Supporting Information

Multi-Cavity Carbon Fiber Film Decorated with Co-N_x Doped CNTs for Lithium-Sulfur Batteries with High-Areal-Capacity

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I. Supporting Experimental Details

Visualized adsorption experiment: Li_2S_6 solution was synthesized by mixing sulfur and lithium sulfides (Li_2S) at a molar ratio of 5:1 in 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) (v:v = 1:1). Co-NCNTs@CNF-0.42 and CP with the same mass were added to 2 mL of Li_2S_6 solution (1 mmol L^{-1}), respectively.

Li_2S nucleation test: Li_2S_8 solution (0.2 mol L^{-1}) was prepared by mixing sulfur and Li_2S at a molar ratio of 7:1 with 1.0 mol L^{-1} LiTFSI in diglyme for 48 h. Then, 25 μL of Li_2S_8 catholyte was dropped onto the Co-NCNTs@CNF-0.42 or CP cathode, and 25 μL of blank electrolyte was dropped onto the lithium anode. For Co-NCNTs@CNF-0.42/CP cathode, the cells were discharged to 2.12 / 2.09 V under a galvanostatic current of 0.112 mA and then kept at 2.10 / 2.07 V until the current dropped to below 10^{-5} A.

II. Supporting Figures

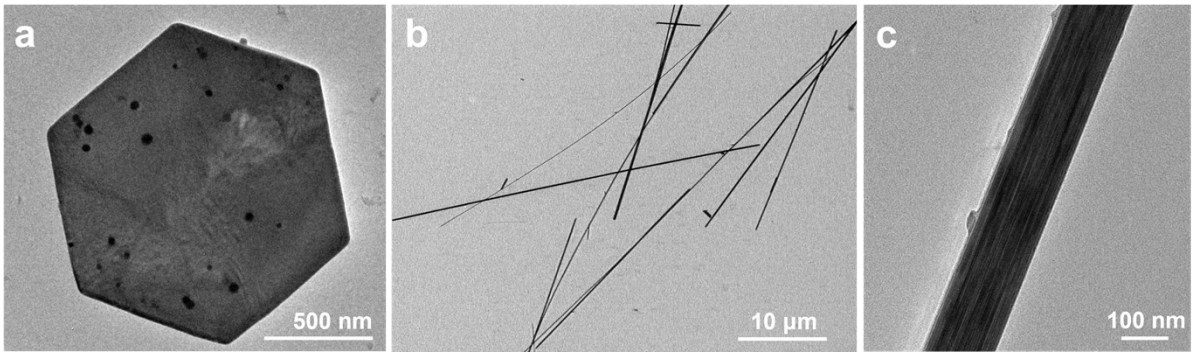

Fig. S1 TEM images of (a) Co-Al LDH and (b-c) MnO_2 nanowires.

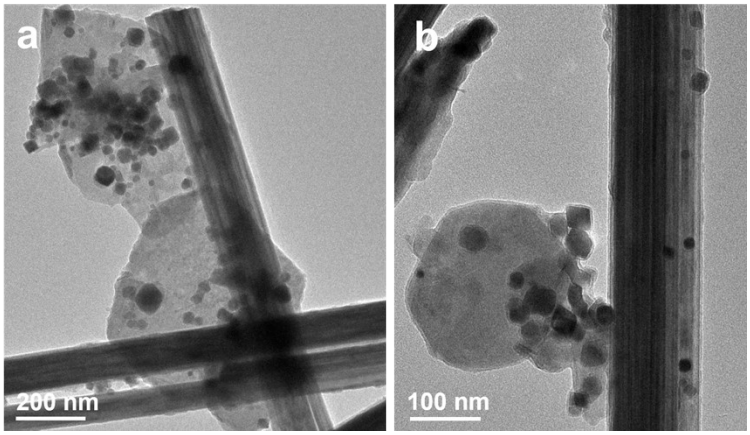

Fig. S2 TEM images of MnO_2@Co-Al LDH film.

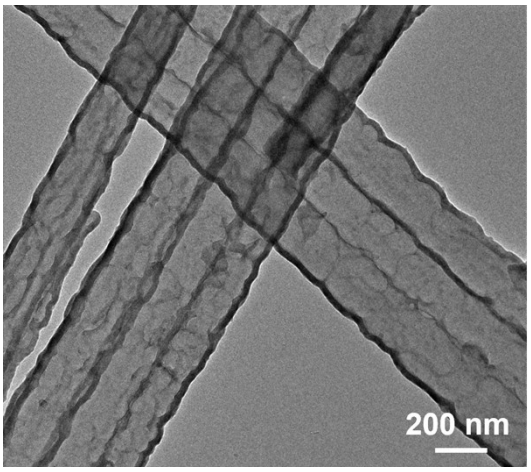

Fig. S3 TEM image of CNF.

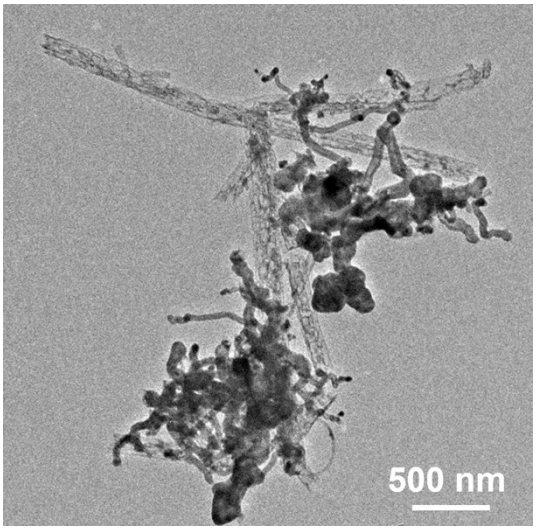

Fig. S4 TEM image of Co-NCNTs@CNF-0.84.

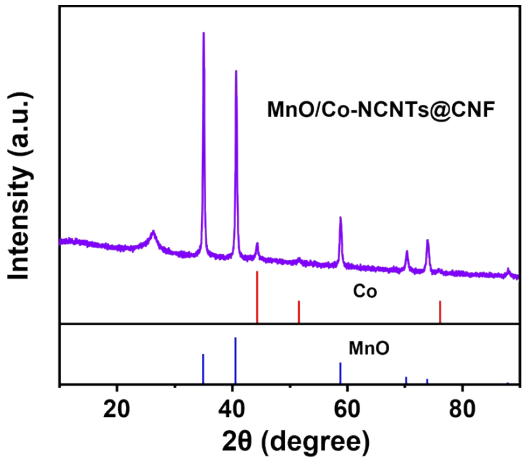

Fig. S5 XRD pattern of MnO/Co-NCNTs@CNF.

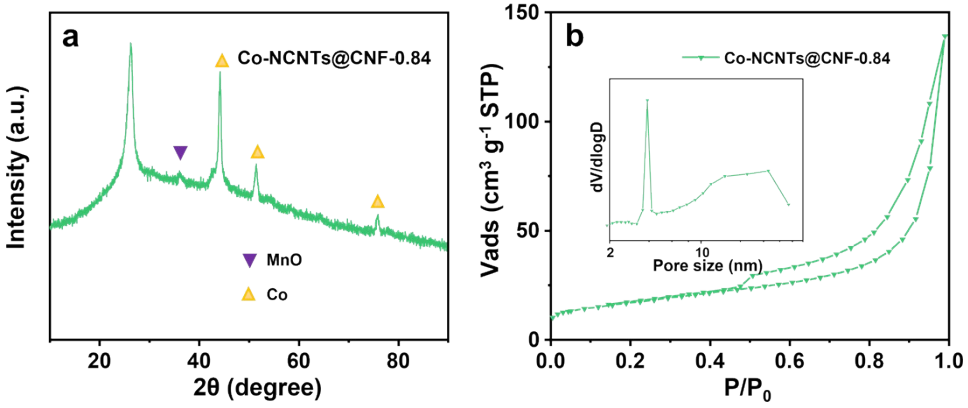

Fig. S6 (a) XRD pattern and (b) N_2 sorption isotherm and pore size distribution of Co-NCNTs@CNF-0.84.

Table S1 Pore structure parameters of Co-NCNTs@CNF-x and CNF.

Samples	S_{BET}	S_{micro}	V_{total}	V_{micro}	V_{meso}/V_{total}
	$m^2\ g^{-1}$		$cm^3\ g^{-1}$		%
CNF	57.8	29.3	0.18	0.015	91.67
Co-NCNTs@CNF-0.21	49.8	21.9	0.15	0.010	93.33
Co-NCNTs@CNF-0.42	42.4	12.3	0.19	0.006	96.84
Co-NCNTs@CNF-0.84	59.6	6.1	0.21	0.003	98.57

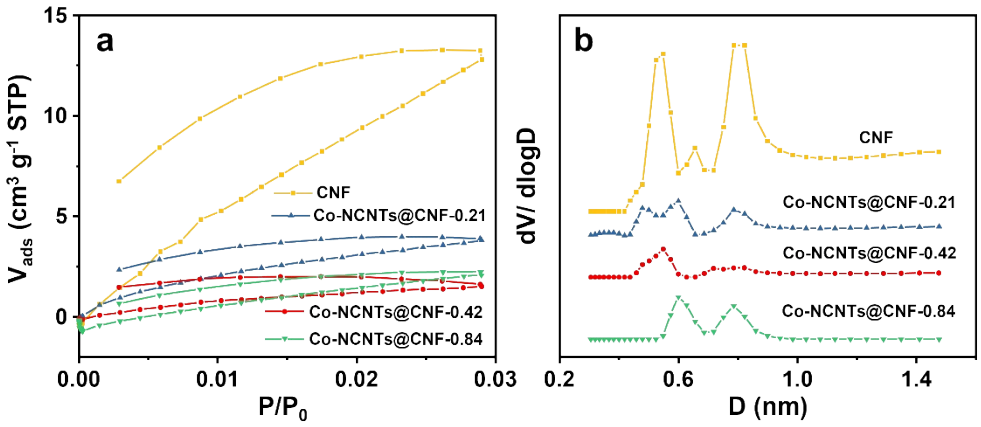

Fig. S7 (a) CO_2 adsorption isotherms at 273 K and (b) corresponding micropore size distributions of Co-NCNTs@CNF-x and CNF.

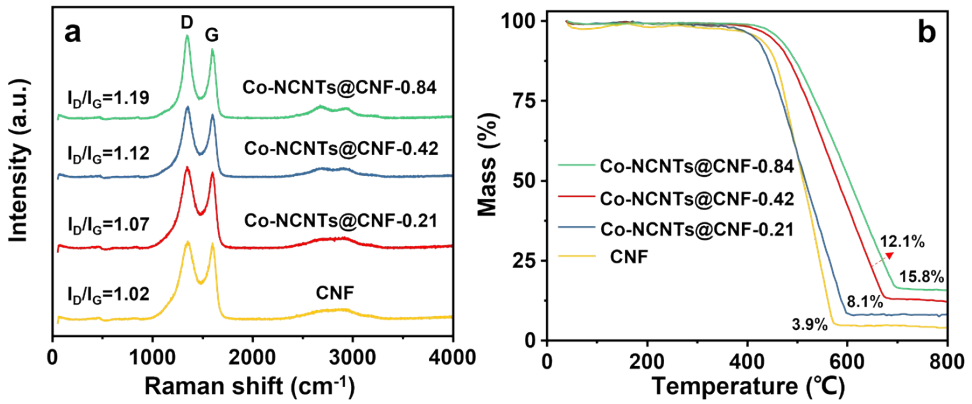

Fig. S8 (a) Raman spectra and (b) TG curves in airflow of Co-NCNTs@CNF-x and CNF.

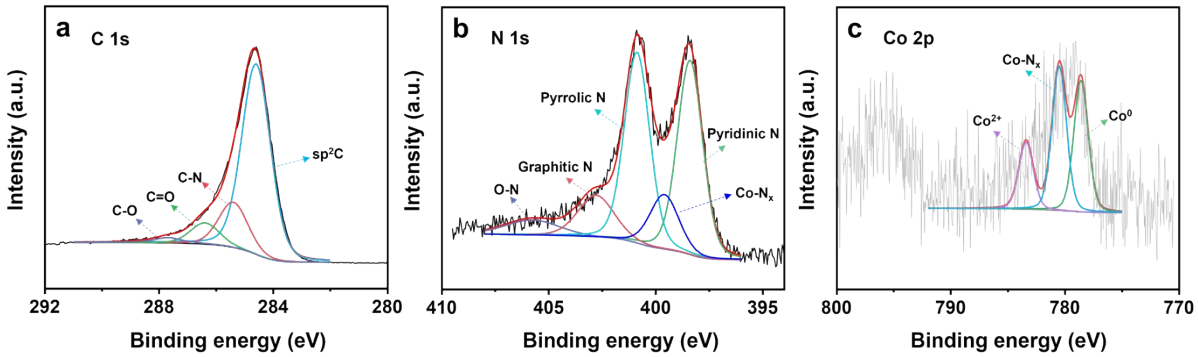

Fig. S9 (a) C 1s, (b) N 1s, and (c) Co 2p XPS spectra of Co-NCNTs@CNF-0.42.

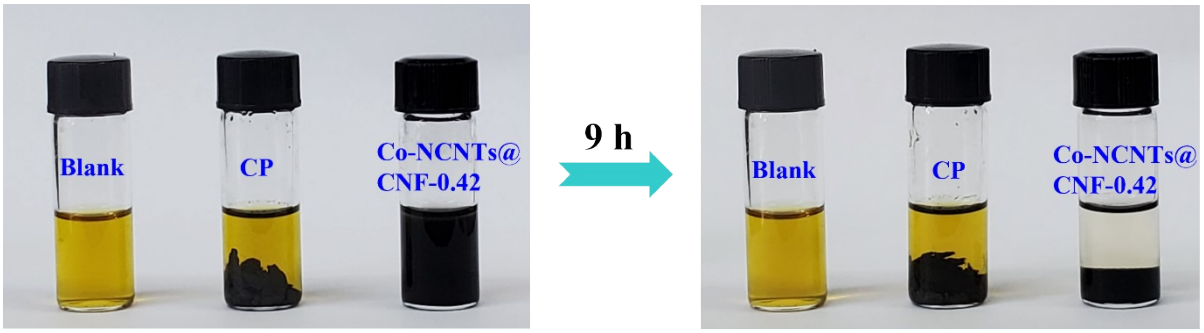

Fig. S10 Digital photographs of an adsorption experiment between Li_2S_6 and Co-NCNTs@CNF-0.42 or CP.

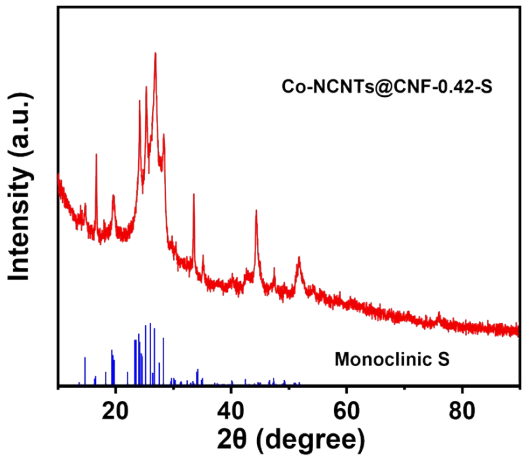

Fig. S11 XRD pattern of Co-NCNTs@CNF-0.42-S.

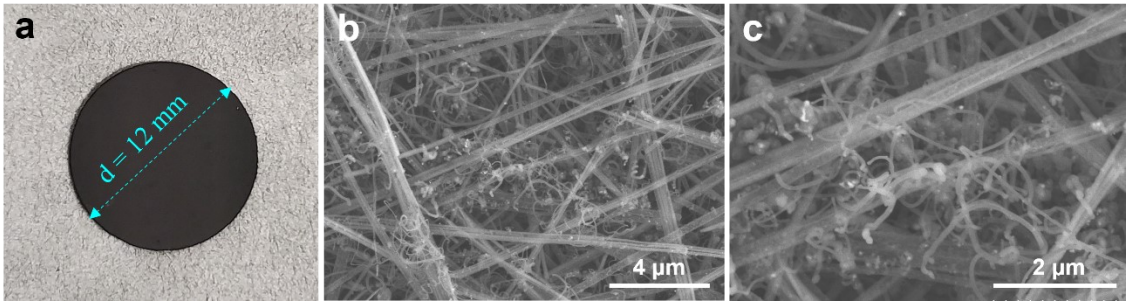

Fig. S12 (a) Macroscopic picture and (b, c) SEM images of Co-NCNTs@CNF-0.42-S.

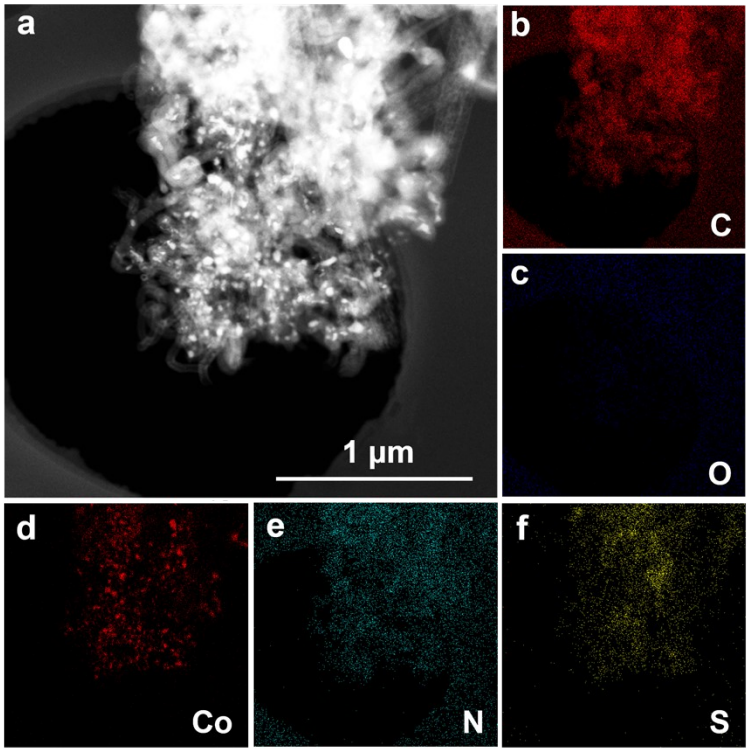

Fig. S13 (a) STEM image of Co-NCNTs@CNF-0.42-S and corresponding elemental mappings for (b) C, (c) O, (d) Co, (e) N, and (f) S.

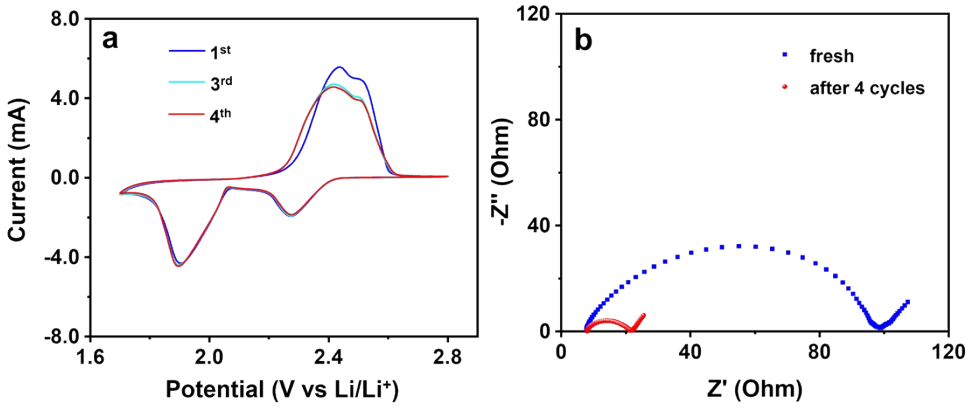

Fig. S14 (a) CV curves at 0.1 mV s^{-1} and (b) Nyquist plots of CP-S electrodes.

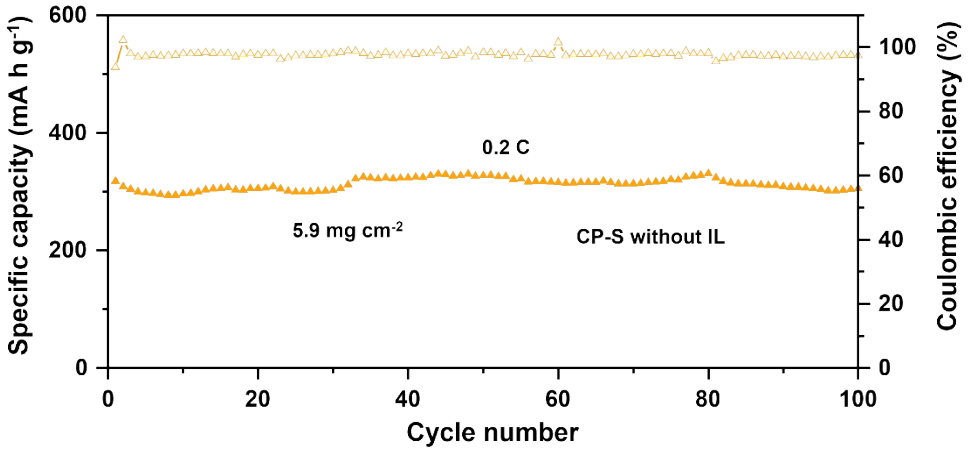

Fig. S15 Cycling performance of CP-S electrode without an IL at 0.2 C.

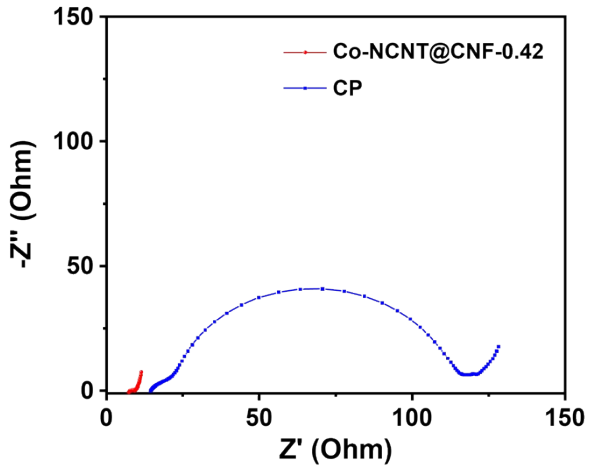

Fig. S16 Nyquist plots of Co-NCNTs@CNF-0.42 and CP symmetric batteries.

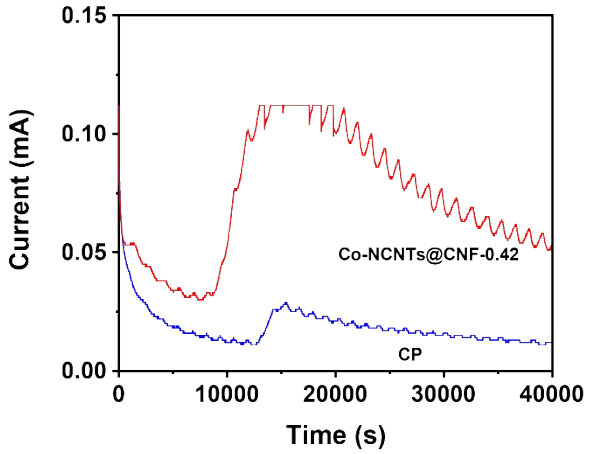

Fig. S17 Potentiostatic discharging curves of Li_2S_8/diglyme solution at 2.10 / 2.07 V on the surfaces of Co-NCNTs@CNF-0.42 and CP electrodes.

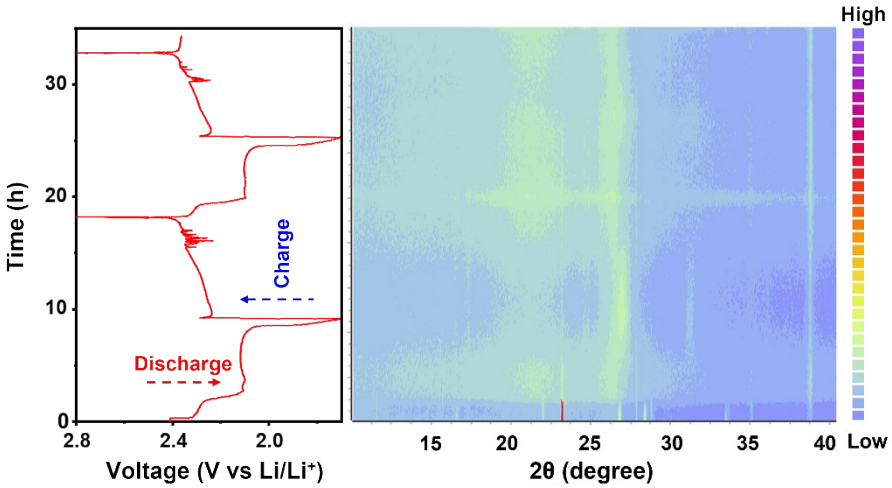

Fig. S18 *In-situ* XRD contour plot of Co-NCNTs@CNF-0.42-S electrode with the corresponding discharge-charge curves on the left and the diffraction intensity chart on the right.

Table S2 Comparison of electrochemical performances of Li/S cells with Co-NCNTs@CNF-0.42-S and results from references.

Samples	S areal loading mg cm^{-2}	Cycle number	Reversible capacity mA h cm^{-2}	Refs.
Co-NCNTs@CNF-0.42-S	6.5	100 (0.2 C)	5.14	This work
OVs-TiO_2@PP separator	3.6	100 (0.2 C)	4.50	[1]
FeP/rGO/CNTs	3.5	200 (1 C)	1.40	[2]
rGO@WO_3	3.7	200 (1 C)	1.61	[3]
MoO_2–Mo_2N interlayer	4.0	100 (0.2 C)	2.36	[4]
C_2N@$NbSe_2$/S	5.6	80 (0.2 C)	3.70	[5]
MTQ@3DG/S	4.9	100 (0.1 C)	4.70	[6]
SAZ-AF separator	4.0	100 (2 C)	2.30	[7]
In_2O_3-G-CNT/S	5.9	200 (0.5 C)	3.90	[8]
$NiMoO_4$@NSCC/S	5.0	100 (0.2 C)	2.80	[9]
Ni-Co-P@C//PP	4.5	80 (0.2 C)	3.60	[10]
w/o DPDSe	5.0	55 (0.1 C)	3.75	[11]
Li_2S_6/ZnS_{1-x}-CC	5.0	100 (0.1 C)	3.25	[12]
CoSA-N-C@S	4.9	120 (0.2 C)	4.20	[13]
S/$Fe_{3-x}C$@C-500	3.0	50 (0.2 C)	3.00	[14]
S@Co/SA-Zn@N-C/CNTs	5.1	100 (0.2 C)	4.50	[15]

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