

SO₃-COF@Al₂O₃ modified cathode electrode materials enhance the cycling ability of lithium sulfur batteries

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Section A. Material and methods

All commercially available reagents and solvents were used as received without further purification, unless otherwise noted. 1,3,5-Triformylphloroglucinol was purchased from Alfa, 2,5-diaminobenzenesulfonic was purchased from San bang Chemical. All solvents used, pure sulfur, conductive carbon black, and polyvinylidene fluoride (PVDF) were purchased from Aladdin.

Fourier transforms Infrared (FT-IR) spectra were recorded on a Perkin-Elmer model FT-IR-frontier infrared spectrometer. For all FT-IR tests, a small amount of sample can be directly mixed with potassium bromide and ground into a powder, compressed, and the pressed product can be directly tested. The solid-state UV-visible analyzer was used for Jasco V-770 spectrometer Solid-state. ¹³C cross-polarization/magic angle spinning nuclear magnetic resonance (CP/MAS NMR) analysis was conducted using AVANCEIII/WB-400. Field-emission scanning electron microscopy (FE-SEM) images were performed on a JEOL model JSM-6700 operating at an accelerating voltage of 5.0 kV. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from $2\theta = 2.5^\circ$ up to 40° with 0.02° increment. TG analysis was carried out by using a Q5000IR analyzer (TA Instruments) with an automated vertical overhead thermobalance. Before measurement, the samples were heated at a rate of $10^\circ\text{C min}^{-1}$ under a nitrogen atmosphere. X-ray photoelectron spectra (XPS) were recorded on an ESCALAB250Xielectron spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA). Nitrogen sorption isotherms were measured at 77 K with Bel Japan Inc. Model BELSORP-max analyzer. Before measurement, the samples were degassed in vacuum at 120°C for more than 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume. The nonlocal density functional theory (NLDFT) method was applied for the estimation of pore size and pore size distribution. Before measurement, the samples were also degassed in vacuum at 120°C for more than 10 h. Evaluate the wettability of the membrane by measuring the contact angle between the electrolyte and the membrane at room temperature using a contact

angle measurement system (SL200 KB, Kino Industry, USA). All processes were carried out in an Ar-filled glovebox ($\text{H}_2\text{O} < 0.1$ ppm, $\text{O}_2 < 0.1$ ppm). The battery test system (LANHE CT2001A, Wuhan LAND Electronics Co.) was employed to evaluate the cycling performance with a voltage range from 1.7 to 2.8 V. CV (0.1 mV s^{-1} , 1.7 - 2.8 V), electrochemical impedance spectra (EIS) (10^{-1} - 10^5 Hz) and I-t curves were measured on CHI 660E, Chenhua.

Section B. Synthetic procedures

Synthesis of $\text{SO}_3\text{-COF}$

Synthesis of $\text{SO}_3\text{-COF}$ was accomplished by reacting 1,3,5-triformylphloroglucinol (TFP, 21 mg, 0.1 mmol) and 2,5-diaminobenzenesulfonic acid (Pa- SO_3H , 28 mg, 0.15 mmol), 1 mL (4:1, v/v) solvent mixture of mesitylene and 1,4-dioxane with acetic acid (6 M, 0.2 mL). After sonication for 10 mins, the tube was flash frozen at 77 K using liquid nitrogen bath and degassed by three freeze-pump-freeze cycles, sealed under vacuum, and then heated at 120 °C for 72 h, which was isolated by filtration, washed with anhydrous acetone for 3 times, and vacuum drying at 80 °C to afford $\text{SO}_3\text{-COF}$. The isolated yield of red powder is 86%.

Synthesis of $\text{SO}_3\text{-COF@Al}_2\text{O}_3$

Synthesis of $\text{SO}_3\text{-COF@Al}_2\text{O}_3$ was accomplished by reacting $\theta\text{-Al}_2\text{O}_3\text{-CHO}$ (12.6 mg, 0.06 mmol), 1,3,5-triformylphloroglucinol (TFP, 21 mg, 0.1 mmol) and 2,5-diaminobenzenesulfonic acid (Pa- SO_3H , 28 mg, 0.15 mmol), 1 mL (4:1, v/v) solvent mixture of mesitylene and 1,4-dioxane with acetic acid (6 M, 0.2 mL). After sonication for 10 mins, the tube was flash frozen at 77 K using liquid nitrogen bath and degassed by three freeze-pump-freeze cycles, sealed under vacuum, and then heated at 120 °C for 72 h, which was isolated by filtration, washed with anhydrous acetone for 3 times, and vacuum drying at 80 °C to afford red powder $\text{SO}_3\text{-COF@Al}_2\text{O}_3$, the isolated yield is 84%.

Section C. Preparation of cathode and its assembly for lithium-sulfur batteries

Preparation of modified SO₃-COF/S, and SO₃-COF@Al₂O₃/S

Through a melting diffusion method, SO₃-COF and SO₃-COF@Al₂O₃ and elemental sulfur (mass ratio = 8:1) was quickly placed in a preheated horizontal furnace at 155 °C under an ambient atmosphere for 20 h and then cooled down to room temperature.

SO₃-COF/S, SO₃-COF@Al₂O₃/S were mixed with Super-P and polyvinylidene fluoride (PVDF) in the mass ratio of 8:1:1, and then N-methyl-2-pyrrolidone (NMP) was added, and the slurry was mixed uniformly and prepared, and then coated on the carbon aluminum foil collector, and then dried in a vacuum drying oven at 60 °C for 12 h. After drying, it was cut into 12 mm diameter wafers to prepare positive electrode wafers. (Sulfur content of 1 ~ 1.5 mg cm⁻²)

Li-S battery assembly

In a glove box filled with argon gas (O₂ < 0.01 ppm, H₂O < 0.01 ppm), assemble in the following order: a. Put in the cathode shell; b. Put in the cathode pole piece; c. Drop in 40 μL of electrolyte, which is a conventional electrolyte containing 1 M LiTFSI and 1 wt% LiNO₃ as the solute, and v (DOL): v (DME) = 1:1 as the solvent; d. put in the separator; e. put in the lithium wafers; f. put in the spacer; g. put in the shrapnel; h. put in the negative shell. The battery was encapsulated using a battery sealer, applying a pressure of about 5 MPa. The electrochemical characteristics of the battery were determined after the battery was left for 10 h. Cathode/electrolyte weight ratio: The areal sulfur loading was 1.2 mg cm⁻² and cathode/electrolyte ratio was 19 μL mg⁻¹.

Electrochemical Evaluation

The cells were galvanostatically cycled in the cut-off potential of 1.7 – 2.8 V on a Land battery tester under different C-rates. The cyclic voltammetry (CV) curves were recorded on a CHENHUA electrochemical workstation at a scanning rate of 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was also performed on a CHENHUA electrochemical workstation with a frequency range of 0.01 to 10⁶ Hz.

Section D. FT-IR of SO₃-COFs and SO₃-COF@Al₂O₃

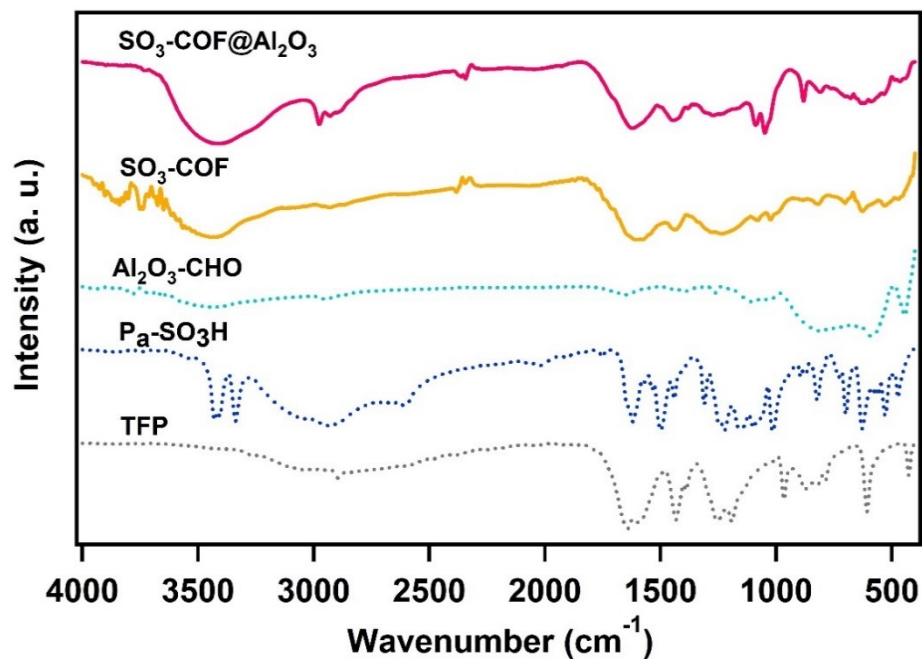


Fig. S1. Fourier transform infrared spectra of TFP, Pa-SO₃H, Al₂O₃-CHO, SO₃-COF and SO₃-COF@Al₂O₃.

Section E. ¹³C NMR spectra of SO₃-COF

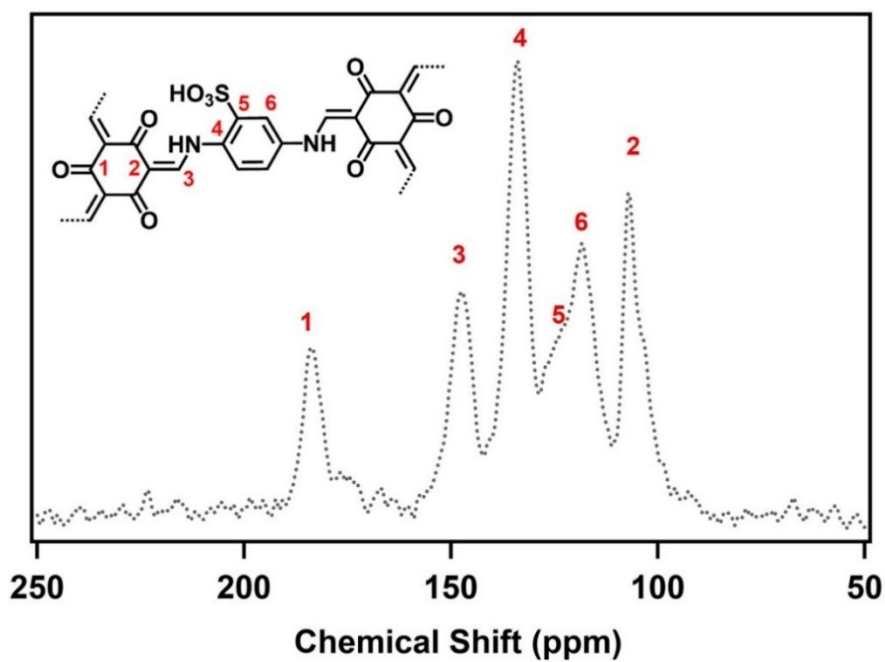


Fig. S2. Solid-state ¹³C NMR spectra of SO₃-COF.

Section F. TG

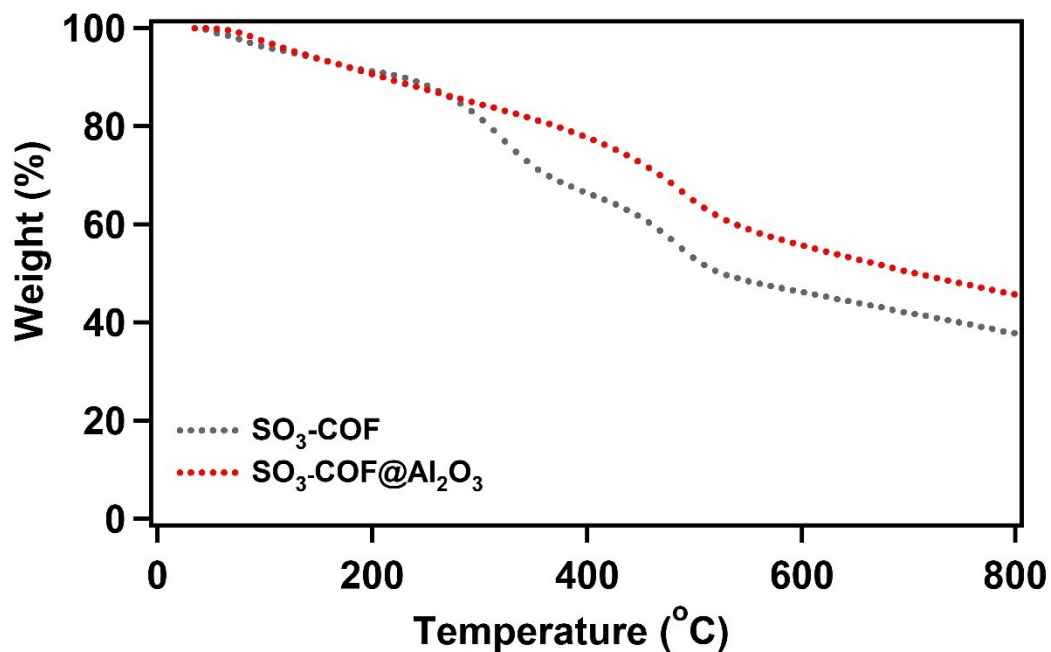


Fig. S3. The TG curves of SO₃-COF and SO₃-COF@Al₂O₃.

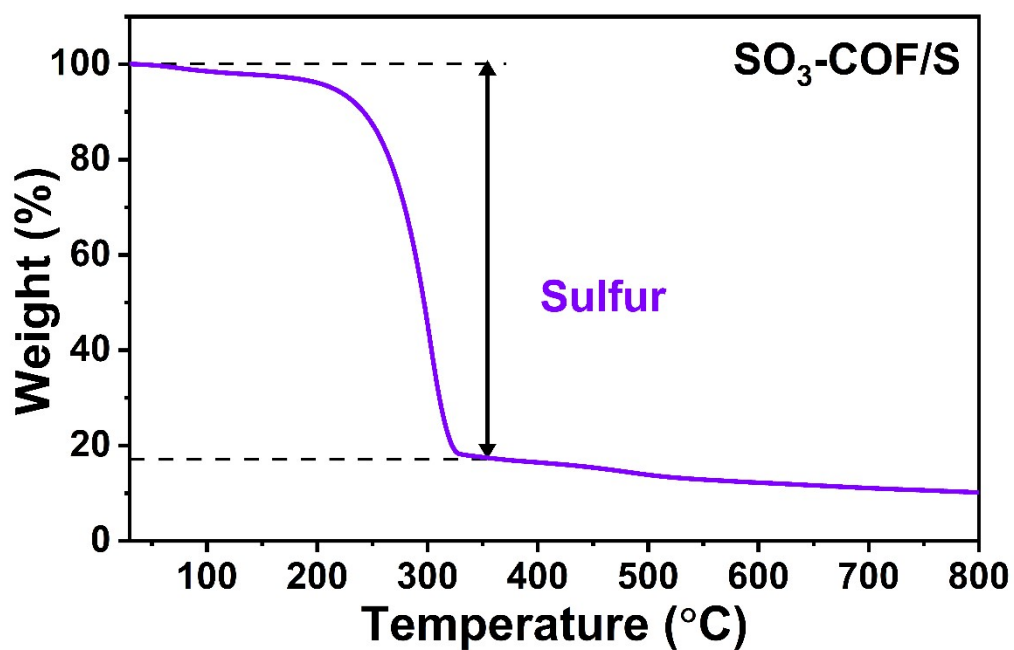


Fig. S4. The TG curves of SO₃-COF/S.

Section G. SEM

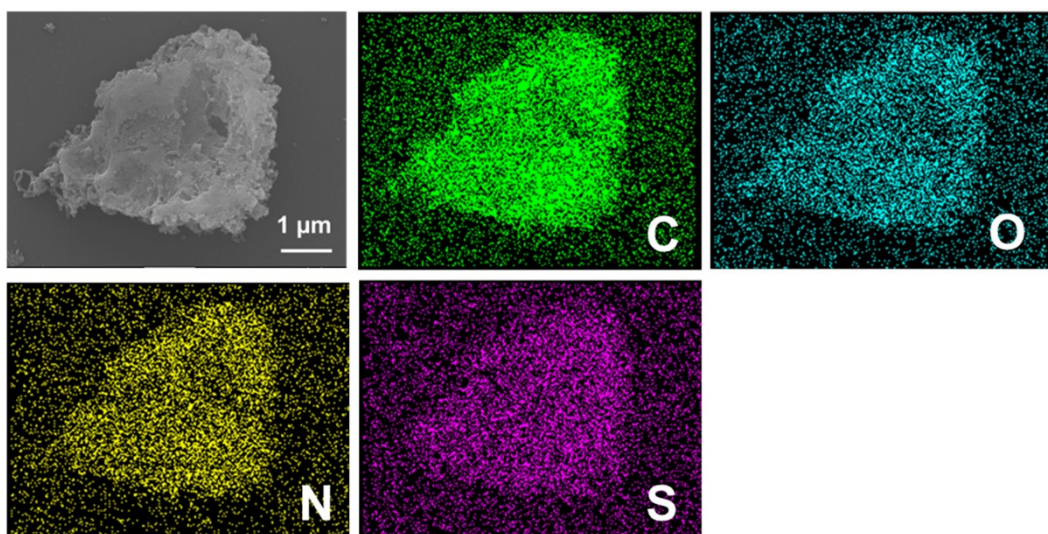


Fig. S5. EDS of SO₃-COF.

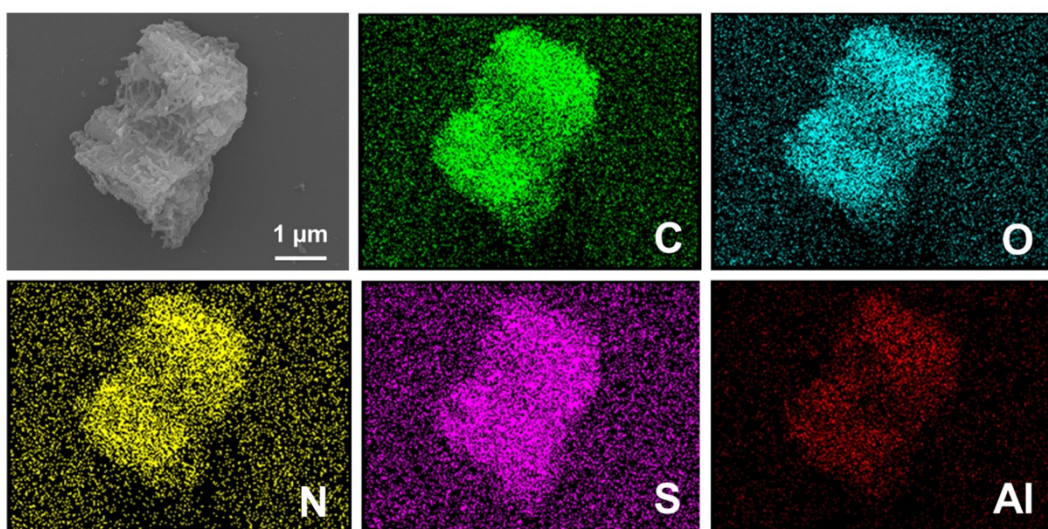


Fig. S6. EDS of SO₃-COF@Al₂O₃.

Section H. XPS

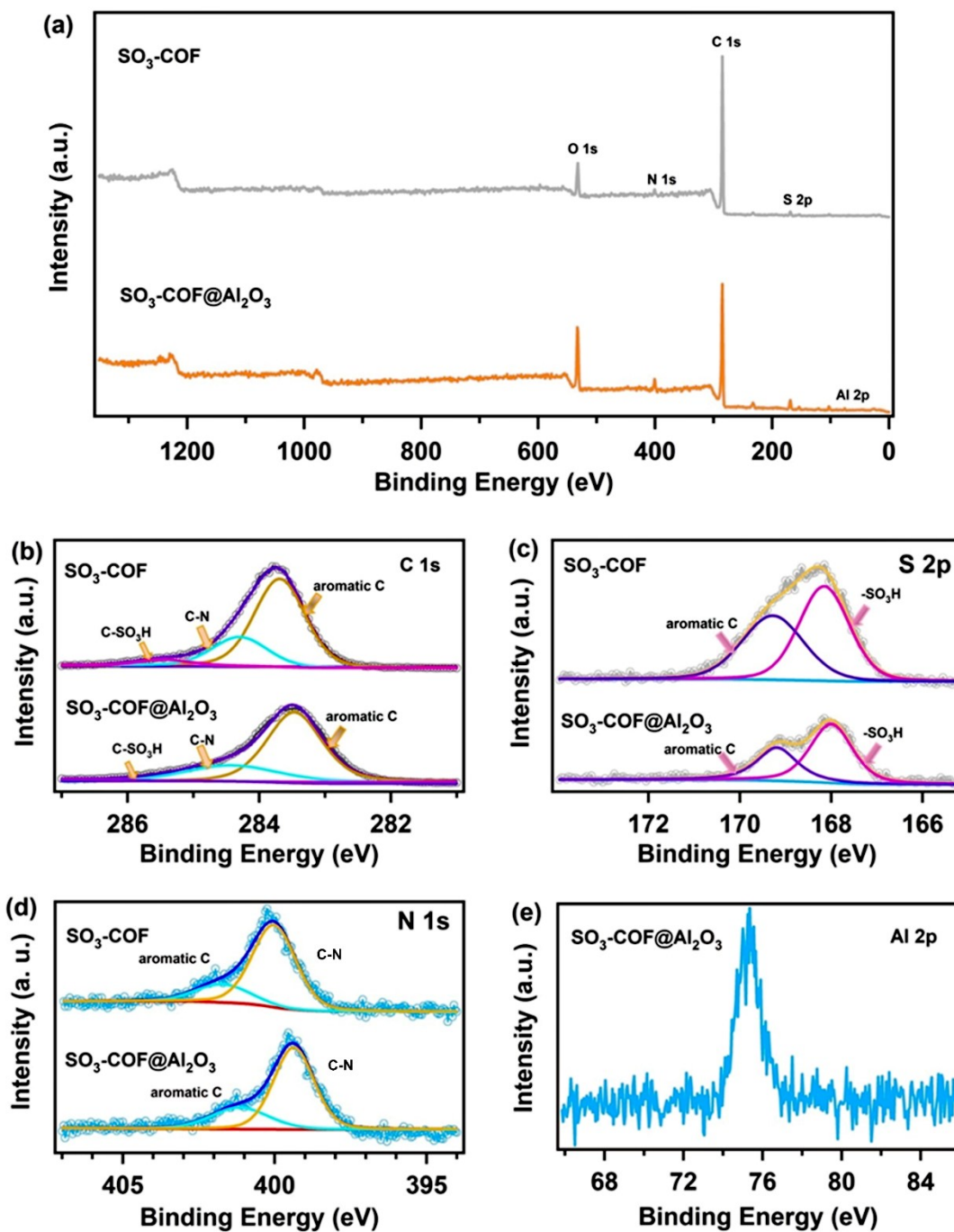


Fig. S7. (a) XPS spectra of $\text{SO}_3\text{-COF}$ and $\text{SO}_3\text{-COF@Al}_2\text{O}_3$. High-resolution XPS spectra of (b) C 1s, (c) S 2p, (d) N 1s and (e) Al 2p for $\text{SO}_3\text{-COF}$ and $\text{SO}_3\text{-COF@Al}_2\text{O}_3$.

Section I. N₂ adsorption isotherms and pore size distributions

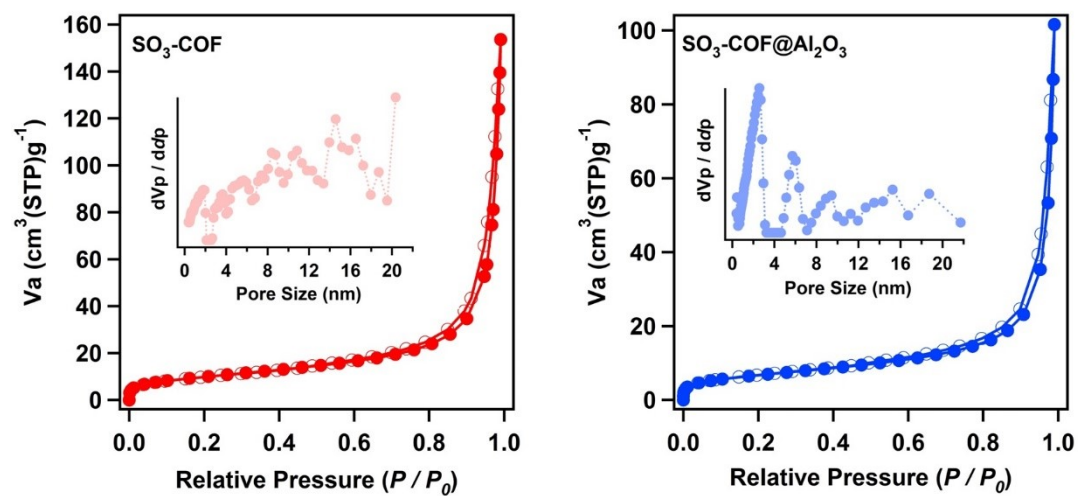


Fig. S8. N₂ adsorption isotherms of SO₃-COF (red) and SO₃-COF@Al₂O₃ (blue), and their pore size distribution curves are inserted into their respective nitrogen adsorption curves.

Section J. Mechanical property test

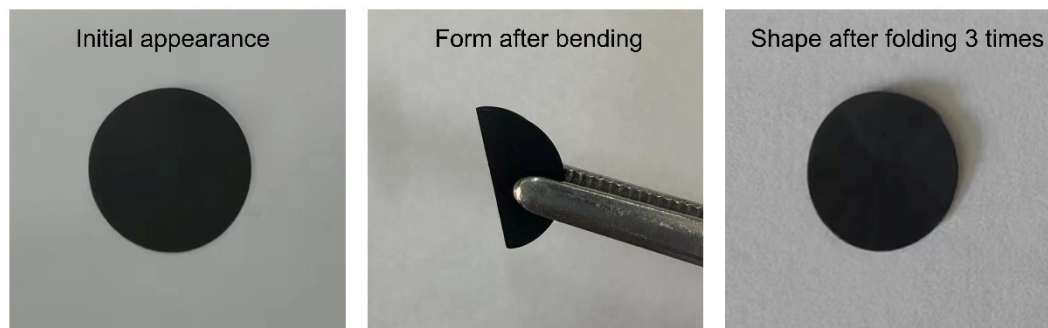


Fig. S9. Mechanical properties testing chart of SO₃-COF@Al₂O₃ composite cathode.

Section K. CV curves

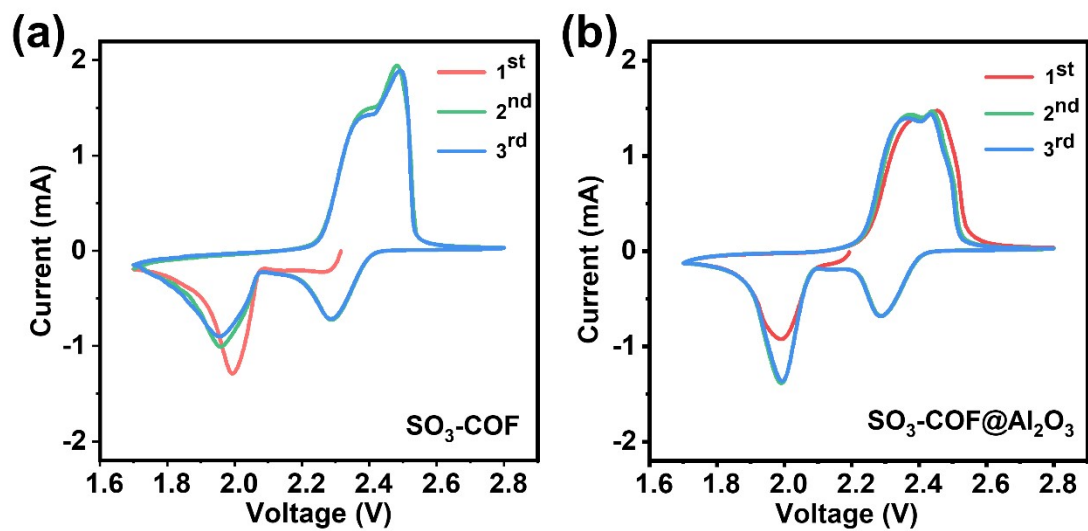


Fig. S10. CV plots of the Li-S batteries with (a) $\text{SO}_3\text{-COF}$ and (b) $\text{SO}_3\text{-COF@Al}_2\text{O}_3$ (scan rate: 0.1 mV s^{-1}).