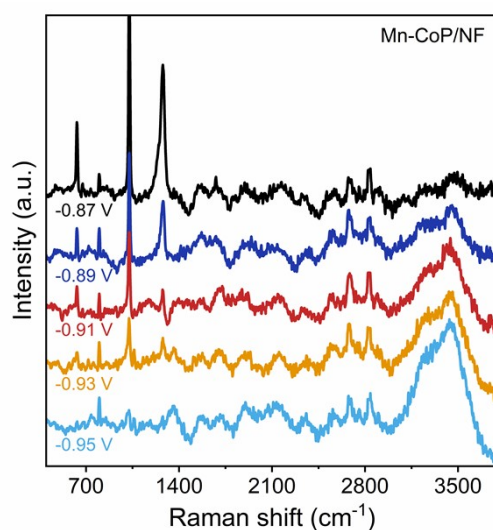


Figure S6. In-situ Raman spectra of Mn-CoP/NF recorded in 3.4 M KHCO_3 electrolyte under HER conditions at various applied potentials (from -0.87 to -0.95 V vs. Ag/AgCl).

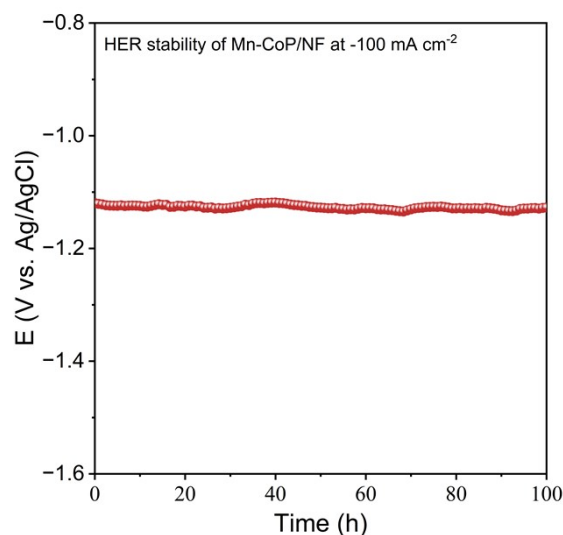


Figure S7. Chronopotentiometry test of Mn-CoP/NF at a constant cathodic current density of -100 mA cm^{-2} .

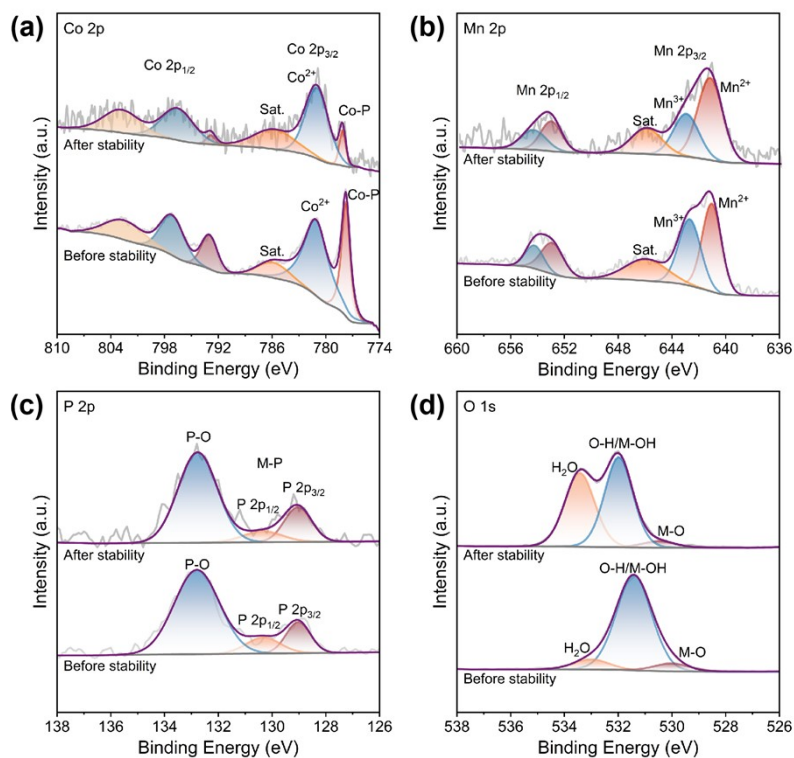


Figure S8. XPS spectra of Mn-CoP/NF before and after 100 h of continuous HER operation at -100 mA cm^{-2} in 3.4 M KHCO_3 . (a) Co 2p, (b) Mn 2p, (c) P 2p and (d) O 1s.

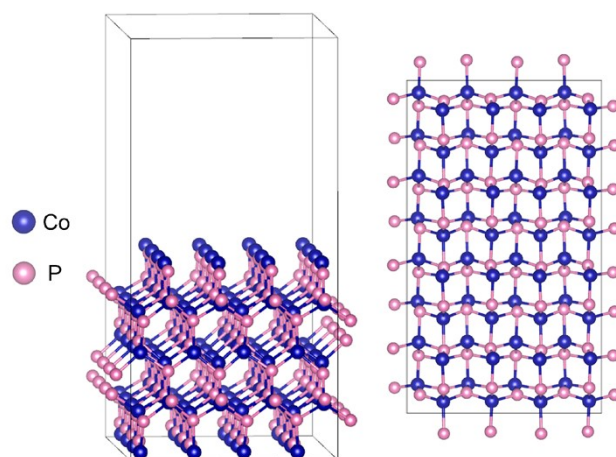


Figure S9. Schematic structure of CoP (001) lattice plane.

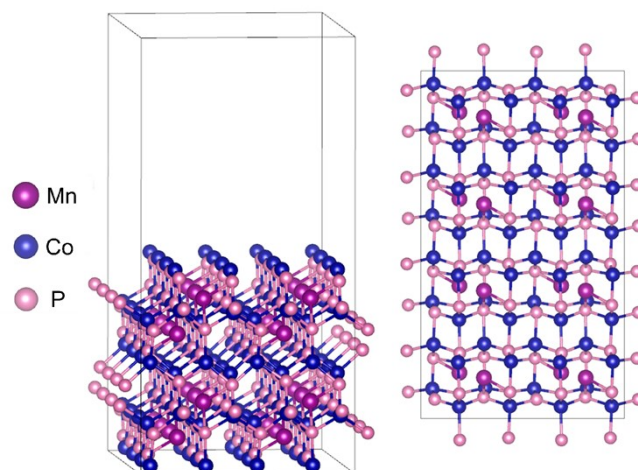


Figure S10. Schematic structure of Mn-CoP (001) lattice plane.

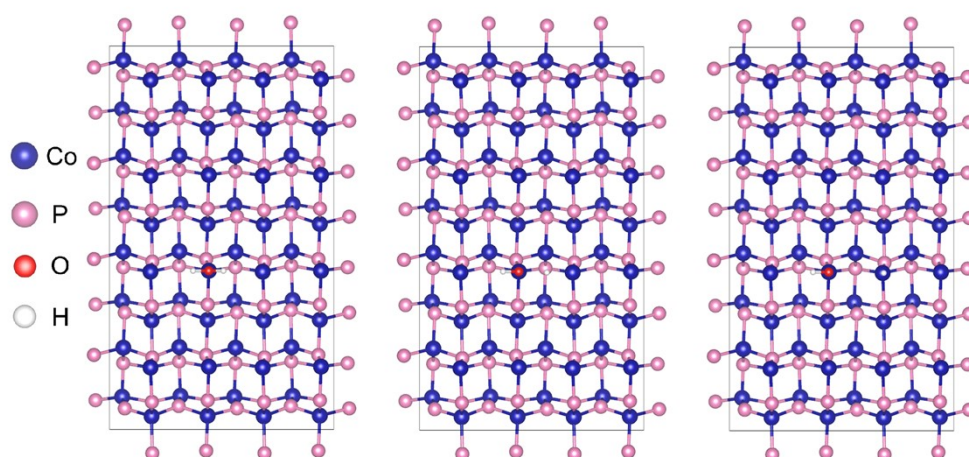


Figure S11. The atomic configurations of the intermediates on the (001) surface of CoP during water dissociation.

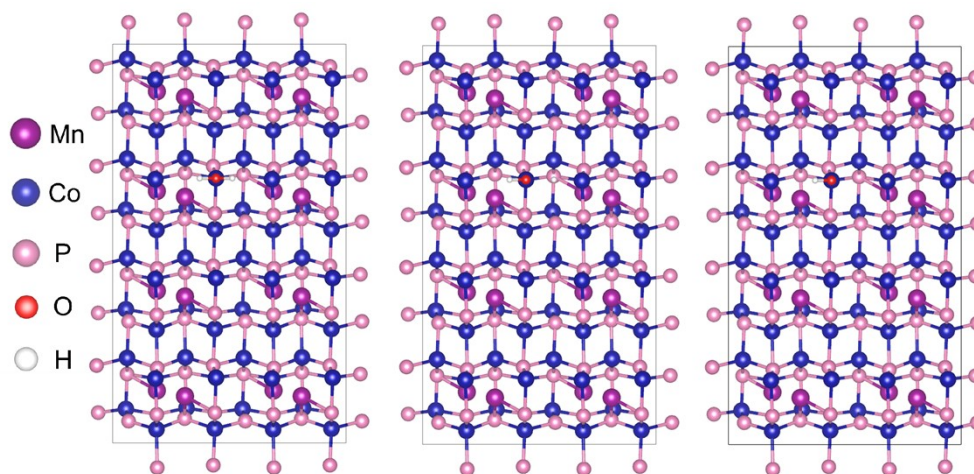


Figure S12. The atomic configurations of the intermediates on the (001) surface of Mn-CoP during water dissociation.

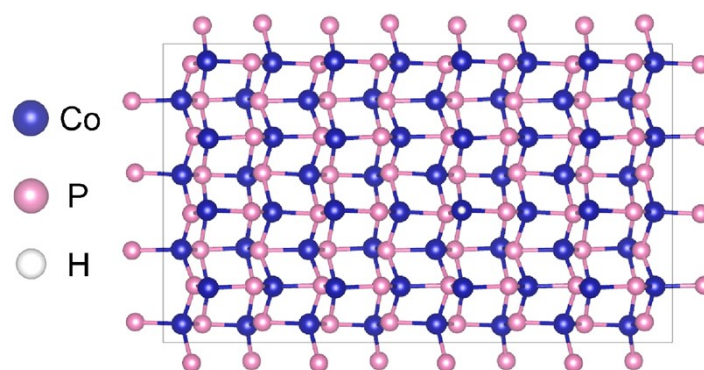


Figure S13. The atomic configurations of the H adsorption configuration of CoP.

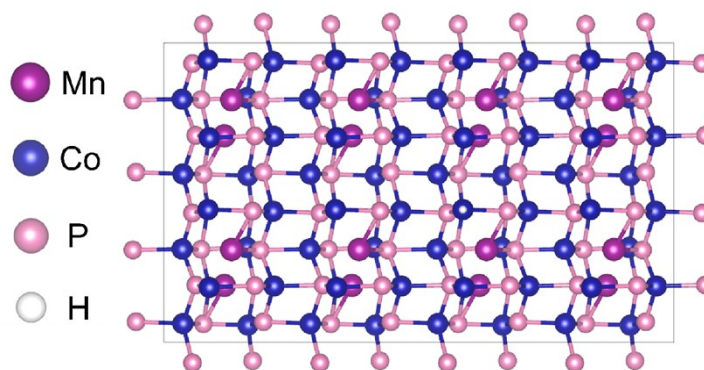


Figure S14. The atomic configurations of the H adsorption configuration of Mn-CoP.

Caption for Video S1

Video S1. The Zn-CO₂ system lighting LED board while generating H₂ gas (LED operate 1V)