

Supporting Information

Amorphous/crystalline heterostructure design enables highly efficient adsorption-diffusion-conversion of polysulfides for lithium–sulfur batteries

Xiangpeng Wu,^{a,1} Zewei Shen,^{a,1} Daoping Cai,^{a,*} Ban Fei,^a Mincai Zhao,^a Junjie Fu,^a

Qidi Chen,^a and Hongbing Zhan^{a*}

^a College of Materials Science and Engineering, Fuzhou University, Fujian 350108, China.

*Corresponding authors: Daoping Cai and Hongbing Zhan.

E-mail addresses: dpcai@fzu.edu.cn and hbzhan@fzu.edu.cn.

¹ These authors contribute equally to this work.

Experimental Section

1.1. Synthesis of BiOBr nanosheets

In a typical synthesis, 1 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 0.4 mL of HBr and 0.7 g of polyethylene glycol (PEG) were dissolved in 10 mL of ethylene glycol, after stirring for 10 minutes, a homogeneous solution was obtained. After that, the mixture was transferred into a Teflon-lined stainless steel autoclave (50 mL) and sealed tightly, the autoclave was maintained at a temperature of 160 °C for 6 h. When the reaction was completed, the resulting product was collected by centrifugation, washed with ethanol and water for at least three times and then dried at 70 °C overnight.

1.2. Synthesis of Bi_2Se_3 nanosheets

20 mg of BiOBr nanosheets, 20 mg of 1,10-phenanthroline and 50 mg of SeO_2 were mixed in 10 mL oleylamine in the 25 mL round flask under continuous magnetic agitation and then heated to 180 °C within 3 h to get a black solution. The obtained sample was collected by filtration and washed with ethanol and hexyl hydride several times, then dried at 70 °C overnight.

1.3. Synthesis of c- Bi_2Se_3 /a- BiO_x nanosheets

20 mg of Bi_2Se_3 nanosheets was dispersed in 16 mL of deionized water. Then 1 mL of hydrogen peroxide (H_2O_2) was added to the solution under 30 min stirring. The product was collected after centrifugation, thoroughly washed with deionized water and ethanol several times, and finally dried in an oven at 70 °C for overnight. The procedure for synthesizing the c- Bi_2Se_3 /a- BiO_x -5 product was similar to that of c- Bi_2Se_3 /a- BiO_x except that the amount of H_2O_2 was adjusted to 5 mL.

1.3. Synthesis of KB/S and CNT/S cathodes

The Ketjen black (KB)/S composite was prepared by the melt-diffusion method. The KB mixed with sublimed sulfur (weight ratio of 1:3) were placed into a sealed glass bottle and the KB/S composite was obtained after heating at 155 °C for 12 h. The sulfur cathode was prepared by the slurry-coating method. The slurry was prepared by mixing KB/S composite, KB, and polyvinylidene fluoride (PVDF) with a mass ratio of 8:1:1 in 1-methyl-2-pyrrolidinone (NMP) solvent. The slurry was then spreaded on carbon

coated aluminum foil and dried in a vacuum oven at 60 °C for 12 h, then punched into circle disks with a parameter of 12 mm. The areal sulfur loading for each disk was controlled around 1.0 mg cm⁻². The CNT/S composite was prepared for high sulfur loading battery via the same strategy.

1.4. Preparation of the modified separator

The c-Bi₂Se₃/a-BiO_x layer uniformly coated on a separator was obtained by the vacuum filtration method. 4.2 mg of c-Bi₂Se₃/a-BiO_x, 1.2 mg of PVDF and 0.6 mg of rGO were dispersed in 10 mL NMP by sonication for 2 h to obtain a homogeneous suspension, which was filtered through a polypropylene (PP) membrane (Celgard 2500). The obtained modified separator was dried at 60 °C overnight under vacuum. Eventually, the modified separator was cut into discs with a diameter of 19 mm. The c-Bi₂Se₃/a-BiO_x-5 and Bi₂Se₃ modified separators were prepared using the same method. The mass loadings of the separator modifiers was around 0.45 mg cm⁻².

1.5. Lithium polysulfide (Li₂S₆) solution and visualized adsorption test

0.1 M Li₂S₆ solution was prepared by dissolving S and Li₂S (the molar ratio is 5:1) in a mixed solvent of 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) (1:1 in volume) under vigorous stirring at 70 °C for 24 h. Then 20 mg of c-Bi₂Se₃/a-BiO_x, c-Bi₂Se₃/a-BiO_x-5 and Bi₂Se₃ were put into 3 mL Li₂S₆ solution (5 mM) for visualized adsorption test. All the above operations were carried out in an argon-filled glove box.

1.6. Symmetric cell assembly and kinetic evaluation of polysulfide conversion

0.2 M Li₂S₆ electrolyte was prepared by same method as above. The electrodes for symmetric cells were prepared by mixing active materials (c-Bi₂Se₃/a-BiO_x, c-Bi₂Se₃/a-BiO_x-5 and Bi₂Se₃) and PVDF with a weight ratio of 9:1 in NMP solvent followed by coating the slurry onto aluminum foil. Two identical electrodes were used as the working and the counter electrodes with a mass loading of about 1.0 mg cm⁻², and 40 μL of Li₂S₆ (0.2 M) was used as electrolyte. The cyclic voltammetry (CV) measurements of the symmetric cells were measured by electrochemical workstation (CHI660E) with a voltage window between -1.0 ~ 1.0 V at 5 mV s⁻¹.

1.7. Li₂S nucleation and decomposition measurements

For the study of liquid-solid conversion kinetics, Li_2S_8 solution (0.5 M) was prepared by mixing sulfur and Li_2S (molar ratio of 7:1) and dissolving the mixture in DME and DOL (1:1 in volume) solution containing 1.0 M LiTFSI under vigorous stirring for 24 h. Nucleation and decomposition experiments of Li_2S on different reactive surfaces were investigated in 2032-type coin cells with PP separator. Carbon papers (CP) were used as current collector to load the different materials. c- $\text{Bi}_2\text{Se}_3/\text{a-BiO}_x$, c- $\text{Bi}_2\text{Se}_3/\text{a-BiO}_x$ -5 and Bi_2Se_3 on CP were applied as cathode and Li foil was used as anode. 20 μL of Li_2S_8 (0.5 M) was dropped onto the cathode, and blank electrolyte with 1.0 M LiTFSI and 1 wt% LiNO_3 but without Li_2S_8 was dropped onto anode side.

For Li_2S nucleation, the cells were firstly potentiostatically discharged to 2.19 V at 0.112 mA and then potentiostatically discharged at 2.05 V until the discharging current decreased to 10^{-5} A. For Li_2S decomposition, the assembled cells were charged galvanostatically to 1.70 V at 0.112 mA for complete transformation of LiPSs into solid Li_2S and then charged potentiostatically at 2.35 V until the charge current was below 10^{-5} A.

1.8. Materials characterization

The information of composition, microstructure and morphology of the products were analyzed by X-ray diffractometer (XRD, Rigaku, D/max-Ultima III diffractometer, Cu $\text{K}\alpha$ radiation, $\lambda = 0.15418$ nm), X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, ESCALAB 250), field emission scanning electron microscope (FESEM, Germany, Zeiss Supra 55), high-resolution transmission electron microscope (HRTEM, FEI, Talos F200i), and the thermogravimetric analysis (TGA, NETZSCH, STA449-F5).

1.9. Electrochemical measurements

CR2032 coin cells were assembled in an Ar-filled glovebox (<0.5 ppm of O_2 , <0.5 ppm of H_2O) by using the KB/S or CNT/S cathodes, modified PP separators, and Li foil anodes. The electrolyte was 1.0 M LiTFSI in DME: DOL (1:1 in volume) with LiNO_3 (1 wt%). Galvanostatic charge-discharge tests were conducted on LAND CT2001A within a potential range from 1.7 to 2.8 V. The specific capacity was

calculated based on the weight of sulfur in each cell ($1\text{ C} = 1675\text{ mA g}^{-1}$). CV curves and electrochemical impedance spectroscopy (EIS) were measured by an electrochemical workstation (CHI660E). EIS spectra were tested with the frequency range from 10^{-2} to 10^5 Hz.

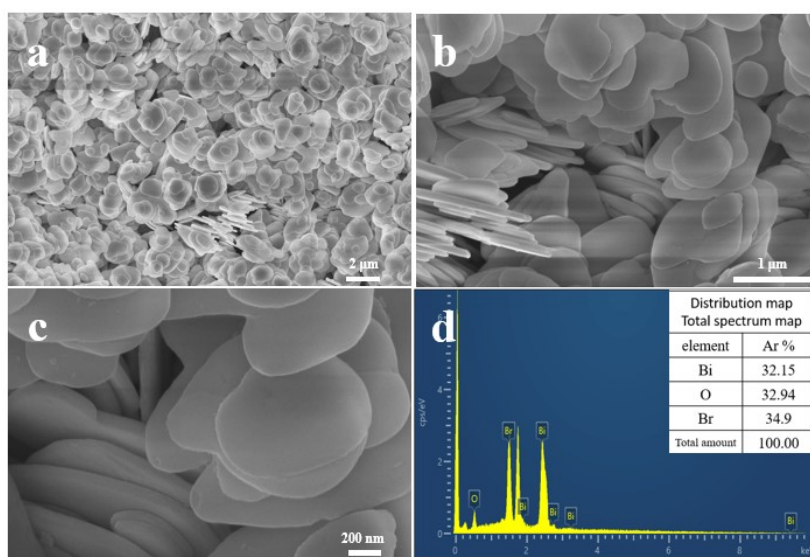


Fig. S1. (a-c) SEM images and (d) EDS spectrum of the BiOBr nanosheets.

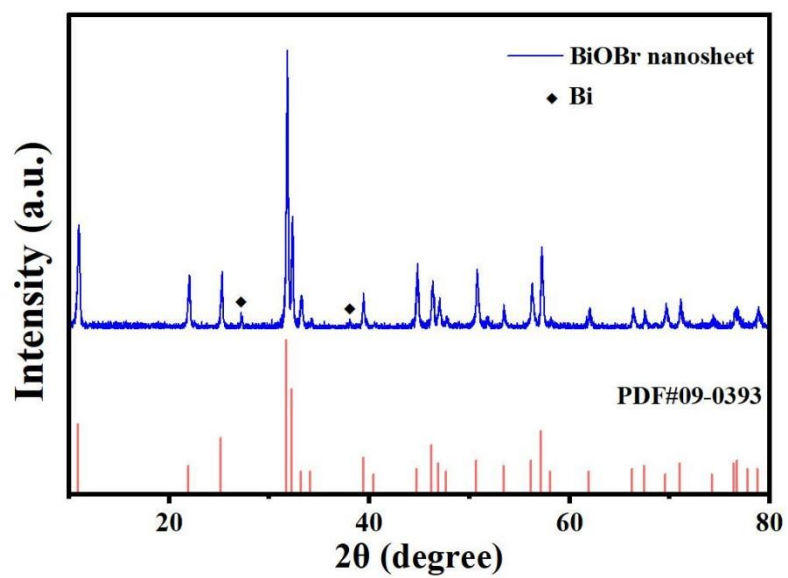


Fig. S2. XRD pattern of the BiOBr nanosheets.

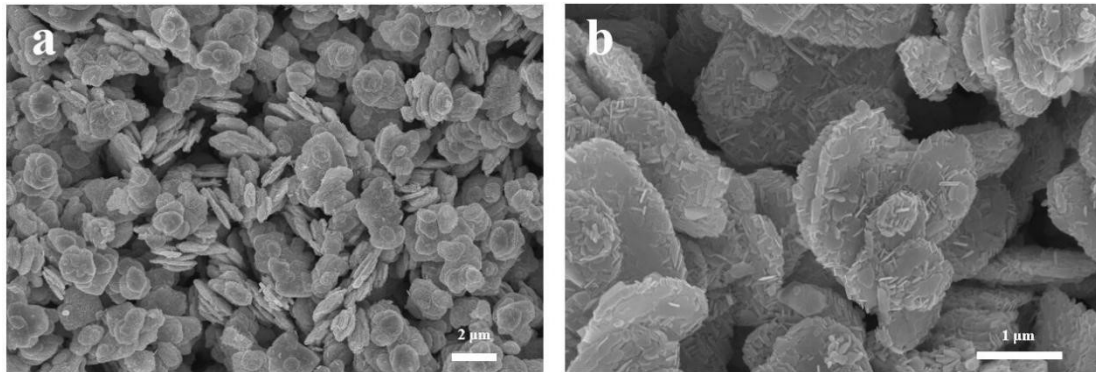


Fig. S3. (a, b) SEM images of the Bi_2Se_3 nanosheets.

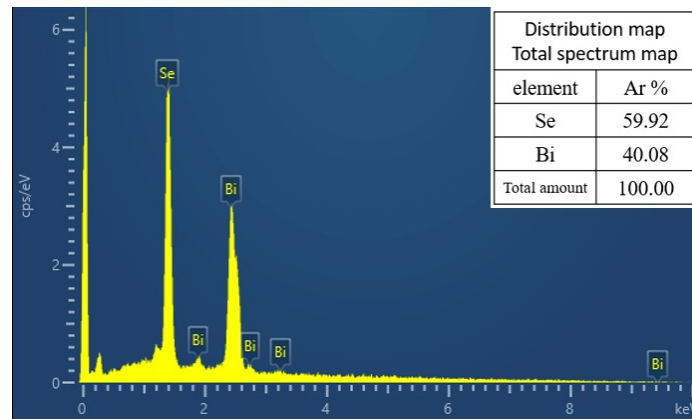


Fig. S4. EDS spectrum of the Bi_2Se_3 nanosheets.

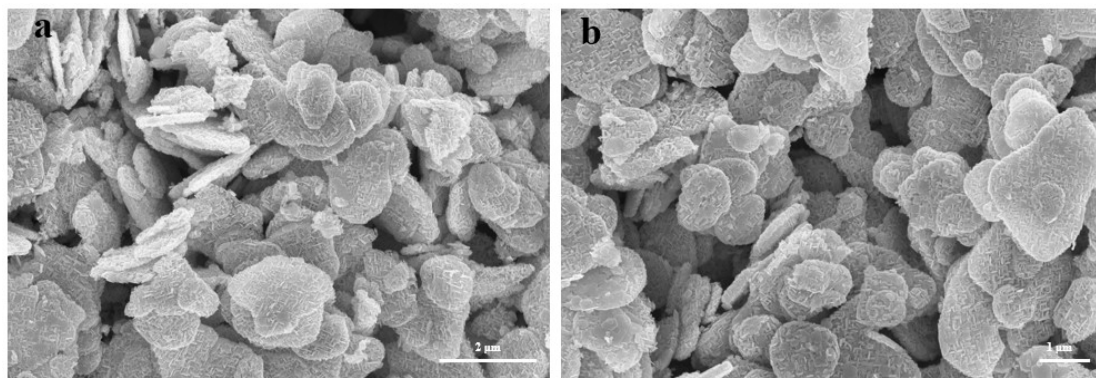


Fig. S5. (a, b) SEM images of the $\text{c-Bi}_2\text{Se}_3/\text{a-BiO}_x$ heterostructure.

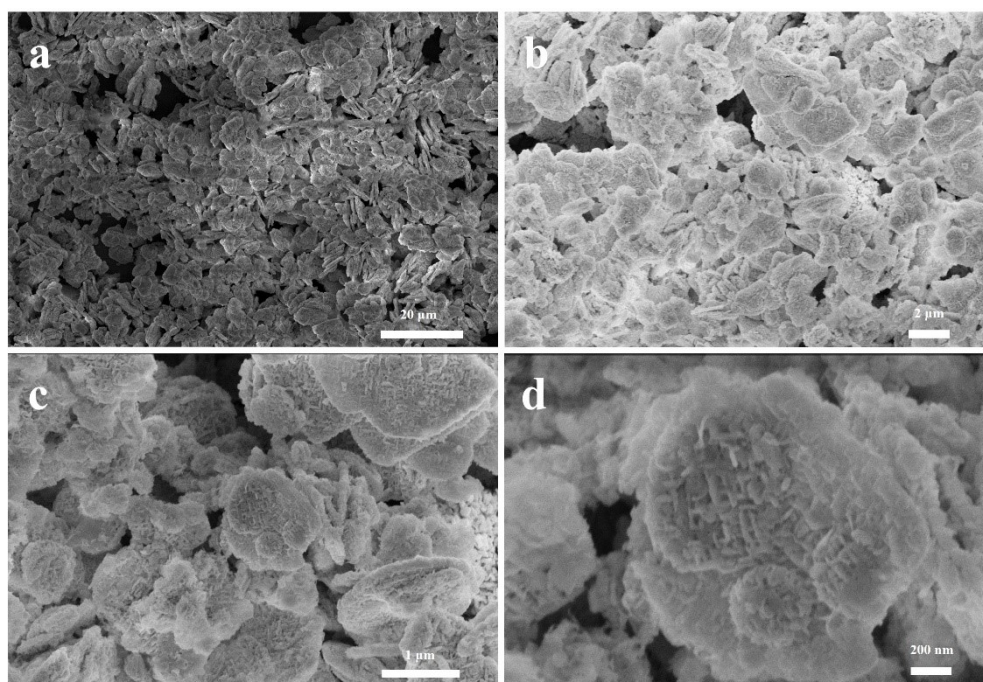


Fig. S6. (a-d) SEM images of the c-Bi₂Se₃/a-BiO_x-5.

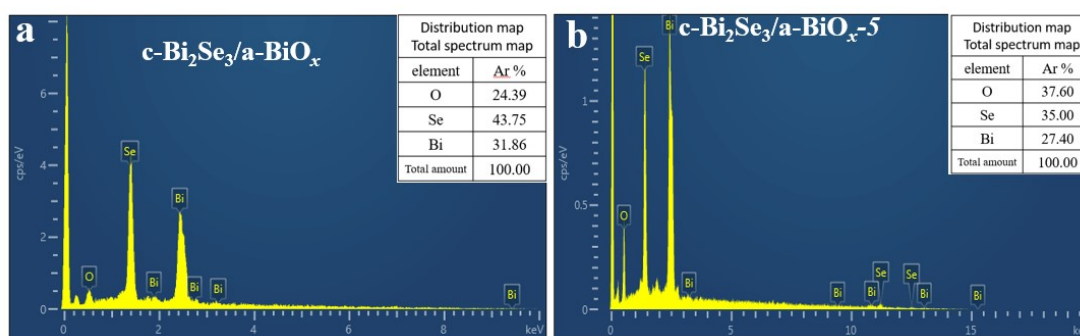


Fig. S7. EDS spectra of the (a) c-Bi₂Se₃/a-BiO_x and (b) c-Bi₂Se₃/a-BiO_x-5 products.

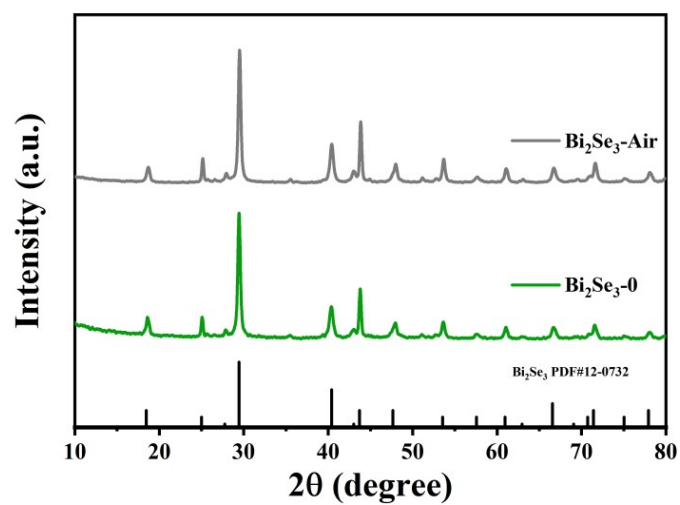


Fig. S8. XRD patterns of the Bi_2Se_3 before and after exposed in air for 30 days.

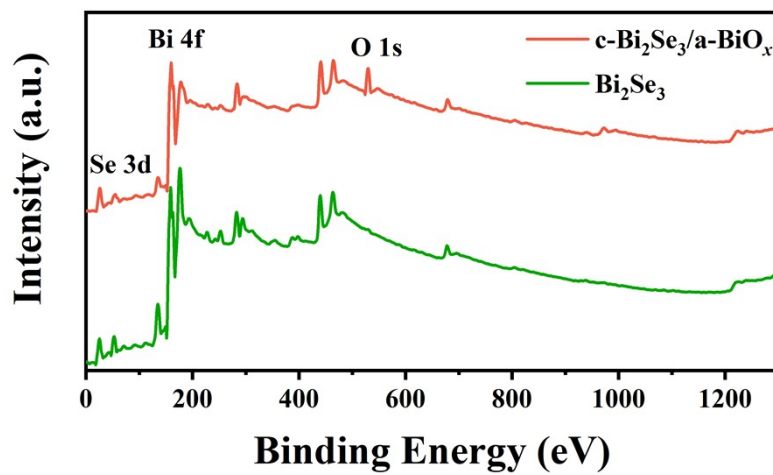


Fig. S9. XPS full spectra of the Bi_2Se_3 and $\text{c-Bi}_2\text{Se}_3/\text{a-BiO}_x$.

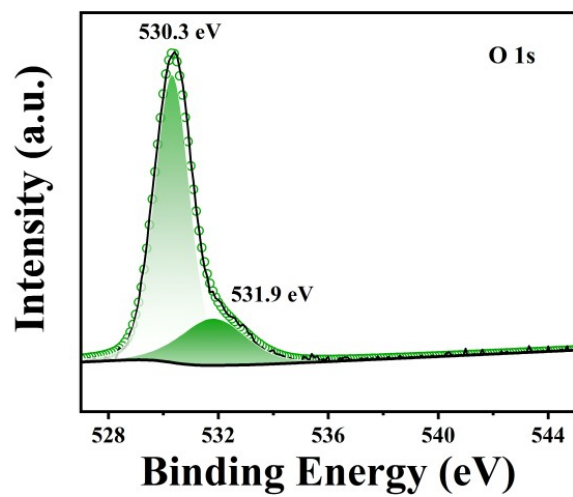


Fig. S10. High-resolution XPS O 1s spectrum of the c-Bi₂Se₃/a-BiO_x.



Fig. S11 The electrolyte wettability test of PP and c-Bi₂Se₃/a-BiO_x-PP separators.

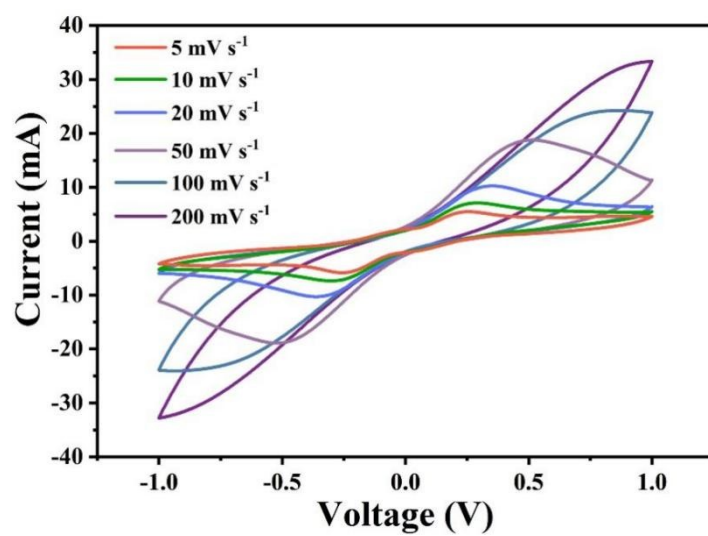


Fig. S12. CV curves of the Li_2S_6 symmetrical cells with $\text{c-Bi}_2\text{Se}_3/\text{a-BiO}_x$ at different scan rates.

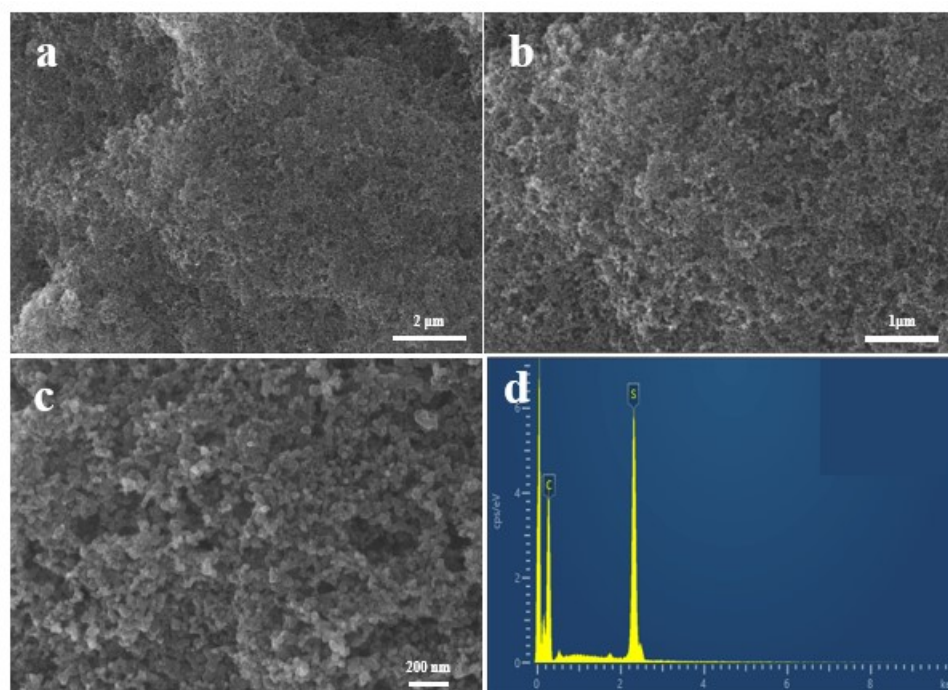


Fig. S13. (a-c) SEM images and (d) EDS spectrum of the KB/S composite.

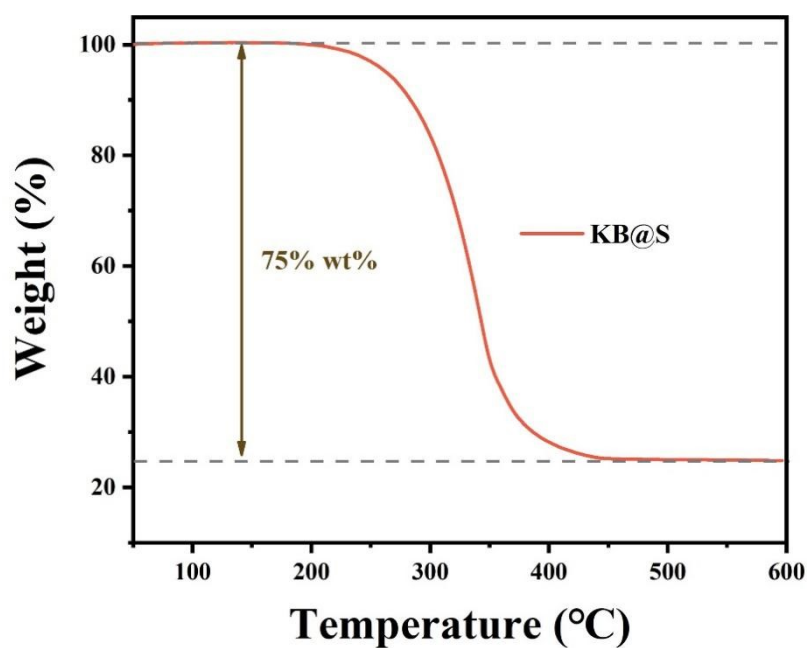


Fig. S14. TGA curve of the KB/S composite.

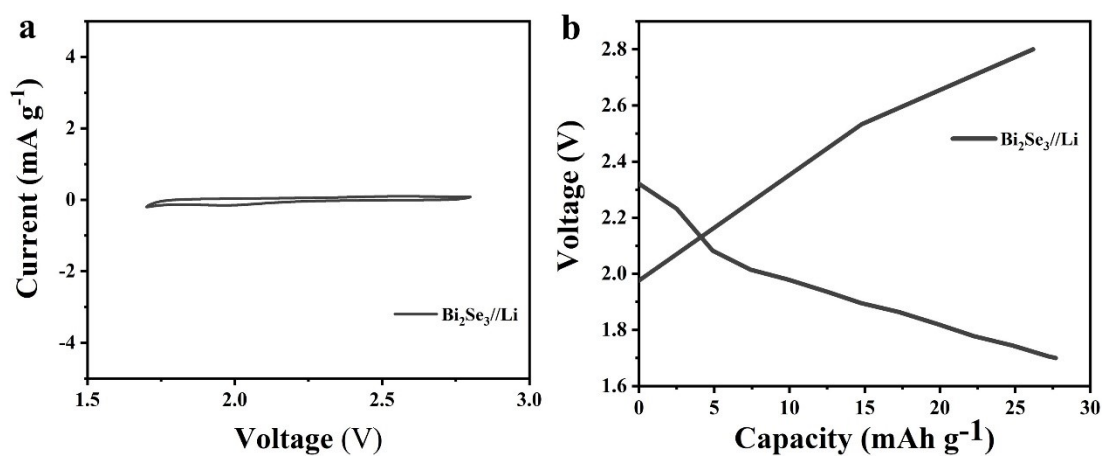


Fig. S15. (a) CV curve at 0.2 mV s^{-1} and (b) GCD curve at 0.2 C of the c-Bi₂Se₃/a-BiO_x.

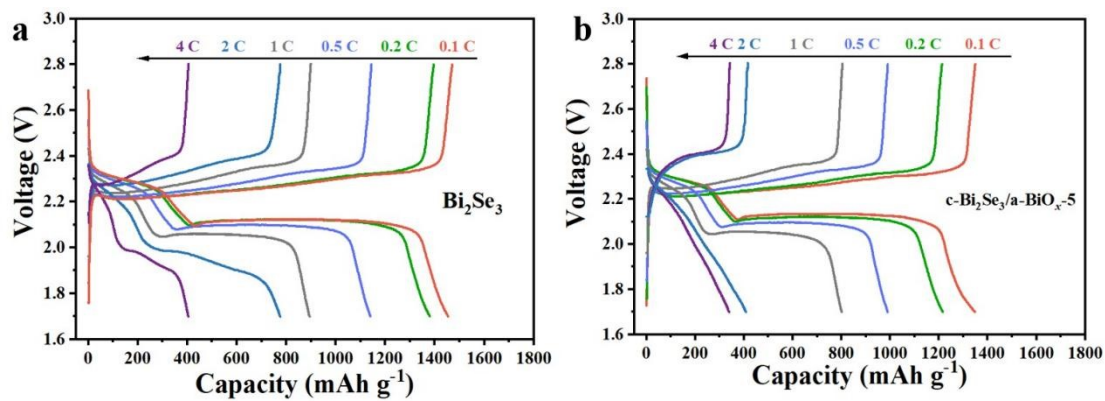


Fig. S16. GCD curves of the (a) Bi₂Se₃ and (b) c-Bi₂Se₃/a-BiO_x-5 batteries at various rates.

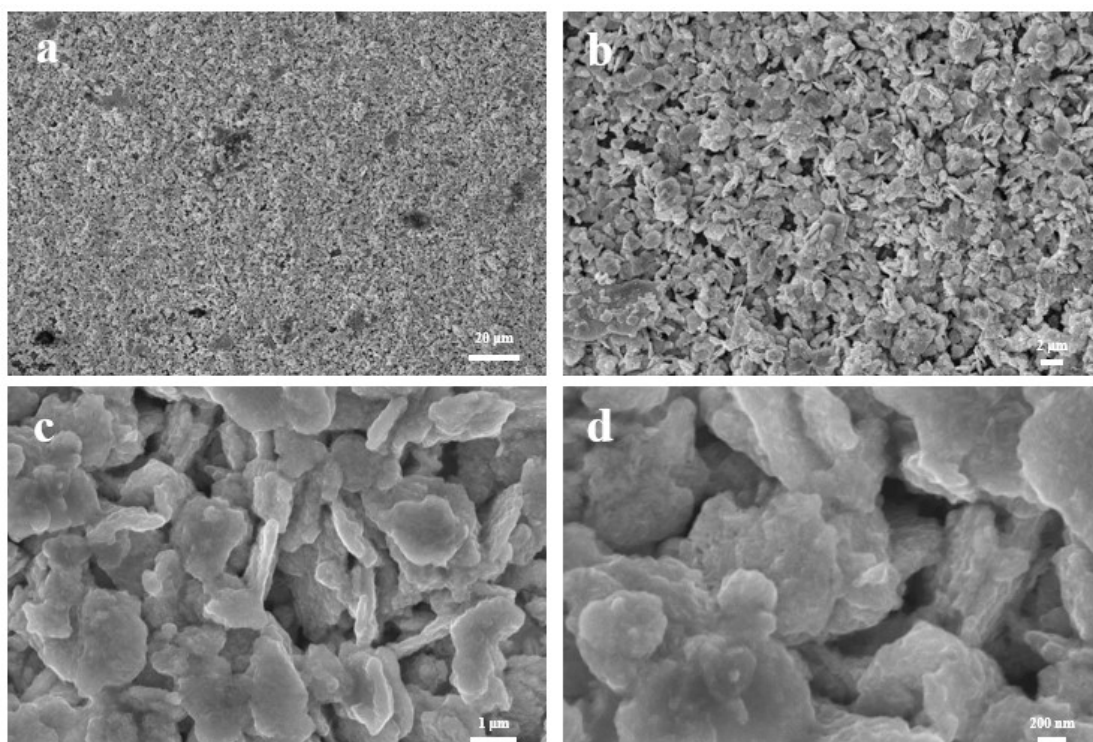


Fig. S17. (a-d) SEM images of the c-Bi₂Se₃/a-BiO_x-PP after 100 cycles.

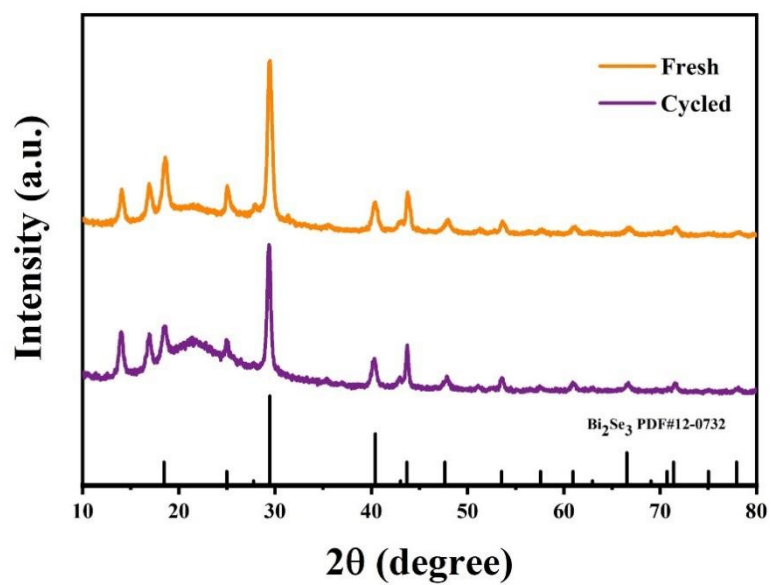


Fig. S18. XRD patterns of the c-Bi₂Se₃/a-BiO_x-PP before and after cycling.

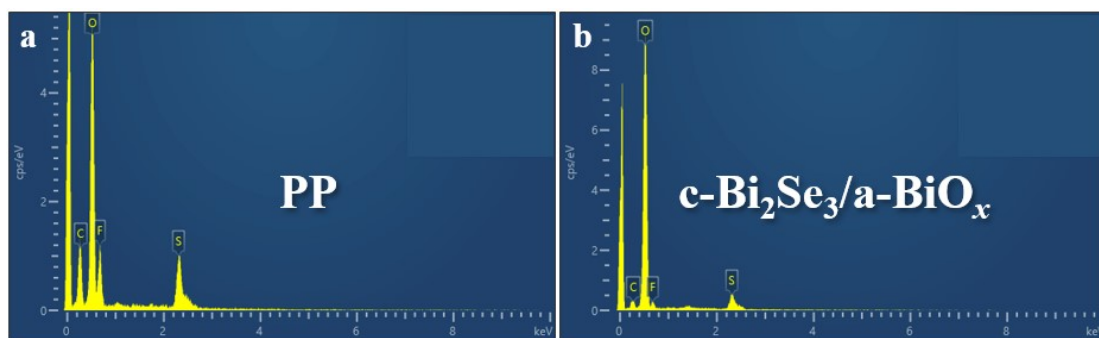


Fig. S19. EDS spectra of the surface of Li anode after 100 cycles with (a) PP and (b) c-Bi₂Se₃/a-BiO_x-PP.

Table S1. Lithium-ion diffusion rates (D_{Li^+} , $\text{cm}^2 \text{s}^{-1}$) of the Li-S batteries with different separators.

Sample	Peak A	Peak B	Peak C
PP	1.81×10^{-8}	1.72×10^{-8}	0.99×10^{-7}
c-Bi ₂ Se ₃ /a-BiO _x	9.04×10^{-8}	2.87×10^{-7}	6.94×10^{-7}
Bi ₂ Se ₃	8.94×10^{-8}	1.34×10^{-7}	4.81×10^{-7}

Table S2. Comparison of the electrochemical performance of this work with recently reported Li-S batteries.

Modified materials	Sulfur loading (mg cm ⁻²)	Long cycle Stability (mAh g ⁻¹)	Capacity Decay Rate (cycle ⁻¹)	Low rate (Initial capacity) mAh g ⁻¹	High rate (Initial capacity) mAh g ⁻¹	Ref.
BNNs@CNFs	1.2	500/1C/800	0.046%	1244 (0.1C)	450 (5C)	8
Co ₉ S ₈	1.5	518/1C/500	0.077%	1276(0.1C)	706 (2C)	10
ZnO-ZnS/rGO	1.0	636/1C/500	0.060%	1201 (0.2C)	749 (3C)	14
PE@CuS/CNTs	1.0	568/2C/1000	0.050%	1292 (0.1C)	868 (2C)	15
Co/Mo ₂ C	1.0	640/1C/600	0.072%	1186 (0.2C)	553 (4C)	48
CoO/NiO@C-NC	1.2-1.4	377/1C/500	0.075%	1343 (0.1C)	738 (3C)	49
NiSA-N-PGC	N.A.	480/0.5C/600	0.069%	1299 (0.2C)	415 (1C)	50
ZIF-67/SA-PAN	1.0	445/1C/500	0.089%	1187 (0.1C)	707 (2C)	51
FeSC@NSC	1.5-2.0	466/1C/700	0.065%	1100 (0.1C)	483 (5C)	52
Gr-MoSe ₂ @GF	~1.3	390/2C/400	0.128%	1118 (0.2C)	553 (3C)	53
MXene/MoS ₂	2.0	443/1C/500	0.056%	1336 (0.1C)	810 (2C)	54
Co@N-CNTs/N-Mo _x C	1.0	610/1C/500	0.090%	1351 (0.1C)	496 (5C)	55
CeO ₂ /KB	1.3	300/2C/1000	0.060%	1242 (0.1C)	627 (3C)	56
d-Ti ₃ C ₂ T _x / Cu-TCPP	1.5	313/0.5C/350	0.186%	917 (0.1C)	504 (1C)	57
MoN-Mo ₂ N	0.4	622/1C/800	0.049%	1350 (0.2C)	698 (4C)	58
CoSe@CNTs	N.A.	50/1C/800	~0.110%	1500 (0.1C)	655 (3C)	59
m-Mn ₂ O ₃ /SP	2.0	500/1C/200	0.250%	1100 (0.2C)	677 (2C)	60
Ni ₃ S ₂ @C	N.A.	490/1C/600	0.080%	1229 (0.2C)	745 (2C)	61
c-MoS ₂	1.5-2.0	590/1C/500	0.082%	1301 (0.25C)	858 (5C)	62
c-Bi ₂ Se ₃ /a-BiO _x	1.0	612/1C/1000	0.041%	1518 (0.1C)	873 (4C)	This work

Table S3. Comparison of the electrochemical performance at high sulfur loading of this work with recently reported Li-S batteries.

Electrocatalysts	Sulfur loading (mg cm ⁻²)	E/S ratio	Rate/Cycles	Discharge capacity (mAh cm ⁻²)	Ref.
Co ₉ S ₈	4.63	7	0.5C/100	2.99	10
CuS	4.5	9.4	1C/100	1.98	15
MoS ₂ /MoO ₃	5.9	-	0.2C/100	2.95	17
ZnSe	5.8	-	0.5C/120	3.6	20
NiS ₂ /WS ₂	4.1	-	0.1C/100	3.2	31
I-Bi ₂ Se ₃	5.2	8	0.5C/300	3.0	44
ZIF-67/SA-PAN	5.45	-	0.1C/100	3.7	51
Co@N-CNTs/ N-Mo _x C	4.4	10	0.1C/100	3.21	55
CeO ₂ /KB	6.6	-	0.2C/100	3.6	56
MXene/ Cu-TCPP	3.45	9.13	0.05C/30	2.7	57
MoN-Mo ₂ N	5.1	5	0.1C/100C	2.8	58
TiO@C-HS	4.0	-	0.1C/50	2.9	65
c-Bi ₂ Se ₃ /a-BiO _x	5.5	7.3	0.2C/100	3.85	This work