

Phosphorus-Doped Cobalt sulphide Nanocubes as a Efficient Electrocatalyst for Hydrogen evolution Reaction

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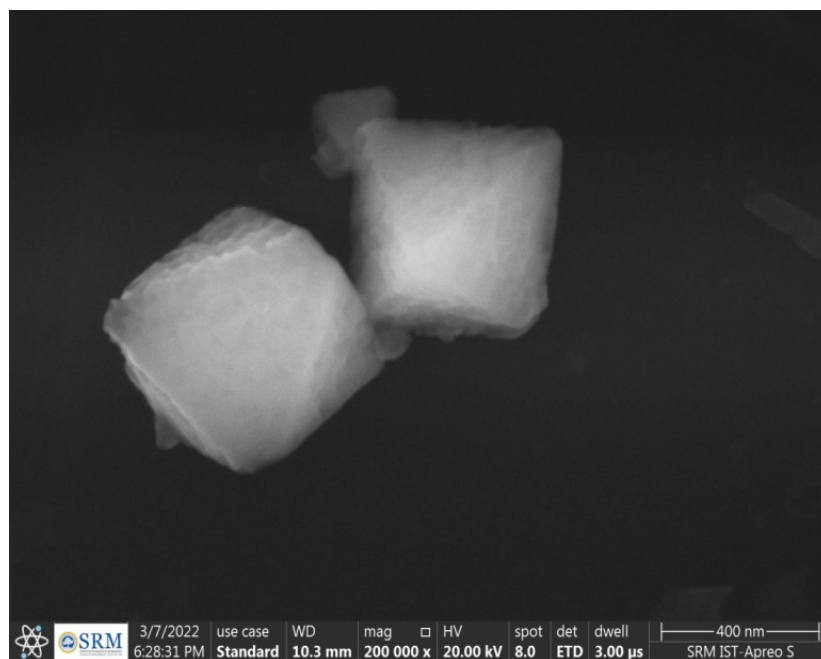


Fig. S1 SEM image of CoS₂.

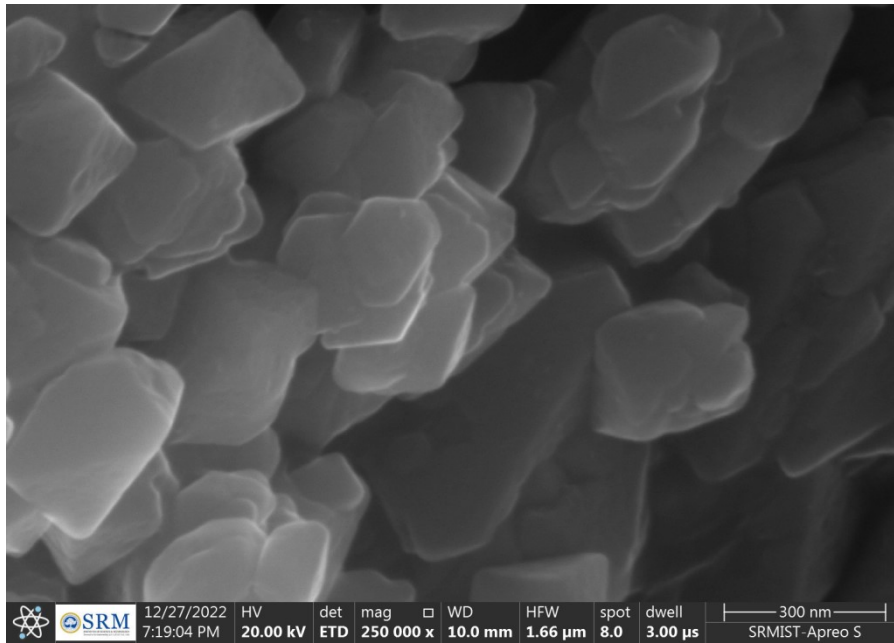


Fig. S2 SEM image of P doped CoS₂-1.

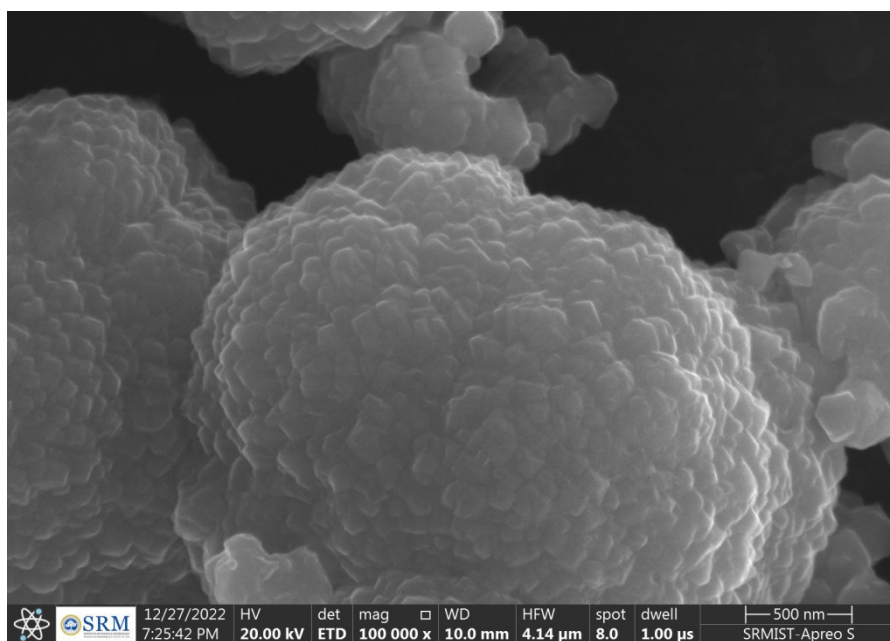
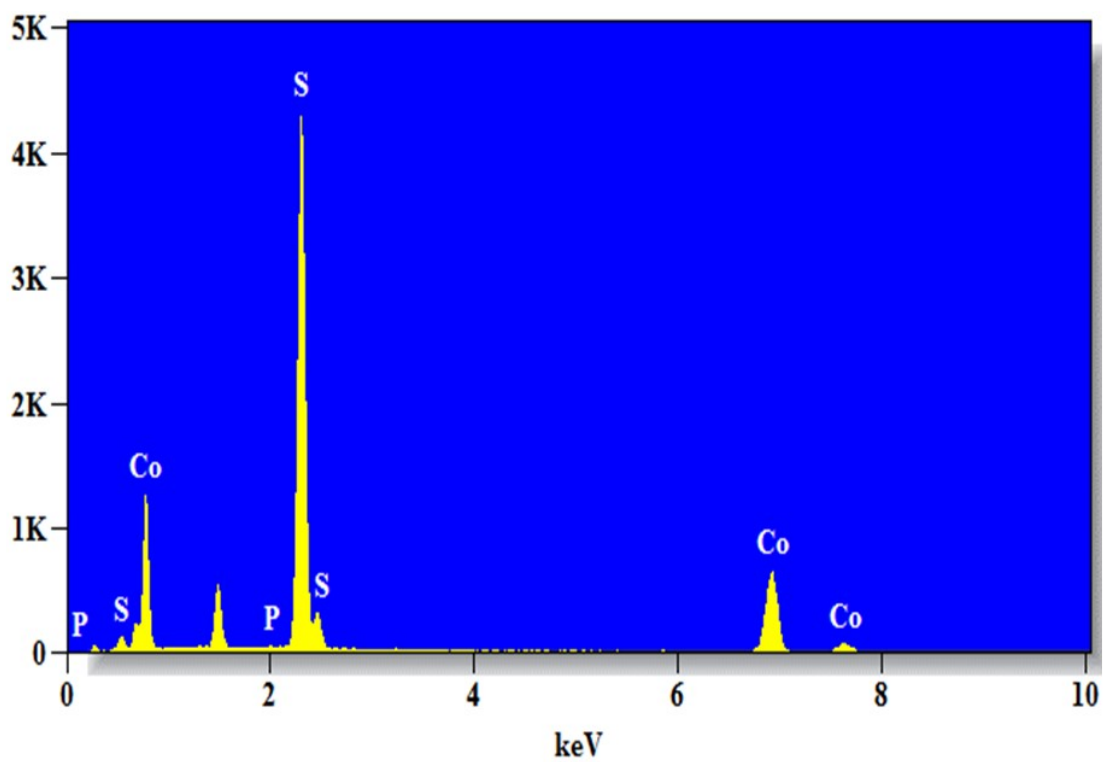
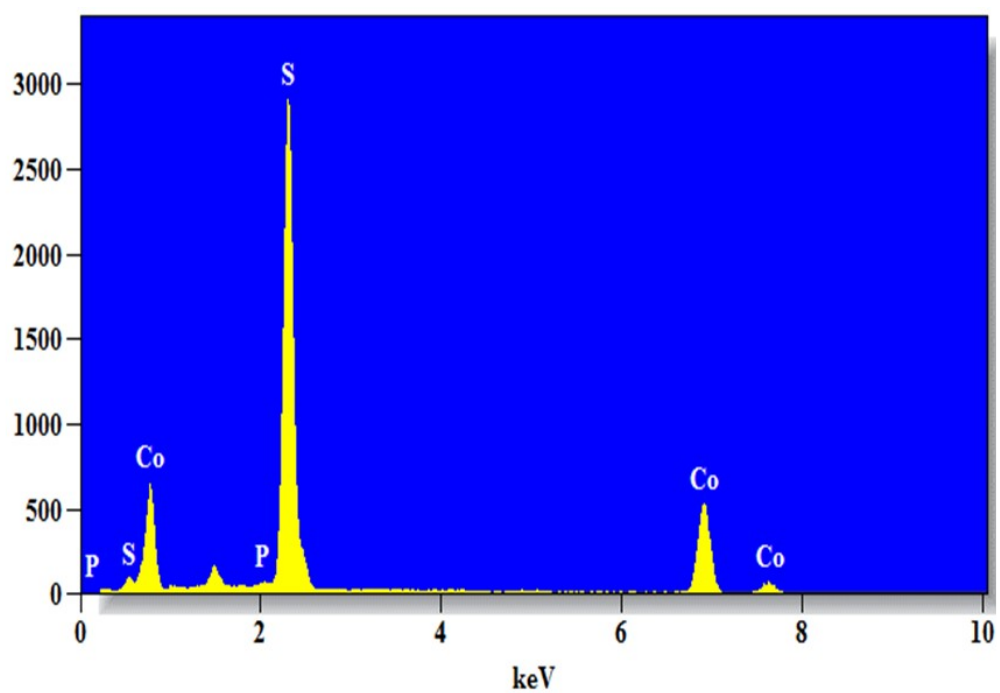


Fig. S3 SEM image of P doped CoS₂-3



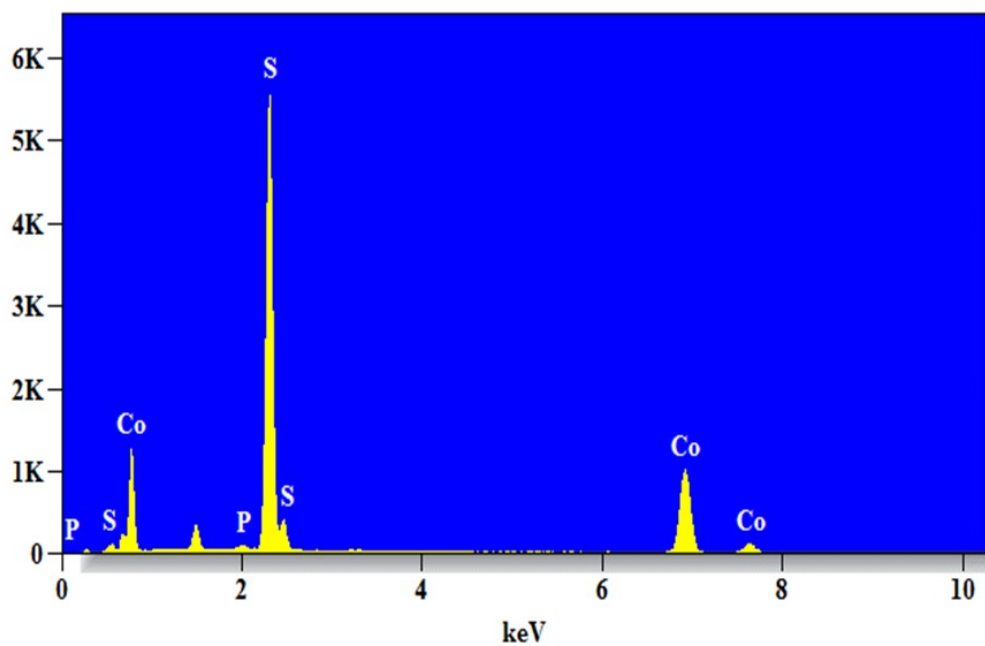
Element	Net Counts	Weight %	Atom %	Formula
P	169	0.20	0.26	P
S	47683	53.97	68.22	S
Co	10510	45.83	31.52	Co
Total		100.00	100.00	

Fig. S4 EDX spectrum of P doped CoS₂-1



Element	Net Counts	Weight %	Atom %	Formula
P	267	0.33	0.44	P
S	43001	49.30	63.99	S
Co	11692	50.37	35.57	Co
Total		100.00	100.00	

Fig. S5 EDX spectrum of P doped CoS₂-2



Element	Net Counts	Weight %	Atom %	Formula
P	766	0.65	0.86	P
S	62834	49.81	64.33	S
Co	16609	49.54	34.81	Co
Total		100.00	100.00	

Fig. S6 EDX spectrum of P doped CoS₂₋₃

Table S1 The electrocatalytic HER performance of synthesized P-doped CoS₂-2 with other recently reported cobalt sulphide-based electrocatalysts in 1M KOH electrolyte.

Catalyst	Overpotential (mV) at J=10mA cm²	Tafel slope (mV/dec)	Reference
P doped CoS ₂ /NF	138	96.2	This work
Mo-CoS ₂ /NC	158	123	40
CoS ₂ @NHCs-800	118	74	41
Sn-CoS ₂ /CC	132	179.9	42
CoS ₂ @N-ASC@NF	165.6	67.8	43
Co/CoS ₂ @NC	188	-	44
CoS ₂ NTA/CC	193	88	45
CoS ₂ @WS ₂ /NF	127	177	46
CoS _{1.25} Se _{0.75} @NC	134	86	47
CoS _x /Ni ₃ S ₂ @NF	201	113.13	48

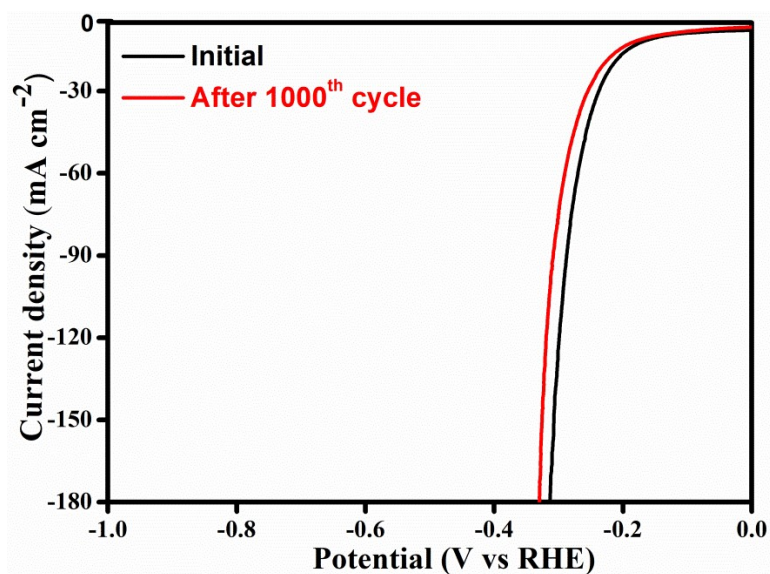


Fig. S7 Polarization curves of P doped CoS₂-2 initially and after 1000 cycles CV with a scan rate of 100 mV s⁻¹ in 1M KOH.

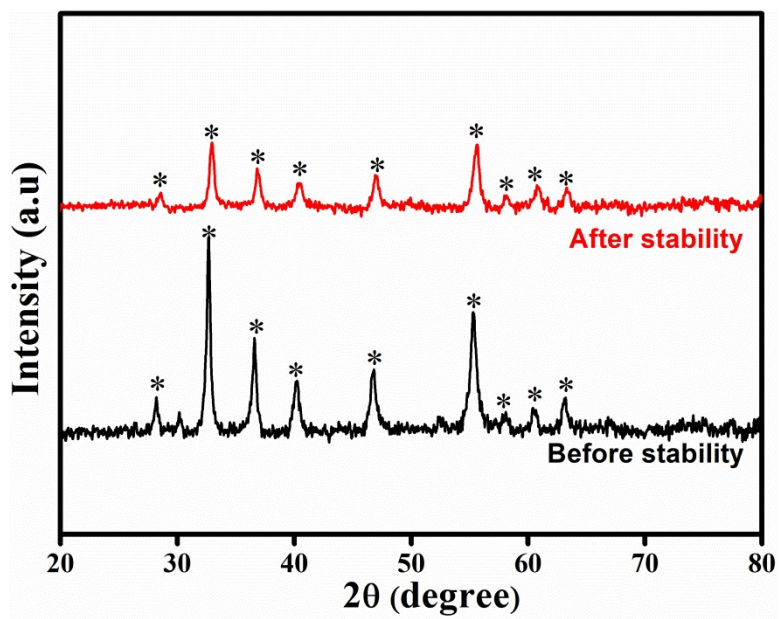


Fig. S8 XRD analysis of P doped CoS₂-2 initially and after 1000 cycles.

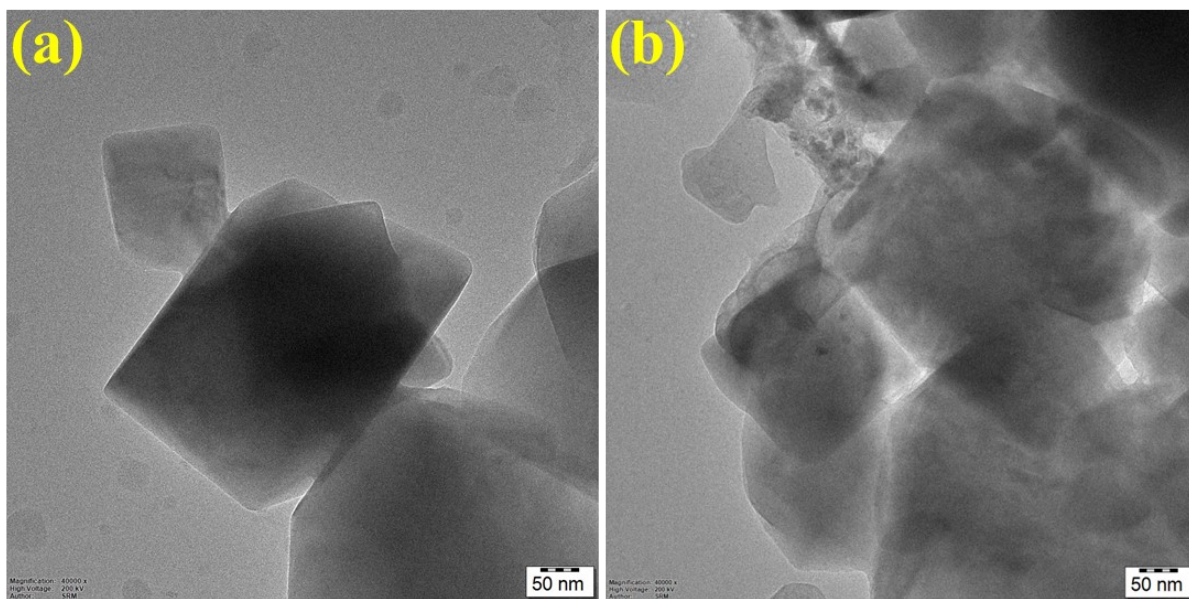


Fig. S9 TEM image of post HER studies for P doped CoS₂-2

Section S1. Calculation of the Electrochemical Active Surface Area (ECSA)

The prepared electrocatalysts double layer capacitance (C_{dl}) values were determined from the cyclic voltammetry (CV) curves recorded (non-faradaic region) at different scan rates. The ECSA of the prepared catalysts was calculated according to equation (1).

$$C_{dl} = \frac{\text{Cathodic} - \text{Anodic}}{2} \text{ ----- (1)}$$

$$\text{ECSA} = \frac{C_{dl}}{C_s} \text{ ----- (2)}$$

The catalyst's C_{dl} values were derived from the slope of linearly fitted curves by plotting capacitive current density versus scan rate. Where C_s - is the specific capacitance (0.040 mF cm^{-2}) and C_{dl} - is the double-layer capacitance [1].

Section S2. Calculate of the TOF of the electrocatalysts, Equations (2) and (3) were used.

$$n = \frac{m_{mass}}{M} \text{ ----- (3)}$$

$$\text{TOF} = \frac{J \times A}{2 \times F \times n} \text{ ----- (4)}$$

Where n is the number of moles of the active sites on the electrode, m_{mass} - is mass loading of active materials and M - is molar mass of active materials, respectively. J is the current density at overpotential of 250 mV in A cm^{-2} , and F is the Faraday constant (96485 C mol^{-1}), [2-4].

Table S2. Represents the intrinsic catalytic activity of the electrochemical HER performance of P doped CoS_2 -2, P doped CoS_2 -3, P doped CoS_2 -1 and bare CoS_2 electrocatalysts in 1M KOH electrolyte.

Catalyst	C_{dl} (mF cm^{-2})	ECSA (cm^2)	TOF @ $\eta=250 \text{ mV}$ (S^{-1})
P doped CoS_2 -2	5.44	136	2.43
P doped CoS_2 -3	3.62	90.5	1.88

P doped CoS ₂ -1	3.47	86.75	1.18
Bare CoS ₂	3.26	81.5	1.03

Reference

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2. Chen, J., Zhao, G., Chen, Y., Rui, K., Mao, H., Dou, S. X., & Sun, W. (2019). Iron-doped nickel molybdate with enhanced oxygen evolution kinetics. *Chemistry—A European Journal*, 25(1), 280-284.
3. Babar, P., Patil, K., Mahmood, J., Kim, S. J., Kim, J. H., & Yavuz, C. T. (2022). Low-overpotential overall water splitting by a cooperative interface of cobalt-iron hydroxide and iron oxyhydroxide. *Cell Reports Physical Science*, 3(2).
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