Electronic Supplementary Material (ESI) for New Journal of Chemistry.

1. Calculation Methods

In one method, the electron transfer number (n) of the ORR process were calculated by the Koutecky-Levich (K-L) equation:

$$J^{-1} = J_k^{-1} + (Bw^{\frac{1}{2}})^{-1}$$

$$B = 0.2 \times n \times F \times Co_2 \times D_{O_2}^{\frac{2}{3}} \times v^{-\frac{1}{6}}$$

where J is the measured current density during ORR, Jk is the kinetic current density, ω is the electrode rotating angular velocity (ω = 2πN, N is the linear rotation speed), B is the slope of K-L plots, n represents the electron transfer number, F is the Faraday constant (F = 96485 C mol^{-1}), D_0 is the diffusion coefficient of O_2 in 0.1 M KOH (1.9 × 10-5 cm^2 s^{-1}), ν is the kinetic viscosity (0.01 cm2 s-1), C_0 is the bulk concentration of O_2 (1.2 × 10-3 mol L^{-1}).

In another method, the electron transfer number (n) and peroxide yield were quantified by the RRDE measurements. The ring potential was set constantly at 1.55 V vs. RHE. The peroxide yield (H_2O_2 %) and electron transfer number (n) were determined by the followed equations

$$n = 4 \times \frac{I_d}{I_d + \frac{I_r}{N}}$$

$$H_2O_2\% = \frac{200 \times \frac{i_r}{N}}{i_d + \frac{i_r}{N}}$$

Where i_d and i_r stand for the disk and ring current, respectively, and N is the current collection efficiency (0.37) of the Pt ring of the RRDE electrode.

2. Test method of zinc-air battery

First, 0.01 g catalyst was suspended in 0.74 mL purified water, 0.2 mL isopropanol, and 60 μL 5 wt% Nafion solution to produce catalyst ink. Then, the air-cathode was fabricated via dropping 100 μL catalyst ink onto 1 cm^{-2} hydrophobic carbon cloth. Thus, the catalyst loading is ~0.001 g cm^{-2}. Combined with the Zn-foil anode and 6 M KOH/0.2 M $(CH_3COO)_2Zn$ electrolyte, the liquid ZABs can be obtained. Discharge and charge performance of liquid ZAB was test by LSV technique at a scan rate of 10 mV s^{-1} on a Chenhua CHI 660E electrochemical work station in ambient atmosphere. The galvanostatic discharge and charge-discharge cycling (10 min charge and 10 min discharge) were recorded by using a LAND testing system at a current density of 10 mA cm^{-2} The specific capacity and the energy density were calculated normalized to the mass of the consumed zinc according the following equations:

$$Specific\ capacit = \frac{Current\ \times\ Discharge\ time}{Weight\ of\ comsumed\ Zn}$$

$$Energy\ density = \frac{Current\ \times\ Discharge\ time\ \times\ Average\ discharge\ voltage}{Weight\ of\ comsumed\ Zn}$$

3. Supplementary Figures and Tables

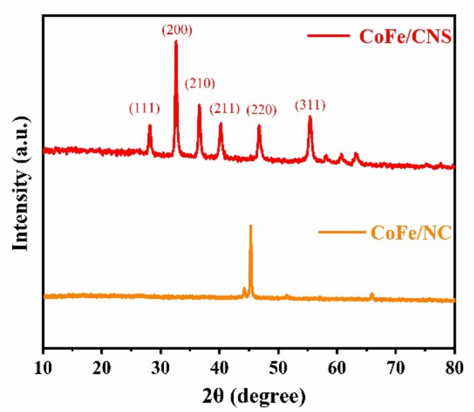

Figure S1. the XRD of (Co,Fe)S_2/CNS and CoFe/CN

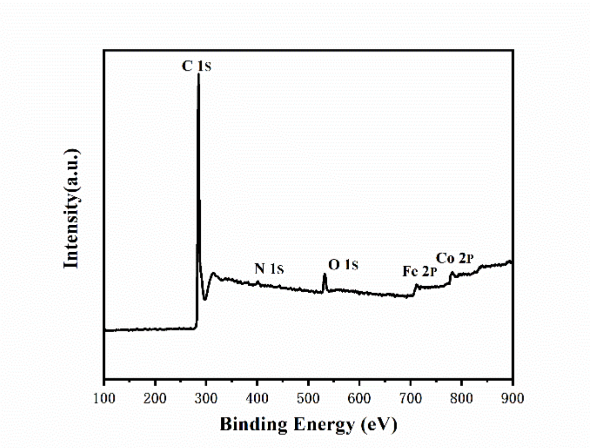

Figure S2. XPS survey spectrum of CoFe/CN

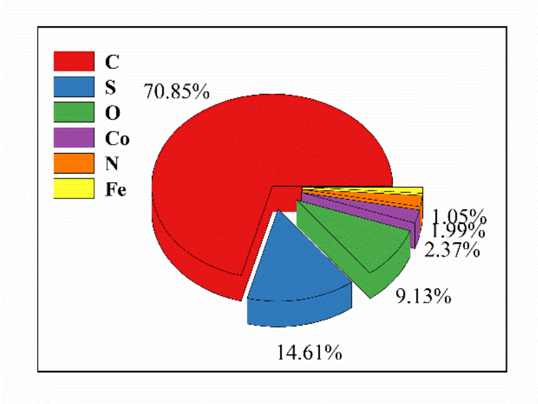

Figure S3. Elemental analysis of $(Co,Fe)S_2$/CNS by xps

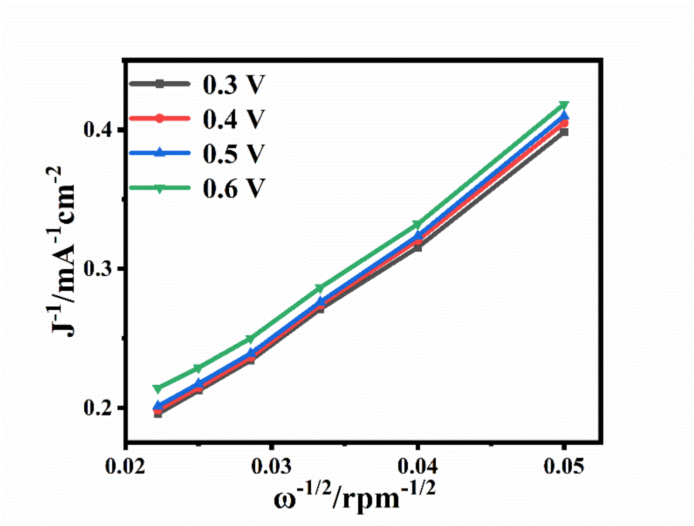

Figure S4. K-L plots of $(Co,Fe)S_2$/CNS at different potentials

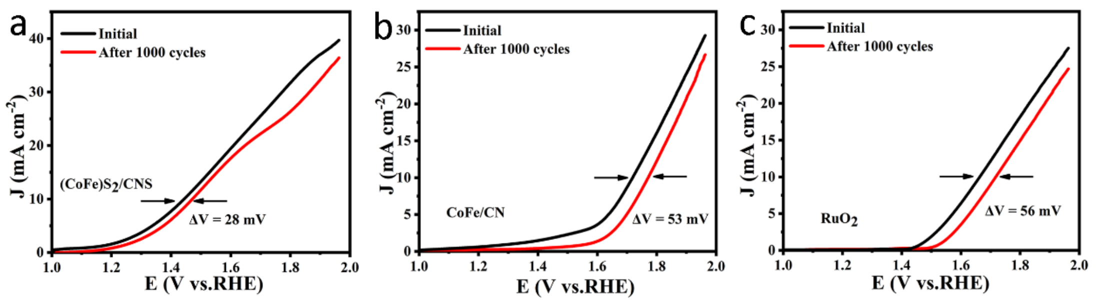

Figure S5 Polarization curves of the (a) $(Co,Fe)S_2$/CNS catalyst, (b) CoFe/CN catalyst, and (c) commercial RuO_2 catalysts before and after 1000 cycles in 0.1 M KOH solution.

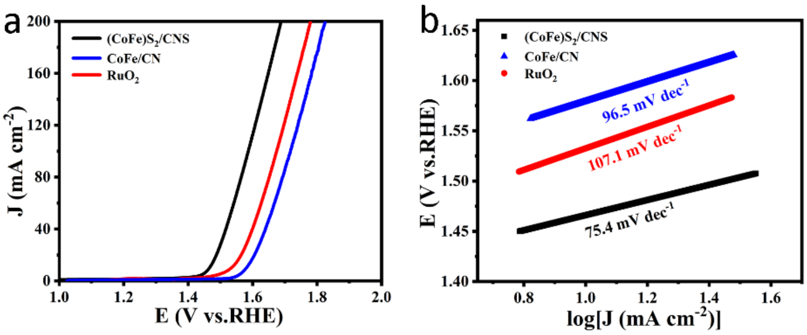

Figure S6 (a) LSV curves for the OER of the (Co,Fe)S_2/CNS, CoFe/CN, and RuO_2 catalysts in 1 M KOH; (b) The corresponding Tafel plots.

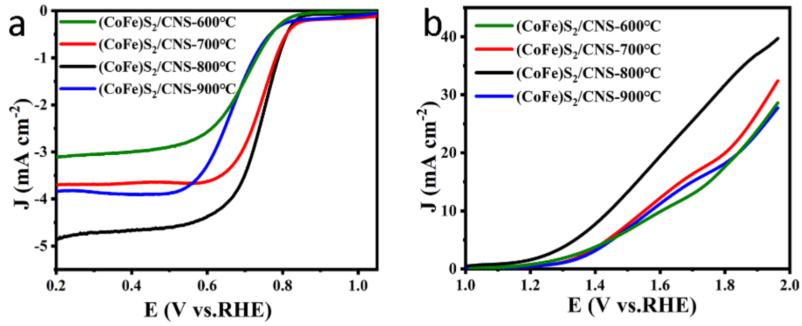

Figure S7 (a-b) (Co,Fe)S_2/CNS catalyst was cured at 600℃, 700℃, 800℃, and 900℃ with ORR and OER.

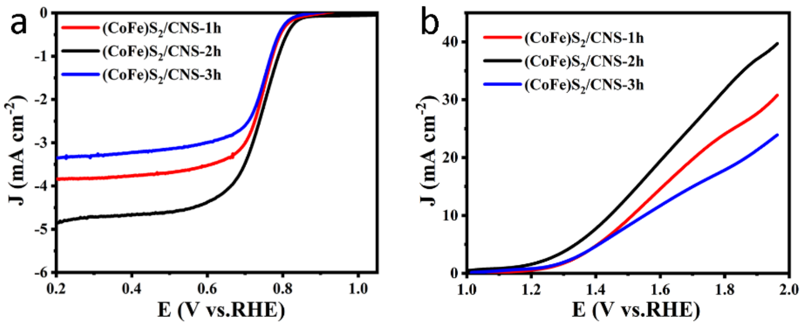

Figure S8 (a-b) Curing time is 1h, 2h and 3h at 800℃, respectively. ORR and OER of (Co,Fe)S_2/CNS catalyst.

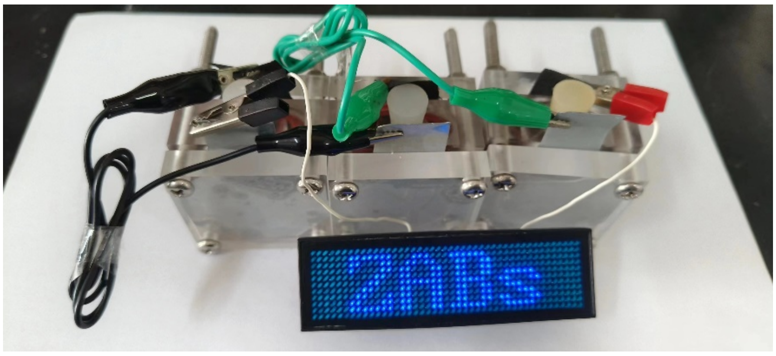

Figure S9. An LED display lighted by three Zn–air batteries connected in series.

Table S1. List of the ORR/OER catalytic properties of the $(Co,Fe)S_2$/CNS and previously reported state-of-the-art catalysts in 0.1 M KOH.

Catalyst	Electrolyte	ORR E_{onset}/V(vs RHE)	ORR $E_{1/2}$/V (vs RHE)	OER E_{onset}/V(vs RHE)	OER $E_{(j=10)}$/V(vs RHE)	E=E(j=10) $E_{1/2}$/V(vs RHE)	Ref
$(Co,Fe)S_2$/CNS	0.1 MKOH	0.84	0.74	1.30	1.42	0.68	Our work
$(Ni,Co)S_2$	0.1 MKOH	0.82	0.71	1.47	1.50	0.79	1
CoFe/N-GCT	0.1 MKOH	0.94	0.70	1.51	1.64	0.88	2
$Co_3FeS_{1.5}(OH)_6$	0.1 MKOH	0.87	0.72	N.A.	1.59	0.87	3
Co-Ni-S@NSP	0.1 MKOH	0.95	0.82	1.57	1.7	0.88	4
Fe@C-NG/NCNTs	0.1 MKOH	N.A.	0.84	N.A.	1.62	0.84	5
N-CoS_2 YSSs	1 M KOH	0.95	0.81	1.50	1.52	0.71	6

Table S2. Comparative summary of the energy efficiency of currently available ZABs with our work.

Electrocatalysts	Electrolytes	OCP (V)	Power density (mW cm^{-2})	Specific capacity (mAh g^{-1})	Cyclic stability	Ref
(Co,Fe)S_2/CNS	6 M KOH+0.2 M Zn^{2+}	1.453 V	115	759.1	360 cycles(120h)	Our work
Co-N,B-CSs	6 M KOH+0.2 M Zn^{2+}	1.49	103	403	40 cycles (15 h)	7
FeCo@MNC	6 M KOH+0.2 M Zn^{2+}	1.41	115	N.A.	144 cycles (24 h)	8
Co_9S_8/CNT	6 M KOH+0.2 M Zn^{2+}	1.43	197.6	N.A.	576 cycles (96 h)	9
S-GNS/$NiCo_2S_4$	6 M KOH+0.2 M Zn^{2+}	N.A.	188.6	N.A.	150 cycles (100 h)	10
Co/N-CNSNs	6 M KOH+0.2 M Zn^{2+}	1.471	81.7	638.4	100 cycles (100 h)	11
$Co_3FeS_{1.5}(OH)$	6 M KOH+0.2 M Zn^{2+}	N.A.	113.12	898	108 cycles (36 h)	3
FeCo/FeCoNi@ NCNTs-HF	6 M KOH+0.2 M Zn^{2+}	1.469	156.2	783	180 cycles (120 h)	12
Fe-SAs/NPS-HC	6 M KOH+0.2 M Zn^{2+}	1.45	195.0	N.A.	500 cycles (200,000 s)	13

References

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