

Supporting Information

Grain-boundary-rich cobalt selenide hollow multi-shelled structure as a highly efficient electrocatalyst for lithium-sulfur batteries

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Experimental Section

1.1. Synthesis of $\text{Co}_2\text{V}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ NPs

0.234 g of NH_4VO_3 was dissolved in 40 mL of deionized water at 70 °C, and stirred continuously at this temperature to form a light yellow solution, then 0.095 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 1.2 g of hexamethylenetetramine were added and stirred continuously at 80 °C for 4 h. After cooling to room temperature, the orange precipitates were collected by centrifuging and then wash three times by deionized water and absolute ethanol. Finally, it was dried at 70 °C for 12 h in air to obtain the $\text{Co}_2\text{V}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ NPs.

1.2. Synthesis of GB-CoSe HoMS and normal CoSe NPs

0.1 g of Na_2SeO_3 and 0.02 g of $\text{Co}_2\text{V}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ NPs were dispersed in 35 mL of ethylene glycol by magnetic stirring, and after stirring for 10 min, 1 mL hydrazine hydrate was added to the solution and stirred for 5 min. Afterward, the solution was transferred to a 40 mL autoclave and maintained at 180 °C for 2 h. After cooling to room temperature, it was washed several times with deionized water and ethanol, and finally dried at 70 °C for 12 h, and finally GB-CoSe HoMS was obtained. As a contrast, the $\text{Co}_2\text{V}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ NPs in the above preparation process were replaced with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and the normal CoSe NPs were obtained.

1.3. Synthesis of GB-CoSe HoMS and CoSe NPs modified separators

The GB-CoSe HoMS and CoSe NPs modified separators (GB-CoSe HoMS/PP and CoSe/PP) were obtained by the vacuum filtration method. In short, GB-CoSe HoMS (4.2 mg) was ultrasonically dispersed into N-methyl-2-pyrrolidone (NMP) (10 mL) with polyvinylidene fluoride (PVDF) (1.2 mg) and Ketjen black (KB) (0.6 mg). The powder samples were filtered on the polypropylene (PP) membrane (Celgard 2400) followed by drying at 60 °C overnight under a vacuum. Eventually, the functionalized separators were cut into discs with a diameter of 19 mm. The average

mass loading of the GB-CoSe HoMS on modified separator is around 0.3 mg cm^{-2} .

1.4. Synthesis of the KB@S and CNT/S cathodes

The KB/S composite was prepared by the melt-diffusion method. Sulfur powder (S_8) and KB were ground together (weight ratio of 3:1) and after heating at $155 \text{ }^\circ\text{C}$ for 12 h using melt diffusion. Afterwards, a slurry containing KB/S composite (80 wt.%), KB (10 wt.%), and polyvinylidene fluoride (PVDF) (10 wt.%) was prepared followed by adding small amounts of NMP and spread on carbon coated aluminum foil and dried in a vacuum oven at $60 \text{ }^\circ\text{C}$ for 6 h. The areal sulfur loading for each disk was controlled around 1.0 mg cm^{-2} .

Commercial carbon nanotube (CNT) and sublimed sulfur (weight ratio of 1:3) was ground uniformly in a mortar to obtain a CNT/S mixture. The CNT/S mixture was then heated at $155 \text{ }^\circ\text{C}$ for 12 h to obtain a CNT/S composite. Generally, CNT/S cathode slurry was fabricated by mixing 80 wt.% CNT/S composite, 10 wt.% KB, and 10 wt.% PVDF in NMP. The obtained slurry was coated onto the surface of carbon paper and dried at $60 \text{ }^\circ\text{C}$ for 12 h.

1.5. Lithium polysulfide (Li_2S_6) solution and visualized adsorption test

Li_2S_6 solution was prepared by dissolving S_8 and Li_2S (the molar ratio is 5:1) in 1:1 volume ratio of DOL/DME solvents under vigorous stirring at $70 \text{ }^\circ\text{C}$ for 24 h. The resulting 0.1 M Li_2S_6 solution was utilized for adsorption test. Certain amount of samples were put into 3 mL Li_2S_6 solution (5 mM) to observe the color change of the solution. All the above operations were carried out in an argon-filled glove box.

1.6. Symmetrical cells assembling and testing

0.25 M Li_2S_6 electrolyte was prepared by vigorous stirring S_8 and Li_2S (the molar ratio is 5:1) in electrolyte (1 M LiTFSI in a mixed solvent of DOL/DME under a volumetric ratio of 1:1) and stirring at $70 \text{ }^\circ\text{C}$ for 24 h. Mixing active materials (GB-

CoSe HoMs and CoSe NPs) and PVDF with a weight ratio of 9:1 in NMP and then coated onto aluminum foil to both serve as anode and cathode. 0.25 M Li_2S_6 electrolyte was electrolyte and commercial PP was used as the separator. The cyclic voltammetry (CV) measurements of the symmetric cells were tested by electrochemical workstation (CHI660E) with a voltage window between -1.0 to 1.0 V at scan rates of 5 mV s^{-1} .

1.7. Li_2S nucleation measurements

For the study of liquid-solid conversion kinetics, 0.5 M Li_2S_8 electrolyte was prepared by mixing Li_2S and S_8 at a molar ratio of 7:1 and dissolved into DME and DOL (1:1 in volume) solution with 1.0 M LiTFSI by stirring for 24 h. GB-CoSe HoMs or CoSe were uniformly dispersed in ethanol and then dropped onto carbon paper to obtain the cathode. Nucleation experiments of Li_2S on different reactive surfaces were investigated in 2032-type coin cells with Celgard 2400 PP membrane as separator and the lithium foil as anode. 20 μL Li_2S_8 electrolyte was added to the cathode side, and 20 μL 1M LiTFSI electrolyte was dropped onto the lithium anode side. The batteries were first discharged to 2.19 V at 0.112 mA followed by maintaining at 2.05 V until the current was below 1.0×10^{-5} A.

1.8. Materials characterization

X-ray diffraction (XRD) was conducted to characterize the crystal structure of products under Cu $K\alpha$ radiation source (D/max-Uitima III Rigaku). The microscopic morphology of products was explored through field-emission scanning electron microscopy (FESEM, Germany, Zeiss Supra 55) and high-resolution transmission electron microscope (HRTEM, FEI, Talos F200i). The surface chemical states of products were detected through X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, ESCALAB 250). Simultaneous thermal analyzer (TG-DSC, NETZSCH, STA449-F5) was performed on thermogravimetric analysis (TGA). The

specific surface area (BET) and pore size distribution (BJH) were obtained on a N₂ adsorption analyzer (Micromeritics-ASAP 2460).

1.9. Electrochemical measurements

CR2032 coin batteries were assembled with KB/S or CNT/S cathodes, modified PP separators, and Li foil anodes in the Ar-filled glove box. LiTFSI of 1.0 M in a DME-DOL solution (1:1 in volume) with 1 wt.% LiNO₃ was used as the electrolyte for lithium-sulfur (Li-S) batteries. Galvanostatic charge and discharge (GCD) tests of the batteries were measured within a potential range from 1.7 to 2.8 V using Neware battery testing system (Neware, China). CV curves and electrochemical impedance spectroscopy (EIS) were measured by electrochemical workstation (CHI660E) with the frequency range from 10⁻² to 10⁵ Hz.

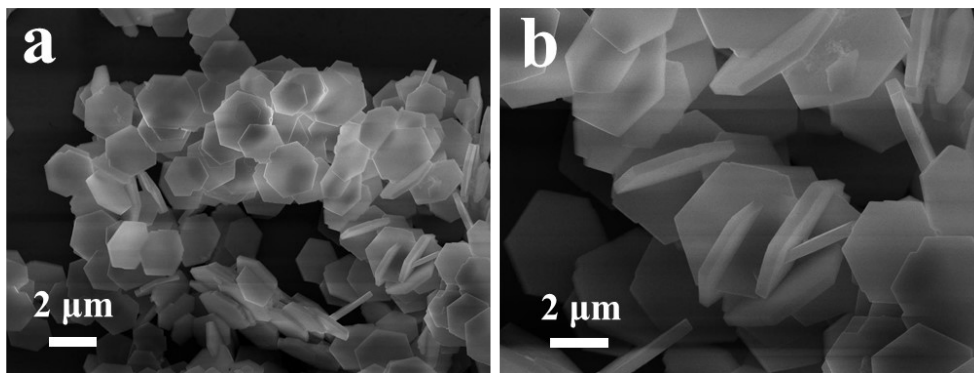


Figure S1. (a, b) SEM images of the $\text{Co}_2\text{V}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ NPs.

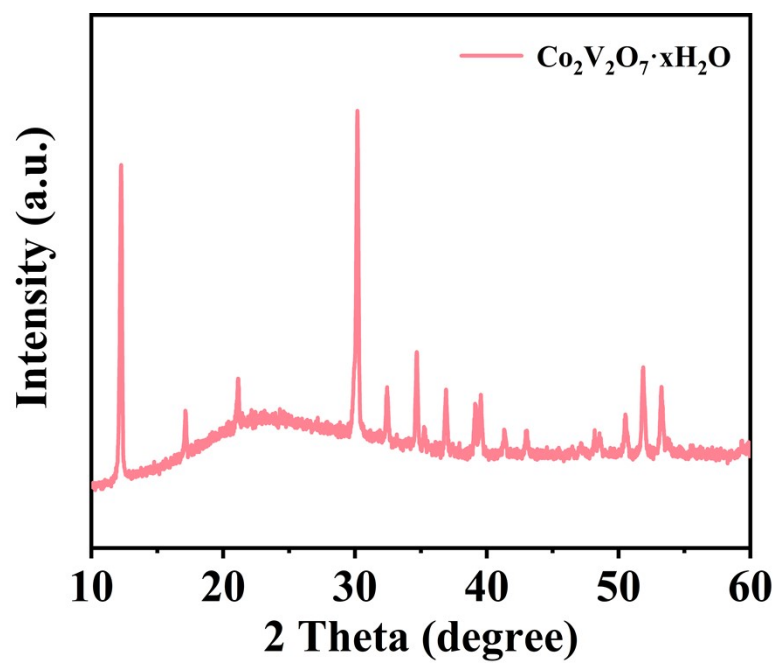


Figure S2. XRD pattern of the $\text{Co}_2\text{V}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ NPs.

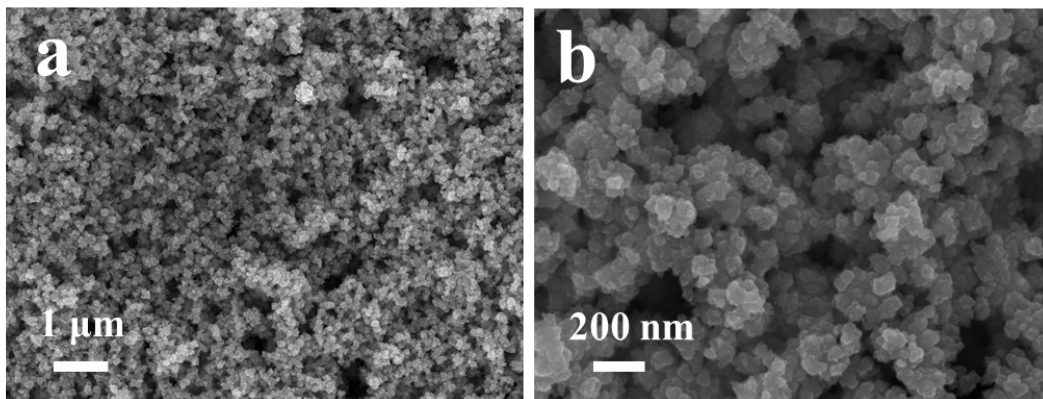


Figure S3. (a, b) SEM images of the normal CoSe NPs.

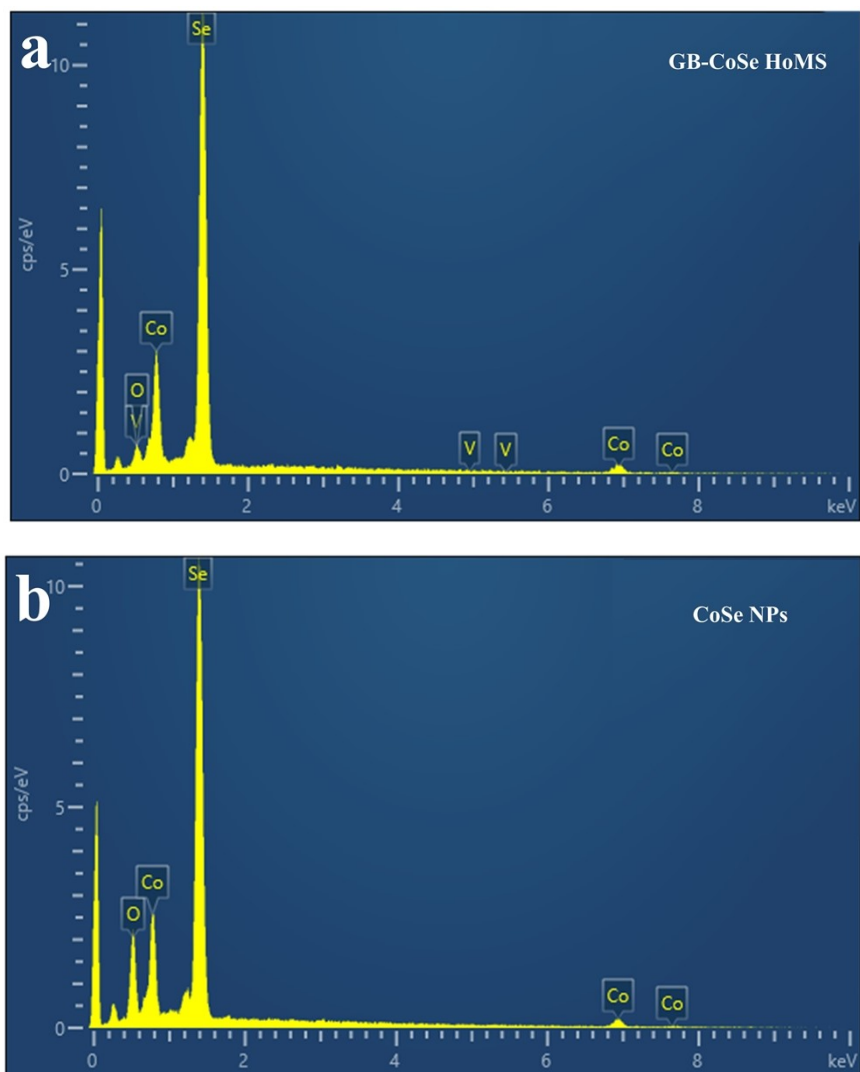


Figure S4. EDS spectra of the (a) GB-CoSe HoMS and (b) CoSe NPs.

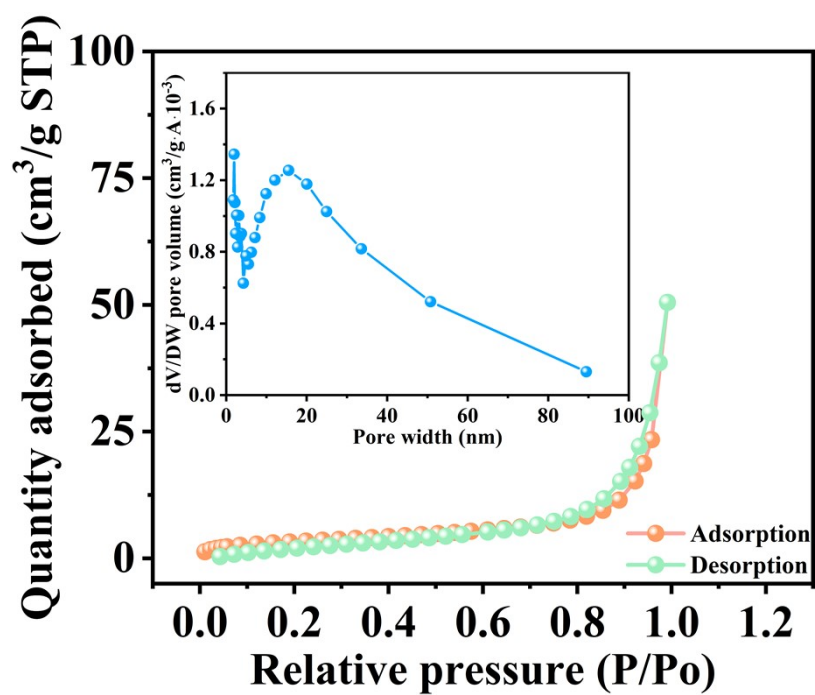


Figure S5. N₂ adsorption-desorption isotherm of the GB-CoSe HoMS (inset shows the size distribution curve).

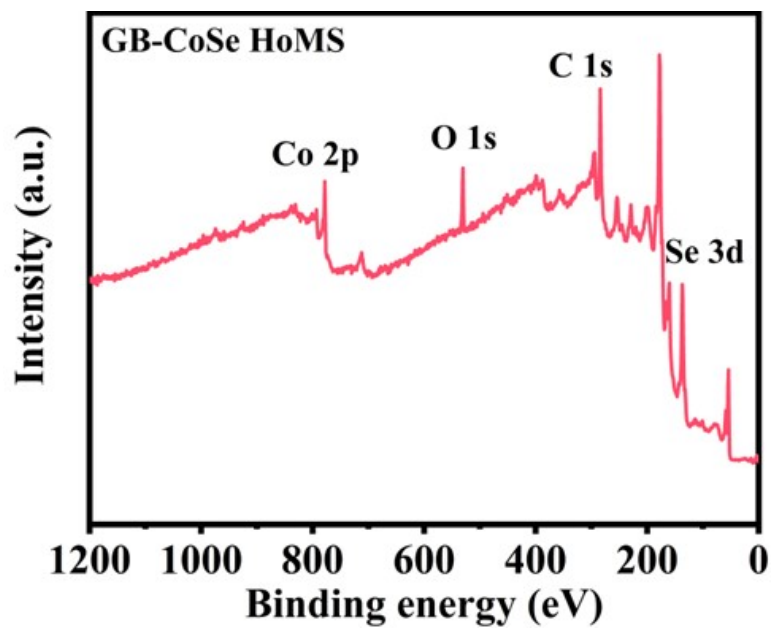


Figure S6. XPS survey spectrum of the GB-CoSe HoMS.

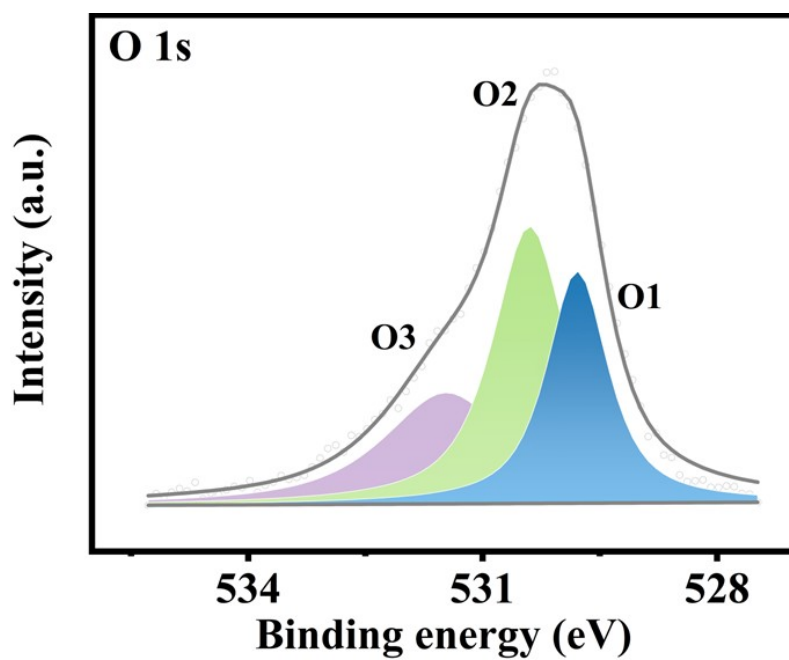


Figure S7. High-resolution O 1s XPS spectrum of the GB-CoSe HoMS.

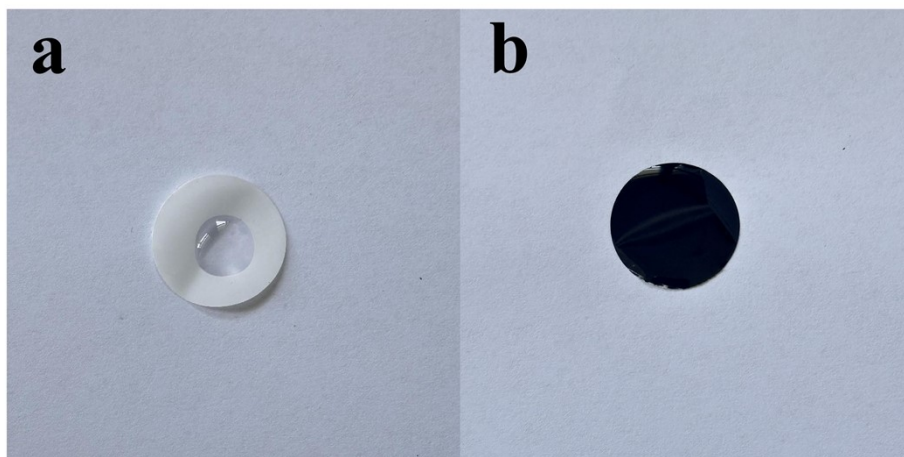


Figure S8. The electrolyte wettability test for the (a) PP and (b) GB-CoSe HoMS/PP separators.

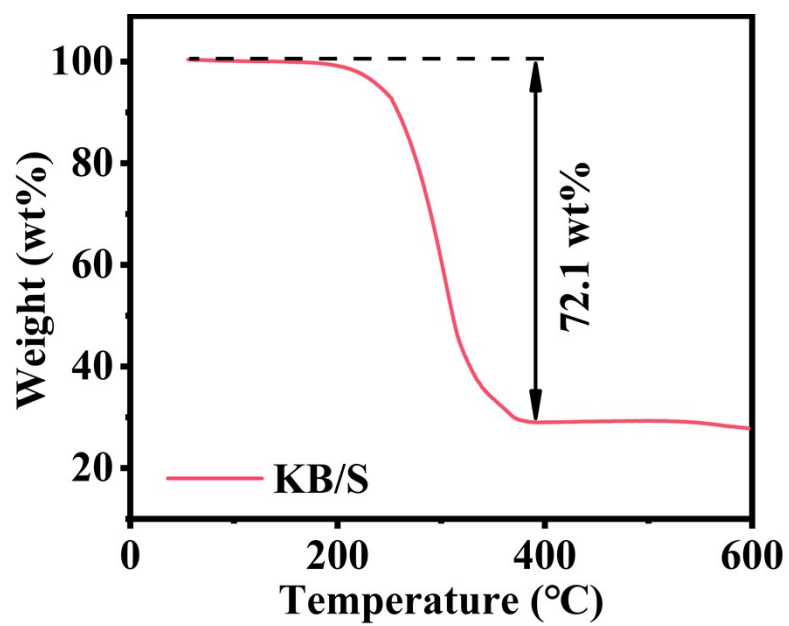


Figure S9. TGA curve of the KB/S composite under nitrogen atmosphere.

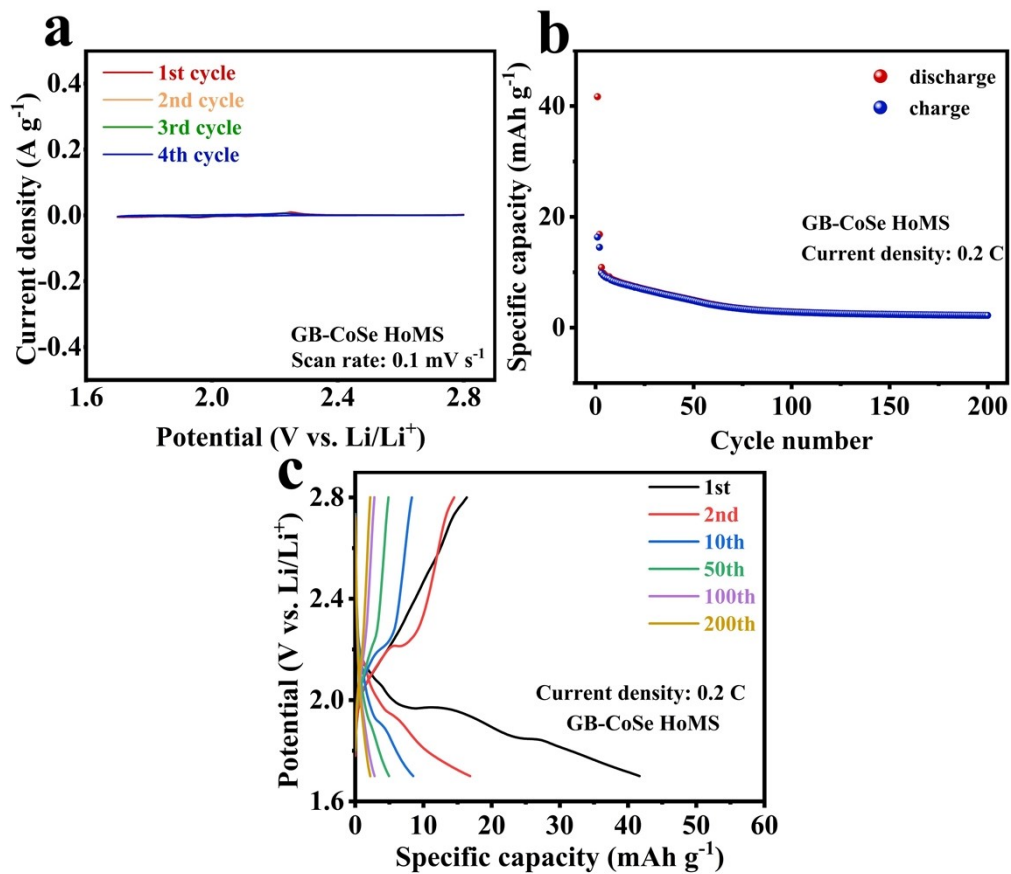


Figure S10. (a) CV curve at 0.1 mV s^{-1} , (b) cycle performance and (c) GCD profiles at 0.2 C of the GB-CoSe HoMS//Li cells (without sulfur loading) in the voltage range of $1.7\text{-}2.8 \text{ V}$.

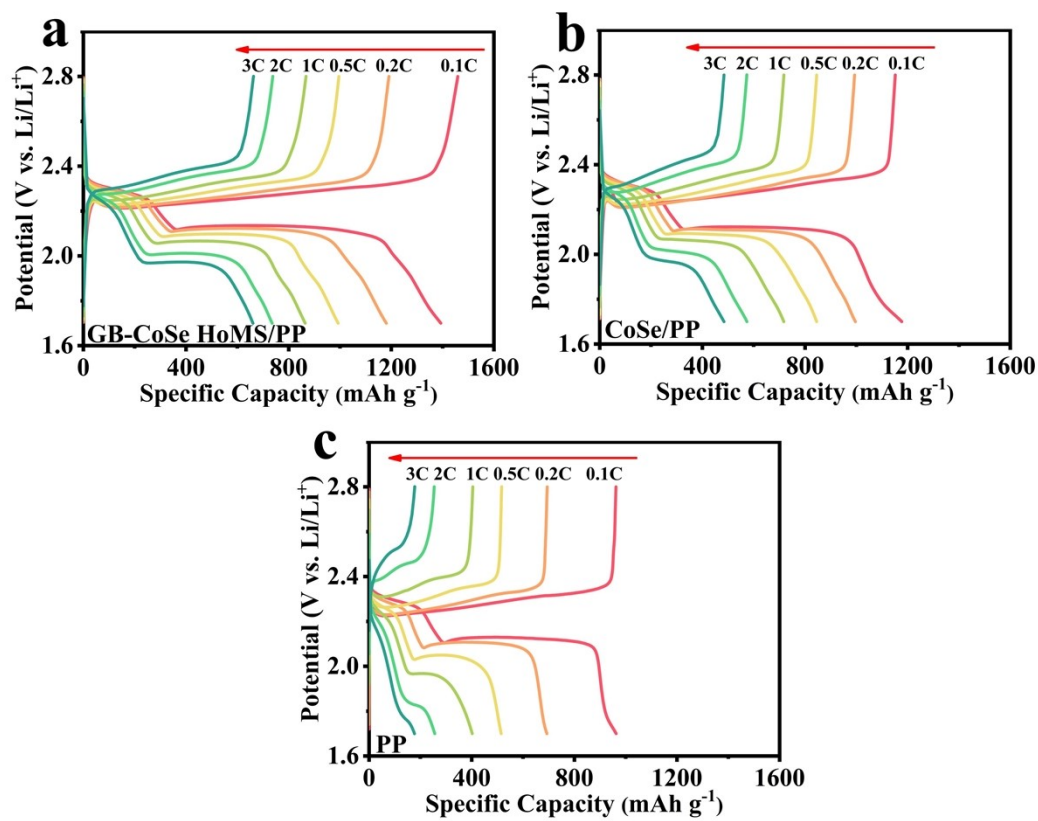


Figure S11. GCD profiles of the Li-S batteries with (a) GB-CoSe HoMs/PP, (b) CoSe/PP, and (c) PP separators at different C rates.

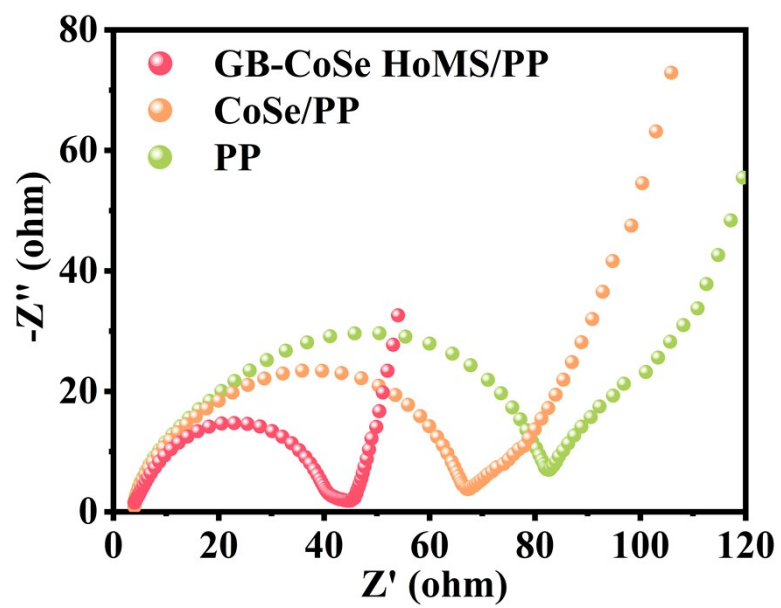


Figure S12. EIS spectra of the Li-S batteries with different separators.

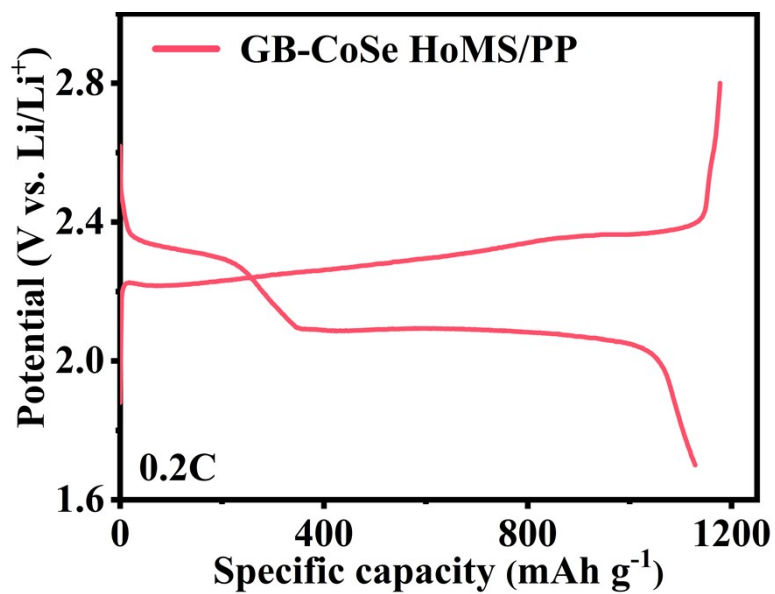


Figure S13. GCD profiles of the high-sulfur-loading battery at 0.2 C.

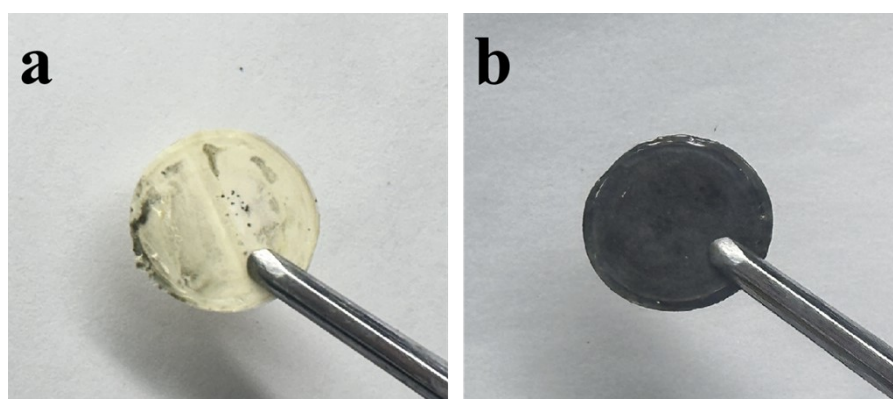


Figure S14. Post-mortem analysis of the Li-S batteries after 100 cycles. Digital photographs of the (a) PP, (b) GB-CoSe HoMS/PP.

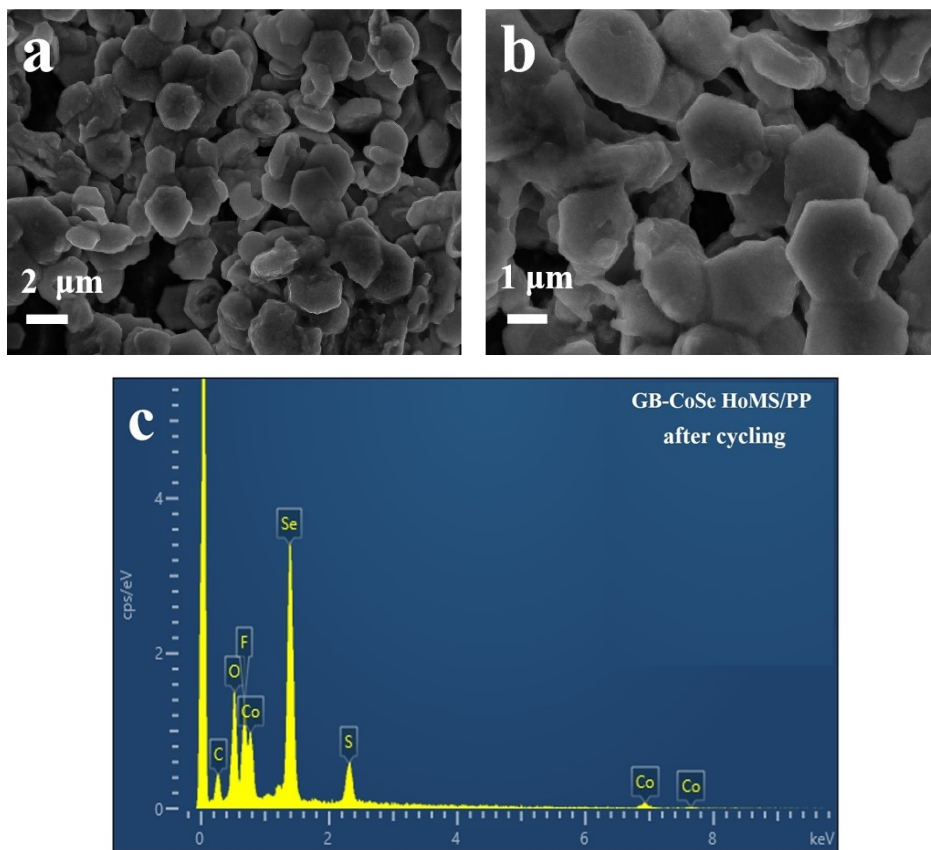


Figure S15. (a, b) SEM images and (c) EDS spectrum of the GB-CoSe HoMS/PP after cycling.

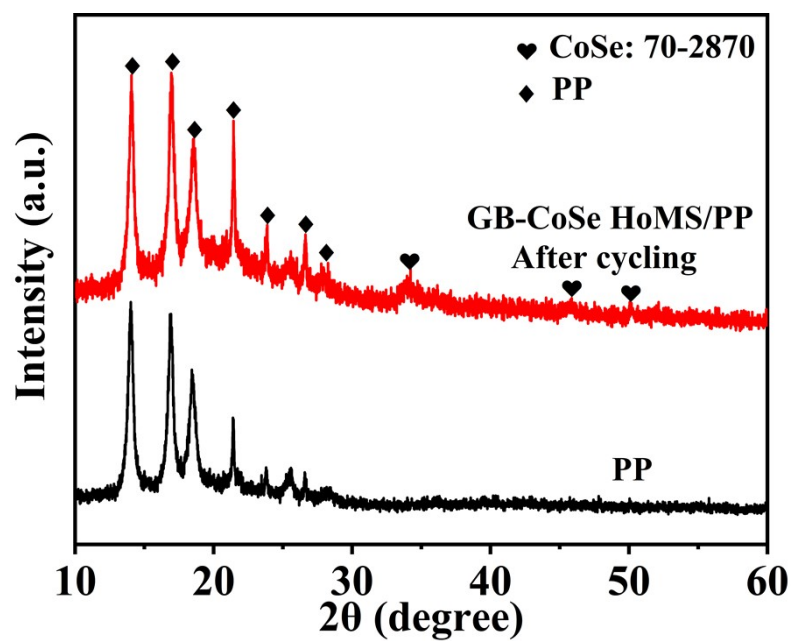


Figure S16. XRD patterns of the pristine PP separator and the GB-CoSe HoMS/PP separator after cycling.

Table S1. Comparison of the electrochemical performance of GB-CoSe HoMS with other recently reported materials.

Catalytic materials	Sulfur loading (mg cm ⁻²)	Long cycle stability (mAh g ⁻¹)	Capacity decay rate (cycle ⁻¹)	Low rate (mAh g ⁻¹)	High rate (mAh g ⁻¹)	References
GB-CoSe HoMS	1.0	486.7/1C/1000	0.046%	1393.3 (0.1C)	660.9 (3C)	This work
TiO@C	1.5	630.0/0.5C/500	0.08%	1146.0 (0.1C)	655.0 (2C)	11
NiO-NiCo ₂ O ₄	-	716.9/0.5C/500	0.059%	1063.2 (0.2C)	697.9 (2C)	12
C-MoSe _{2-x}	1.1-1.3	470.2/1C/500	0.09%%	1341.5 (0.1C)	663.8 (1C)	19
ZnCo-MOF	1.6	688.0/0.5C/300	0.048%	1076.0 (0.1C)	552.0 (2C)	23
3DP-Ni ₂ P	1.8	500.0/1C/400	0.125%	973.8 (0.2C)	637.6 (2C)	28
ZIF-67/SA-PAN	1.0	≈400.0/1C/500	0.089%	1187.0 (0.1C)	707.0 (2C)	45
Ni _{0.1} Zn _{0.1} Co _{0.8} Se	1.0	≈500.0/1C/400	0.065%	1219.4 (0.1C)	681.74 (2C)	46
2						
SnS ₂ @NHCS	1.0	395.0/1C/500	0.065%	947.4 (0.2C)	569.5 (2C)	47
SnS ₂ /TiO ₂	1.2	572.0/0.5C/500	0.064%	1174.9 (0.2C)	449.3 (2C)	48
CoF ₂	2.0	542.4/1C/300	0.076%	1096.0 (0.1C)	737.1 (2C)	49
Ti ₃ AlC ₂	1.5	313.0/0.5C/350	0.186%	917.0 (0.1C)	504.0 (1C)	50

Table S2. Summary of Li⁺ ion diffusion rates (D_{Li^+} , cm² s⁻¹) of different separators.

Separators	Peak A	Peak B	Peak C
PP	7.72×10^{-9}	8.83×10^{-9}	5.17×10^{-8}
CoSe/PP	1.85×10^{-8}	2.69×10^{-8}	6.31×10^{-8}
GB-CoSe HoMS/PP	4.98×10^{-8}	5.86×10^{-8}	2.42×10^{-7}

Table S3. Comparison of the areal capacities and sulfur loading with other previously reported Li-S batteries in literatures.

Catalytic materials	Sulfur loading (mg cm ⁻²)	Areal capacity (mAh cm ⁻²)	E/S ratio (μL mg ⁻¹)	References
GB-CoSe HoMS	5.5	6.2	8.0	This work
Fe _{3-x} C@C-500	5.0	5.0	-	13
FeCFeOC-FeCFeOC	4.3	4.6	-	14
CS@HPP	4.4	4.0	15.0	17
C-MoSe _{2-x}	5.0	≈3.5	-	19
VSe ₂ -VG	5.5	4.0	8.4	20
G _L -CoSe	4.5	3.0	14.0	53
MoSe ₂ /CoSe ₂ @NC	3.6	2.1	12.0	54
MXene@CoSe ₂ /NC	5.0	2.6	5.0	55
Ti ₃ C ₂ T _x @CoSe ₂	4.0	4.3	9.0	56