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RESEARCH ARTICLE

Co_4S_3/Co_9S_8@rGO as catalyst to enhance the redox kinetics of polysulfide conversion for Li-S batteries

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Supporting Information

Experimental section

Preparation of S@cobalt sulfides@rGO composite

The precursor of cobalt sulfides@rGO was prepared as the precursor of Co_4S_3/Co_9S_8@rGO a thermal method and then was heated at 200°C for 2 h to obtained the cobalt sulfides@rGO. Finally, cobalt sulfides@rGO was uniformly mixed with S powder (sulfur content: 70 wt%; cobalt sulfides@rGO content: 30 wt%), and then was kept in Teflon-lined stainless steel autoclave and treated under 155°C for 12 h to prepare the S@cobalt sulfides@rGO composite.

Preparation of Li_2S_6 and Li_2S_8 solutions

The Li_2S_6 solution (0.2 M) was prepared through the stoichiometric ratio of Li_2S and sulfur (S_8) (the molar ratio between Li_2S and S was 1:5), which were dissolved in the electrolyte of DME and DOL (the volume ratio was 1:1) with the magnetic stirring at 25 ℃ for 36 h. The preparation process of Li_2S_8 solution (80 mM) was similar to the Li_2S_6 solution (the molar ratio between Li_2S and S was 1:7) [1].

The symmetric battery and catalytic performance of catalysts

Firstly, the Co_4S_3/Co_9S_8@rGO (or rGO, accounting for 90 wt%) and polyvinylidene fluoride (PVDF, accounting for 10 wt%) were mixed in N-methylpyrrolidone (NMP) through ball milling for 2h (200 r/min). Then, the mixture was coated onto the surface of carbon paper, which served as the current collector. After drying at 80°C for 12 h, the Co_4S_3/Co_9S_8@rGO@carbon paper (or rGO@carbon paper) electrodes were obtained. The same mixture above-mentioned was also coated onto both sides of a PP separator, and after drying at 70°C for 24 hours, a Co_4S_3/Co_9S_8@rGO interlayer was produced. In the symmetric battery, the electrode materials of the working electrode and the counter electrode were identical (*i.e.* Co_4S_3/Co_9S_8@rGO@carbon paper), with separators being polypropylene (PP) and the Co_4S_3/Co_9S_8@rGO interlayer, respectively. It should be noted that the Co_4S_3/Co_9S_8@rGO@carbon paper (or rGO@carbon paper) electrode was abbreviated as the Co_4S_3/Co_9S_8@rGO electrode in the literature [1,2]. The electrolyte consisted of 80 μL of Li_2S_6 solution (0.2 M) and 20 μL of regular electrolyte without Li_2S_6, which were evenly dispensed onto the working electrode and the counter electrode. To investigate the redox reactions of polysulfides in the symmetric battery, cyclic voltammetry (CV) was performed with a voltage range of -1.5 V to 1.5 V at a scan rate of 2 mV/s.

The nucleation of Li_2S

The stoichiometric ratio of Co_4S_3/Co_9S_8@rGO (or rGO, accounting for 90 wt%) and polyvinylidene fluoride (PVDF, accounting for 10 wt%) was mixed in N-methylpyrrolidone (NMP) through ball milling for 2h (200 r/min). The mixture was then coated onto the surface of carbon paper. After drying the carbon paper at 80℃ for 12 h, Co_4S_3/Co_9S_8@rGO (or rGO) served as the cathode. The same mixture above-mentioned was coated onto both sides of a PP separator, and after drying at 70℃ for 24 h, the Co_4S_3/Co_9S_8@rGO interlayer was obtained. Polypropylene (PP) and the Co_4S_3/Co_9S_8@rGO interlayer were used as separators respectively, with lithium foil as the anode, to assemble the symmetric batteries. Meanwhile, 20 μL of Li_2S_8 solution (80 mM) and 20 μL of blank electrolyte without Li_2S_8 were dropped onto the cathode and lithium anode sides, respectively [3]. To investigate the nucleation process of Li_2S, the assembled batteries were discharged at a constant current of 0.6 mA to 2.11 V, allowing Li_2S_8 to convert to Li_2S_6. After stewing 2 min, these batteries were followed by potentiostatic discharging at 2.05 V to ensure complete conversion of polysulfides into Li_2S until the current decreased to 1.0×10^{-3} mA [3].

Calculation of lithium ions diffusion coefficient

The calculation is carried out by Eq. S1 as follows:

Eq. S1: $D_{Li+} = \frac{I^2}{(2.69\times10^5)^2 A^2 n^3 C_{Li+}^2 v}$

where A is the area of the electrode surface (1.13 cm^2), n is the electron number corresponding to the reaction of the lithium ions (2) and C_{Li+} is the molar concentration of Li^+ ions (1.3×10^{-3} mol cm^{-3}).

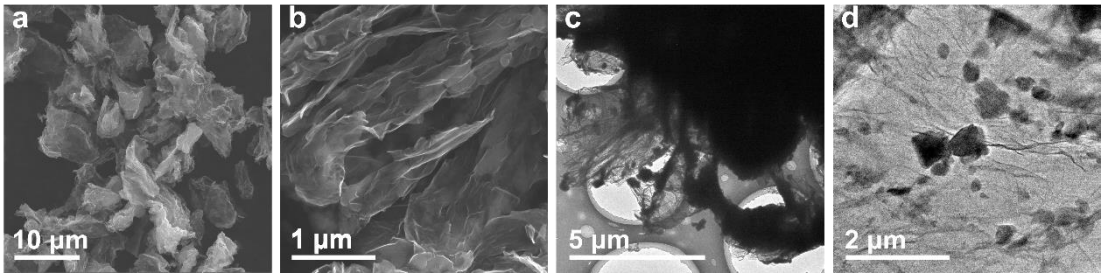


Fig. S1 (a,b) SEM images and (c,d) TEM images of the synthesized Co_4S_3/Co_9S_8@rGO.

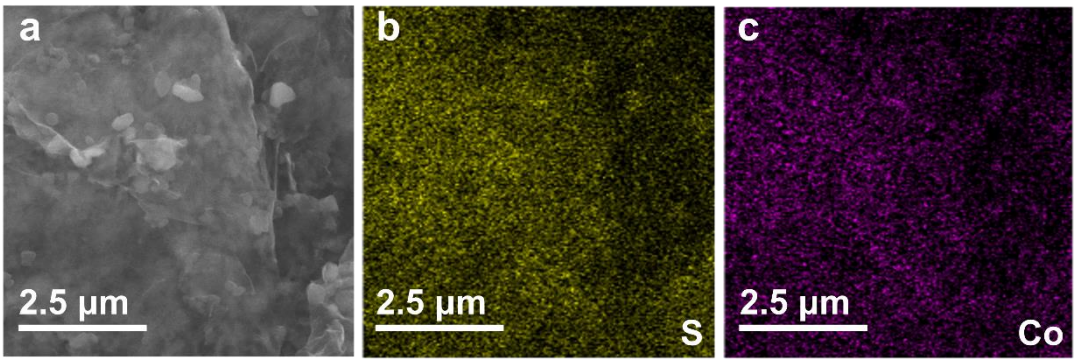


Fig. S2 (a) the SEM image of Co_4S_3/Co_9S_8@rGO for the elemental mapping images of (b) S and (c) Co.

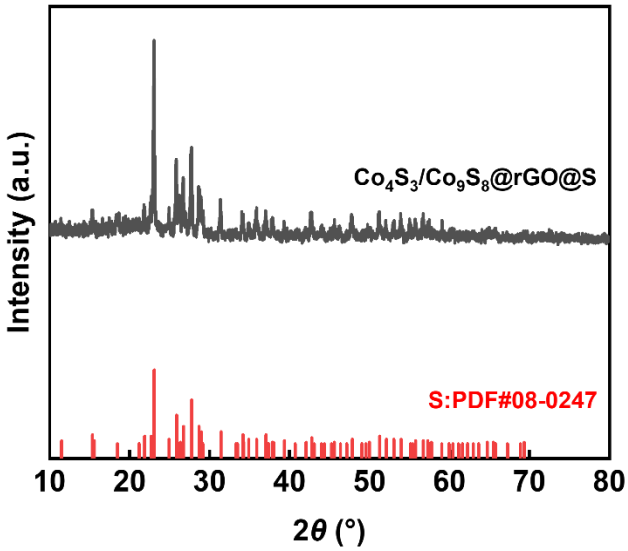


Fig. S3 The XRD of the as-prepared Co_4S_3/Co_9S_8@rGO@S (S content: 70%)..

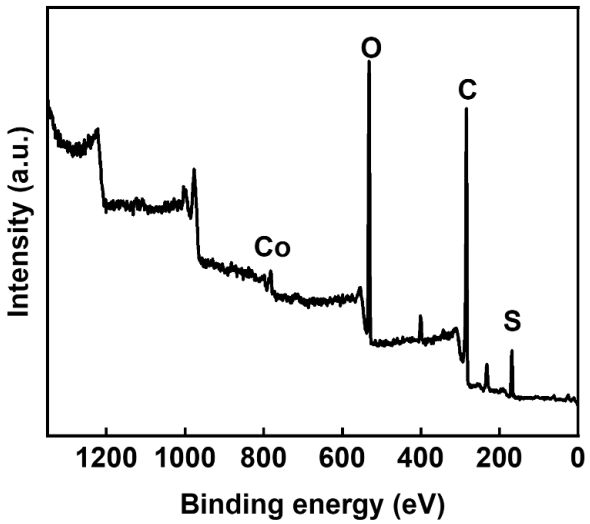


Fig. S4 The survey XPS spectra of Co_4S_3/Co_9S_8@rGO.

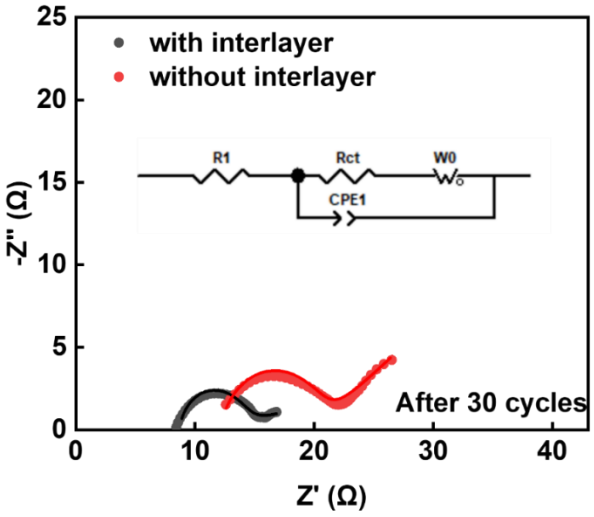


Fig. S5 The EIS of the electrodes with/without Co_4S_3/Co_9S_8@rGO interlayer after 30 cycles.

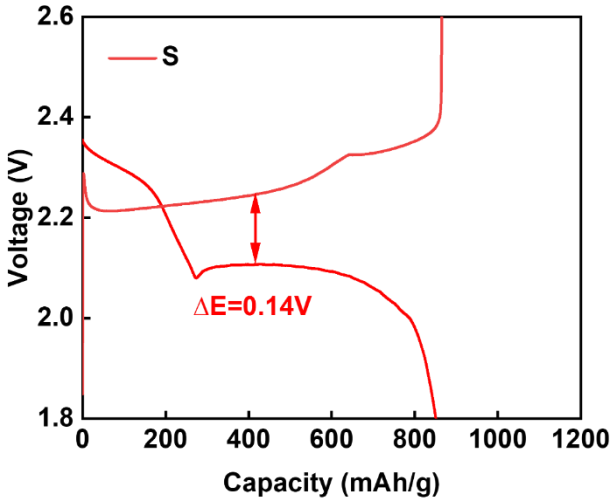


Fig. S6 The galvanostatic charge-discharge curves at 0.1 C for the sulfur electrodes.

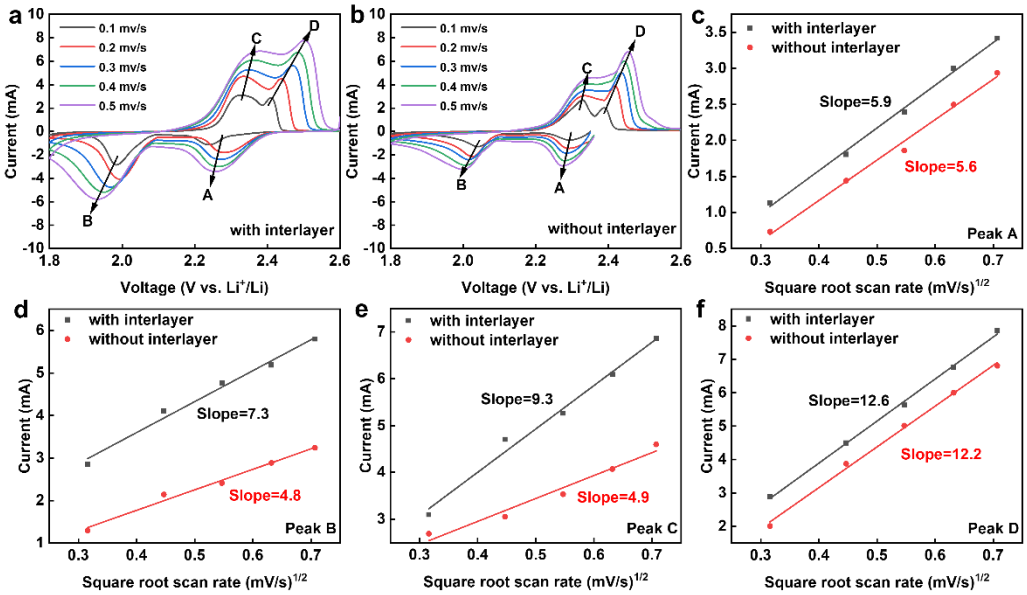


Fig. S7 The CV curves of the Li−S batteries with/without interlayer at various scan rates. (a) with interlayer and (b) without interlayer. Plots of CV peak current of peak A (c), peak B (d), peak C (e) and peak D (f) vs. square root of the scan rates.

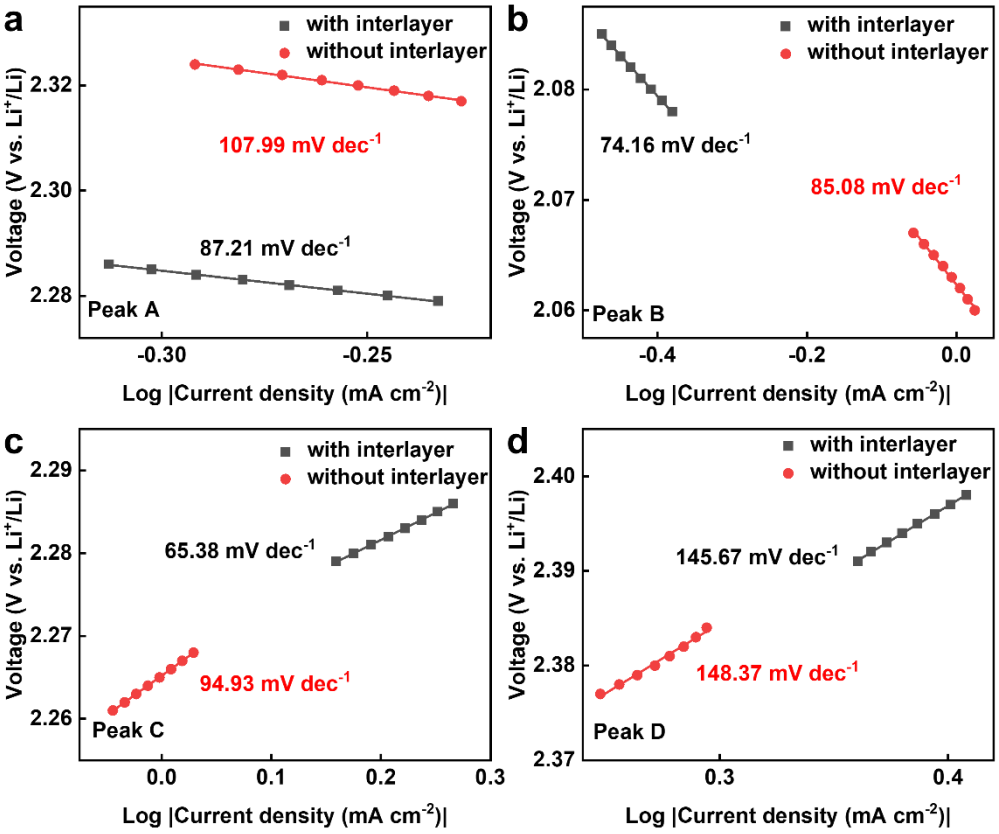


Fig. S8 Tafel plots calculated from CV results for with/without interlayer.

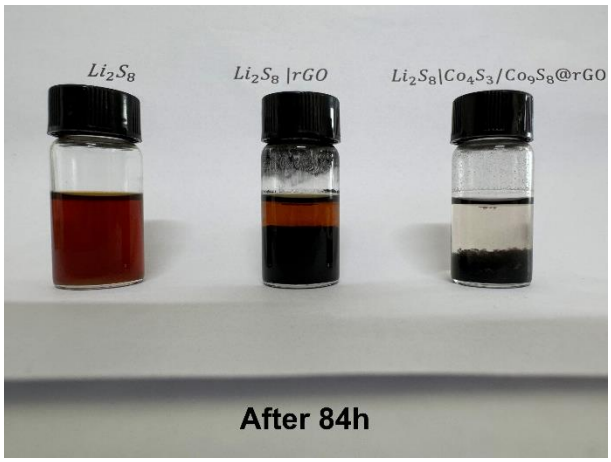


Fig. S9 Visual discrimination experiment of a Li_2S_8 solution containing blank electrolyte, rGO and Co_4S_3/Co_9S_8@rGO left to stand for 84 h.

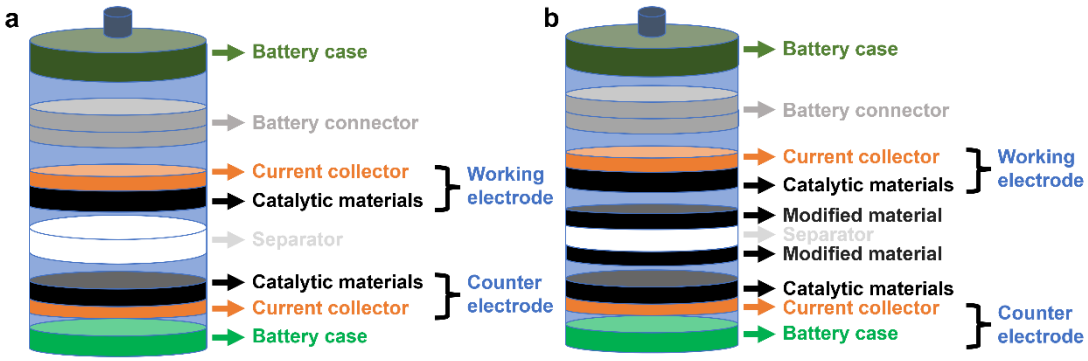


Fig. S10 The scheme of symmetric battery (a) without interlayer and (b) with interlayer.

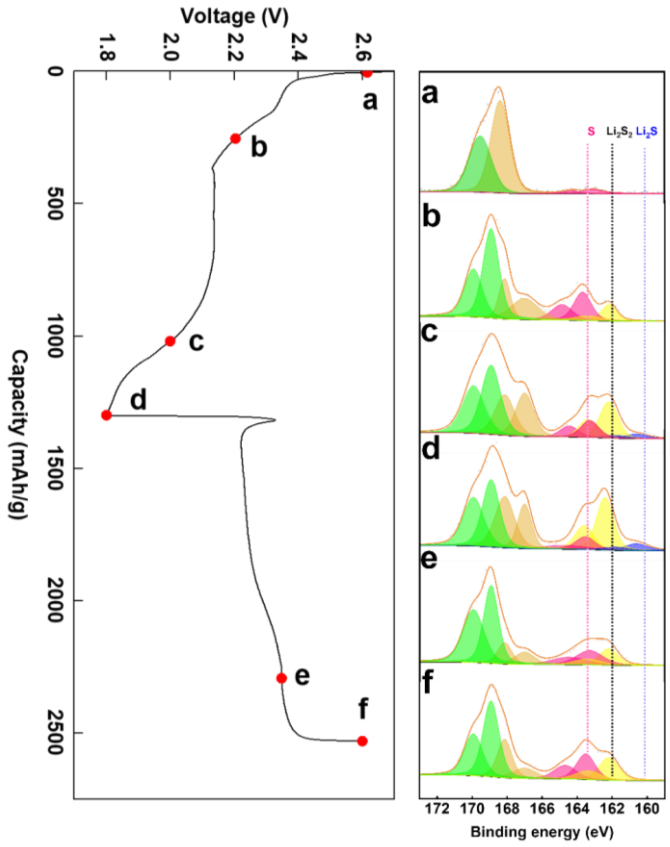


Fig. S11 Ex situ XPS spectra of S@Co_4S_3/Co_9S_8@rGO cathode at different voltage states (discharged/charge rate is 0.1 C).

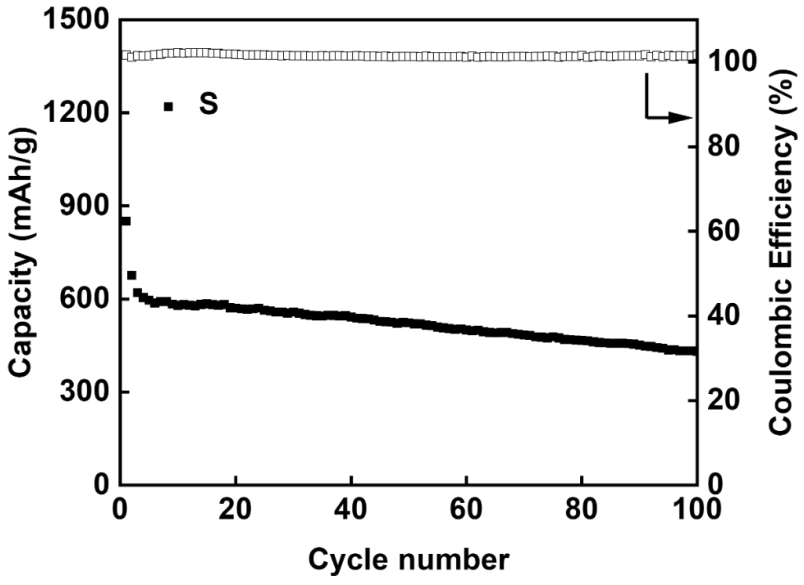


Fig. S12 The cycle performance at 0.2C (activated at 0.1C in the 1st cycle) of sulfur electrode.

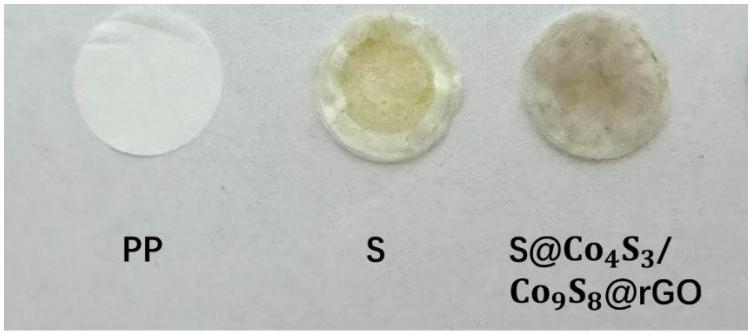


Fig. S13 Morphology characterization of separators after 200 cycles.

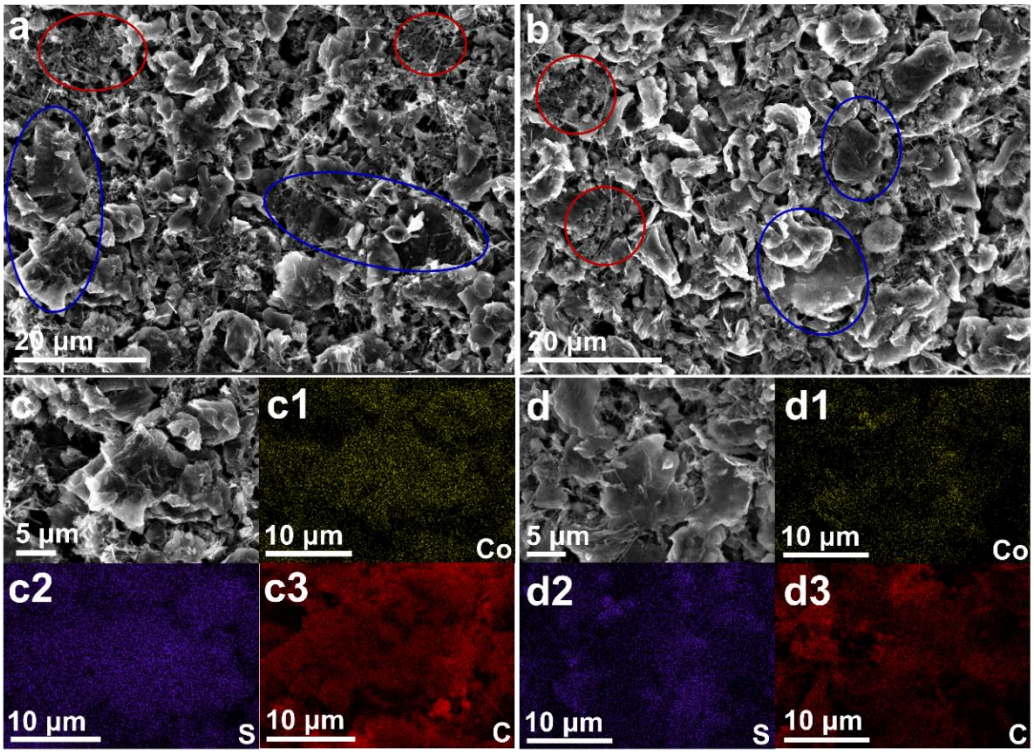


Fig. S14 The SEM images of electrodes with (a) and without (b) interlayer. The SEM images (c) and the corresponding elemental mapping images of (c1) Co, (c2) S and (c3) C in the electrode with interlayer. The SEM images (d) and the corresponding elemental mapping images of (d1) Co, (d2) S and (d3) C in the electrode without interlayer.

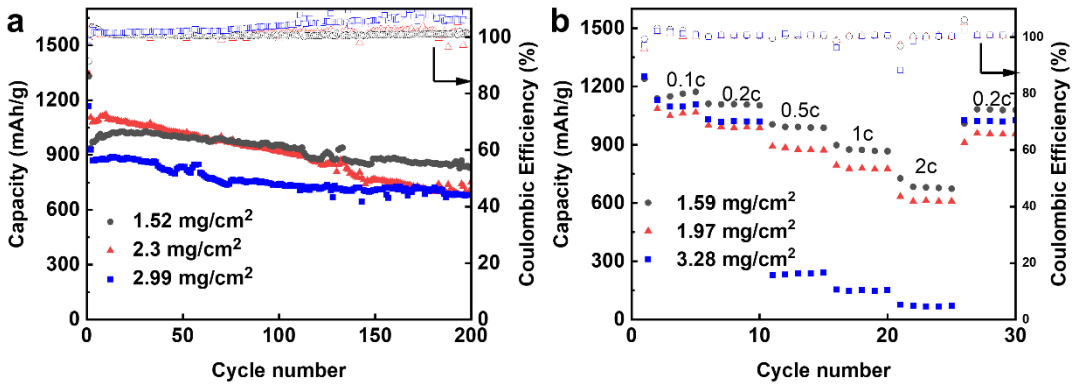


Fig. S15 The cycle performance (a) at 0.2C (activated at 0.1C in the 1st cycle) and (b) rate capability of S@Co_4S_3/Co_9S_8@rGO electrode with high sulfur loading.

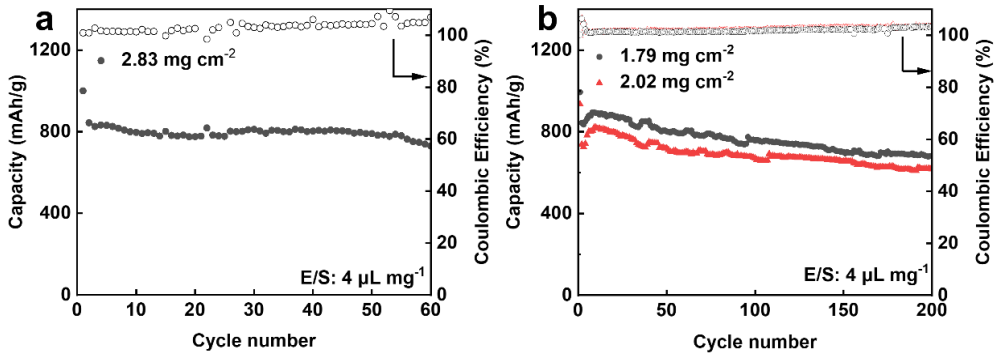


Fig. S16 The cycling performance under lean electrolyte (E/S: 4 μL mg^{-1}) at 0.2C (activated at 0.1C in the 1st cycle) (a,b) S@Co_4S_3/Co_9S_8@rGO electrodes with different sulfur loading.

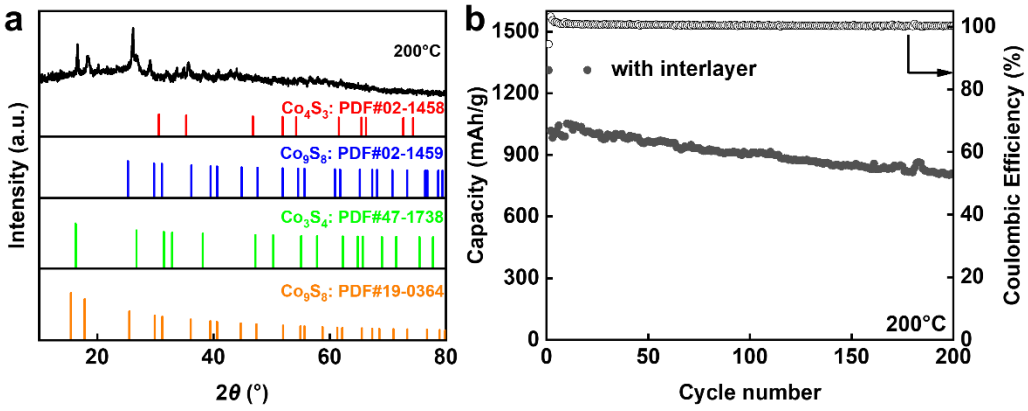


Fig. S17 The XRD of cobalt sulfides@rGO and the cycling performance at 0.2C (activated at 0.1C in the 1st cycle) of S@cobalt sulfides@rGO.

Table S1 Electrochemical impedance fitted parameters.

	R_s (Ω)	R_{ct} (Ω)
Fresh cell with interlayer	2.28	22.56
Fresh cell without interlayer	2.33	34.9
After 30 cycles with interlayer	8.43	7.39
After 30 cycles without interlayer	12.59	9.47

Table S2 Lithium ions diffusion coefficient.

	D_{Li+} (cm^2 s^{-1}) with interlayer	D_{Li+} (cm^2 s^{-1}) without interlayer
Peak A	27.87×10^{-6}	25.1×10^{-6}
Peak B	42.66×10^{-6}	18.44×10^{-6}
Peak C	69.24×10^{-6}	19.22×10^{-6}
Peak D	127.09×10^{-6}	119.15×10^{-6}

Table S3 Electrochemical performances summaries of heterostructures based LSB.

Sample	S loading	Initial	Reversilble	Decay	Ref.

	(mg/cm^{-2})	Capacity ($mAh\ g^{-1}$)	Capacity ($mAh\ g^{-1}$/Cycles/C)	rate (%)	
NiS_2-MoS_2@MXene	1.2	926.9	575.6/900/1	0.042	[4]
GeS_2-NiS_2/rGO	N / A	878.5	474.6/1000/2	0.046	[5]
MoS_2@C	N / A	711.5	392.1/1000/2	0.055	[6]
NiS-$NiCo_2O_4$	2.2	778.1	450.6/500/1	0.084	[7]
MnO_2-ZnS	N / A	811.1	421.8/1000/2	0.048	[8]
$Co_{0.1}Fe_{0.9}S_2$	1.48	854.7	440.8/920/1	0.052	[9]
Co_4S_3/Co_9S_8@rGO	1.2	621.69	387.21/1000/2	0.038	This work

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