Electronic Supplementary Material (ESI) for Nanoscale.

SUPPLEMENTARY INFORMATION

Structural combination of polar hollow microspheres and hierarchical N-doped carbon nanotubes for high-performance Li-S batteries

Jun Yeob Lee,[‡a] Gi Dae Park,[‡a] Jae Hun Choi[a] and Yun Chan Kang*[a]

[a]*Department of Materials Science and Engineering, Korea University, Anam-Dong, Seongbuk-Gu, Seoul 136-713, Republic of Korea.*

‡ These authors contributed equally to this work

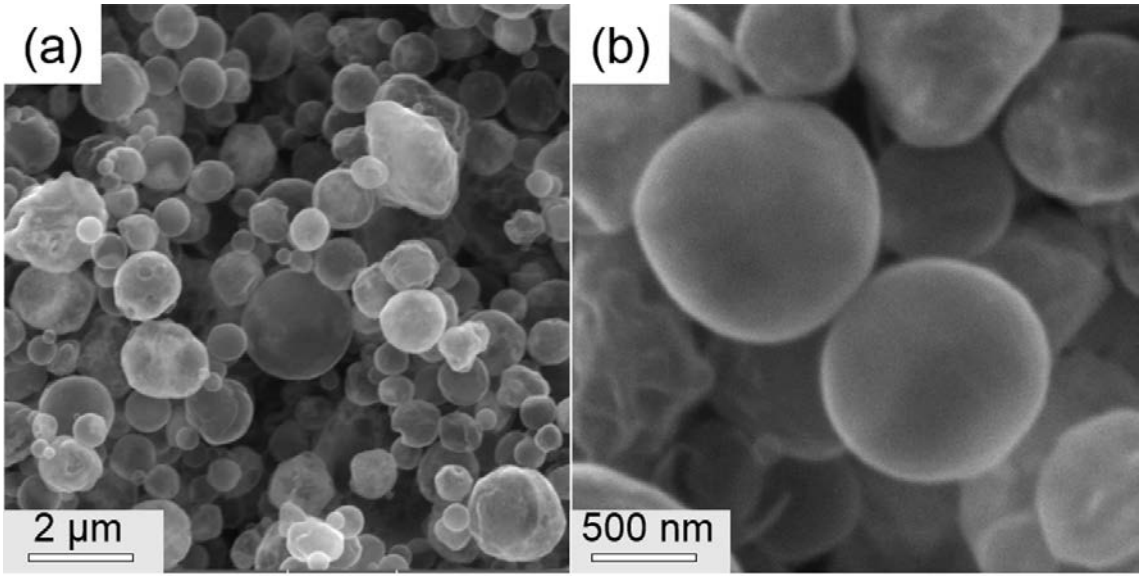

Fig. S1 Morphologies of precursor $CoFe_2O_4$-C microspheres with the hollow structure.

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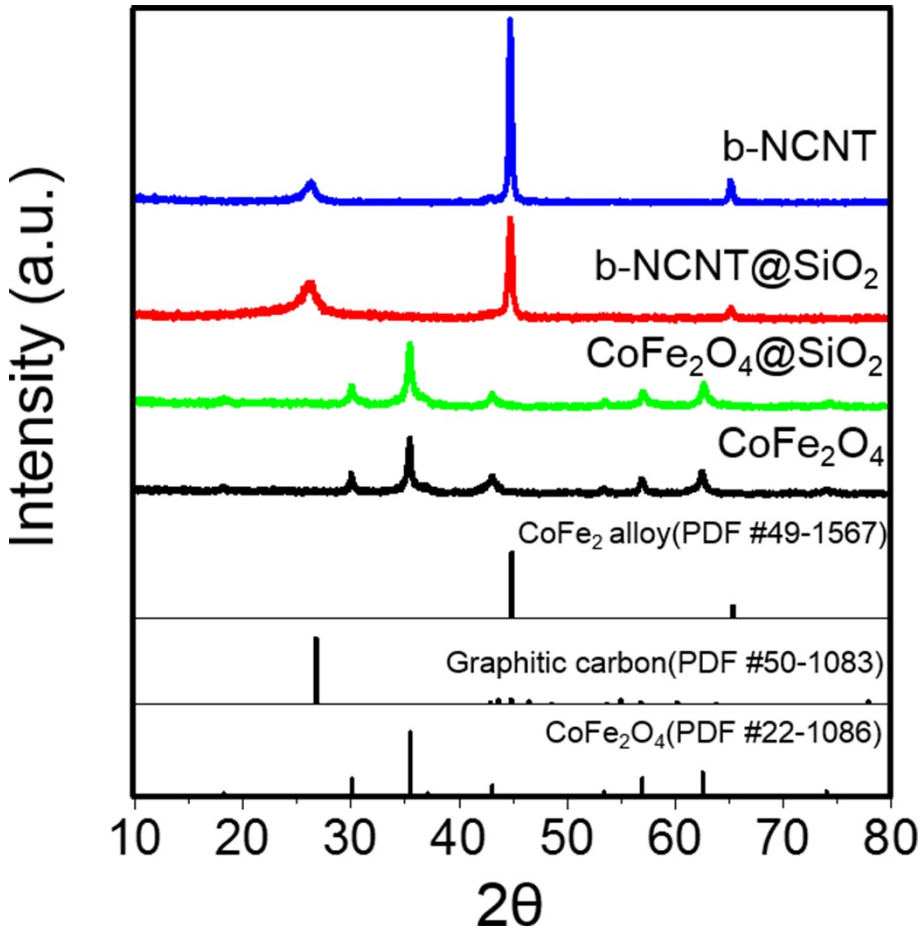

Fig. S2 XRD patterns of precusor $CoFe_2O_4$, SiO_2-coated $CoFe_2O_4$ ($CoFe_2O_4$@SiO_2), micelle-like b-NCNT@SiO_2, and ciliate-like b-NCNT microspheres.

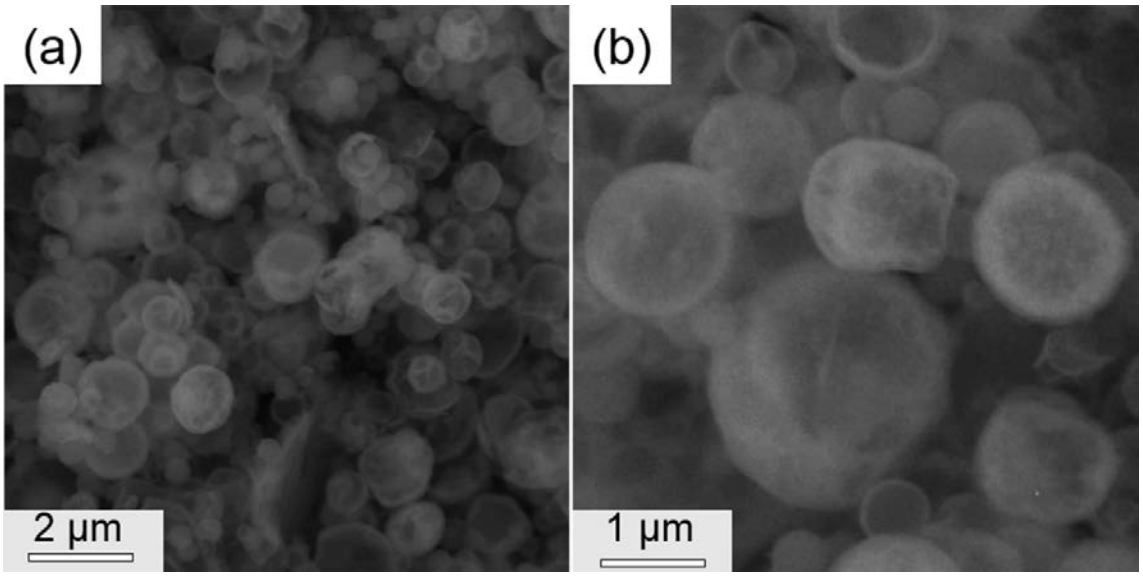

Fig. S3 SEM images of SiO_2-coated $CoFe_2O_4$-C microspheres.

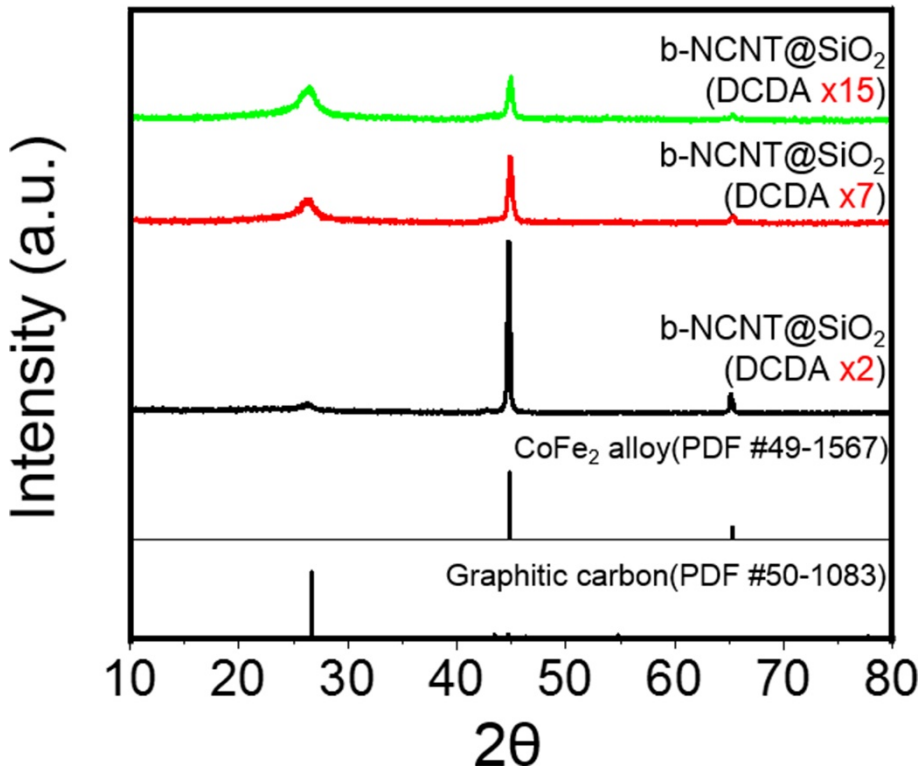

Fig. S4 XRD patterns of b-NCNT@SiO_2 according to amount of DCDA (2–15 times of the precursor microsphere amount).

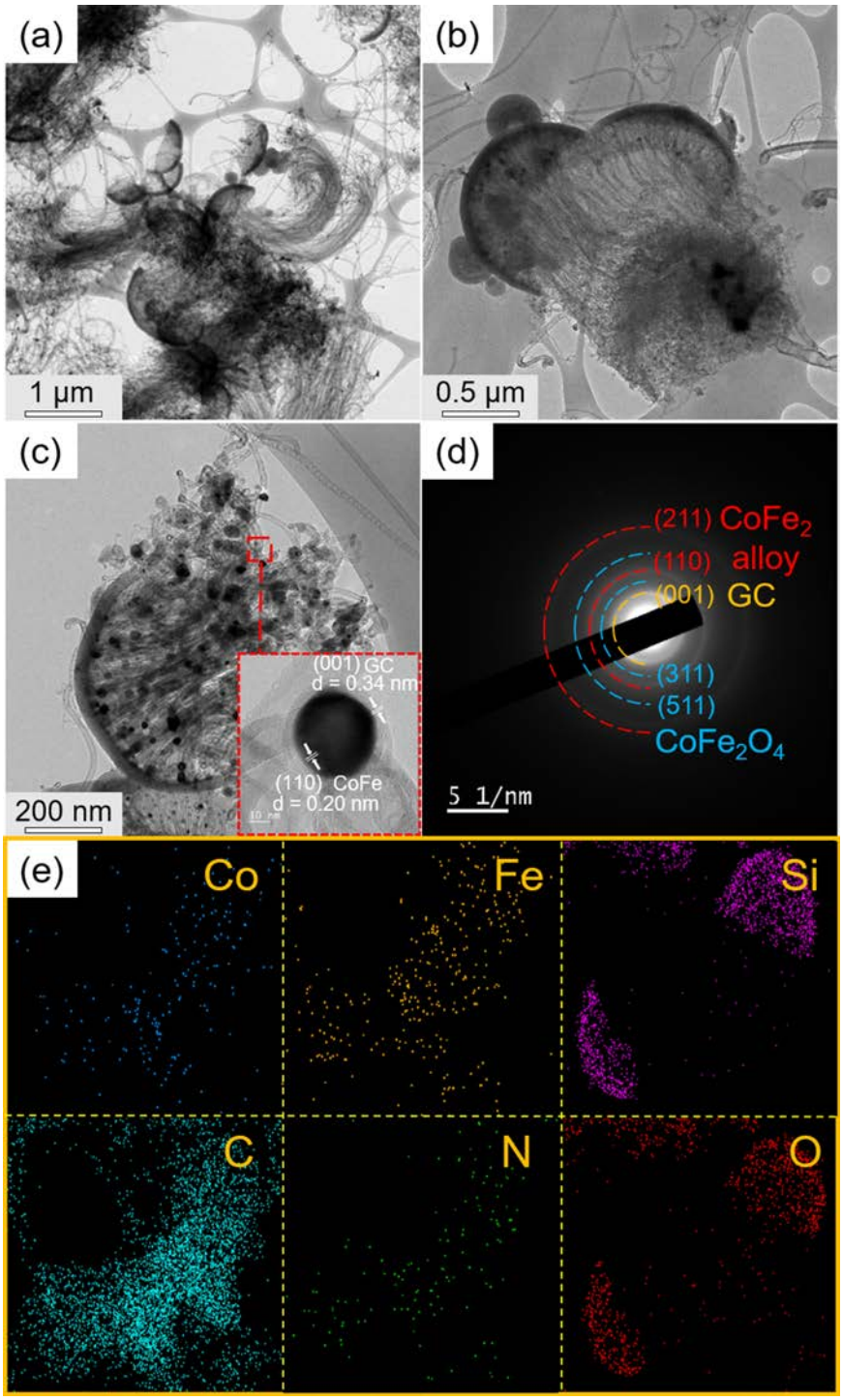

Fig. S5 Morphologies, SAED pattern, and elemental mapping images of broken micelle-like b-NCNTs@SiO_2 microspheres obtained when the amount of DCDA was 15 times that of the precursor microspheres: (a) and (b) TEM images, (c) HR-TEM image, (d) SAED pattern, and (e) elemental mapping images.

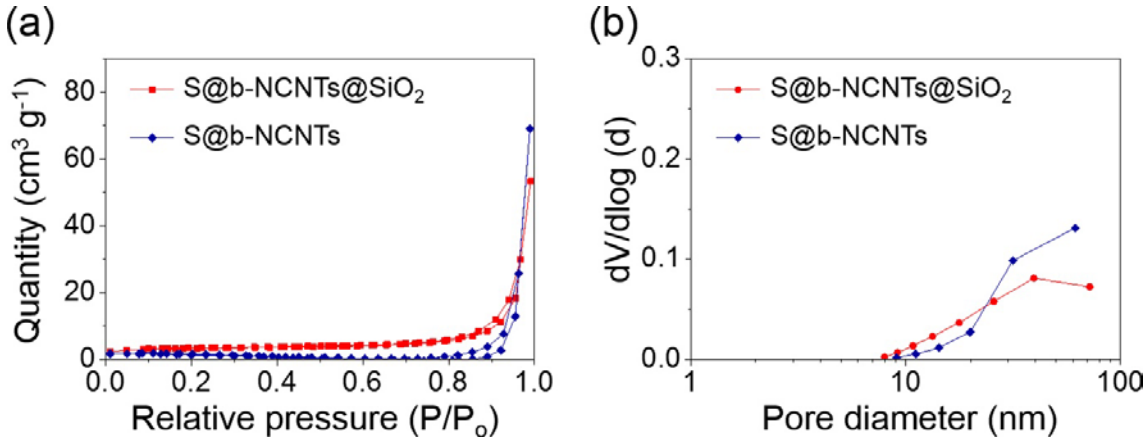

Fig. S6 (a) N_2 gas adsorption and desorption isotherms and (b) BJH pore-size distributions of S-loaded micelle-like b-NCNTs@SiO_2 (S@b-NCNTs@SiO_2) and S-loaded ciliate-like b-NCNTs microspheres (S@b-NCNTs).

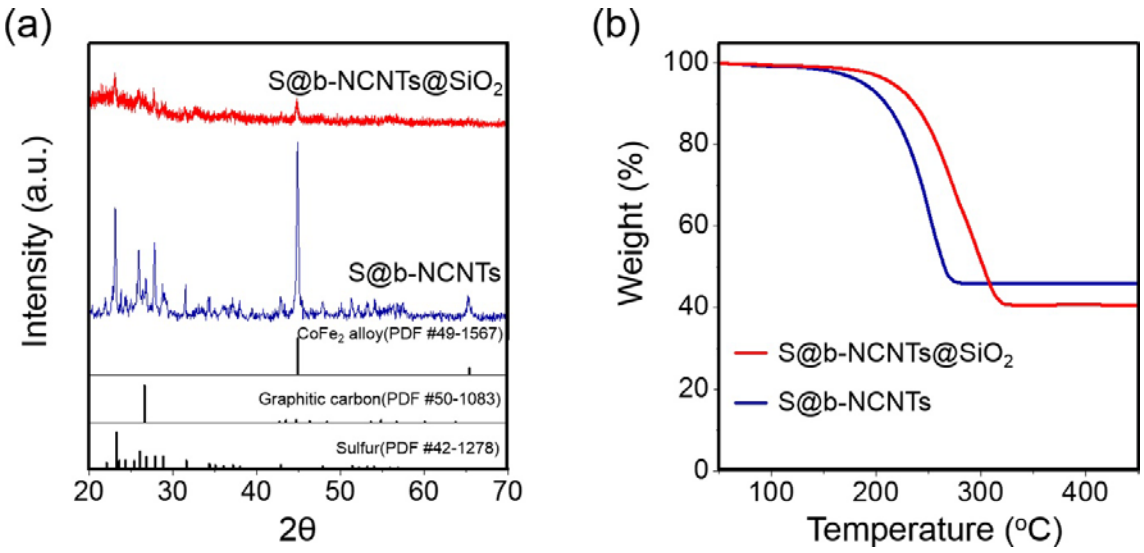

Fig. S7 (a) XRD patterns and (b) TG curves of S-loaded micelle-like b-NCNTs@SiO_2 (S@b-NCNTs@SiO_2) and S-loaded ciliate-like b-NCNTs microspheres (S@b-NCNTs).

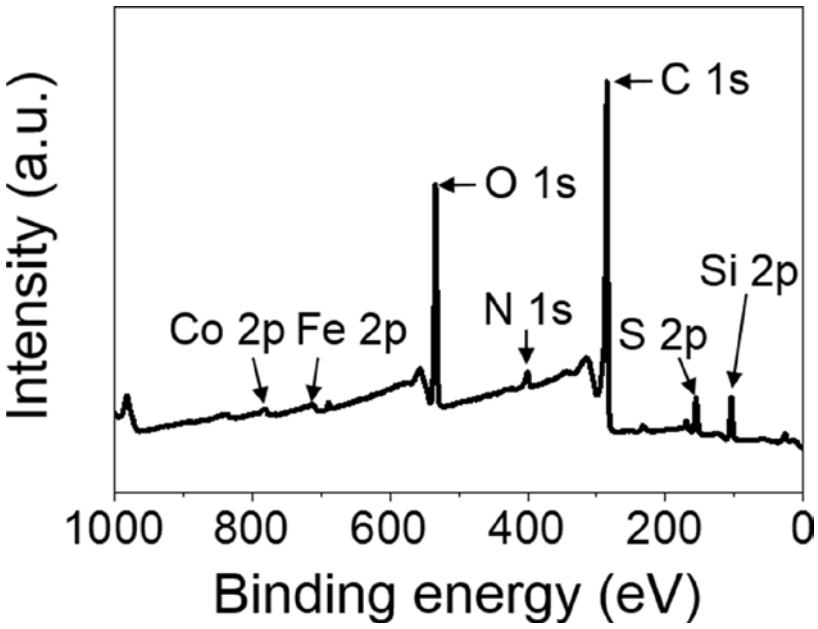

Fig. S8 XPS survey scan of S-loaded micelle-like b-NCNTs@SiO_2 microspheres.

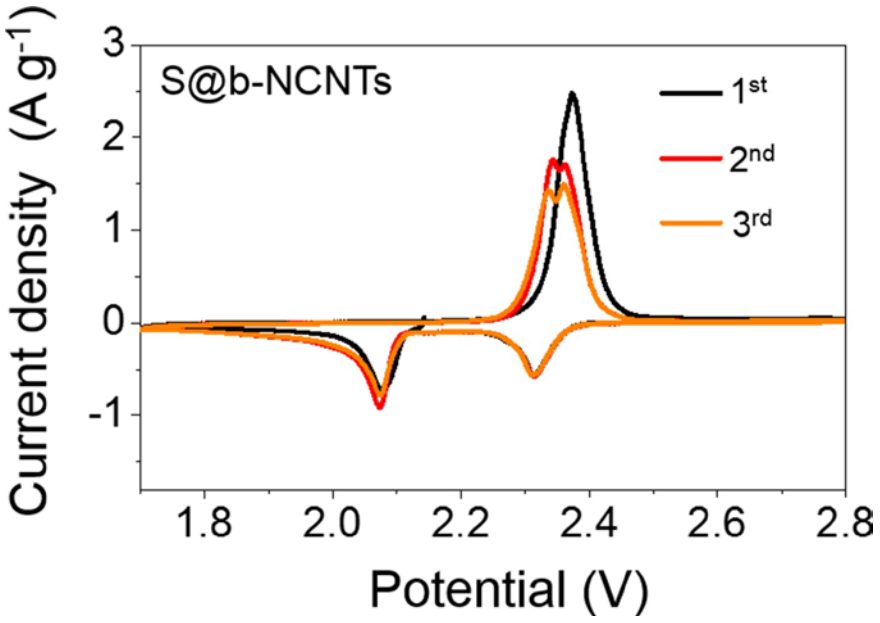

Fig. S9 CV curves of S-loaded ciliate-like b-NCNTs microspheres (S@b-NCNTs).

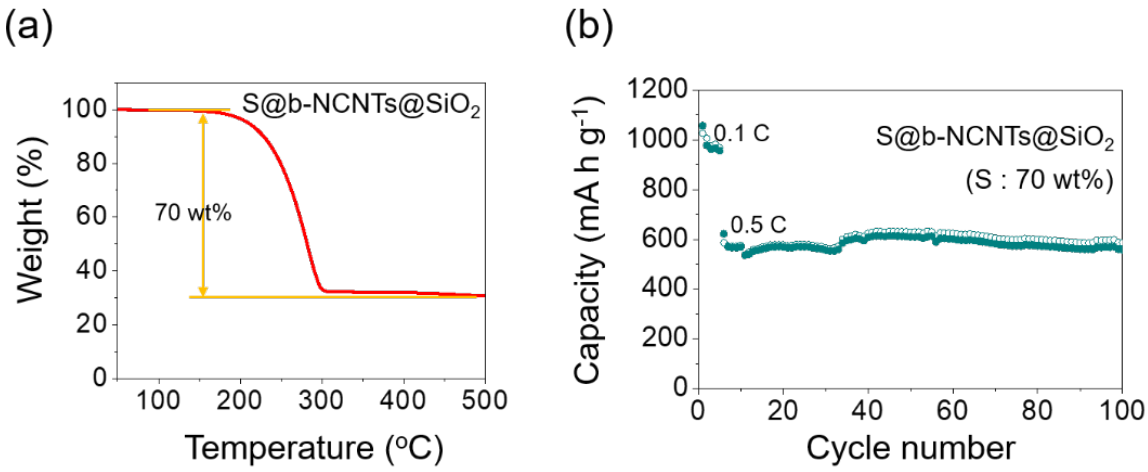

Fig. S10 (a) TG curves and (b) cycle performance of S@b-NCNTs@SiO_2 with 70 wt% sulfur.

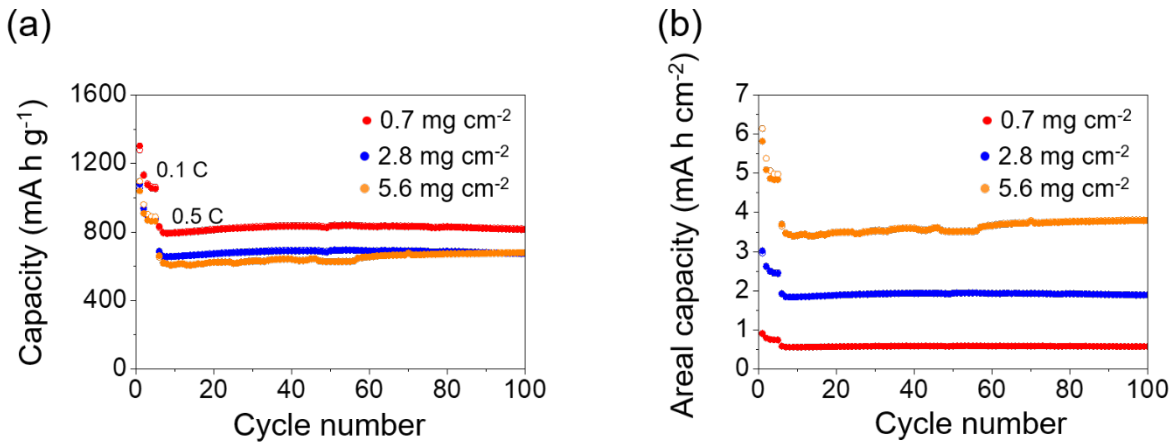

Fig. S11 Cycling performances of S@b-NCNTs@SiO_2 with different sulfur loading of 0.7, 2.8 and 6.5 mg cm^{-2}: (a) gravimetric capacities and (b) areal capacities.

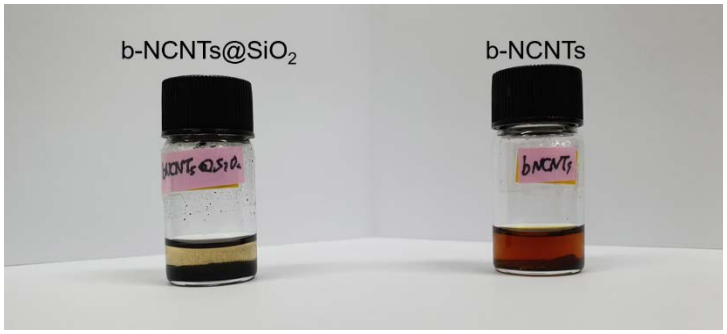

Fig. S12 Optical photographs of b-NCNTs@SiO_2 and b-NCNTs soaked in the catholyte after 24 h (catholyte: 0.05M Li_2S_6-DOL/DME solution).

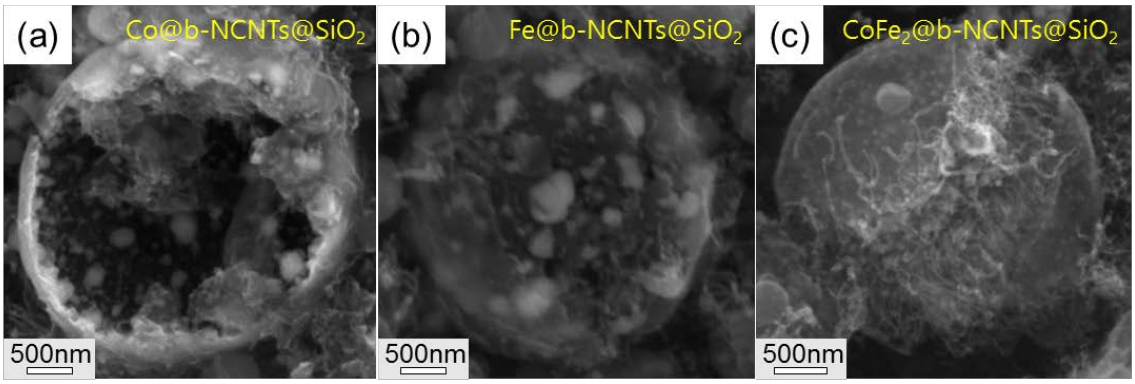

Fig. S13 SEM images of Co@b-NCNTs@SiO_2, Fe@b-NCNTs@SiO_2, and $CoFe_2$@b-NCNTs@SiO_2.

Table S1. Electrochemical properties of various hierarchical sulfur-loaded carbon materials applied as lithium-sulfur batteries reported in the previous literatures.

Materials	Current rate	Discharge capacity [mA h g^{-1}] and (cycle number)	Rate capacity [mA h g^{-1}] (current rate)	Ref
Hierarchical structure carbon fiber/sulfur (HCF/S) composite	0.25 C	657 (100)	438 (2C)	[S1]
Hierarchical porous graphene material	0.5 C	434(150)	357 (5C)	[S2]
Nitrogen-doped hierarchical porous carbon nanosheets	1 C	576 (500)	493(4C)	[S3]
Hierarchical micro/mesoporous carbonaceous nanotube	0.5 A g^{-1}	618.5(100)	616(3.2Ag^{-1})	[S4]
Graphene oxide wrapped, multi-cavity walnut-like carbon spheres	0.2 C	808 (100)	680(2C)	[S5]
Hierarchical porous carbon rods constructed by vertically oriented porous graphene-like nanosheets	1 C	700 (300)	646(5C)	[S6]
Honeycomb-like nitrogen and sulfur dual-doped hierarchical porous biomass-derived carbon/sulfur composites (NSHPC/S)	1 C	496(500)	1201(1C)	[S7]
Hierarchical porous carbon, intrinsically doped with nitrogen and oxygen,	0.5 C	460(800)	710(1C)	[S8]
Sulfur embedded in one-dimensional French fries like hierarchical porous carbon	0.5 C	751(200)	763(2C)	[S9]
Nitrogen and phosphorus co-doped hierarchical porous carbon (N, P-HPC)	1 C	464(400)	303(5C)	[S10]
Micelle-like b-NCNTs@SiO_2 microspheres	**0.5 C**	**771(200)**	**486(5C)**	**Our work**

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