Supporting Information

A simple method for the preparation of nickel selenide and cobalt selenide mixed catalyst to enhance bifunctional oxygen activity for Zn-air battery

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Fig. S1 The unit cell of $\mathrm{Ni}_{0.85}\mathrm{Se}$ and $\mathrm{Co}_{0.85}\mathrm{Se}$



Fig. S2 SEM of (a, b) NHCS, (c, d) $Ni_{0.85}$ Se-NHCS, (e, f) $Co_{0.85}$ Se -NHCS, (g, i) $Ni_{0.85}$ Se/Co_{0.85}Se-NHCS-2, and (j, k) 50% Ni-Co_{0.85}Se-NHCS



Fig. S3 EDX of $\mathrm{Ni}_{0.85}\mathrm{Se}\text{-NHCS}$ and corresponding element content

| | 6— | Element | wt% | wt% Sigma |
|------|------|---|-----------------------------------|--------------------------|
| | | С | 97.75 | 0.30 |
| s/eV | | N | 0.28 | 0.27 |
| | 4- C | Со | 0.90 | 0.08 |
| | - | Se | 1.07 | 0.11 |
| cb | | Se • • • • • • • • • • • • • • • • • • • | Se 1 ' ' ' ' ' ' ' ' ' ' 15 | I ' I ' I ' I ' keV |

Fig. S4 EDX of Co_{0.85}Se-NHCS and corresponding element content



Fig. S5 (a) the XRD patterns of $Ni_{0.85}$ Se/Co_{0.85}Se-NHCS-2 and (b) Raman patterns of $Ni_{0.85}$ Se/Co_{0.85}Se-NHCS-2 and NHCS, (c) N₂ adsorption/desorption isotherms and (d) corresponding pore size distributions curves of $Ni_{0.85}$ Se/Co_{0.85}Se-NHCS-2.



Fig. S6 X-ray photoelectron spectroscopy and corresponding C1s spectra



Fig. S7 LSV curves for ORR varying the 400 rpm to 2025 rpm and LSV curves for OER of NHCS.



Fig. S8 EIS spectra of Ni_{0.85}Se-NHCS, Co_{0.85}Se-NHCS, and Ni_{0.85}Se/Co_{0.85}Se-NHCS-2.



Fig. S9 LSV curves for (a) ORR, corresponding (b, c) Tafel curves, LSV curves for (d) OER and corresponding (e, f) Tafel curves of the as-synthesized catalysts.



Fig. S10 CV curves of (a) $Ni_{0.85}$ Se-NHCS, (b) $Co_{0.85}$ Se-NHCS, (c) $Ni_{0.85}$ Se/Co_{0.85}Se-NHCS-1, (d) $Ni_{0.85}$ Se/Co_{0.85}Se-NHCS-2 and (e) $Ni_{0.85}$ Se/Co_{0.85}Se-NHCS-3 at different scan rates.



Fig. S11 The methanol tolerance of $Ni_{0.85}$ Se/Co_{0.85}Se-NHCS-2 and 20 % Pt/C by the chronoamperometric test at 0.3 V *vs*. RHE in O₂-saturated 0.1 M KOH solution



Fig. S12 The chronoamperometric test of $Ni_{0.85}$ Se/Co_{0.85}Se-NHCS-2 and 20 % Pt/C at 0.3 V vs. RHE in O₂-saturated 0.1 M KOH solution



Fig. S13 The photo of the zinc-air battery assembled with $Ni_{0.85}Se/Co_{0.85}Se-NHCS-2$ driving a timer.

| | E _{onset} (V) | $E_{1/2}(V)$ | J _{limiting} (mA cm ⁻²) | $E_{j=10}\left(V ight)$ | $\Delta E(V)$ |
|--|------------------------|--------------|---|-------------------------|---------------|
| Ni _{0.85} Se-NHCS | 0.79 | 0.69 | 3.71 | 1.62 | 0.93 |
| Co _{0.85} Se-NHCS | 0.89 | 0.76 | 4.67 | 1.65 | 0.89 |
| Ni _{0.85} Se/Co _{0.85} Se- NHCS-1 | 0.84 | 0.76 | 4.34 | 1.64 | 0.88 |
| Ni _{0.85} Se/Co _{0.85} Se- NHCS-2 | 0.90 | 0.77 | 4.66 | 1.63 | 0.86 |
| Ni _{0.85} Se/Co _{0.85} Se- NHCS-3 | 0.86 | 0.75 | 4.02 | 1.63 | 0.88 |
| 20 % Pt/C & RuO ₂ | 0.94 | 0.82 | 5.05 | 1.59 | 0.77 |

Table S1. The bifunctional activity of as-synthesized catalysts for ORR and OER

| catalyst | Mass | Electroly | ORR | ORR | OER | OER | Refe |
|---|--------------------|-------------------|-------|---------------------|------------------|---------------------|----------|
| | loadi | te (mol | half- | Tafel | potenti | Tafel | renc |
| | ng | L ⁻¹) | wave | slope | al at 10 | slope | e |
| | (mg | | poten | (mV | mA | (mV | |
| | cm ⁻²) | | tial | dec ⁻¹) | cm ⁻² | dec ⁻¹) | |
| | | | (V) | | (V) | | |
| Ni So | 0.12 | 0.1 M | | 71.7 | | 141.6 | This |
| NHCS | | KOH | 0.69 | | 1.62 | | wor |
| NIICS | | | | | | | k |
| Cos or Se- | | 0.1 M | | | | | This |
| NHCS | 0.12 | KOH | 0.76 | 62.7 | 1.65 | 136 | wor |
| MICS | | KOII | | | | | k |
| Ni _{0.85} Se/Co _{0.8} | 0.12 | 0.1 M | 0.78 | 58.2 | 1.63 | 118.3 | This |
| ₅ Se-NHCS-2 | | KOH | | | | | wor |
| | | | | | | | k |
| Ni _x Co _{0.85-x} Se | 0.60 | 0.1 M | 0.78 | / | 1.54 | 62 | 1 |
| | | KOH | | | | | |
| Co _{0.85} Se@N | 0.40 | 1 M | / | / | 1.55 | 75 | 2 |
| С | | КОН | | | | | |
| $Co_{0.85}Se@C$ | 0.23 | 0.1 M | 0.82 | 69 | 1.58 | 61 | 3 |
| NFs | | КОН | | | | | |
| coral-like | 0.28 | 0.1 M | / | / | 1.53 | 40 | 4 |
| CoSe | | КОН | | | | | - |
| $\mathrm{Co}_{0.7}\mathrm{Fe}_{0.3}\mathrm{Se}_2$ | 0.51 | 0.5 M | 0.584 | 110 | / | / | 5 |
| | | H_2SO_4 | | | | | 6 |
| $CoSe_2$ | 1 | 0.1 M | / | / | 1.74 | 67 | 6 |
| | | КОН | | | | | <i>.</i> |
| NiSe ₂ | 1 | 0.1 M | / | / | 1,64 | 50 | 6 |
| | | КОН | | | | | - |
| $(Ni, Co)Se_2$ | 0.17 | 0.1 M | 0.7 | / | 1.59 | 86 | 7 |
| | | КОН | | | | | 0 |
| NiCo ₂ Se ₄ | 0.39 | 1 M | 0.77 | / | 1.56 | 56 | 8 |
| | | KOH | | | | | |

Table S2. Comparison with the bifunctional activity of different catalysts for ORR and OER

| Catalyst | Open circuit potential (V) | Maximum power density (mW cm ⁻²) | Reference |
|--|-------------------------------|---|-----------|
| Ni _{0.85} Se/Co _{0.85} Se-NHCS-2 | 1.40 | 118.34 | This work |
| 20% Pt/C | 1.46 | 154.13 | This work |
| (Ni, Co)Se ₂ | 1.38 | 110 | 7 |
| IOSHs-NSC-Co ₉ S ₈ | 1.49 | 113 | 9 |
| N-CoS ₂ YSSs | 1.41 | 81 | 10 |
| Co/Co ₃ O ₄ @PGS | 1.45 | 118.27 | 11 |
| $Co/Co_x M_y$ (M=P, N) | 1.43 | 125.2 | 12 |
| Ni _{0.6} Co _{0.4} Se ₂ -O | 1.41 | 110 | 13 |
| $O-Co_{1-x}Mo_xSe_2$ | 1.53 | 120.28 | 14 |
| FeCo-N-C-700 | 1.39 | 150 | 15 |
| Co-MOF-800 | 1.38 | 144 | 16 |

Table S3. Comparison with the performance of zinc-air batteries of nonprecious catalysts.

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