Supporting Information

Naturally-derived Honeycomb-like N, S-codoped Hierarchical Porous Carbon with MS₂

(M=Co, Ni) Decoration for High-performance Li-S Battery

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Fig. S1 FE-SEM images at different magnifications: (a, b) Ginkgo-nut with large spherical particles; (c, d) Nano-sized CaCO₃ template with agglomerated nanoparticles with an average size about 50 nm.



Fig. S2 Characterization results of GC: (a, b) FE-SEM images at different magnifications. It is apparent that GC shows an interconnected honeycomb-like porous structure possessing abundant internal space with void diameter ranging from 30-90 nm, matching well with the size of the CaCO₃ nanotemplates. (c, d) TEM images at different magnifications. This confirms that GC consists of homogeneous micropores and macropores with an average porous size of 90 nm. (e-g) the corresponding elemental mappings of C, S and N, verifying the existence and uniform distribution of C, N and S elements in GC, as well as the *in-situ* doping of N and S in GC. Such a unique porous architecture with N and S doping not only provides enough internal voids to relieve the volume expansion of sulfur during the cycling, but also creates enough surface active sites and abundant polar locations to confine and trap the polysulfides and graft the MS₂ nanoparticles.¹ Furthermore, the numerous interconnected conductive networks not only are beneficial for the fast charge transport, but also provide the sufficient active sites for increased sulfur loading and better sulfur utilization.¹



Fig. S3 EDS results of (a) GC and (b) GC-CoS₂. The atomic contents of the doping N and S elements in the pristine GC are 0.62 % and 0.68 %, respectively.



Fig. S4 (a-b) SEM images of GC-NiS₂ at different magnifications, (e-h) corresponding EDX elemental mapping images of C, N, Ni and S elements.



Fig. S5 XRD patterns of (a) GC and (b) GC-NiS₂, (c) N_2 adsorption and desorption isotherms of GC and the corresponding pore size distribution (the inset).



Fig. S6 Thermogravimetrical analysis of (a) GC under air atmosphere and (b) GC-CoS₂/S under Ar atmosphere.



Fig. S7 (a) CV curves of GC/S cathodes at different scan rates and (b) the corresponding b-values of the redox peaks, (c) CV curves of GC-CoS₂/S cathodes at different scan rates and (d) the corresponding b-values of the redox peaks.



Fig. S8 (a-d) capacitive (red) and diffusion-controlled (blue) contributions of GC-CoS₂/S cathodes at different scan rates, (e) the contribution rates of capacitance and diffusion of GC-CoS₂/S cathodes at different scan rates.

In order to investigate the dynamic mechanism of redox reaction, a series of CV measurements of GC/S and GC-CoS₂/S electrodes were carried out at various scan rates from 0.10 to 0.60 mV s⁻¹. All the CV curves present two cathodic peaks and one anodic peak. In the first reduction peak located at about 2.03 V is attributed to the reduction of sulfur into the soluble high-order long chain lithium polysulfides (Li₂S_n, ($4 \le n \le 6$)). The second reduction peak at about 2.31 V is assigned to the further reduction of the long chain lithium polysulfides into insoluble low-order short chain lithium sulfides (Li₂S₂ and Li₂S). One anodic peak located at approximately 2.40 V is originated to the oxidation of Li₂S₂ and Li₂S to Li₂S₈ and S₈.² As shown in Fig. S7a and c, GC-CoS₂/S exhibits the more sharp and symmetrical redox peaks, and the increased cathodic potential and decreased anodic potential (the lower voltage polarization), attesting the more effective utilization of sulfur species and better electrochemical reversibility of electrode reaction, enhanced polysulfide conversion and redox reaction kinetics and electrocatalytic effect,³ while GC/S demonstrates the broad redox peaks with the increase of scan rates. The redox processes of two electrodes can be well investigated from CV curves at various scan rates based on the following law:⁴

$$i = av^{b}$$
(1)
$$\log (i) = b \times \log (v) + \log (a)$$
(2)

Where a and b are adjustable parameters, i and v are the current density (A) and sweep rate (mV s⁻¹), respectively. When b=0.5, the process is controlled by ion diffusion. When 0.5 < b < 1.0, both ion diffusion and capacitive effect are involved. If b=1.0, the process is controlled via a capacitive

effect.⁵ Fig. S7b and d give the log i versus log v plots of GC/S and GC-CoS₂/S, respectively. The calculated b values of GC-CoS₂/S are 0.714, 0.759 and 0.541 for peak 1, 2 and 3, which are higher than those of 0.433, 0.632 and 0.509 for GC/S. This result explicitly confirms that CoS₂ could effectively catalyze the conversion of soluble lithium polysulfide to solid Li_2S_2/Li_2S and further converting them to Li_2S_8/S_8 , thus promoting redox kinetics process to alleviate the accumulation of LiPSs.⁵ It is reported that the enhanced capacitive contributions can make the electrode material to obtain the higher rate performance and remarkable long cycling stability. The contributions of the capacitive capacity can be estimated according to the following equation:⁴

$$i(V) = k_1 V + k_2 V^{1/2} \tag{3}$$

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Where v is the scan rate, k_1 and k_2 are constants determined by linearly fitting the above equation at a fixed voltage. Subsequently, the contribution of capacitive capacity ($k_1 \times v$) can be obtained. The detailed capacitive contributions at different scan rates are displayed in Fig. S8a-d. The capacitive contributions of the GC-CoS₂/S cathode are calculated to be 60.4 %, 66.3 %, 70.1 % and 77.2 % at scan rates of 0.1, 0.2, 0.4, and 0.6 mV s⁻¹, respectively. As shown in Fig. S8e, along with the increase of voltage scan rates, the capacitive contribution keeps increasing. Compared with GC/S, the capacitive capacity contributions are more dominant in the total capacity for GC-CoS₂/S, which is conducive to the superior cycling stability originated from the well-suppressed polysulfide dissolution in electrolyte.⁵



Fig. S9 EIS spectra: (1, 2) GC/S and GC-CoS₂/S at the first cycle, and (3, 4) GC/S and GC-CoS₂/S after 500 cycles, and the equivalent circuit curve (the inset). Apparently, all of the EIS curves exhibit the similar constituent parts, namely consisting of a intercept at real axis in the high frequency region, a depressed semicircle at the high-to-medium frequency region accompanied with a short inclined line in the low frequency region. The equivalent circuit is also depicted in the inset of Fig. S9, which can be used to fit the constituent parameters of EIS curves, in which R_s is the ohmic resistance, R_{ct} is assigned to charge-transfer resistance, CPE represents the constant phase element and W₀ corresponds to Warburg impedance.⁶ It can be seen from the curves that both two electrodes show the relatively lower and approximately equal R_s and R_{ct} at first cycle. However, the R_{ct} significantly increases after 500 cycles, especially for GC/S cathode. In contrast, the R_{ct} of GC-CoS₂/S electrode is distinctly less than that of GC/S cathode after 500 cycles, proving the lower charge-transfer resistance weak after 500 cycles, and approximately enhanced kinetics processes of electrons and ions transfer as well as electrode reactions.⁶



Fig. S10 Electrochemical performance: (a) the rate performance and (b) cycling performance of the different mass ratio of GC and NiS₂, (I) m C: m NiS₂ = 100:0, (II) m C: m NiS₂ = 90:10, (III) m C: m NiS₂ = 85:15, (IV) m C: m NiS₂ = 80:20.



Fig. S11 The galvanostatic charge-discharge profiles of (a) GC-NiS₂/S and (b) GC-CoS₂/S cathodes at various current rates. The galvanostatic charge-discharge curves of (c) GC-NiS₂/S and (d) GC-CoS₂/S cathodes at different cycles at 0.1 C rate. The GC-CoS₂/S electrode shows clear charge-discharge plateaus, and longer charge-discharge plateaus and negligible voltage drop of discharge plateaus even at 2 C and 4 C, indicating a minimal electrochemical polarization. In contrast, GC-NiS₂/S presents shortened charge-discharge plateaus and apparent voltage drop of discharge plateaus, implying a severe electrochemical polarization. The galvanostatic charge-discharge curves of the cell with GC-CoS₂/S also exhibit the distinct charge-discharge plateaus at different cycles even up to 400th despite of the somewhat widening of the potential gap between charge and discharge plateaus. However, by contrast, the cell based on GC-NiS₂/S discloses the severer electrochemical polarization with larger potential gaps, further proving the superiority of GC-CoS₂/S in promoting the sulfur redox reaction.⁷



Fig. S12 UV-Vis adsorption spectra of pure Li_2S_6 solution and adding GC, GC- NiS₂ and GC-CoS₂ after resting 12 h. Strong absorbance in the 250-300 nm region can be observed for fresh polysulfide solution, which is attributed to the high degree of S_6^{2-} ions.⁸ Nevertheless, the solution exposed to GC-CoS₂ shows the lowest absorbance, indicating the best adsorption characteristics for polysulfides.



Fig. S13 Digital photographs of cathode, membrane and lithium foil of (a_1-a_3) GC-CoS₂/S and (b_1-b_3) GC-NiS₂/S after 400 cycles at 0.1 C.



Fig. S14 (a, b) SEM images of GC-CoS₂/S electrode after 400 cycles at 0.1 C rate and corresponding EDX elemental mapping images (d-g) of C, Co, S and Li. (h, i) SEM images of GC-NiS₂/S electrode after 400 cycles at 0.1 C rate and corresponding EDX elemental mapping images (k-n) of C, Ni, S and Li.

The morphological evolution of GC-CoS₂/S and GC-NiS₂/S electrodes at the discharge state after 400 cycles was investigated by SEM to further gain insights into their catalytical and conversional function for polysulfides. As shown in Fig. S14a and b, the GC-CoS₂/S composite still maintains the porous structure with clean surface without the obvious presence of irregular particle aggregates. By contrast, the surface of GC-NiS₂/S is vastly covered by the gathered particles and almost lost its

porous structure (Fig. S14h and i), which may be derived from the aggregation of insoluble LiPSs $(Li_2S_2 \text{ and } Li_2S)$.⁶ Elemental mapping images show that the elemental distributions are uniformly for both GC-CoS₂/S (Fig. S14d-g) and GC-NiS₂/S (Fig. S14k-n). It is noteworthy that the lithium and sulfur signals of GC-NiS₂/S are slightly stronger than those of GC-CoS₂/S. These observations further validate that GC-CoS₂ can not only suppress the shuttle effect, but also effectively facilitate the conversion kinetics of solid Li₂S₂ and Li₂S.⁵

Ref.	Sulfur host materials	Sulfur loading (mg cm ⁻²)	Current density (C*)	Initial capacity (mAh g ⁻¹)	Cycle number	Capacity retention (%)
This work	GC-CoS ₂ /S	2.2-2.5	0.1 2 4	1252 899.8 683.4	500 1000 1000	81.4 67.8 60.4
9	Litchi Shells-C	1.2	0.2	1105	100	65.3
10	Agar -C	1.5	0.2	1240	100	80.2
11	Gum Arabic-C	1.1	1	731.7	250	41
12	CoS ₂ /rGO	5.6	0.5	993.5	110	81.2
13	S/CoS ₂ N-C	1.3	0.5	1081	250	76.3
14	S/CoS ₂ /G	1.5	0.5	1368	150	73.5
15	CHPC/CoS ₂	2	0.2	1231	250	85.2
16	Silk Cocoon-C	1.5	0.5	1279	100	37.8
17	CoS ₂ -N-C	1.68	0.2	1288	200	69.7
18	Bagasse-derived NBC	3.2	0.2	1169	200	77
19	Cassava- derived C sheet	1.6	0.5	1318	100	60
20	CoS ₂ @N-doped Nanoshells-C	1.5	0.1	1300	100	69.3

Table S1 Electrochemical performance comparison of GC-CoS₂/S with other representative sulfur host materials for Li-S batteries in the literatures.

*1C=1675 mAh g⁻¹

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