

Electronic Supplementary Information

Fe/P Dual Doping Boosts the Activity and Durability of CoS₂ Polycrystalline

Nanowires for Hydrogen Evolution

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This file includes Fig. S1-S8 and Table S1-S3.

Experimental Method

Preparation of Fe-CoS₂ PCNW. Carbon cloth (CC, Wuhan Instrument, Wuhan) was carefully cleaned with concentrated HNO₃ to remove impurities on surface, then rinsed by deionized water and ethanol before use. 1.5 mmol cobalt nitrate hexahydrate (Acros Organics 99+%), 0.15 mmol ferric chloride (Alfa Aesar 98+%), 3.78 mmol ammonium fluoride (Alfa Aesar 98.0%), and 7.5 mmol urea (Acros Organics 99%) were dissolved in 40 mL deionized water. After stirring for 30 min, the solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave with a piece of clean CC and maintained at 120 °C for 6 h. After the autoclave cooled down to room temperature, the sample was collected and washed with water and ethanol several times and dried at 60 °C, followed by annealing at 300 °C for 2 h in air to obtain the Fe-Co₃O₄/CC precursor. To convert Fe-Co₃O₄ into Fe-CoS₂, Fe-Co₃O₄/CC in a quartz boat was loaded in a quartz tube which was positioned at the downstream of a two-zone furnace. Sulfur powder (0.5 g) in another quartz boat was then positioned in the tube at the upstream of the furnace. The temperature for downstream zone was set at 400 °C with a ramp rate of 3 °C·min⁻¹, while upstream zone was set at 400 °C with a ramp rate of 3 °C·min⁻¹. After 2 h under Ar (100 sccm) atmosphere, the Fe-CoS₂/CC was obtained.

Preparation of Fe/P-CoS₂ PCNW. The prepared Fe-CoS₂/CC was then thermally phosphorized to prepare Fe/P-CoS₂/CC through a vapor phase phosphorization process in a tube furnace. The NaH₂PO₂·H₂O (Alfa Aesar 97+%) was put in the upstream side of the furnace and heated to 400 °C for 1 h under a steady Ar gas flow with a flow rate of 100 sccm.

Preparation of control catalyst CoS₂ PCNW. CoS₂/CC was prepared in parallel by the same method as Fe-CoS₂/CC except for no addition of ferric chloride.

Preparation of control catalyst P-CoS₂ PCNW. P-CoS₂/CC was prepared through the

same process as Fe/P-CoS₂ except for using CoS₂/CC as precursor instead of Fe-CoS₂/CC.

Material characterization.

Morphology characterization was conducted using a Hitachi S-4800 field emission scanning electron microscope (FESEM) operated at 10 kV. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images were recorded on a JEOL-2100F microscope operating at 200 kV. Elemental mapping was performed with an EDS detector equipped on the JEOL-2100F TEM. X-ray diffraction (XRD) experiments were carried out on a PANalytical high resolution X-ray diffraction system (model EMPYREAN) with a Cu K α radiation ($\lambda = 0.15406$ nm). X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo Scientific ESCALab250Xi using 300 W monochromated Mg K α radiation. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. The Raman spectra were recorded on a LabRAM HR Evolution spectroscope (HORIBA, France).

Electrochemical measurement.

All electrochemical measurements were performed on a CHI 660E bipotentiostat in a standard three-electrode setup. In a typical measurement, Fe/P co-doped CoS₂/CC hybrid electrode (0.5 \times 0.5 cm) was used as a working electrode, a graphite rod as the counter electrode, and a mercuric oxide electrode (MOE) as the reference electrode in 0.5 M H₂SO₄. The loading of catalyst on the electrode is 14.5, 15.7, 14.3, 14.1 mg cm⁻² for CoS₂, Fe-CoS₂, P-CoS₂ and Fe/P-CoS₂, respectively and commercial Pt/C catalyst (20 wt.% Pt, Johnson Matthey) with a loading of 0.35 mg cm⁻² were also measured for comparison. The electrochemical analysis was performed through linear sweep voltammograms at a scan rate of 5 mV s⁻¹. Cyclic voltammetry (CV) measurements were applied to probe the electrochemical double layer capacitance at

non-Faradaic region for estimating the effective electrochemical surface area (ECSA).

Calculation of active sites. The voltammetric charges (cathodic and anodic) of active components can be obtained from the CV curves recorded between 0.16 V and 0.23 V vs. RHE in 0.5 M H₂SO₄ at a scan rate of 90 mV s⁻¹. The number of active sites (n) of the catalysts was got at non-Faradaic region according the following equation:¹⁻³

$$n = \frac{Q}{2F}$$

F: Faraday constant (96485 C/mol)

Q: Whole charge of CV curve (C)

Assessment of turnover frequency (TOF). When the number of active sites is obtained, the per-site turnover frequencies (in s⁻¹) were calculated with the following equation:¹⁻³

$$\text{TOF} = \frac{I}{2Fn}$$

I: Current during the linear sweep measurement (A) at a given overpotential

n: Number of active sites (mol)

References:

- 1 Y. Yan, X. Ge, Z. Liu, J.-Y. Wang, J.-M. Lee and X. Wang, *Nanoscale*, 2013, **5**, 7768-7771.
- 2 J. Yin, P. Zhou, L. An, L. Huang, C. Shao, J. Wang, H. Liu and P. Xi, *Nanoscale*, 2016, **8**, 1390-1400.
- 3 J. Zhang, W. Xiao, P. Xi, S. Xi, Y. Du, D. Gao and J. Ding, *ACS Energy Lett.*, 2017, **2**, 1022-1028.

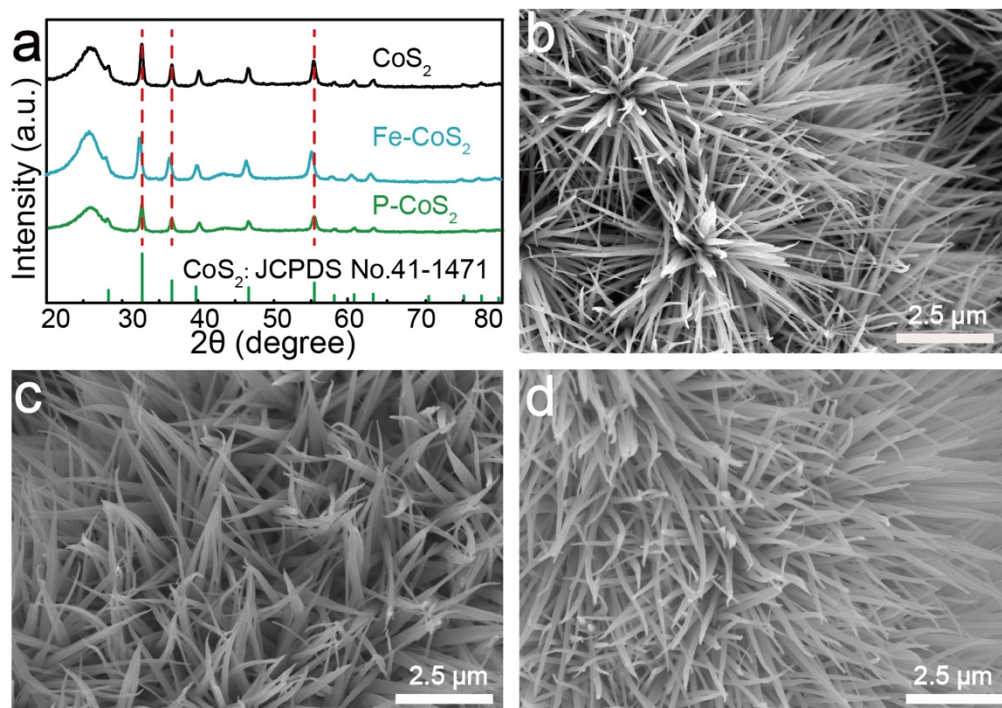


Fig. S1 (a) XRD patterns of CoS_2 , Fe-CoS_2 , and P-CoS_2 PCNWs. Low-magnification SEM images of (b) CoS_2 , (c) Fe-CoS_2 , and (d) P-CoS_2 PCNWs.

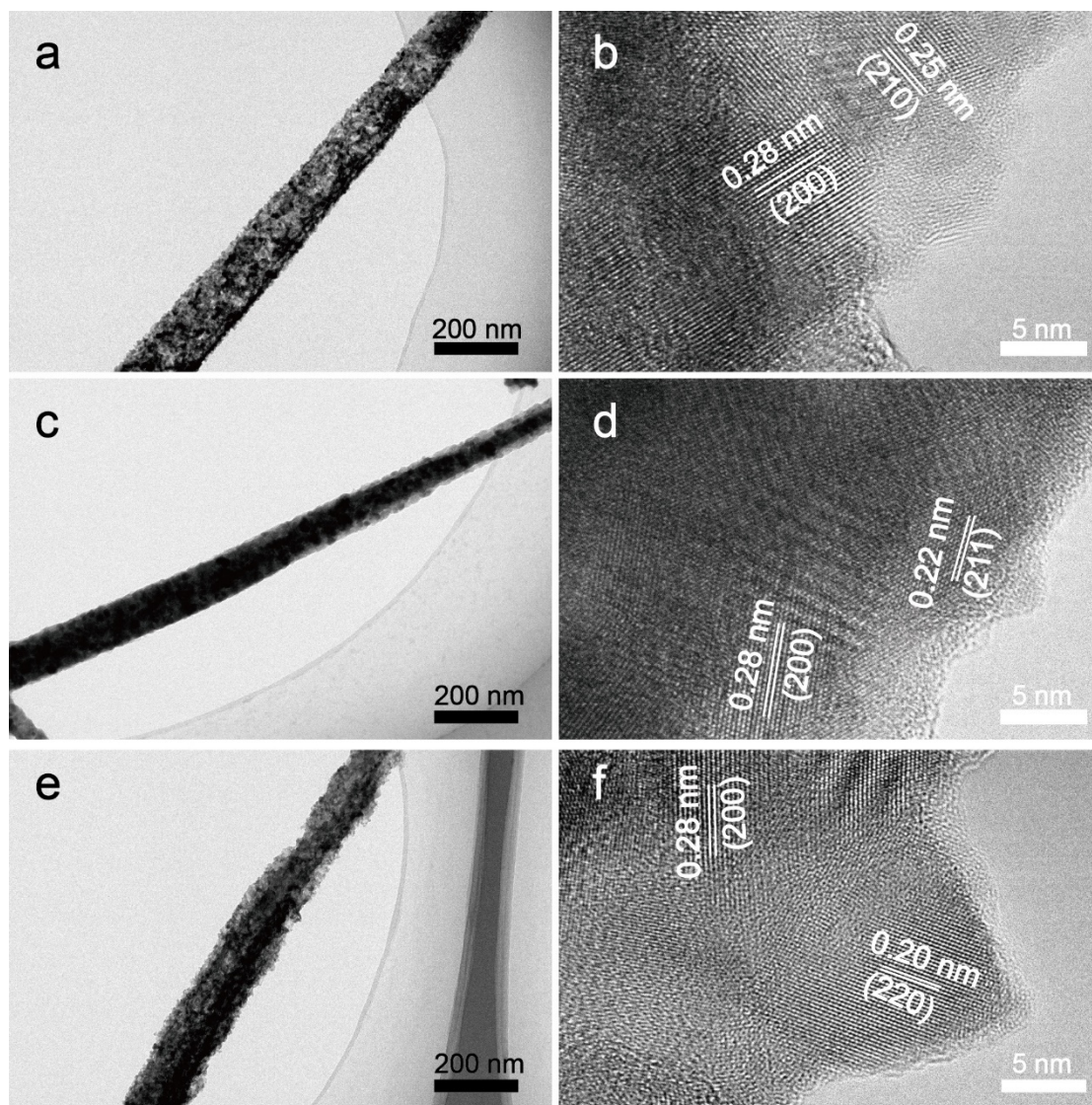


Fig. S2 TEM and HRTEM images of (a, b) CoS₂, (c, d) Fe-CoS₂, and (e, f) P-CoS₂.

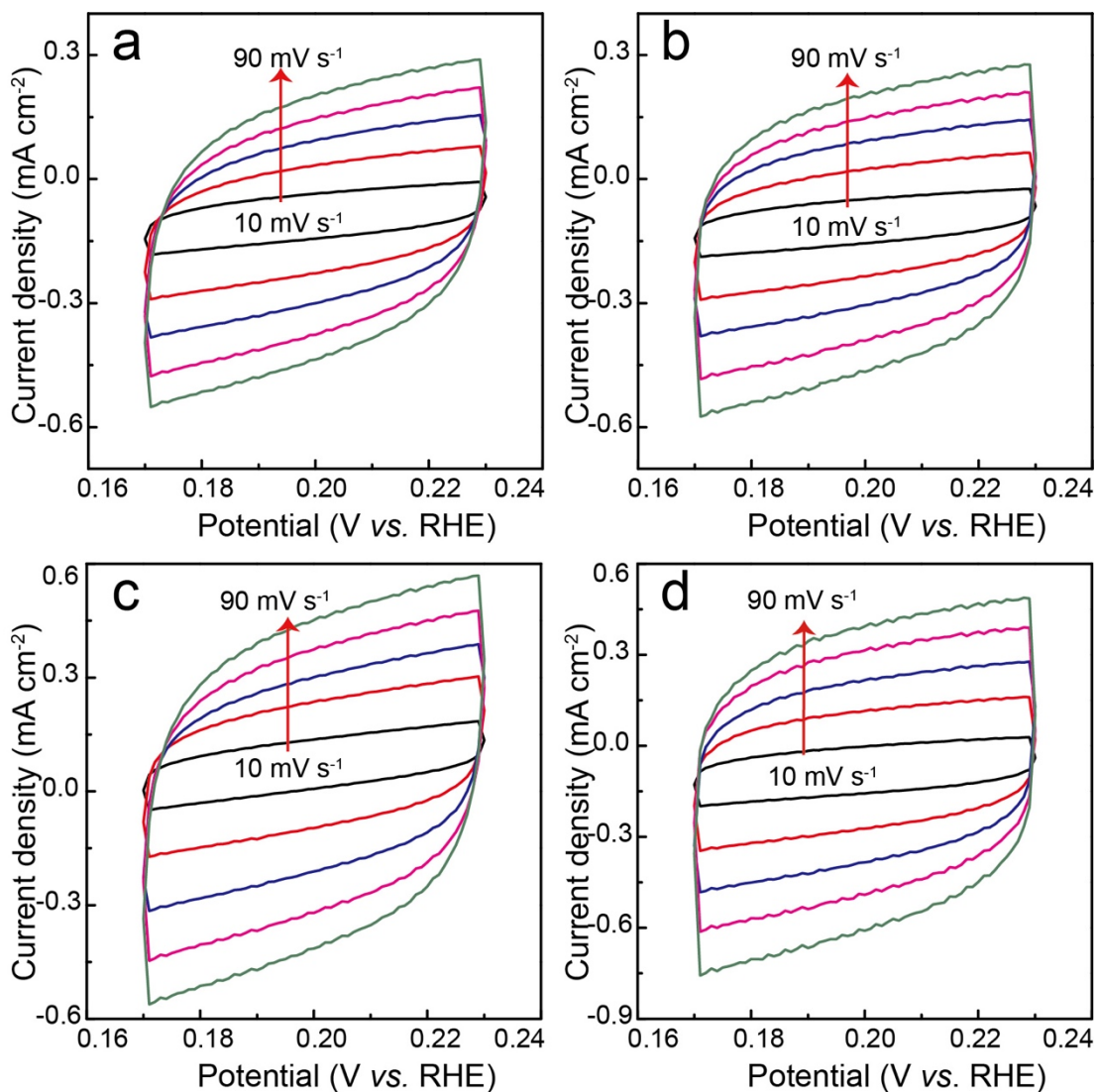


Fig. S3 CV curves measured at different scan rates from 10, 30, 50, 70 to 90 mV s⁻¹ in 0.5 M H₂SO₄ for (a) CoS₂, (b) P-CoS₂, (c) Fe-CoS₂, and (d) Fe/P-CoS₂.

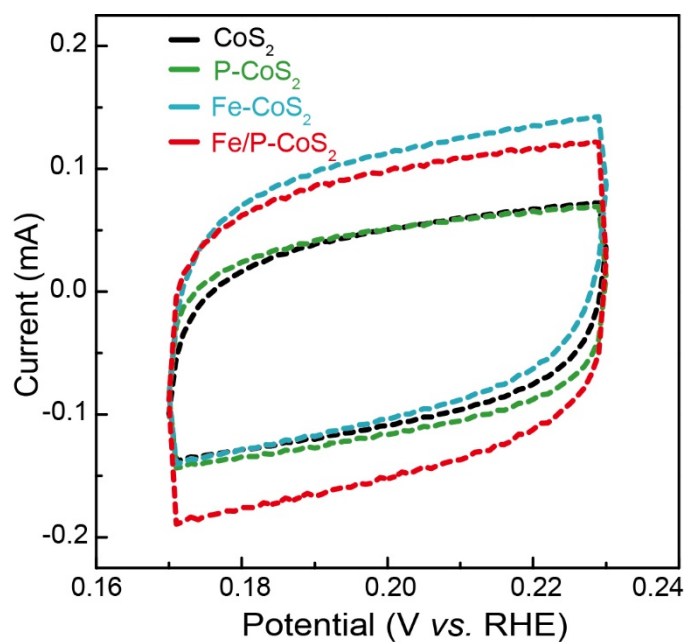


Fig. S4 CV curves measured between 0.16 V and 0.23 V (vs. RHE) in 0.5 M H₂SO₄ at a scan rate of 90 mV s⁻¹ for CoS₂, P-CoS₂, Fe-CoS₂, and Fe/P-CoS₂.

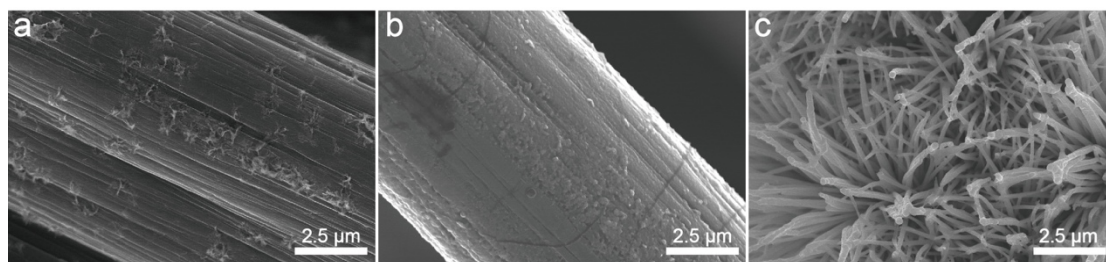


Fig. S5 SEM images for (a) CoS₂, (b) Fe-CoS₂, and (c) P-CoS₂ after stability test.

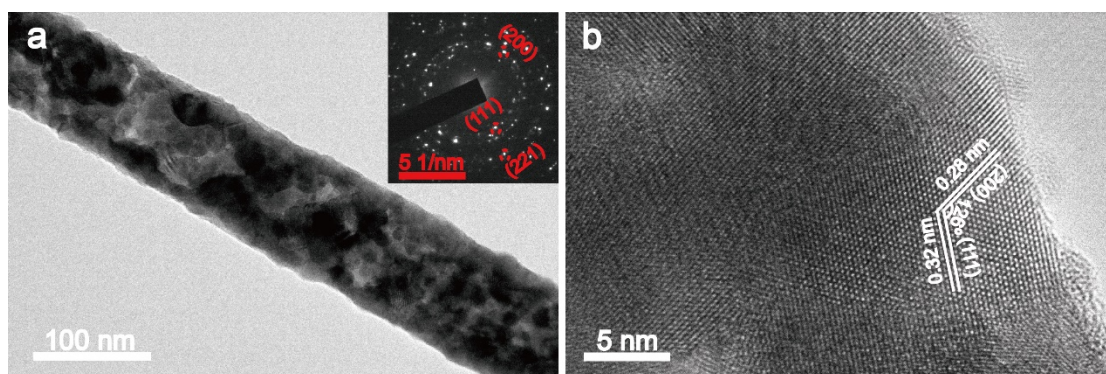


Fig. S6 (a) TEM and (b) HRTEM images for Fe/P-CoS₂ after consecutive hydrogen evolution for 10 h at a current density of 25 mA cm⁻². Inset in (a) is a corresponding SAED pattern.

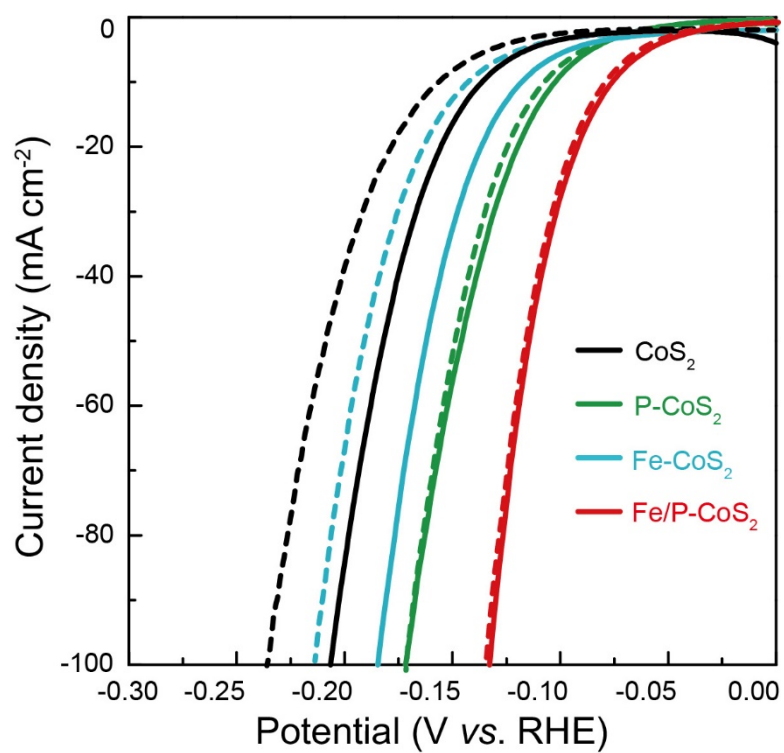


Fig. S7 LSV curves recorded with iR correction for CoS₂, Fe-CoS₂, P-CoS₂ and Fe/P-CoS₂ before and after 2000 cycles of CV scanning between 0 and -300 mV (vs. RHE).

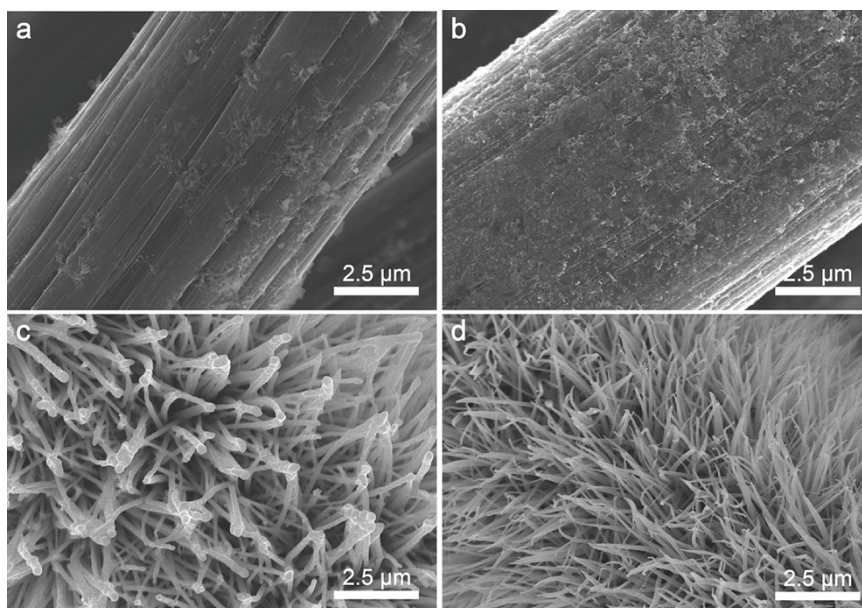


Fig. S8 SEM images of (a) CoS₂, (b) Fe-CoS₂, (c) P-CoS₂, and (d) Fe/P-CoS₂ after 2000 CV scans.

Table S1. Elemental contents of different catalysts calculated from XPS spectra.

Catalysts	Co (at.%)	S (at.%)	P (at.%)	Fe (at.%)
CoS₂	20.5	79.5	-	-
P-CoS₂	21.7	49.2	29.1	-
Fe-CoS₂	20.7	77.3	-	2.0
Fe/P-CoS₂	21.5	52.9	23.6	2.0

Table S2. Comparison of HER activity of different catalysts.

Catalysts	Overpotential (mV at 10 mA cm⁻²)	Tafel slope (mV dec⁻¹)	TOF (s⁻¹ at -0.12 V)
CoS₂	137	90	0.17
P-CoS₂	104	57	0.55
Fe-CoS₂	118	73	0.17
Fe/P-CoS₂	80	56	1.03

Table S3. EIS results of different catalysts.

Catalysts	R_s (Ω)	R_{ct} (Ω)
CoS₂	2.10	87.4
P-CoS₂	1.74	49
Fe-CoS₂	1.26	27
Fe/P-CoS₂	2.06	10.9

Table S4. HER activity comparison of CoS₂ based catalysts.

Electrocatalysts	Overpotential (mV) at 10 mA cm ⁻²	Tafel slop (mV dec ⁻¹)	Electrolyte	Ref.
Fe/P-CoS₂	80	56	0.5 M H ₂ SO ₄	This work
CoS₂ NW	145	51.6	0.5 M H ₂ SO ₄	<i>J. Am. Chem. Soc.</i> , 2014, 136, 10053
CoS₂/RGO-CNT	142	82	0.5 M H ₂ SO ₄	<i>Angew. Chem. Int. Ed.</i> , 2014, 53, 12594
CoS₂@MoS₂/RG O	98	37.4	0.5 M H ₂ SO ₄	<i>Adv. Funct. Mater.</i> , 2017, 1602699
Ni-doped CoS₂	156	52	0.5 M H ₂ SO ₄	<i>Electrochim. Acta</i> , 2017, 228, 428-435
CoS₂@WS₂/CC	97.2	66	0.5 M H ₂ SO ₄	<i>J. Mater. Chem. A</i> , 2017, 5, 15552
CoS₂/CoSe₂	80	33.6	0.5 M H ₂ SO ₄	<i>J. Mater. Chem. A</i> , 2017, 5, 2504
CoS₂ NA/Ti	140	107	1.0 M KOH + 0.3 M urea	<i>Electrochim. Acta</i> , 2017, 246, 776
CNF@CoS₂	110	66.8	0.5 M H ₂ SO ₄	<i>Inorg. Chem. Front.</i> , 2016, 3, 1280
Co_{1-x}V_xSP	55	50	0.5 M H ₂ SO ₄	<i>Adv. Energy Mater.</i> , 2018, 1702139
N-doped CoS₂	57	48	0.5 M H ₂ SO ₄	<i>ACS Energy Lett.</i> , 2017, 2, 1022
Ni-doped CoS₂ nanoneedle	350 mV at 30 mA cm ⁻²	76	1 M KOH	<i>Catalysts</i> , 2017, 7, 366
CoS P/CNT	48	55	0.5 M H ₂ SO ₄	<i>Nat. Commun.</i> , 2016, 7, 10771
CoS₂-CFN	136	73	0.5 M H ₂ SO ₄	<i>Catal. Sci. Technol.</i> , 2016, 6, 4545-
CoS₂ nanopyramid array	70	64.5	0.5 M H ₂ SO ₄	<i>J. Mater. Chem. A</i> , 2015, 3, 6306
P-doped CoS₂	67	50	0.5 M H ₂ SO ₄	<i>Chem. Commun.</i> , 2015, 51, 14160
Fe_{0.54}Co_{0.46}S_{0.92}/C NTs/CC	70	64	1 M KOH	<i>ACS Energy Lett.</i> , 2017, 2, 2778
CoS_{2x}Se_{2(1-x)}	129.5	44	0.5 M H ₂ SO ₄	<i>Nanoscale</i> , 2016, 8, 4699