Supporting Information

## Promoting the Sulfur Immobilization by a Hierarchical Morphology of Hollow Carbon Nanospheres Cluster for High-stability Li-S Battery

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Figure S1. SEM image of HCNCs.



Figure S2. TEM images of HCNCs obtained with different RF precursor concentration.

*Additional explanation:* RF precursor concentration of sample 1 (**Fig. S2**a) is 1.5 times that of sample 2 (**Fig. S2**b).



**Figure S3**. TGA curves of pomegranate-like SiO<sub>2</sub>/C clusters and single SiO<sub>2</sub>/C nanosphere under air atmosphere.



Figure S4. X-ray photoelectron spectroscopy (XPS) analysis of HCNCs-1.



Figure S5. TGA curves of MHCSs and HCNCs under air atmosphere.



Figure S6. Raman spectra of HCNCs and MHCSs.

*Additional discussion:* Only two characteristic carbon peaks at 1350 cm<sup>-1</sup> (D-band) and 1580 cm<sup>-1</sup> (G-band) are observed, which are generally related to structural defects and graphitic structure, respectively []. The intensity ratio of the D-band to G-band  $I_D/I_G$  of HCNCs-2 is 0.79, indicating the lower graphitization degree. Similarly, HCNCs-1 and MHCSs show an amorphous carbon structure.



Figure S7. XRD patterns of MHCSs and HCNCs.



Figure S8. (a-d) SEM images of MHCSs, MHCSs/S, HCNCs-1 and HCNCs-1/S, respectively.



Figure S9. High-resolution S 2p spectra of HCNCs-2/S.



**Figure S10**. Nyquist plots of MHCSs/S and HCNCs/S electrode (a)before cycling and (b)after 100 cycles at 0.5 C rate.



**Figure S11**. SEM image of the fresh (a, c) and cycled (b, d) electrodes in a charge state after 200 cycles at 1 C. Insets of (a-d) are corresponding local magnification SEM images.



**Figure S12.** (a) Cycle performance of HCNCs/S and MHCSs/S electrodes with a high-sulfur-loading of 4 mg cm<sup>-2</sup> at 0.2 C. (b) Rate performance of HCNCs-2/S electrode with a high-sulfur-loading of 4 mg cm<sup>-2</sup> at varied current rates.

Sample	S at.%	C at.%	O at.%
MHCSs	36.11	56.27	7.62
HCNCs-1	23.77	69.41	6.82
HCNCs-2	14.71	78.75	6.54

Table S1. XPS results of MHCSs/S and HCNCs/S.

G 1	С	Н	0
Samples	wt.%	wt.%	wt.%
HCNCs-1	90.79	2.60	6.61
HCNCs-2	90.40	2.27	7.33
MHCSs	91.58	1.92	6.50

Table S2. Elemental analysis of MHCSs/S and HCNCs/S.

Samples		HCNCs-1/S	HCNCs-2/S	MHCSs/S
D (O)	Fresh	1.4	2.4	4.5
$\mathbf{K}_0$ (22)	After cycling	2.3	1.4	2.5
Rct (\Omega)	Fresh	62.4	47.9	80.7
	After cycling	4.1	3.9	18.0

Table S3. Electrode resistance obtained from equivalent circuit fitting of the HCNCs/S and MHCSs/S cathode.

`	Sulfur content (wt%)	C-rate	Cycle number	Initial capacity (mA h g <sup>-1</sup> )	Reversible capacity (mA h g <sup>-1</sup> )	Capacity decay rate per cycle	High-rate capability (mA h g <sup>-1</sup> )	Ref.
HCNCs	73%	0.2 C	500	1311	695	0.094%	715 (2 C)	This
		1 C	300	1196	630	0.158%	<b>592 (5 C)</b>	work
PHC/S	69.75%	0.5 C	100	1071	947	0.116%	450 (3 C)	[1]
P-AB@S	66%	0.06 C	500	1221	577	0.106%	521 (0.6 C)	[2]
S@rGO-HCS	65%	0.5 C	400	901	712	0.052%	770 (4 C)	[3]
DHCSs/S	64%	0.1 C	100	-	690	-	350 (1 C)	[4]
G-NDHCS-S	62%	0.2 C	100	1360	940	0.309%	800 (1 C)	[5]
		0.5 C	200	-	520	0.19%	600 (2 C)	
S/HCSF@C	70.7%	0.6 C	300	-	780	0.14%	535 (1.2 C)	[6]
S/HICS-75	75%	0.5 C	800	933	441	0.066%	480 (1 C)	[7]
HGs/S	90%	1 C	600	-	-	0.08%	676 (2 C)	[8]
		0.5 C	200	1109	910	0.03%		
HCS–S	57%	0.12 C	100	1098	844	0.23%	-	[9]
HCSs/S-LBL	65%	0.6 C	200	850	575	0.162%	698 (2.4 C)	[10]
m-DSHCS/S (containing N)	75%	0.2 C	200	1289	876	0.16%	900 (1 C)	[11]
		1 C	1000	~1090	386	0.07%	800 (2 C)	

 Table S4.
 Electrochemical performances comparison of HCNCs/S with the reported hollow carbon/sulfur cathodes.

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