# Supplementary Information

## In-situ encapsulation engineering boosts electrochemical performance of highly graphitized N-doped porous carbon-based copper-cobalt selenides for bifunctional oxygen electrocatalysis

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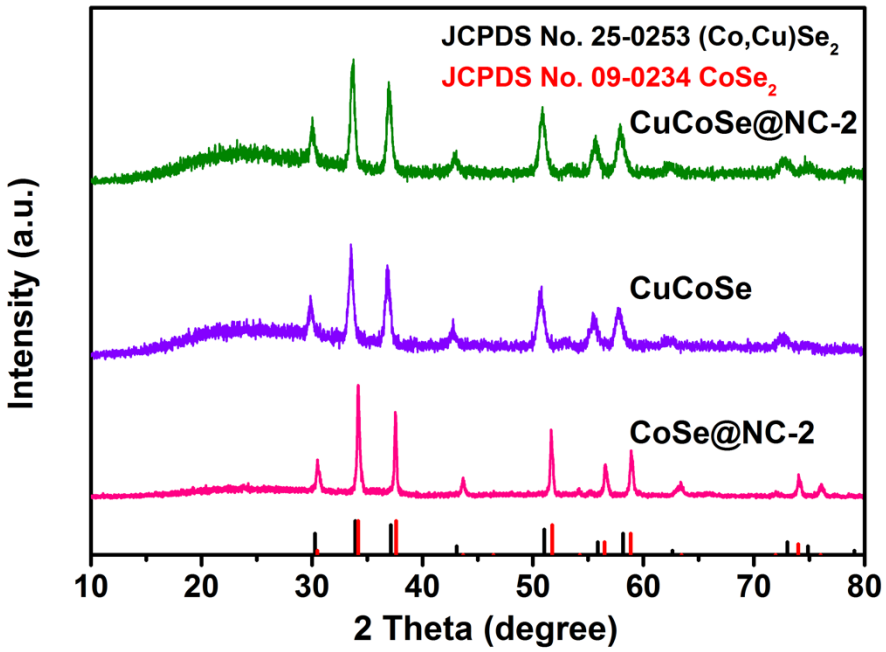


**Fig. S1**. XRD patterns of CuCoSe@NC-2, CuCoSe and CoSe@NC-2.

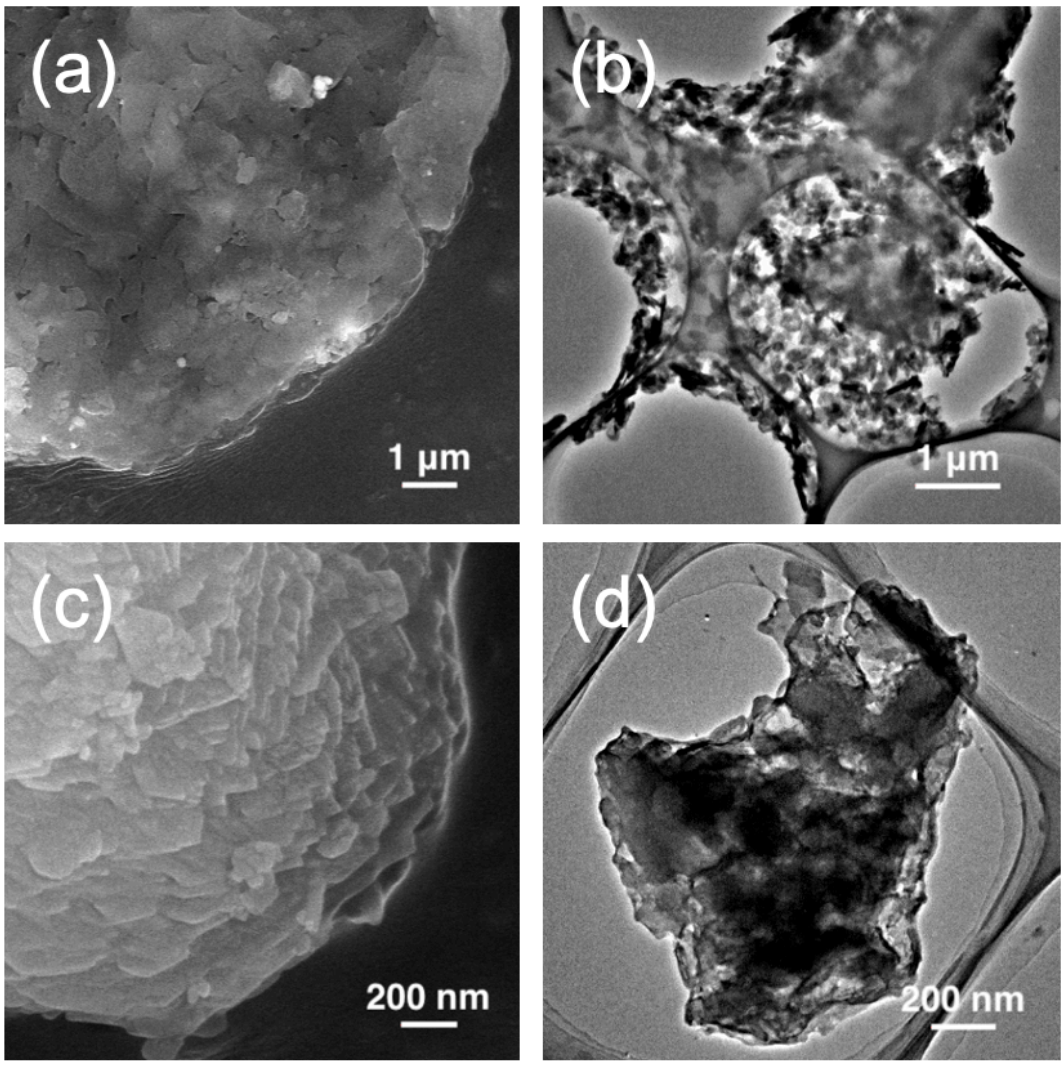


**Fig. S2**. SEM and TEM images of (a, b) CuCo-BDC and (c, d) CuCo-BDC-2@2-MIM.

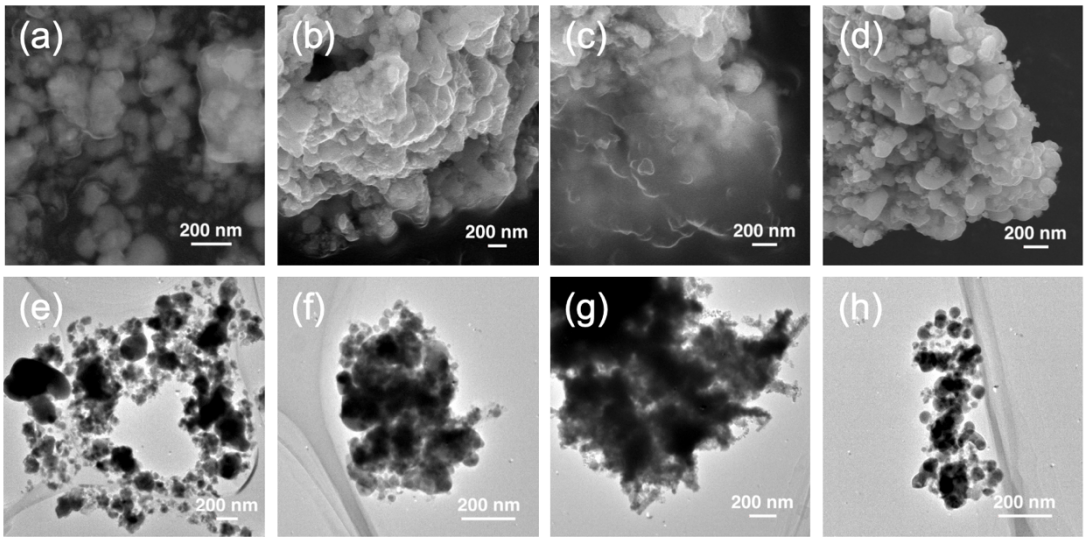


**Fig. S3**. SEM and TEM images of (a, e) CuCoSe@NC-1, (b, f) CuCoSe@NC-3, (c, g) CoSe@NC-2 and (d, h) CuCoSe.

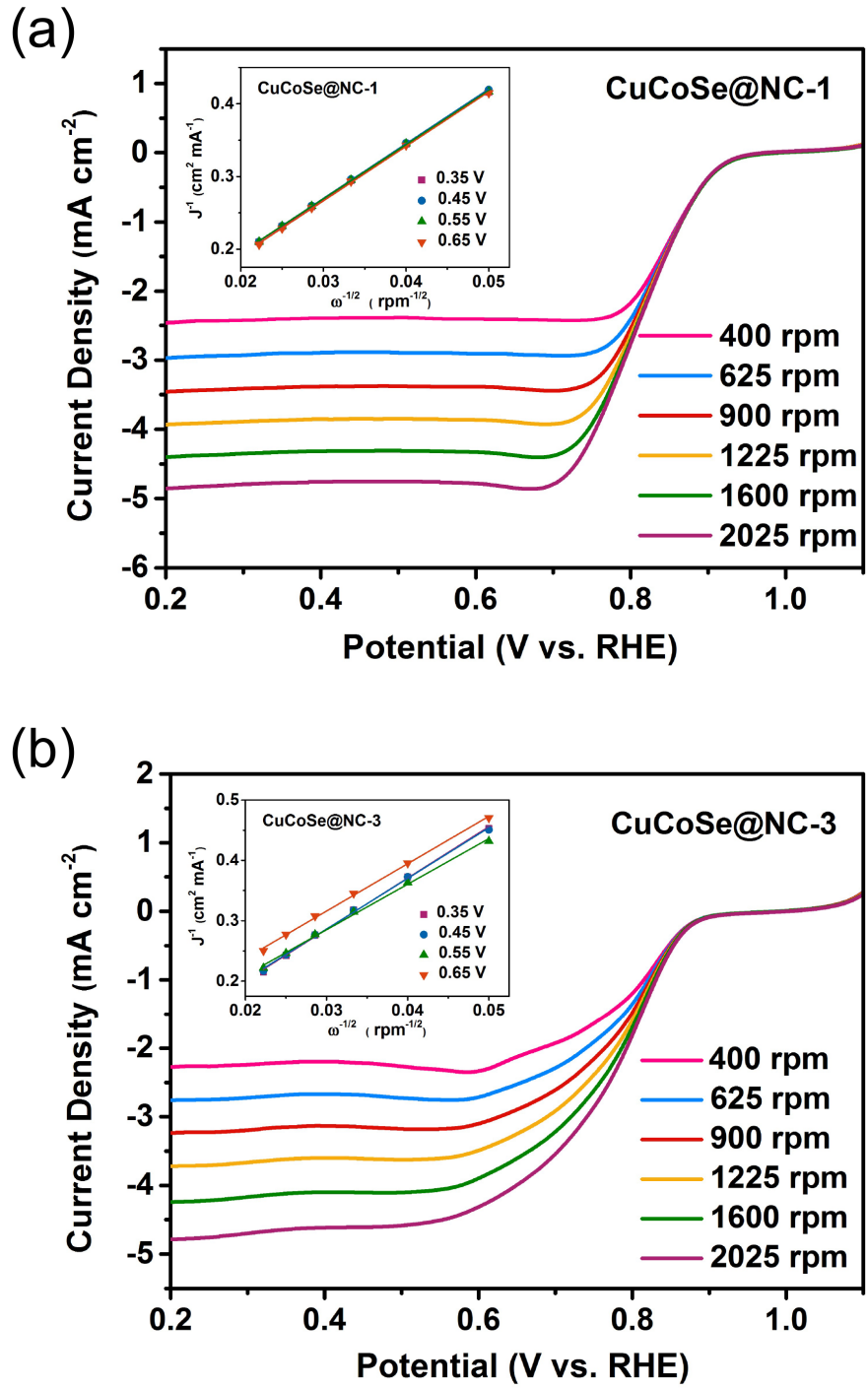


**Fig. S4**. ORR polarization curves of (a) CuCoSe@NC-1 and (b) CuCoSe@NC-3 measured at different rotating speeds in 0.1 M KOH solution and the corresponding K-L plots at different potentials (inset).

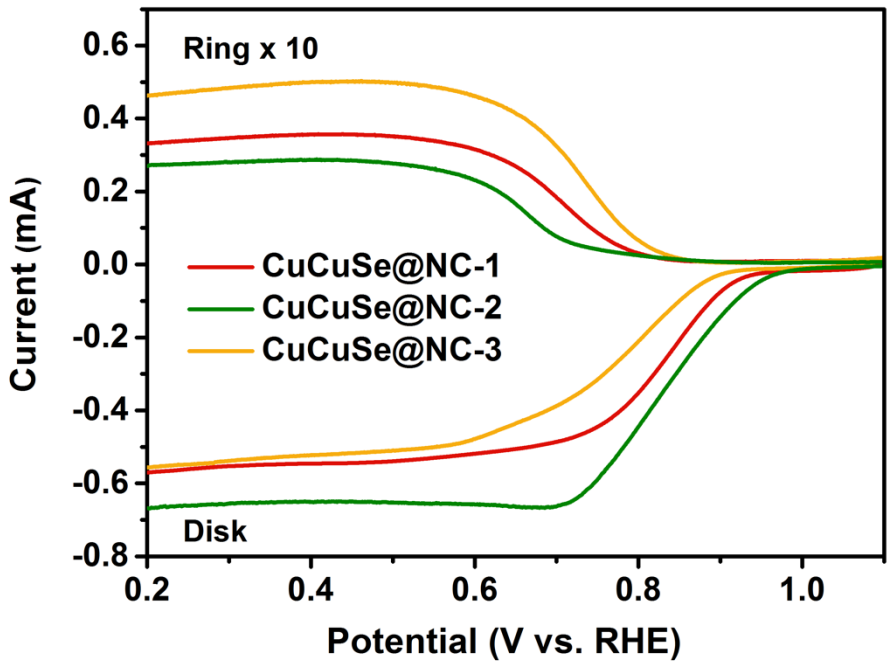


**Fig. S5**. RRDE voltammograms and amperometric responses of CuCoSe@NC-*x* at a scan rate of 10 mV $s^{-1}$ and a rotating speed of 1600 rpm in $O_2$ saturated 0.1 M KOH solution.

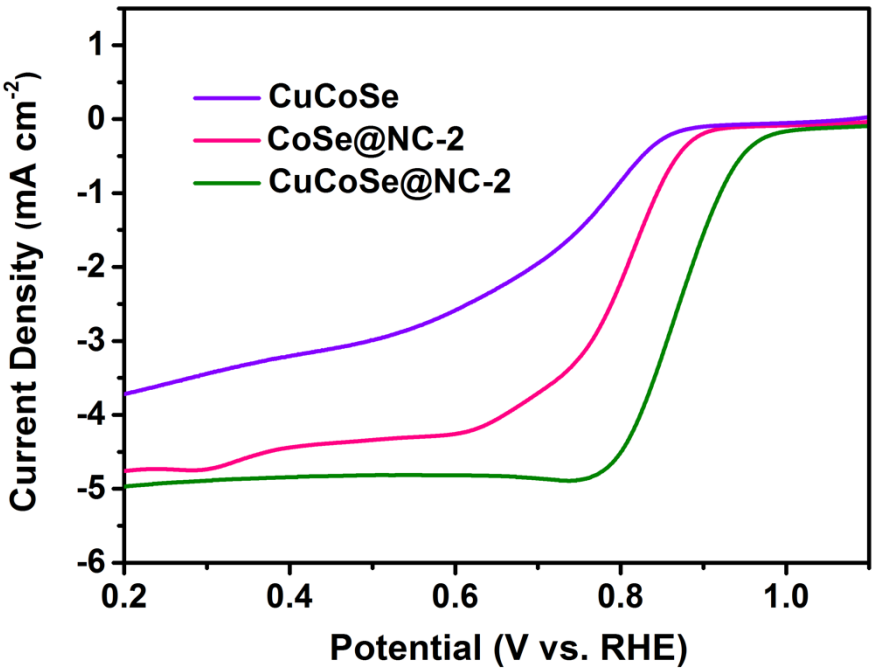


**Fig. S6**. LSV curves of CuCoSe, CoSe@NC-2 and CuCoSe@NC-2 at a rotating speed of 1600 rpm in $O_2$-saturated 0.1 M KOH solution.

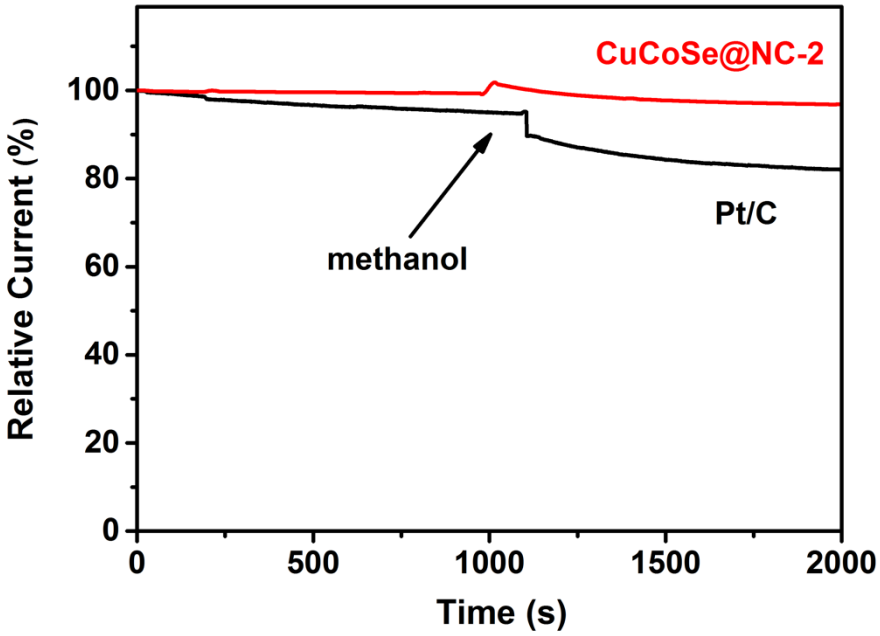


**Fig. S7**. *I-t* plots of CuCoSe@NC-2 and Pt/C for the evaluation of anti-methanol poisoning performance.

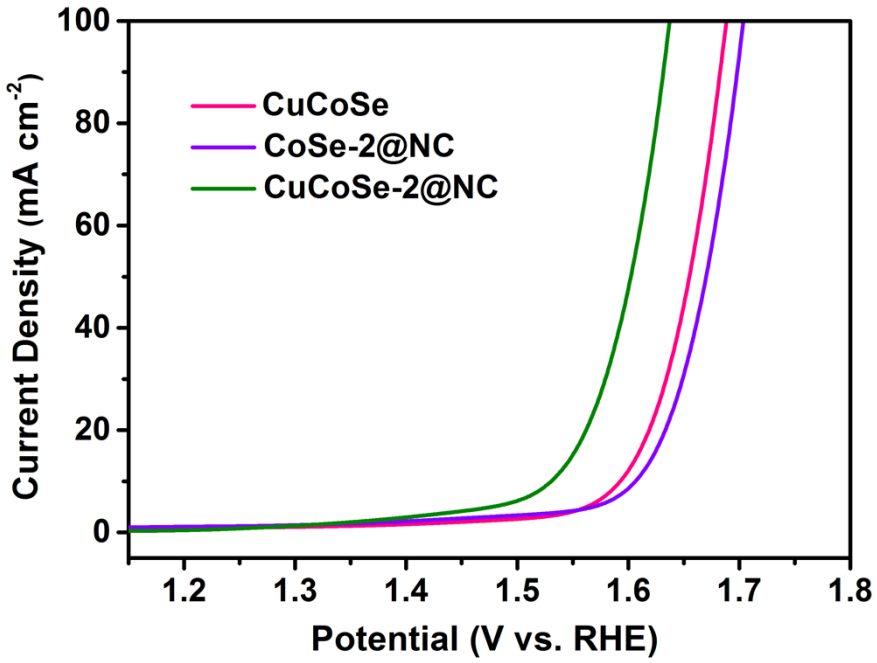


**Fig. S8**. LSV curves of CuCoSe, CoSe@NC-2 and CuCoSe@NC-2 in 1 M KOH solution toward the OER.

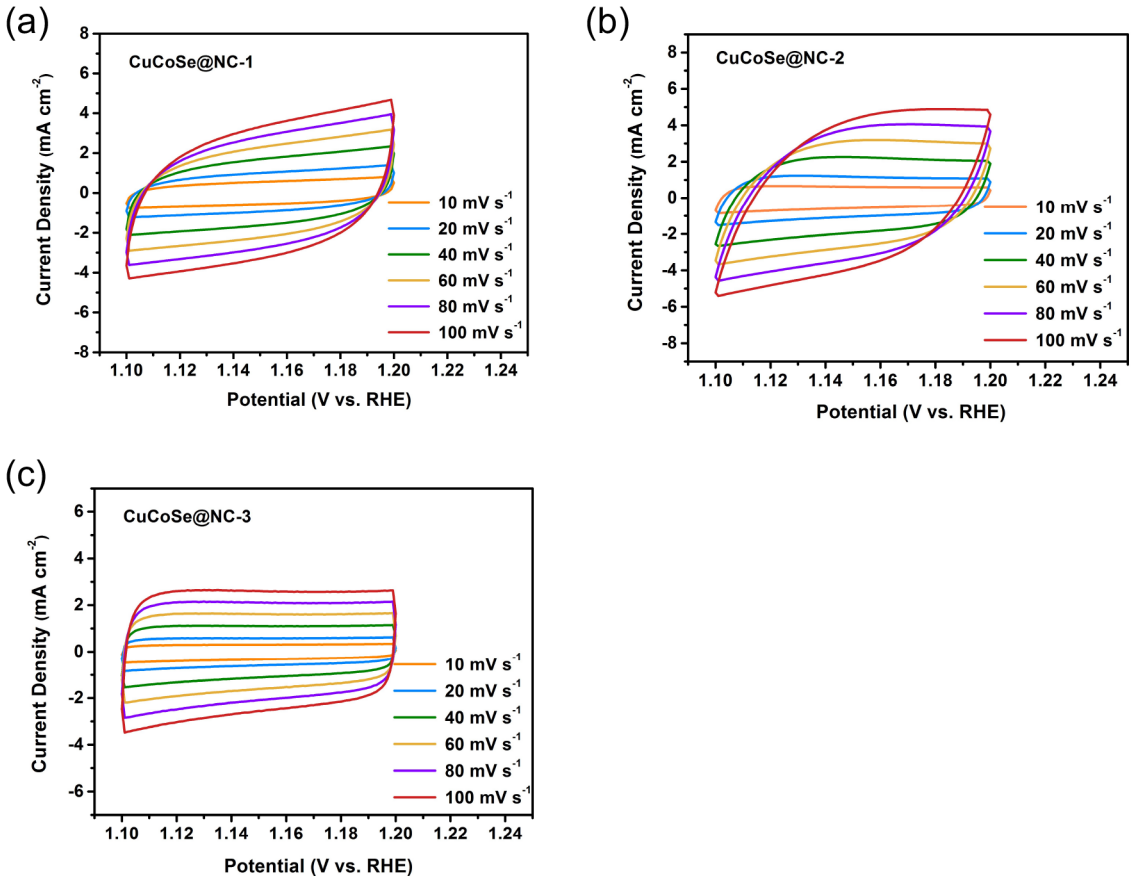


**Fig. S9**. CV curves of CuCoSe@NC-1, CuCoSe@NC-2 and CuCoSe@NC-3 at different scan rates in 1 M KOH solution.

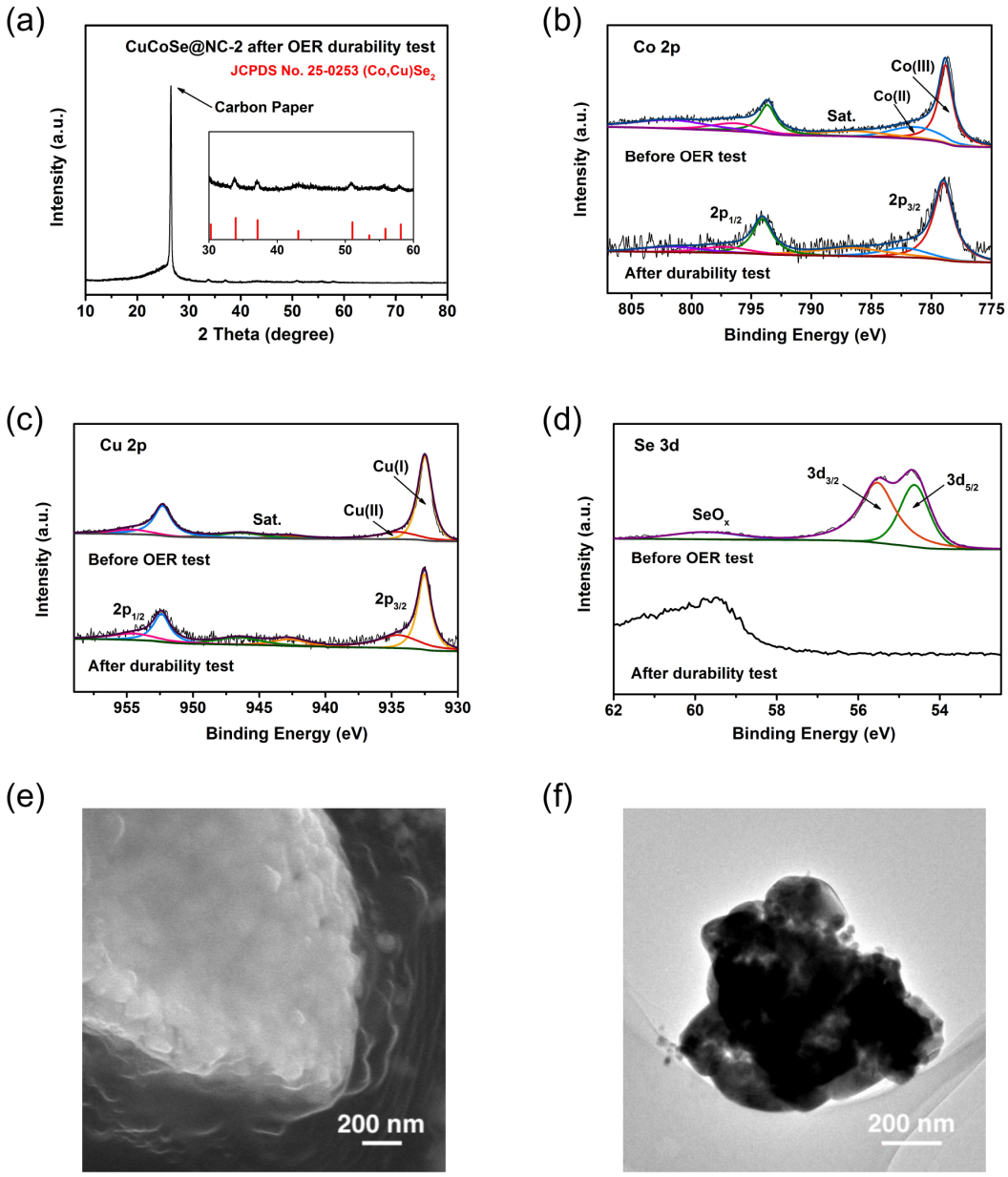


**Fig. S10**. (a) XRD spectrum of CuCoSe@NC-2 after OER durability test. XPS spectra for (b) Co 2p, (c) Cu 2p and (d) S 2p of CuCoSe@NC-2 before and after OER durability test. (e) SEM image and (f) TEM image of CuCoSe@NC-2 after OER durability test.

**Table S1**. The BET specific surface area of CuCoSe@NC-*x*.

| Samples | $S_{BET}$ ($m^2$ $g^{-1}$) |
|---|---|
| CuCoSe@NC-1 | 226 |
| CuCoSe@NC-2 | 342 |
| CuCoSe@NC-3 | 169 |

**Table S2**. Comparison of the ORR performance of CuCoSe@NC-2 and other metal selenide electrocatalysts reported in the literature.

| Samples | Electrolyte | Onset Potentials (V *vs.* RHE) | Half-wave Potentials (V *vs.* RHE) | References |
|---|---|---|---|---|
| CuCoSe@NC-2 | 0.1 M KOH | 0.951 | 0.846 | **This work** |
| $Co_{0.85}Se$@CNFs | 0.1 M KOH | 0.84 | 0.82 | *Chem. Eur. J.*, 2019, 25: 1-8 |
| $Ni_xCo_{0.85-x}Se$ | 0.1 M KOH | 0.89 | 0.82 | *Sci. China Mater.*, 2020, 63(3): 347-355 |
| $(Ni,Co)Se_2$ | 0.1 M KOH | / | 0.70 | *Journal of Energy Chemistry*, 2019, 38: 34-40 |
| Co-Fe-P-Se/NC | 0.1 M KOH | / | 0.76 | *Nanoscale*, 2019, 11(42): 20144-20150 |
| $Co_{0.62}Zn_{0.38}$-ZIF@NCF-800 | 0.1 M KOH | 0.913 | 0.78 | *ACS Sustainable Chem. Eng.*, 2020, 8, 8391-8401 |
| $CoIn_2Se_4$ | 0.1 M KOH | 0.88 | 0.77 | *ACS Appl. Mater. Interfaces*, 2020, 12(7): 8115-8123 |
| Cu-14-$Co_3Se_4$/GC | 0.1 M KOH | 0.892 | 0.782 | *ACS Catal.*, 2019, 9(12): 10761-10772 |
| $Ni_{0.85}Se$-NHCS | 0.1 M KOH | 0.850 | / | *J. Mater. Sci.*, 2019, 54(12): 9063-9074 |

**Table S3**. Comparison of the OER performance of CuCoSe@NC-2 and other metal selenide electrocatalysts reported in the literature.

| Samples | Electrolyte | Overpotentials at 10 mA $cm^{-2}$ (mV) | References |
|---|---|---|---|
| CuCoSe@NC-2 | 1.0 M KOH | 300 | **This work** |
| CoIn2Se4 | 1.0 M KOH | 305 | *ACS Appl. Mater. Interfaces*, 2020, 12(7): 8115-8123 |
| $Co_{0.85}$Se-NC/C-T | 1.0 M KOH | 298 | *Chemical Engineering Journal*, 2021,420(15):130461 |
| $Ni_{0.85}$Se-NHCS | 1.0 M KOH | 353 | *J. Mater. Sci*., 2019, 54(12): 9063-9074 |
| Cu-14-Co3Se4/GC | 1.0 M KOH | 280 | *ACS Catal.*, 2019, 9(12): 10761-10772 |
| $Ni_xCo_{0.85-x}Se$ | 0.1 M KOH | 305 | *Sci. China Mater.*, 2020, 63(3): 347-355 |
| $(Ni,Co)Se_2$ | 0.1 M KOH | 360 | *Journal of Energy Chemistry,* 2019, 38: 34-40 |
| FeSe/NC-PoFeSe | 0.1 M KOH | 350 | *ACS Appl. Mater. Interfaces*, 2018, 10(38):32133-32141 |

**Table S4**. Comparison of the Zn-air baterries performance of CuCoSe@NC-2 and other metal selenide electrocatalysts reported in the literature.

| Samples | Power density (mW $cm^{-2}$) | Durability @ J (mA $cm^{-2}$) | References |
|---|---|---|---|
| CuCoSe@NC-2 | 137.1 | Cycle times over 75 h @ 10 | **This work** |
| $Ni_xCo_{0.85-x}Se$ | / | Cycle times over 84 h @ 10 | *Sci. China Mater.*, 2020, 63(3): 347-355 |
| $(Ni,Co)Se_2$ | 110 | Cycle times over 120 h @ 2 | *Journal of Energy Chemistry,* 2019, 38: 34-40 |
| CoIn2Se4 | 107 | Cycle numbers over 410 @ 10 | *ACS Appl. Mater. Interfaces*, 2020, 12(7): 8115-8123 |
| $Ni_{0.85}Se$-NHCS | 89.41 | Cycle times over 18 h @ 20 | *J. Mater. Sci*., 2019, 54(12): 9063-9074 |
| Co-Fe-P-Se/NC | 104 | Cycle numbers over 120 @ 10 | *Nanoscale*, 2019, 11(42): 20144-20150 |
| Ni-Fe-$Se_{1:1}$-180 | 148.6 | Cycle times over 300 h @ 10 | *Electrochimica Acta*, 2018, 291: 64-72. |