

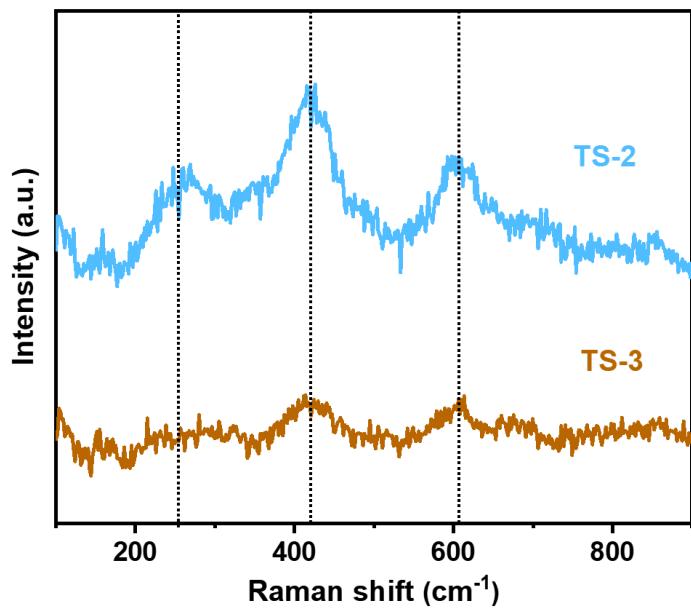
## Supporting Information

# *In Situ* Synthesis of Vacancy-Rich Titanium Sulfide Confined in a Hollow Carbon Nanocage as an Efficient Sulfur Host for Lithium–Sulfur Batteries

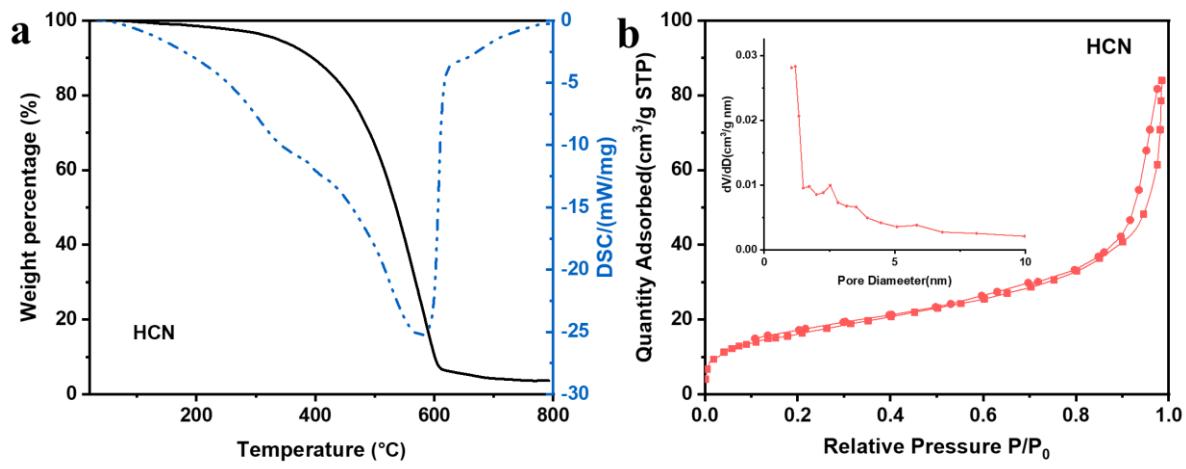
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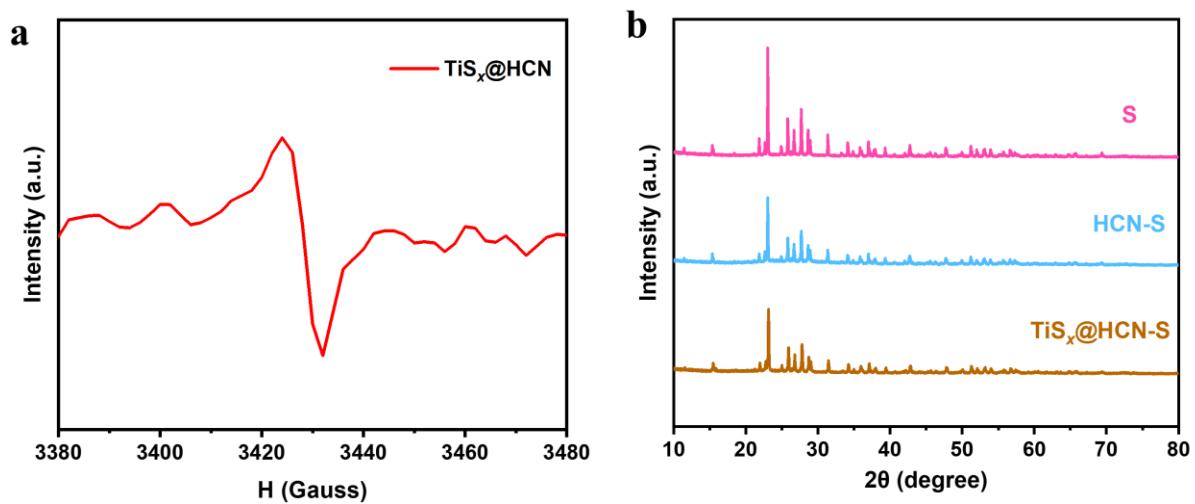
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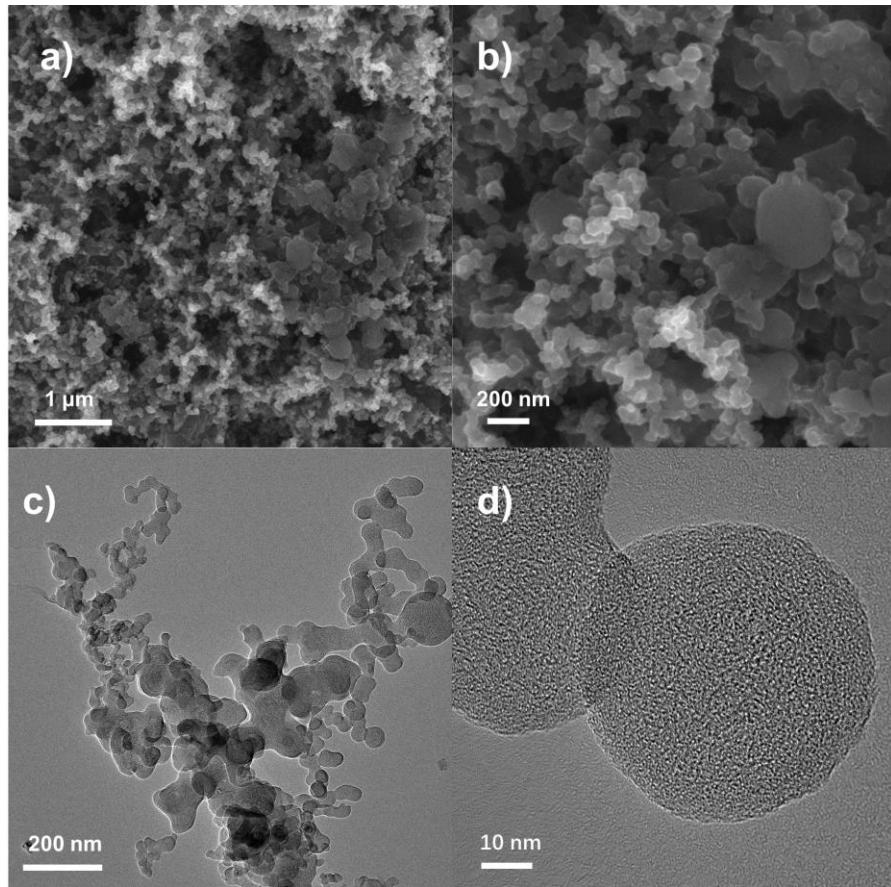
**Figure S1.** Raman spectra of  $\text{TiS}_x@\text{HCN}$  with the different ratios (1:2 & 1:3) of titanium and sulfur powder denoted as TS-2 and TS-3, respectively.



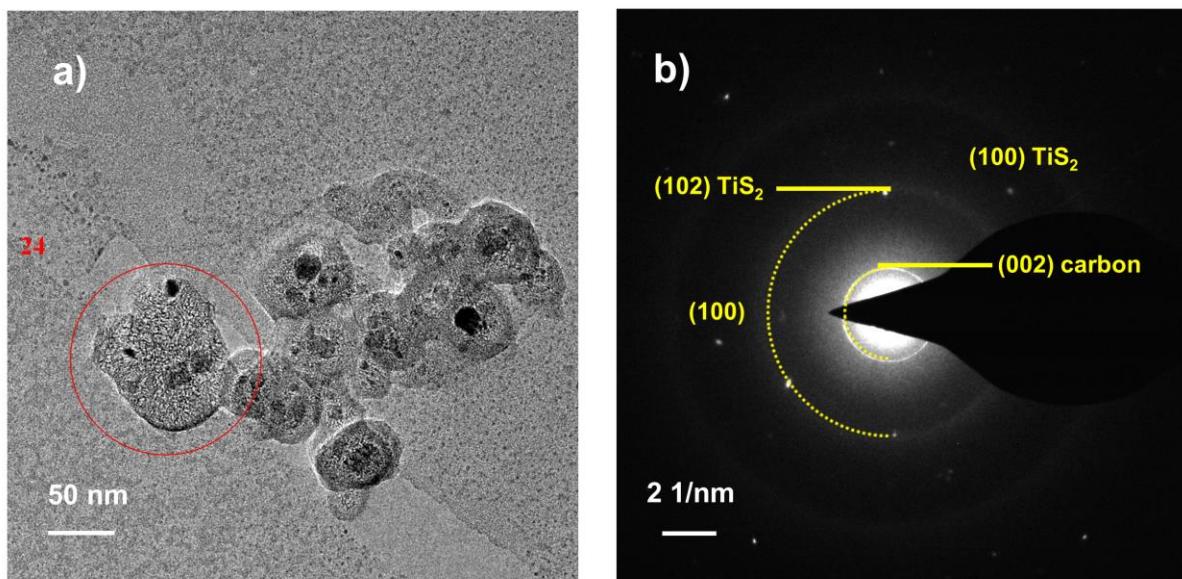
**Figure S2.** a) TG curve and DTA analysis of HCN; b)  $\text{N}_2$  adsorption-desorption isotherms and pore size distributions (insert) of HCN.



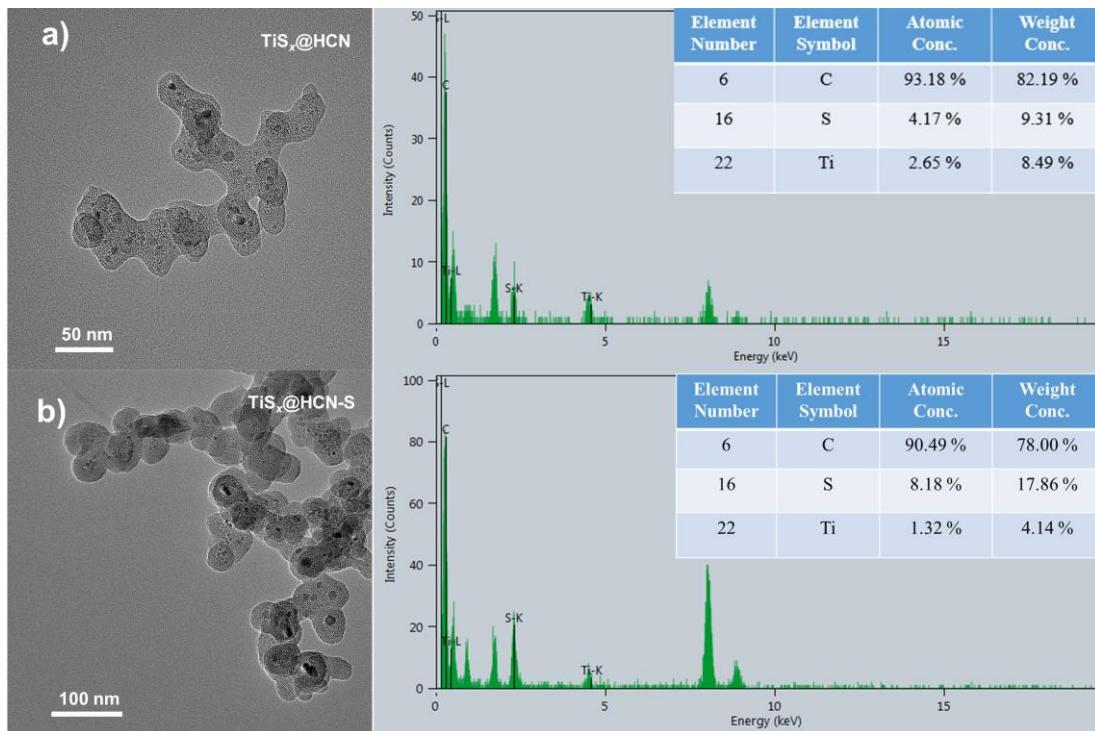
**Figure S3.** a) EPR spectra of  $\text{TiS}_x@\text{HCN}$ . b) XRD patterns of S, HCN-S, and  $\text{TiS}_x@\text{HCN-S}$ .



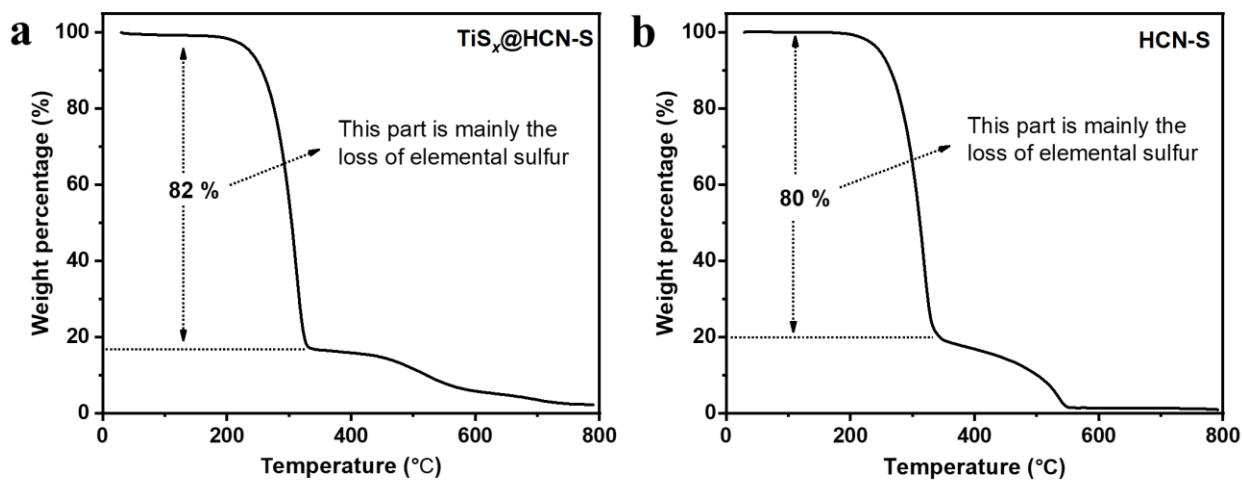
**Figure S4.** SEM images of (a & b) HCN and TEM images of (c & d) HCN.



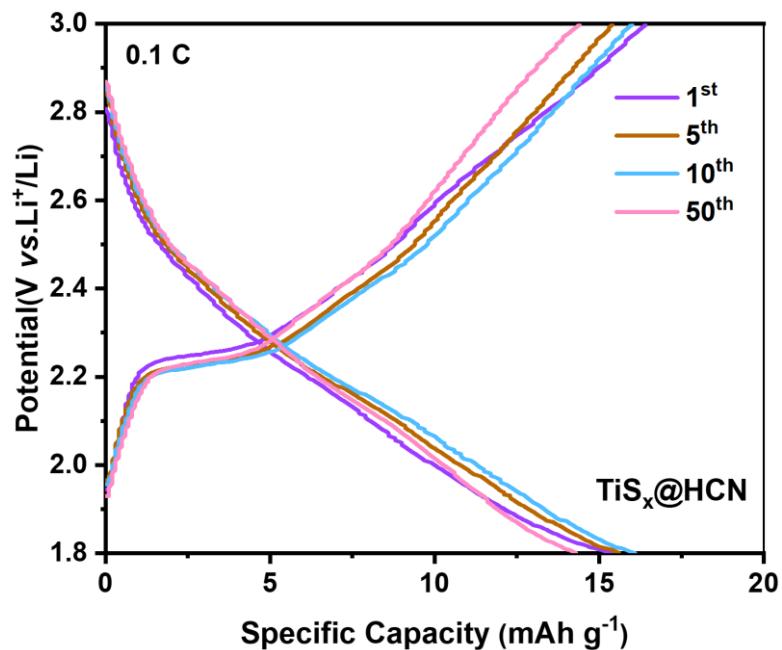
**Figure S5.** a) TEM image and b) SAED pattern of  $\text{TiS}_x@\text{HCN}$ .



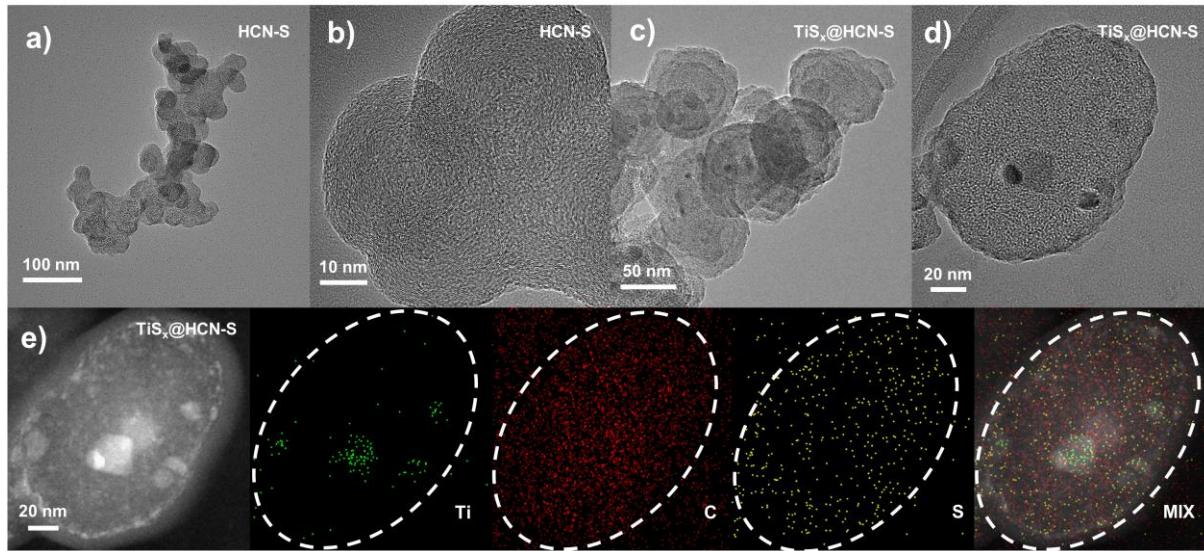
**Figure S6.** a) The low-magnification TEM image and EDX spectrum of amorphous  $\text{TiS}_x@\text{HCN}$ . The atomic ratio of Ti/S is about 2:3. b) The low-magnification TEM image and EDX spectrum of amorphous  $\text{TiS}_x@\text{HCN-S}$ . The atomic ratio of Ti/S is about 1:6.



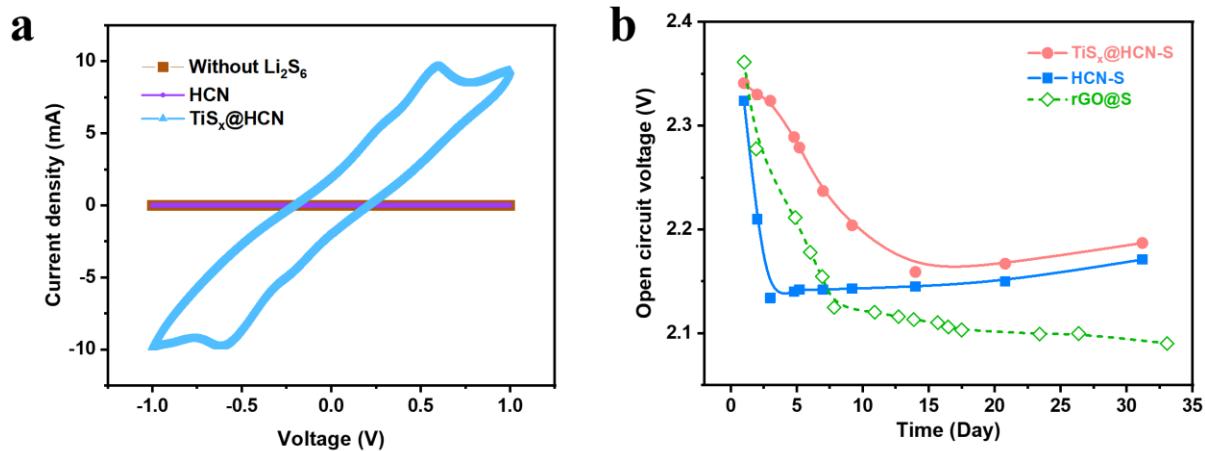
**Figure S7.** TGA curves of  $\text{TiS}_x@\text{HCN-S}$  (a) and HCN-S (b).



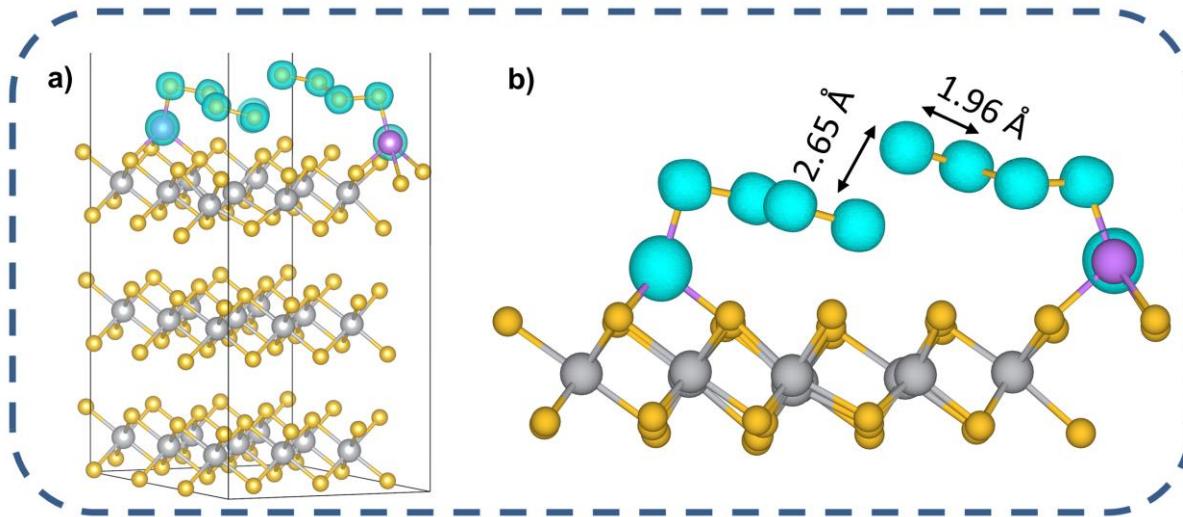
**Figure S8.** The galvanostatic charge-discharge voltage profiles of pure  $\text{TiS}_x@\text{HCN}$  cathode for the initial 50 cycles at the rate of 0.1 C. The specific capacity was measured corresponding to the mass of  $\text{TiS}_x$ . Note: It can be clearly seen that the pure  $\text{TiS}_x$  electrode has no obvious charge/discharge voltage plateaus and shows a negligible capacity less than  $20 \text{ mAh g}^{-1}$ , which has almost no contribution to the measured capacity of Li-S batteries.



**Figure S9.** TEM images of HCN-S (a & b) and TiS<sub>x</sub>@HCN-S (c & d) cathode after 400 cycles at 0.5 C. (e) Elemental mapping (C, Ti, & S) images of TiS<sub>x</sub>@HCN-S cathode after 400 cycles.



**Figure S10.** a) CV plots of the symmetric cells with HCN and TiS<sub>x</sub>@HCN electrodes at a scan rate of 10 mV s<sup>-1</sup>. b) Open-circuit voltages of the cells with TiS<sub>x</sub>@HCN-S, HCN-S, and rGO@S<sup>1</sup> cathodes.



**Figure S11.** The scheme of  $\text{Li}_2\text{S}_8$  adsorbed on the defected- $\text{TiS}_2$  surface. The elongated ( $2.65 \text{ \AA}$ ) and normal S-S bond ( $1.96 \text{ \AA}$ ) are labeled in Figure b.

**Table S1.** Elemental analysis results of  $\text{TiS}_x@\text{HCN}$  based on the SEM-EDS and TEM-EDS.

Method	Element	Atomic Concentration (at. %)	Atomic Error (%)	Weight Concentration (wt. %)	Mass Error (%)
SEM-EDS	Ti K	1.58	/	5.76	/
	S K	2.89	/	7.05	/
TEM-EDS	Ti K	2.65	0.85	9.31	1.89
	S K	4.17	0.41	8.49	1.30

**Table S2.** Elemental analysis results of  $\text{TiS}_x@\text{HCN-S}$  and HCN-S cathodes after 400 cycles at 0.5 C based on the TEM-EDS.

Cathode	Element	Atomic Concentration (at. %)	Atomic Error (%)	Weight Concentration (wt. %)	Mass Error (%)
$\text{TiS}_x@\text{HCN-S}$	S K	2.64	0.53	6.16	1.23
HCN-S	S K	0.26	0.14	0.66	0.30

**Table S3.** Comparison of the cycling stability of this work with other reported works with the similar structure.

Cathode materials	Initial capacity (mAh g <sup>-1</sup> )	Cycle number	Cycling rate	Capacity decay rate per cycle
This work	1118.6	200	0.1 C	0.108%
$\text{MoO}_2/\text{C-S}^2$	734	400	0.5 C	0.1%
S-FeS@G/CNT <sup>3</sup>	705	300	0.5 C	0.175%
S/WO <sub>3</sub> <sup>4</sup>	769	100	0.2 C	0.56%
S/WC <sup>4</sup>	843	100	0.2 C	0.18%
S/MgO <sup>5</sup>	860	100	0.2 C	0.18%
FeS/C-S <sup>6</sup>	870	100	0.1 C	0.338%
$\text{TiS}_{2-x}/\text{S}^7$	1169.8	100	0.2 C	0.21%
rGO/N-YSHCS/S <sup>8</sup>	1100.41	100	0.2 C	0.273%
S@SiO <sub>2</sub> <sup>9</sup>	1153	100	0.2 C	0.292%

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