batteries

Synergistic Effect of Zn–Co Bimetallic Selenide Composites for Lithium–Sulfur Battery

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1. Material characterization

1.1. Scanning electron microscope (SEM)

The field emission scanning electron microscope (JSM-7001F) was selected for all sample morphology analysis tests to observe the microscopic morphology, crystal structure and particle size determination of prepared samples. An energy spectrometer was equipped for qualitative and quantitative testing of the chemical composition of various material micro-regions.

1.2. Transmission Electron Microscopy (TEM)

The transmission microscope, JEOL JEM 2100F, was selected for further testing of the morphology and lattice striations of the samples, including the observation of the morphology and lattice striations of the materials produced.

1.3. X-ray diffraction spectroscopy（XRD）

The X-ray powder diffractometer of model PW3040/60 produced by PANalytic was selected for crystal phase analysis of the prepared sample, and the scanning rate was 10 º min^{-1} in 2θ range of 5~80º wide-angle scanning, and the PDF-2 international powder diffraction database was equipped. Determine the crystal structure of the substance, and perform qualitative and semi-quantitative analysis of the phase and grain size analysis.

1.4. Specific surface area of nitrogen adsorption/desorption（BET）

The experimental test of N_2 adsorption and desorption of the prepared matrix material was carried out by using the ASAP 2460 BET specific surface instrument, and the specific surface area and pore volume of the matrix material were calculated according to BET, and the pore size distribution analysis was obtained according to BJH calculation.

1.5. X-ray electron spectroscopy（XPS）

The chemical composition and valence state of transition metal selenide composites were determined using Thermo Scientific K-Alpha X-ray photoelectron spectroscopy (XPS) from the American company. The test conditions are: the excitation source is Al $K\alpha$ ray, hv =1486.6 eV.

1.6. UV/VIS absorption spectroscopy analysis（UV-vis）

UV/VIS absorption spectroscopy is produced by transitions in valence electrons. The selective absorption of light by substances is used to determine and analyze the composition and structure of substances. In this paper, Shimadzu ultraviolet spectrophotometer UV-3600 was used to determine and analyze Li_2S_6 solution.

1.7. Thermogravimetric Analysis（TG）

NETZSCH STA 449 F3/F5 was used for thermogravimetric analysis of cathode composites to determine the mass percentage of sulfur in cathode composites. The heating rate is 10 °C min^{-1}, the temperature range is 30~600 °C, and nitrogen is used as a protective gas.

1.8. Polysulfide adsorption test

The sulfur powder and lithium sulfide (molar ratio was 5:1) were dissolved in DOL/DME (v/v=1:1) solution, stirred at 60 °C for 48 h, and a Li_2S_6 solution with a concentration of 0.05M was obtained for later use. 20 mg of the active

substance was added to a dilute (0.005 M) Li_2S_6 solution in 5 mL and leave for 12 h， observing the colour change of the solution and record with a mobile phone camera. The supernatant was subjected to ultraviolet-visible absorption spectroscopy.

2. Electrochemical Measurements

2.1. Preparation of positive electrode and assembly of Battery

The laboratory prepared materials, Super P, and polyvinylidene fluoride (PVDF) were mixed and ground in a mass ratio of 8:1:1 for 30 minutes, Then, an appropriate amount of N-methyl pyrrolidone (NMP) was added and stirred to form a uniform slurry, which was then coated on aluminum foil. The coated electrode plate was placed in a vacuum drying oven at 60 ℃, vacuum dried for 12 hours, and then taken out for rolling. It was then punched into a circular plate with a diameter of 12 mm, and the positive electrode plate is prepared for backup. The mass of active substance on the positive electrode was about 3.5 mg cm^{-2}.

The positive plate, negative lithium (0.1 mm thick), diaphragm Celgard 2340, and electrolyte (1.0 mol/L LiTFSI + DME (volume ratio was 1:1) + 0.1 mol/L $LiNO_3$-DOL), were assembled into a CR2032 button type battery in the glove box.

2.2. Constant current charge-discharge test and rate performance test

The Xinwei CT-4008-5V10mA-164 multi-channel battery tester was used for constant current charge and discharge performance testing. Electrochemical cycling tests were carried out at current densities of 0.2 C and 1 C, with voltages ranging from 1.6 V to 2.8 V. Electrodes were tested at current densities of 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C and 5 C for multiplier performance. All cells were first activated at a current density of 0.05 C and then tested.

2.3. Cyclic voltammetry (CV) test

Cyclic voltammetry (CV) tests were carried out on the assembled cells using the Shanghai Chenhua CHI650D electrochemical workstation. The instrument was a Shanghai Chenhua CHI650D electrochemical workstation with a scanning speed of 0.1 mV s^{-1} and a voltage test window of 1.4 V-3.0 V.

2.4. Electrochemical impedance test (EIS)

The AC impedance data for the batteries in the paper was tested using an electrochemical workstation of the type Shanghai Chenhua CHI650D. The AC impedance test parameters were: AC amplitude of 5 mV and frequency range of 10^{-2} to 10^5 Hz. The EIS data were plotted and fitted to the equivalent circuit using Z_{view} software to obtain the resistance values.

2.5. Symmetric cell assembly

The sulphur-free base material, Super P and PVDF are weighed and ground in a ratio of 8:1:1 by mass. Then, an appropriate amount of N-methyl pyrrolidone (NMP) is added and stirred to form a uniform slurry, which is then coated on aluminum foil. The coated electrode plate was placed in a vacuum drying oven at 60 ℃, vacuum dried for 12 hours, and then taken out for rolling. It was then punched into a circular plate with a diameter of 12 mm, and the positive electrode plate was prepared for backup. Two positive electrodes of the same mass were selected to form a symmetrical cell, using Celgard 2340 as the diaphragm, a CR2032 button cell was assembled in the glove box, with a Li_2S_6 solution added to the side of each electrode near the diaphragm, where the solution contains 0.05 M Li_2S_6 solution and 1.0 mol/L-1LiTFSI-DOL/DME-0.1 M $LiNO_3$ (1:1 volume ratio). Electrochemistry For the tests, the electrochemical workstation of Shanghai Chenhua CHI650D was used to record the electrochemistry in a voltage window of -1.0~1.0 V at a scan rate of 5 mV The polarization curves were recorded at a scan rate of 5 mV s^{-1} within a voltage window of -1.0~1.0 V.

3. Figure in Supplementary Material

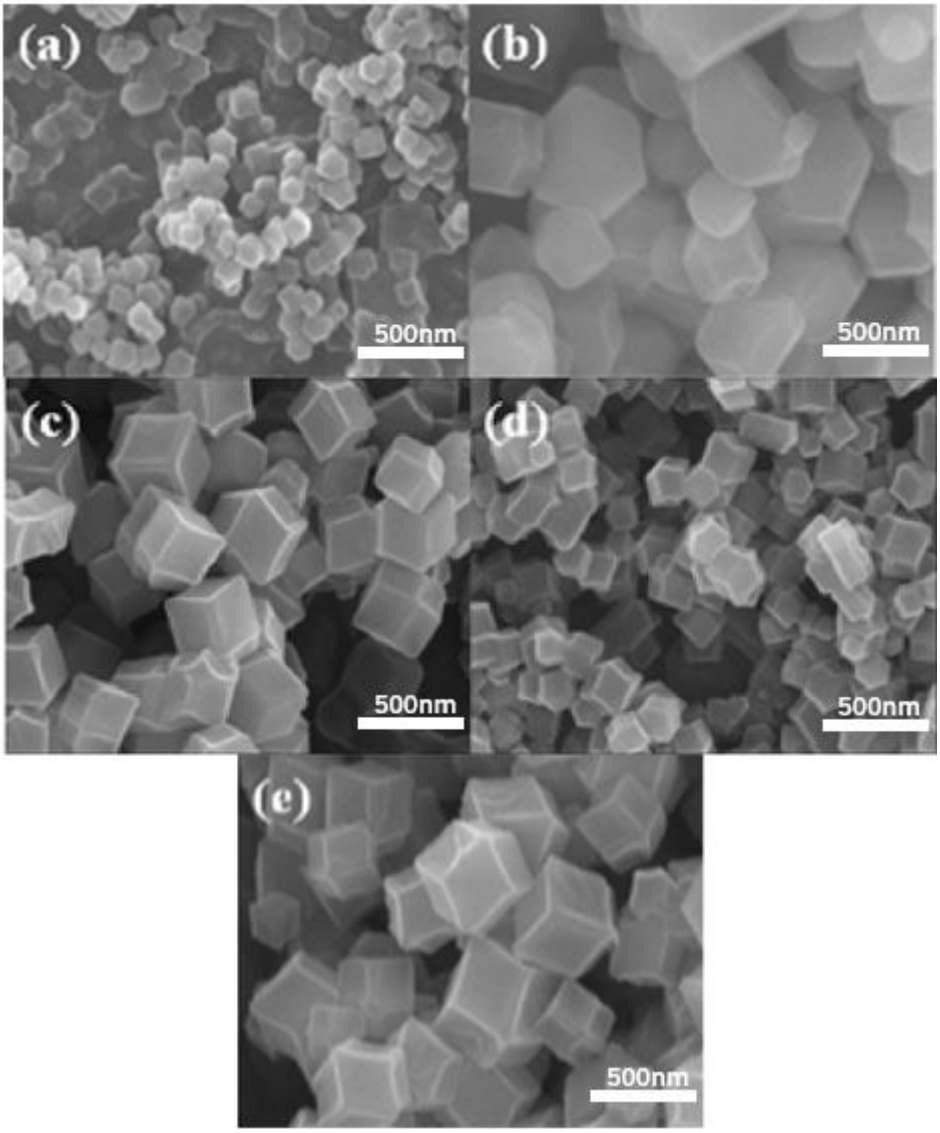
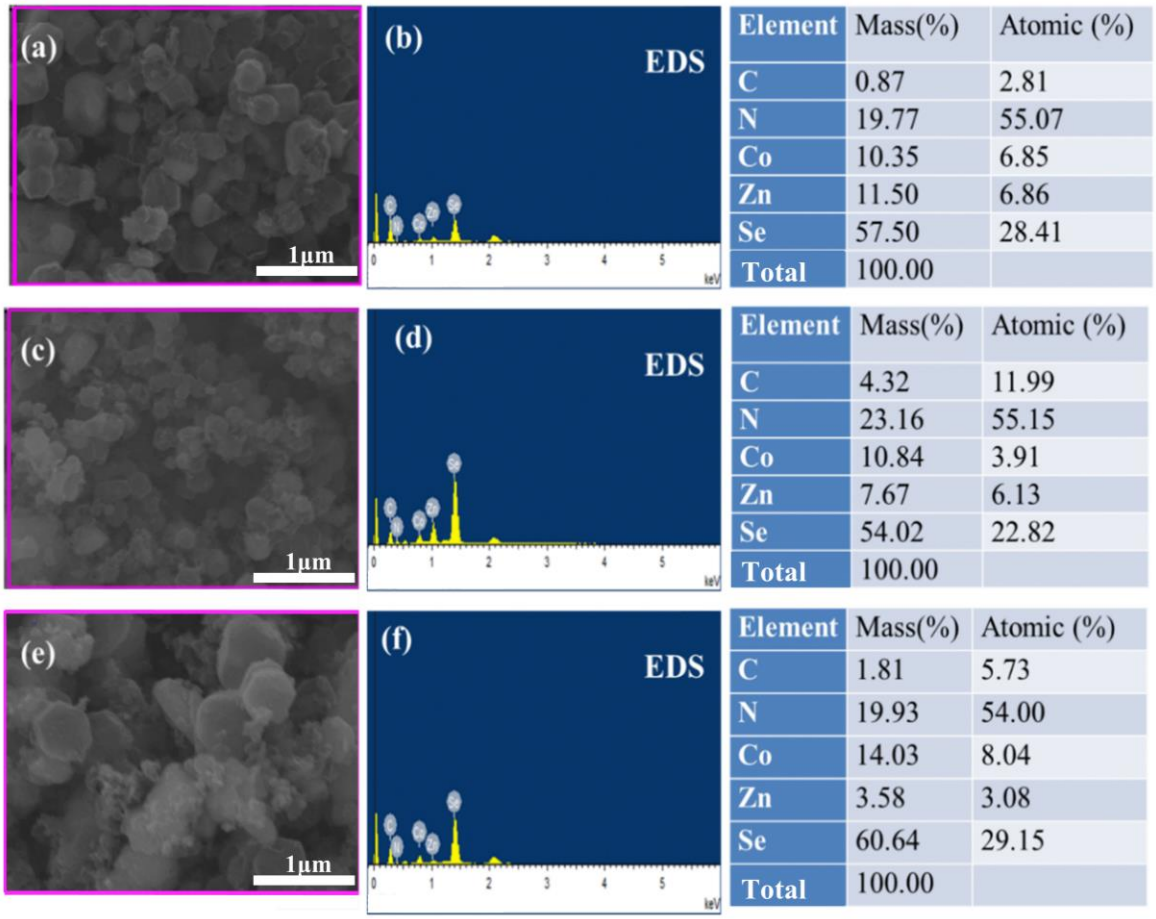


Figure S1. SEM images of (a) ZIF-8, (b) ZIF-67, (c-e) ZIF-8/67 with different Zn to Co ratios are 1:1, 2:1,and 1:2, respectively.



Element	Mass(%)	Atomic (%)
C	0.87	2.81
N	19.77	55.07
Co	10.35	6.85
Zn	11.50	6.86
Se	57.50	28.41
Total	100.00	

Element	Mass(%)	Atomic (%)
C	4.32	11.99
N	23.16	55.15
Co	10.84	3.91
Zn	7.67	6.13
Se	54.02	22.82
Total	100.00	

Element	Mass(%)	Atomic (%)
C	1.81	5.73
N	19.93	54.00
Co	14.03	8.04
Zn	3.58	3.08
Se	60.64	29.15
Total	100.00	

Figure S2. SEM and EDS of (a-b) Zn: Co=1:1, ZnSe/$CoSe_2$ sample, (c-d) Zn: Co=2:1, ZnSe/$CoSe_2$ sample, (e-f) Zn: Co=1:2, ZnSe/$CoSe_2$ sample.

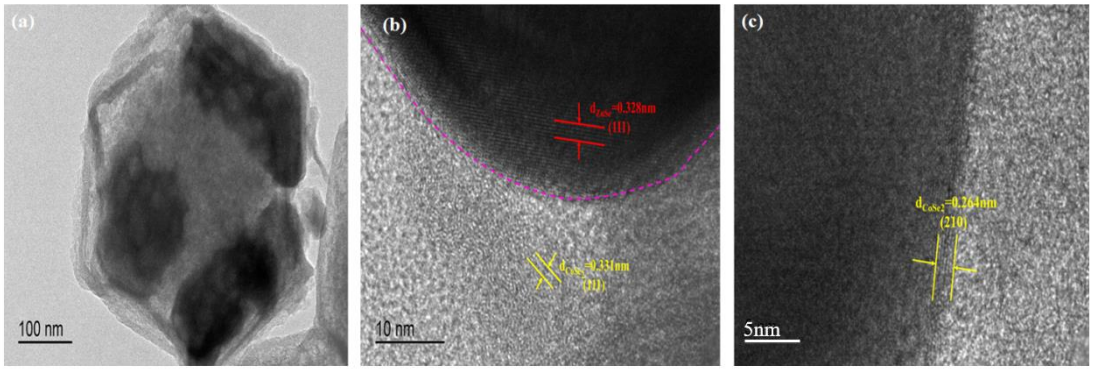


Figure S3. TEM images of (a-c) ZnSe/$CoSe_2$ with Zn: Co=1:1 at low and high magnification.

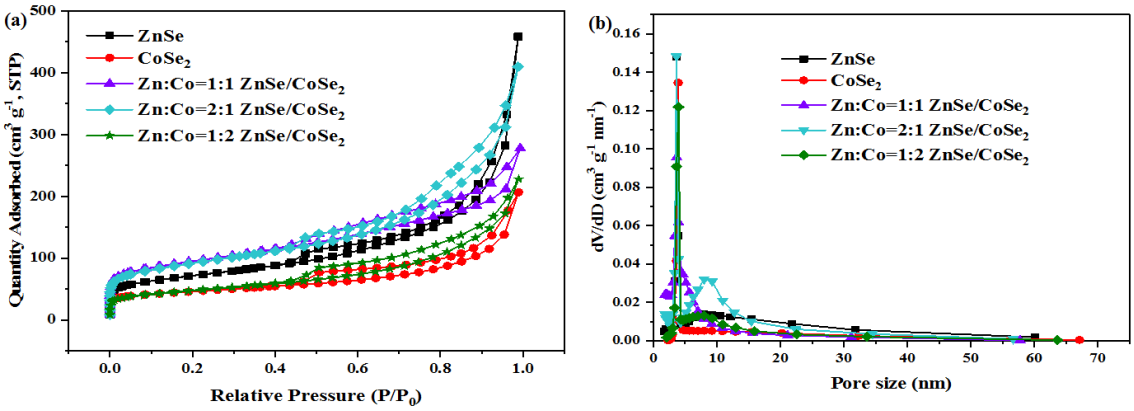


Figure S4. ZnSe, $CoSe_2$, and ZnSe/$CoSe_2$ composites with different Zn/Co ratios (a) N_2 absorption and desorption curves; (b) pore size distribution.

Table S1. BET results of ZnSe, $CoSe_2$, and ZnSe/$CoSe_2$ composites with different Zn/Co ratios.

Sample	BET Surface Area ($m^2 g^{-1}$)	Pore Volume ($cm^3 g^{-1}$)	t-Plot micropore volume ($cm^3 g^{-1}$)
ZnSe	245.835	0.710	0.027
$CoSe_2$	151.788	0.320	0.028
Zn:Co=1:1 ZnSe/$CoSe_2$	317.991	0.430	0.045
Zn:Co=2:1 ZnSe/$CoSe_2$	313.595	0.634	0.035
Zn:Co=1:2 ZnSe/$CoSe_2$	162.089	0.356	0.014

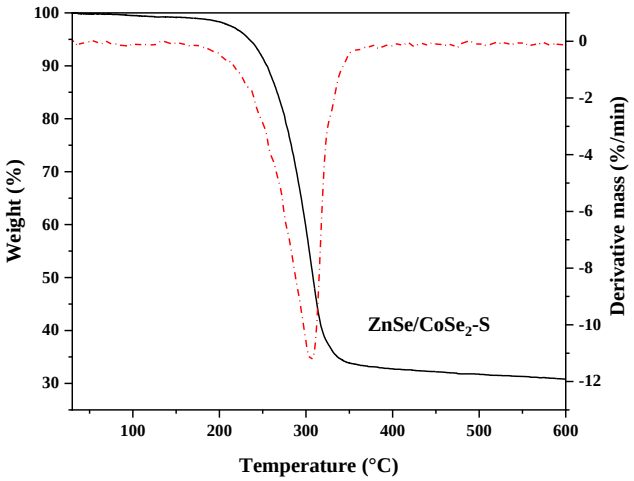


Figure S5. Thermogravimetric curves of Zn: Co=1:1, ZnSe/$CoSe_2$-S composites.

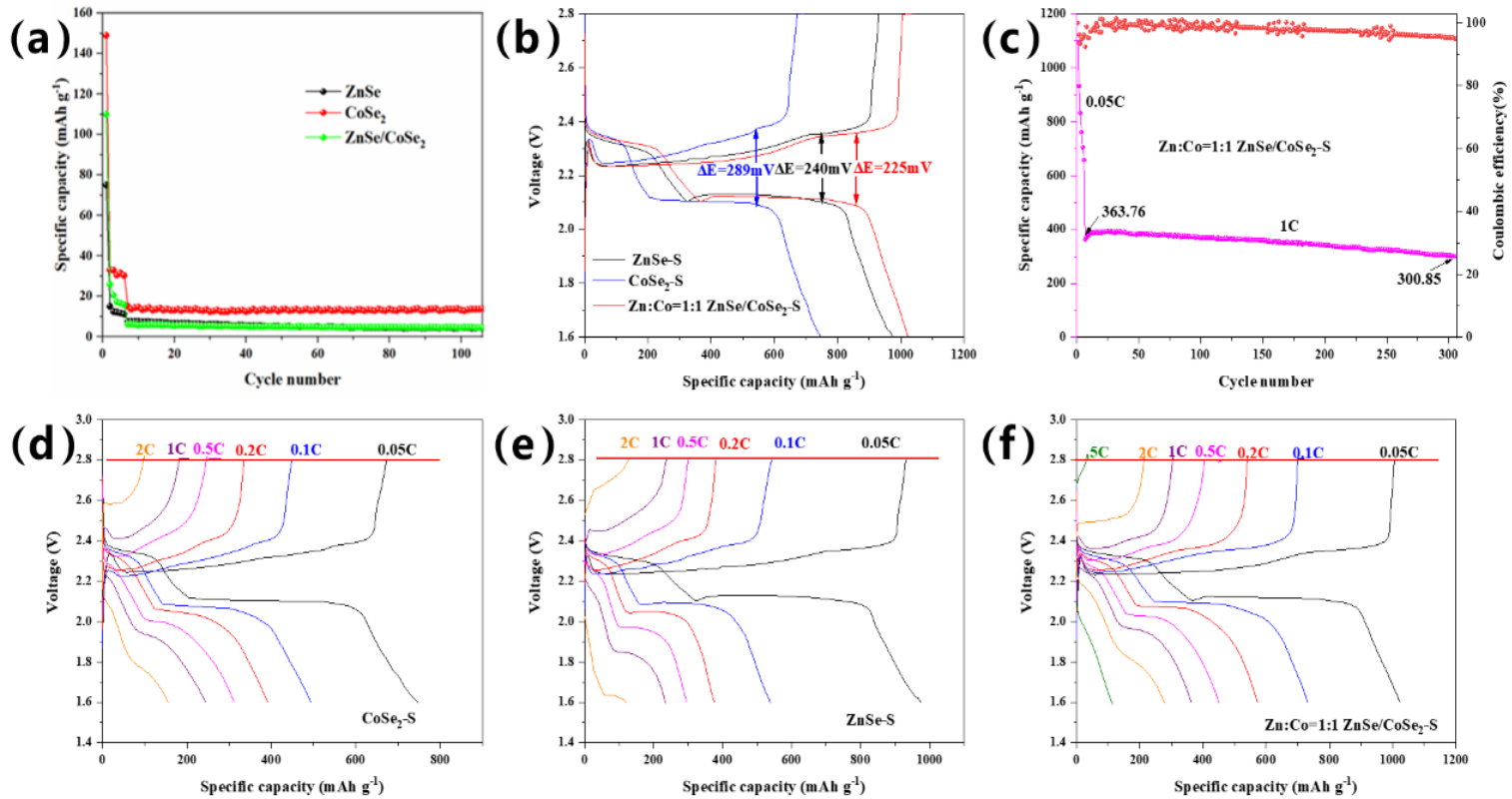


Figure S6. (a) Diagram of cyclic properties of ZnSe、$CoSe_2$ and ZnSe/$CoSe_2$ materials at 0.2C; (b) Charge-discharge curve platform of ZnSe-S, $CoSe_2$-S, and Zn: Co=1:1 for ZnSe/$CoSe_2$-S cathode material composites at 0.05 C; (c) Cyclic properties of Zn: Co=1:1 for ZnSe/ $CoSe_2$-S cathode material at 1 C; Charge and discharge curves of (d) ZnSe-S、(e) $CoSe_2$-S and (f) Zn: Co=1:1 for ZnSe/$CoSe_2$-S cathode material composites at different current densities.

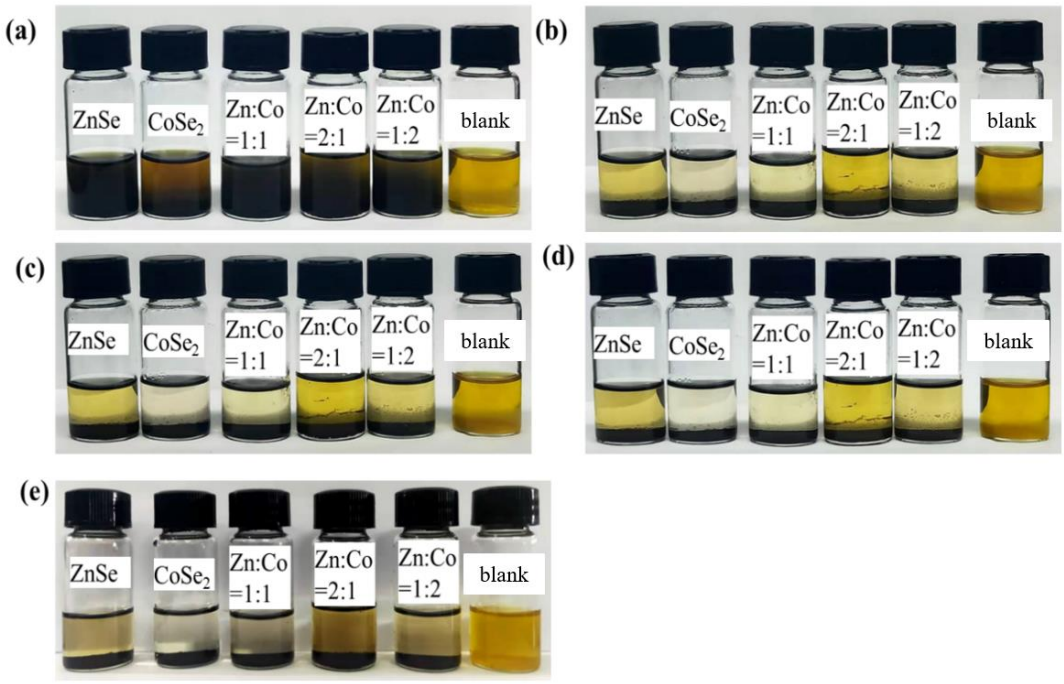


Figure S7. Diagram of the adsorption of Li_2S_6 solution by composite substrate with time change: a. 0 h; B. 2 h; C. 4 h; D. 8 h; e. 12h.

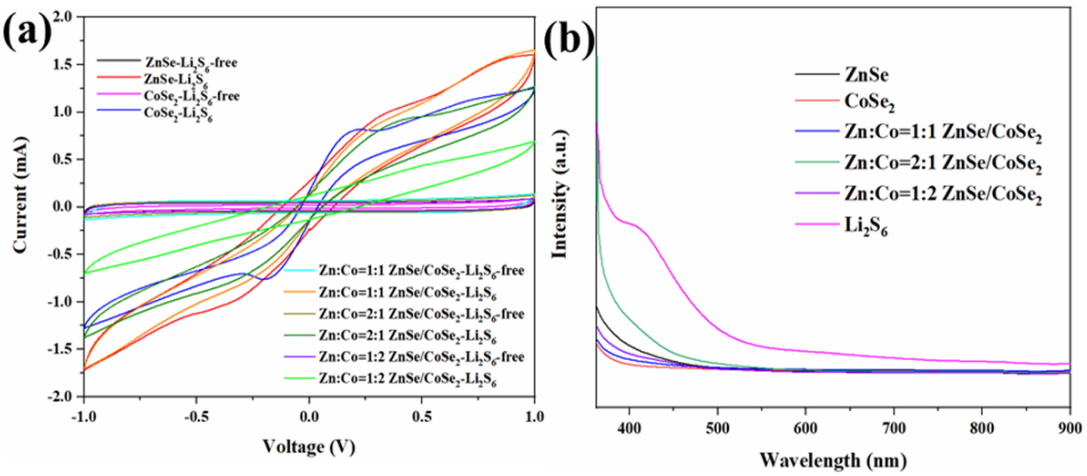


Figure S8. CV curves of ZnSe, $CoSe_2$, and ZnSe/$CoSe_2$ matrix composites with different Zn-Co ratios between −1.0 ~1.0 V at 5 mV s^{-1} scanning rate and (b) UV-vis spectra of adsorbed Li_2S_6 solution by ZnSe, $CoSe_2$ and ZnSe/$CoSe_2$ matrix composites with different Zn-Co ratios.