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Enhancing the catalytic conversion of polysulfides utilizing covalent organic framework-carbon nanotube interlayer

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Experimental section

Fabrication of Modified Separators:

The CTF and CTF-CNT modified separators were prepared via vacuum-assisted filtration. Typically, 50 mg of the as-synthesized CTF or CTF-CNT powder was dispersed in 50 mL of N-methyl-2-pyrrolidone (NMP, 1 mol L^{-1}) containing approximately 5.5 mg of polyvinylidene fluoride (PVDF) as a binder. The mixture was stirred magnetically until homogeneous and further sonicated for several minutes to ensure uniform dispersion. Subsequently, ~5 mL of the dispersion was vacuum-filtered onto a commercial polypropylene (PP) membrane with a diameter of 4.8 cm. The coated separator was then dried at room temperature for 12 h. The resulting coating layer had a thickness of 5–7 μm, and the mass loading of the active material was ~0.3 mg cm^{-2}.

The vacuum filtration process resulted in a compact and uniform coating layer on the PP membrane, as shown in **Figure S10**. The prepared separators were designated as CTF and CTF-CNT, with the latter further labeled according to the CNT content: CTF-CNT-5, CTF-CNT-10, and CTF-CNT-20.

Preparation of Electrolyte

Standard Electrolyte for Li–S Batteries:

The electrolyte typically consists of 1 M LiTFSI and 1 wt% $LiNO_3$ dissolved in a DME/DOL (1:1 by volume) solvent mixture.

Li_2S_6 Electrolyte:

To prepare a 0.2 M Li_2S_6 solution, elemental sulfur (320.6 mg, 0.01 mol) and Li_2S (91.8 mg, 0.002 mol) were weighed and transferred into a glass vial inside an argon-filled glovebox. Then, 10 mL of a DOL:DME solvent mixture (1:1 by volume) was added. The mixture was heated and stirred at 60 °C for 24 hours until a clear yellow solution was obtained. This solution was used for adsorption experiments.

Li_2S_8 Electrolyte Preparation:

0.1 M Li_2S_8 Electrolyte:

A 0.1 M Li_2S_8 electrolyte was prepared in an argon-filled glovebox. Elemental sulfur (2244.6 mg, 0.07 mol) and Li_2S (459.5 mg, 0.01 mol) were weighed and placed into a glass vial. Then, 100 mL of a DOL:DME (1:1 by volume) solvent mixture was added. The mixture was heated and stirred at 60 °C for 24 hours to yield a yellow solution, which was used for adsorption experiments.

0.2 M Li_2S_8 Electrolyte:

To prepare a 0.2 M Li_2S_8 electrolyte under the same solvent conditions, the molar amounts of sulfur and Li_2S were doubled accordingly.

Cathode Preparation:

The main framework of the cathode material was based on porous-walled carbon nanotubes (MWCNTs). Multi-walled carbon nanotubes (MWCNTs) and elemental sulfur were mixed in a mass ratio of 3:7 by ball milling for 1 hour. The mixture was then transferred into a reaction kettle, and the atmosphere was exchanged under an argon-filled glovebox (O_2 and H_2O levels < 0.01 ppm). The sealed vessel was heated at 155 °C for 12 hours to obtain the sulfur–carbon composite material (CNT/S). The sulfur content in the composite was determined to be 69.7% by thermogravimetric analysis (TGA), as shown in **Figure S11**.

The CNT/S composite was then mixed with a conductive agent (Super P) and polyvinylidene fluoride (PVDF) in a mass ratio of 8:1:1. A certain amount of N-methyl-2-pyrrolidone (NMP) was added to the mixture in a ball mill jar for 1 hour of grinding. The PVDF was pre-dissolved in NMP to form a 2 wt% solution (mass ratio 2:98). After grinding, a viscous and homogeneous slurry was obtained, which was uniformly coated onto carbon-coated aluminum foil using a doctor blade. The coated foil was dried in a vacuum oven at 60 °C for 12 hours. Finally, round cathode disks with a diameter of 12 mm were punched out, yielding CNT/S composite sulfur cathodes with a sulfur loading of 0.8–1.2 mg cm^{-2}.

Preparation of COF electrode sheets：

A mixture comprising CTF-CNT, CTF, CNT, Super-P, and PVDF was combined with a specific quantity of NMP in a ratio of 8:1:1. This mixture was subjected to grinding in a ball mill jar for one hour, resulting in the formation of a viscous and homogeneous slurry. Subsequently, the slurry was uniformly applied onto carbon-coated aluminum foil using a scraper. The coated foil was then dried at 60 °C in a vacuum drying oven for 12 hours. After the drying process, the material was cut into small discs with a diameter of 12 mm.

Li_2S Nucleation Experiment

The lithium sulfide nucleation experiment utilized various COF materials coated onto a carbon substrate to function as electrodes. Specifically, a mixture of CTF-CNT or CTF, Super-P, and polyvinylidene fluoride (PVDF) was homogenized in N-methyl-2-pyrrolidone (NMP) at a mass ratio of 7:2:1. The resultant slurry was subsequently cast onto carbon paper. A lithium foil was employed as the counter electrode, with a Celgard 2400 separator placed between the electrodes. The electrolyte comprised a 0.2 M solution of Li_2S_8 dissolved in the electrolyte medium. The battery underwent an initial galvanostatic discharge at a current of 0.112 mA to a voltage of 2.06 V, followed by a potentiostatic discharge at 2.05 V for 10,000 seconds to facilitate the nucleation and growth of Li_2S.

Battery Assembly:

To assemble the battery, a lithium metal foil was first placed onto the negative case. Then, 25 μL of electrolyte was added using a micropipette. A separator was carefully placed on top of the lithium metal, ensuring full coverage and central alignment with the lithium disk. An additional 25 μL of electrolyte was then dropped onto the separator. The sulfur cathode was placed on top of the separator, aligned centrally.

Subsequently, a stainless steel spacer, a spring, and the positive case were sequentially assembled. The entire cell was then pressed using an automatic crimping machine at a pressure of 450 kg. The assembled battery was allowed to rest until the open-circuit voltage stabilized before electrochemical testing was carried out.

The spring ensures tight contact among all internal components, while the stainless steel spacer increases the overall thickness and contributes to better compression of the cell.

Electrochemical measurements.

Electrochemical characterization was performed using standard testing protocols. Galvanostatic charge/discharge measurements were carried out on the LAND 2001A test system at 25°C, with current densities normalized to sulfur mass (1C = 1675 mA g^{-1}). The standard voltage window was set at 1.7-2.8 V (vs Li/Li+), while high-loading electrodes were tested between 1.6-2.7 V. Electrochemical workstation (Metrohm M204) measurements included: (1) cyclic voltammetry at 0.1-0.4 mV s^{-1} scan rates (1.7-2.8 V range), (2) electrochemical impedance spectroscopy (100 kHz-0.1 Hz, 10 mV amplitude), and (3) galvanostatic intermittent titration with 0.1C current pulses (10 min on/20 min off intervals).

In situ time-resolved Raman measurements

The in-situ time-domain Raman measurement of Li_2S_8 solution is conducted using a 0.2M Li_2S_8 electrolyte. The materials' electrode is prepared by mixing CTF-CNT and CTF, carbon black, and PVDF in a mass ratio of 8:1:1 in NMP, and then the slurry is coated on an aluminum mesh. PP is used as a separator. The CTF-CNT and CTF electrodes serve as the cathode. The electrolyte consists of 0.2M Li_2S_8 dissolved in LiTFSI and 1wt% $LiNO_3$ in DOL/DME (1:1). The positive electrode shell has a small hole (diameter: 5 millimeters) and is filled with a quartz piece. After assembly, 50 microliters of Li_2S_8 solution is slowly added through the small hole onto the COF electrode. Finally, a quartz piece is placed on the positive electrode box to cover the small hole. The incident beam is a focused laser beam with a wavelength of 532 nanometers.

Ionic Conductivity Measurements

The ionic conductivity of separators and electrolytes was determined using electrochemical impedance spectroscopy (EIS) in a stainless steel symmetric cell configuration. Measurements were conducted over a frequency range of 0.1 Hz to 100 kHz. The ionic conductivity (σ) was calculated according to the following equation:

$$\sigma = L/(Rb \times A)$$

where L is the thickness of the separator, Rb is the bulk resistance obtained from the EIS Nyquist plot, and A is the contact area between the separator and electrodes.

Lithium-Ion Transference Number Measurements

The lithium-ion transference number (t_{Li+}) was determined using chronoamperometry in a Li||Li symmetric cell configuration. The value was calculated according to the Bruce-Vincent equation:

$$t_{Li^+} = Is\ (\Delta V -\ IR_0)/I_0\ (\Delta V -\ I_S R_S)$$

Is = steady-state current

I_0 = initial current

ΔV = applied potential difference

R_0 = initial interfacial resistance

Rs = steady-state interfacial resistance

Lithium-Ion Diffusion Coefficient Determination

The lithium-ion diffusion coefficient (D_{Li+}) was evaluated through cyclic voltammetry (CV) measurements conducted at multiple scan rates (0.1-0.4 mV s^{-1}). The diffusion coefficient was quantitatively determined using the Randles-Ševčík equation:

$$I_{peak} = 2.69 \times 10^5 \times n^{1.5} \times A \times D_{Li^+}^{0.5} \times C_{Li^+} \times V^{0.5}$$

Ip = peak current (A)

n = number of electrons transferred

A = electrode area (cm^2)

D_{Li+} = lithium-ion diffusion coefficient (cm^2 s^{-1})

C = bulk concentration (mol cm^{-3})

v = scan rate (V s^{-1})

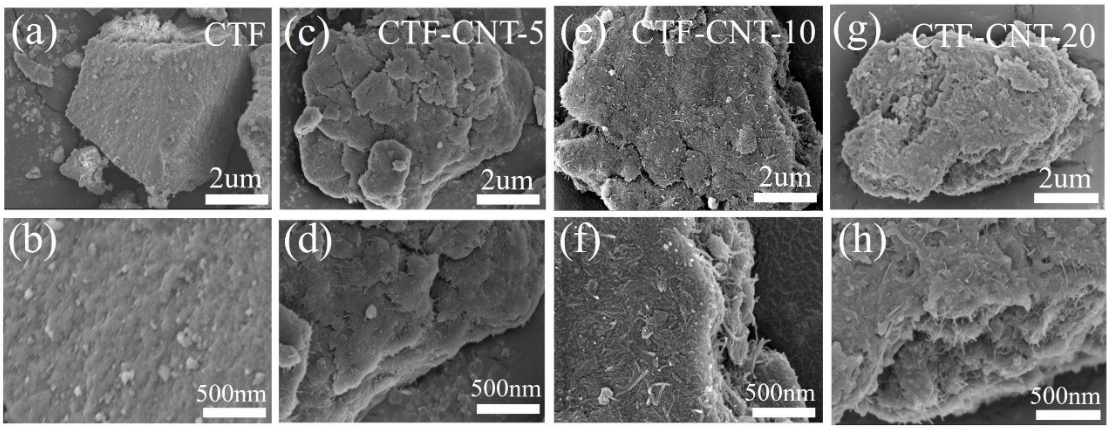


Figure S1. SEM images of (a, b) CTF; (c, d) CTF-CNT-5; (e, f) CTF-CNT-10; and (g, h) CTF-CNT-20, illustrating their respective morphologies and structural features.

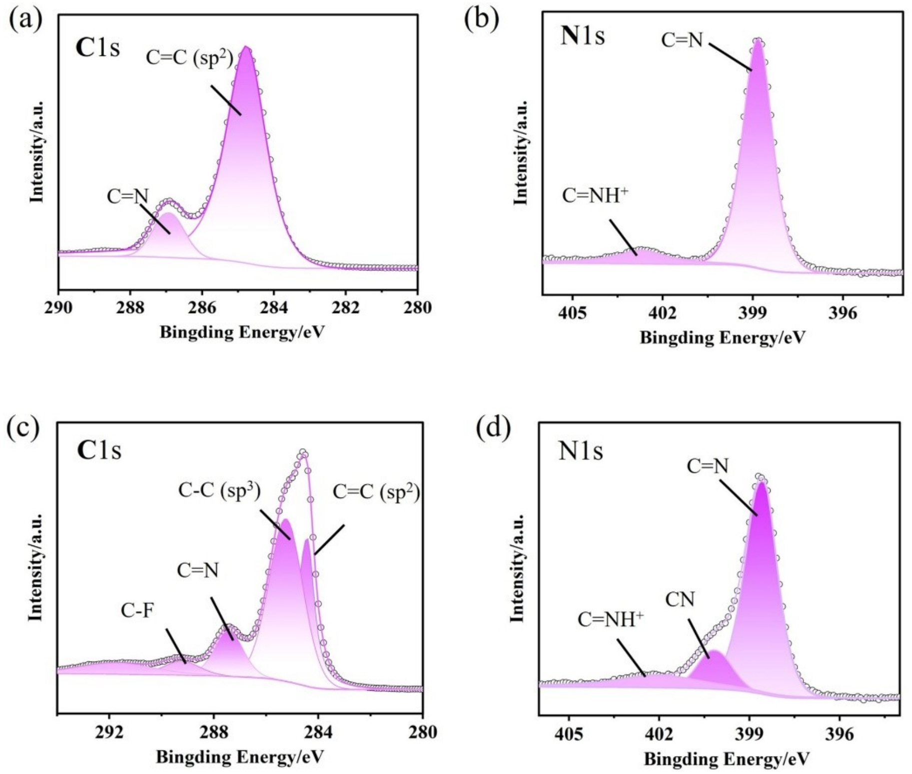
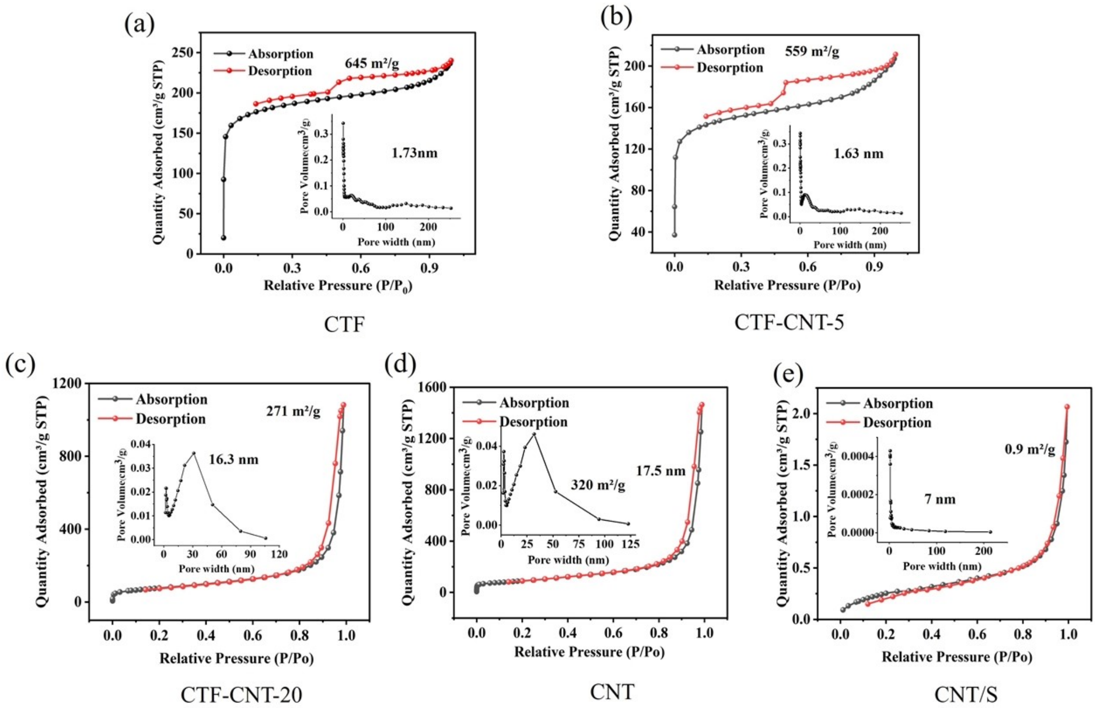


Figure S2. (a, b) C 1s and N 1s XPS spectra of CTF;(c, d) C 1s and N 1s XPS spectra of CTF-CNT.



CTF

CTF-CNT-5

CTF-CNT-20

CNT

CNT/S

Figure S3. Surface area and pore size analysis of the materials:(a) CTF;(b) CTF-CNT-5;(c) CTF-CNT-20;(d) CNT;(e) CTF/S.

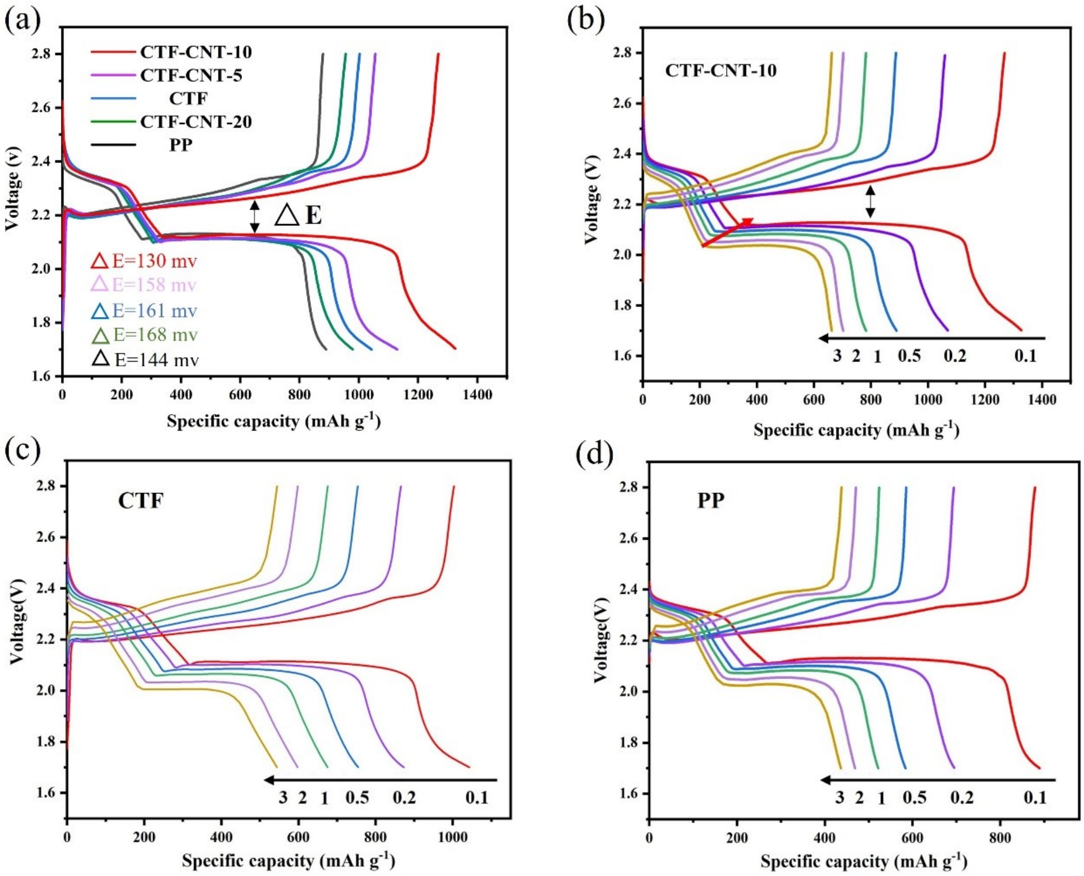


Figure S4. (a) Rate performance of CTF, CTF-CNT-10, CTF-CNT-5, CTF-CNT-20, and unmodified PP separators. (b) Voltage vs. specific capacity curve of CTF-CNT-10 separator.(c) Voltage vs. specific capacity curve of CTF separator.(d) Voltage vs. specific capacity curve of PP separator.

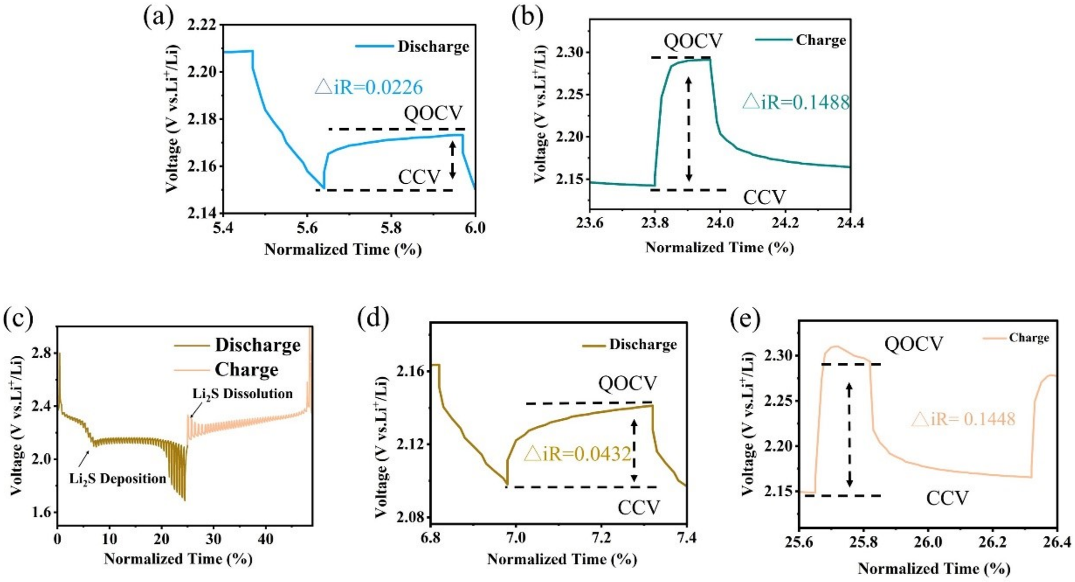


Figure S5. (a) GITT curve during Li$_2$S nucleation.(b) GITT curve during Li$_2$Sdecomposition.(c) GITT curve of CTF separator.(d) GITT curve during Li$_2$S nucleation.(e) GITT curve during Li$_2$S decomposition.

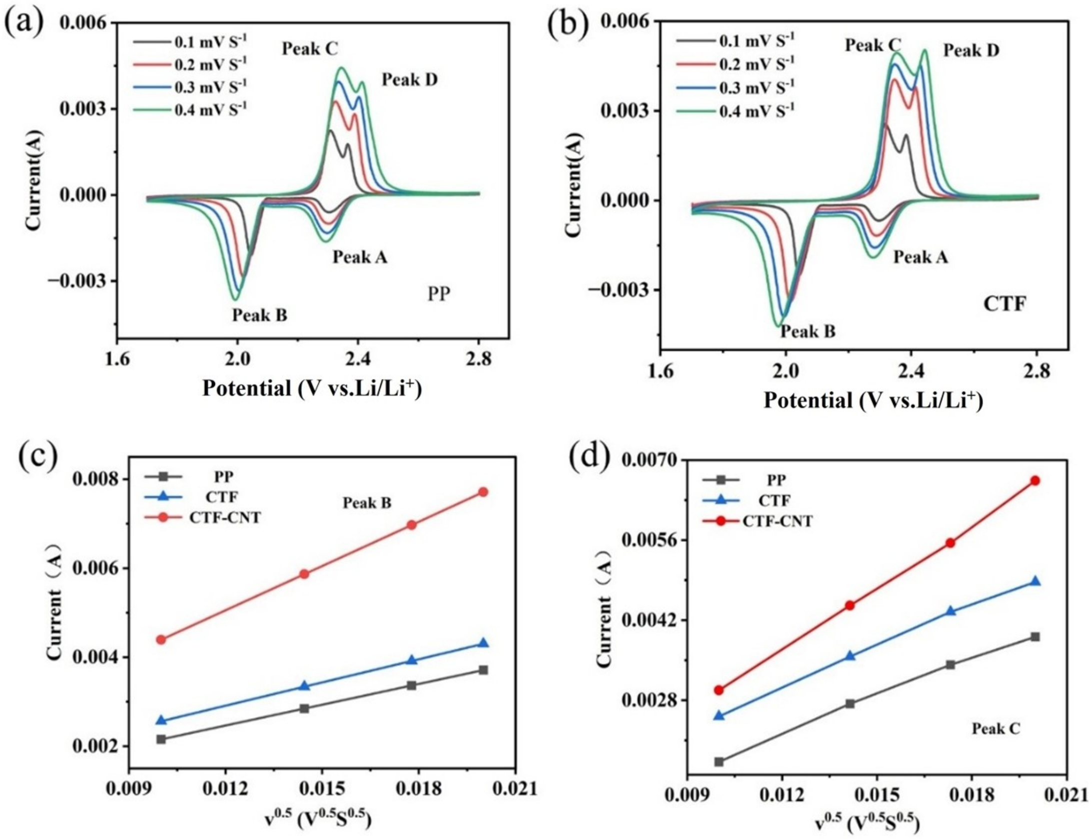


Figure S6. (a,b) CV curves of PP and CTF separators at scan rates of 0.1, 0.2, 0.3, and 0.4 mV s⁻¹.(c,d) Relationship between peak current and square root of scan rate for CTF-CNT, CTF, and PP separators at different scan rates.

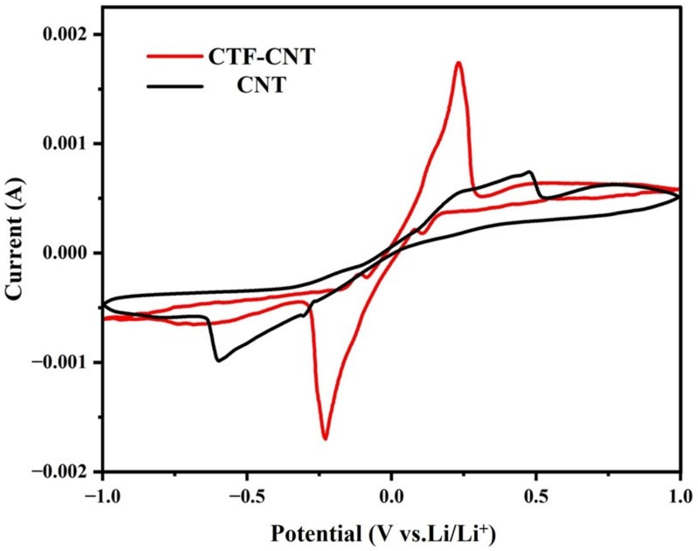


Figure S7.CV tests of CTF-CNT and CNT electrode at a scan rate of 0.1 mV s^{-1}, with a voltage range of -1 V to 1 V.

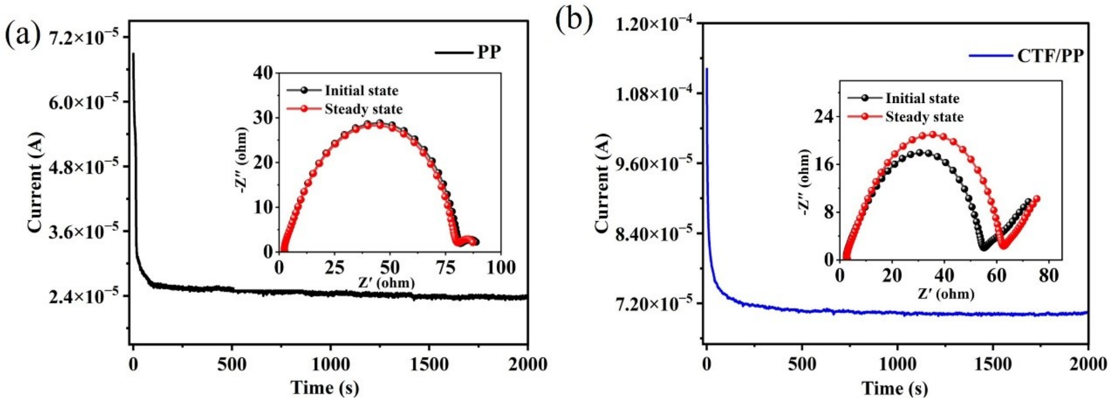


Figure S8. (a) Constant potential discharge curve of PP separator at a voltage of 10 mV.(b) Constant potential discharge curve of CTF separator at a voltage of 10 mV.

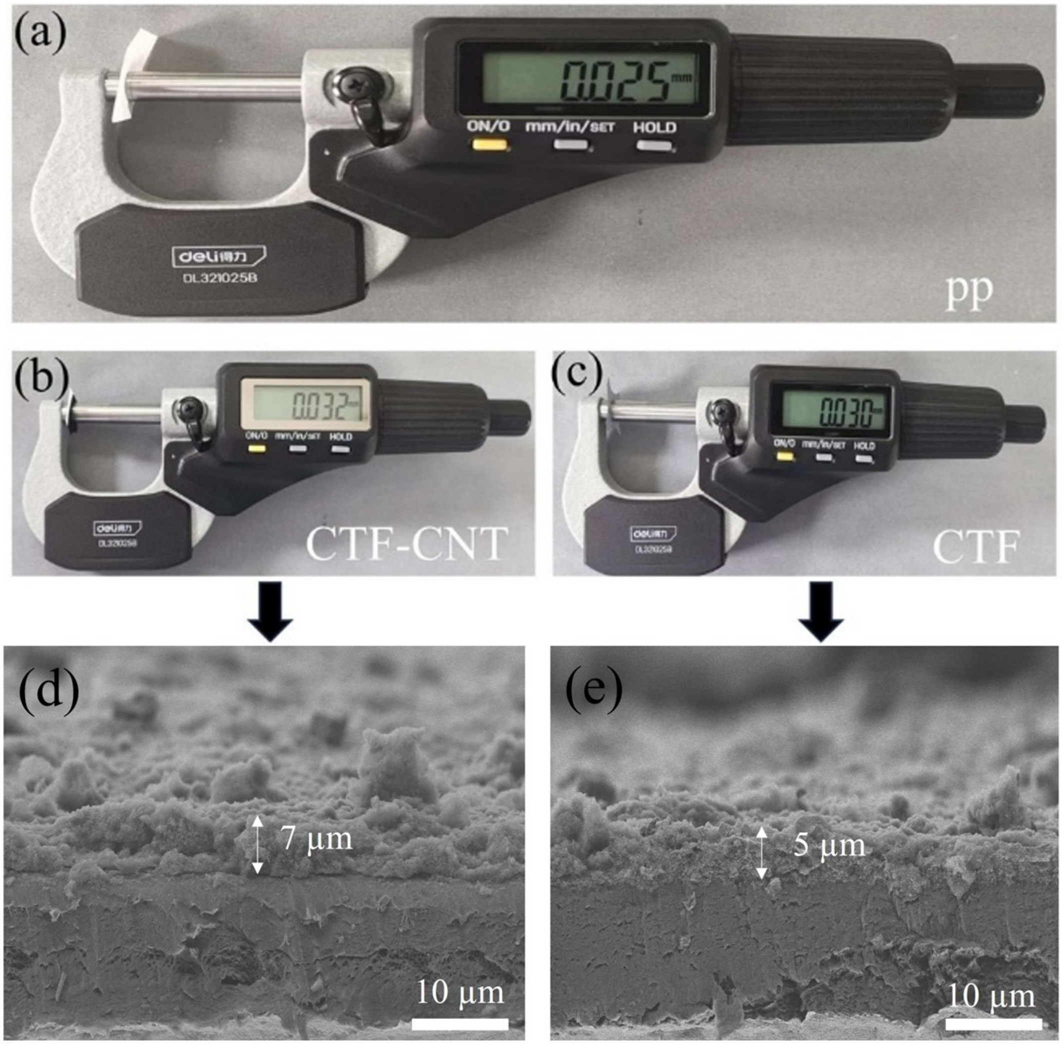


Figure S9.(a) Schematic of the thousandth measurement results for PP separator.(b) Schematic of the thousandth measurement results for CTF-CNT separator.(c) Schematic of the thousandth measurement results for CTF separator.(d) Cross-sectional schematic of the CTF-CNT separator.(e) Cross-sectional schematic of the CTF separator.

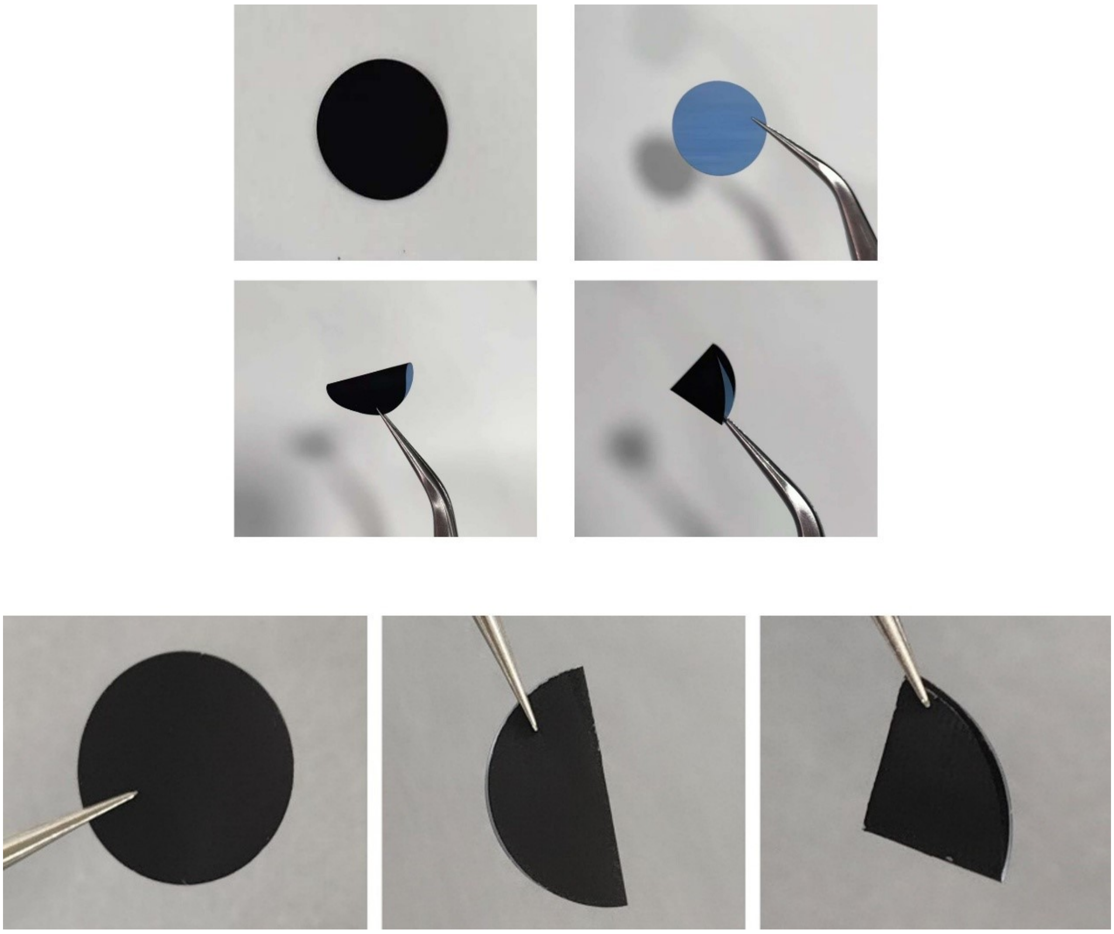


Figure S10. Photographic image showing the vacuum filtration process of CTF-CNT composite onto the separator.

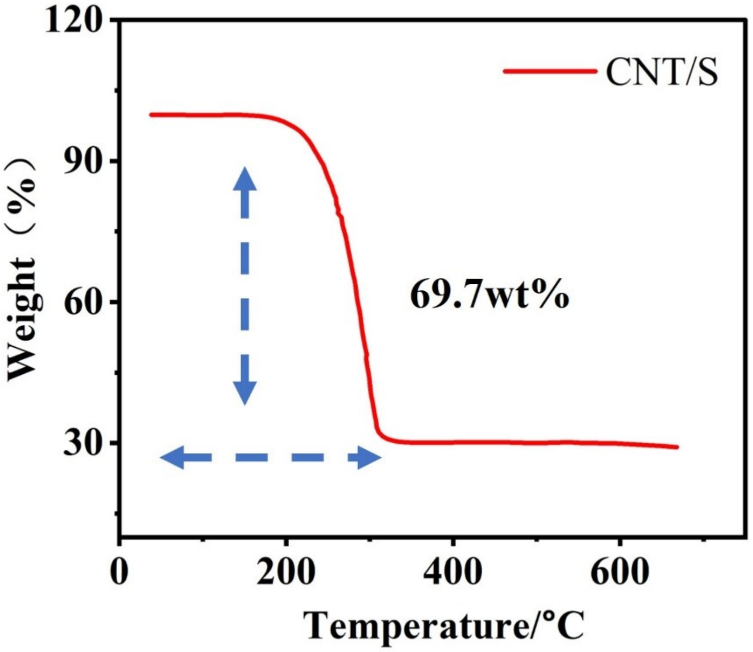


Figure S11. Thermogravimetric analysis (TGA) curve of the CNT/S composite cathode material, showing the sulfur content to be approximately 69.7 wt%.