Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Hierarchical Co_3O_4/CoS microbox heterostructure as highly efficient bifunctional electrocatalyst for rechargeable Zn–air batteries

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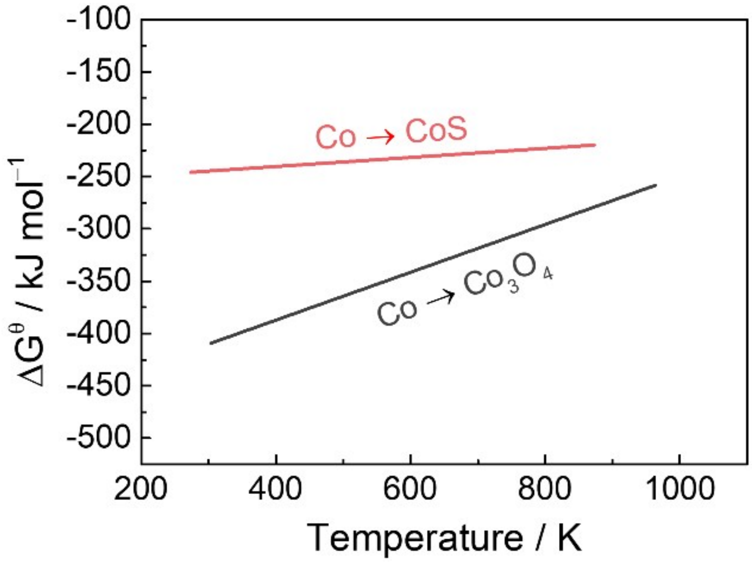

Fig. S1 The Gibbs free energy of formation (ΔG) of the Co based oxide and sulfide based on the Ellingham diagram.

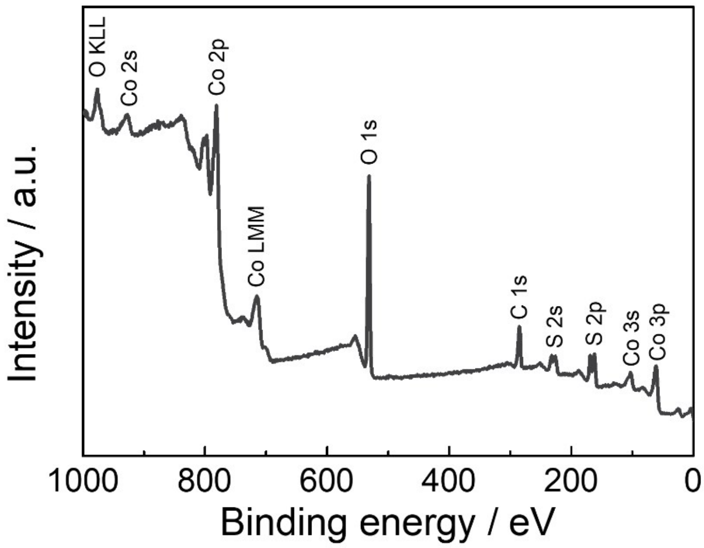

Fig. S2 The XPS survey spectrum Co_3O_4/CoS catalyst.

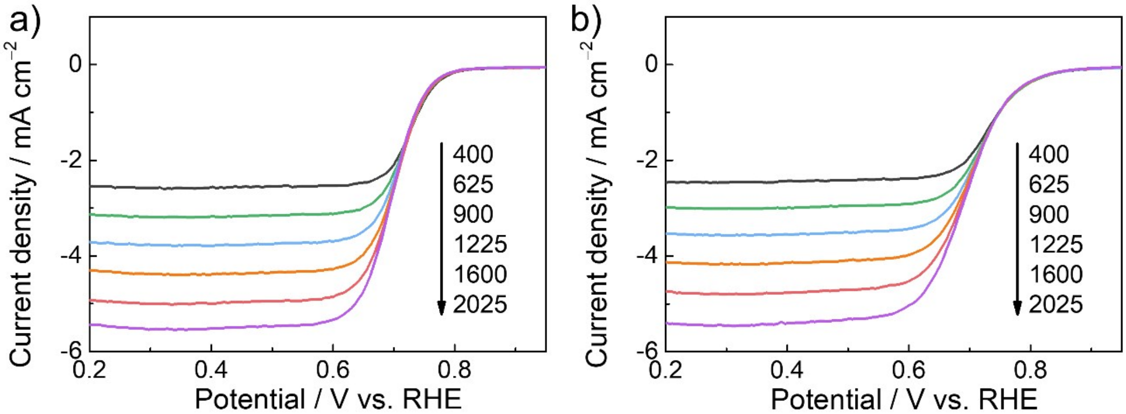

Fig. S3 Rotating disk voltammograms of (a) Co-Co PBA and (b) Co_3O_4 at rotation speeds from 400 to 2025 rpm.

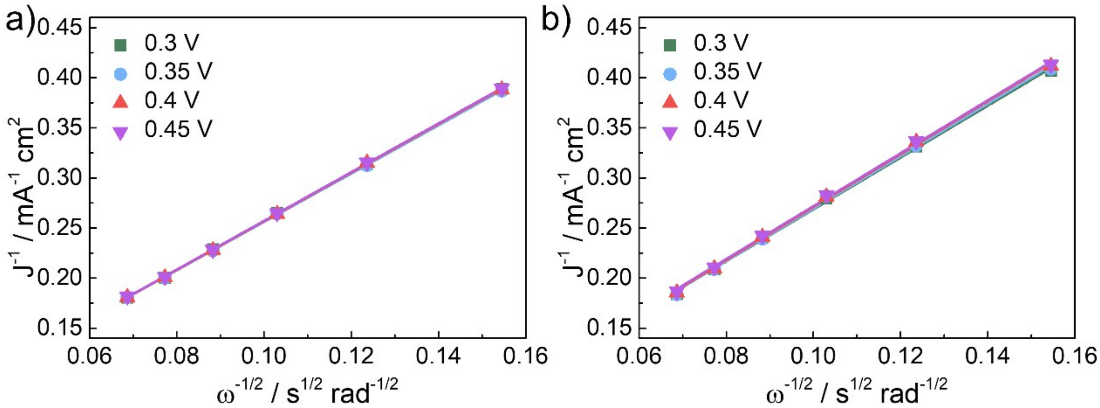

Fig. S4 The Koutecky–Levich plots of (a) Co-Co PBA and (b) Co_3O_4 at different potentials.

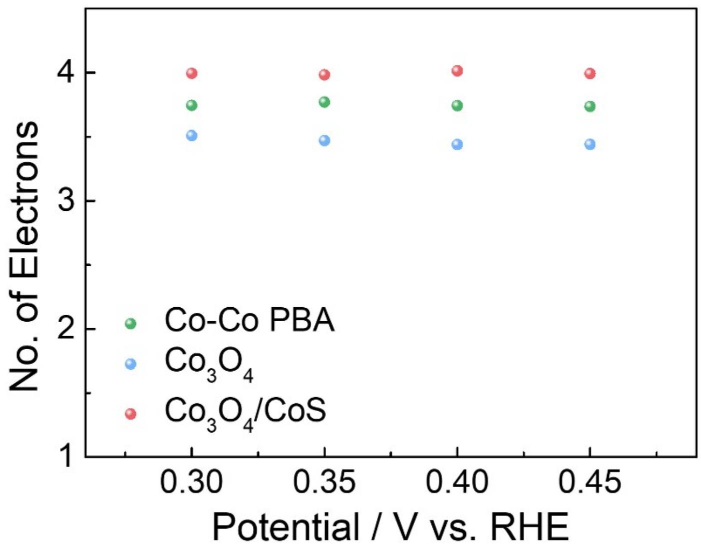

Fig. S5 Electron transfer number of catalysts as a function of applied voltage.

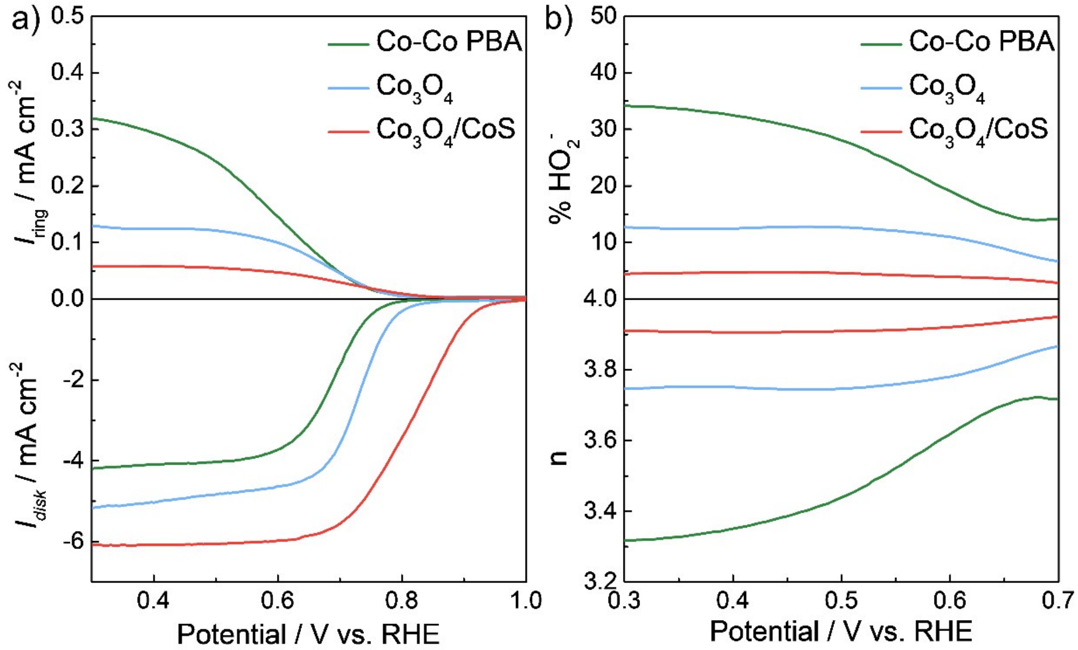

Fig. S6 (a) RRDE ring current and disk current and (b) HO_2^- yields and n values of Co-Co PBA, Co_3O_4, and Co_3O_4/CoS in O_2-saturated 0.1 M KOH at 1600 rpm and sweep rate of 5 mV s^{-1}.

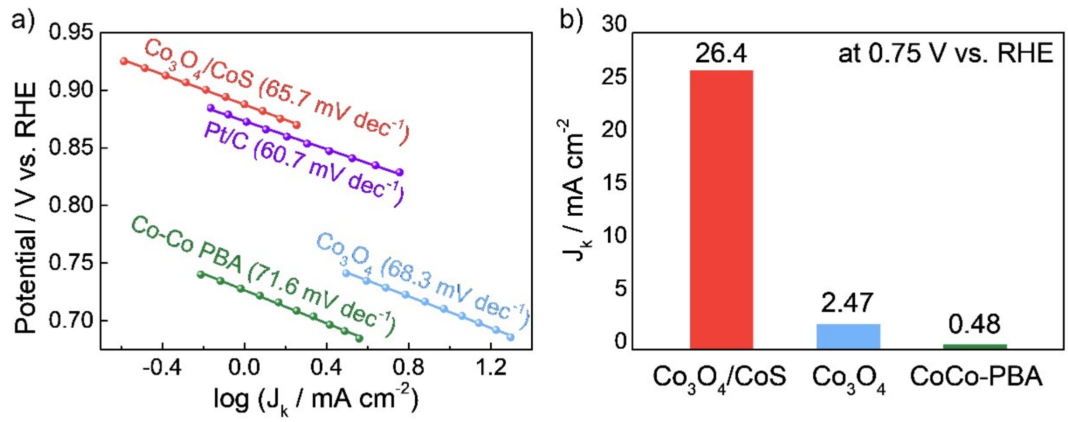

Fig. S7 (a) Tafel plots and (b) kinetic current densities of prepared samples.

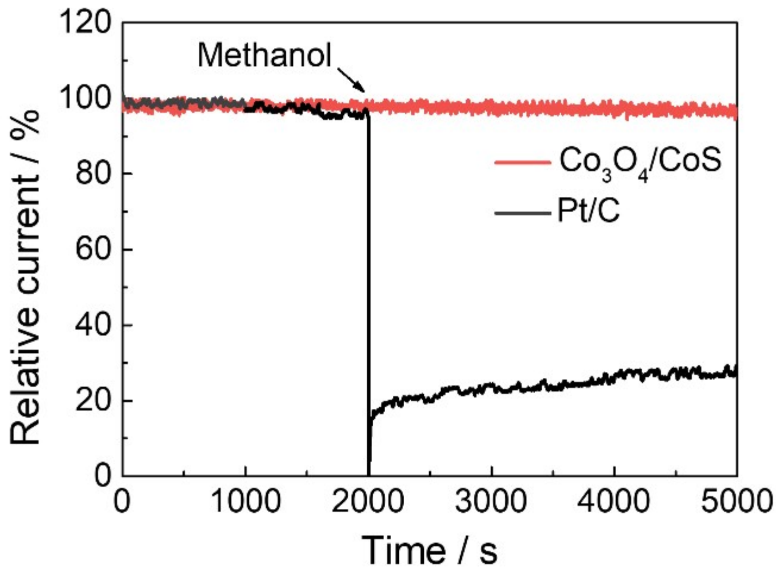

Fig. S8 Methanol-crossover tests performed by adding methanol into the electrolyte at 2000 s.

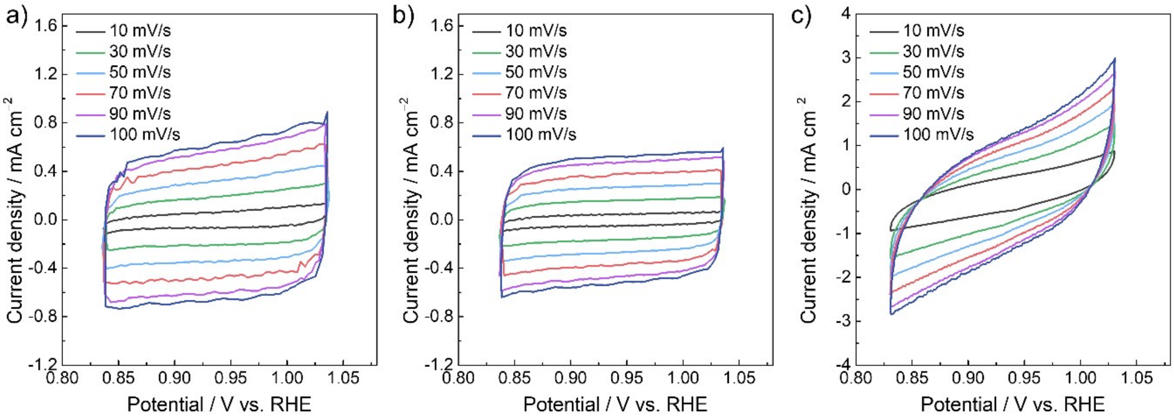

Fig. S9 Typical cyclic voltammograms at different scan rates of the (a) Co-Co PBA, (b) Co_3O_4, and (c) Co_3O_4/CoS samples.

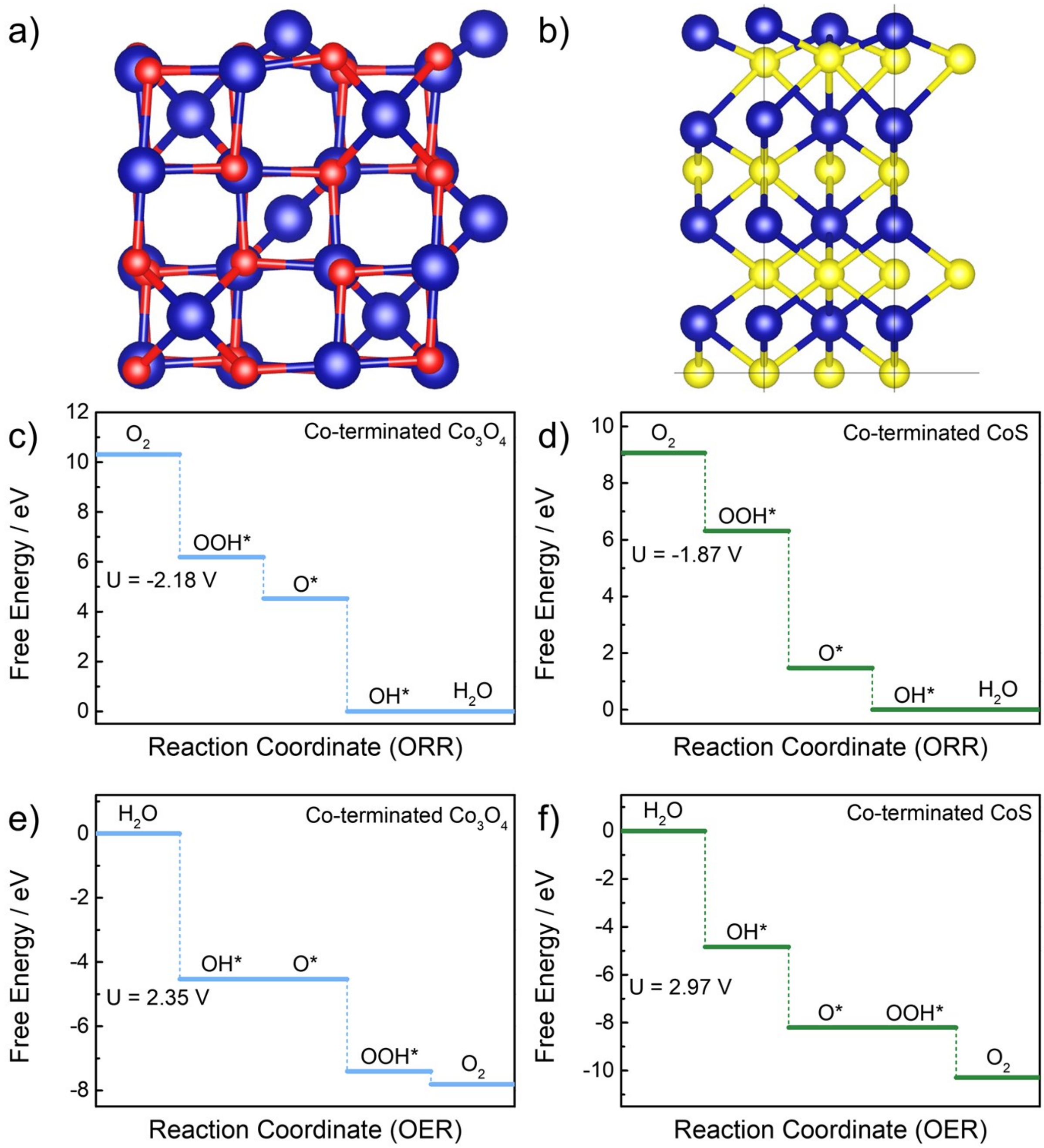

Fig. S10 Structure of (a) Co-terminated Co_3O_4 and (b) Co-terminated CoS. Free energy change diagrams (U = onset potential) of (c), (e) Co-terminated Co_3O_4 (ORR/OER), (d), (f) Co-terminated CoS (ORR/OER) in alkaline condition.

Table S1 Comparison of the ORR and OER performance of Co_3O_4/CoS against previously reported bifunctional catalysts in 0.1 M KOH solution

Catalysts	$E_{j=10}$ (V)	$E_{1/2}$ (V)	ΔE (V)	Reference
Co_3O_4/CoS	1.579	0.820	0.759	This work
Co_3O_4	1.710	0.727	0.983	This work
Co-Co PBA	1.648	0.688	0.960	This work
Pt/C + RuO_2	1.596	0.827	0.769	This work
Co_3O_4/NPGC	1.680	0.842	0.838	*Angew. Chem. Int. Ed.,* 2016, **55**, 4977-4982.
CoO@Co_3O_4/NSG-650	1.690	0.790	0.900	*ACS Appl. Mater. Interfaces*, 2018, **10**, 7180-7190.
Co_3O_4/CNF	1.646	0.851	0.795	J. Energy Storage, 2019, **23**, 269-277.
Co_3O_4-T500	1.610	0.650	0.960	Electrochim. Acta, 2021, **367**, 137490.
Co-Co_3O_4@NAC	1.610	0.795	0.815	*Appl. Catal. B Environ.,* 2020, **260**, 118188.
CoS_2(400)/N,S-GO	1.610	0.790	0.820	*ACS catal.,* 2015, **5**, 3625-3637.
Ni_x-Co_9S_8@HCF-t	1.544	0.860	0.684	*ACS Appl. Mater. Interfaces*, 2021, **13**, 18683-18692.
$Co_{0.5}Fe_{0.5}S$@N-MC	1.640	0.808	0.832	*ACS Appl. Mater. Interfaces*, 2015, **7**, 1207-1218.
Co_3O_4/2.7Co_2MnO_4	1.770	0.680	1.090	*Nanoscale*, 2013, **5**, 5312-5315.
$Co_3FeS_{1.5}(OH)_6$	1.588	0.721	0.867	*Adv. Mater.*, 2017, **29**, 1702327.
FeN_x -embedded PNC	1.625	0.860	0.775	*ACS nano*, 2018, **12**, 1949-1958.

Table S2 Binding energy (ΔE_{ad}) of the reaction intermediates by DFT calculation

Catalysts	**ΔE_{ad}(O) (eV)**	**ΔE_{ad}(OH) (eV)**	**ΔE_{ad}(OOH) (eV)**
Co_3O_4/CoS	−3.59	−2.51	−2.02
O-terminated Co_3O_4	−3.04	−2.20	−1.19
Co-terminated Co_3O_4	−4.22	−5.16	−3.54
S-terminated CoS	−4.40	−2.27	−0.86
Co-terminated CoS	−6.65	−4.84	−2.48

Table S3 Comparison of the performances of Zn-air batteries with various electrocatalysts

Catalysts	**Current density (mA cm^{-2})**	**Power density (mW cm^{-2})**	**Specific capacity (mAh g_{Zn}^{-1})**	**Energy density (Wh kg_{Zn}^{-1})**	**Reference**
Co_3O_4/CoS	119	168	715	840	This work
Pt/C + RuO_2	80	137	690	786	This work
FeNC-S-Fe_xC/Fe	-	149.4	663	795	*Adv. Mater.*, 2018, **30**, 1804504.
NCNF	-	-	626	776	*Adv. Mater.*, 2016, **28**, 3000-3006.
NCNT/CoO-NiO-NiCo	-	-	594	713	*Angew. Chem. Int. Ed.*, 2015, **54**, 9654-9658.
NCNT/ $Co_xMn_{1-x}O$	-	-	581	695	*Nano Energy*, 2016, **20**, 315-325.
CoZn-NC-700	-	152	578	694	*Adv. Funct. Mater.*, 2017, **27**, 1700795.
AgCu-10	-	85.8	572	641	*Electrochim. Acta*, 2015, **158**, 437-445.
$NiCo_2S_4$/N-CNT	107	147	431.1	*554.6*	*Nano Energy*, 2017, **31**, 541-550.
$ZnCo_2O_4$/N-CNT	-	82.3	428	595	*Adv. Mater.*, 2016, **28**, 3777-3784.