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Supplementary Materials for

Sulfur vacancies in Co_9S_{8-x}/N-doped graphene enhancing the electrochemical kinetics for high-performance lithium-sulfur batteries

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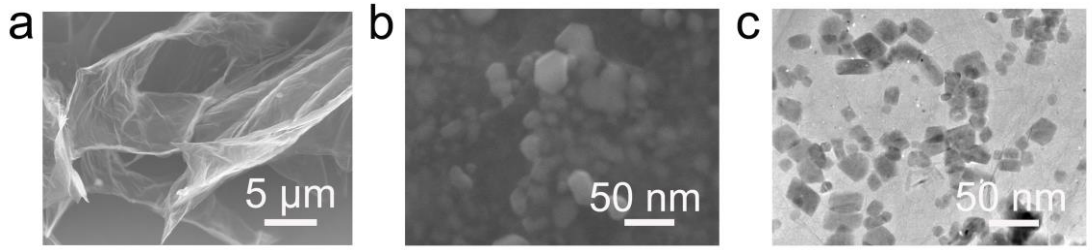

Figure. S1 SEM image of a) N-doped graphene and b) Co_9S_8 /N-doped graphene; c) TEM image of Co_9S_{8-x}/N-doped graphene.

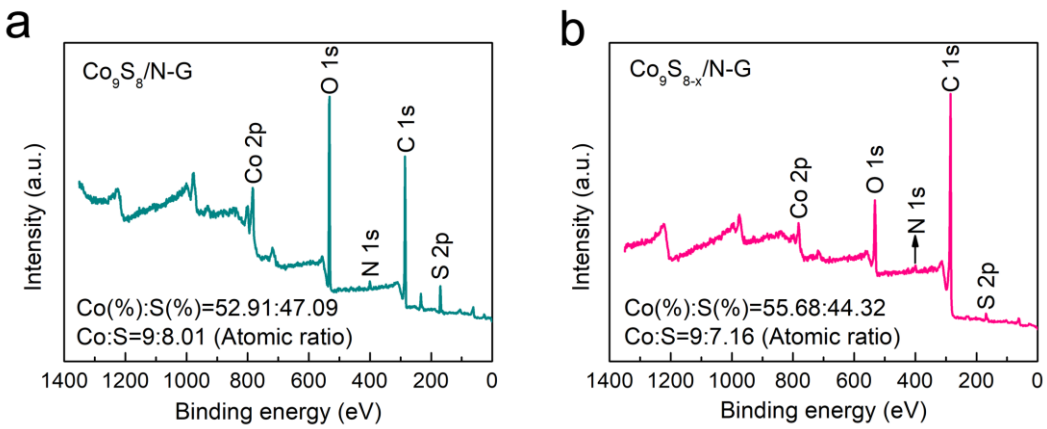

Figure. S2 XPS survey spectra of a) Co_9S_8/N-doped graphene and b) Co_9S_{8-x}/N-doped graphene.

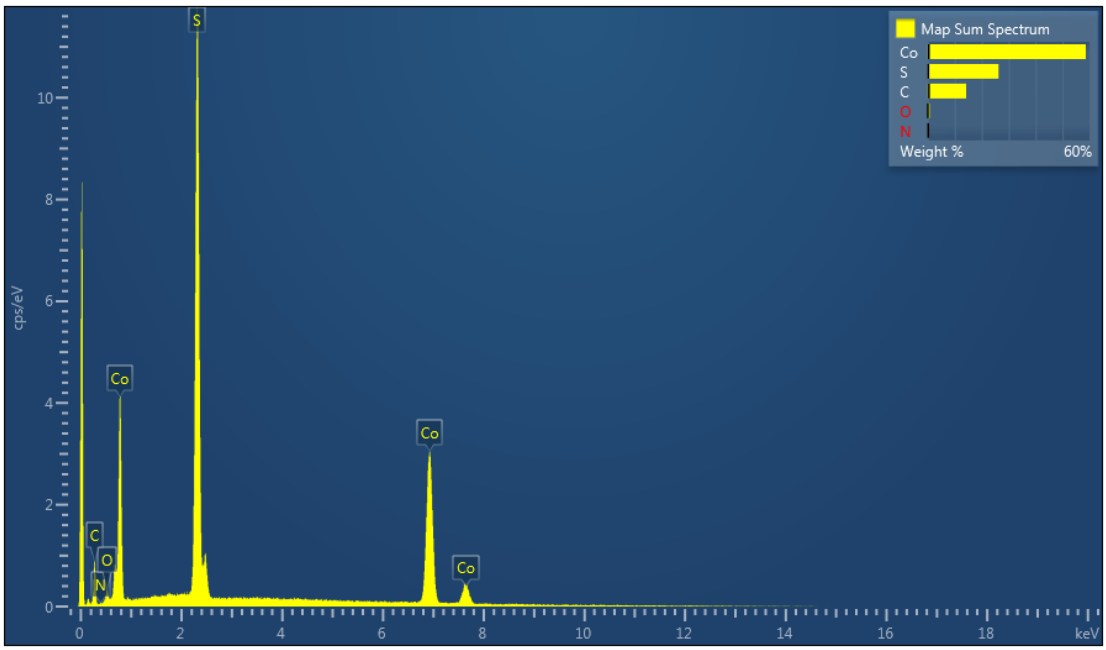

Figure S3 EDS of Co_9S_8/N-G

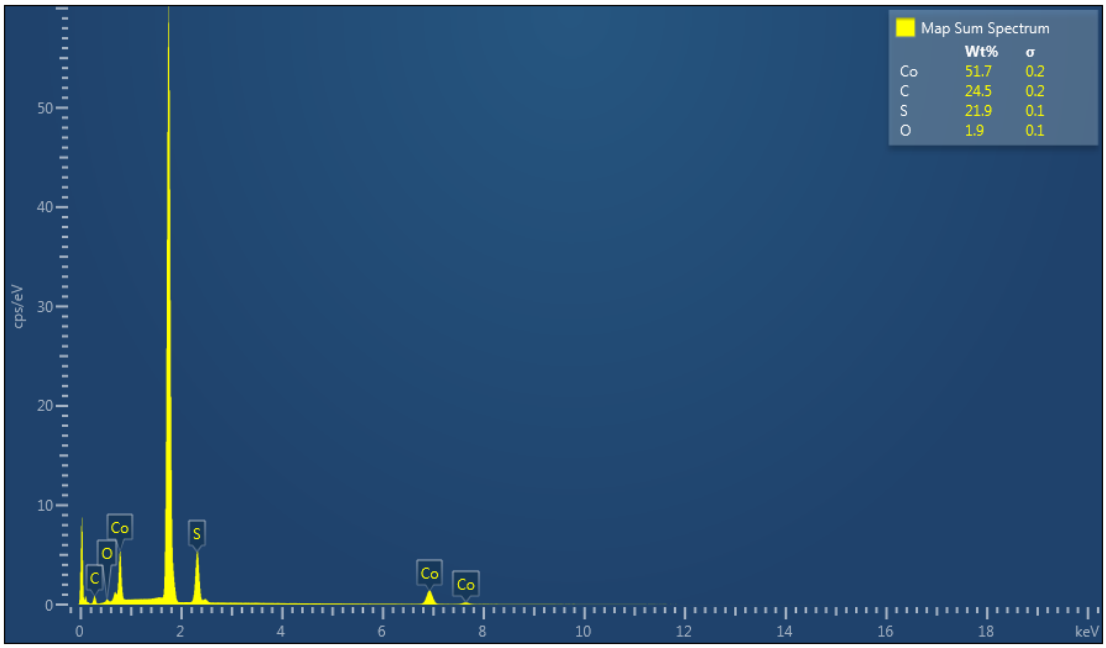

Figure S4 EDS of Co_9S_{8-x}/N-G

Table S1 Amount of element of Co_9S_8/N-G and Co_9S_{8-x}/N-G based on EDS

Sample	EDS				Content	
	Co (wt%)	S (wt%)	C (wt%)	O (wt%)	Mol Ratio (Co:S)	cobalt sulfide Content /(Co+S+C+O)
Co_9S_8/N-G	55.1	24.2	15.6	3.6	1.15 (9:7.8)	80
Co_9S_{8-x}/N-G	51.7	21.9	24.5	1.9	1.28 (9:7.02)	74

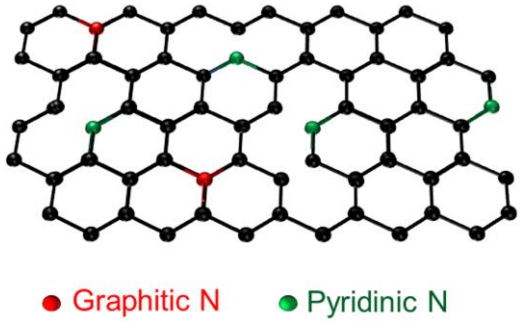

Figure. S5 Schematic structure of N-doped graphene.

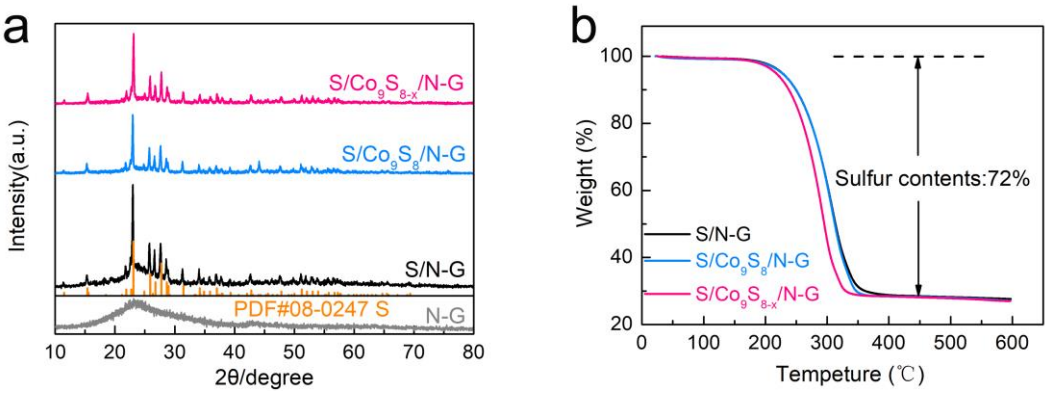

Figure. S6 a) XRD pattern and b) TGA curve of S/Co_9S_{8-x}/N-doped graphene, S/Co_9S_8/N-doped graphene, S /N-doped graphene, as well as N-doped graphene for comparison.

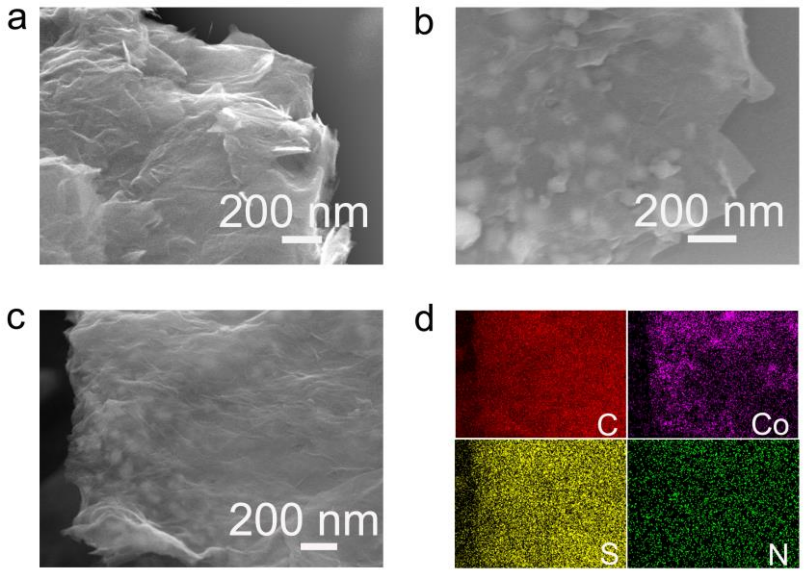

Figure. S7 SEM image of S /N-doped graphene (a), S/Co_9S_8/N-doped graphene (b), and S/Co_9S_{8-x}/N-doped graphene (c); the corresponding EDS element maps of S/Co_9S_{8-x}/N-doped graphene.

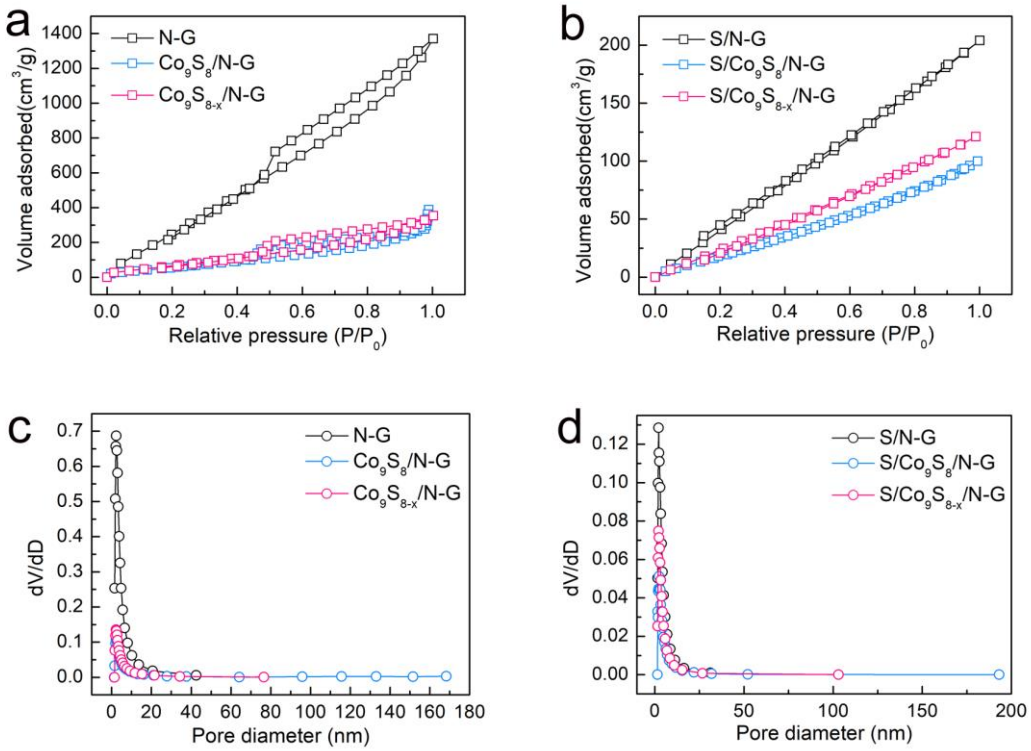

Figure. S8. N_2 adsorption-desorption isotherm and pore size distribution plot of the host materials and after loading sulfur.

Table S2 Specific surface area and pore size data of the host materials and after loading sulfur

Materials	Co_9S_{8-x} /N-G	S/Co_9S_{8-x} /N-G	Co_9S_8 /N-G	S/Co_9S_8 /N-G	N-G	S/N-G
Specific surface areas /m^2 g^{-1}	327	191	273	118	1664	313
Average pore size/nm	6.7	4.0	6.6	4.0	5.8	4.1
Total pore volume/cm^3 g^{-1}	0.61	0.19	0.60	0.16	4.73	0.32

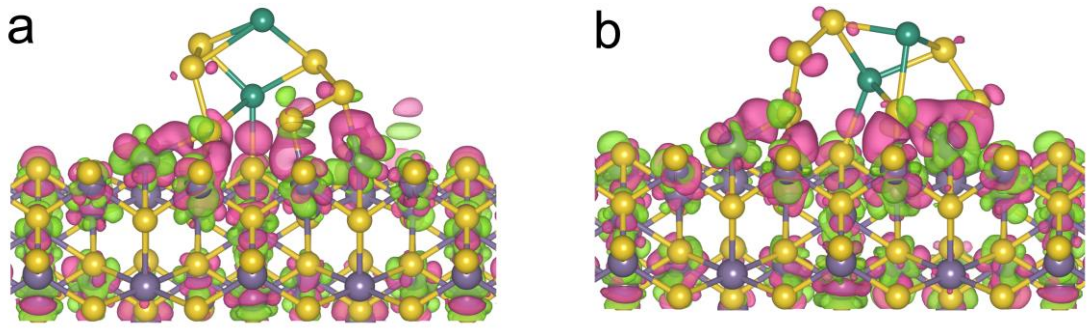

Figure. S9 Visualized vacancy charge difference between the a) Co_9S_8 (311)-Li_2S_6 and b) Co_9S_{8-x} (311)-Li_2S_6 surfaces. Pink isosurface and green isosurface represent the positive and the negative charges migration, and the small pink ball marked was the vacancy. Obviously, a great lack of charges around the vacancy also affected the charge distribution of the nearby Co atoms.

Table S3 Selected bond lengths (Å) of the Li_2S_6@Co_9S_8 (311) and Li_2S_6@Co_9S_{8-x} (311) complexes

Bond length (Å)	Co-S, surf (Avg)	Co-S, int	Li-S	S-S
Co_9S_8 (311)	2.23~2.50 (2.30)	2.20	2.37	2.5185
Co_9S_{8-x} (311)	2.13~2.33 (2.23)	2.07	2.68	2.5200

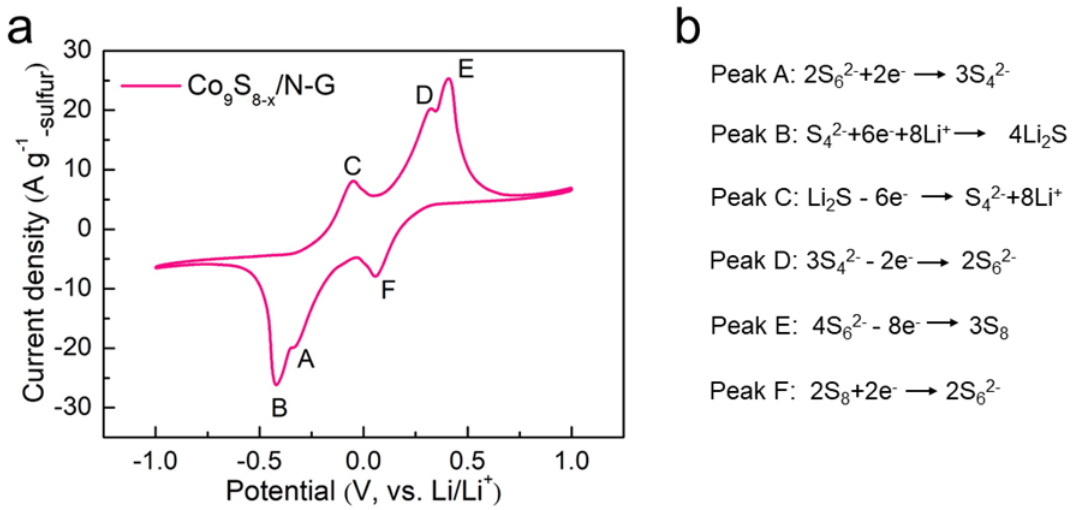

Figure. S10 a) The cyclic voltammograms of the symmetric cell with Co_9S_{8-x}/N-G catalyst; b) The electrode reaction for the redox peaks.

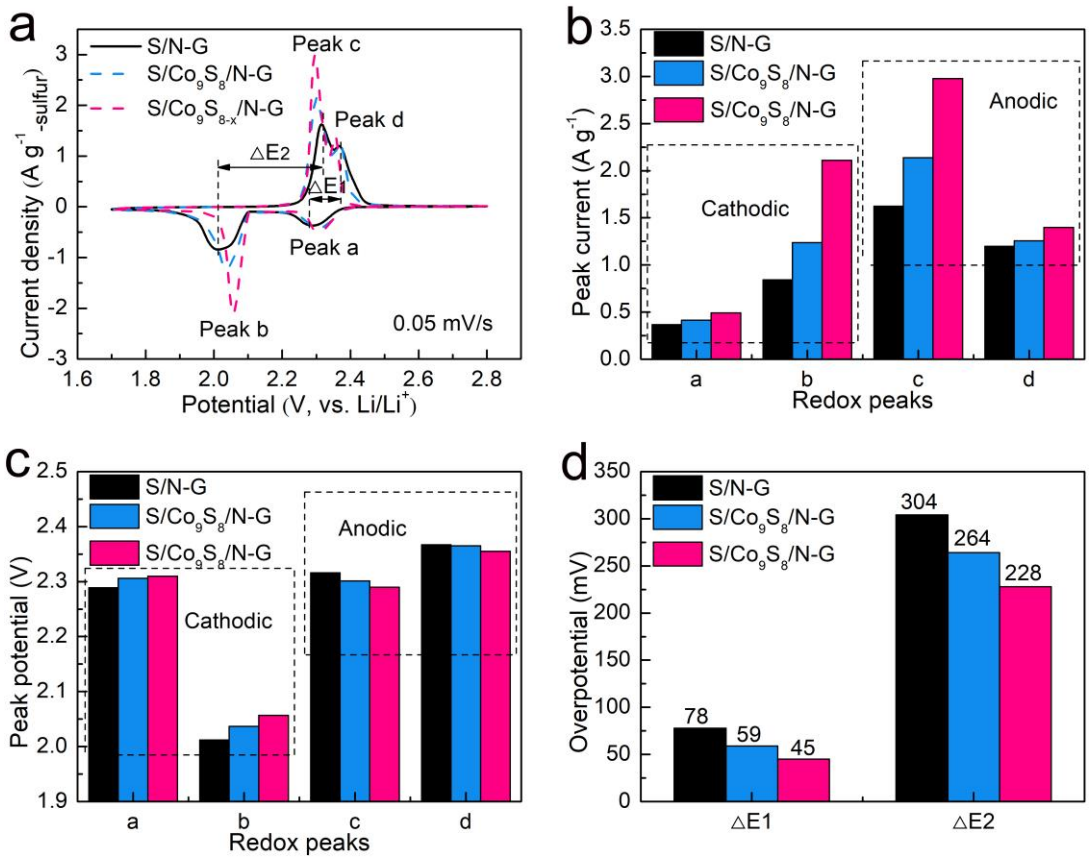

Figure. S11 a) CV profile of S/Co_9S_{8-x}/N-doped graphene, S/Co_9S_8/N-doped graphene, and S/N-doped graphene at a scanning rate of 0.05 mVs^{-1}; comparison of peak current (b), peak potential (c), and potential difference (d).

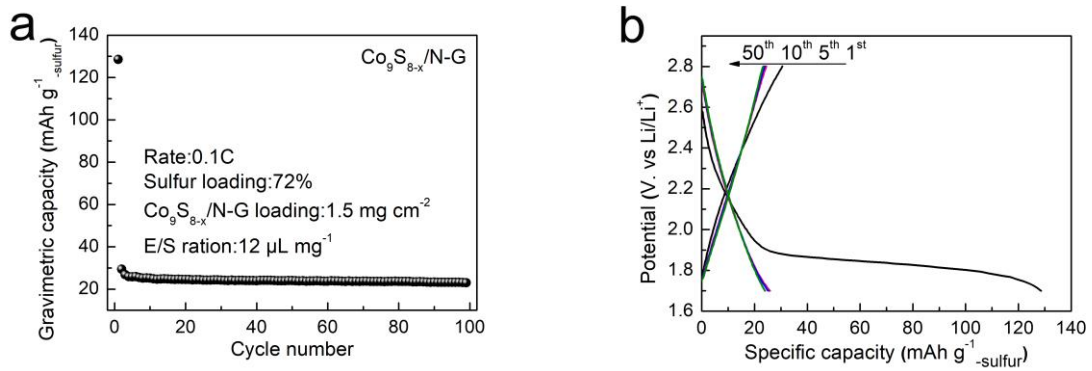

Figure. S12 Cycle performance (a) and charge-discharge curves (b) of Co_9S_{8-x}/N-doped graphene.

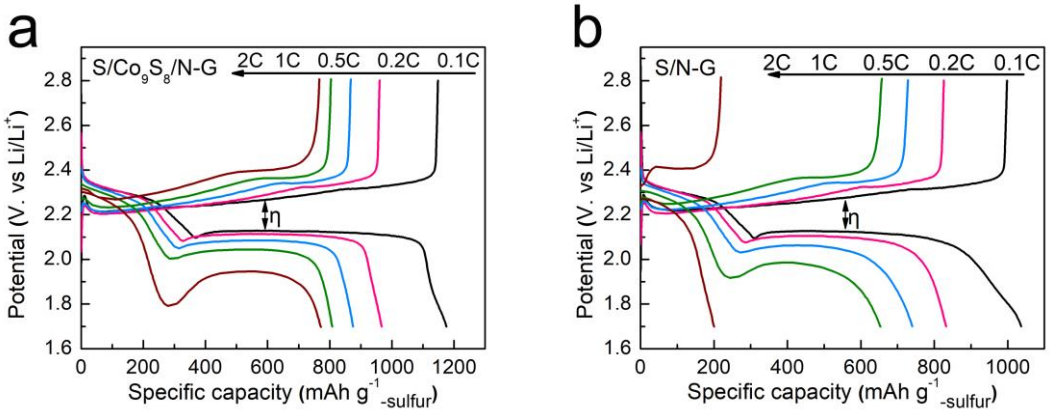

Figure. S13 Charge-discharge curves at various rates of a) S/Co_9S_8/N-doped graphene, and c) S/N-doped graphene; and comparison of the corresponding overpotential (d).

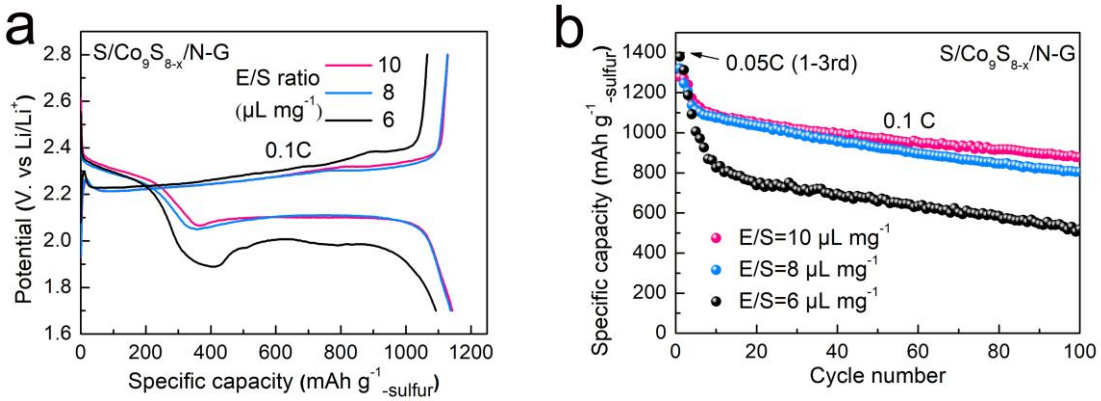

Figure. S14 a) The initial discharge–charge curve of S/Co_9S_{8-x}/N-doped graphene (areal sulfur loading of 1.5 mg cm^{-2}) at 0.1 C rate with various E/S ratios; b) cycling performance with the E/S ratio of 6 μL mg^{-1}.

Table S4 Sulfur loading and area capacity of the reported lithium–sulfur batteries involving metal sulfide as host materials

Sample	**Mass loading (mg cm^{-2})**	**Area capacity (mAh cm^{-2})**	**Reference No.**
Co_9S_{8-x} /N-G	14.6	12.9	This work
Co_9S_8-3DGF	10.4	10.9	[1]
Co_9S_8/C	3	2	[2]
Co_9S_8	4.5	4.3	[3]
N-Co_9S_8	5	4.3	[4]

Co_9S_8 Nanorods	3	3.15	[5]
CNTs/CoS-NSs	3.8	5.05	[6]
NiS	2.3	1.66	[7]
CoS_2-LBLCN	3	4.1	[8]
DCC@MoS_2/PrNP/CNTs	5.2	4.75	[9]
C@SnO_2/MoS_2	5	4.55	[10]
MoS_3	5.5	5.16	[11]
Mo_6S_8	10	7.5	[12]
CC@Co_9S_8	6.1	4.35	[13]
MoS_2-NPs	4	3.9	[14]
MoS_2/rGO	3.6	3.3	[15]
rGO–VS_2/S-89	2.56	2.6	[16]
TiS_2@NSC	7.7	5.9	[17]
ZnS/ Li_2S@G	3.49	3.29	[18]

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