Supporting information

Ultrathin Covalent Organic Polymer-decorated Reduced Graphene Oxide for Enhanced Sulfur Conversion Kinetics in Li–S Batteries

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- ## Materials Preparation:

Synthesis of COP

The COP was synthesized via a solvothermal method. Initially, 3 mmol of terephthalaldehyde (402.39 mg) and 2 mmol of melamine (378 mg) were dissolved in 55 mL of anhydrous ethanol under continuous stirring for 15 minutes. Subsequently, 5 mL of 6 M acetic acid were added to the mixture with stirring for an additional 5 minutes to form a homogeneous liquid. This mixture was sonicated for five minutes and heated at 180 °C for 24h. After the reaction mixture was cooled to room temperature, the precipitate was collected by centrifugation and washed multiple times with THF and ethanol, followed by drying under vacuum at 60 °C for 12 hours.

Synthesis of COP-rGO

The COP-rGO was synthesized via a solvothermal method. Initially, 3 mmol of terephthalaldehyde (402.39 mg) and 2 mmol of melamine (378 mg) were dissolved in 30 mL of anhydrous ethanol under continuous stirring for 15 minutes. Subsequently, 25 mL of graphene oxide dispersion and 5 mL of 6 M acetic acid were added to the mixture with stirring for an additional 5 minutes to form a homogeneous liquid. This mixture was sonicated for five minutes and heated at 180 °C for 24h. After the reaction mixture was cooled to room temperature, the precipitate was collected by centrifugation and washed multiple times with THF and ethanol, followed by drying under vacuum at 60 °C for 12 hours. Moreover, the van der Waals forces and π-π interactions between graphene oxide and monomers of COP, which prevent disordered aggregation of monomers, jointly promote the planar growth of COP.

Preparation of functional separator

The pre-prepared samples, carbon black (CB) and polyvinylidene fluoride (PVDF), were dispersed in 1-methyl-2-pyrrolidinone (NMP) at a mass ratio of 2:7:1 to form a homogeneous slurry. This slurry was then coated onto a Celgard-2500 separator using a bar coater and dried at 60 °C for 12 hours, resulting in a functional separator.

Preparation of C/S cathodes

Sulfur was loaded in CB by the conventional melt-diffusion method. According to the mass ratio of 8:1, mixture of CB and sulfur was heated at 155 °C for 10 h to obtain C/B powder. The C/S cathode was fabricated by mixing the C/B powder with PVDF binder in a mass ratio of 9:1 in NMP to form a slurry, which was subsequently coated onto aluminum foil and dried in vacuum at 60 °C for over 12 hours to form the cathode.

Synthesis of Li_2S_8 electrolyte

0.5 mol L^{-1} Li_2S_8 electrolyte was prepared by dissolving the sulfur and Li_2S in special electrolyte (0.5M LiTFSI, 0.15 M LiNO3 in TETRAGLYME=100 Vol%) with a molar ratio of 7:1 and stirring for 24 hours at 55 °C.

- ## Methods:

Characterizations

X-ray powder diffraction (XRD) patterns were acquired using a Bruker D8 Advance diffractometer with Cu Kα radiation (40 kV, 40 mA). Raman spectra were collected on a WITec alpha300 Via confocal Raman system with a 532 nm laser over the range of 100–2000 cm^{-1}. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Perkin-Elmer PHI 5000C ESCA system equipped with an Al Kα source operating at 250 W. Transmission electron microscopy (TEM) was performed using a JEM-ARM200F microscope and field emission scanning electron microscopy (FE-SEM) was carried out on a ZEISS ULTRA-55 instrument.

Symmetrical cell assembly and measurements

The COP-rGO, COP and rGO were loaded on carbon cloth (CC) as the electrodes in symmetrical cells, respectively. For comparison, the symmetrical cells assembled with CC were also prepared. The cyclic voltammetry (CV) curves were performed to evaluate the catalytic effect of the symmetrical cells on the Autolab 302N electrochemical working station at the voltage range of −1.0 to 1.0 V. In addition, the electrochemical impedance spectroscopy (EIS) spectra were also collected by Autolab 302N electrochemical working station with 0.01~106 Hz. The Tafel plots were obtained by CHI 760E electrochemical working station with the voltage range of −2.0 V to +2.0 V.

Lithium diffusivity

The lithium diffusivity was calculated according to the Randles-Sevcik equation:

$$I_p = (2.69 \times 10^5) n^{1.5} A D_{Li^+}^{0.5} C_{Li^+} v^{0.5} \quad \text{(S1)}$$

where I_P is the peak current (A), n is the number of electrons transferred in the reaction (for lithium-sulfur battery, n=1), A is the electrode area (0.785 cm^2), D_{Li^+} is the lithium-ion diffusion coefficient ($cm^2\ s^{-1}$), C_{Li^+} is the concentration of Li^+ in the electrolyte (1 mol L^{-1}), and v is the sweeping rate (V s^{-1}).

Li_2S nucleation

CR2032 coin cells were assembled with Li foil as the anode and COP-rGO, COP, and rGO as the cathode, respectively. For each cell, 20 μL of Li_2S_8 electrolyte was injected into the cathode side, while 20 μL of conventional electrolyte was injected into the anode side. The discharge process was initiated with a constant current step at 112 μA until the voltage reached 2.06 V, followed by a constant voltage hold at 2.05 V until the current decreased to the cut-off value of 0.01 mA. The current-time curve was recorded throughout the process, and the nucleation capacity of lithium sulfide was subsequently determined through fitting analysis.

Cell assembly and electrochemical measurements

The assembly of cells should be carried out in an argon glove box, ensuring that the water and oxygen content in the glove box is less than 1 ppm. Cells were assembled using a C/S cathode, a lithium foil as the anode, a DME/DOL (1:1, v/v) mixed solution containing 1 M LiTFSI and 0.1M $LiNO_3$ as the electrolyte, and a functional separator for galvanostatic charge-

discharge (GCD), CV, and EIS testing. The voltage window for GCD testing is 1.8~2.7 V. The voltage range for CV testing is 1.8~2.7 V, with scan speeds including 0.1, 0.2, 0.3, 0.4, 0.5 mV s^{-1}. The conditions for EIS testing are 0.01~100000Hz and 5 mV.

- **Supporting Figures:**

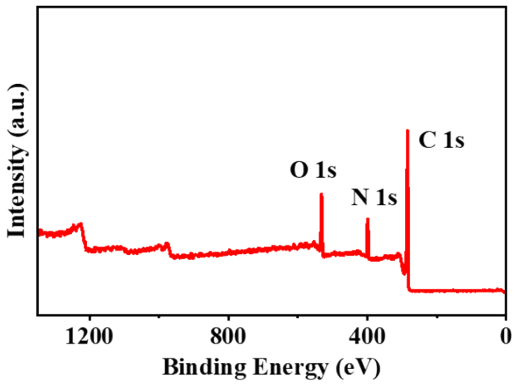

Figure S1. XPS survey spectrum of COP-rGO.

Figure S2. Digital images of COP-rGO modified separator.

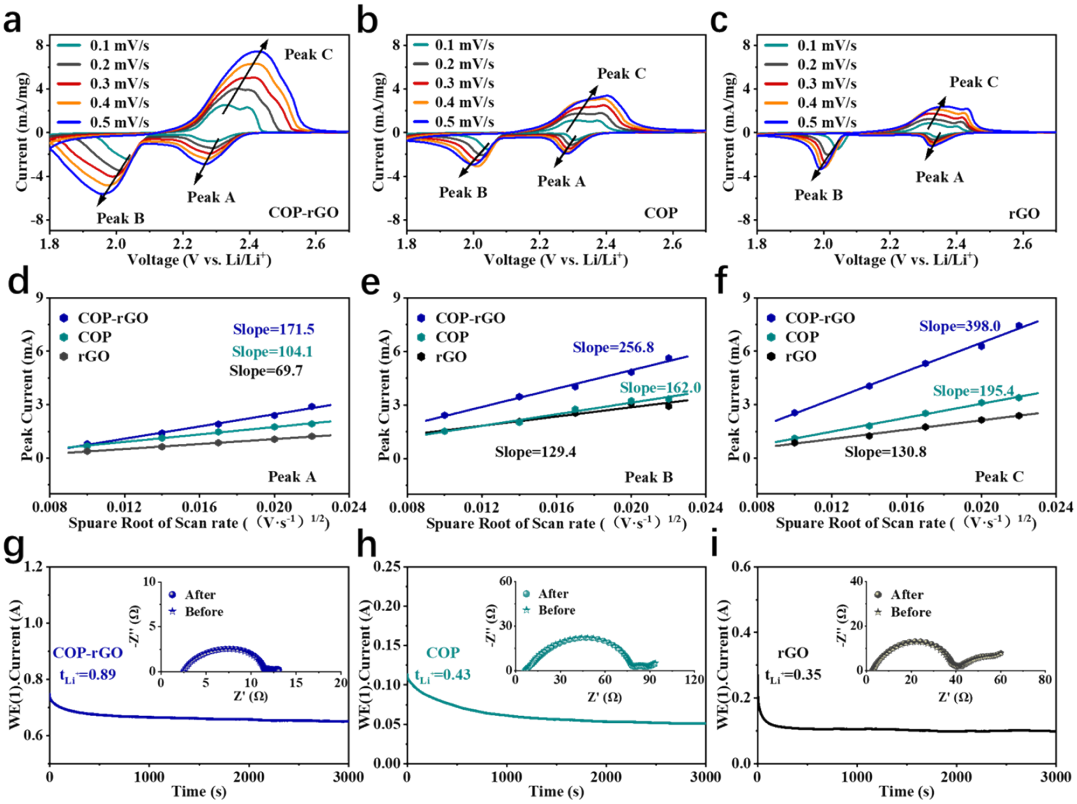

Figure S3. a-c) CV curves of the different cells at various scan rates. d-f) Curves of the peak current versus the square root of the potential scan rate of the cells with different separators. g-i) Li^+ transference number of COP-rGO, COP and rGO-based separator.

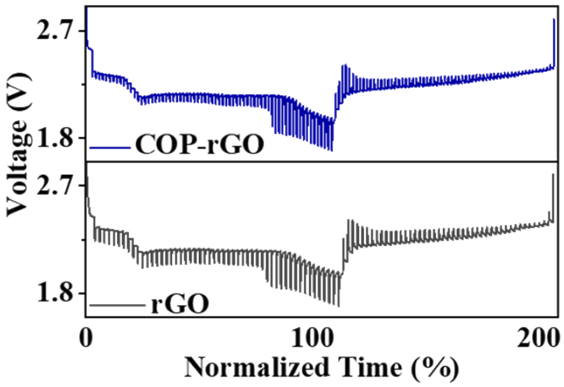

Figure S4. GITT curves of Li–S batteries with different catalyst systems.

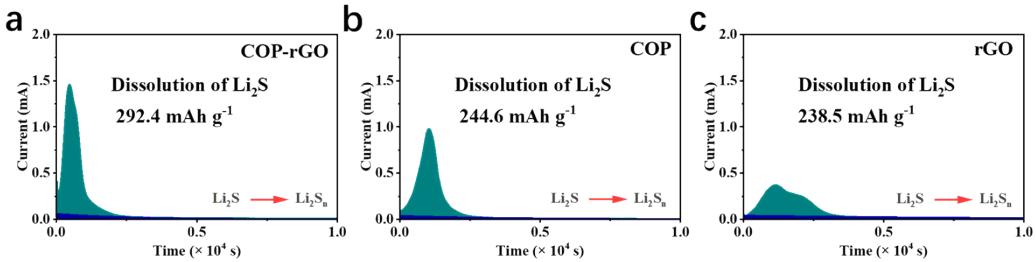

Figure S5. The Li_2S dissolution test of a) COP-rGO, b) COP, c) rGO.

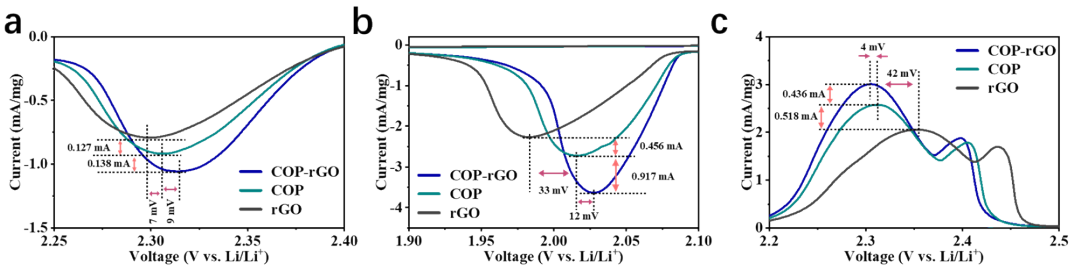

Figure S6. The Magnified CV curves: (a) Peak A, (b) Peak B and (c) Peak C.

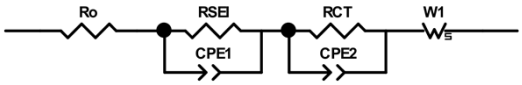

Figure S7. Equivalent circuit model of Li-S batteries.

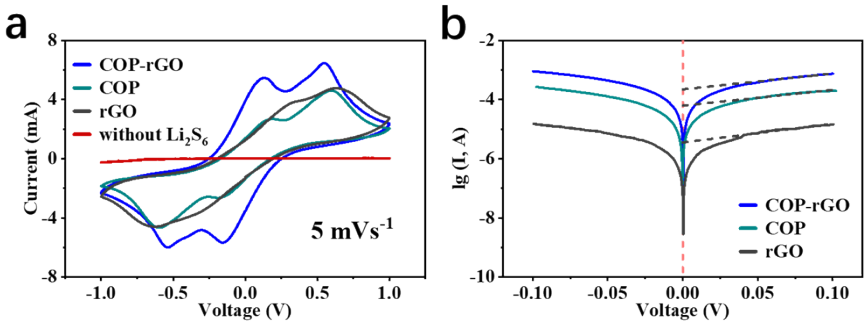

Figure S8. a) CV curves and b) tafel curves of symmetric cells with different catalyst.

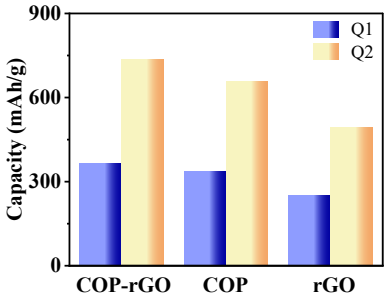

Figure S9. Capacity contributed by different discharge stages.

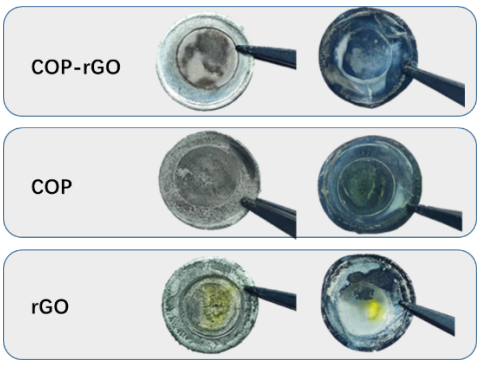

Figure S10. Images of Li sheets and separators disassembled from the cells after cycling.

Table S1. Lithium-ion diffusion rates (D_{Li^+}) of Li-S batteries paired with different separators.

D_{Li^+}	**Peak A** ($cm^2\ s^{-1}$)	**Peak B** ($cm^2\ s^{-1}$)	**Peak C** ($cm^2\ s^{-1}$)
COP-rGO	$6.558*10^{-13}$	$1.479*10^{-12}$	$1.552*10^{-12}$
COP	$2.430*10^{-13}$	$5.885*10^{-13}$	$8.563*10^{-13}$
rGO	$1.089*10^{-13}$	$3.755*10^{-13}$	$3.837*10^{-13}$