Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Combined Physical Confinement and Chemical Adsorption on Co-doping Hollow TiO_2 for Long-Term Cycle Lithium-sulfur Batteries

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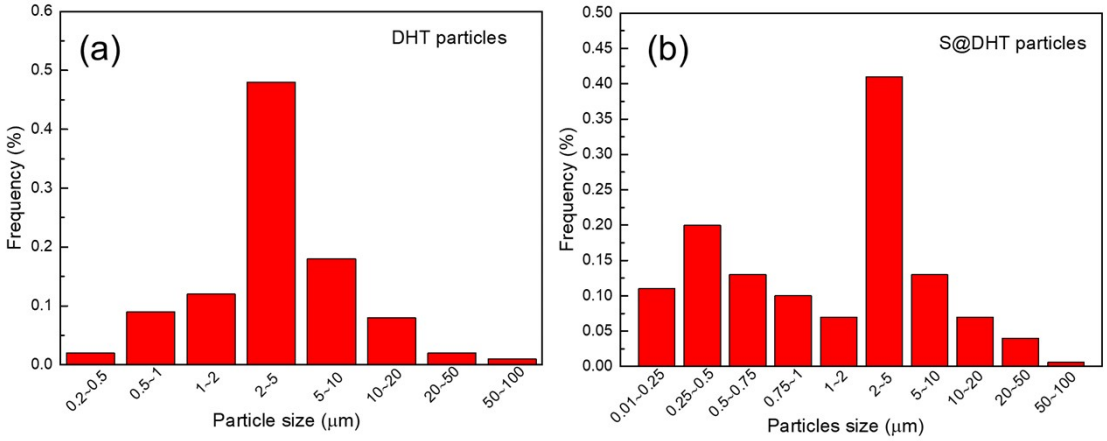


Figure S1. Size distribution of (a) DHT, and (b) S@DHT composite as determined by particle density analysis instrument.

Table S1. Specific surface area, total pore volume and pore diameter of the four samples (S@DHT, S/DHT, DHT, and elemental sulfur)

Samples	S_{BET} (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	pore diameter (nm)
S@DHT	249.23	0.37	12.28
S/DHT	210.81	0.29	13.56
DHT	652.57	0.92	5.96
Sulfur	16.39	0.17	16.23

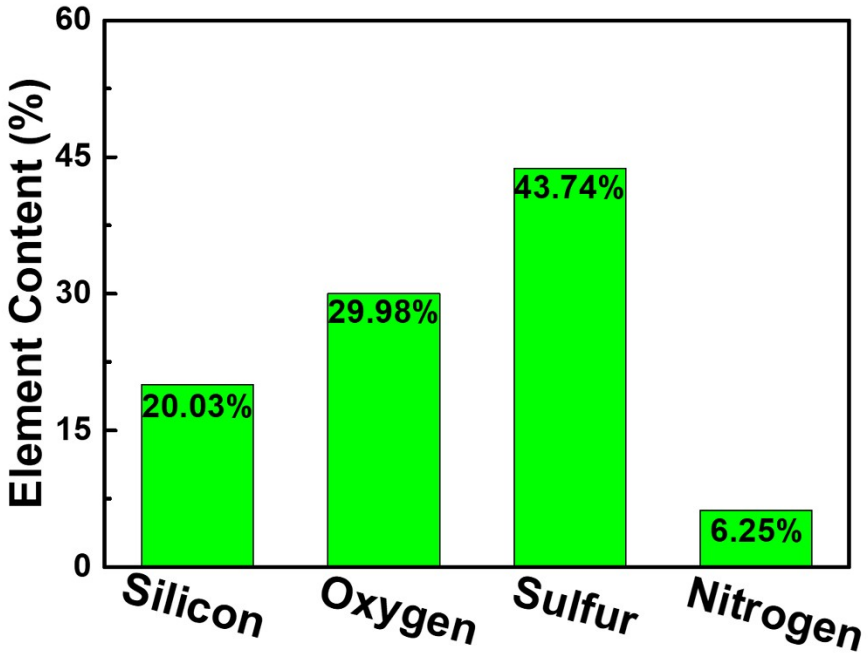


Figure S2. The summary of the elemental content histogram in the S@DHT sample.

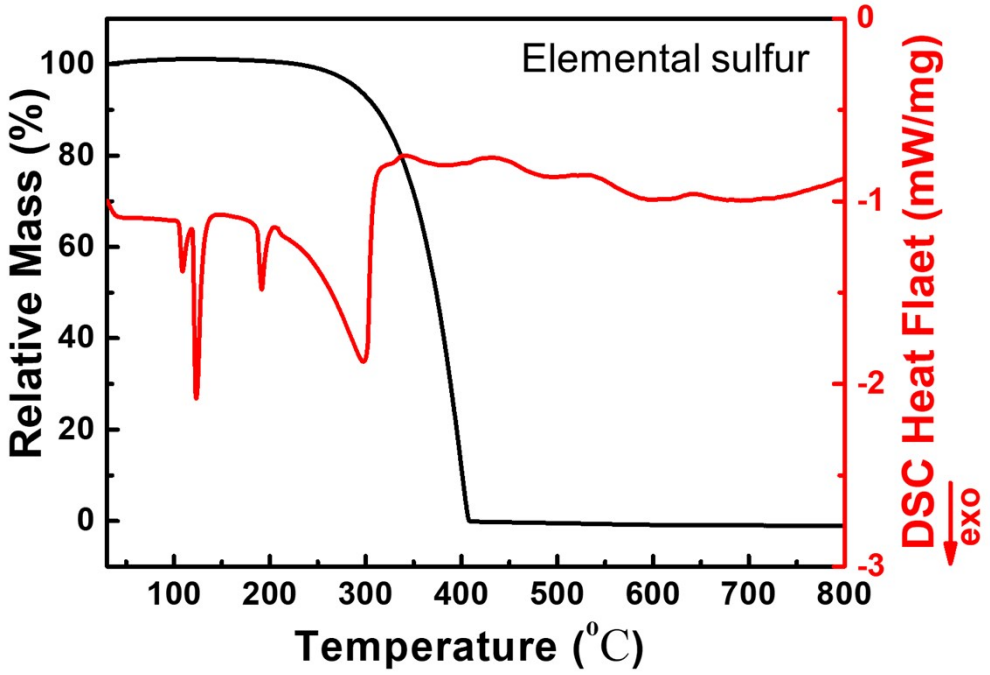


Figure S3. TGA/DSC curves of elemental sulfur [1].

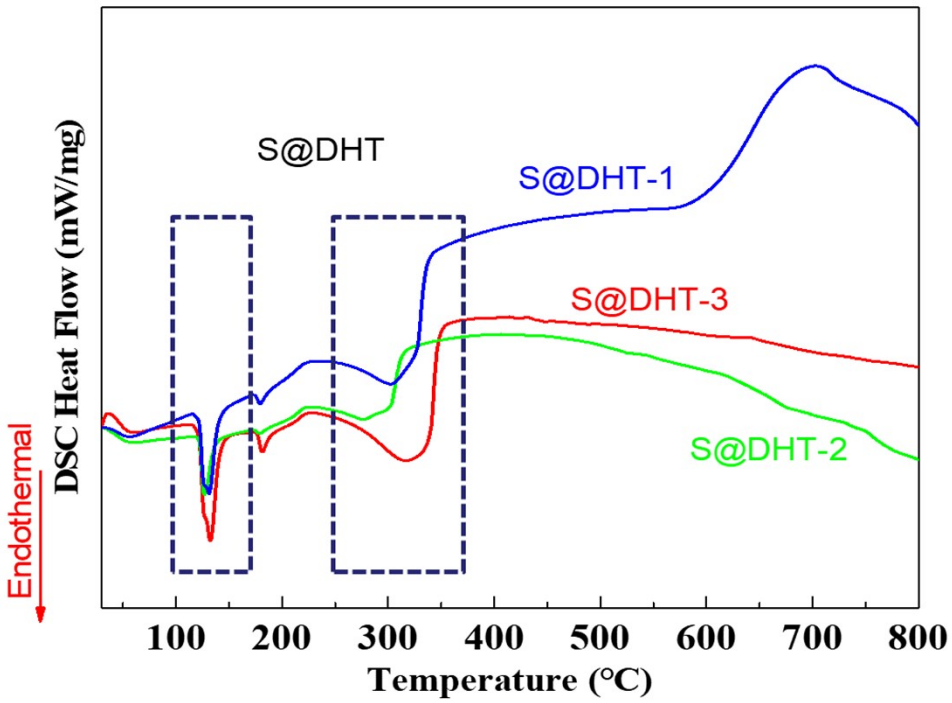


Figure S4. DSC curves of the three S@DHT samples.

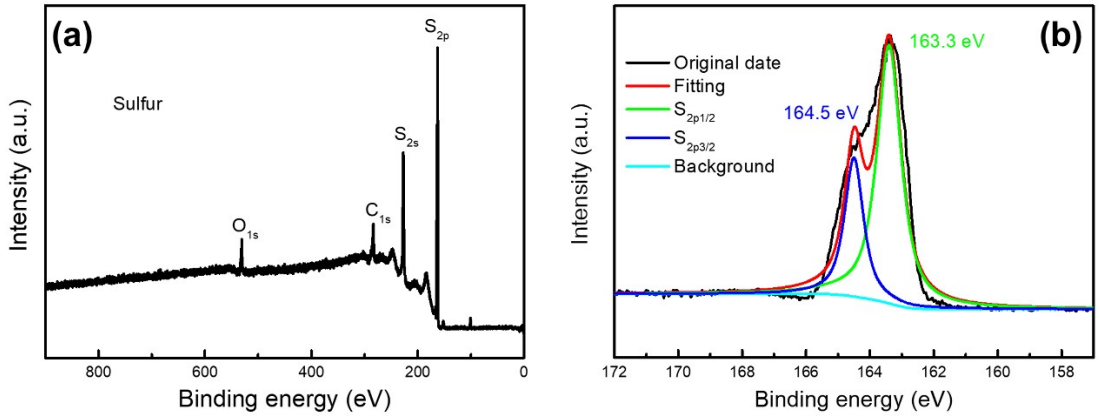


Figure S5. (a) XPS survey spectrum of elemental sulfur, (b) High-resolution fitting spectrum of elemental S 2p.

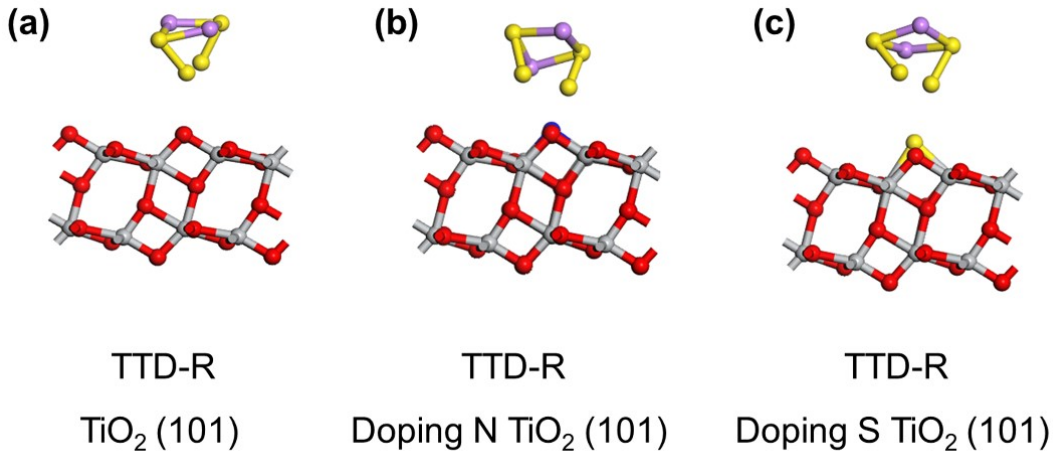


Figure S6. Different viewpoints optimized configurations of (a) between TiO_2 and Li_2S_4, (b) between N-doped TiO_2 and Li_2S_4, (c) between S-doped TiO_2 and Li_2S_4.

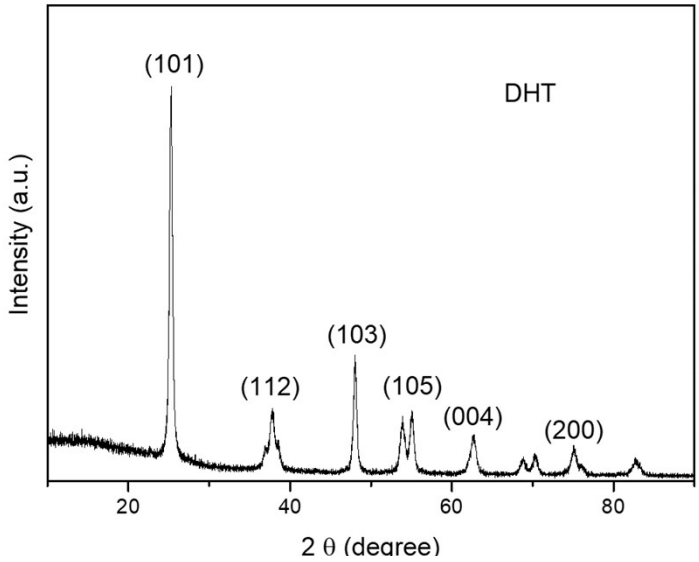


Figure S7. XRD pattern of DHT.

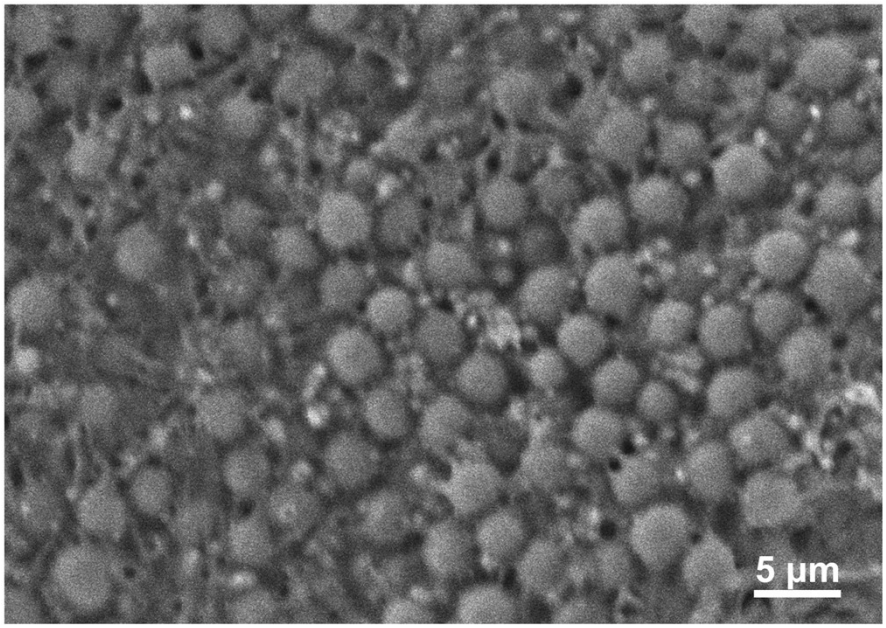


Figure S8. SEM image of sulfur electrode with S@DHT cathode.

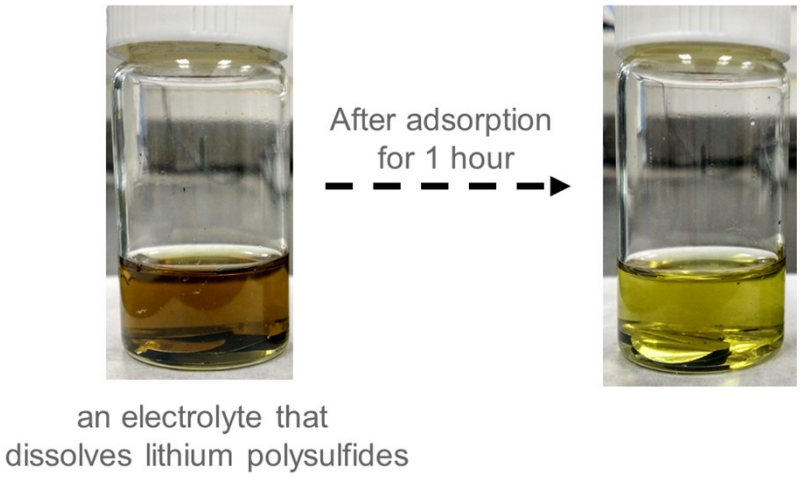


Figure S9. Illustration of electrodes placed in an electrolyte that dissolves lithium polysulfides. The electrolyte was configured using with 1.0 mol L^{-1} lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) with 0.1 mol L^{-1} of $LiNO_3$ in 1,3-dioxolane and 1,2-dimethoxyethane (v/v = 1:1). Further, We prepared Li_2S_8 which was synthesis using calculated stoichiometry of Li_2S and elemental sulfur. Then the 1 mol L^{-1} Li_2S_8 was dissolves in above electrolyte. Finally, The prepared five electrodes are added to the final solution. All the above experimental steps are performed in a glove box filled with argon gas.

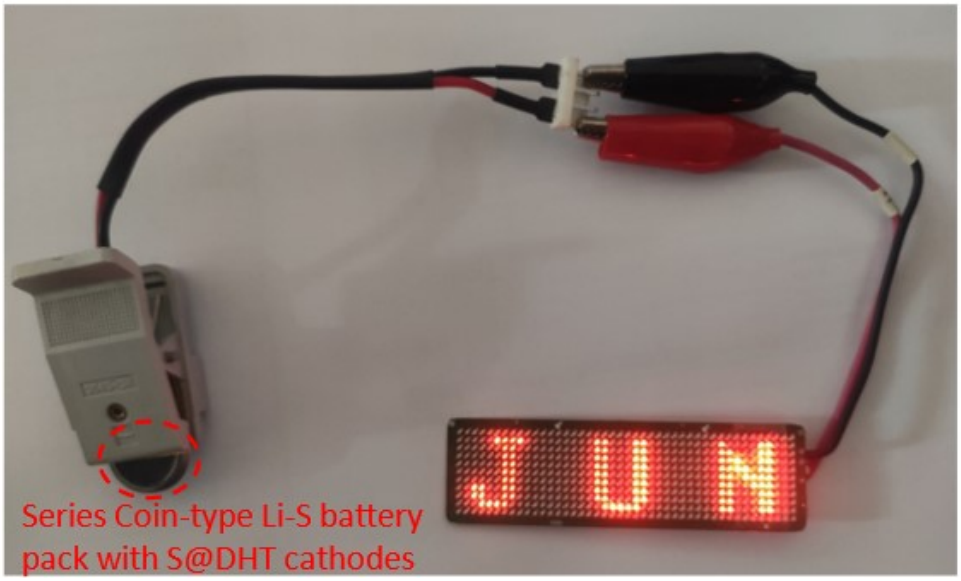


Figure S10. Practical demonstration of Li-S batteries with the S@DHT cathode.

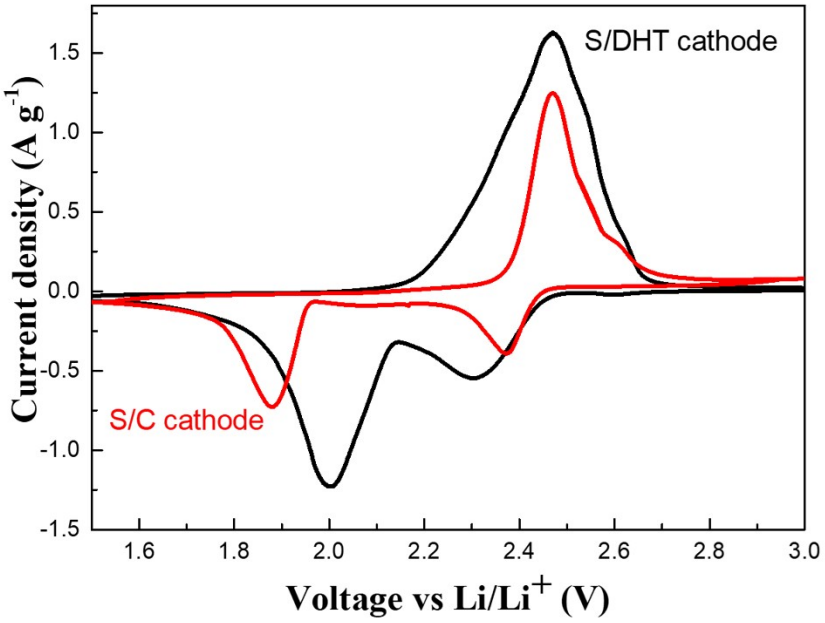
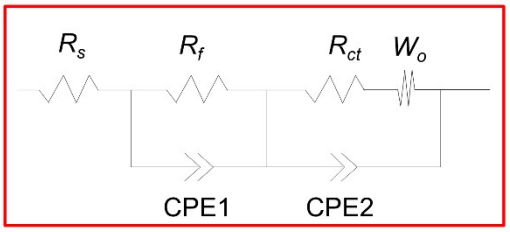


Figure S11. CV curves of Li-S batteries with prefabricated S/DHT, S/C cathodes at scan rate of 0.2 mV s^{-1} and in the scan voltage range of 1.5～3.0 V *vs* Li/Li^+.

Table S2 (a) equivalent circuit for S@DHT, S/DHT and S/C cathodes, (b) charge-transfer resistance (R_{ct}) of different electrodes by fitting impedance spectroscopy. The high-frequency intercept on the real axis represents the ohmic resistance (R_f) of the cell, including the electrolyte and electrode resistances. The semicircles in the high-frequency region along with a radial oblique line in the low-frequency region correspond to the charge-transfer resistance (R_{ct}) and the Warburg impedance (W_0).

(a)



(b)

Electrodes	R_f (Ω)	R_{ct} (Ω)
S@DHT	4.1	37
S/DHT	4.3	174
S/C	8.6	198

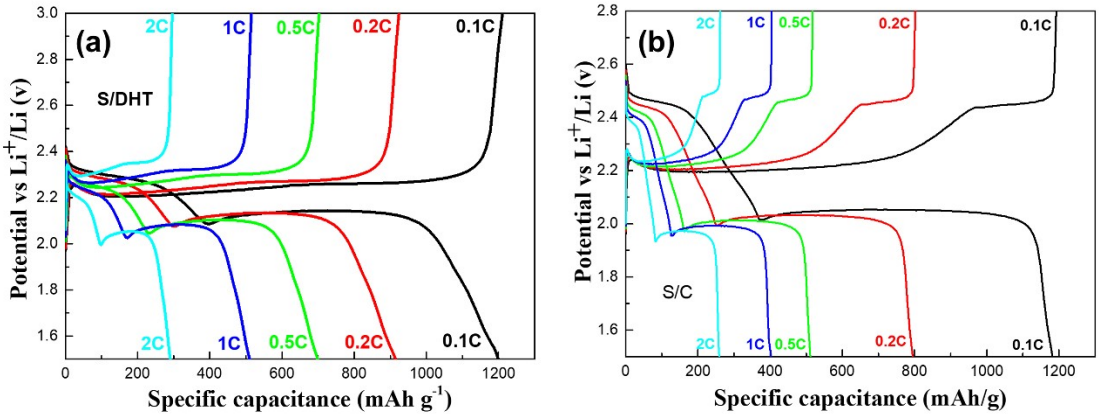


Figure S12. The charge and discharge of S/DHT and S/C cathodes at rate-current densities from 0.1 C to 2 C.

Table S3. The discharge capacity of the three electrodes (S/C, S/DHT, and S@DHT electrodes) with various current densities (0.1 C, 0.2 C, 0.5 C, 1 C, 2 C, and back to 0.1 C).

Samples electrode	0.1 C ($mAh\ g^{-1}$)	0.2 C ($mAh\ g^{-1}$)	0.5 C ($mAh\ g^{-1}$)	1 C ($mAh\ g^{-1}$)	2 C ($mAh\ g^{-1}$)	Back to 0.1 C ($mAh\ g^{-1}$)
S/C	1189.6	800.2	513.7	400.9	260.1	613.4
S/DHT	1198.4	917.4	703.2	512.5	296.7	943.8
S@DHT	1258.1	1086.4	904.3	738.6	571.8	1133.9

Table S4. The electrochemical performances comparison of prepared Li-S batteries by different literatures in recent years.

References	First Discharge Capacity (mAh/g)	C-Rate Capacity (mAh/g)	Total Cycle Number	Degradation Rate Per Cycle	Coulombic Efficiency	Sulphur Loading in electrode
This work	1,258 (0.1 C)	1086 (0.2 C); 904 (0.5 C); 738 (1 C); 571 (2 C)	500	0.0478%	~100%	3.8 mg/cm²
Small, 2020, 1906634	1,382 (0.1C)	1293 (0.2 C);1181 (0.5 C); 929 (1 C); 679 (2 C)	400	0.038%	--	3.61 mg cm⁻²
J. Energy Chem., 2020, 51, 262-271	1353 (0.1C)	1110 (0.2 C);1014 (0.5 C); 950 (1 C); 886 (2 C)	500	0.05%	100%	1.5 mg cm⁻² 67.5 wt%
Angew. Chem. Int. Ed., 2021, 202114671	1017 (0.2 C)	903 (0.5 C); 873 (1 C); 771 (2 C); 309 (3 C); 293 (4 C)	250	~0.084%	100%	1.2 mg cm⁻²
ACS Appl. Energy Mater. 2020, 3, 11893−11899	1211 (0.2 C)	967 (0.3 C); 908 (0.5 C); 734 (1 C); 545 (2 C)	400	~0.109%	100%	72.8 wt%

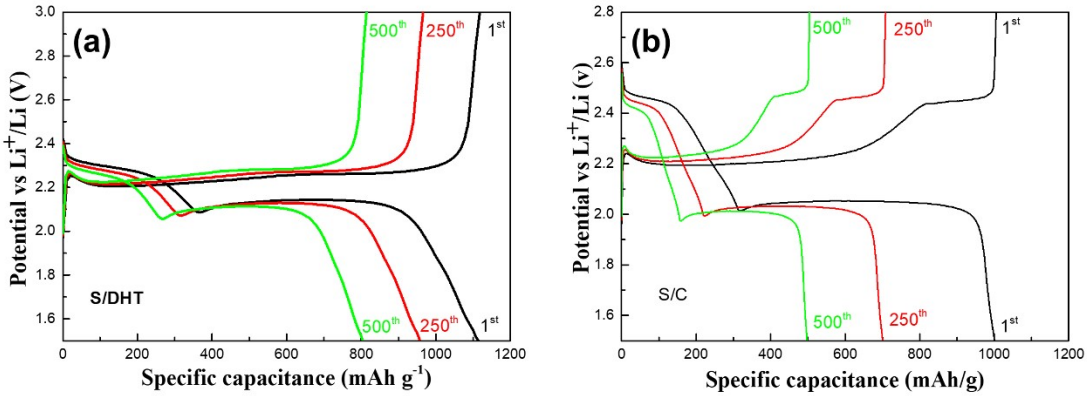


Figure S13. The different cycles (1st, 250th, 500th) discharge-charge curves of Li-S batteries with (a) S/DHT cathode, (b) S/C cathode at 0.1 C at the sulfur loading of 3.8 mg cm^{-2}.

References

1. S. B. Zeng, L. G. Li, L. H. Xie, D. K. Zhao, N. Zhou, N. Wang, S. W. Chen,. *Carbon,* **2017**, 122, 106-113.