Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Space−Confinement and Chemisorption Co−Involved in Encapsulation of Sulfur for Lithium−Sulfur Batteries with Exceptional Cycling Stability

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Keywords: Lithium-sulfur batteries, graphene, carbon nanotubes, tube-in-tube, polydopamine

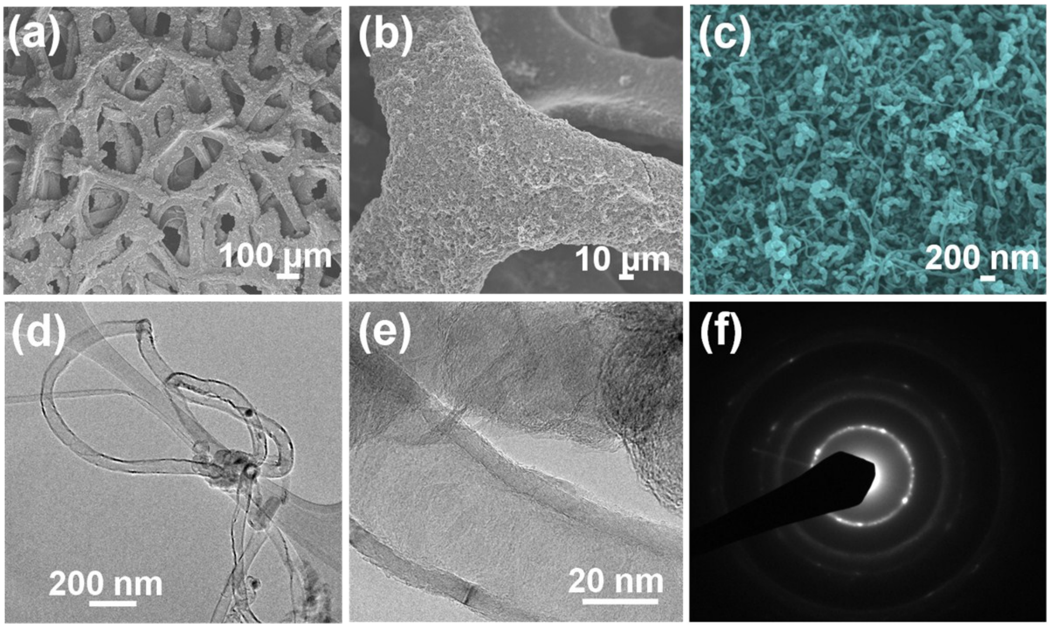

Figure S1 (a), (b), (c) SEM images of CNT/GF. (d)-(e) TEM images of CNTs in CNT/GF. (f) Selected area electron diffraction (SAED) pattern of CNTs.

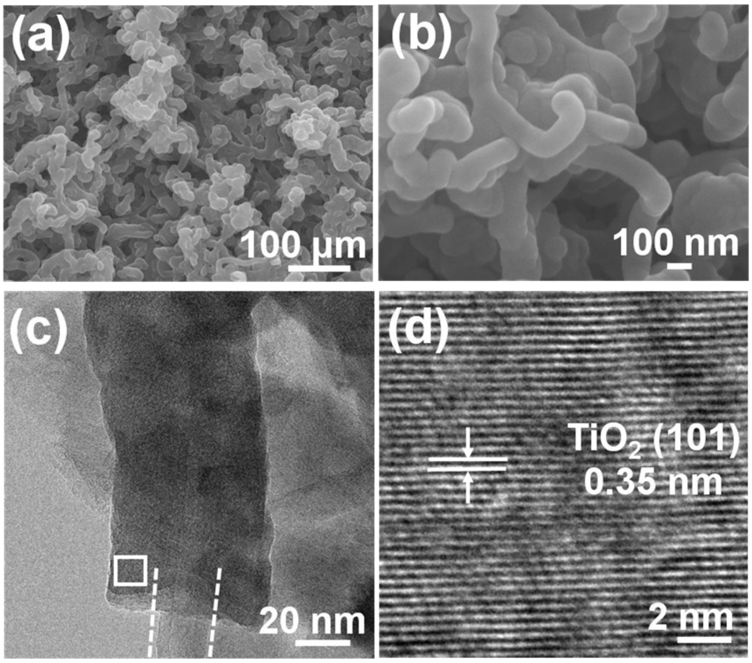

Figure S2. (a) and (b) SEM images of CNT/GF after ALD coating of TiO_2 (80 cycles).

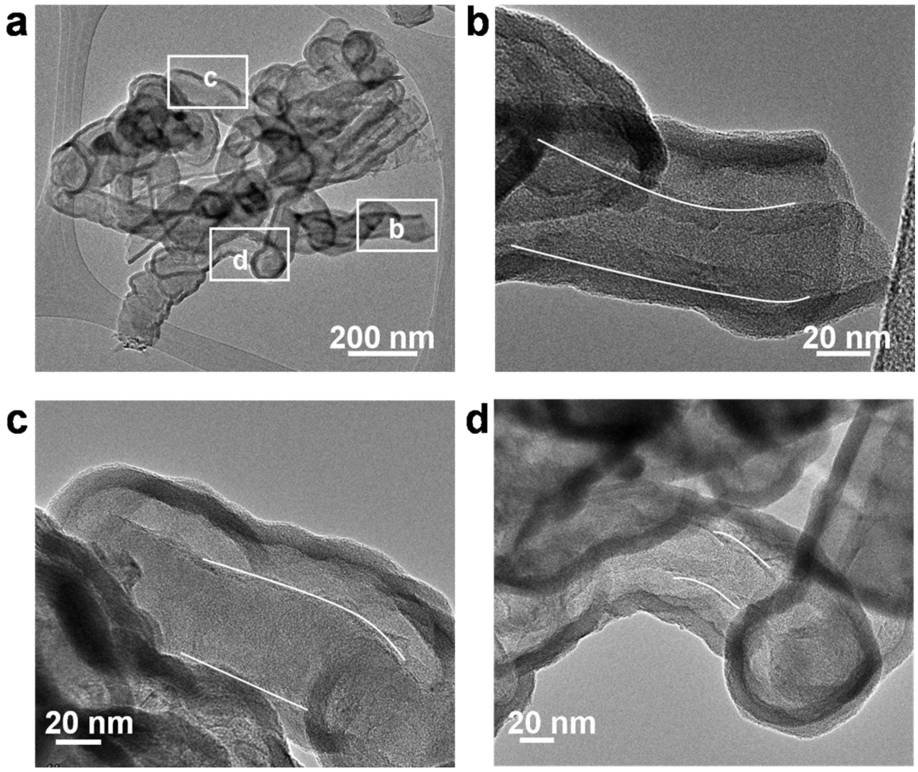

Figure S3. (a) TEM images of NC⊙CNTs in NC⊙CNT/GF. (b)-(d) HRTEM images at different areas of Figure (a), clearly showing a tube-in-tube structure.

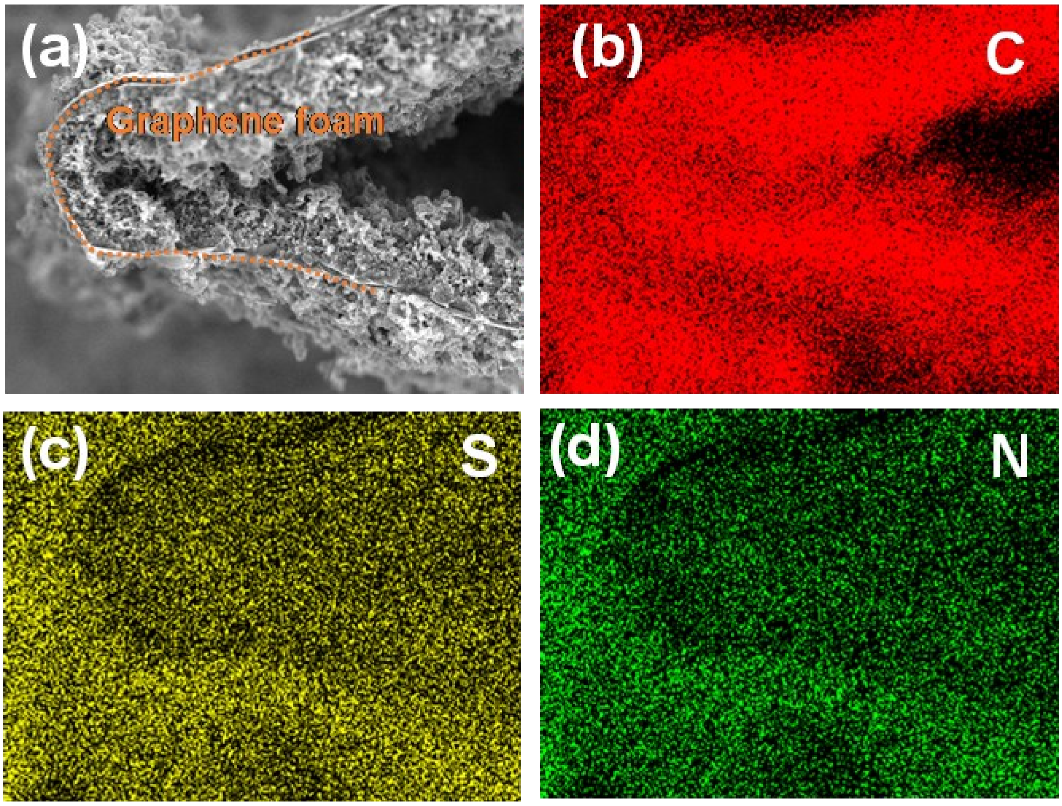

Figure S4. (a) SEM images of cross-sectional images of NC⊙CNT/GF branch. Corresponding elemental mapping images of C (b), S (c) and N (d), indicating the uniform encapsulation of sulfur in NC⊙CNT/GF.

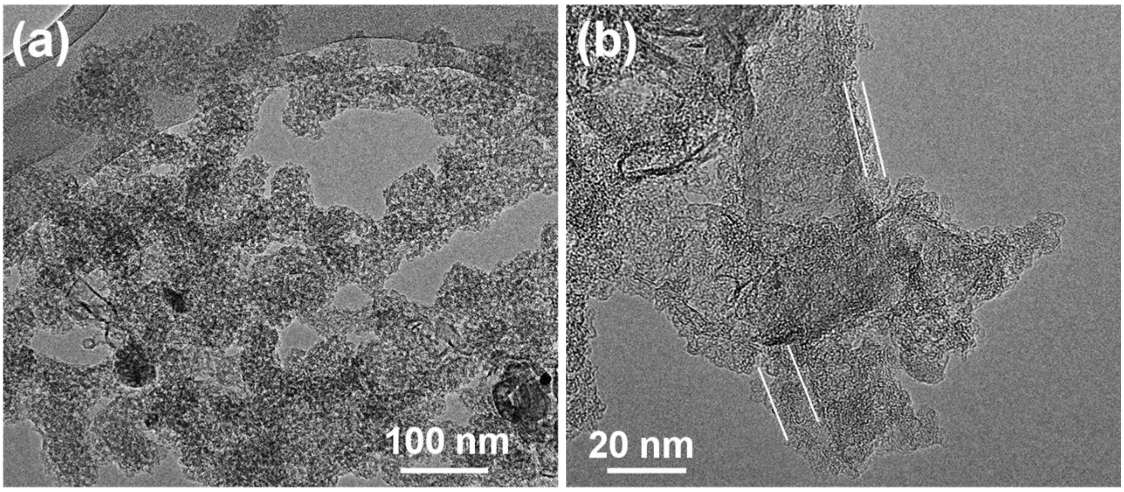

Figure S5. TEM images of (a) and (b) PD@CNT in the NC@CNT/GF films.

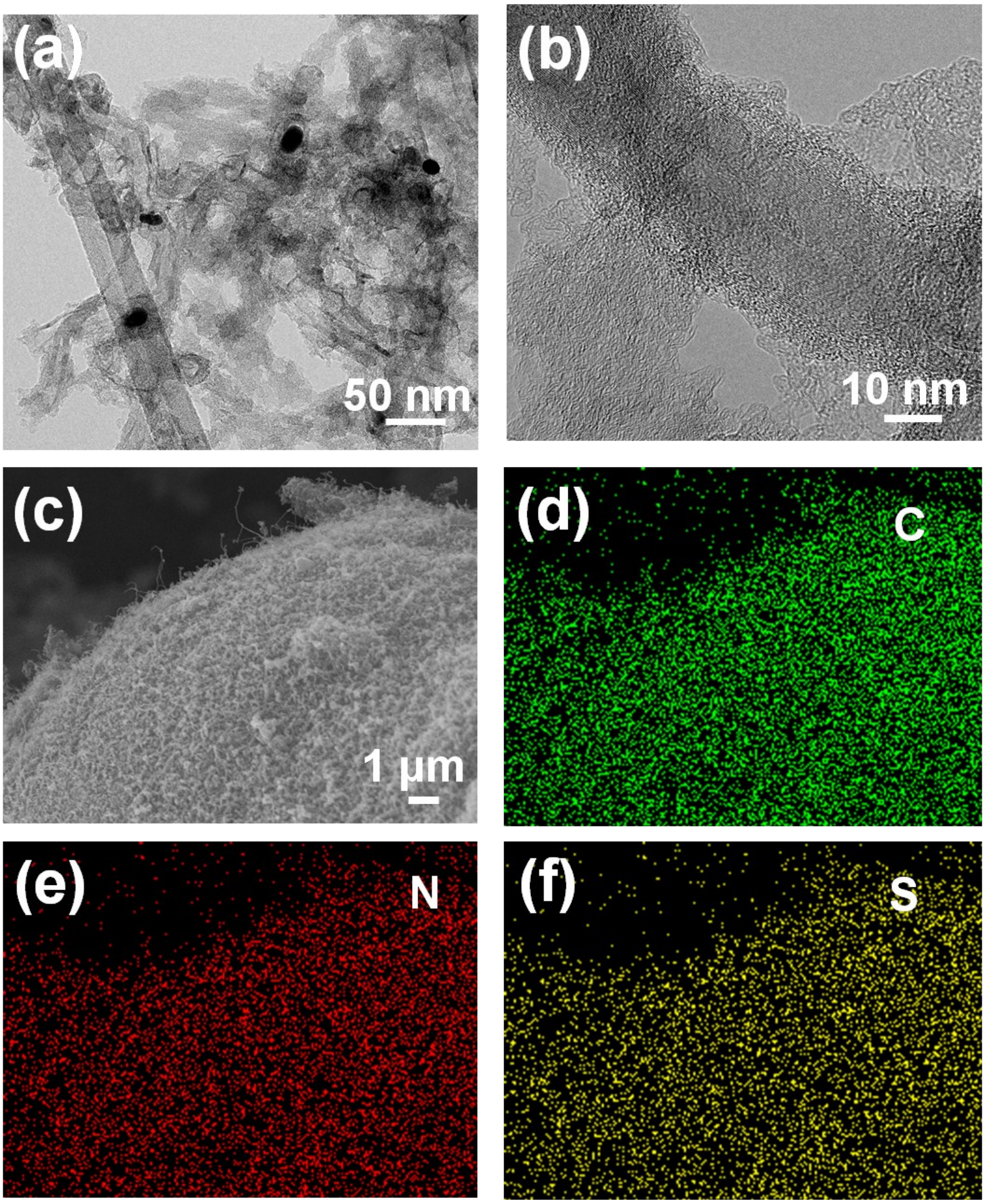

Figure S6. TEM images of (a) and (b) NC@CNT in the NC@CNT/GF films. (c) SEM image of the S−NC@CNT/GF hybrid. EDS elemental mapping of (c) for: d) carbon, e) nitrogen, and g) sulfur of the S−NC@CNT/GF hybrid.

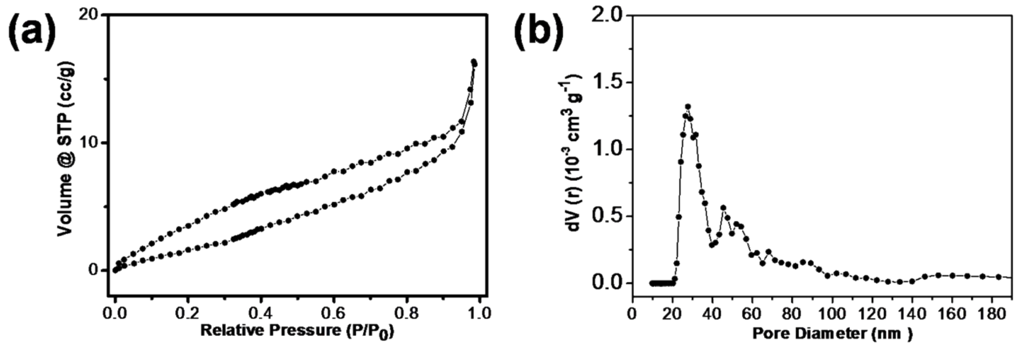

Figure S7. (a) Nitrogen adsorption—desorption isotherms, and (b) pore size distribution curves of S-NC⊙CNT/GF composites.

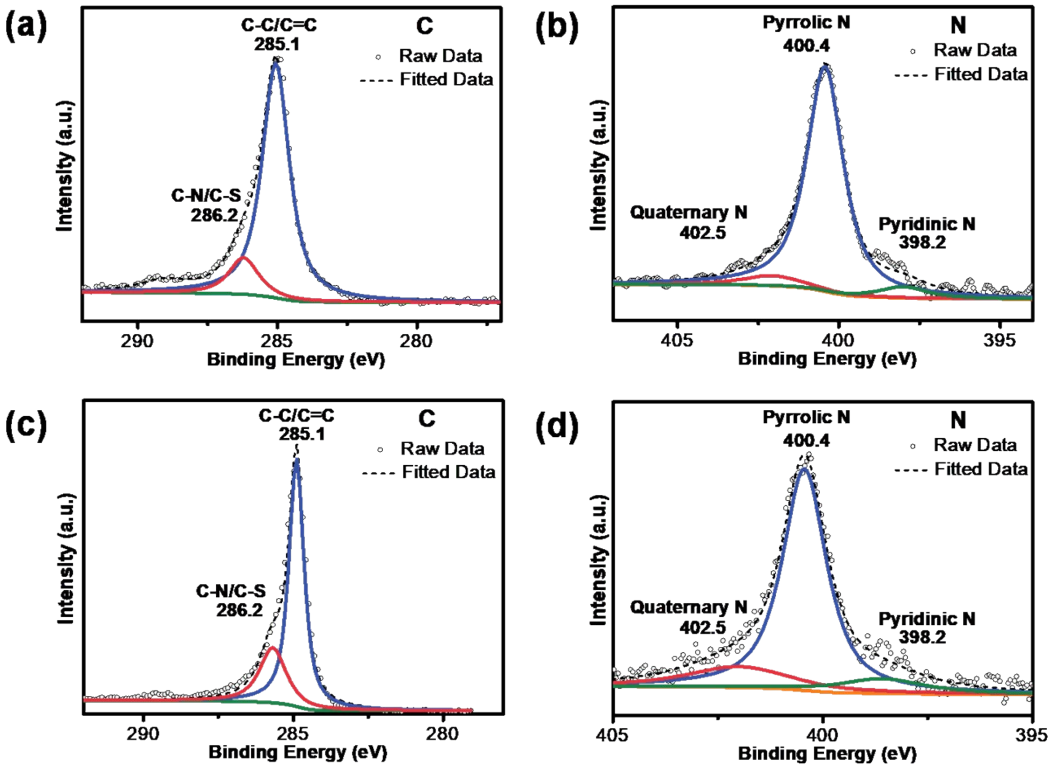

Figure S8. XPS spectrum of NC⊙CNT/GF and S- NC⊙CNT/GF composites. (a) C 1s XPS spectrum of NC⊙CNT/GF. (b) N 1s XPS spectrum of NC⊙CNT/GF. (a) C 1s XPS spectrum of S-NC⊙CNT/GF. (b) N 1s XPS spectrum of S-NC⊙CNT/GF.

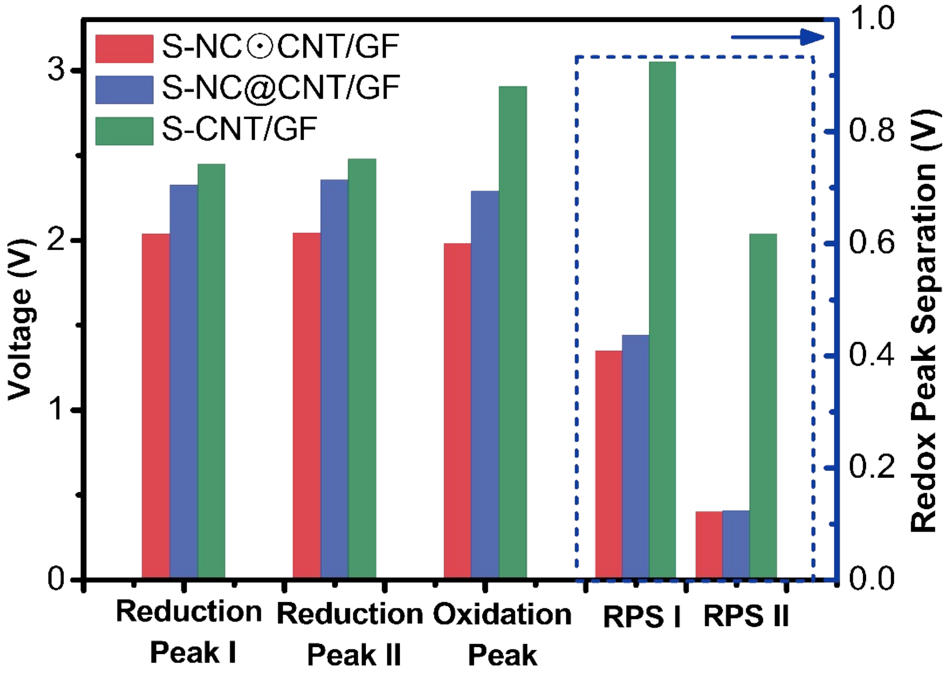

Figure S9. Peak potentials and redox peak separation value of the S-NC⊙CNT/GF, S–NC@CNT/GF and S@CNT/GF electrodes from the second CV cycle. Redox peak separation I (RPS I) is referring to peak separation value between the reduction peak at the lower voltage and oxidation peak. Redox peak separation II (RPS II) is referring to peak separation value between the reduction peak at the higher voltage and oxidation peak.

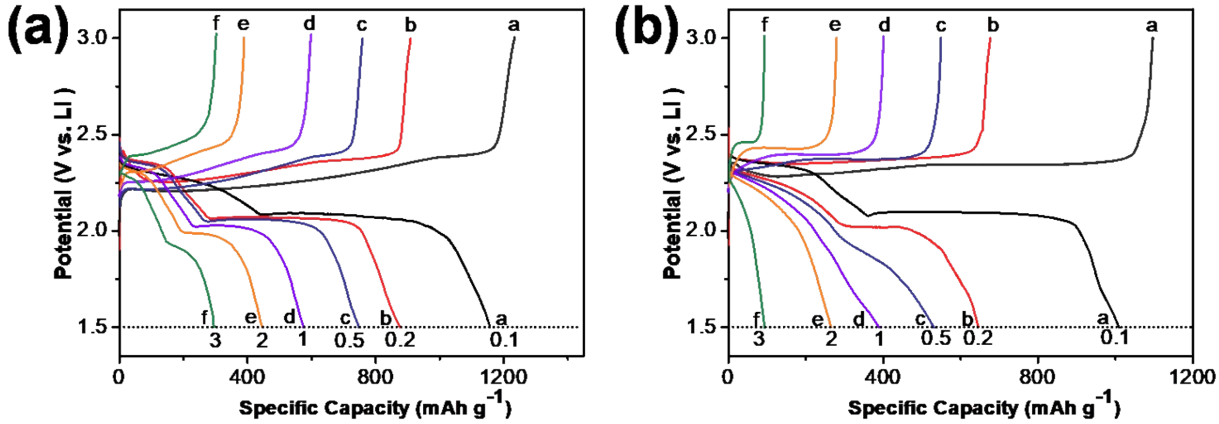

Figure S10. Galvanostatic charge-discharge voltage profiles of (a) S–NC@CNT/GF and (b) S@CNT/GF electrodes at various current rates within a potential window of 1.5–3 V versus Li^+/Li_0.

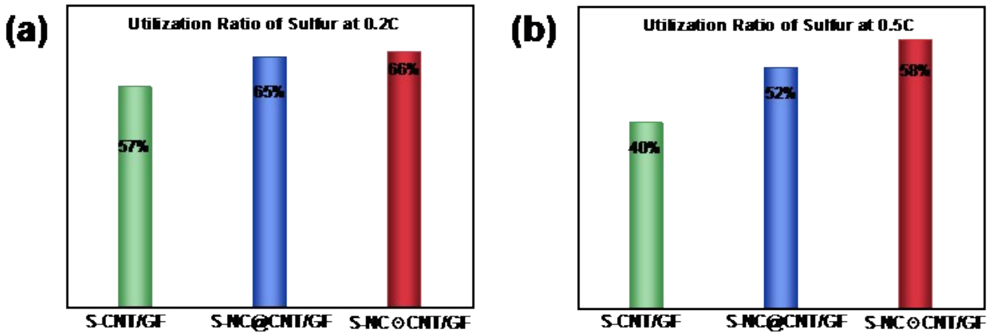

Figure S11. Sulfur utilization ratio for the S–CNT/GF, S–NC@CNT/GF and S–NC⊙CNT/GF electrodes at current rates of (a) 0.2C and (b) 0.5C.

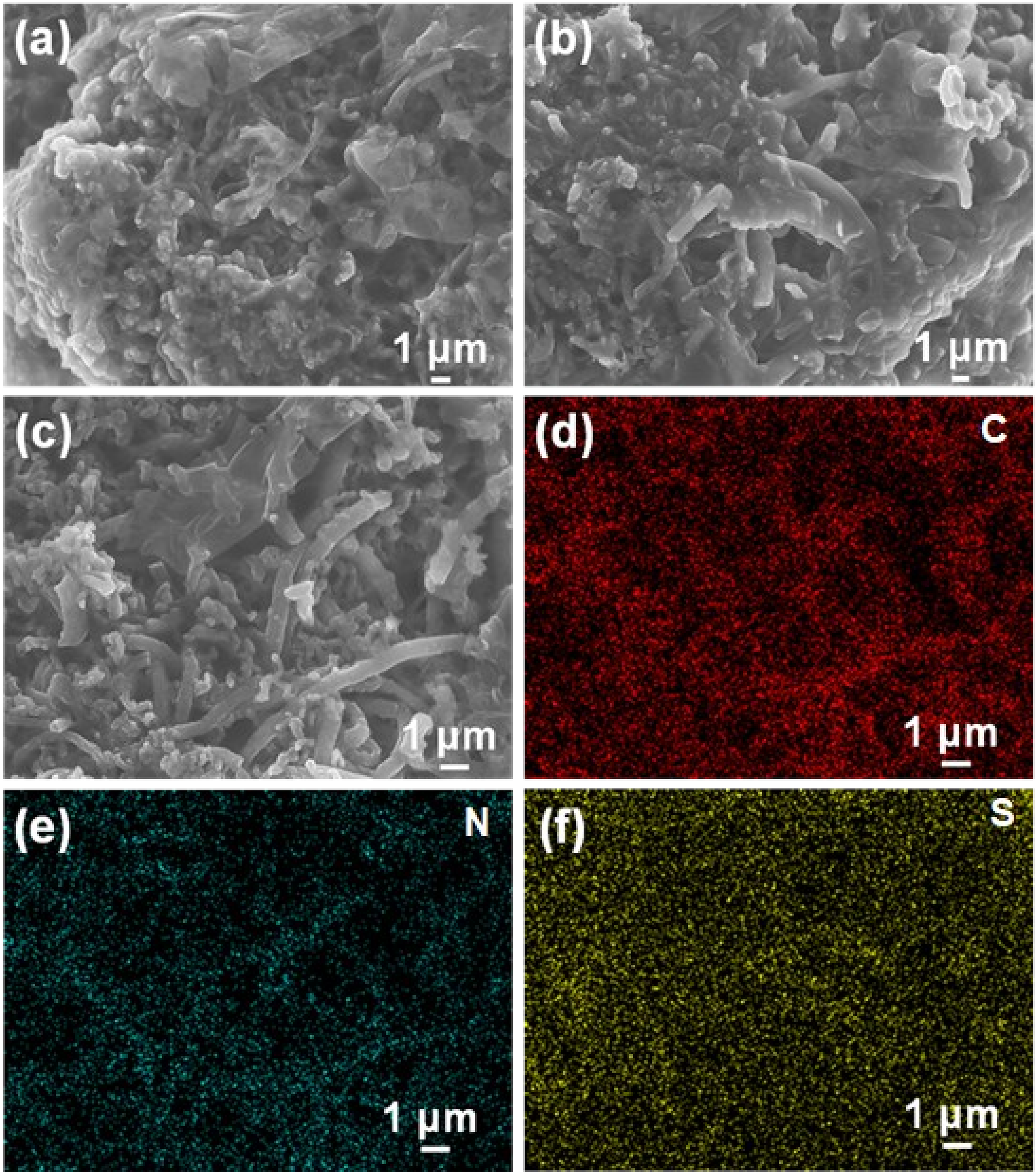

Figure S12. SEM images of the cathode surface after 100 cycles in the (a) S–CNT/GF, (b) S–NC@CNT/GF, (c) S–NC⊙CNT/GF electrodes, and (d)-(f) EDS mapping images of S–NC⊙CNT/GF electrodes after 100 cycles.

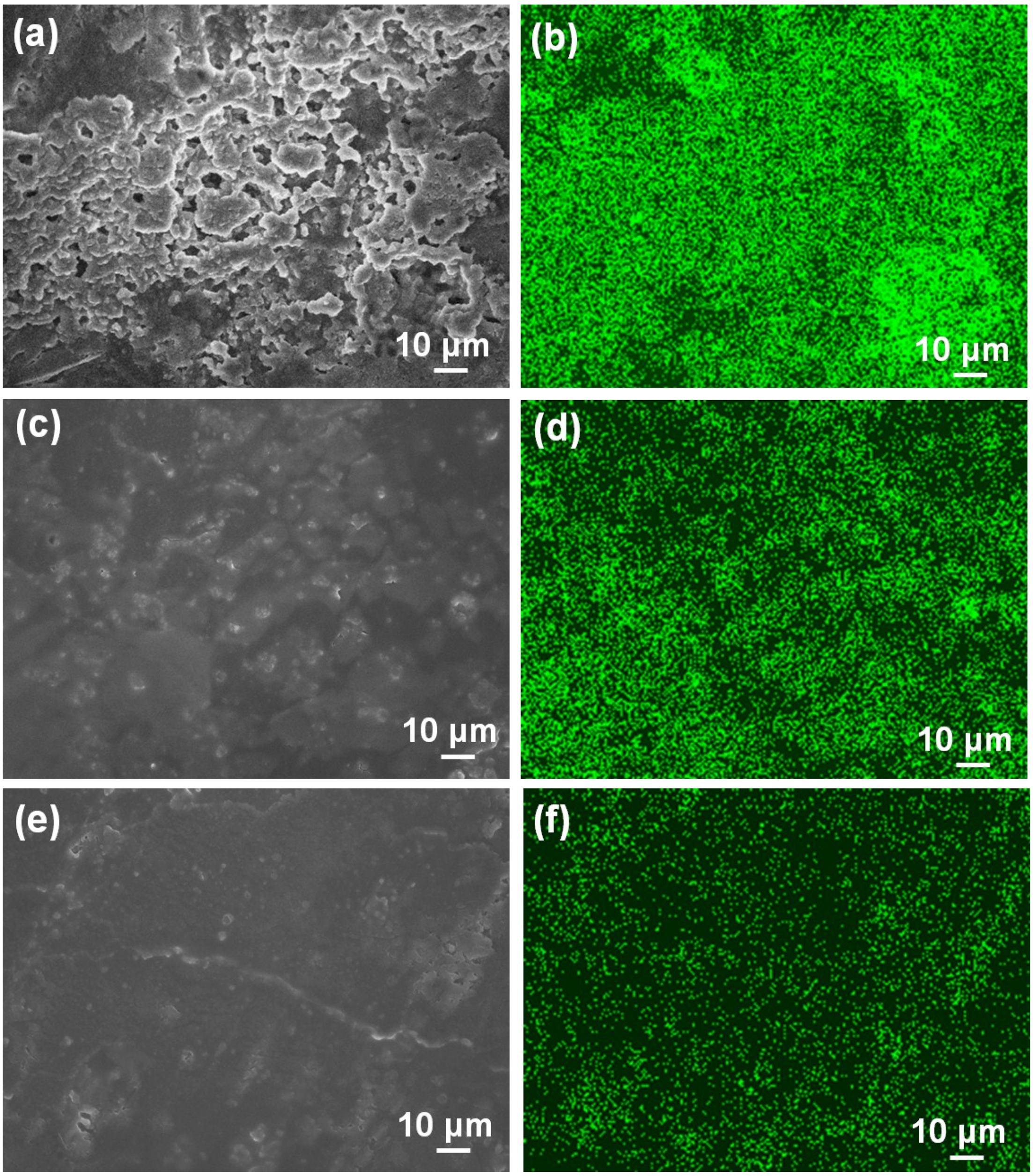

Figure S13. SEM images and EDS mapping images of the lithium-metal surface after 100 cycles in the (a)-(b) S–CNT/GF, (c)-(d) S–NC@CNT/GF, and (e)-(f) S–NC⊙CNT/GF electrodes. EDS mapping of sulfur element was scanned using the same time (200 s) for a comparison.

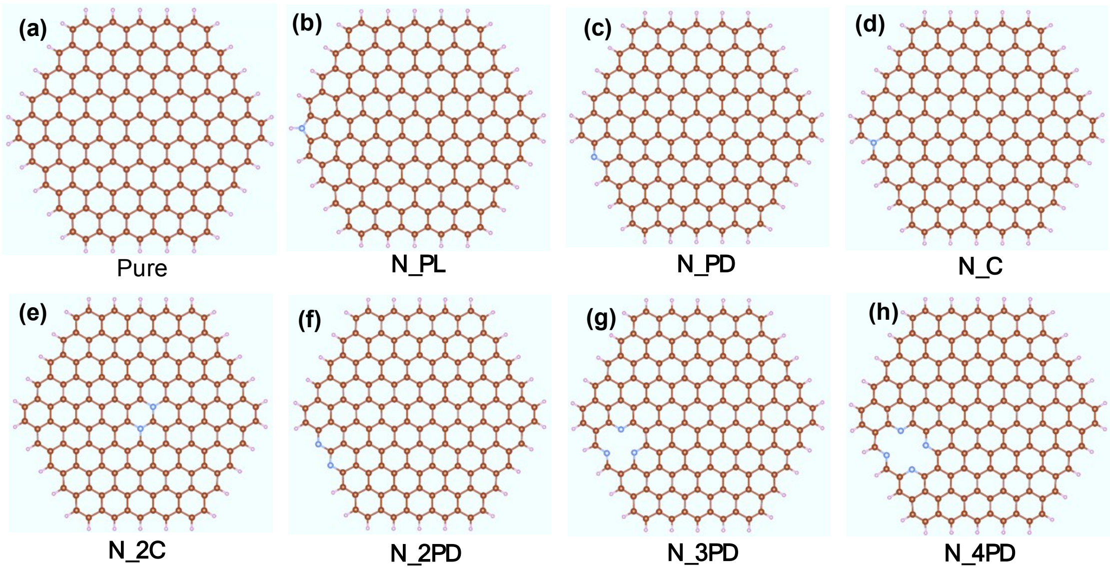

Figure S14. Structural diagrams of N-doped carbon with different doping configurations. (a) Pure carbon. (b) N_{PL} doped carbon. (c) N_{PD} doped carbon. (d) N_{C} doped carbon. (e) Two N_{C} doped carbon. (f) Two N_{PD} doped carbon. (g) Three N_{PD} doped carbon. (h) Four N_{PD} doped carbon. The full names of all abbreviations are given in the main text. The C, N and H atoms are denoted by brown, purple and pink balls, respectively.

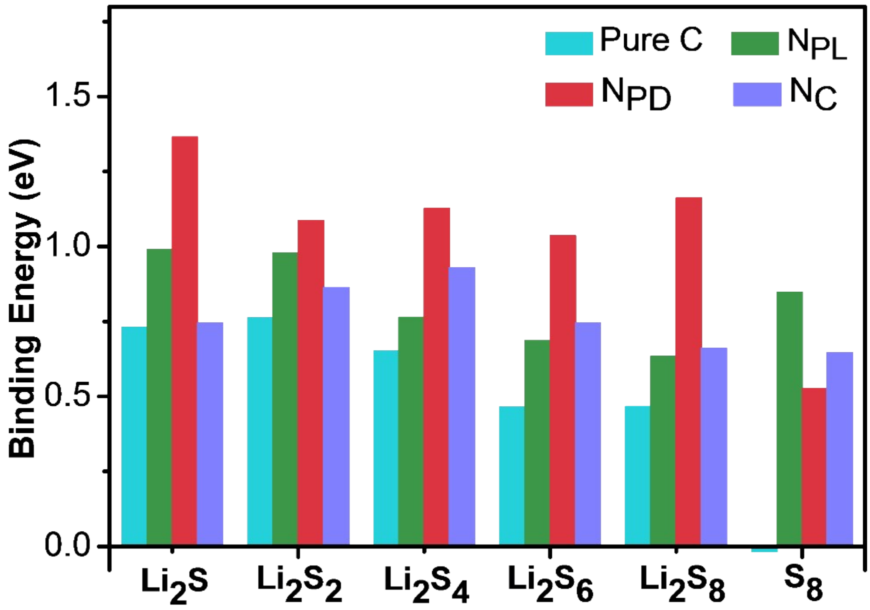

Figure S15. DFT calculated binding energies between lithium polysulfides and N-doped carbon with different doping configurations.

Table S1. A survey of electrochemical properties of sulfur cathode for Li-S batteries. Only sulfur cathodes with sulfur loading above 2 mg cm^{-2} is chose for comparasion.

Electrode description	Sulfur loading	Cycling stability	Rate performance
Our Work	5.6 mg cm^{-2}	898 mAh g^{-1} at 0.2C after 100 cycles; 795 mAh g^{-1} at 0.5C after 100 cycles; 663 mAh g^{-1} at 1C after 500 cycles	1367, 1153, 993, 851, 699, and 550 mAh g^{-1} at 0.1C, 0.2C, 0.5C, 1C, 2C, and 3C
Phosphorene as a polysulfide immobilizer for lithium–sulfur batteries [1]	3.3 mg cm^{-2}	660 mA h g^{-1} at 1C after 500 cycles	1262, 1092, 1027, 985, 865, and 785 mAh g^{-1} at 0.2C, 0.5C, 0.8C, 1C, 2C, and 3C
Double-shelled nanocages for lithium–sulfur batteries [2]	3 mg cm^{-2}	491 mA h g^{-1} at 0.5C after 100 cycles.	900, 800, 650 and 500 mAh g^{-1} at 0.1C, 0.2C, 0.5C and 1C
Graphene-supported nitrogen and boron rich carbon layer [3]	NA	556 mA h g^{-1} at 0.5C after 500 cycles	1050, 833, 699, 555, and 480 mAh g^{-1} at 0.2C, 0.5C, 1C, 2C, and 3C
Nitrogen rich hierarchically organized porous carbon/S composites [4]	2.2 mg cm^{-2}	832 mA h g^{-1} at 0.2C after 500 cycles; 519 mA h g^{-1} at 0.5C after 500 cycles.	1140, 962, 805, 681, 515 and 310 mAh g^{-1} at 0.05C, 0.1C, 0.25C, 0.5C, 1C and 2C
3D vertically aligned and interconnected porous carbon nanosheets [5]	6 mg cm^{-2}	620 mA h g^{-1} at 0.1C after 60 cycles	1250, 1105, 1020, 930 and 738 mAh g^{-1} at 0.1C, 0.2C, 0.5C, 1C and 2C
3D CNT current collectors [6]	4.1 mg cm^{-2}	850 mAh g^{-1} at 0.2C after 100 cycles	NA
g-C_3N_4/S electrode [7]	4.5 mg cm^{-2}	643 mAh g^{-1} at 2C after 400 cycles	1130, 890, 895 and 863 mAh g^{-1} at 0.05C, 0.5C, 1C and 2C
MOF derived sulfur host containing cobalt and N-doped graphitic carbon [8]	2.0-2.5 mg cm^{-2}	625 mAh g^{-1} at 1C after 600 cycles	1670, 1350, 1145, 925, 795, 685 and 565 mAh g^{-1} at 0.05C, 0.1C, 0.2C, 0.5C, 1C, 2C and 5C
Sulfur@3D porous graphitic carbon [9]	2.36 mg cm^{-2}	670 mAh g^{-1} at 2C after 1000 cycles	1382, 1242, 1115 and 500 mAh g^{-1} at 0.5C, 1C, 2C and 5C

MWCNT-S with N-doped porous carbon [10]	3 mg cm^{-2}	750 mAh g^{-1} at 1C after 300 cycles	1278, 1078, 964, 900 and 685 mAh g^{-1} at 0.1C, 0.2C, 0.5C, 1C and 3C
GF–rGO hybrid nested hierarchical network [11]	9.8 mg cm^{-2}	645 mAh g^{-1} at 0.2C after 350 cycles	NA
Boronate ester COF [12]	NA	770 mAh g^{-1} at 0.5C after 200 cycles	1411, 1062, 822 and 620 mAh g^{-1} at 0.1C, 0.2C, 0.5C and 1C
Nitrogen doped CNT-graphene nanostructures [13]	4.2-4.4 mg cm^{-2}	665 mAh g^{-1} at 2C after 200 cycles	1314, 1009, 922, 696 and 480 mAh g^{-1} at 0.2C, 0.5C, 1C, 2C and 5C
Holey-CNT/S Cathodes[14]	NA	879 mAh g^{-1} at 0.5C after 200 cycles; 870 mAh g^{-1} at 10C after 200 cycles	1176, 679 and 424 mAh g^{-1} at 0.2C, 3C and 6C
Nitrogen doped mesoporous–hollow carbon nanospheres[15]	0.5-0.7 mg cm^{-2}	980 mAh g^{-1} at 0.2C after 100 cycles	1139, 920, 720 and 250 mAh g^{-1} at 0.2C, 0.5C, 1C and 2C
Nitrogen-doped double-shelled hollow carbon spheres and wrapped with graphene[16]	3.9 mg cm^{-2}	940 mAh g^{-1} at 0.2C after 100 cycles	1360, 800, 600 and 430 mAh g^{-1} at 0.2C, 1C, 2C and 3C
Nitrogen/sulphur-codoped graphene sponge[17]	4.6 mg cm^{-2}	670 mAh g^{-1} at 0.5C after 200 cycles	1157, 912, 675 and 430 mAh g^{-1} at 0.2C, 0.5C, 1C and 2C
Leaf-like graphene-oxide-wrapped sulfur[18]	2.7 mg cm^{-2}	670 mAh g^{-1} at 0.5C after 500 cycles	1250, 1130, 930, 753, 685 and 468 mAh g^{-1} at 0.1C, 0.2C, 0.5C, 1C, 2C and 4C
An aligned and laminated nanostructured carbon hybrid cathode[19]	20 mg cm^{-2}	400 mAh g^{-1} at 2C after 1000 cycles	1206, 912, 729, 593, and 473 mAh g^{-1} at 0.1C, 0.2C, 0.5C, 1C and 2C
CNT-interpenetrated mesoporous nitrogen-doped carbon spheres[20]	5 mg cm^{-2}	1200 mAh g^{-1} at 0.2C after 200 cycles	NA
Nitrogen and sulfur dual-doped carbon derived from polyrhodanine@cellulose [21]	NA	925 mAh g^{-1} at 0.2C after 500 cycles	1370, 1280, 1135 and 830 mAh g^{-1} at 0.05C, 0.2C, 0.5C and 2C
Vertically aligned sulfur-graphene nanowall[22]	NA	1210 mAh g^{-1} at 0.125C after 120 cycles	1100 and 410 mAh g^{-1} at 0.5C, and 8C
CMK-S[23]	NA	920 mAh g^{-1} at 0.2C after 100 cycles	1150, 1021, 870 and 814 mAh g^{-1} at 0.1C, 0.2C, 0.5C

			and 1C
A hollow carbon fiber foam for Li-S batteries[24]	10.8 mg cm^{-2}	852 mAh g^{-1} at 0.2C after 100 cycles	1352, 1122, 1092, and 947 mAh g-1 at 0.05 C, 0.1 C, 0.2 C, and 0.5 C

Table S2. BET surface area, pore volume and the calculated volume content of sulfur in pores.

Samples	Weight content of sulfur (%)	BET surface area [m^2 g^{-1}]	Total pore volume [cm^3 g^{-1}]	Volume content of sulfur in pores	Weight percent of sulfur in pores
CNT/GF	/	58.2	0.12	/	/
NC@CNT/GF	/	387.5	0.64	/	/
NC⊙CNT/GF	/	1033.9	1.78	/	/
S-CNT/GF	67	9.7	0.037	0.065	0.015
S-NC@CNT/GF	69.1	10.2	0.069	0.65	0.454
S-NC⊙CNT/GF	69.8	10.8	0.19	0.64	0.695

Here, we consider the volume decrease is all related with the sulfur impregnation into the pores. According to the pore volume before and after sulfur impregnation, we can calculate the volume content of sulfur in pores. The detailed calculation can be expressed as following:

(1) For the sample S-CNT/GF:

Before sulfur impregnation, the pore volume of CNT/GF is 0.12 cm^3 g^{-1}. V_{pore}, V_{Sulfur} and M_c are pore volume, sulfur volume in pores and carbon weight.

$V_{pore}/M_C=0.12$ (1)

After sulfur impregnation, the pore volume of S-CNT/GF is 0.037 cm^3 g^{-1}. Then, we can obtain equation (2).

$(V_{pore}-V_{Sulfur})/(M_C+67/33M_C) = 0.037$ (2)

Equation (2) can be simplified as Equation (3)

$(V_{pore}-V_{Sulfur})/M_C = 0.1121$ (3)

According to equations (1) and (3),

We can obtain equations (4).

$V_{Sulfur} = 0.065\ V_{pore}$ (4)

Then, according to the density of sulfur (2 g cm^{-3}), we can get the sulfur content (W_t) by equations (5).

$W_t = 0.13\ V_{pore}/(0.13\ V_{pore}+1)$

Then, the sulfur content in pores is only 1.5%.

(2) For the sample S-NC@CNT/GF:

Before sulfur impregnation, the pore volume of NC@CNT/GF is 0.64 cm^3 g^{-1}. V_{pore}, V_{Sulfur} and M_c are pore volume, sulfur volume in pores and carbon weight.

$V_{pore}/M_C=0.64$ (6)

After sulfur impregnation, the pore volume of S-CNT/GF is 0.069cm^3 g^{-1}. Then, we can obtain equation (7).

$(V_{pore}-V_{Sulfur})/(M_C+69.1/30.9M_C) = 0.069$ (7)

Equation (7) can be simplified as Equation (8)

$(V_{pore}-V_{Sulfur})/M_C = 0.2233$ (8)

According to equations (6) and (8),

We can obtain equations (9).

$V_{Sulfur} = 0.65\ V_{pore}$ (9)

Then, according to the density of sulfur (2 g cm^{-3}), we can get the sulfur content (W_t) by equations (10).

$W_t = 1.3\ V_{pore}/(1.3\ V_{pore}+1)$ (10)

Then, the sulfur content in pores is 45.4%.

(3) For the sample S-NC⊙CNT/GF:

Before sulfur impregnation, the pore volume of NC⊙CNT/GF is 1.78 cm^3 g^{-1}. V_{pore}, V_{Sulfur} and M_c are pore volume, sulfur volume in pores and carbon weight.

$V_{pore}/M_C=1.78$ (11)

After sulfur impregnation, the pore volume of S-CNT/GF is 0.19 cm^3 g^{-1}. Then, we can obtain equation (12).

$(V_{pore}-V_{Sulfur})/(M_C+69.8/30.2M_C) = 0.19$ (12)

Equation (12) can be simplified as Equation (13)

$(V_{pore}-V_{Sulfur})/M_C = 0.63$ (13)

According to equations (11) and (13),

We can obtain equations (14).

$V_{Sulfur} = 0.64\ V_{pore}$ (14)

Then, according to the density of sulfur (~2 g cm^{-3}), we can get the sulfur content (W_t) by equations (15).

$W_t = 1.28V_{pore}/(1.28V_{pore}+1)$ (15)

Then, the weight percent of sulfur in pores is 69.5%.

Table S3 The fitted resistance parameters of SEI film (R_{sf}) and charge-transfer resistance (R_{ct}) for the S-CNT/GF, S−NC@CNT/GF and S-NC⊙CNT/GF three electrodes.

Electrode description	R_{sf} (Ω)	R_{ct} (Ω)
S-CNT/GF	31.8	139.5
S−NC@CNT/GF	14.1	42.2
S-NC⊙CNT/GF	8.6	20.7

Table S4 The calculated E_b (eV) for different Li_2S_x species and virous N-doped carbon configurations.

Doping configurations	**S_8**	**Li_2S_8**	**Li_2S_6**	**Li_2S_4**	**Li_2S_2**	**Li_2S**
Pure	-0.017	0.467	0.465	0651	0.763	0.731
N_C	0.647	0.661	0.746	0.930	0.863	0.745
N_{2C}	0.816	0.813	0.569	0.687	0.806	0.722
N_{PD}	0.526	1.162	1.037	1.127	1.087	1.366
N_{2PD}	0.531	1.173	1.231	1.523	2.010	2.117
N_{PL}	0.848	0.635	0.686	0.764	0.980	0.991
N_{3PD}	0.839	2.103	2.291	2.360	2.906	2.816
N_{4PD}	0.221	2.885	2.855	2.980	3.492	3.164

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