

Supporting Information

Core-shell polyoxometalate-based zeolite imidazole framework-derived multi-interfacial MoSe₂/CoSe₂@NC enabling multi-functional polysulfide anchoring and conversion in lithium-sulfur batteries

Lunan Zhang,^{*a†} Tangsuo Li,^{a†} Xuecheng Zhang,^a Zhiyuan Ma,^a Qiuping Zhou,^a Yi Liu,^a Xinyuan Jiang,^a Hangyu Zhang,^a Lubin Ni^{*a} and Guowang Diao^{*a}

^a *School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, 225002 (P.R. China)*

*Corresponding authors

E-mail address: zhangln@yzu.edu.cn (L.N. Zhang), lbni@yzu.edu.cn (L.B. Ni), gwdiao@yzu.edu.cn (G.W. Diao)

Postal address: Yangzhou University, Siwangting Road No. 180, Yangzhou, Jiangsu Province, 225002, P. R. China

Table of contents

Section	Page
Experimental Section	S2-S7
Theoretical Section	S7
Supporting Figures	S8-S24
Supporting Tables	S25-S26
References	S27

Experimental Section

Chemicals and reagents

Cobalt nitrate (99.99%, AR), phosphomolybdic acid $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$ and sublimed sulfur powder were obtained from Aladdin (China), Methanol (99.5%, AR) and 2-methylimidazole were purchased from Shanghai Chemical Reagents Company (Shanghai, China). Lithium sulfide (Li_2S) was purchased from Sigma Aldrich (USA).

Synthesis of $\text{PMo}_{12}@ZIF-67$ with different feeding ratios and pure ZIF-67

Briefly, a methanol (25 mL) solution of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.72 g, 2.48 mmol) and an aqueous solution of PMo_{12} (10 mL DI H_2O , the masses of PMo_{12} were 25 mg, 50 mg and 100 mg, respectively) were mixed and stirred vigorously at room temperature for 30 minutes. Then 2-methylimidazole (1.63 g, 19.84 mmol) in 25 mL methanol was quickly added to the above solution, stirring for further 2.5 h. Finally, the obtained precipitates were centrifugally collected, and washed several times with methanol and deionized water. The solids were dried at 75 °C for 10 h to obtain the desired products. The obtained $\text{PMo}_{12}@ZIF-67$ with three different feeding ratios are noted as $\text{PMo}_{12}@ZIF-67$ (25 mg), $\text{PMo}_{12}@ZIF-67$ (50 mg) and $\text{PMo}_{12}@ZIF-67$ (100 mg). The procedure for the synthesis of pure ZIF-67 follows the same procedure in the absence of PMo_{12} .

Synthesis of NC

ZIF-67 was transferred to a porcelain boat in a tube furnace and heated at 350 °C for 2 h with a ramping rate of 2 °C min^{-1} . After that, the temperature was raised to 600 °C with the rate of 5 °C min^{-1} and maintained for 2 h. The entire heating process takes place in an atmosphere of Ar. After cooling down to room temperature, $\text{Co}@NC$ was

collected. The Co@NC was etched with 2M HCl and further dried at 60 °C for 10 h to obtain the desired product of NC.

Synthesis of Mo-doped CoSe₂@NC

The synthesis of Mo-doped CoSe₂@NC is similar to that of the MoSe₂/CoSe₂@NC described in the manuscript, except that the precursor used was changed from PMo₁₂@ZIF-67 to PMo₁₂@ZIF-67 (25mg).

Materials Characterization

The structure of the sample was investigated by XRD (WAXD, D8 Advance, Bruker, Cu K α , $\lambda = 1.54 \text{ \AA}$). TGA (Netzsch TG209 F3) measurements were collected from room temperature to 800 °C with a heating rate of 10 °C min⁻¹ under N₂/air flow. An XPS (Thermo Escalab 250 system) was used to determine the elemental composition of nanoparticles with Al K α radiation ($h\nu = 1486.6 \text{ eV}$) and the chamber pressure was kept below 2×10^{-9} Torr. SEM (Zeiss Supra-55 VP) was used to characterize the external morphology. TEM (Philips TECNAI-12) was used to characterize the microscopic structure of the samples. HRTEM and HAADF-STEM were measured under 200 kV by an FEI Themis Z (USA). BET surface areas of the sample were measured by the equipment of JW-BK 200 static nitrogen adsorption (Beijing Jingwei Gaobo Science and Technology Co. Ltd. China). UV-vis absorption spectra (UV/vis, Shimadzu UVmini-1280 spectrophotometer) were used to detect the concentration and elemental chemical states of the LiPSs.

LiPSs adsorption test

As a representative LiPSs, Li₂S₄/DME solution (0.04 M) was prepared by adding

384 mg of sulfur (12 mmol) and 184 mg of Li_2S (4.0 mmol) into 100 mL of DME solution under vigorous stirring according to previous reports. Before the adsorption experiment, 9 mL DME was added to the 1 mL prepared 0.04 M $\text{Li}_2\text{S}_4/\text{DME}$ solution to dilute it 10-fold. Poured 50 mg of $\text{MoSe}_2/\text{CoSe}_2@\text{NC}$, $\text{CoSe}_2@\text{NC}$ and NC into 10 mL of diluted $\text{Li}_2\text{S}_4/\text{DME}$ solution separately, and stirred vigorously for 1 h. Then the solution was left to stand for 30 min and all supernatants after treatment with various sulfur hosts were analyzed by UV-vis spectroscopy. All operations were conducted in an argon-filled glove box.

Oxidation of Lithium Sulfide (Li_2S) Test

Firstly, Li_2S (20 mg) was added into DME (6 mL) solvent with stirring in a 20 mL penicillin bottle. Then 40 mg of various host materials ($\text{MoSe}_2/\text{CoSe}_2@\text{NC}$, $\text{CoSe}_2@\text{NC}$ and NC) were also added to the reaction system separately with continuous stirring for 10 h. The solution was then left to stand for 30 min and all supernatants after treatment with various sulfur hosts were analyzed by UV-vis spectroscopy. All operations were conducted in an argon-filled glove box.

Li_2S_6 electrolyte based Symmetric Battery Assembly and Measurements

The electrodes of Li_2S_6 symmetric battery were composed of electrode materials ($\text{MoSe}_2/\text{CoSe}_2@\text{NC}$, $\text{CoSe}_2@\text{NC}$ and NC), Super P, and polyvinylidene fluoride (PVDF) binder with the mass ratio of 7:2:1. The areal loading was all controlled around 1.5 mg cm^{-2} . The Li_2S_6 electrolyte (0.5 M) was prepared by adding sulfur (8 g) and Li_2S (2.3 g) in 100 mL of Li-S battery electrolyte (0.5 M lithium trifluoromethanesulfonate (LiCF_3SO_3) and 0.5 M LiNO_3 dissolved in 1,3-dioxolane (DOL) and

dimethoxymethane (DME) (volume ratio = 1: 1)) followed by vigorous mixing at room temperature for two weeks. Two identical electrodes ($\text{MoSe}_2/\text{CoSe}_2@\text{NC}$, $\text{CoSe}_2@\text{NC}$ and NC), a Celgard 2500 separator and $40.0 \mu\text{L}$ Li_2S_6 electrolyte (0.5 M) were assembled into a standard CR2032 coin cell. The CV of symmetric cell was performed voltage window from -1.0 to 1.0 V at a scan rate of 10 mV s^{-1} .

In Situ UV-Vis Measurement

The cathode slurry was composed of the $\text{S}@\text{MoSe}_2/\text{CoSe}_2@\text{NC}$ or $\text{S}@\text{CoSe}_2@\text{NC}$, Super P, and PVDF binder with a mass ratio of 7:2:1. Then, the nickel foam was selected as the collector ($0.8 \times 0.8 \text{ cm}^2$). The areal sulfur loading was around 5.0 mg cm^{-2} . The in-situ UV-Vis cells were assembled using the $\text{S}@\text{MoSe}_2/\text{CoSe}_2@\text{NC}$ or $\text{S}@\text{CoSe}_2@\text{NC}$ electrode as the cathode and lithium metal as the anode, using a custom made in situ cuvette. The in-situ cuvette battery was assembled in an argon-filled glove box and further sealed in 3 mL of Li-S battery electrolyte (0.5 M LiCF_3SO_3 and 0.5 M LiNO_3 dissolved in the mixture of 1,3-DOL and DME with volume ratio of 1: 1). In situ cuvette cell discharges at 0.02 C constant current in the potential range of 1.8-2.8 V. UV-vis spectra were recorded every 15 minutes from the beginning to the end of discharge in situ cuvette batteries.

Li-S Battery Assembly and Electrochemical Measurements

The active substances ($\text{S}@\text{MoSe}_2/\text{CoSe}_2@\text{NC}$, $\text{S}@\text{CoSe}_2@\text{NC}$ and $\text{S}@\text{NC}$) were mixed with super P li (TIMCAL) and PVDF (HSV900) with a weight ratio of 7:2:1 in N-methyl pyrrolidone (NMP) to form a homogeneous slurry. After that, the obtained slurry was directly coated on carbon paper (GDL 28 AA, SGL) current collectors with

a diameter of 16.0 mm, which was further dried at 60 °C for 12 h. The low sulfur loading on each carbon paper is about $\approx 1.5 \text{ mg cm}^{-2}$. For comparison, a high area sulfur loading of $\approx 3.6 \text{ mg cm}^{-2}$. The 2032-type coin cells were assembled using the prepared electrode (S@MoSe₂/CoSe₂@NC, S@CoSe₂@NC and S@NC) as the cathode, Celgard 2500 microporous polypropylene (PP) as a separator and lithium foil as the anode (diameter: 16 mm; thickness: 0.6 mm) in an Ar-filled glove box. The Li-S battery electrolyte was prepared by 0.5 M LiCF₃SO₃ and 0.5 M LiNO₃ dissolved in DOL and DME (volume ratio = 1: 1). In addition, the amount of the electrolyte was strictly controlled for performance evaluation, and the cell contained an electrolyte to sulfur (E/S) ratio of $\approx 12 \text{ } \mu\text{L mg}^{-1}$. The galvanostatic charge/discharge tests were conducted on Neware Battery Measurement System CT 4008W (Neware, China) from 2.8 to 1.7 V at room temperature. The GITT tests of the second cycle were recorded, the closed-circuit voltage (CCV) was measured with a current pulse of 0.1 C for 5 min, and then the quasi-open circuit voltage (QOCV) was obtained by resting the battery for 20 min. For PITT measurements, the 2032-type coin cells were performed on the PITT module of the Gamry Electrochemical Workstation. The voltage range is 2.4-1.7 V, the voltage interval is -50 mV, and the cutoff condition is that the current response is less than 0.05 mA or the run time is greater than 15 min. Then the battery was left for 15 minutes to reach equilibrium. The charging procedure is similar to the discharging PITT, except that the voltage interval is 50 mV. Electrochemical impedance spectra (EIS) and cyclic voltammetry (CV) measurements were measured on a Chenhua CHI-660E electrochemical workstation. CV curves was performed from 2.8 V to 1.7 V (vs Li⁺/Li)

at a scanning rate of 0.1 mV s^{-1} , and the frequency of EIS was performed from 100 kHz to 0.01 Hz at open-circuit potential.

Theoretical Section

Computational Methods

All the calculations results based on the DFT. The Geometry Optimizatio of the system used CASTEP module. And the plane wave code CASTEP with the generalized gradient approximation by Perdew-Burke-Ernzerhof. After the energy convergence testament, $3 \times 3 \times 1$ and $4 \times 4 \times 1$ Monkhorst-Pack meshes were used for the sampling of the Brillouin zone with a kinetic energy cut-off energy of 408.19 and 408.19 eV. The threshold for self-consistent-field (SCF) density convergence is 1.0×10^{-6} eV per atom. One Li_2S_4 molecule was adsorbed on only one side of the exposed surfaces, with the dipole moment corrected accordingly along the (100) and (100) directions. The binding energy (E_b) of the Li_2S_4 on MoSe_2 or CoSe_2 monolayer was calculated as follows: $E_{b1} = E(\text{MoSe}_2/\text{Li}_2\text{S}_4) - E(\text{Li}_2\text{S}_4) - E(\text{MoSe}_2)$, $E_{b2} = E(\text{CoSe}_2/\text{Li}_2\text{S}_4) - E(\text{Li}_2\text{S}_4) - E(\text{CoSe}_2)$, where $E(\text{MoSe}_2)$, $E(\text{CoSe}_2)$, $E(\text{Li}_2\text{S}_4)$, $E(\text{MoSe}_2/\text{Li}_2\text{S}_4)$, and $E(\text{CoSe}_2/\text{Li}_2\text{S}_4)$ represent the total energies of the MoSe_2 and CoSe_2 substrate, the Li_2S_4 molecule, and the adsorption pair of the MoSe_2 substrate and Li_2S_4 , CoSe_2 and Li_2S_4 , respectively.

Supporting Figures

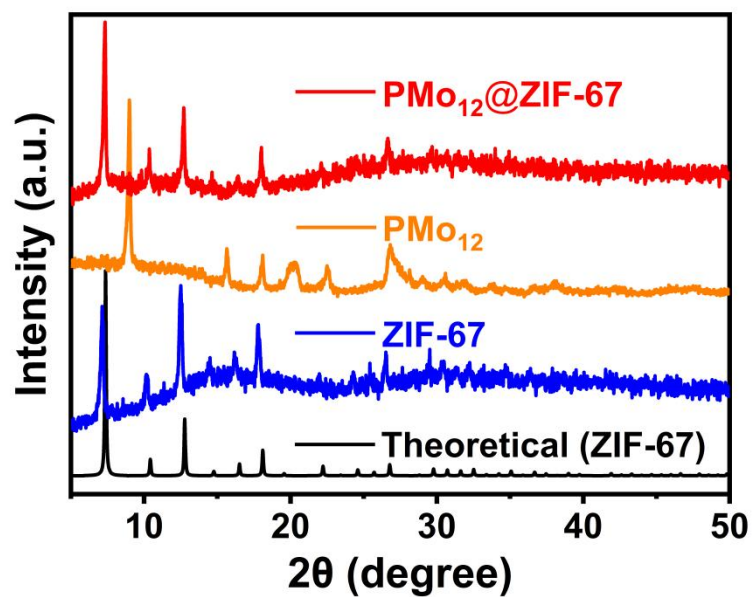


Fig. S1. The PXRD patterns of ZIF-67, PMo₁₂ and PMo₁₂@ZIF-67.

As shown in **Fig. S1**, the PXRD pattern of obtained ZIF-67 matches well with the theoretical value, indicating the successful synthesis of ZIF-67. In addition, the characteristic peaks belonging to ZIF-67 and PMo₁₂ can be clearly observed in the PXRD pattern of PMo₁₂@ZIF-67, which reflects that PMo₁₂ has been encapsulated in the channel of ZIF-67 without changing its original crystal structure.

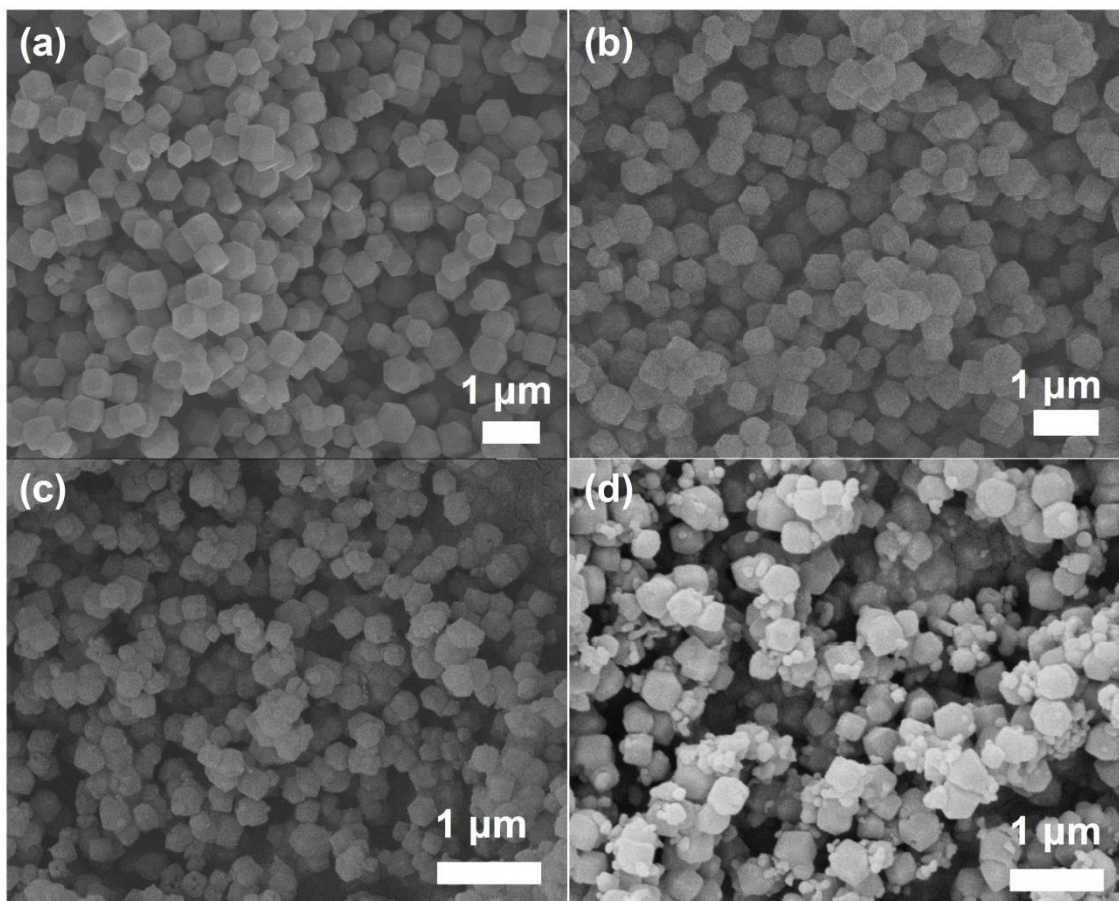


Fig. S2. (a) SEM image of ZIF-67; (b) SEM image of $\text{PMo}_{12}@ZIF-67$ (25mg); (c) SEM image of $\text{PMo}_{12}@ZIF-67$ (50mg); (d) SEM image of $\text{PMo}_{12}@ZIF-67$ (100mg).

The SEM image of pure ZIF-67 is shown in **Fig. S2a**, the regular polyhedral morphology can be found. As displayed in **Fig. S2b-S2c**, it is unambiguous to discover that the regular polyhedral shape of ZIF-67 can be well maintained after the encapsulation of 25 mg or 50 mg PMo_{12} . However, as shown in **Fig. S2d**, a large number of PMo_{12} nanoparticles were found on the surfaces of ZIF-67 after the addition of 100 mg PMo_{12} , indicating that the cavity of ZIF-67 was filled with PMo_{12} .

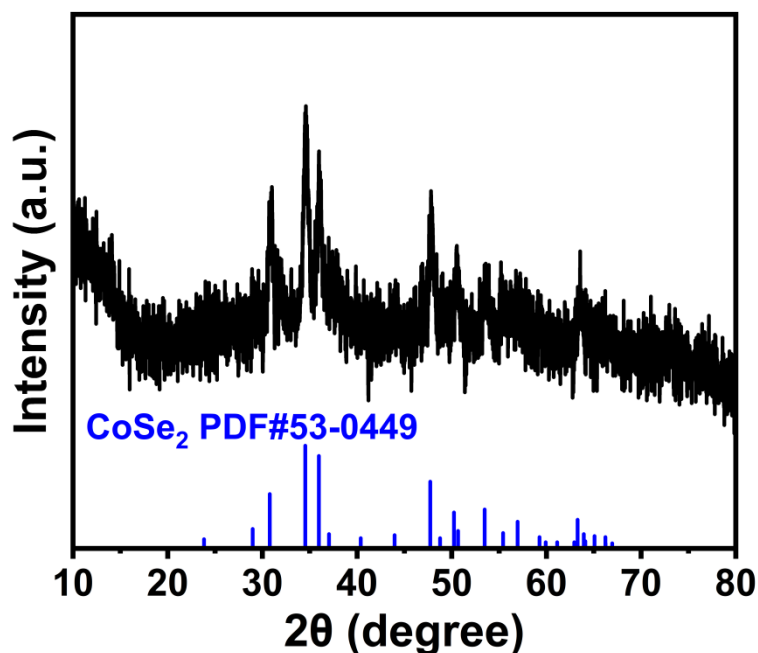


Fig. S3. The PXRD pattern of Mo-doped CoSe₂@NC.

The PXRD spectra of Mo-doped CoSe₂ was analyzed. There are several strong diffraction peaks appeared at 30.8, 34.5, 35.9 and 47.7 should be attributed to (101), (111), (120) and (211) planes of CoSe₂ (PDF#53-0449), respectively. Meanwhile, there exists several weak peaks located at 50.2, 53.5 and 63.3 degree are ascribed to (002), (031) and (122) lattice planes of CoSe₂. However, no diffraction peaks corresponding to MoSe₂ were observed, which may be due to the low Mo content in the precursor of PMo₁₂@ZIF-67 (25mg), which prevented the formation of crystalline MoSe₂ phase during selenization.

Considering the above results presented in **Fig. S2-S3**, we choose PMo₁₂@ZIF-67 (50mg) as the precursor for subsequent selenization in this work. Additionally, all of the PMo₁₂@ZIF-67 (50mg) mentioned in this article are simplified as PMo₁₂@ZIF-67.

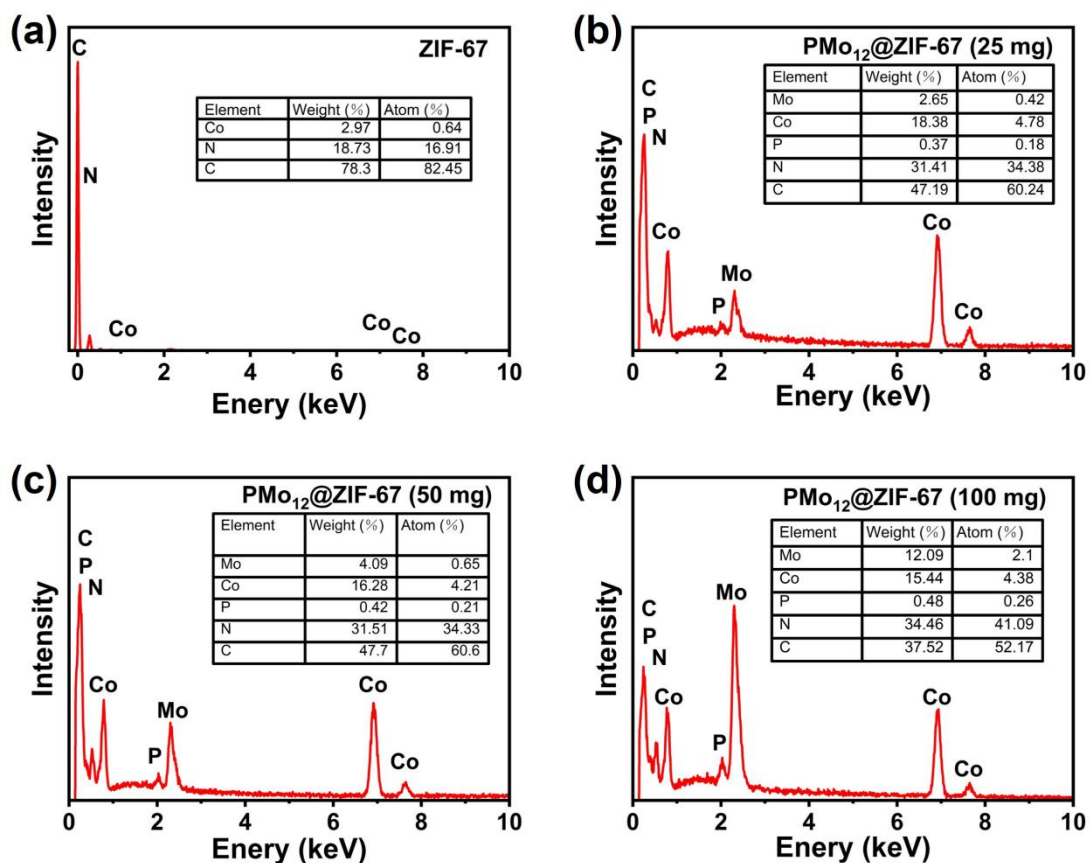


Fig. S4. EDAX spectra of (a) ZIF-67, (b)-(d) series of PMo₁₂@ZIF-67 with different PMo₁₂ mass loading.

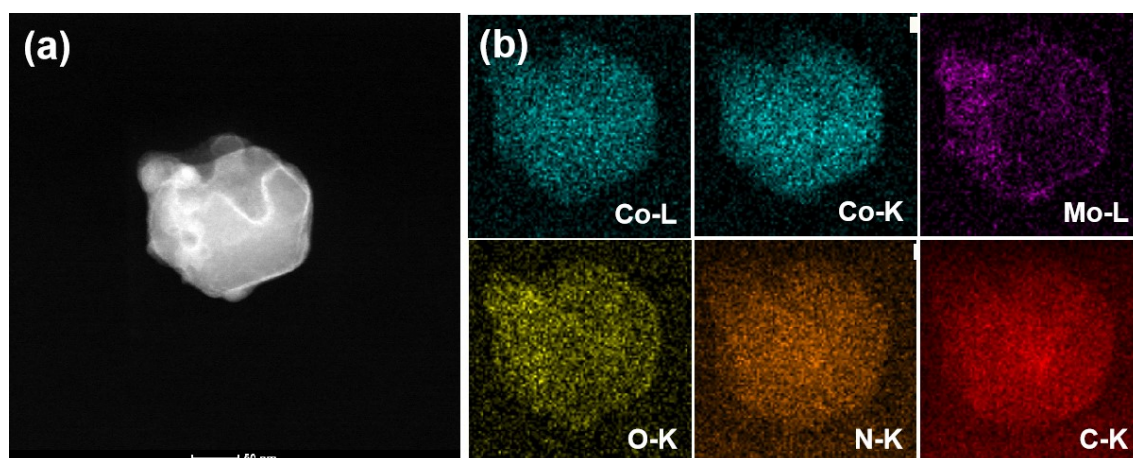


Fig. S5. (a-b) Dark field STEM images of the PMo₁₂@ZIF-67 and EDX elemental mapping on Co, Mo, O, N and C.

The Energy-dispersive X-ray spectroscopy (EDX) elemental mapping give an

effective demonstration of the $\text{PMo}_{12}@ZIF-67$, confirming the $\text{PMo}_{12}@ZIF-67$ contains Co, Mo, O, N and C elements. The uniform distribution of elements further proves that $\text{PMo}_{12}@ZIF-67$ has been prepared.

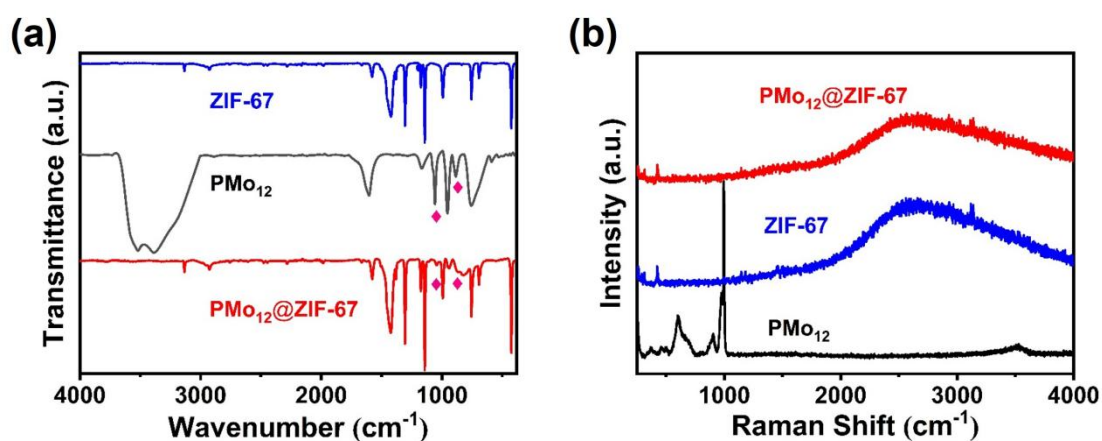


Fig. S6. (a) IR spectra and (b) Raman spectra of ZIF-67, PMo_{12} and $\text{PMo}_{12}@ZIF-67$.

In the infrared (IR) spectrum of $\text{PMo}_{12}@ZIF-67$, two new peaks indexing to PMo_{12} can be observed, which is absent for ZIF-67, implying that PMo_{12} is indeed encapsulated in ZIF-67 cage. Furthermore, the Raman spectra are also tested.

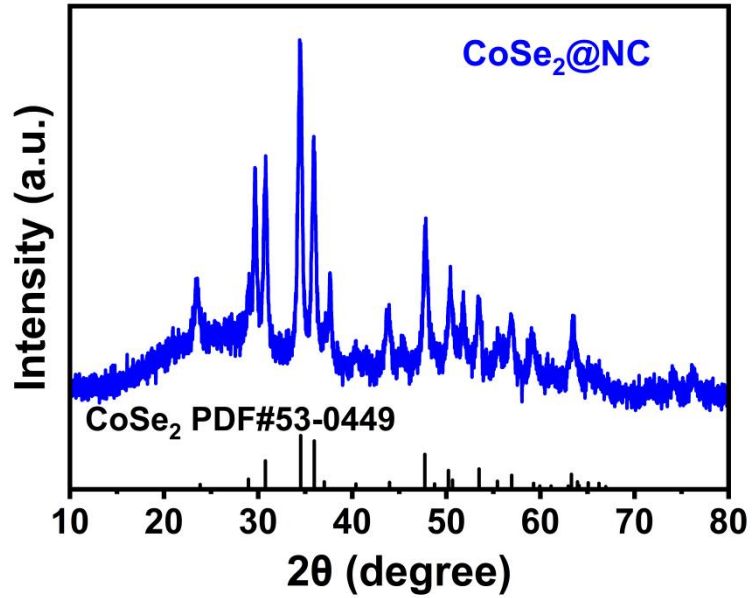


Fig. S7. PXRD pattern of CoSe₂@NC.

The PXRD of CoSe₂@NC was analyzed. There are several strong diffraction peaks at $2\theta \approx 30.8, 34.5, 35.9, 47.7$ and 50.6 degree, which are attributed to (101), (111), (120), (211) and (130) lattice planes of CoSe₂ (PDF#53-0449). Meanwhile, there exists several weak peaks located at $50.2, 53.5$ and 63.3 degree are ascribed to the (002), (031) and (122) lattice planes of CoSe₂.

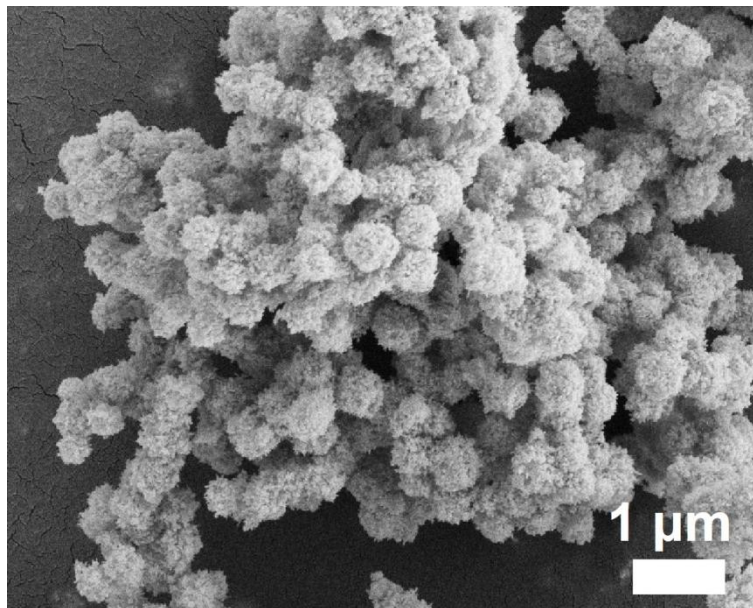


Fig. S8. SEM image of the CoSe₂@NC.

Fig. S8 shows the SEM image of the $\text{CoSe}_2@\text{NC}$, we can find that the morphology of $\text{CoSe}_2@\text{NC}$ is similar to that of $\text{MoSe}_2/\text{CoSe}_2@\text{NC}$, and basically inherits the polyhedral morphology of $\text{PMo}_{12}@\text{ZIF-67}$.

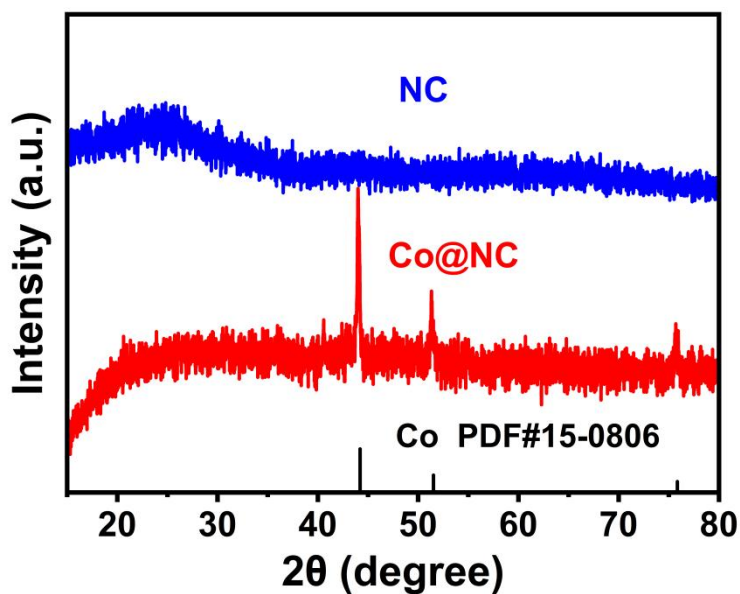


Fig. S9. PXRD patterns of the $\text{Co}@\text{NC}$ and NC.

In the PXRD pattern of $\text{Co}@\text{NC}$, there are three strong diffraction peaks appeared 44.2, 51.5 and 75.8, which should be attributed to (111), (200), and (220) lattice planes of Co (PDF#15-0806). After acid etching, these characteristic peaks both disappeared, implying that all of the Co nanoparticles are removed and the NC skeleton is obtained.

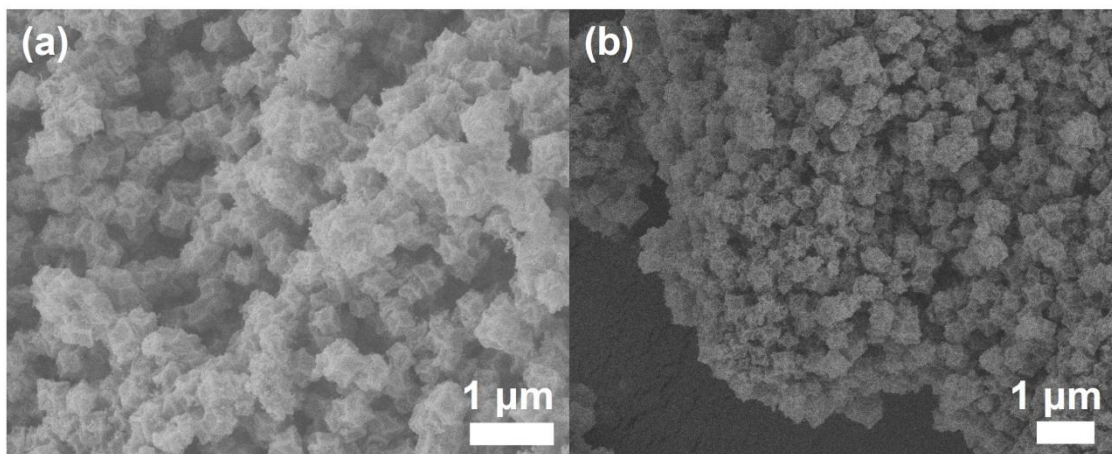


Fig. S10. (a) SEM image of the Co@NC; (b) SEM image of the NC.

As displayed in **Fig. S10**, Co@NC and NC show similar polyhedral morphology with crumpled surfaces.

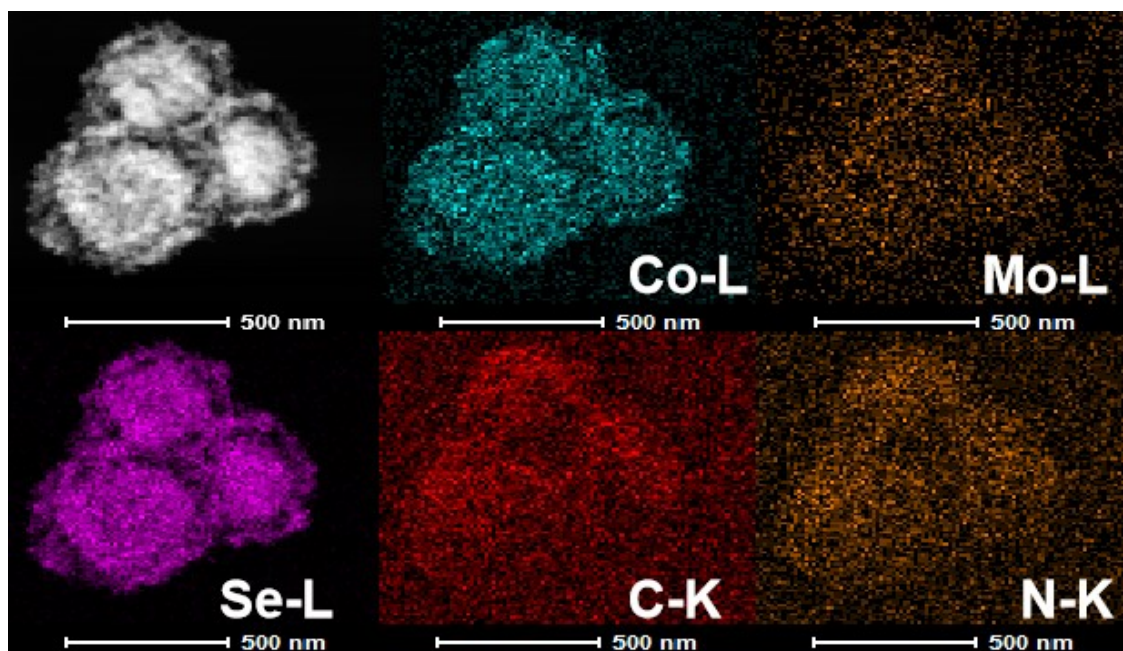


Fig. S11. Dark field STEM images of MoSe₂/CoSe₂@NC and the corresponding EDX elemental mapping of Co, Mo, Se, C and N.

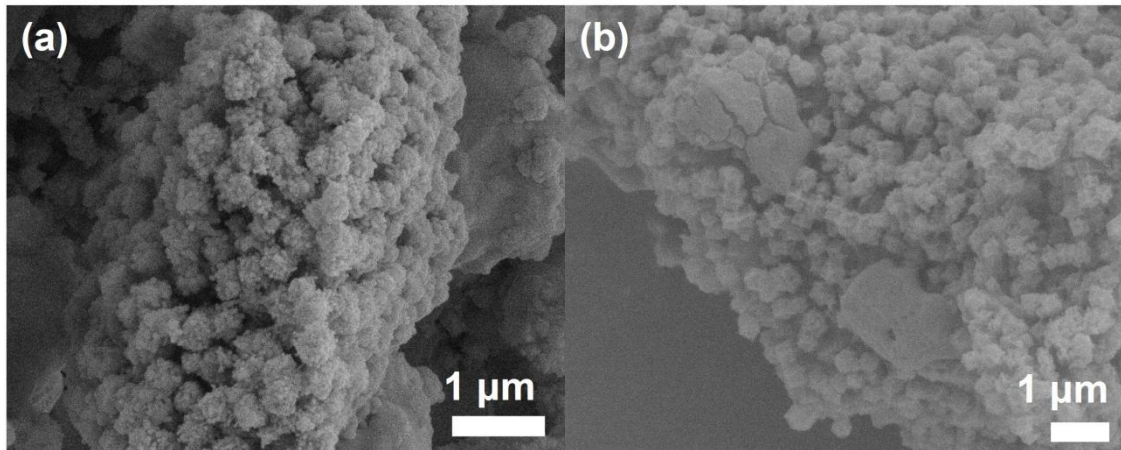


Fig. S12. (a) SEM image of the S@CoSe₂@NC; (b) SEM image of the S@NC.

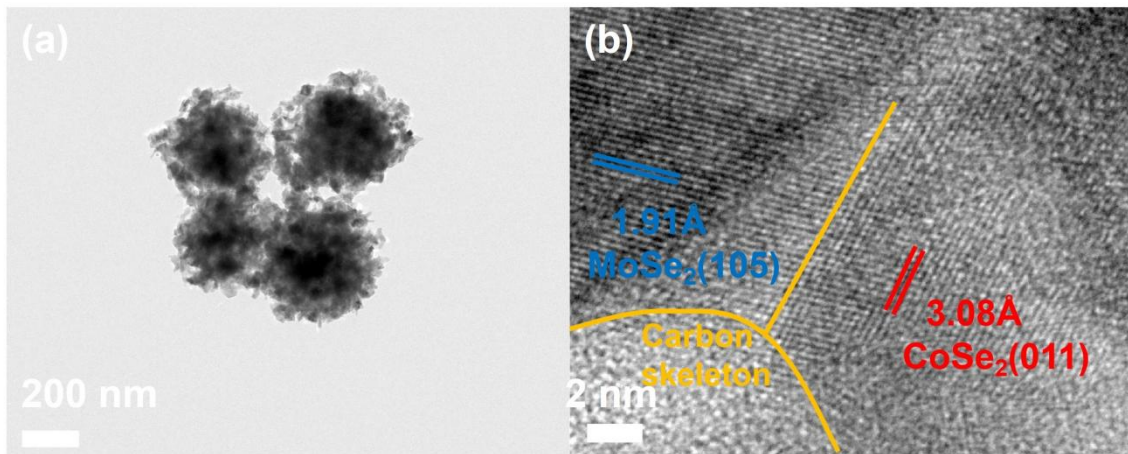


Fig. S13. (a) TEM and (b) HRTEM image of the S@MoSe₂/CoSe₂@NC.

Fig. S13 shows TEM image of the S@MoSe₂/CoSe₂@NC. Comparing with the MoSe₂/CoSe₂@NC, the core-shell structure of S@MoSe₂/CoSe₂@NC can still be clearly observed in several polyhedrons. The HRTEM image represents the lattice fringes with interplanar distances of 3.08 Å is associated with the (011) facets of CoSe₂, and the others with 1.91 Å correspond to the (105) crystallographic planes of MoSe₂.

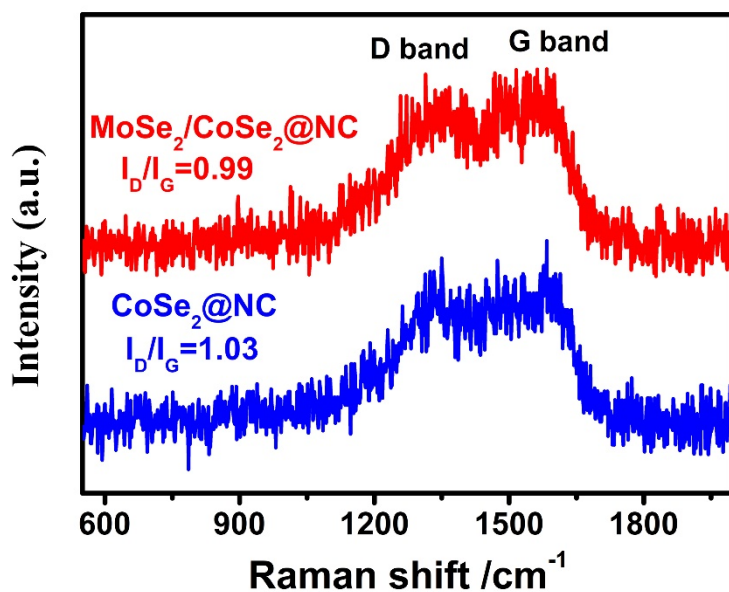


Fig. S14. Raman spectra of MoSe₂/CoSe₂@NC and CoSe₂@NC.

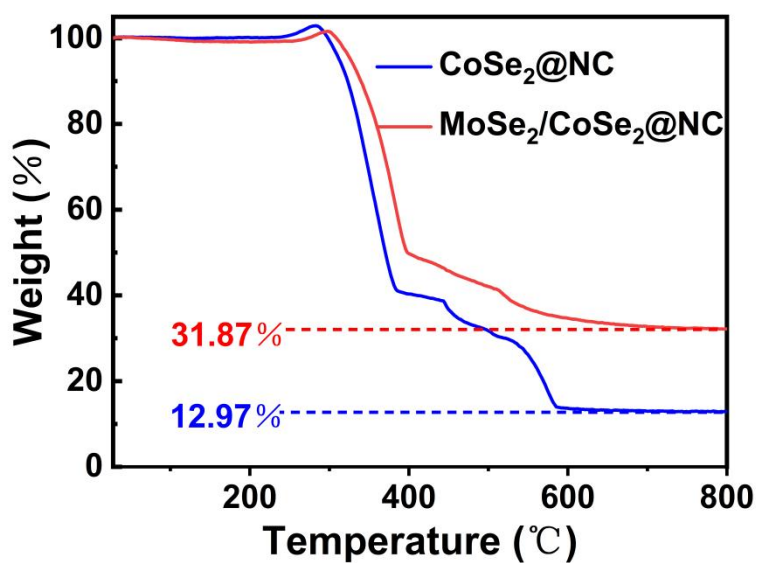


Fig. S15. TGA curves of CoSe₂@NC and MoSe₂/CoSe₂@NC in air.

The TGA curves reflect the decomposition of N-doped carbon species, and the oxidation of CoSe₂ and MoSe₂. It can be thermally decomposed at about 300 °C, indicating that CoSe₂@NC and MoSe₂/CoSe₂@NC have good thermal stability at the battery test temperature. The final residual amounts of Co₃O₄ and MoO₃ content at 700 °C for CoSe₂@NC and MoSe₂/CoSe₂@NC are 12.97 wt % and 31.87 wt%, respectively, which reflect that there are more host materials in MoSe₂/CoSe₂@NC than

in $\text{CoSe}_2@\text{NC}$.

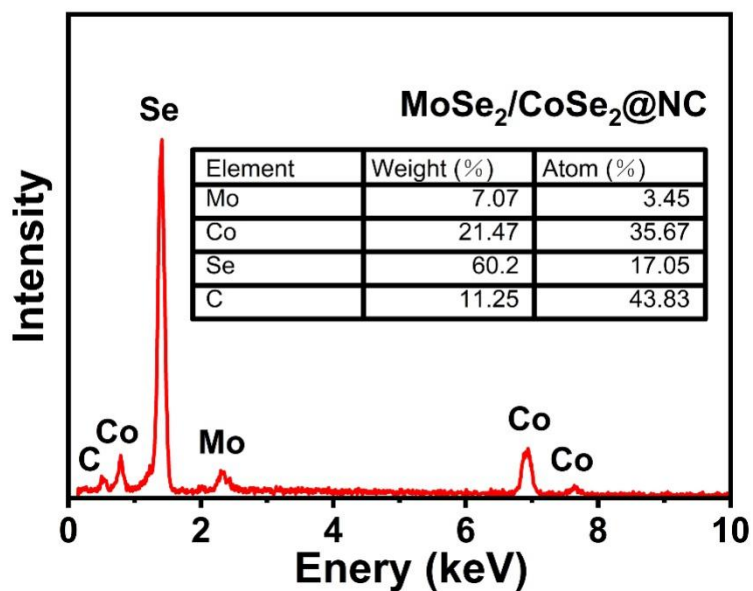


Fig. S16. EDX spectra of $\text{MoSe}_2/\text{CoSe}_2@\text{NC}$.

As can be seen from the results listed in the above table, the mass content of carbon in $\text{MoSe}_2/\text{CoSe}_2@\text{NC}$ is approximately 11.25%, while the element of N is not detected due to the low content and the limited accuracy of the instrument. However, the real presence of N has been confirmed in **Fig. 11** of the manuscript. The atomic ratio of Co and Mo is 4.94, which is close to 5. Therefore, we conclude that the molar ratio of CoSe_2 phase to MoSe_2 phase in $\text{MoSe}_2/\text{CoSe}_2@\text{NC}$ composite is approximately 5:1.

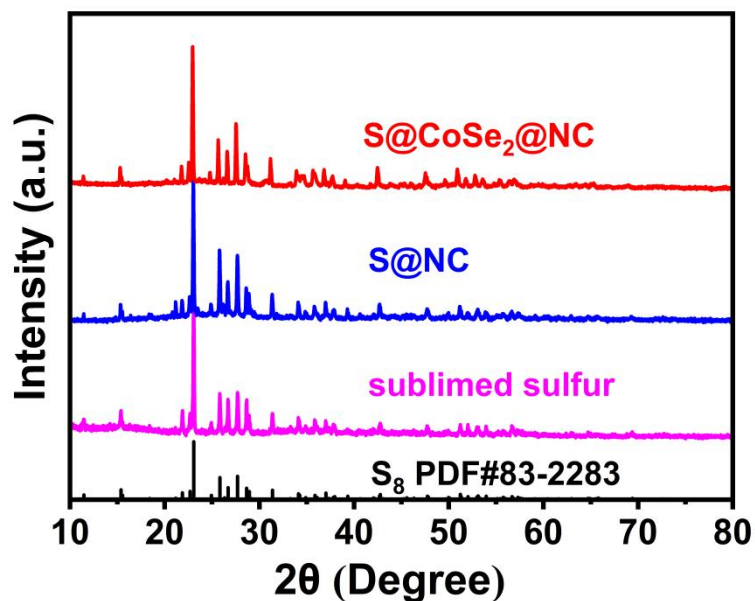


Fig. S17. The PXRD patterns S@CoSe₂@NC, S@NC composites and sublimed sulfur.

The strong diffraction peaks of sublimed sulfur are discovered in the PXRD pattern of S@NC and S@CoSe₂@NC, showing the successful loading of sulfur.

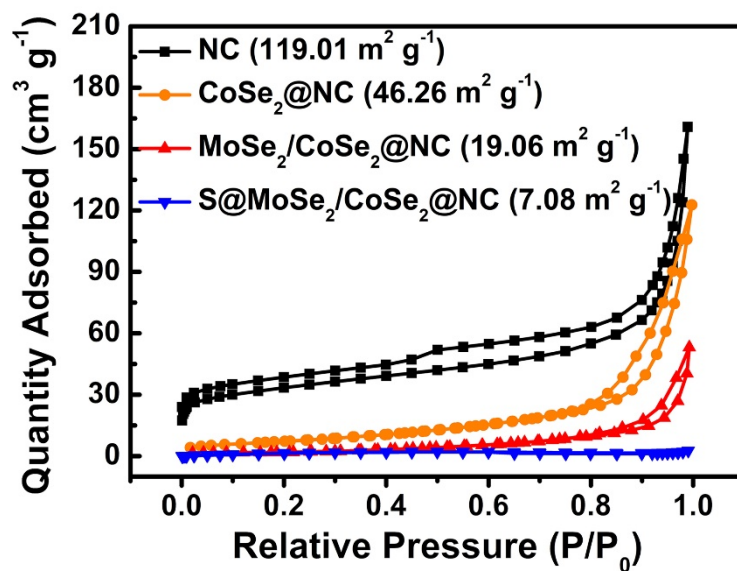


Fig. S18. N₂ adsorption - desorption isotherms for NC, CoSe₂@NC, MoSe₂/CoSe₂@NC and S@MoSe₂/CoSe₂@NC.

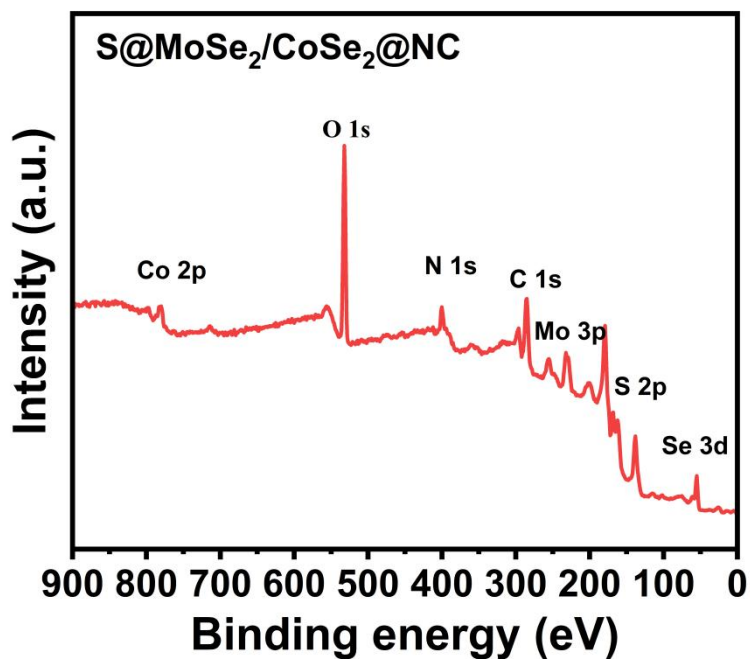


Fig. S19. XPS survey spectrum of the as-prepared S@MoSe₂/CoSe₂@NC composite.

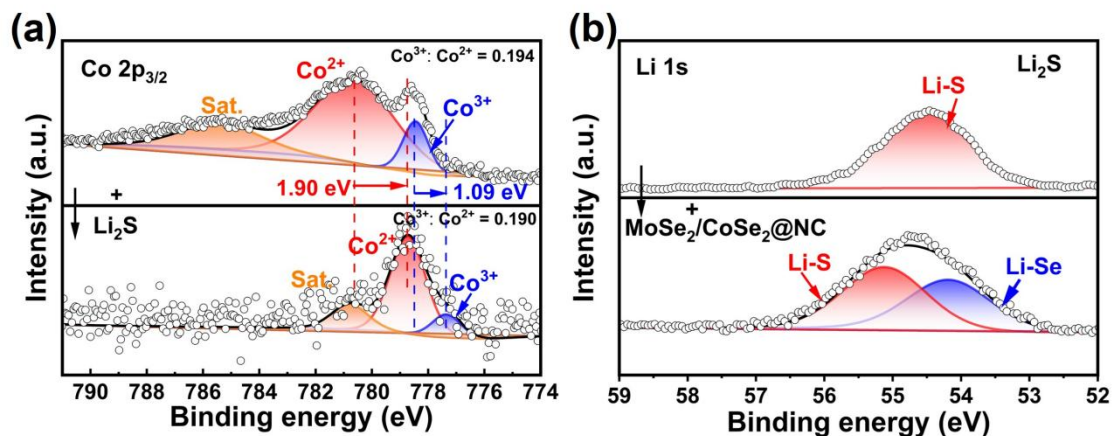


Fig. S20. (a) Co 2p_{3/2} XPS spectra of MoSe₂/CoSe₂@NC and MoSe₂/CoSe₂@NC+Li₂S; (b) Li 1s XPS spectra of pristine Li₂S and MoSe₂/CoSe₂@NC+Li₂S.

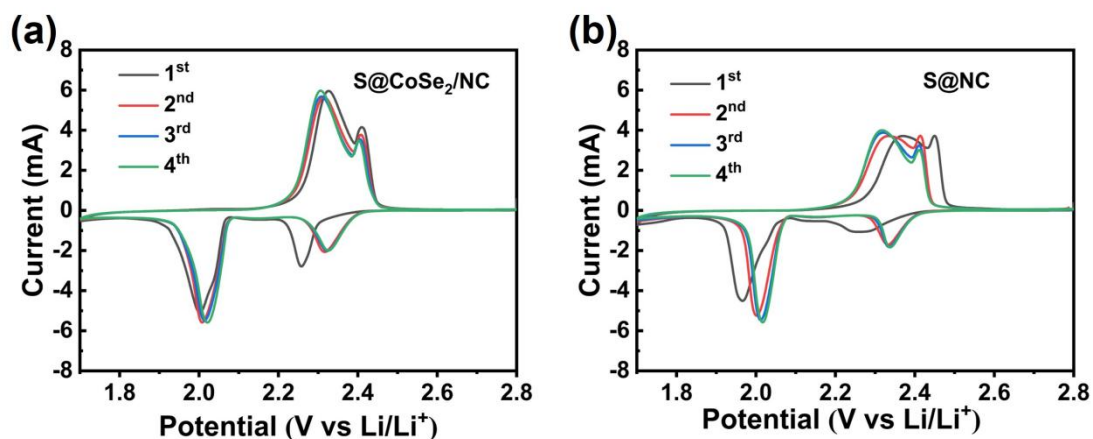


Fig. S21. (a) The CVs of S@CoSe₂@NC cathode material for the first four cycles; (b) The CVs of S@NC cathode material for the first four cycles.

The cyclic voltammograms (CVs) of the first four cycles of Li-S cells with S@CoSe₂@NC and S@NC composites at a scanning rate of 0.1 mV s⁻¹. Two peaks of reduction were observed in the reduction of S@CoSe₂@NC and S@NC, and two peaks of oxidation were also observed in the oxidation process, which was the same as for S@MoSe₂/CoSe₂@NC.

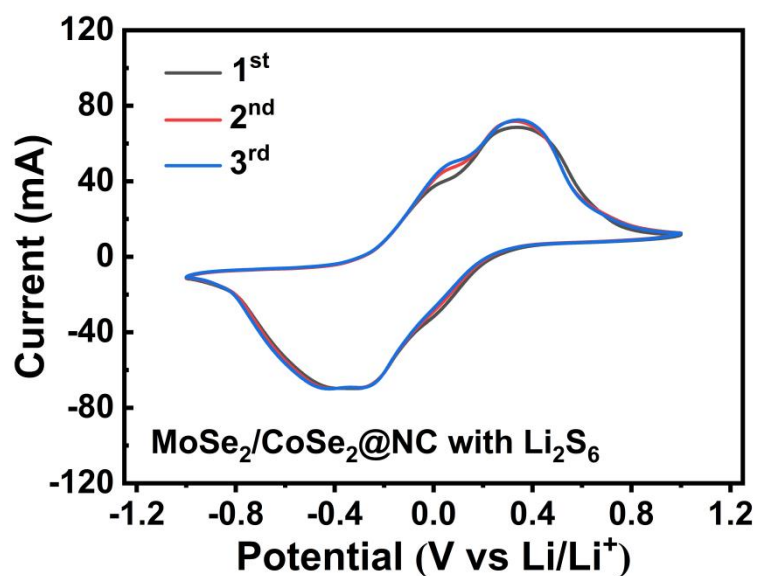


Fig. S22. The CVs of CoSe₂@NC symmetrical cells with Li₂S₆ electrolyte for the

first three cycles.

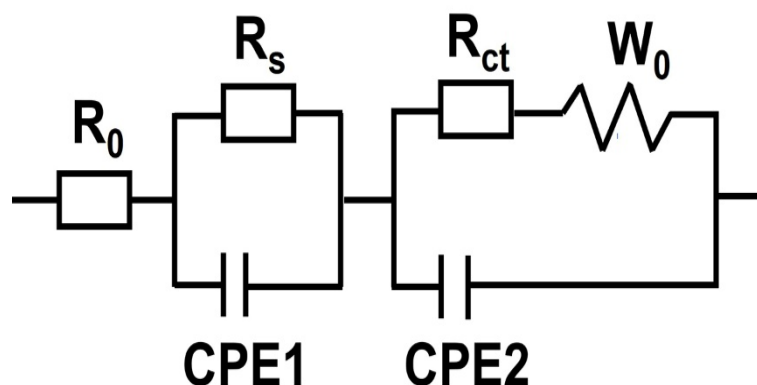


Fig. S23. The equivalent circuit of EIS.

R_0 : The intercept at real axis Z' represents the Ohmic resistance R_0 , corresponding to the intrinsic resistance of current collectors, active materials, electrolyte and separator;

R_s : The internal resistance of the solid electrolyte interface (SEI) film correlated with insoluble $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$, related to the electrode's surface resistance between the electrolyte and sulfur electrodes;

R_{ct} : The charge-transfer resistance of sulfur electrode, related to the electrode reaction kinetics;

CPE1: Capacitance of the electrode bulk in high-frequency region;

CPE2: Capacitance of the charge transfer process at the interface between sulfur and electrolyte;

W_0 : The inclined line in the low frequency is attributed to Warburg impedance (W_0).

The semi-infinite Warburg diffusion impedance of long-chain LiPSs.

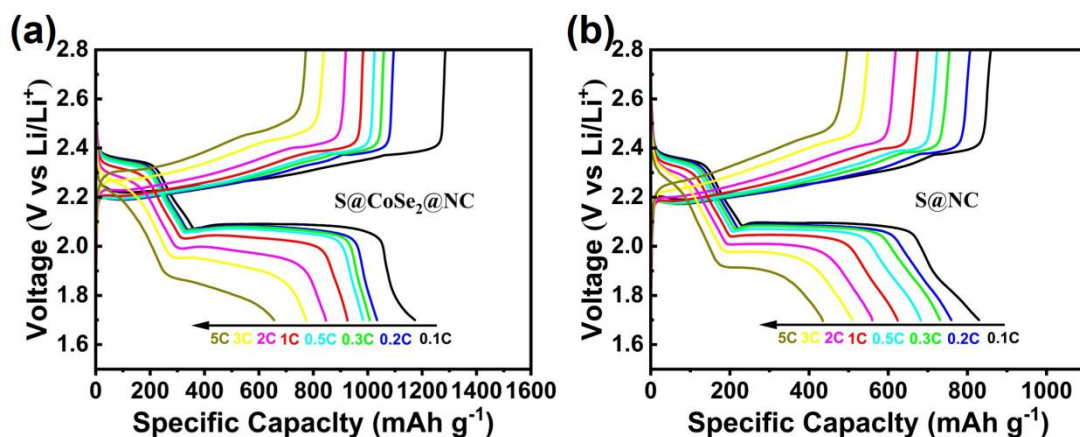


Fig. S24. (a) The charge-discharge curves of S@CoSe₂@NC from 0.1 to 5 C; (b) The charge-discharge curves of S@NC from 0.1 to 5 C.

The corresponding galvanostatic discharge/charge plots of S@CoSe₂@NC and S@NC cathode materials at a series of current densities. The S@CoSe₂@NC cathode delivers initial discharge specific capacity of 1173.47, 1034.14, 1007.20, 982.43, 925.61, 846.62, 774.04 and 655.77 mAh g⁻¹ at different rates of 0.1, 0.2, 0.3, 0.5, 1, 2, 3 and 5 C, respectively. However, the S@NC cathode delivers initial discharge specific capacity of 846.04, 759.24, 730.74, 682.31, 623.92, 559.77, 509.21 and 435.00 mAh g⁻¹ at different rates of 0.1, 0.2, 0.3, 0.5, 1, 2, 3 and 5 C, respectively.

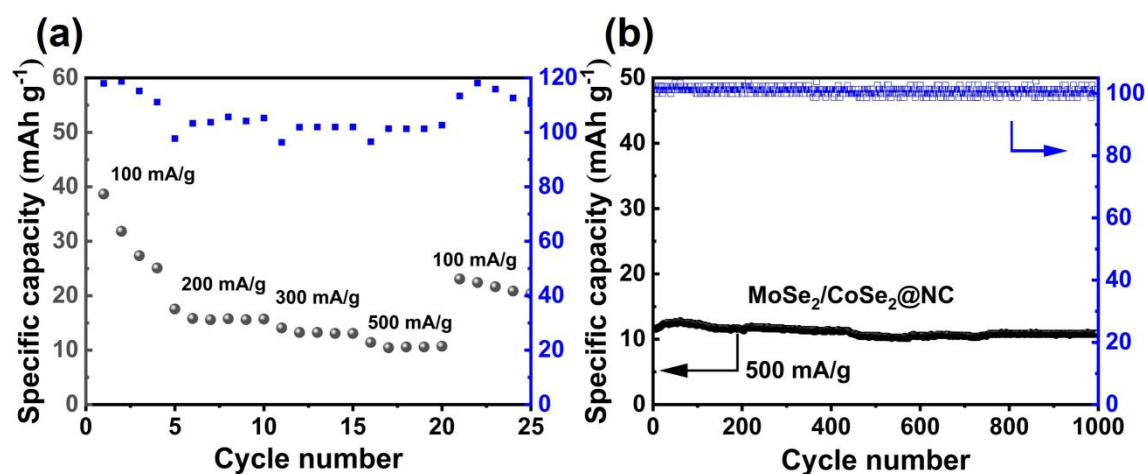


Fig. S25. (a) Rate performance of MoSe₂/CoSe₂@NC composites at different C-rate,

ranging from 100 to 500 mA g⁻¹; (b) Cycling performance and Coulombic efficiency of MoSe₂/CoSe₂@NC cathodes at a current rate of 500 mA g⁻¹.

The MoSe₂/CoSe₂@NC cathode only delivers 38.66, 15.81, 14.08, and 11.41 mAh g⁻¹ at current densities of 100, 200, 300, and 500 mA g⁻¹, respectively, which can be ignored.

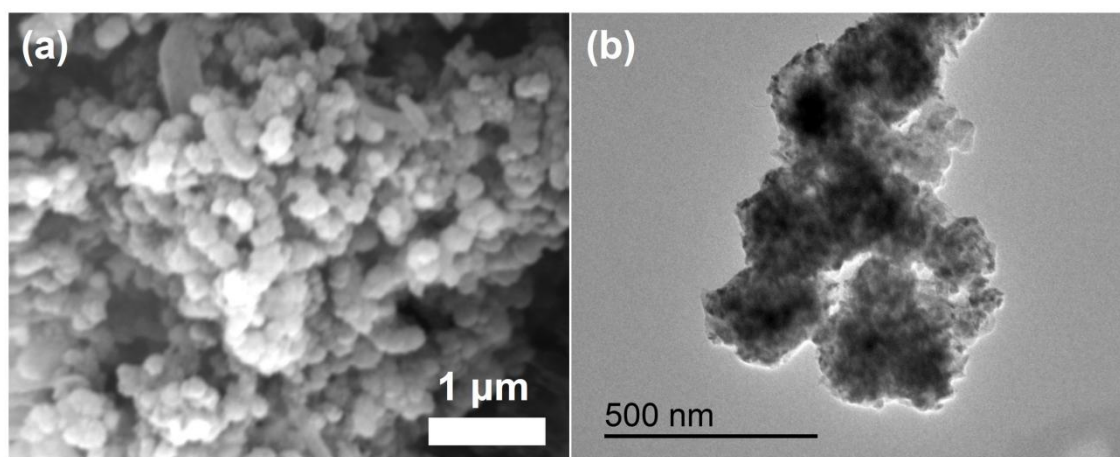


Fig. S26. (a) SEM and (b) TEM images of S@MoSe₂/CoSe₂@NC cathode after 100 cycles at 1 C.

Supporting Tables

Table S1. Comparison of equivalent circuit parameters for S@NC, S@CoSe₂@NC and S@MoSe₂/CoSe₂@NC electrodes.

Sample	χ^2	R_0 (Ω)	R_s (Ω)	R_{ct} (Ω)
S@NC	1.52×10^{-3}	6.67	0.95	121.8
S@CoSe ₂ @NC	2.68×10^{-3}	1.77	0.87	65.24
S@MoSe ₂ /CoSe ₂ @NC	2.72×10^{-3}	1.40	0.74	36.61

Table S2. The initial discharge specific capacity (mAh g⁻¹) of S@NC, S@CoSe₂@NC and S@MoSe₂/CoSe₂@NC electrodes at different rates is compared in the rate performance.

	S@NC	S@CoSe ₂ @NC	S@MoSe ₂ /CoSe ₂ @NC
0.1 C	846.04	1173.47	1352.54
0.2 C	759.24	1034.14	1260.62
0.3 C	730.74	1007.20	1197.92
0.5 C	682.31	982.43	1138.49
1 C	623.92	925.61	1051.06
2 C	559.77	846.62	952.79
3 C	509.21	774.04	867.56
5 C	435.00	655.77	729.97
0.1 C	653.71	848.16	986.97

Table S3. Comparison of the electrochemical performance of Li-S batteries with different catalyst.

Host materials	Sulfur content (wt%)	Areal S loading (mg cm ⁻²)	Discharge current rate	DIS. capacity (mAh g ⁻¹)		Ref.
				Initial	After (<i>n</i> th)	
		3.6	1 C	594	472 (100)	
S@MoSe₂/CoSe₂@NC	70	1.5	3 C	820	515 (500)	This work
		1.5	1 C	993	768 (300)	
S@CoSe ₂ -PNC	60	1.5	1 C	790	546 (300)	1
S-Co ₃ O ₄ @MCR	70	1.32	2 C	600	324 (300)	2
S@Co/Co ₃ O ₄ -NHC	70	1.2	1 C	617	553 (500)	3
NMCS@MoS ₂ /S	70	1.2	0.5 C	894	826 (200)	4
MoS ₂ -rGO/S	80	0.85	1 C	872	480 (300)	5
Ni _{0.1} Zn _{0.1} Co _{0.8} Se ₂ -S	60	1.0	1 C	679	503 (400)	6
S/ZnSe-CoSe ₂ @NC	80	1.23	1 C	810	619 (400)	7
CoSe@HPP/S	70	1.2	1 C	912	716 (300)	8
MoSe ₂ /N-rGO/S	60	1.1	0.2 C	981	692 (100)	9
MoSe ₂ @C/rGO/S	70	1.2	1 C	851	583 (300)	10

References

1. F. L. Zhang, H. Wang, S. Ji, V. Linkov, X. Y. Wang and R. F. Wang, *Chemphyschem*, 2022, **23**, 202100811.
2. S. F. Wang, X. H. Hou, Z. M. Zhong, K. X. Shen, G. Z. Zhang, L. M. Yao and F. M. Chen, *Scientific Reports*, 2018, **8**, 16133.
3. Y. Jeon, J. Lee, H. Jo, H. Hong, L. Y. S. Lee and Y. Z. Piao, *Chemical Engineering Journal*, 2021, **407**, 126967.
4. S. X. Jiang, M. F. Chen, X. Y. Wang, Z. Y. Wu, P. Zeng, C. Huang and Y. Wang, *Acs Sustainable Chemistry & Engineering*, 2018, **6**, 16828.
5. Y. You, Y. W. Ye, M. L. Wei, W. J. Sun, Q. Tang, J. Zhang, X. Chen, H. Q. Li and J. Xu, *Chemical Engineering Journal*, 2019, **355**, 671.
6. L. P. Chen, Y. H. Xu, G. Q. Cao, H. M. K. Sari, R. X. Duan, J. J. Wang, C. Xie, W. B. Li and X. F. Li, *Advanced Functional Materials*, 2022, **32**, 2107838.
7. J. Xu, L. L. Xu, Z. L. Zhang, B. Sun, Y. Jin, Q. Z. Jin, H. Liu and G. X. Wang, *Energy Storage Materials*, 2022, **47**, 223.
8. Z. Q. Ye, Y. Jiang, L. Li, F. Wu and R. J. Chen, *Advanced Materials*, 2020, **32**, 2002168.
9. H. L. Wong, X. W. Ou, M. H. Zhuang, Z. J. Liu, M. D. Hossain, Y. T. Cai, H. W. Liu, H. B. Lee, C. Z. Wang and Z. T. Luo, *Acs Applied Materials & Interfaces*, 2019, **11**, 19986.
10. C. C. Li, W. N. Ge, S. Y. Qi, L. Zhu, R. Z. Huang, M. W. Zhao, Y. T. Qian and L. Q. Xu, *Advanced Energy Materials*, 2022, **12**, 2103915.