

Supporting Information

Oxygen-incorporated crystalline/amorphous heterophase cobalt vanadium selenide nanoplates with dense interfacial sites for robust lithium-sulfur batteries

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Experimental Section

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

In a typical synthesis procedure, 0.234 g of NH_4VO_3 was dissolved into 40 mL deionized water at 70 °C and maintained at this temperature with incessant stirring. After forming a canary yellow solution, 0.095 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 1.2 g of hexamethylenetetramine (HMTA) were added into the solution successively with incessant stirring for 4 h at 80 °C. After cooling to room temperature, the orange precipitates were collected by centrifuging and then rinsed with distilled water and absolute ethanol several times. The samples were dried at 70 °C for 12 h in the air.

Synthesis of DC/A O-CoVSe NPs and SC/A O-CoVSe NPs

In a typical preparation, 0.095 g of Se, 0.228 g of NaBH_4 , 0.08 g of NaOH and 0.02 g of $\text{Co}_2\text{V}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ NPs were added in 30 mL of deionized water by magnetic agitation for 30 min. Afterward, the solution was transferred to a 40 mL autoclave. Subsequently, the autoclave was maintained at 120 °C for 6 h. After cooling to room temperature, the material was washed repeatedly with deionized water and ethanol, then dried at 70 °C for 12 h. SC/A O-CoVSe NPs went through the same process by changing the selenization temperature to 160 °C.

Synthesis of modified separators

The DC/A O-CoVSe NPs and SC/A O-CoVSe NPs modified separators (DC/A O-CoVSe NPs/PP and SC/A O-CoVSe NPs/PP) were prepared through a simple vacuum filtration method. In short, DC/A O-CoVSe NPs (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 sample was deposited on the Celgard-2400 polypropylene (PP) separator followed by drying at 60 °C overnight under a vacuum. Finally, the functionalized separator was cut into the 19 mm diameter discs for further use.

Synthesis of the KB@S and CNT/S cathodes

To obtain Ketjen black (KB)/S composite, sulfur powder (S_8) and KB) were ground together in an 8:2 mass ratio and heated at 155 °C for 12 h using melt diffusion. Afterward, 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 coated on carbon coated aluminum foil drying under vacuum at 60 °C overnight prior to use. The areal sulfur loading with a diameter of 12 mm was around 1.0 mg cm⁻².

Commercial carbon nanotube (CNT) and sublimed sulfur with a 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 °C for 12 h to obtain a CNT/S composite. CNT/S cathode slurry was prepared through mixing 80% CNT/S, 10% KB, and 10% PVDF in NMP. The obtained slurry was coated onto the surface of carbon paper and dried at 60 °C for 12 h.

Lithium polysulfide (Li₂S₆) solution and visualized adsorption test

Li₂S₆ solution was prepared by dissolving S₈ and Li₂S with a molar ratio of 5:1 in 1:1 volume ratio of DOL/DME solvents and stirring at 70 °C for 24 h. The resulting 0.1 M Li₂S₆ solution was utilized for adsorption test. Certain amount of samples were added into 3 mL Li₂S₆ solution (5 mM) to observe the color change of the solution.

Symmetrical cells assembling and testing

0.25 M Li₂S₆ electrolyte was prepared by dissolving S₈ and Li₂S with a molar ratio of 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 °C for 24 h. Mixing active materials (DC/A O-CoVSe NPs and SC/A O-CoVSe NPs) and PVDF were uniformly dispersed in NMP and then coated onto aluminum foil to both serve as anode and cathode. 0.25 M Li₂S₆ electrolyte was electrolyte and commercial Celgard-2400 polypropylene (PP) was used as the separator. The as-prepared symmetric cells were measured by cyclic voltammetry (CV) at scan rate of 5 mV s⁻¹ and voltage range from -1.0 to 1.0 V.

Li₂S nucleation measurements

First, 0.5 M Li₂S₈ electrolyte was prepared by mixing Li₂S and sulfur powders at a molar ratio of 1:7 and dissolved into DME and DOL (1:1 in volume) solution with 1.0 M LiTFSI by stirring for 24 h. DC/A O-CoVSe NPs or SC/A O-CoVSe NPs were uniformly dispersed in ethanol and then dropped onto carbon paper to obtain the cathode. For the Li₂S nucleation, CR 2032 cells were assembled with the commercial PP as separator, and the lithium foil as anode. 20 μL Li₂S₈ 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.

Materials characterization

The crystal structure of products was examined by X-ray diffraction (XRD) under Cu Ka radiation source (D/max-Uitima III Rigaku). The surface chemical states of products were detected through X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, ESCALAB 250). 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). Simultaneous thermal analyzer (TG-DSC, NETZSCH, STA449-F5) was performed on thermogravimetric analysis (TGA).

Electrochemical Characterization

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.% LiNO_3 was used as the electrolyte for lithium-sulfur (Li-S) batteries. The rate and cyclic performances of batteries were measured with a galvanostatic mode at a voltage window of 1.7–2.8 V using Neware battery testing system (Neware, China). Cyclic voltammetry of Li-S batteries was performed on a CHI660 electrochemical station. Electrochemical impedance spectroscopy of batteries was also measured with CHI660 electrochemical station, with the frequency range of 10^{-2} - 10^5 Hz.

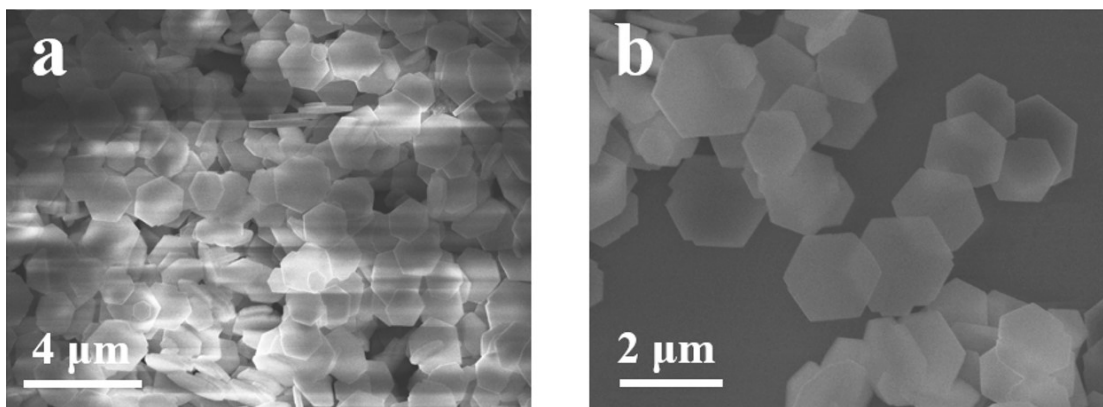


Figure S1. (a, b) SEM images of the $\text{Co}_2\text{V}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ NPs.

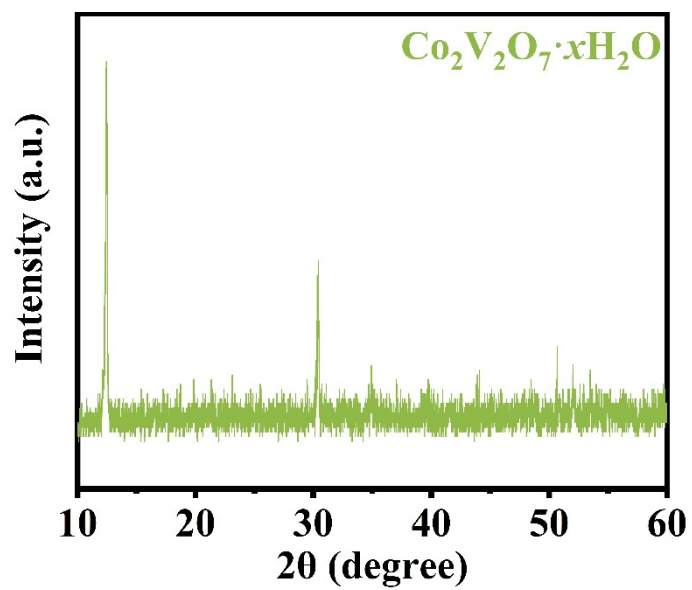


Figure S2. XRD pattern of the $\text{Co}_2\text{V}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ NPs.

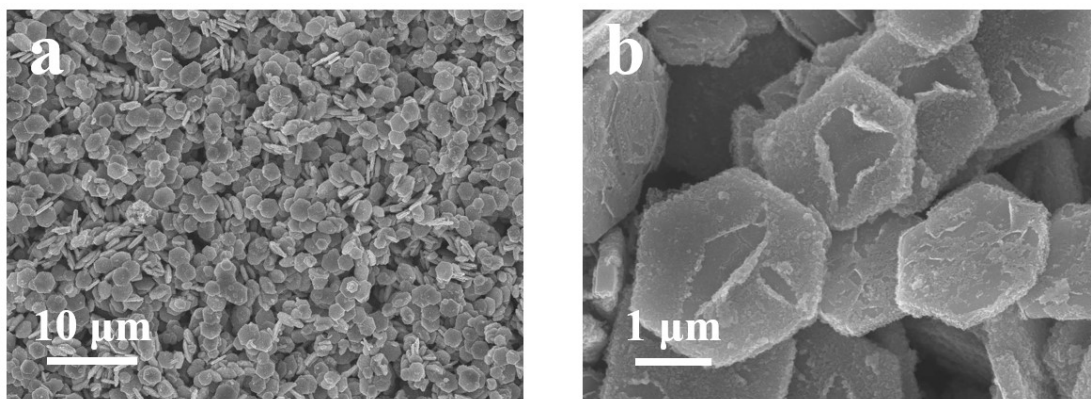


Figure S3. (a, b) SEM images of the SC/A O-CoVSe NPs.

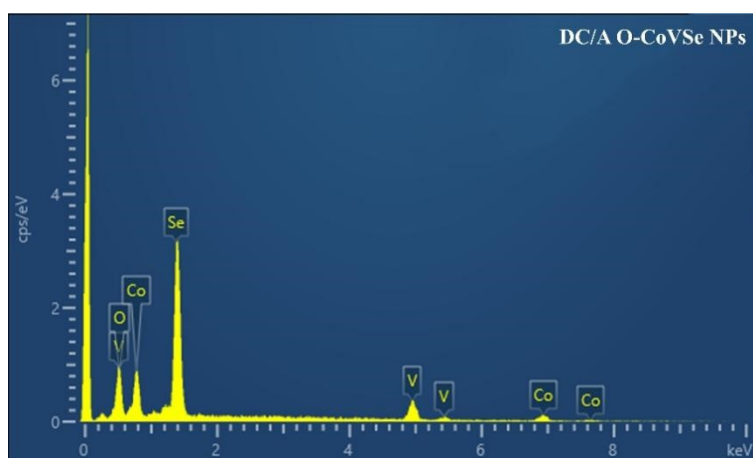


Figure S4. EDS spectrum of the DC/A O-CoVSe NPs.

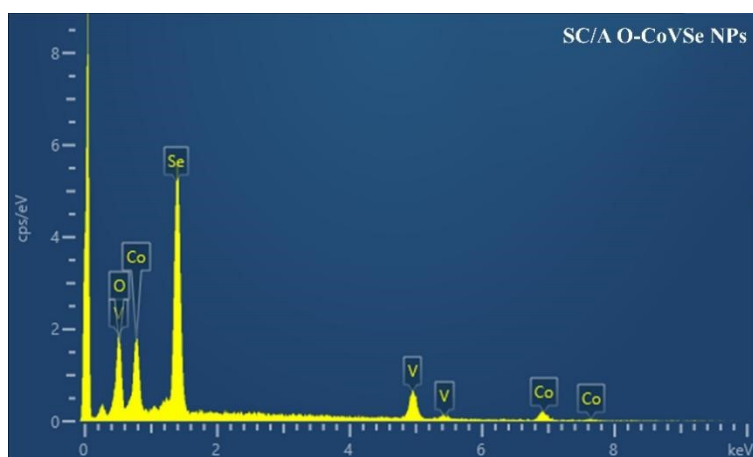


Figure S5. EDS spectrum of the SC/A O-CoVSe NPs.

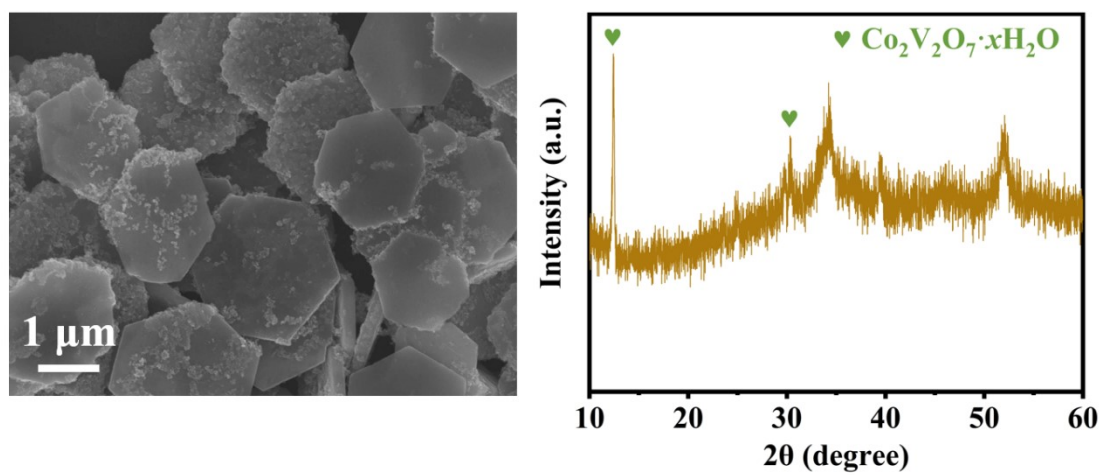


Figure S6. SEM image and XRD pattern of the product obtained at 100 °C.

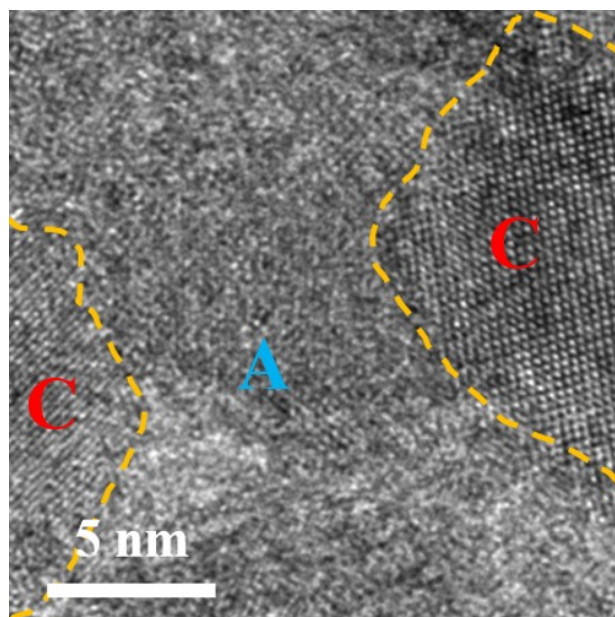


Figure S7. HRTEM image of the DC/A O-CoVSe NPs.

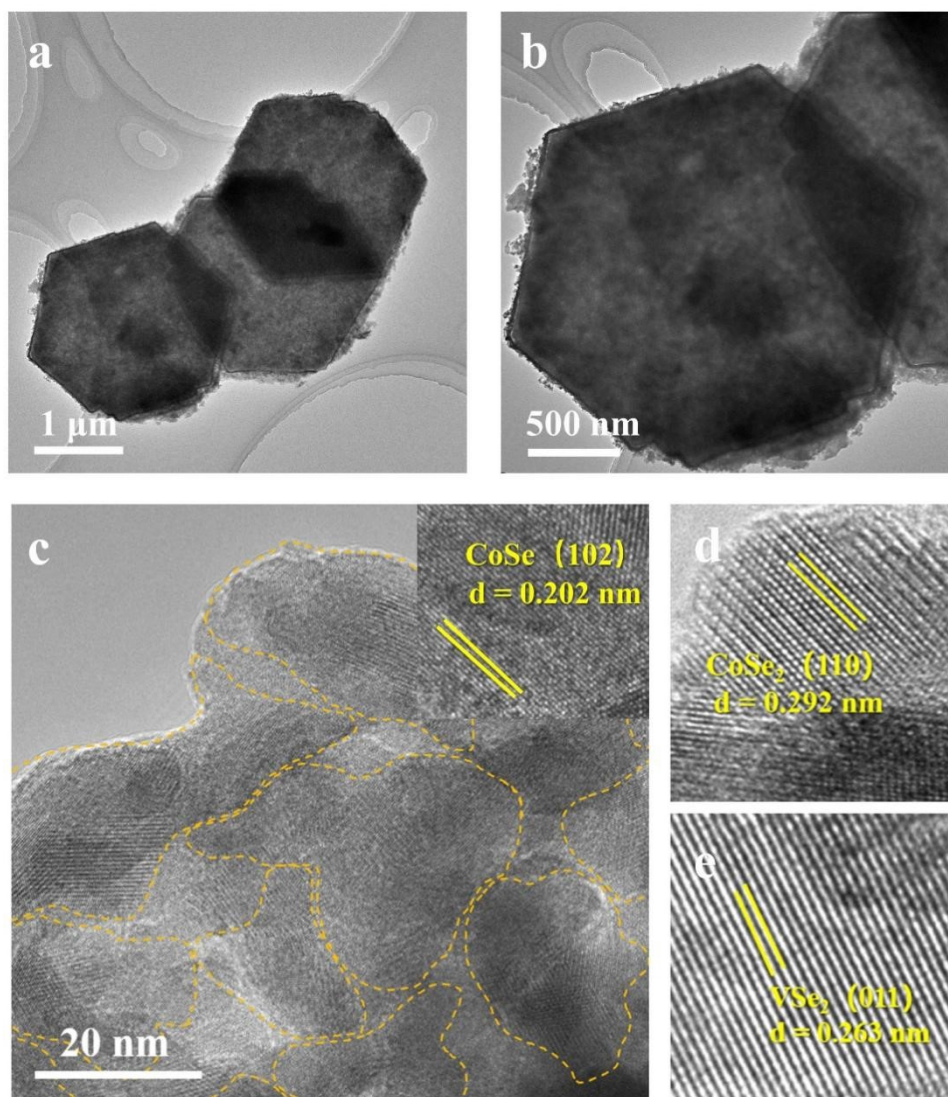


Figure S8. TEM and HRTEM images of the SC/A O-CoVSe NPs.

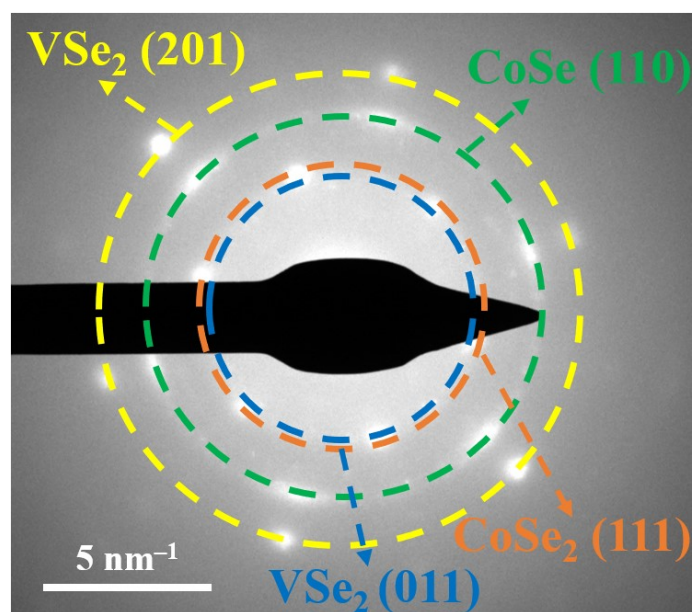


Figure S9. SAED pattern of the SC/A O-CoVSe NPs.

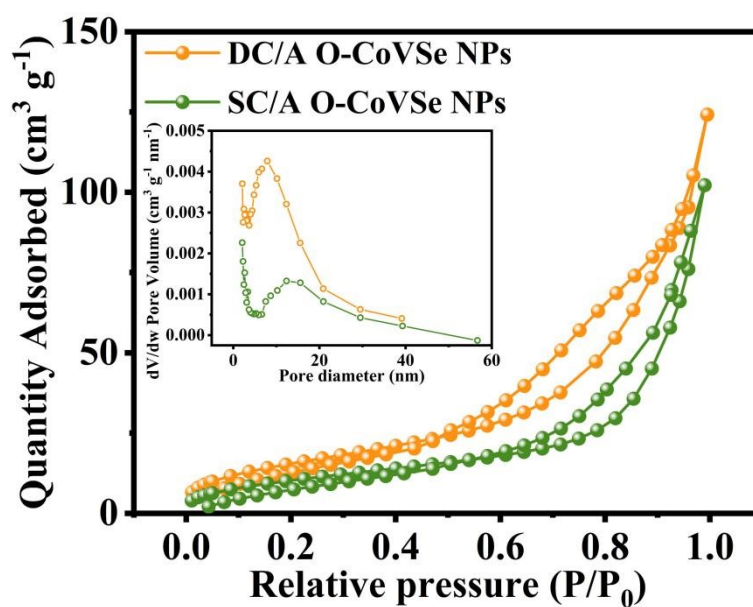


Figure S10. N_2 adsorption-desorption isotherm of the DC/A O-CoVSe NPs and SC/A O-CoVSe NPs (insert shows the size distribution curves).

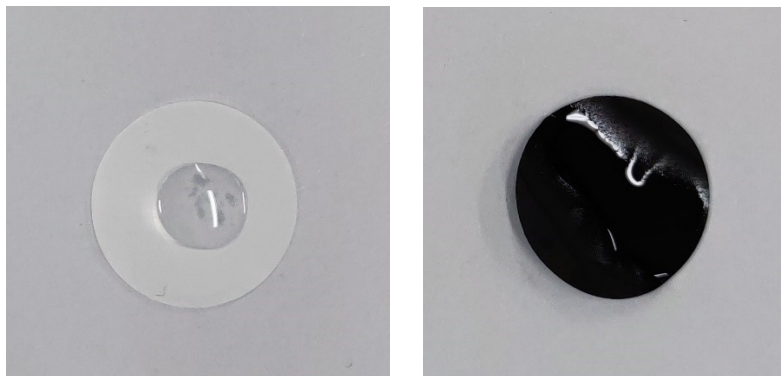


Figure S11. The electrolyte wettability test for the PP (left) and DC/A O-CoVSe NPs/PP (right) separators.

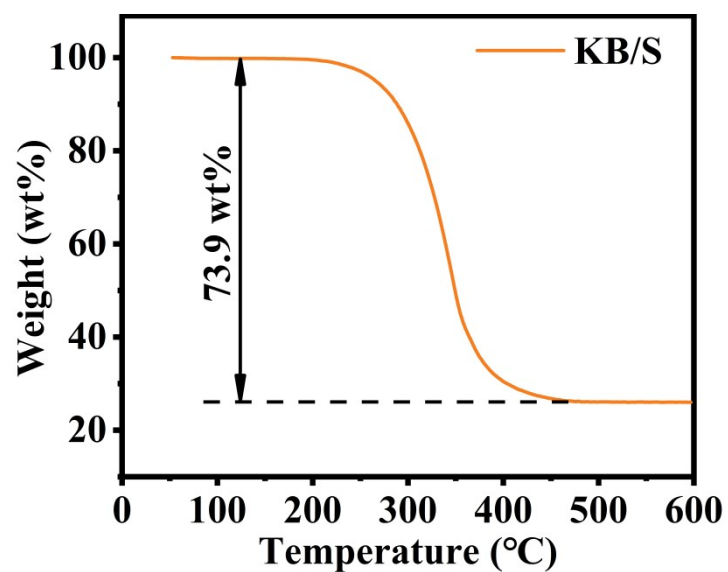


Figure S12. TGA curve of the KB/S composite under nitrogen atmosphere.

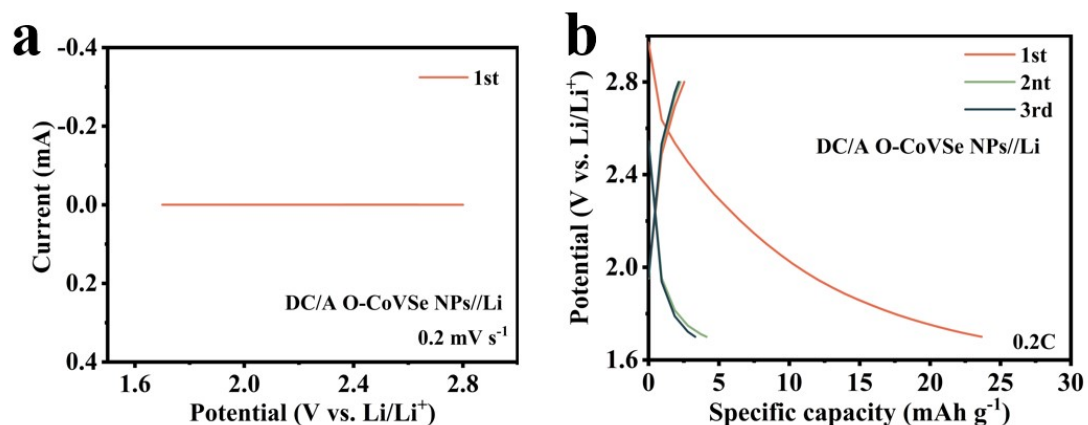


Figure S13. (a) CV curve and (b) GCD profiles of the DC/A O-CoVSe NPs//Li cell (without sulfur loading) in the voltage range of 1.7-2.8 V.

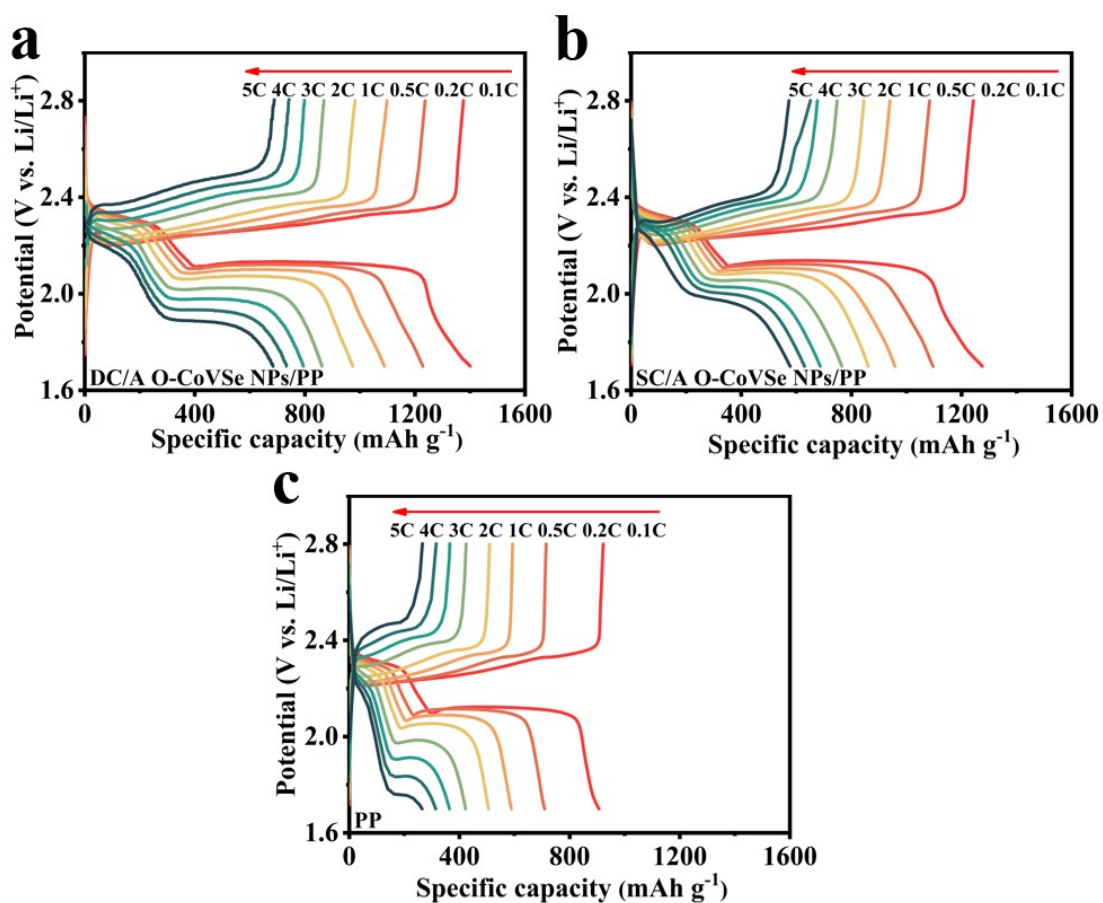


Figure S14. GCD profiles of the Li-S batteries with (a) DC/A O-CoVSe NPs/PP, (b) SC/A O-CoVSe NPs/PP and (c) PP separators at different current densities.

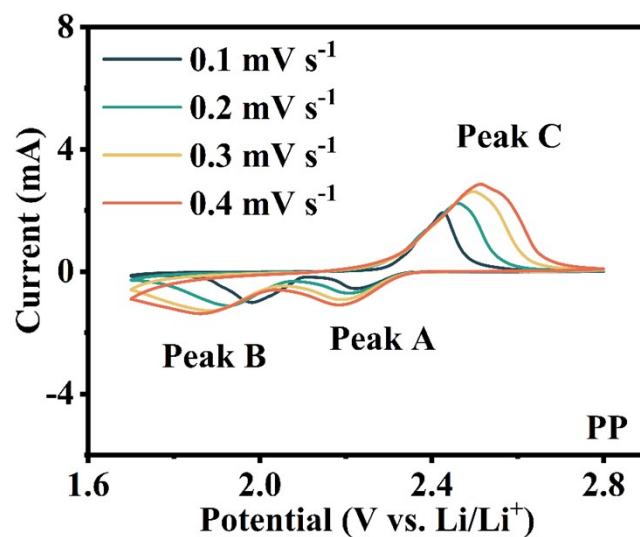


Figure S15. CV curves of Li-S battery with PP separator at various scan rates from 0.1 to 0.4 mV s^{-1} .

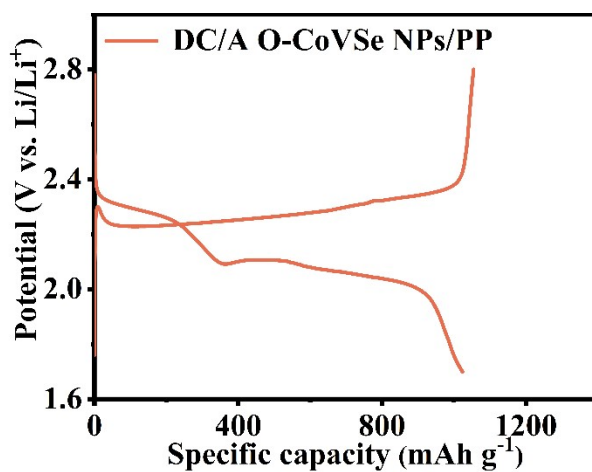


Figure S16. GCD profiles of the high-sulfur-loading battery at 0.2C.

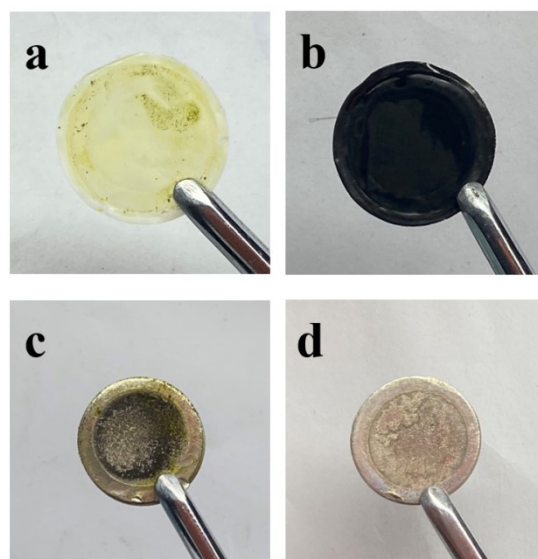


Figure S17. Post-mortem analysis of the Li-S battery after 100 cycles. Digital photographs of the (a) PP, (b) DC/A O-CoVSe NPs/PP and (c, d) corresponding lithium metal anodes.

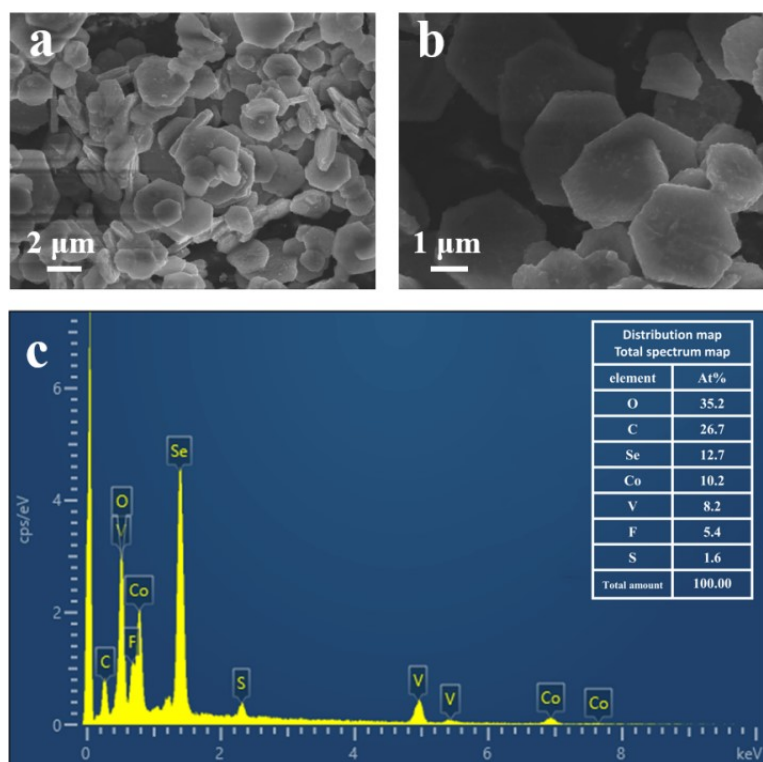


Figure S18. (a, b) SEM images and (c) EDS spectrum of the DC/A O-CoVSe NPs/PP after cycling.

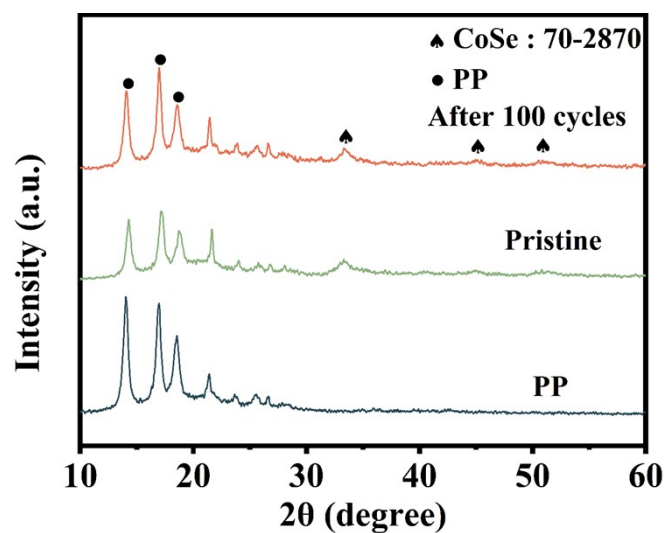


Figure S19. XRD patterns of the PP, DC/A O-CoVSe/PP separators before and after cycling.

Table S1. Elemental composition of samples according to the ICP and element analysis results:

Sample	Co/ atomic%	V/ atomic%	Se/ atomic%
SC/A O-CoVSe NPs	34.59	27.03	38.38
DC/A O-CoVSe NPs	36.58	23.39	40.03

Table S2. Summary of lithium-ion diffusion rates (D_{Li^+} , $\text{cm}^2 \text{s}^{-1}$) of different separators:

Sample	Peak A	Peak B	Peak C
PP	3.66×10^{-9}	2.16×10^{-9}	1.25×10^{-8}
SC/A O-CoVSe NPs/PP	1.79×10^{-8}	1.73×10^{-8}	1.27×10^{-7}
DC/A O-CoVSe NPs/PP	6.19×10^{-8}	9.15×10^{-8}	3.67×10^{-7}

Table S3. Comparison of the electrochemical properties the modified materials for 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.
LC-Ni _x Fe _y @OCNT/NG	2.4	~490/3C/600	0.08%	1379(0.1C)	855.7(3C)	36
KB/Mo ₂ C	1.2	439/1C/600	0.076%	1299(0.1C)	437(3.5C)	54
3D P-MoS ₂ -G	1	629.4/0.5C/300	0.14%	1099.7(0.1C)	667.5(4C)	55
STO-W/S	1.2	541/1C/500	0.067%	1242(0.1C)	492(2C)	56
Zn ₂ W ₂ @2CD	1.5	720/1C/500	0.064%	1355(0.1C)	552(5C)	57
Ti ₃ C ₂ T _x	0.9	535/1C/500	0.070%	1282(1C)	677(2C)	58
H-CMP	1.2	653.1/1C/500	0.0668%	1216(0.1C)	770.5(3C)	59
Bi ₂ Te _{2.7} Se _{0.3}	4	560/2C/300	0.10%	1284(0.1C)	756(2C)	60
CoF ₂	2	542.4/1C/300	0.076%	1096(0.1C)	737.1(2C)	61
Co/Mo ₂ C	1	640/1C/600	0.072%	1186(0.2C)	553(4C)	62
DC/A O-CoVSe NPs	1	672.4/1C/500	0.066%	1400.1(0.1C)	683.8(5C)	This work

Table S4. Comparison of the areal capacities and sulfur loading with other previously reported Li-S batteries in literatures.

Modified materials	Sulfur loading (mg cm ⁻²)	Areal Capacity (mAh cm ⁻²)	E/S ratio (μL mg ⁻¹)	Ref.
MoO ₂ -Mo ₂ N	4	3.19	6-7	12
Ni-Co-P@C	4.5	~3.4	5	14
Mo ₂ C/CHS	5	4.52	7	17
ZnSe-CoSe ₂ @NC	6.08	~2.7	4.1	19
7TiN:3TiO ₂ -G	4.3	2.12	Not mentioned	22
CoNiO ₂ /Co ₄ N	3.1	2.5	10	24
MoS ₂ -MoO ₃ /CS	5.9	3.78	Not mentioned	25
Co ₇ Mo ₃ B	4.53	4.96	5	33
LC-Ni _x Fe _y @OCNT/NG	5.37	4.1	4.9	36
3D P-MoS ₂ -G	3.7	4.3	Not mentioned	55
Ti ₃ C ₂ T _x	2.42	2.4	Not mentioned	58
CoF ₂	4	2.79	8	61
DC/A O-CoVSe NPs	5.6	5.75	8	This work