

MOF-derived CoS_x as a bifunctional electrocatalyst for efficient sulfide oxidation and coupled ammonia synthesis

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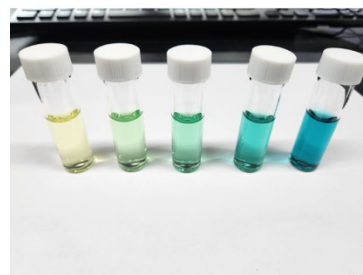
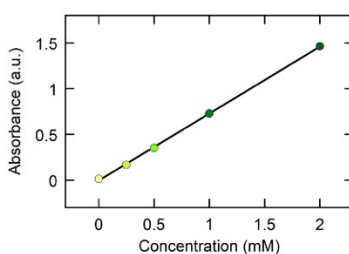
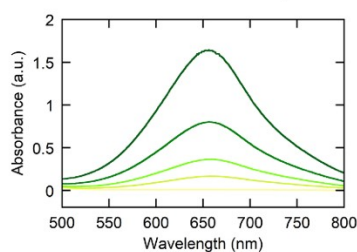
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a Ammonium quantification – Indophenol reagent



b Nitrite quantification – Griess reagent

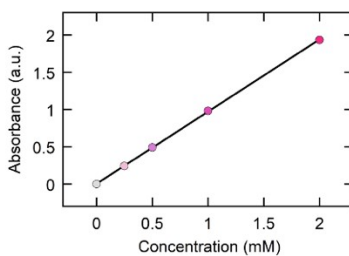
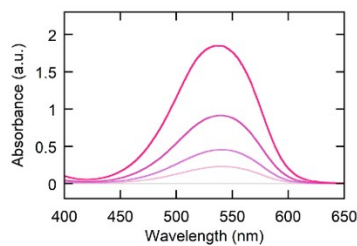


Figure S1. Calibration curves of (a) NH_4^+ and (b) NO_2^- using UV-vis spectrophotometry.

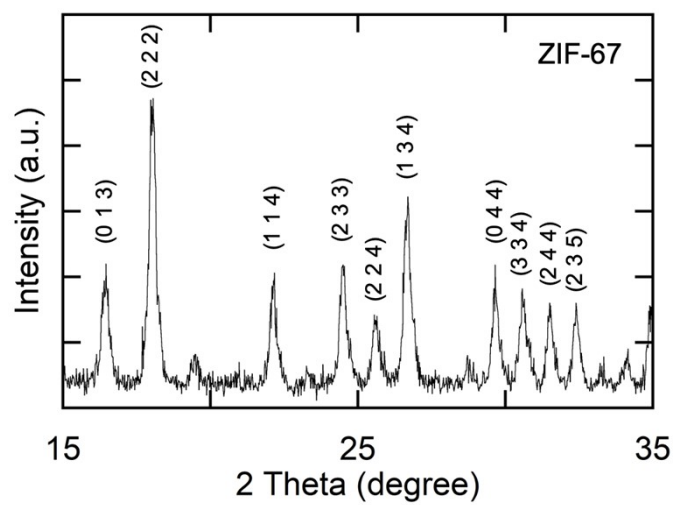


Figure S2. A XRD pattern of the synthesized ZIF-67.

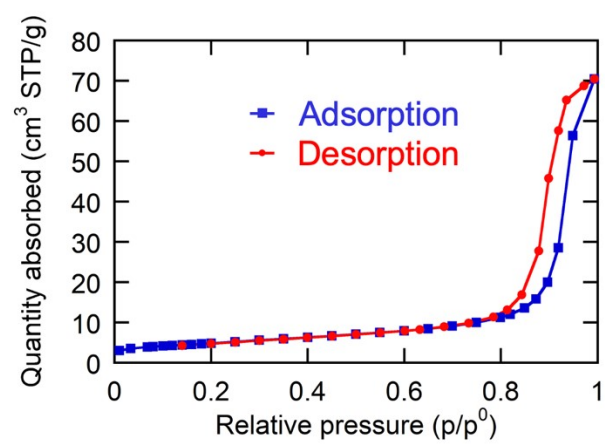


Figure S3. Nitrogen adsorption–desorption isotherm of MOF-derived CoS_x.

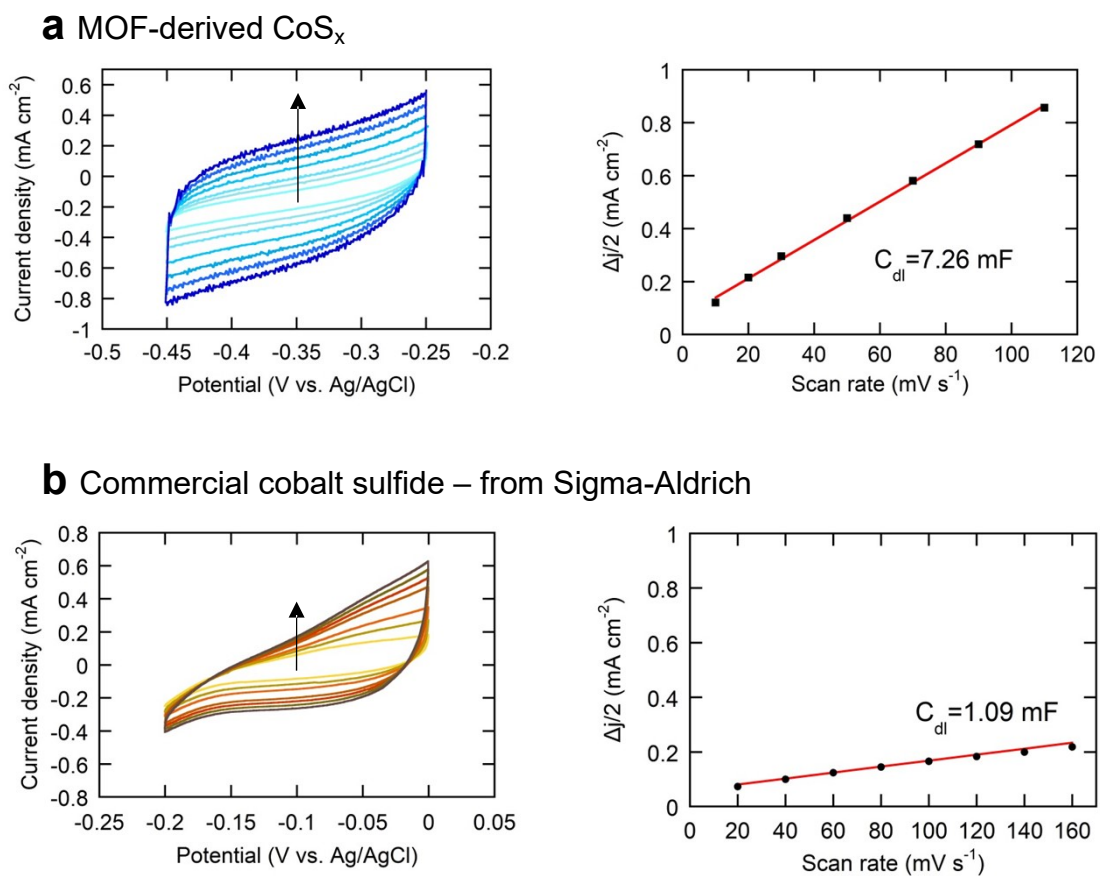


Figure S4. Electrochemical surface area estimated by cyclic voltammetry for (a) MOF-derived CoS_x and (b) commercial cobalt sulfide.

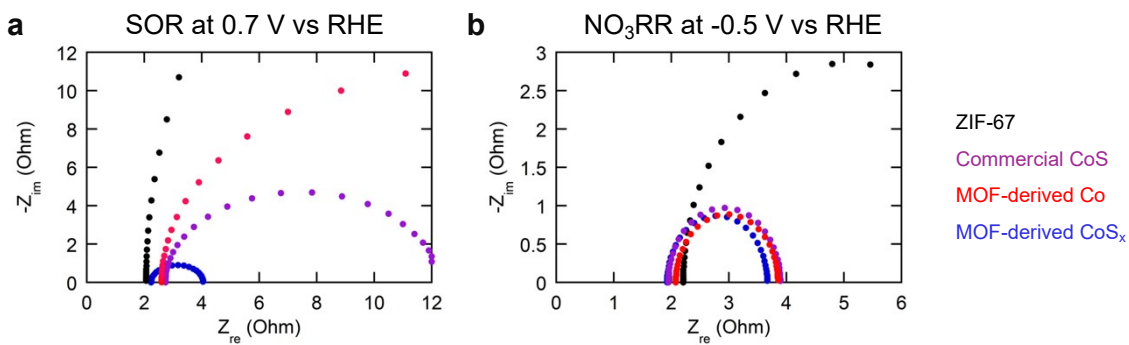


Figure S5. (a) Nyquist plots of various catalysts recorded at 0.7 V vs RHE in 1 M NaOH containing 1 M Na₂S for SOR. (b) Nyquist plots of various catalysts recorded at -0.5 V vs RHE in 1 M NaOH containing 0.1 M NaNO₃ for NO₃RR.

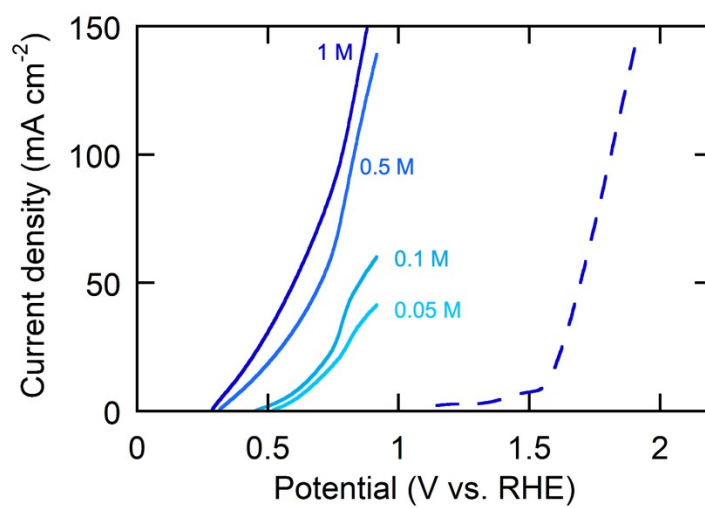


Figure S6. LSV curves of MOF-derived CoS_x for SOR at different initial Na₂S concentrations in 1 M NaOH. The dashed line indicates LSV for OER.

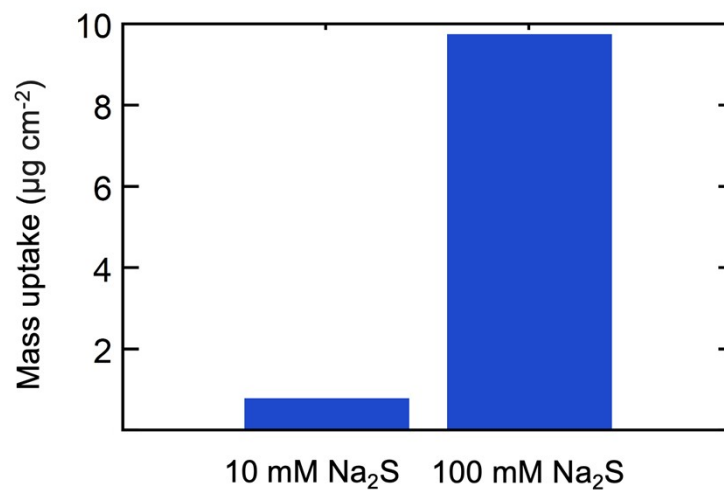


Figure S7. Uptake of sulfide ion by MOF-derived CoS_x measured using EQCM. The mass loading of the catalyst on quartz crystals was 1 mg.

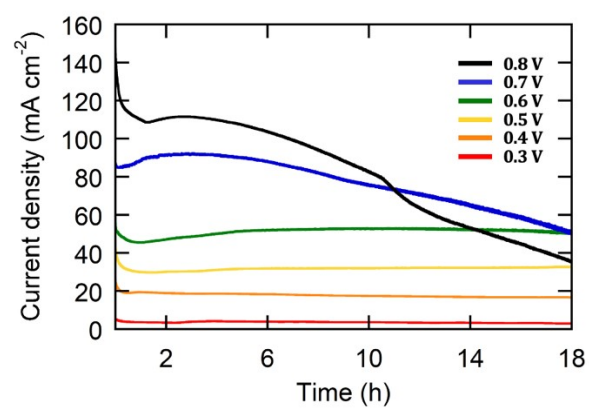


Figure S8. *Current density–time* curves during chronoamperometric operation for SOR at different applied potentials for 18 h. The analyte was 1 M Na₂S + 1 M NaOH.

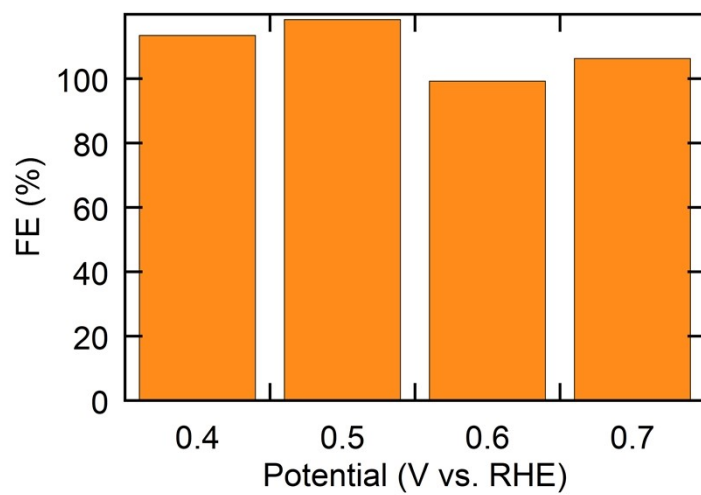


Figure S9. FE of 2e⁻ SOR at different applied potentials. The calculations were based on *i-t* curve shown in **Figure S8**.

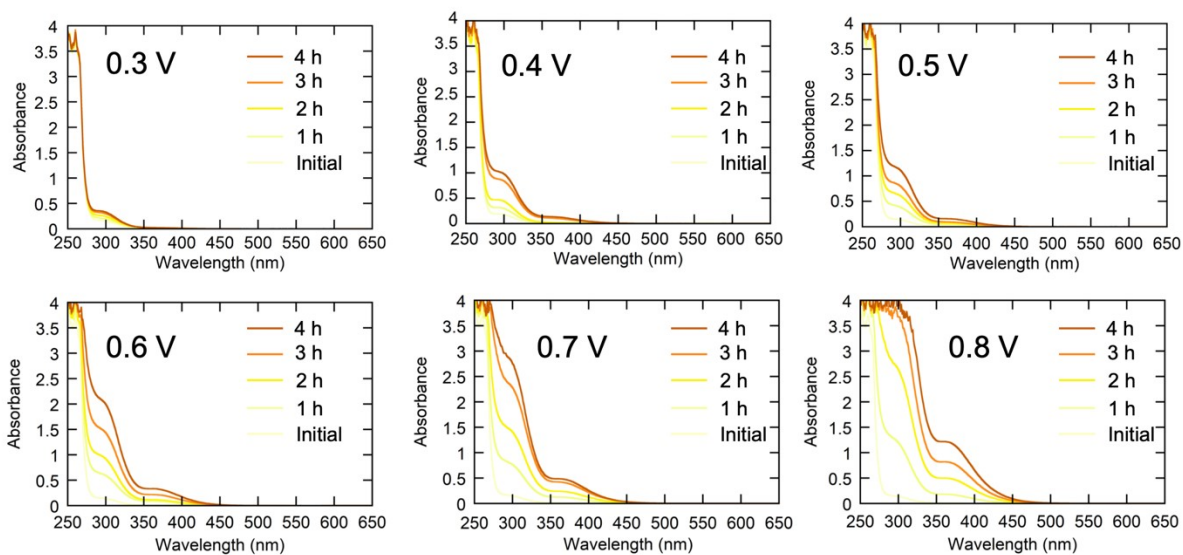


Figure S10. UV-vis UV-vis spectra of the anolyte diluted 25 times at various applied potentials for SOR.

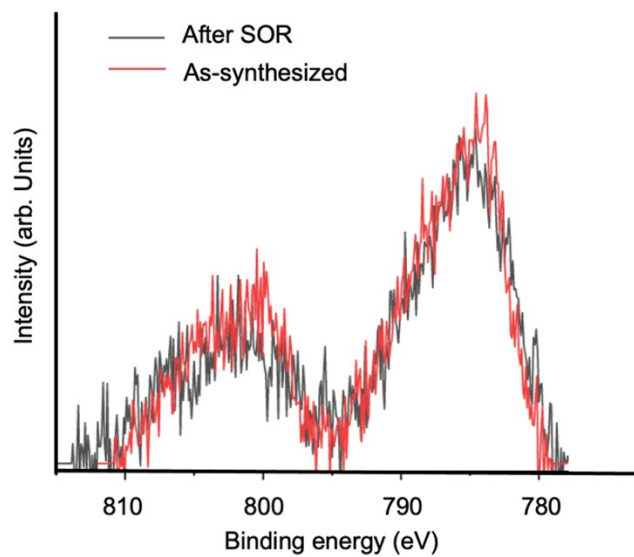


Figure S11. XPS Co 2p spectra of as-synthesized catalyst and MOF-derived CoS_x after 150 h durability test at 0.8 V vs RHE.

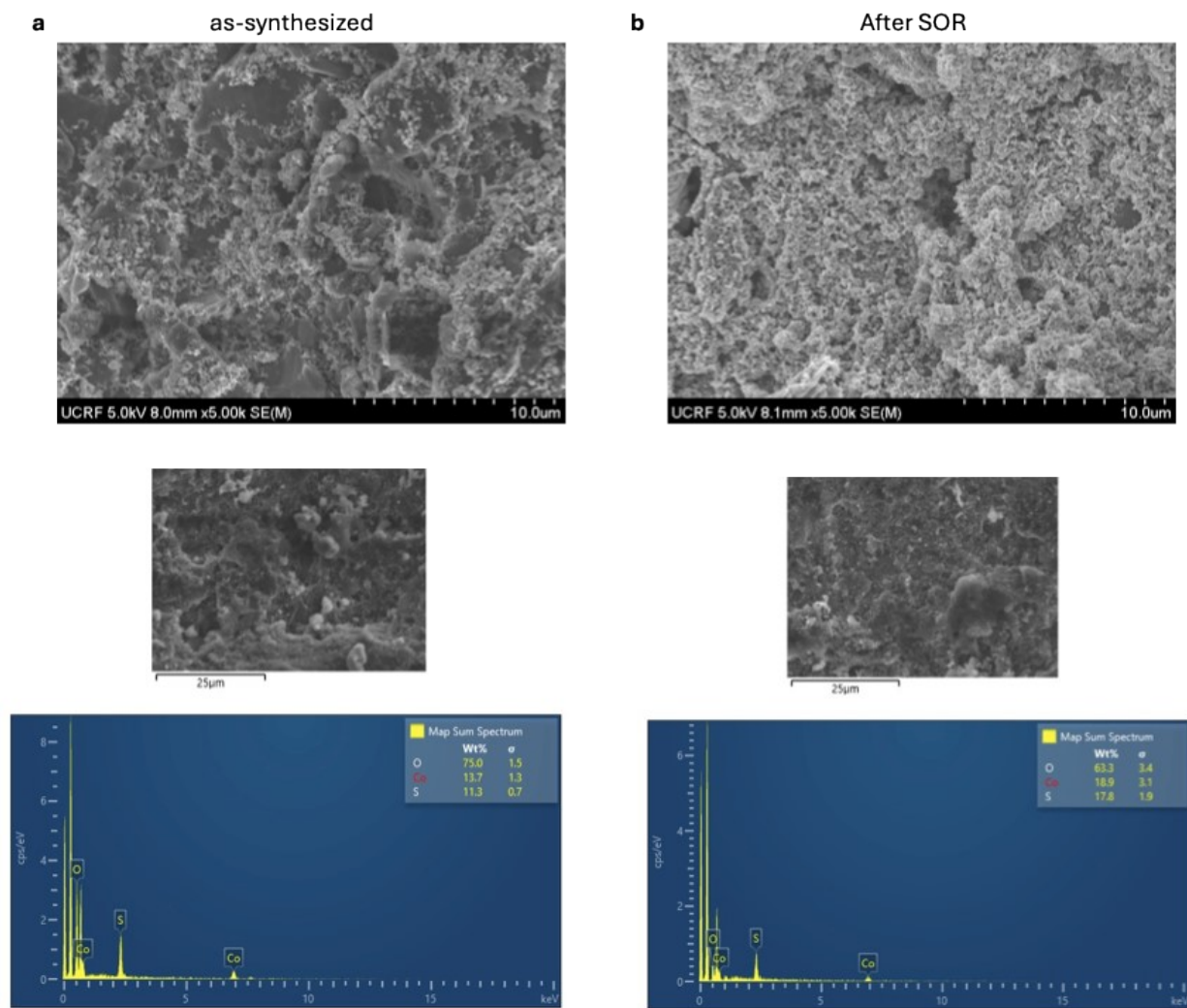


Figure S12. SEM and EDS analysis of MOF-derived CoSx (a) before and (b) after 150 h durability test.

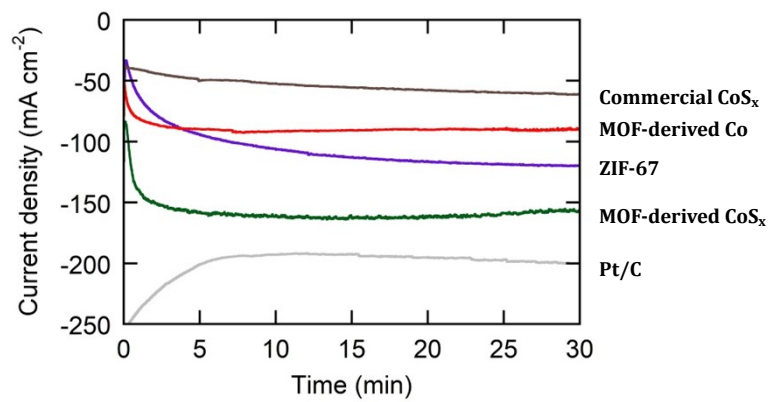


Figure S13. *i-t* curve during NO₃RR at -0.5 V vs RHE using various electrode materials.

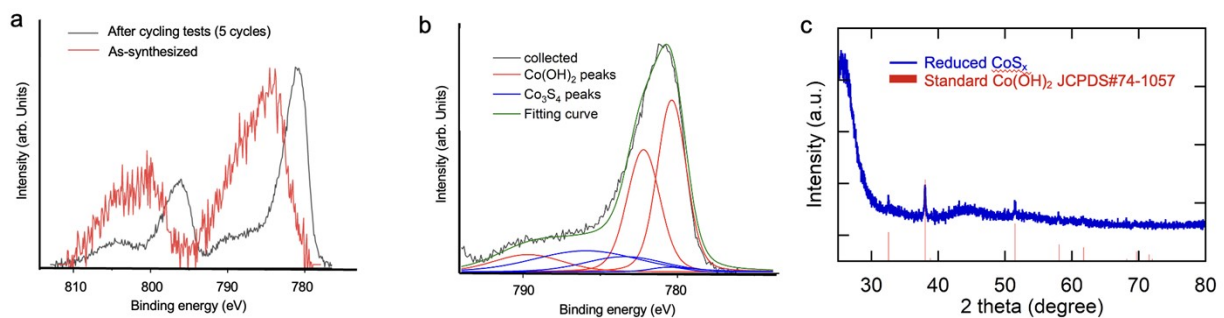


Figure S14. (a) XPS Co 2p spectra of the as-synthesized catalyst (red) and MOF-derived CoS_x after five cycles of testing at -0.5 V vs. RHE (black). (b) Fitted curves of the spent catalyst from (a). (c) XRD pattern of the spent MOF-derived CoS_x after electrochemical reduction.

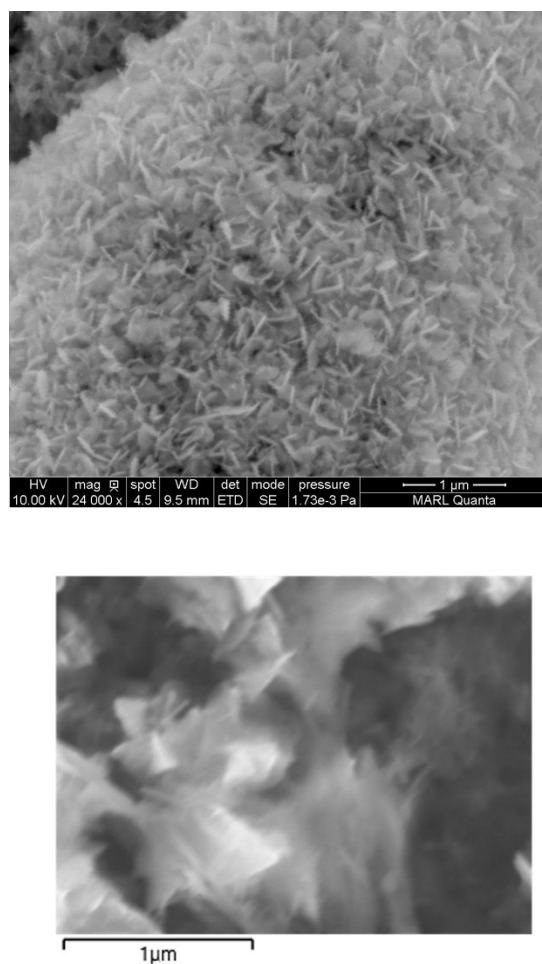


Figure S15. A SEM image and EDS analysis result of MOF-derived CoS_x after 5 cycles of testing at -0.5 V vs. RHE.

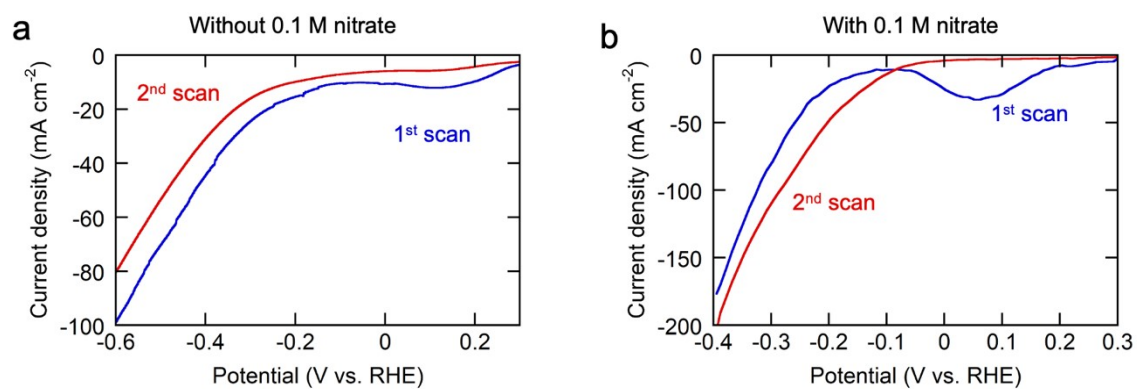


Figure S16. LSV curves of MOF-derived CoS_x (a) without nitrate and (b) with 0.1 M nitrate in background 1 M NaOH.

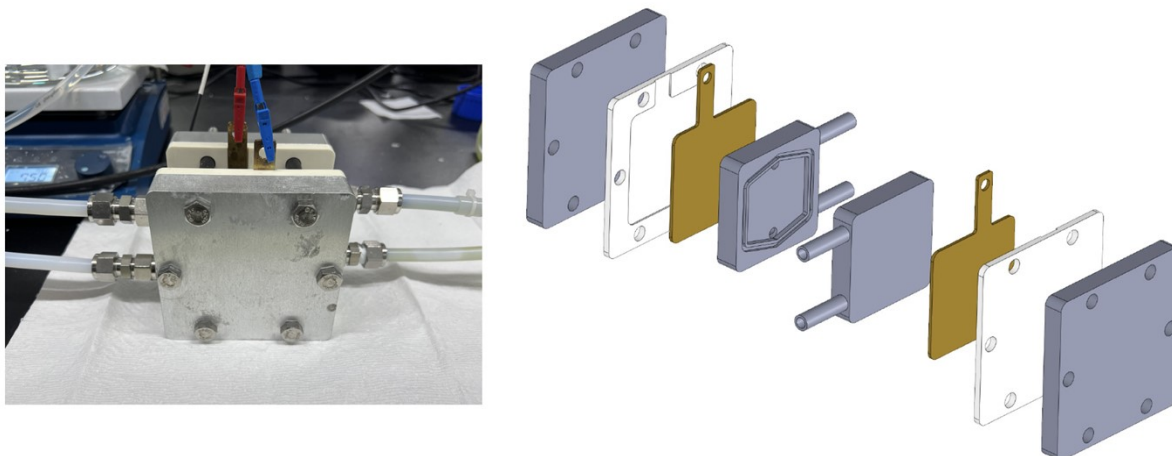


Figure S17. Flow electrolyzer setup. (Left) Photograph of the assembled flow electrolyzer used for coupled SOR-NO₃RR, showing inlet and outlet tubing connections and electrical wiring. (b) Exploded schematic diagram illustrating the components of the flow electrolyzer, including end plates, current collector, and flow channels.

Table S1. Summary of elemental composition analysis of MOF-derived CoS_x using Energy Dispersive X-ray Spectroscopy (EDX) at 50,000× magnification.

	at%			
Label	O	S	Co	Total
MOF derived CoS area 1 50000x 1	41.49	32.5	26.01	100
MOF derived CoS area 1 50000x 2	44.21	31.09	24.7	100
MOF derived CoS area 1 50000x 3	37.52	30.19	32.29	100
MOF derived CoS area 1 50000x 4	41.18	34.18	24.64	100
MOF derived CoS area 1 50000x 5	40.7	34.03	25.27	100
MOF derived CoS area 1 50000x 6	42.48	31.16	26.36	100

Table S2. Performance of the state-of-the-art SOR catalysts.

Material	Electrolytes	Potential at. j (V@mA cm ⁻²)	Duration of stability (h@mA cm ⁻² or V)	Cell voltage (V@mA cm ⁻²)	Ref.
MOF-derived CoS_x	1.0 M Na₂S + 1.0 M NaOH	0.46 V @50 mA cm⁻²	150 h@0.8 V	0.57 V@10 mA cm⁻² (SOR-NO₃RR)	This work
CoNi ₂ S ₄ NFs	1.0 M Na ₂ S + 1.0 M NaOH	0.53 V @50 mA cm ⁻²	20 h@10 mA cm ⁻²	0.3 V@10 mA cm ⁻²	[1]
WS ₂ NSs	1.0 M Na ₂ S + 1.0 M NaOH	0.6 V @57.60 mA cm ⁻²	192 h@1.3 V	1.17 V@10 mA cm ⁻²	[2]
Vpd·Pd ₄ SMNRs	4.0 M Na ₂ S + 1.0 M NaOH	0.65 V @100mA cm ⁻²	120 h@0.5 V	0.77 V @100 mA cm ⁻²	[3]
Fe ₃ C@N- CNTs/IF	1.0 M Na ₂ S + 1.0 M NaOH	0.46 V @10mA cm ⁻²	/	0.99 V@10 mA cm ⁻² (SOR-NO ₃ RR)	[4]
CoNi@NGs	1.0 M Na ₂ S + 1.0 M NaOH	0.52 V @100mA cm ⁻²	500 h@30 mA cm ⁻²	/	[5]
SnSe ₂	1.0 M Na ₂ S + 1.0 M NaOH	0.42 V @10 mA cm ⁻²	18 h@10 mA cm ⁻²	/	[6]
Co-Ni ₃ S ₂	1.0 M Na ₂ S + 1.0 M NaOH	0.59 V @100 mA cm ⁻²	24 h@50 mA cm ⁻²	0.80 V@50 mA cm ⁻²	[7]
CuCoS/CC	4.0 M Na ₂ S + 1.0 M NaOH	1.33 V @100 mA cm ⁻²	20 h@10 mA cm ⁻²	0.75 V@100 mA cm ⁻²	[8]
HEDP-Rh metallene	4.0 M Na ₂ S + 1.0 M NaOH	0.538 V @100 mA cm ⁻²	125 h@0.8 V	1 V@100 mA cm ⁻²	[9]
Fe, F-NiO	1.0 M Na ₂ S 1.0 M KOH	0.63 V @100 mA cm ⁻²	100 h@1.74 V	/	[10]
SP-Rhlene	4.0 M Na ₂ S + 1.0 M KOH	0.38 V @10 mA cm ⁻²	120 h@0.8 V	0.385 V@10 mA cm ⁻²	[11]
MFe ₂ O ₄	1.0 M Na ₂ S + 1.0 M NaOH	0.45 V @10 mA cm ⁻²	25 h@10 mA cm ⁻²	1.14 V@10 mA cm ⁻² (SOR-NO ₃ RR)	[12]

Table S3. Performance of the state-of-the-art NO₃RR catalysts.

Material	Electrolytes	Highest FE (%)	NH ₃ yield rate (mg h ⁻¹ cm ⁻²)	Ref.
MOF-derived CoS_x	0.1 M NaNO₃ + 1.0 M NaOH	93.4	9.1	This work
BCN@Ni	0.1 M KNO ₃ + 0.1 M KOH	91.1	2.3	[13]
RM (Fe ₂ O ₃ +Al _x Si _y O)	1.0 M KNO ₃ + 1.0 M PBS	92.8	2.7	[14]
Fe ₃ O ₄ /SS	0.1 M NaNO ₃ + 0.1 M NaOH	91.5	10.1	[15]
Fe SAC	0.5 M KNO ₃ + 0.1 M K ₂ SO ₄	75	7.8	[16]
PTCDA/O-Cu	500 ppm NaNO ₃ + 0.1 M PBS	77	0.43	[17]
Cu-N-C	0.1 M KNO ₃ + 0.1 M KOH	84.7	4.5	[18]
Co-Fe@Fe ₂ O ₃	1000 ppm NaNO ₃ + 0.1M Na ₂ SO ₄	85.8	1.5	[19]
Cu@C	1.0 mM NaNO ₃ + 1.0 M KOH	72	0.47	[20]
Co NPs@C	0.05 M NaNO ₃ + 0.2 M NaHCO ₃	54.3	2.21	[21]
Ir NTs	1.0 M NaNO ₃ + 0.1 M HClO ₄	84.7	0.92	[22]
Cu ₂ O+Cu ₃ O ₄	0.1 M NaNO ₃ + 0.1 M NaOH	85.4	12.76	[23]
Cu@NF	200 ppm KNO ₃ -N + 1 M KOH	96.6	4.28	[24]

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