

**1. High resolution TEM images and EDS mapping of the Co SACs and Co
SACs + Co₉S₈ catalysts.**

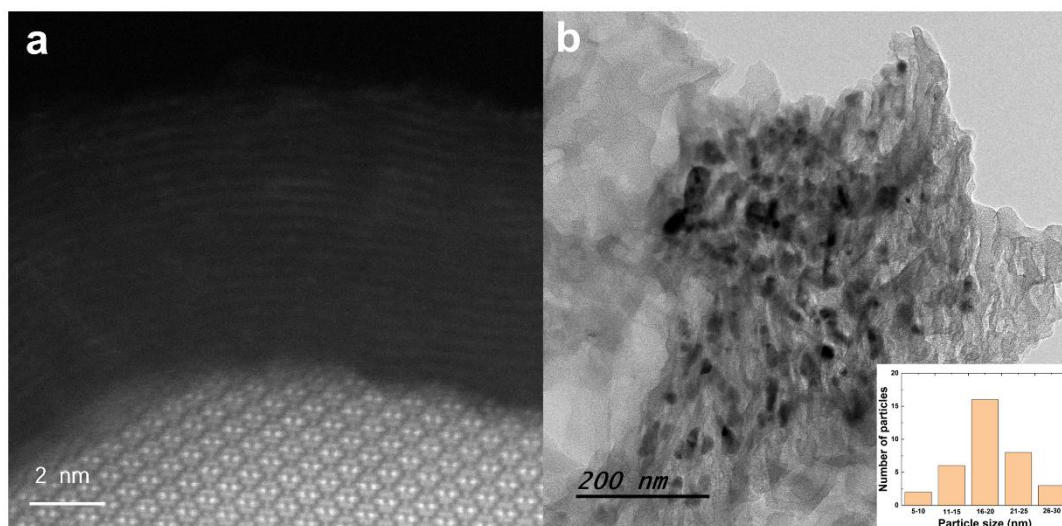


Figure S1 (a) HAADF-STEM image of Co SACs + Co₉S₈ catalyst. (b) size distribution of Co₉S₈ nanoparticles.

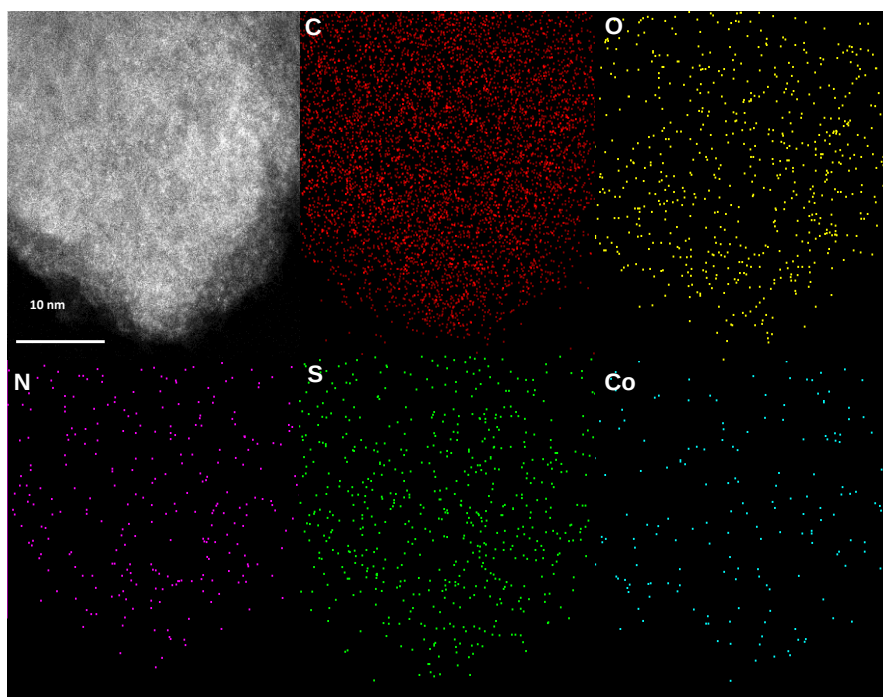


Figure S2 EDS mapping of the Co SACs + Co₉S₈ catalyst.

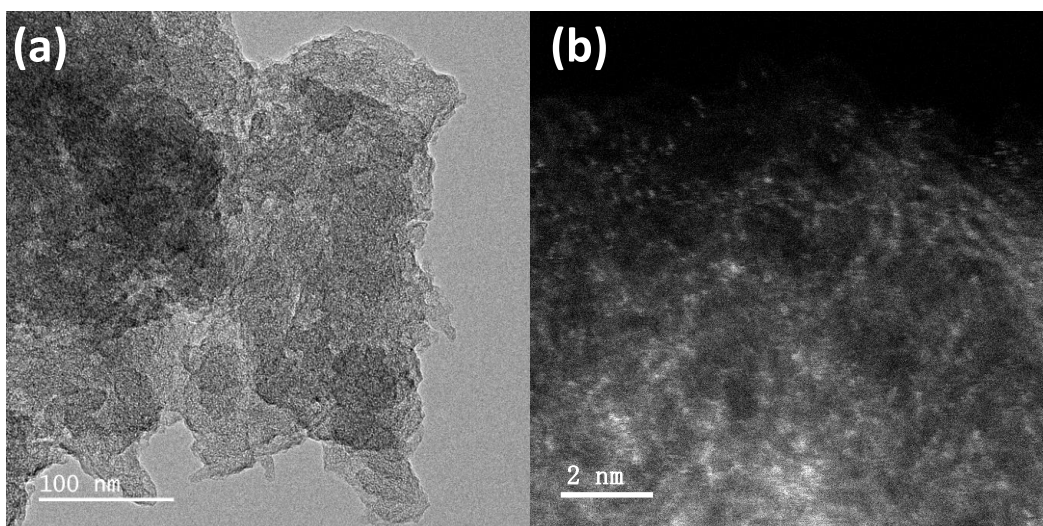


Figure S3 (a) HRTEM image and (b) HAADF-STEM image of the Co SACs catalyst.

2. Raman spectra in lower wavenumber range of the Co SACs and Co SACs + Co₉S₈ catalysts.

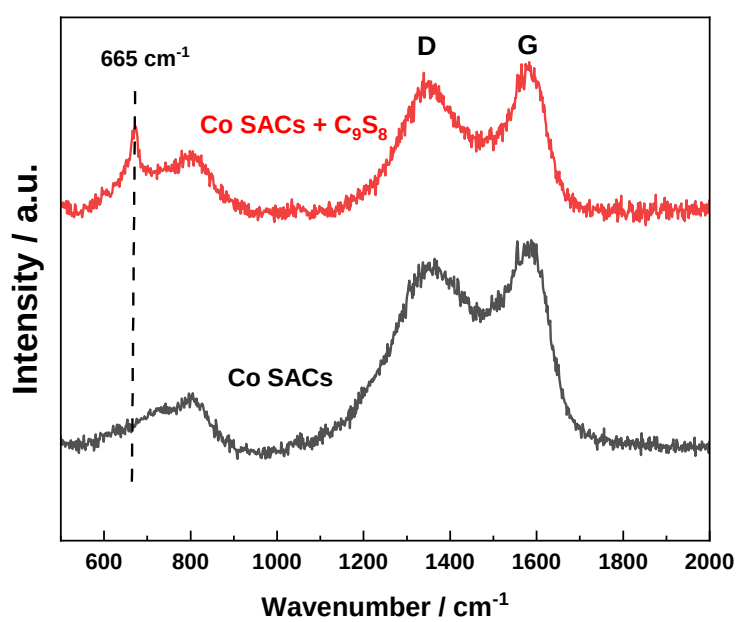


Figure S4 Raman spectra of the Co SACs and Co SACs + Co₉S₈ catalysts.

3. Table S1: External, microporous, and total surface area of the Co SACs and Co SACs + Co₉S₈ catalysts determined by N₂ adsorption.

Catalyst	External SA [m ² g ⁻¹]	Microporous SA [m ² g ⁻¹]	Total SA [m ² g ⁻¹]
Co SACs	91.7	228.3	320
Co SACs + Co ₉ S ₈	70.6	338.6	409.2

Table S2: Average pore size and pore volume of the Co SACs and Co SACs + Co₉S₈ catalysts determined by N₂ adsorption.

Catalyst	Average pore size [nm]	Pore volume [cm ³ g ⁻¹]
Co SACs	5.85	0.46
Co SACs + Co ₉ S ₈	4.11	0.51

4. XPS survey spectra, S 2p and Co 2p spectra of the Co SACs and Co SACs + Co₉S₈ catalysts

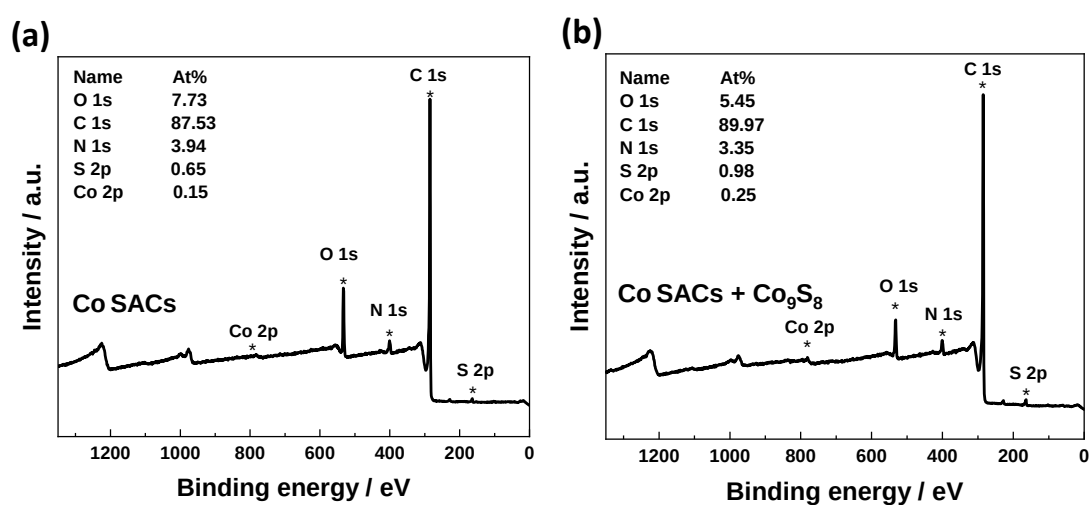


Figure S5 XPS survey spectrum of (a) Co SACs and (b) Co SACs + Co₉S₈ catalyst.

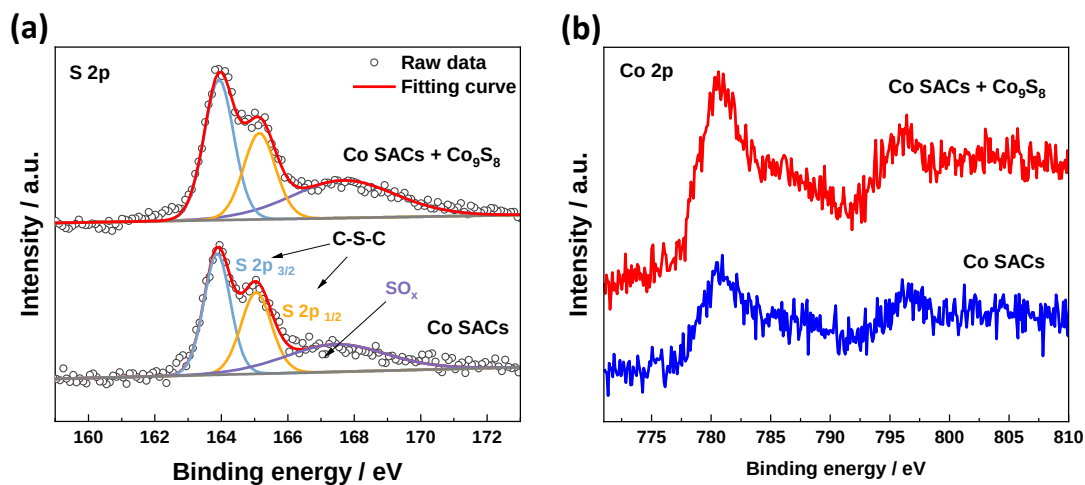


Figure S6 High-resolution (a) S 2p and (b) Co 2p XPS spectra of the Co SACs and Co SACs + Co₉S₈ catalysts.

5. EXAFS fitting results of the Co SACs and Co SACs + Co₉S₈ catalyst

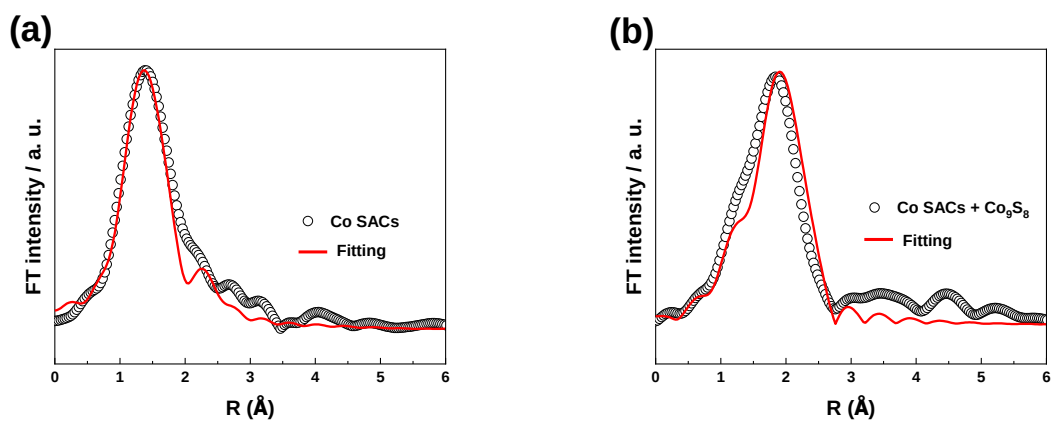


Figure S7 The EXAFS fitting curves of the (a) Co SACs and (b) Co SACs + Co₉S₈.

Table S3 Co K-edge EXAFS curve fitting parameters for the Co SACs and Co SACs + Co₉S₈

Sample	Bond type	Coordination number	Bond length (Å)	Bond disorder σ^2 (Å ²)	R factor
Co SACs	Co-N	2.1	1.88	0.0067	0.003
	Co-C	1	2.15	0.0007	
Co SACs + Co ₉ S ₈	Co-N	2.8	1.89	0.016	0.008
	Co-S	0.85	2.22	0.007	
	Co-Co	3.6	2.49	0.005	

6. Steady-state RRDE measurements investigating the 2nd heat treatment effect on the Co SACs and Co SACs + Co₉S₈ catalysts

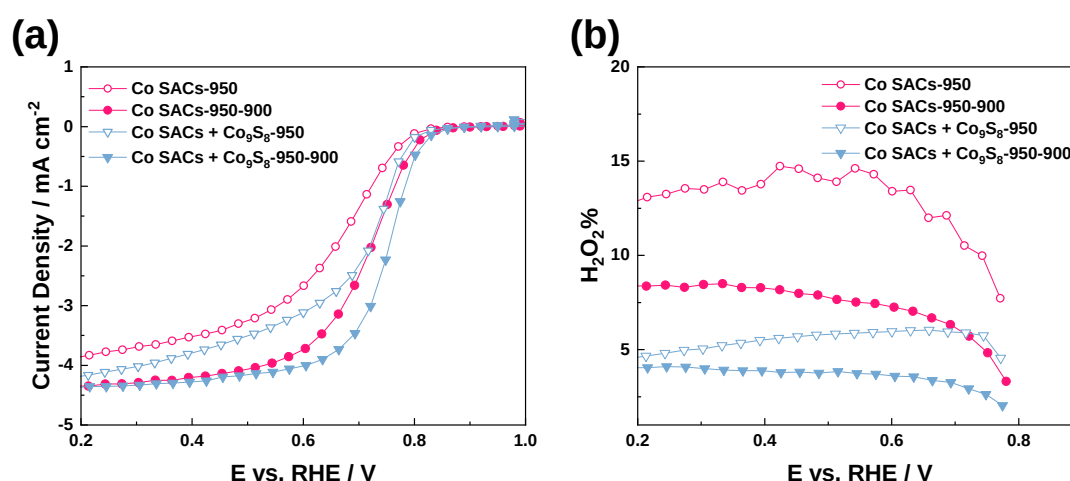


Figure S8 Steady-state RRDE measurements of the Co SACs and Co SACs + Co₉S₈ catalysts in O₂-saturated 0.5 M H₂SO₄ after the first and second heat treatment, catalyst loading: 750 μg cm⁻², rotating speed: 1600 rpm, 30 mV step potential, 30s hold.

7. Co 2p, N 1s, and S 2p XPS spectra of the Co SACs and Co SACs + Co₉S₈ catalysts after the first and second heat treatment

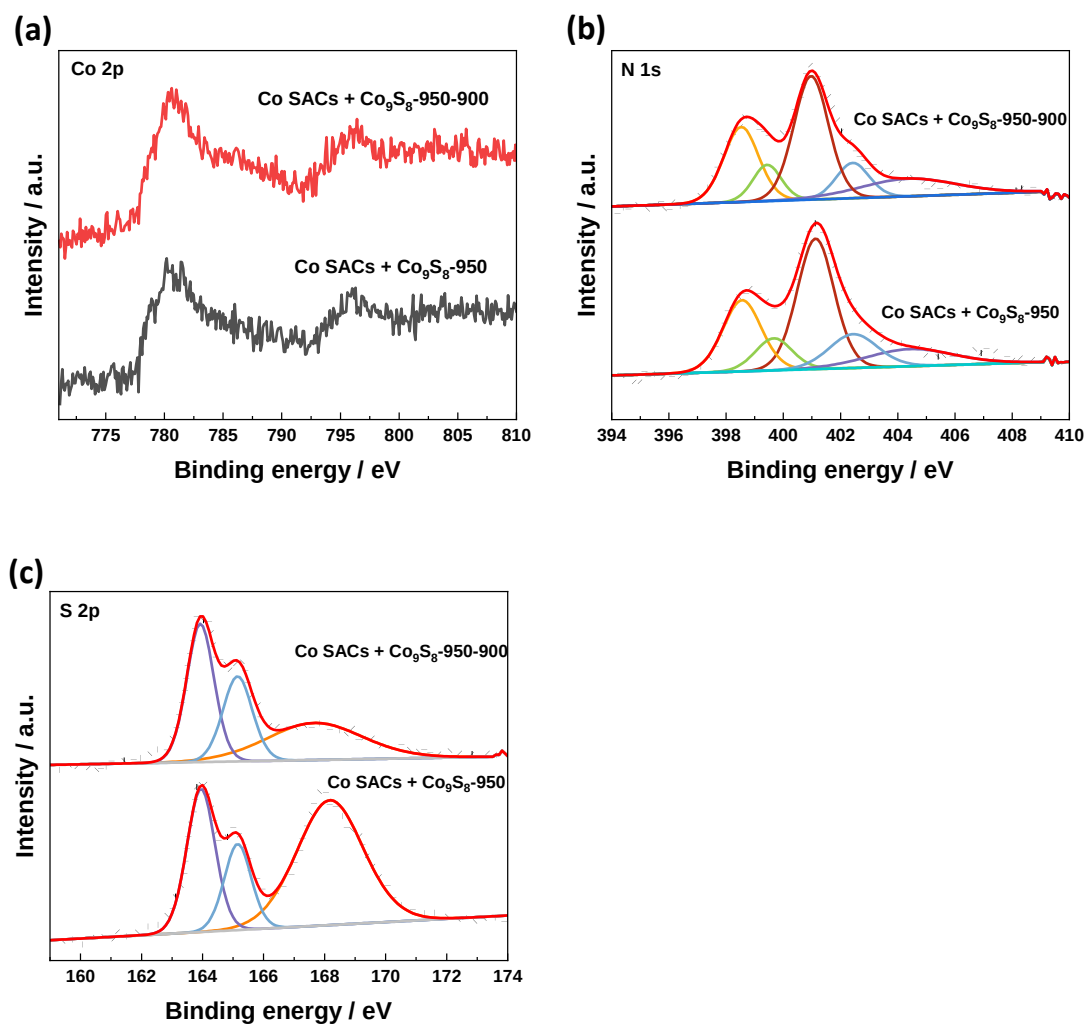


Figure S9 High resolution (a) Co 2p, (b) N 1s, and (c) S 2p XPS spectra of the Co SACs and Co SACs + Co₉S₈ catalysts after first and second heat treatment

8. Table S4: Surface elemental composition of the best acid performing catalysts before and after the second heat treatment as detected by XPS

Catalysts	C [at%]	N [at%]	O [at%]	S [at%]	Metal [at%]
Co SACs-950	86.78	3.97	7.85	1.34	0.06
Co SACs-950-900	87.53	3.94	7.73	0.65	0.15
Co SACs+Co ₉ S ₈ -950	87.32	3.38	7.23	1.98	0.09
Co SACs+Co ₉ S ₈ -950-900	89.97	3.35	5.45	0.98	0.25

9. Long term chronoamperometry test on the Co SACs + Co₉S₈ catalyst.

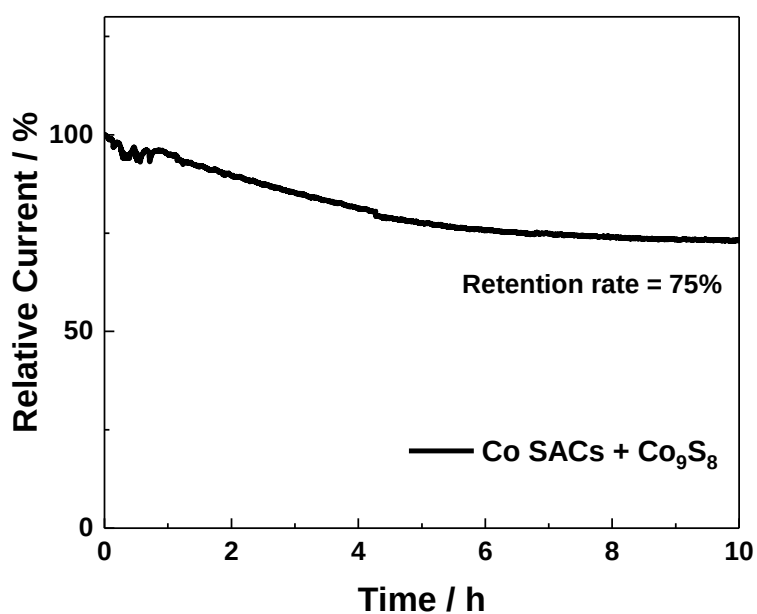


Figure S10 Chronoamperometry responses (in O₂-saturated 0.5 M H₂SO₄) of Co SACs + Co₉S₈

catalysts coated carbon paper, catalysts loading: 1 mg cm⁻².

10. Physical characterization on the post-ORR test Co SACs + Co₉S₈ catalyst

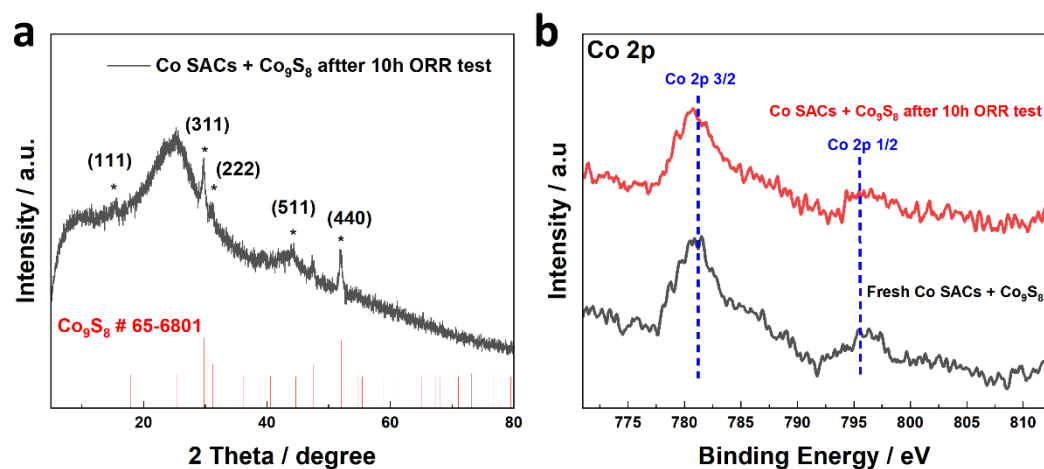


Figure S11 (a) XRD pattern and (b) Co 2p region XPS spectra of Co SACs + Co₉S₈ catalysts after 10h ORR tests.

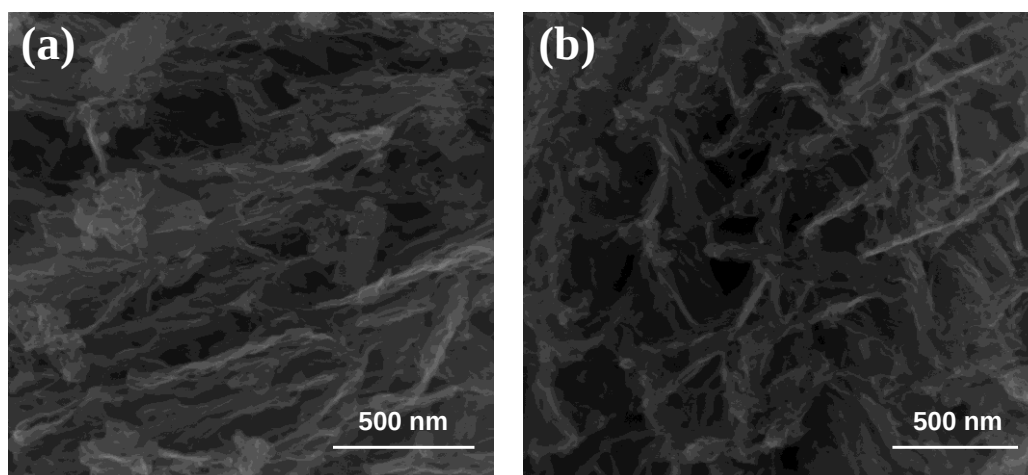


Figure S12 SEM images of the fresh Co SACs + Co₉S₈ catalysts and after 10h ORR tests.

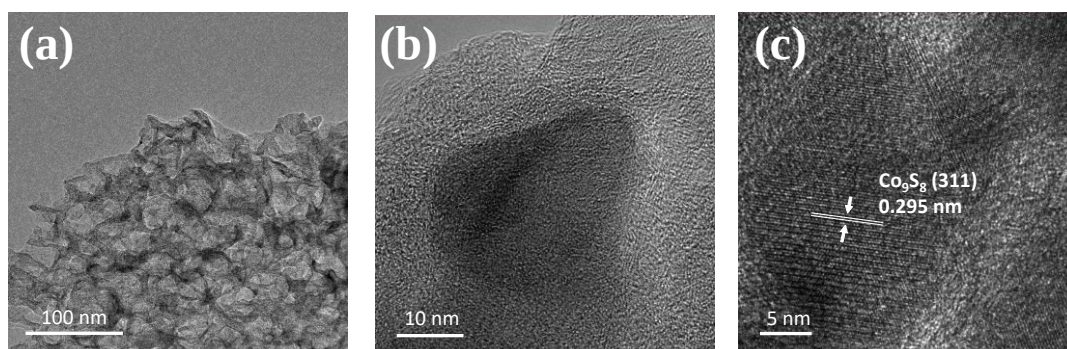


Figure S13 TEM images of the fresh Co SACs + Co₉S₈ catalysts and after 10h ORR tests.

11. RRDE nitrite poisoning experiments on the Co SACs and Co SACs + Co₉S₈ catalysts.

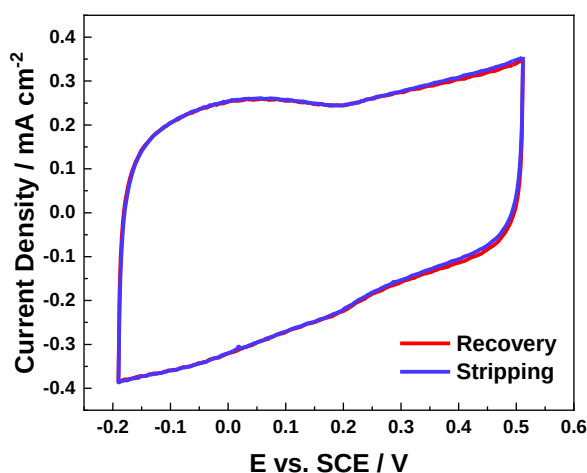


Figure S14 wide range baseline scan (avoid nitrite reduction area) for the catalyst layer before, during and after nitrite adsorption. All experiments were performed in a 0.5 M acetate buffer at pH 5.2 for the Co SACs + Co₉S₈ catalyst using a rotating disk electrode setup; catalyst loading: 0.2mg cm⁻².

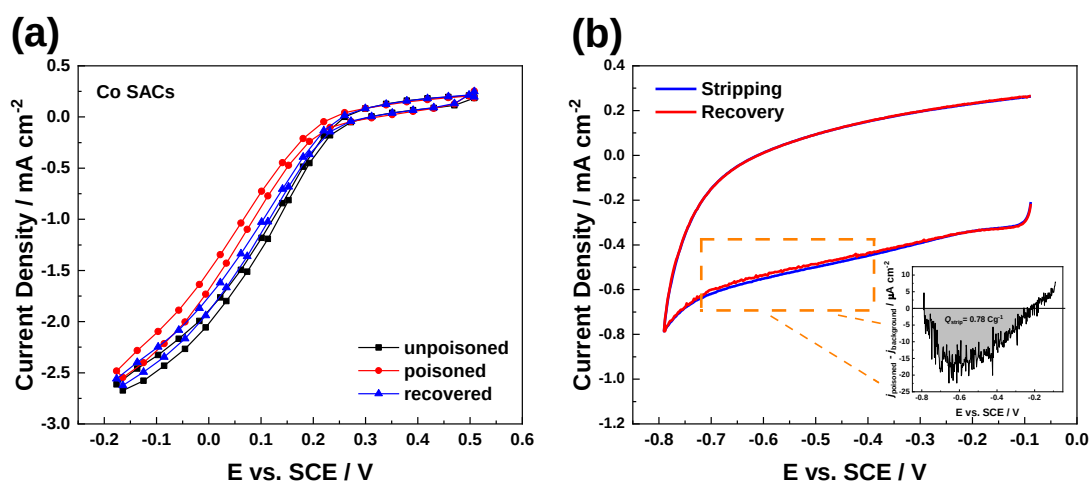


Figure S15 (a) Steady state ORR tests of catalyst layer before, during and after nitrite adsorption. (b) Narrow baseline scan in the nitrite reductive stripping region during and after nitrite adsorption. Inset is the stripping charge calculated by subtracting the recovered from poisoned curve in Figure S15b. All experiments were performed in a 0.5 M acetate buffer at pH 5.2 for the bare Co SACs catalyst using a rotating disk electrode setup; catalyst loading: 0.2 mg cm⁻².

12. Physical characterizations on the Co SACs + high loading Co₉S₈ catalyst.

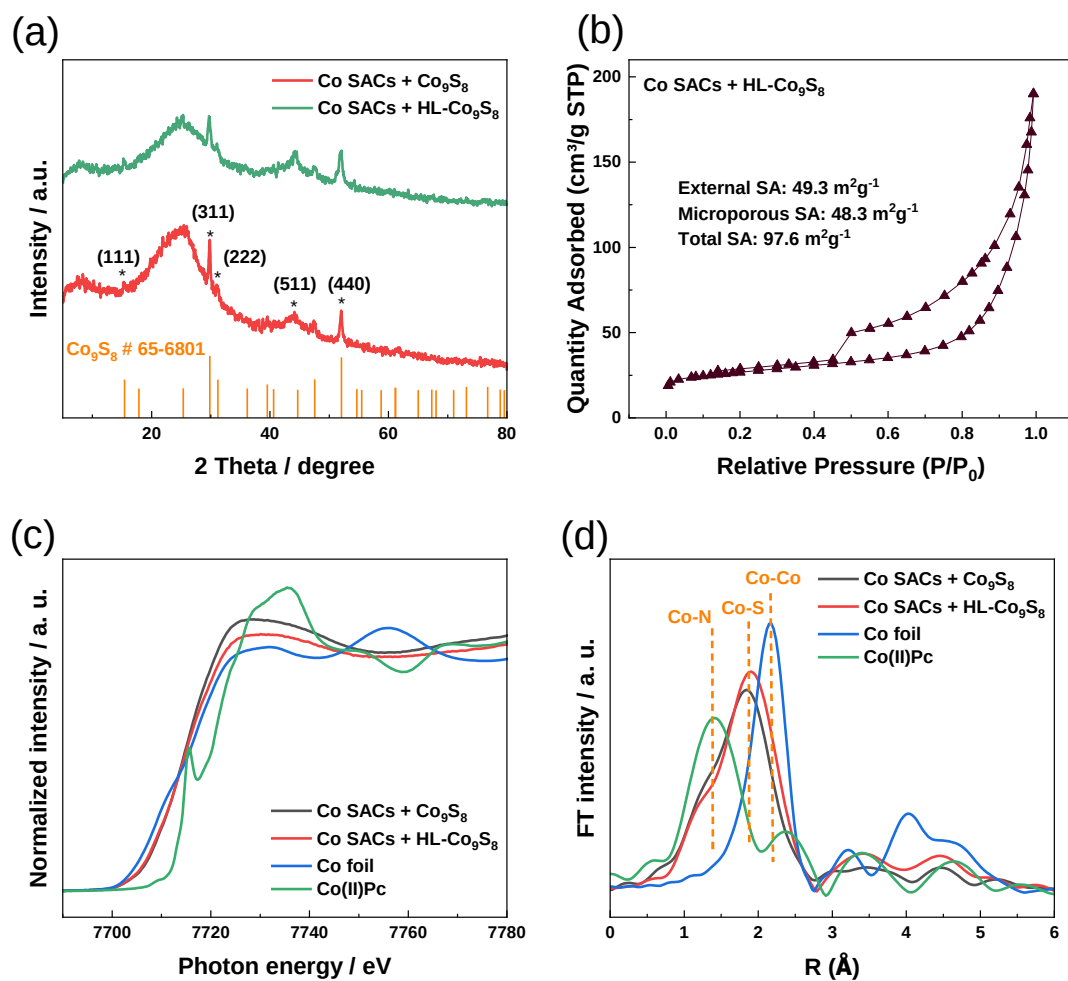


Figure S16 (a) XRD patterns of the Co SACs + Co₉S₈ and Co SACs with high loading Co₉S₈ catalysts. (b) N₂ isotherms of the Co SACs with high loading Co₉S₈ catalysts. (c) Co K-edge XANES spectra and (d) Fourier transforms of *k*²-weighted Co-K-edge EXAFS spectra of the Co SACs + Co₉S₈ and Co SACs with high loading Co₉S₈ catalysts, and the references samples.

13. EXAFS fitting results of the Co SACs + HL-Co₉S₈ catalyst

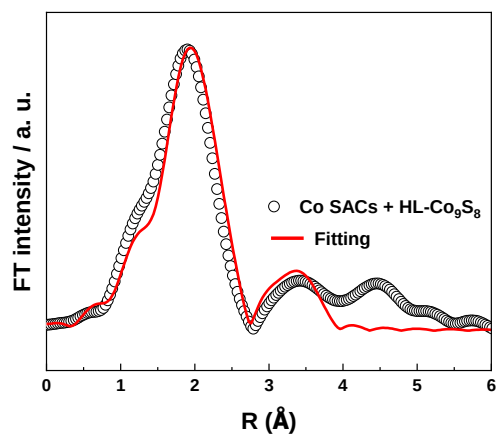


Figure S17 The EXAFS fitting curves of the Co SACs + HL Co₉S₈.

Table S5 Co K-edge EXAFS curve fitting parameters for the Co SACs + HL Co₉S₈.

Sample	Bond type	Coordination number	Bond length (Å)	Bond disorder σ^2 (Å ²)	R factor
Co SACs + HL Co₉S₈	Co-N	2.56	1.89	0.016	0.008
	Co-S	1	2.22	0.007	
	Co-Co ₁	3.66	2.49	0.005	
	Co-S-Co ₂	1.2	3.63	0.002	

14. Steady-state ORR polarizations on the Co SACs + high loading Co₉S₈ catalyst.

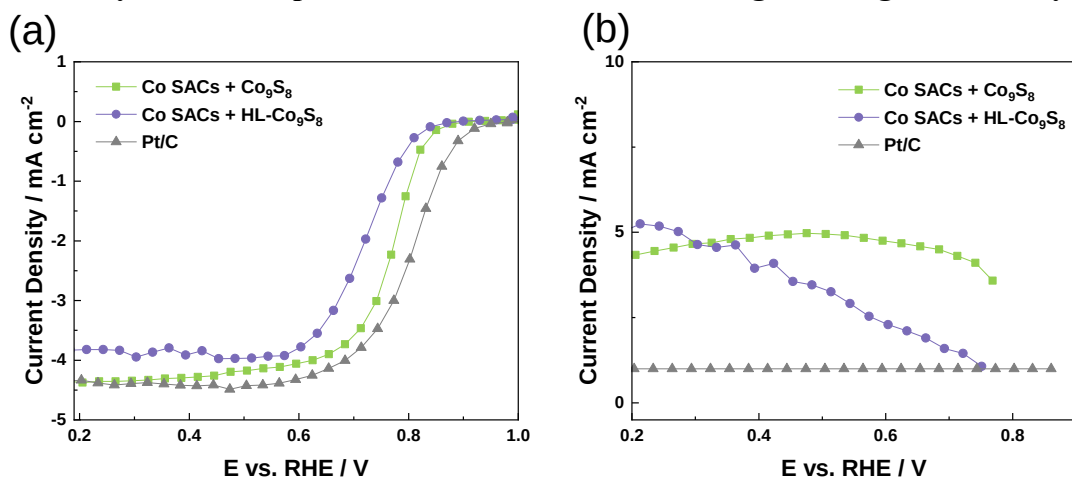


Figure S18 (a) Steady-state RRDE measurements of the Co SACs + Co₉S₈ and Co SACs with high loading Co₉S₈ catalysts in O₂-saturated H₂SO₄, catalysts loading: 750 μg cm⁻², rotating speed: 1600 rpm, 30 mV step potential, 30s hold.

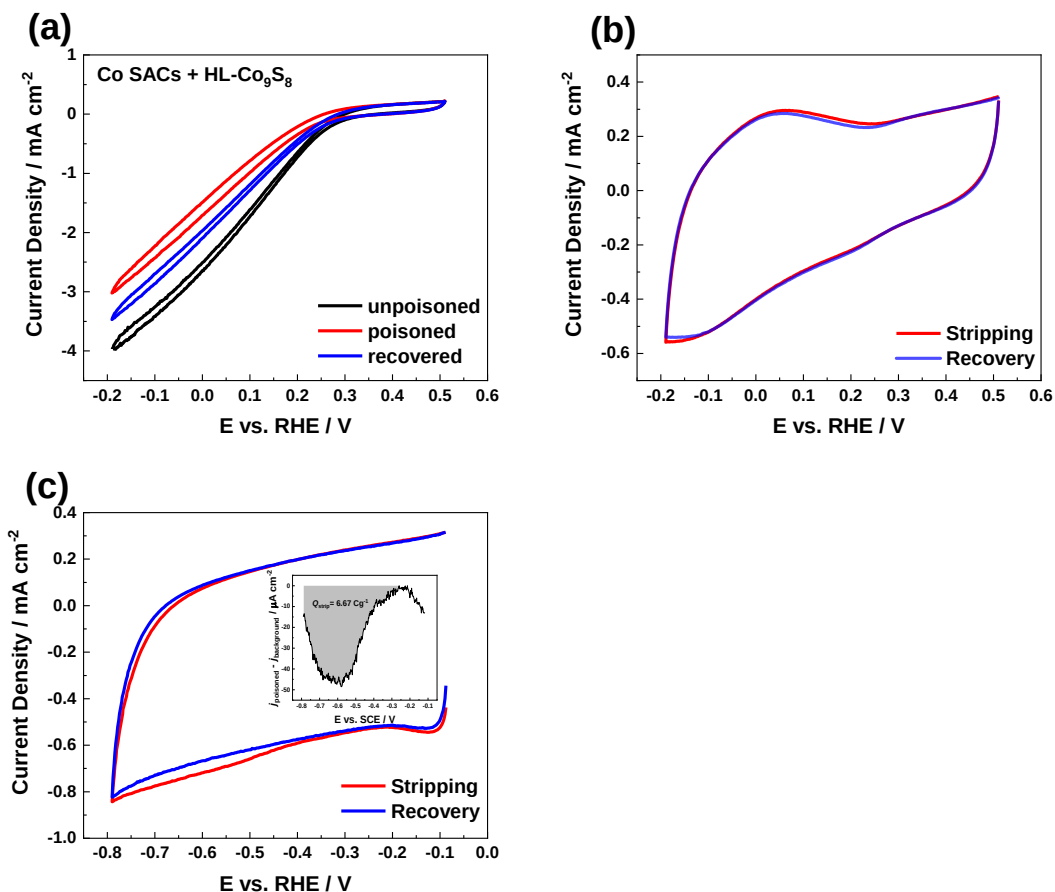


Figure S19 (a) Steady state ORR tests of catalyst layer before, during and after nitrite adsorption. (b) Wide range baseline scan (avoid nitrite reduction area) for the catalyst layer during and after nitrite adsorption. (c) Narrow baseline scan in the nitrite reductive stripping region during and after nitrite adsorption.

nitrite adsorption. Inset is the stripping charge calculated by subtracting the recovered from poisoned curve in Figure S19c. All experiments were performed in a 0.5 M acetate buffer at pH 5.2 for the bare Co SACs catalyst using a rotating disk electrode setup; catalyst loading: 0.2 mg cm⁻².

15. Comparison of H₂-O₂ PEMFC performance of the highest performing Co SACs + Co₉S₈ catalyst with other reported non-Fe PGM-free catalysts

Table S6: Comparison of H₂-O₂ PEMFC performance of the highest performing Co SACs + Co₉S₈ catalyst with other reported non-Fe PGM-free catalysts

Catalysts	Catalyst loading	Back pressure	P _{max}
	[mg cm ⁻²]	[bar]	[W cm ⁻²]
3wt%-Co-N _x /C	4.0	2.0	0.61
CoNC@KL600 ¹	4.0	1.0	0.72
Co (mlm)-NC (1.0) ²	6.3	1.0	0.64
H@CoNC ³	3	1.5 ^a	0.66
<i>d</i> -(Co _{NP} /Co _{SA} -N-C) ⁴	4	2.0	1.207
Co-N-C@F127 ⁵	4	1.0	0.87
1.6%CoNC-ArNH ₃ ⁶	3	2.0	0.8

^a 22 psi

16. Comparison of H₂-Air PEMFC performance of the highest performing Co SACs + Co₉S₈ catalyst with other reported non-Fe PGM-free catalysts

Table S7: Comparison of H₂-Air PEMFC performance of the highest performing Co SACs + Co₉S₈ catalyst with other reported non-Fe PGM-free catalysts

Catalysts	Catalyst loading	Back pressure	P _{max}
	[mg cm ⁻²]	[bar]	[W cm ⁻²]
3wt%-Co-N _x /C	4.0	2.0 bar	0.25
Co (mlm)-NC (1.0) ²	6.3	1.0 bar	0.32
<i>d</i> -(Co _{NP} /Co _{SA} -N-C) ⁴	4.0	1.0 bar	0.454
Co-N-C@F127 ⁵	4.0	1.0 bar	0.27
20Co-NC-1100 ⁷	4.0	2.1 bar ^a	0.28
Co-N-PCNF ⁸	4.0	1.0 bar	0.4
1.6%CoNC-ArNH ₃ ⁶	3	2.0 bar	0.305

^a 30 psi

Reference

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