Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Synthesis of Co_9S_8 nanoflakes by one-step solvent-free solid-state method for multiple electrocatalytic reactions

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Experimental section

Chemicals: Cobalt power was purchased from Alfa Aesar. RuO_2 (99.9% metals basis), Sulfur power (99.99% metals basis), and $CoCl \cdot 6H_2O$ (AR) were purchased from Aladdin. Urea (AR, 99%), Pt/C (20%), and $Na_2S \cdot 9H_2O$ (AR, ≥ 98.0%) were obtained from Shanghai Macklin Biochemical Co., Ltd. Commercial active carbon YP-50 was obtained from Toray.

Turnover frequency (TOF) calculation: The per-site TOF values were calculated based on the following equation:

$$\text{TOF}= \frac{\text{total hydrogen turnover / cm}^{-2}\text{ geometric area}}{\text{number of active sites / cm}^{-2}\text{ geometric area}}$$

The total number of hydrogen turnovers was calculated from the current density according to the:

$$\text{no. of } H_2 = j\ \frac{mA}{cm^2} \left(\frac{1\ C\ s^{-1}}{1000\ mA}\right) \left(\frac{1\ mol\ e^{-1}}{96485.3\ C}\right) \left(\frac{1\ mol\ H_2}{2\ mol\ e^-}\right) \left(\frac{6.02 \times 10^{23}\ molecules\ H_2}{1\ mol\ H_2}\right) =$$

$$3.12 \times 10^{15}\ \frac{H_2\ s^{-1}}{cm^2}\ per\ \frac{mA}{cm^2}$$

Considering that it was difficult to determine the exact quantity of active sites on the catalyst surface, the total number of surface Co sites was assumed as the number of active sites according to the reference. The molar volume of Co was obtained by the equation of the molar mass of Co divided by the density of Co, and thus the molar volume of Co is determined to be 6.62 $cm^3\ mol^{-1}$. The average surface atoms per 1 square centimeter could be required by the following equation [1]:

$$\text{surface sites}= \left(\frac{1\times 6.02\times 10^{23}\text{atoms}}{1\text{ mol}} \times \frac{1\text{ mol}}{6.62\text{ cm}^3}\right) = 2.02 \times 10^{15}\ \frac{\text{atoms}}{\text{cm}^2}$$

Thus, the current density from the LSV polarization curves can be converted into the TOF values according to the following equation:

$$\text{TOF} = \frac{\left(3.12 \times 10^{15}\ \frac{\text{H}_2\text{s}^{-1}}{\text{cm}^2}\ \text{per}\ \frac{\text{mA}}{\text{cm}^2}\right) \times |\text{j}|}{\text{surface sites} \times \text{A}_{\text{ECSA}}}$$

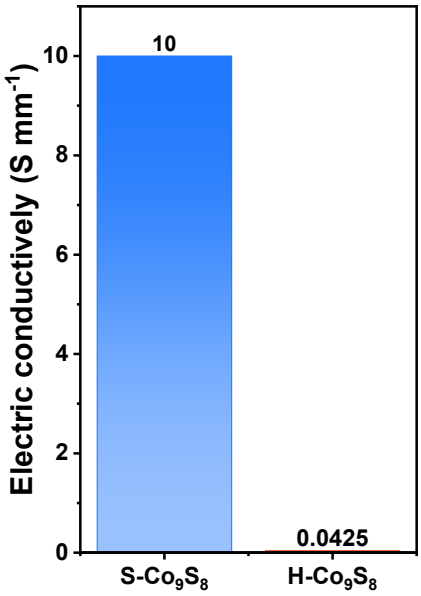

Figure S1. Values of electronic conductivity for S-Co_9S_8 and H-Co_9S_8.

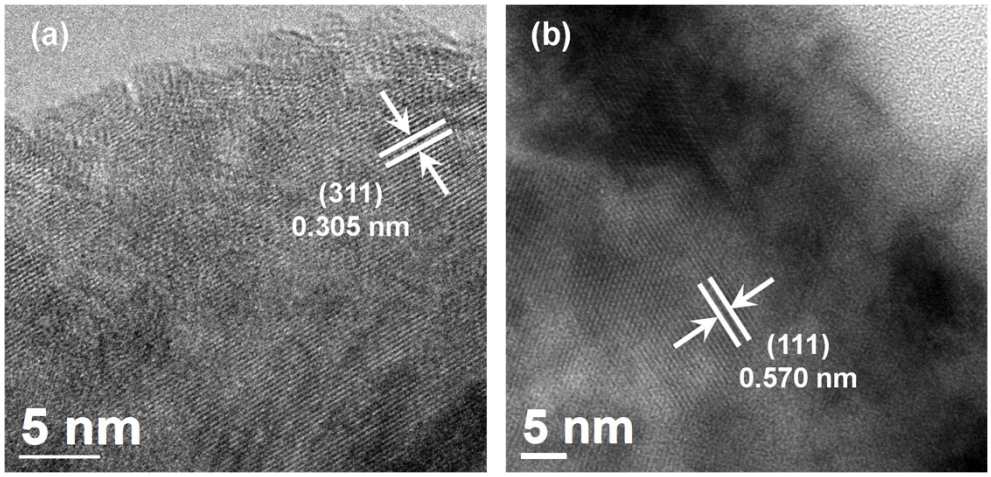

Figure S2. HRTEM images of (a) S-Co_9S_8 and (b) H-Co_9S_8.

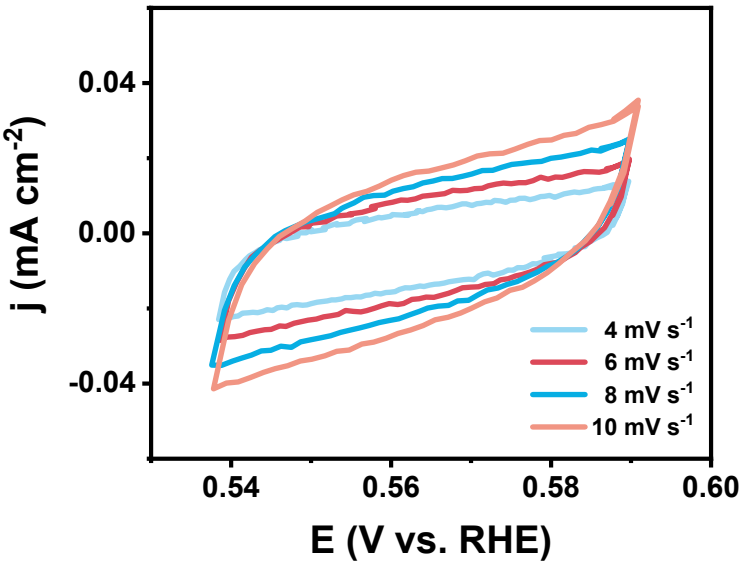

Figure S3. CV curves of S-Co_9S_8 at different sweep rates in 0.5 M H_2SO_4.

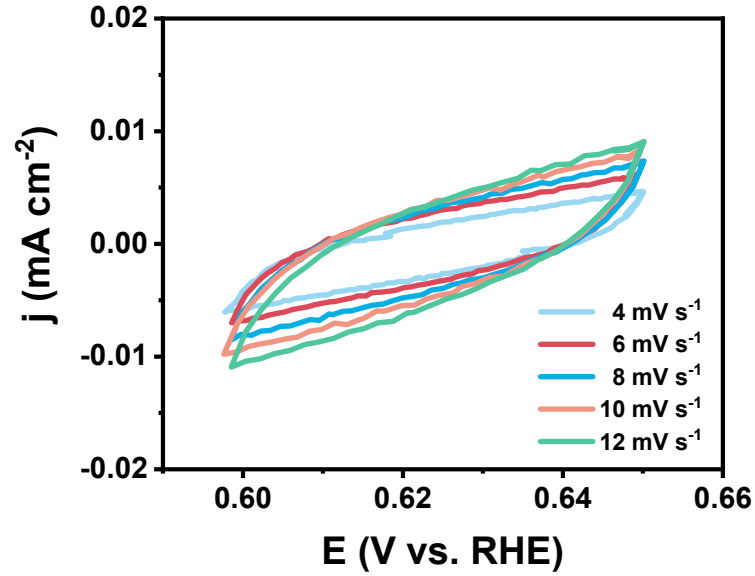

Figure S4. CV curves of H-Co_9S_8 at different sweep rates in 0.5 M H_2SO_4.

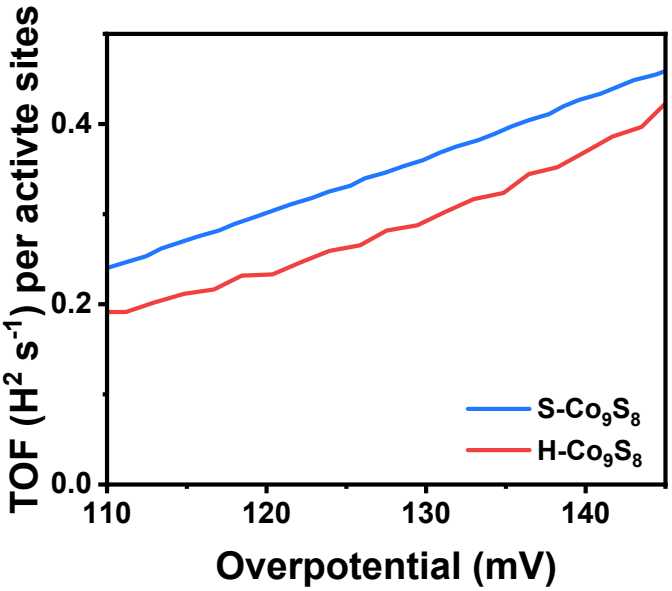

Figure S5. TOF values of S-Co_9S_8 and H-Co_9S_8 electrodes.

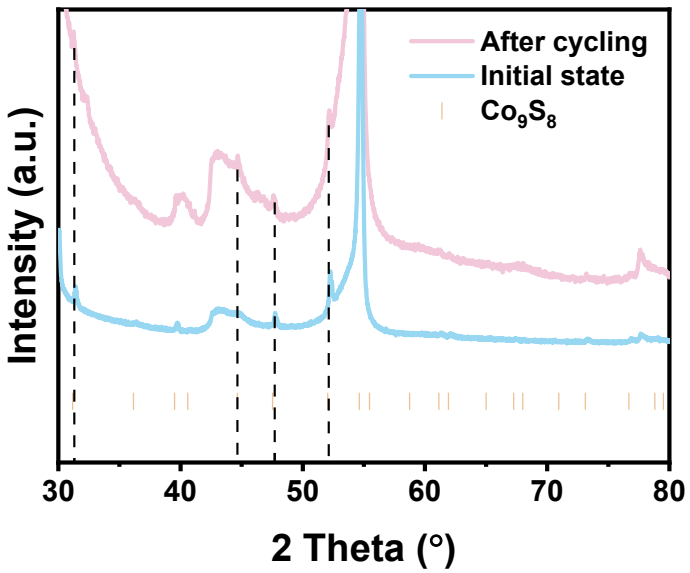

Figure S6. XRD patterns of S-Co_9S_8 before and after the cycling stability test in acidic HER.

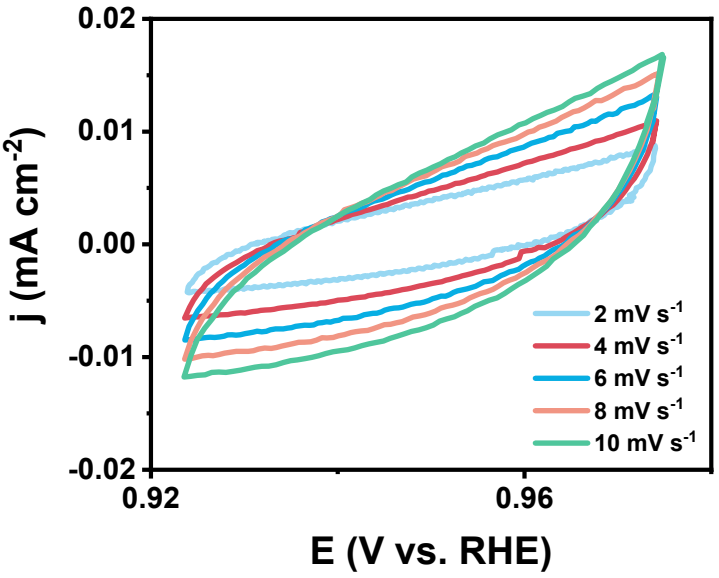

Figure S7. CV curves of S-Co_9S_8 at different sweep rates in 1 M KOH.

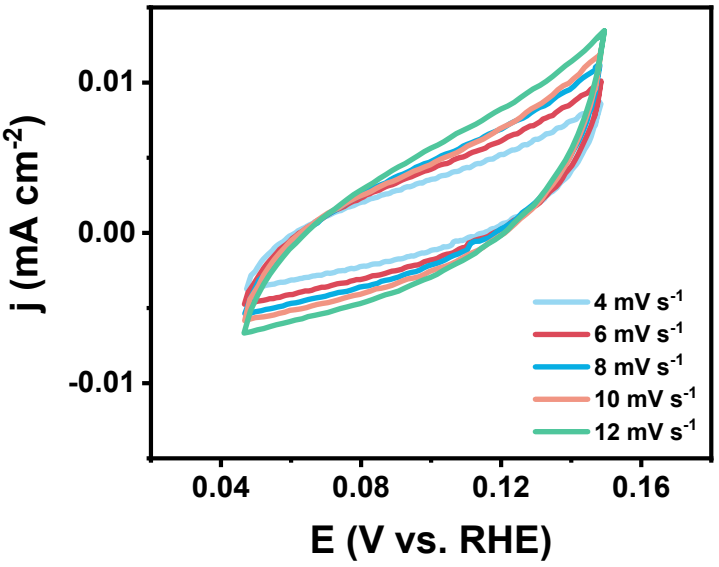

Figure S8. CV curves of H-Co_9S_8 at different sweep rates in 1 M KOH.

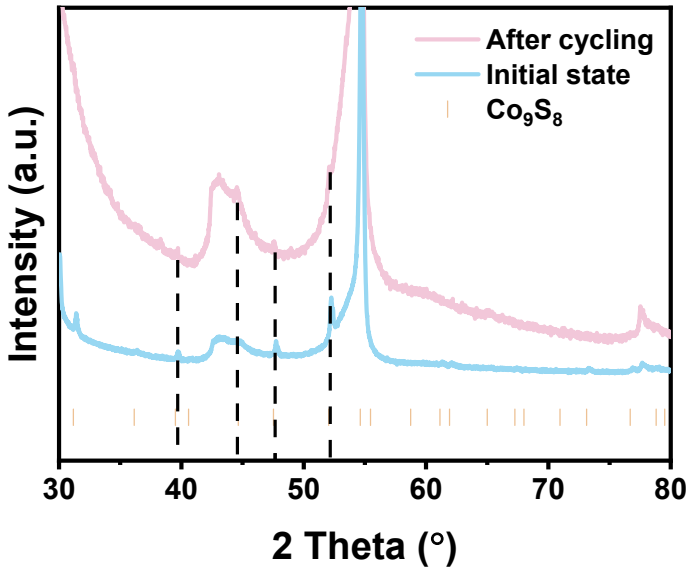

Figure S9. XRD patterns of S-Co_9S_8 before and after the alkaline OER test.

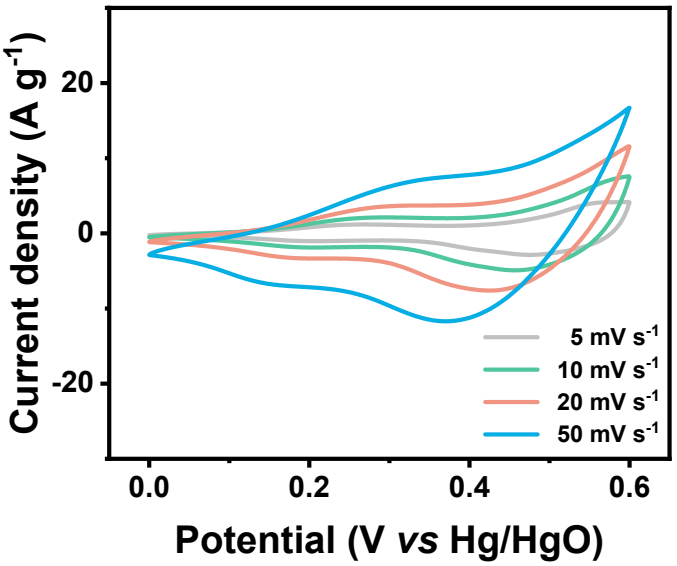

Figure S10. CV curves of H-Co_9S_8 measured in 1M KOH at the range of current densities between 5 – 50 mV s^{-1}.

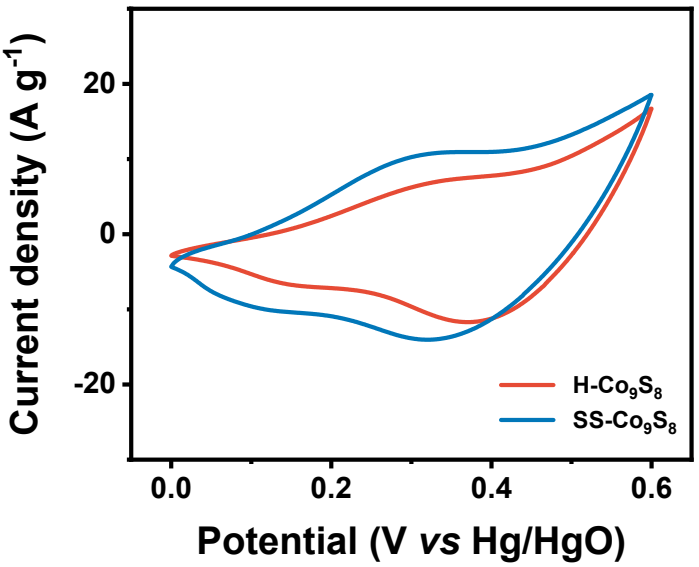

Figure S11. The comparison of CV curves was measured at 50 mV s^{-1} for S-Co_9S_8 and H-Co_9S_8.

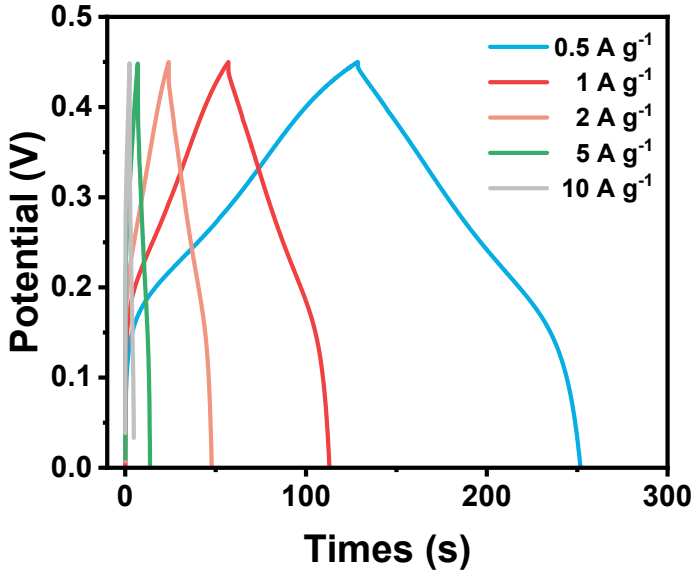

Figure S12. GCD curves under various current densities of the H-Co_9S_8 electrode by using 1 mol L^{-1} KOH aqueous electrolyte.

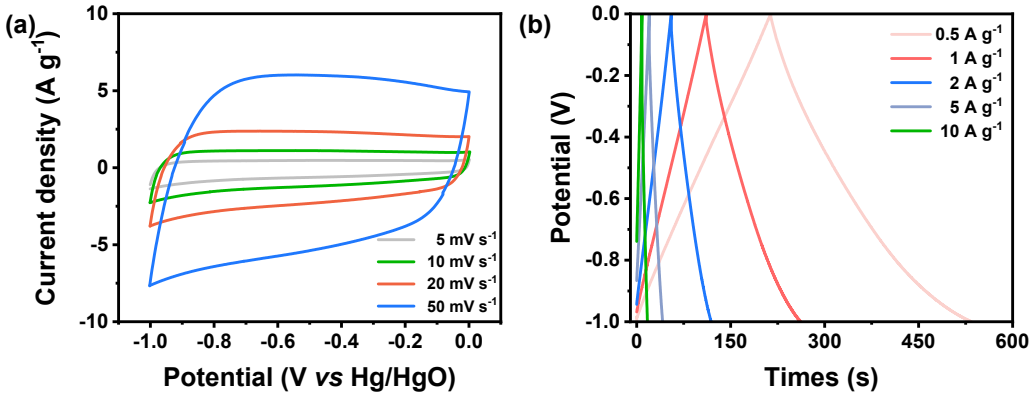

Figure S13. CV curves and GCD curves of the YP-50 electrode by using 1 mol L^{-1} KOH aqueous electrolyte.

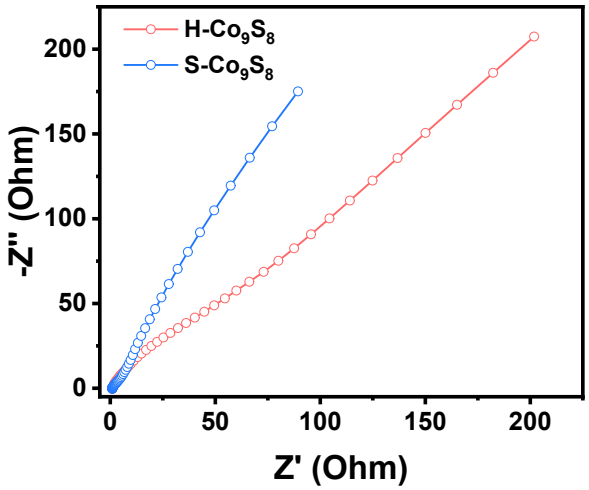

Figure S14. Nyquist plots for S-Co_9S_8 and H-Co_9S_8.

Table S1. Structural parameters of S-Co_9S_8. The space group is Fm-3m (No. 225), a = b = c = 9.93 Å.

Atom	*x*	*y*	*z*	Occupancy
Co1(Co)	0.5	0.5	0.5	1.0
Co2(Co)	0.126087	0.126087	0.126087	1.0
S1(S)	0.25	0.25	0.25	1.0
S2(S)	0.277277	0.0	0.0	1.0

Table S2. Structural parameters of H-Co_9S_8. The space group is Fm-3m (No. 225), a = b = c = 8.52 Å.

Atom	*x*	*y*	*z*	Occupancy
Co1(Co)	0.5	0.5	0.5	1.0
Co2(Co)	0.12623	0.12623	0.12623	1.0
S1(S)	0.25	0.25	0.25	1.0
S2(S)	0.26230	0.0	0.0	1.0

Table S3. Comparison of Tafel slope and overpotential (η) for S-Co_9S_8 and other Co_9S_8-based acidic HER electrocatalysis.

Materials	η at 10 mA cm^{-2} (mV vs RHE)	Reference
Co_9S_8@C	240	***ACS Appl. Mater. Interfaces***, 2015, 7, 980–988
Co_9S_8/NC@MoS_2	117	***ACS Appl. Mater. Interfaces***, 2017, 9, 28394–28405
Co_9S_8-MoS_2 HNBs	106	***Chem.–Asian J.***, 2018, 13, 413–420
Co_9S_8@MoS_x/CC	98	***Nano Energy***, 2017, 32, 470–478

Co_9S_8/1L MoS_2 (3.5%)	97	***Adv. Mater.***, 2018, 30, 1707301
Fe-Co_9S_8 NSs/CC	65	***Electrochim. Acta*, 2018, 264, 157–165**
Co_9S_8/WS_2	138	***J. Mater. Chem. A*, 2017, 5, 23361–23368**
Co_9S_8/CNFs	165	***Part. Part. Syst. Charact.*, 2017, 34, 1700189**
Co_9S_8@MoS_2 - 750	171	***ACS Appl. Mater. Interfaces*, 2018, 10, 1678–1689**
S-Co_9S_8	96.3	This work

Reference:

[1] H. Sun, Z. Yan, C. Tian, C. Li, X. Feng, R. Huang, Y. Lan, J. Chen, C. Li, Z. Zhang, M. Du, Bixbyite-type Ln_2O_3 as promoters of metallic Ni for alkaline electrocatalytic hydrogen evolution, *Nat. Commun.*，2022, **13**, 3857.