Supplementary Information

Rational Integration of Spatial Confinement and Polysulfide Conversion Catalyst for High Sulfur Loading Lithium-Sulfur Batteries

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Fig. S1 a, b) SEM image of ZnCo-ZIF nanoparticles; and c) SEM image of nanofibers in typical ZnCo-ZIF@PAN film prepared *via* electrospinning; d) Optical image of typical as-spun ZnCo-ZIF@PAN film.



Fig. S2 Photographs of a) the Co/N-PCNF film after carbonization of ZnCo-ZIF@PAN film; b) the Co/N-PCNF film bent for 180°.



Fig. S3 a, b) SEM images of typical N-PCNF film.



Fig. S4 a, b) TEM images of N-PCNF fiber.



Fig. S5 a, b) Elemental mappings of N-PCNF fiber, the corresponding color of C and N elemental are cyan and purple, respectively.



Fig. S6 High-resolution XPS spectra of Co/N-PCNF: a) C 1s spectrum, b) Co2p spectrum, c) N 1s spectrum and d) Zn2p spectrum.



Fig. S7 High-resolution XPS spectra of N-PCNF: a) N 1s spectrum, b) Zn2p spectrum.



Fig. S8 a) Nitrogen adsorption/desorption isotherms of the N-PCNF and Co/N-PCNF films; b) BJH pore size distribution curves of the N-PCNF and Co/N-PCNF films analyzed from N_2 adsorption/desorption measurement.



Fig. S9 Raman spectrum of the Co/N-PCNF and N-PCNF.



Fig. S10 a, b) Photographs of Co/N-PCNF@S disk cathodes; c) Cross-section SEM image of Co/N-PCNF@S disk cathode.



Fig. S11 a, b) Low magnification and high magnification SEM image of N-PCNF@S films, respectively.



Fig. S12 SEM image and elemental mappings of N-PCNF@S fiber, the corresponding color of C, S and N element are cyan, yellow and purple, respectively.



Fig. S13 The initial 5 cycle cycles voltammetry of the Co/N-PCNF@S disk cathode against Li foil under a scanning rate of 0.1 mV s^{-1} .



Fig. S14 The DFT calculation results of interaction between Co-N-graphene and different lithiumpolysulfides: c) Li₂S₈, d) Li₂S₄.



Fig. S15 a, b) SEM image of Co/N-PCNF@S film after 300 cycles; c, d) SEM image of N-PCNF@S films after 300 cycles.



Fig. S16 a) SEM images and c) elemental mapping of S element of the Li anode matched with Co/N-PCNF@S cathode after 200 cycles; b) SEM images and d) elemental mapping of S element of the Li anodes matched with N-PCNF@S cathode after 200 cycles.



Fig. S17 a) Cyclic voltammetry (CVs) plots of the Co/N-PCNF@S cathode at different scan rates from 0.1 to 0.8 mV s⁻¹; b) Cyclic voltammetry (CVs) plots of the N-PCNF@S cathode at different scan rates from 0.1 to 0.8 mV s⁻¹.



Fig. S18 The relationships between the peak current and square root of scan rate in different reaction processes of the Co/N-PCNF@S and N-PCNF@S cathodes. (a) Peak a: $S_8 \rightarrow Li_2S_x$, b) Peak b: $Li_2S_x \rightarrow/Li_2S$, (c) Peak c: $Li_2S_x \rightarrow S_8$ ($4 \le x \le 8$)



Fig. S19 XPS survey spectra of the Co/N-PCNF cathode after its adsorption of Li_2S_6 .

Sample	$R_{ct}(\Omega)$	$\mathbf{R}_{s}(\Omega)$	
Co/N-PCNF@S	34.8	2.0	
N-PCNF@S	65.3	3.8	

Table. S1 The fitted parameters for R_s and R_c	t
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Table. S2 The quantitative elemental analysis of Li anode matched with Co/N-PCNF@S and	1 N-
PCNF@S cathode after 200 cycles by EDS measurement.	

Sample	C (wt%)	O (wt%)	F (wt%)	S (wt%)
LilCo/N-PCNF@S	10.07	55.08	29.08	5.65
N-PCNF@S	11.80	46.82	24.74	16.65

Freestanding nanofibers cathode	Sulfur mass loading (mg cm ⁻²)	Sulfur content (%)	Rate (C)/ Current (A)	Areal capacity (mAh cm ⁻²)	Ref
S-a-MCNF	4.6	80	0.2	5.23	S1
SN-HCSs/S	3.0	76	0.2	2.05	S2
TiN/C@S	10.5	56	0.2	8.30	S3
CNF/S	10.5	79	0.1	7.91	S4
S-CNF	2.0	64	0.5	1.10	S5
C ₃ N ₄ @PCNF/S	1.2	56	0.1A	1.23	S6
Co/N-PCNF@S	9.3	60	0.2	8.35	This work

Table S3. Performance comparison of different Li-S batteries with freestanding carbon nanofiber-based cathodes via electrospinning route

References

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