Supplementary Information

Oversaturated iron sites on mesopore-rich carbon nanocages boost adsorption and transformation of polysulfides for lithium-sulfur batteries

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Experimental Section

Synthesis of ZIF-8 nanocubes. 300 mg of $Zn(CH_3COO)_2 \cdot 2H_2O$ is dissolved in 5 mL of deionized H_2O to form solution A. 1116 mg of 2-methylimidazole and 0.8 mg of cetyltrimethylammonium bromide (CTAB) are dissolved in 5 mL of deionized H_2O to form solution B. Then, solution A is added into solution B, and the mixture is shaken for about 16 s and subsequently left undisturbed at room temperature for 2 h. The resulting ZIF-8 nanocubes are washed with ethanol for several times.

Synthesis of Fe-Phen/ZIF-8/polydopamine (Fe-Phen-ZIF-8@PDA). Typically, $FeSO_4 \cdot 7H_2O$ (13.4 mg) and 1,10-phenanthroline (Phen, 26 mg) are dissolved in ethanol (30 mL) with stirring for 1 h. Subsequently, the as-prepared ZIF-8 nanocubes (200 mg) is added and stirred for another 10 min. The whole reaction mixture is then stirring at 50 °C for 2 h. After cooling to the room temperature, the above mixture and 65 mg of dopamine hydrochloride are added into a Tris solution (10 mM, 200 mL) and stirred for 12 h. The resultant Fe-Phen-ZIF-8@PDA products are collected by centrifugation, washed with ethanol and dried at the vacuum environment.

Synthesis of Fe single atoms on nitrogen-doped carbon nanocages (Fe-NCNC). The as-prepared Fe-Phen-ZIF-8@PDA is heated to 1000 ^oC and maintained for 1 h under Ar atmosphere. The obtained sample is soaked in hydrochloric acid solution for about 6 h at room temperature. The suspension is centrifuged and washed with ethanol for several times.

Synthesis of ZIF-8/polydopamine (ZIF-8@PDA). The as-prepared ZIF-8 nanocubes (200 mg) are dispersed in ethanol (30 mL) with stirring at 50 °C for 2 h. After cooling to the room temperature, the above mixture and 65 mg of dopamine hydrochloride are added into a Tris solution (10 mM, 200 mL) and stirred for 12 h. The resultant ZIF-8@PDA products are collected by centrifugation, washed with ethanol and dried at the vacuum environment.

Synthesis of nitrogen-doped carbon nanocages (NCNC). The as-prepared ZIF-8@PDA is heated to 1000 ^oC and maintained for 1 h under Ar atmosphere. The obtained sample is soaked in hydrochloric acid aqueous solution for about 6 h at room temperature. The suspension is centrifuged and washed with ethanol for several times.

Fabrication of Fe-NCNC/S and NCNC/S composites. The Fe-NCNC/S and NCNC/S composites are fabricated via a melt-diffusion method. Typically, a mixture of sulfur powder and host material (Fe-

NCNC, NCNC) with a mass ratio of 7:3 is sealed in a glass bottle, and then heated at 155 °C for 6 h in an oven under Ar atmosphere.

Adsorption measurements of Li_2S_6. To fabricate the 5 mM of Li_2S_6 solution, Li_2S and sulfur (molar ratio: 1:5) are dissolved in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1, *v*/*v*), and stirred at 50 °C for 24 h to form the brown solution. 5 mg of host material (Fe-NCNC, NCNC) is added into 2.5 mL of Li_2S_6 solution, then waiting for 6 h. The supernatants and precipitates of the mixtures are analyzed by ultraviolet-visible (UV-Vis) spectroscopy and X-ray photoelectron spectroscopy (XPS), respectively.

Li_2S_6 symmetric cell measurements. For the symmetric cells, both anode and cathode are composed of host material (Fe-NCNC, NCNC) and poly(vinylidene fluoride) with a mass ratio of 4:1 coated onto carbon paper, which are dried in a vacuum oven at 60°C for 12 h. The electrolyte is composed of 0.5 M Li_2S_6 and 0.5 M LiTFSI in a mixed solvent of DOL and DME (1:1, *v*/*v*). Cyclic voltammetry (CV) measurements are performed on a CHI 660E electrochemical workstation within the voltage range of -0.8~0.8 V.

Material characterizations. X-ray diffraction (XRD) patterns of samples are analyzed with a powder X-ray diffractometer (Bruker D2 Phaser X-ray Diffractometer with Ni filtered Cu Kα radiation). The morphology of samples is characterized by field-emission scanning electron microscope (FESEM, JEOL-6700) and transmission electron microscope (TEM, JEOL, JEM-1400 and JEM-2100F). Energy-dispersive X-ray (EDX) spectroscopy elemental mapping is recorded with the TEM instrument (FEI Talos F200X G2). N_2 adsorption-desorption isotherms are recorded and analyzed on Micromeritics 3Flex. Thermogravimetric analysis (TGA) is performed on a Shimadzu DRG-60 thermal analyzer under N_2 flow. XPS measurements are carried out on PHI Quantum 2000 to study the chemical states of elements in samples. All binding energies are referenced to the C 1s peak of the surface adventitious carbon at 284.8 eV. UV-Vis spectroscopy (Shimadzu UV 2450 Spectrometer) is performed to analyze the adsorption degree of polysulfides on the host materials. X-ray absorption spectroscopy (XAS) measurements of Fe K-edge are performed at the National Synchrotron Radiation Research Center (NSRRC), Taiwan.

Electrochemical measurements. To prepare the cathodes, the as-prepared composites (Fe-NCNC/S and NCNC/S), Ketjen black, and poly(vinylidene fluoride) binder are mixed in N-methyl pyrrolidone

(NMP) with a weight ratio of 8:1:1. Then, the slurry is spread onto a carbon paper with the areal sulfur loading of 1.1~1.5 mg cm^{-2}. The Li-S coin cells are assembled using as-prepared cathodes, Celgard membrane as separator and Li foil as an anode in an argon-filled glovebox. The electrolyte is comprised of 1.0 M lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) in a mixed solvent of DOL and DME (1:1, *v*/*v*) with 0.2 M of $LiNO_3$. The electrolyte/sulfur ratio used in the coin cell is 30:1 (μL:mg). Galvanostatic discharge/charge tests are performed on a Neware Battery Measurement System (Neware, China) in the voltage range of 1.7~2.8 V (*vs*. Li^+/Li) at room temperature. The current density and specific capacities are based on the weight of sulfur (1.0 C = 1675 mA g^{-1}). CV measurements are conducted at 0.1 mV s^{-1} in the voltage range of 1.7~2.8 V on a CHI 660E electrochemical workstation. Electrochemical impedance spectroscopy (EIS) is obtained by applying a sine wave with an amplitude of 5 mV over the frequency ranging from 100 kHz to 100 mHz on a CHI 660E electrochemical workstation.

Computational details. Density functional theory (DFT) calculations are performed by the Vienna Ab initio Simulation package (VASP)[1], and the exchange-correlation energy is approximately described by Perdew, Burke and Ernzerhof (PBE) functional based on the generalized gradient approximation (GGA)[2]. The plane wave basis sets with projector-augmented wave (PAW) pseudopotentials are applied in structure optimization[3]. The plane-wave cutoff energy is set to be 500 eV. The convergence tolerance of geometry optimization is set to be 1.0×10^{-5} eV for energy, and all the forces on each atom are smaller than 0.02 eV $Å^{-1}$. The spin-polarized condition and van der Waals interaction (Grimme's DFT-D3 method) are adopted for the whole DFT calculations[4]. All Fe single atom supported on the graphene models are constructed based on the graphene basal plane model with the supercell of 3×5×1 (12.78 Å×12.30 Å×15.00 Å). The Gamma-centered Monkhorst-Pack k-points grids for graphene basal plane (Fe-NCNC and NCNC models) is set to 3×3×1. All the structures discussed in this work are visualized in the Visualization for Electronic and Structural Analysis (VESTA)[5].

The Gibbs free energies (*G*) of adsorbed intermediates are calculated by:

$$G\,(\mathrm{ad}) = E\,(\mathrm{ad}) + ZPE\,(\mathrm{ad}) - \mathrm{T}S\,(\mathrm{ad})$$

Total energy (*E*), zero-point energy (*ZPE*) and entropy contribution (T*S*) of each adsorbed state are obtained from DFT calculations.

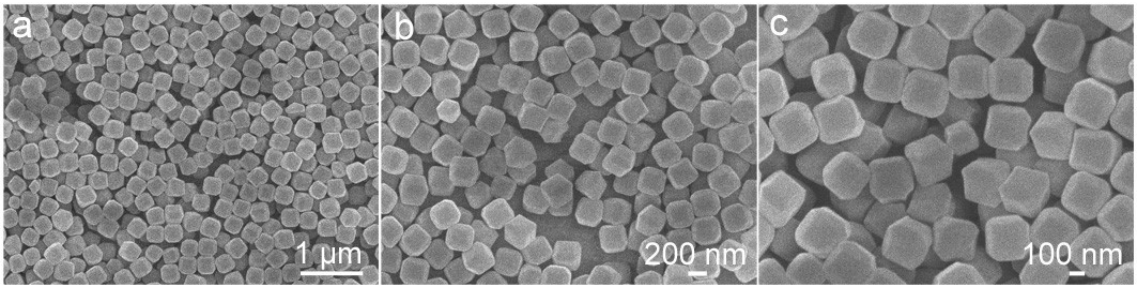

Fig. S1 (a-c) FESEM images of ZIF-8 nanocubes at different magnifications.

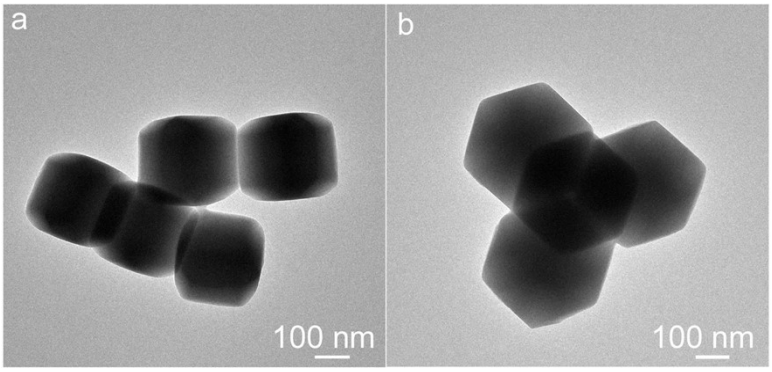

Fig. S2 (a, b) TEM images of ZIF-8 nanocubes at different magnifications.

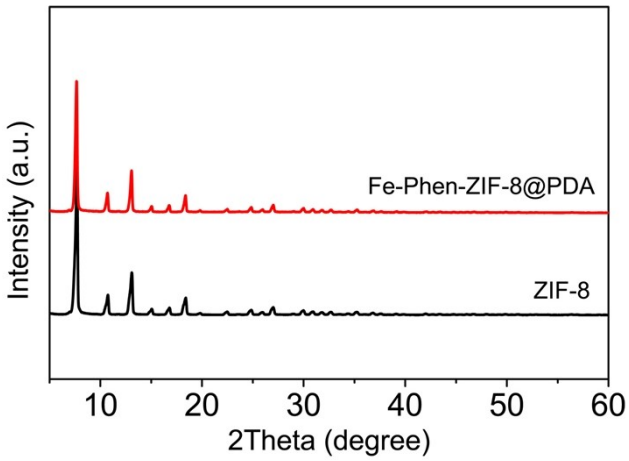

Fig. S3 XRD patterns of ZIF-8 nanocubes and Fe-Phen-ZIF-8@PDA.

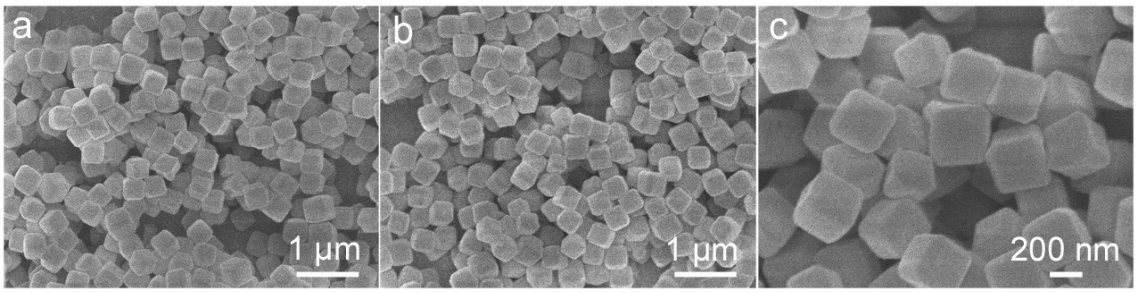

Fig. S4 (a-c) FESEM images of ZIF-8@PDA at different magnifications.

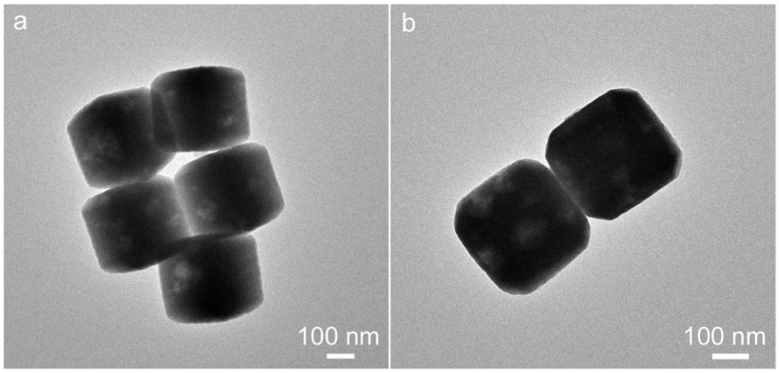

Fig. S5 (a-b) TEM images of ZIF-8@PDA at different magnifications.

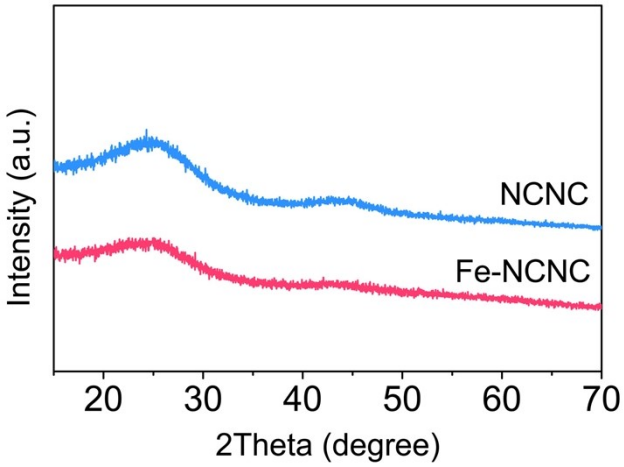

Fig. S6 XRD patterns of the as-prepared Fe-NCNC and NCNC.

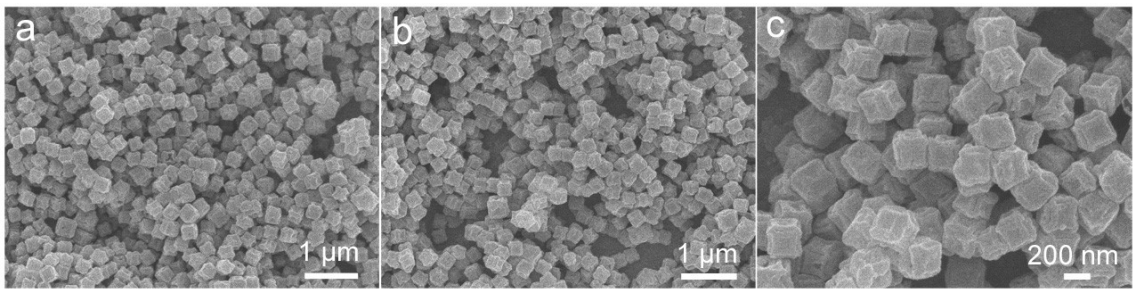

Fig. S7 (a-c) FESEM images of NCNC at different magnifications.

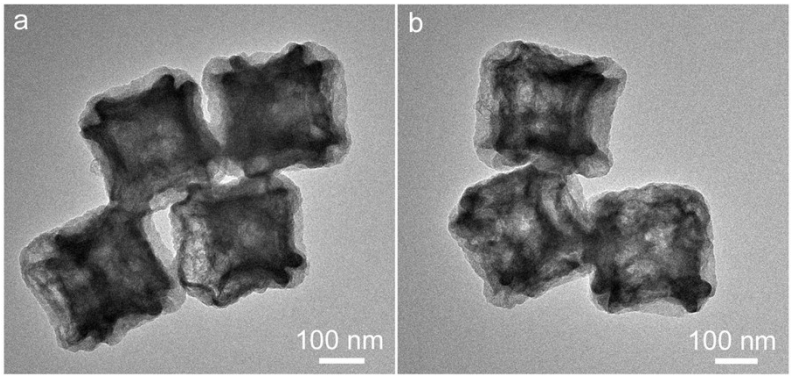

Fig. S8 (a-b) TEM images of NCNC at different magnifications.

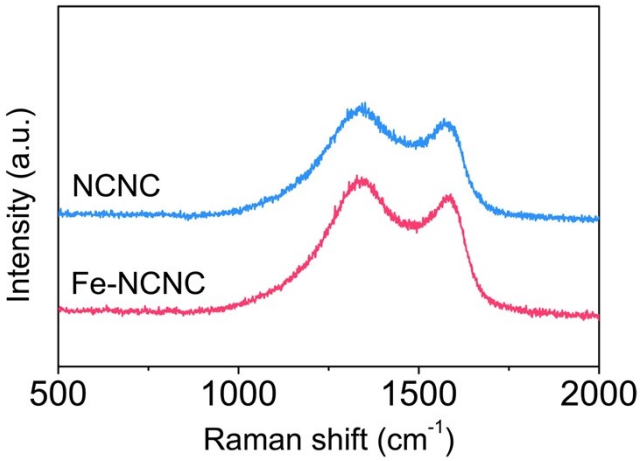

Fig. S9 Raman spectra of the as-prepared Fe-NCNC and NCNC.

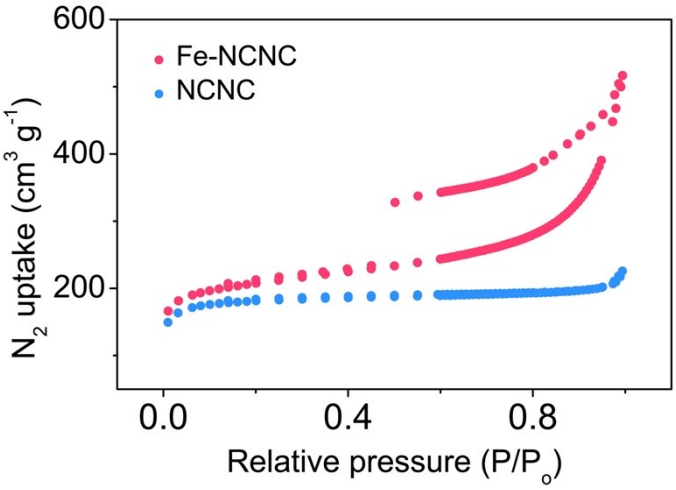

Fig. S10 N_2 adsorption-desorption isotherms of Fe-NCNC and NCNC.

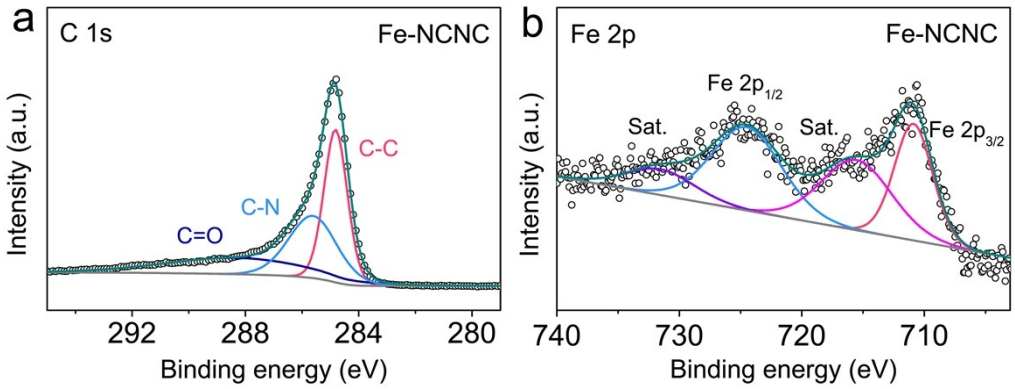

Fig. S11 (a) C 1s and (b) Fe 2p XPS spectra of Fe-NCNC.

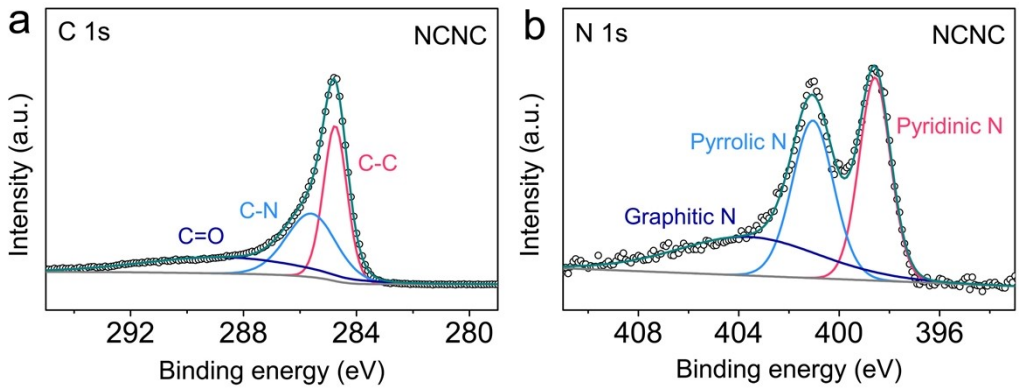

Fig. S12 (a) C 1s and (b) N 1s XPS spectra of NCNC.

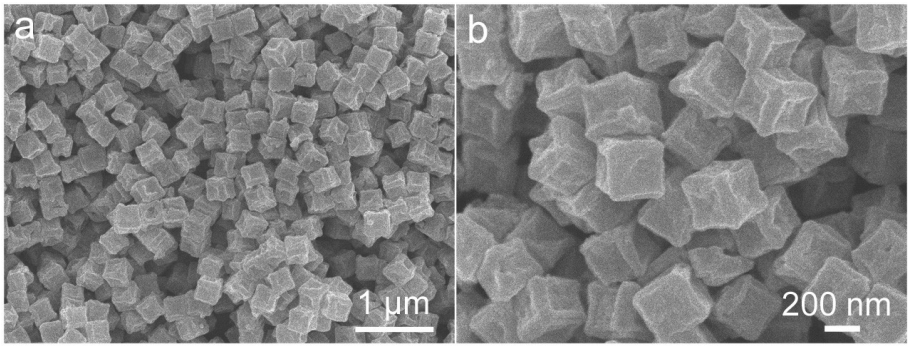

Fig. S13 (a-b) FESEM images of NCNC/S composite at different magnifications.

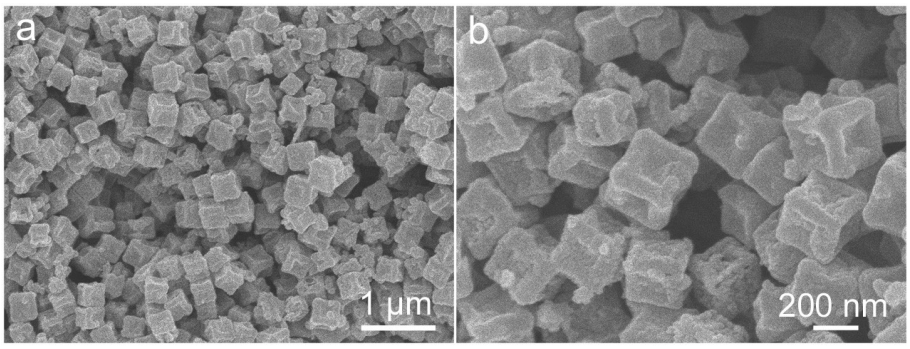

Fig. S14 (a-b) FESEM images of Fe-NCNC/S composite at different magnifications.

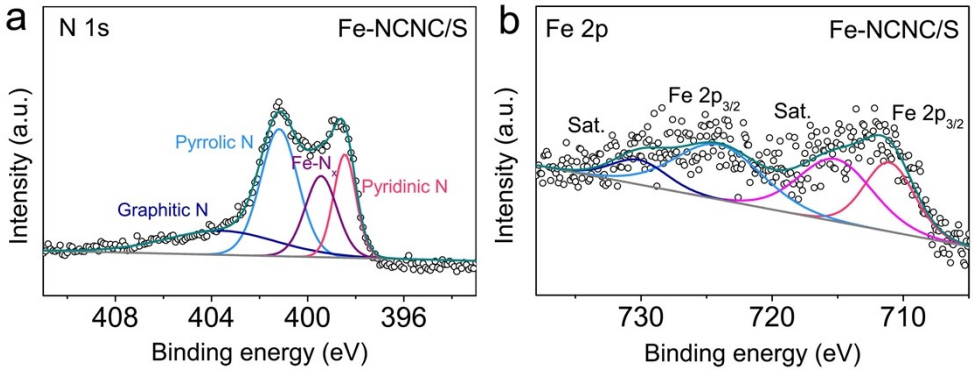

Fig. S15 (a) N 1s and (b) Fe 2p XPS spectra of Fe-NCNC/S composite.

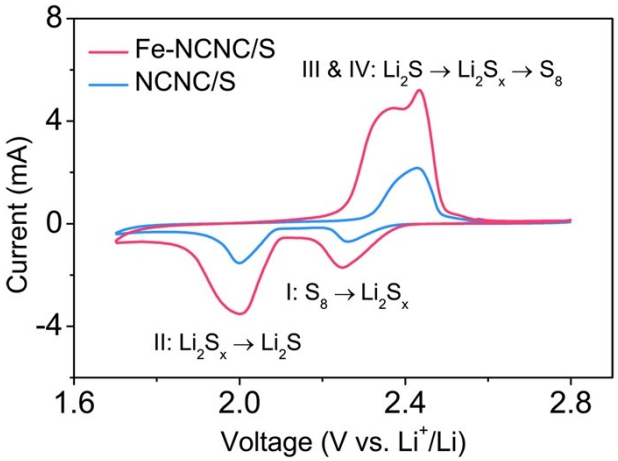

Fig. S16 CV curves for the second cycle of Fe-NCNC/S and NCNC/S electrodes at 0.1 mV s^{-1}.

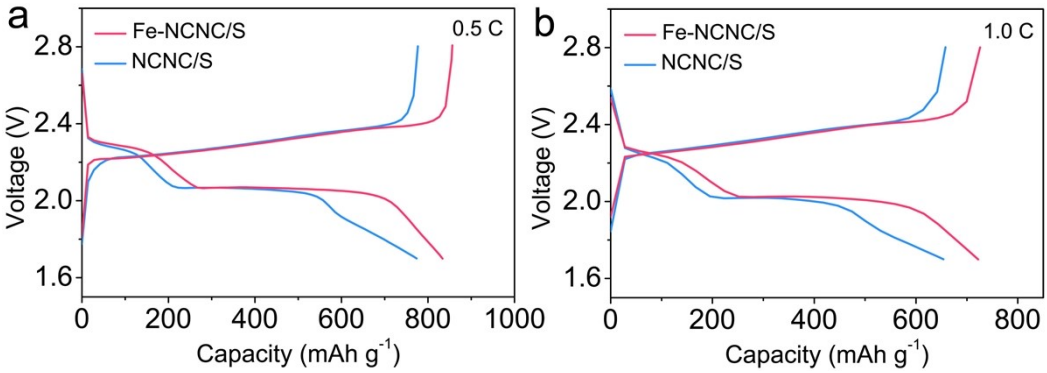

Fig. S17 Discharge-charge voltage profiles of the Fe-NCNC/S and NCNC/S cathodes at 0.5 C and 1.0 C.

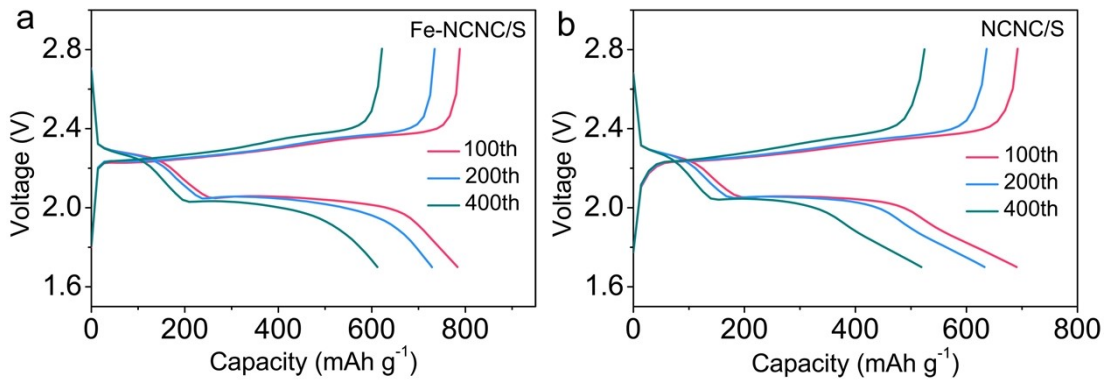

Fig. S18 Discharge-charge voltage profiles of the Fe-NCNC/S and NCNC/S electrodes during cycling of 400 cycles at 0.5 C.

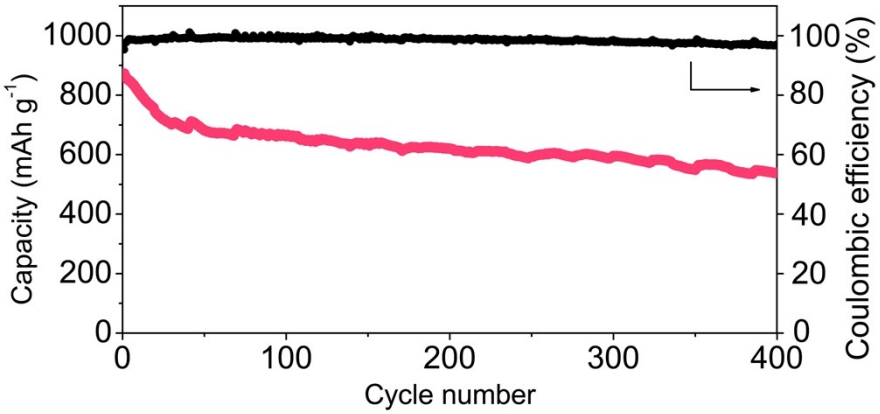

Fig. S19 Long-cycling performance of the Fe-NCNC/S electrode at 1.0 C and the corresponding Coulombic efficiency.

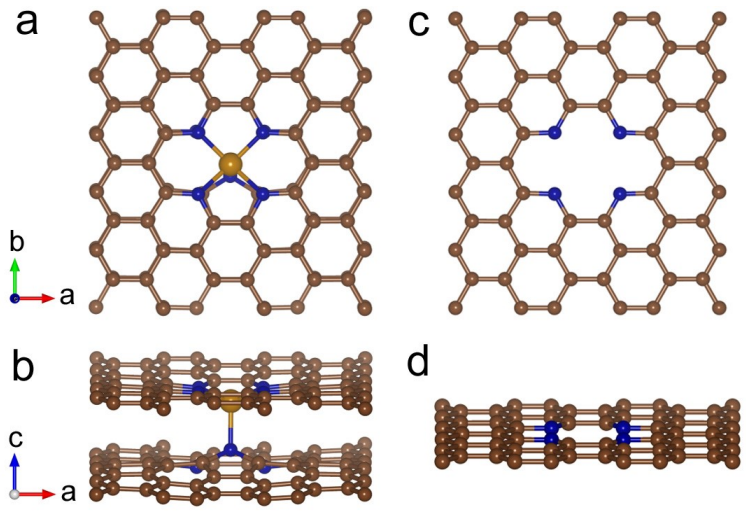

Fig. S20 Optimized structures of (a, b) Fe-NCNC and (c, d) NCNC used in first-principles calculations. The brown, blue and bright brown balls represent C, N and Fe atoms, respectively.

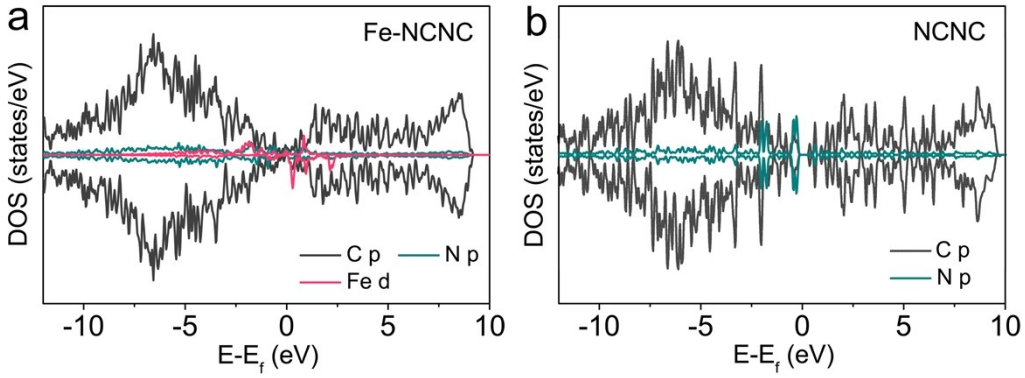

Fig. S21 The calculated density of state (DOS) of Fe-NCNC and NCNC.

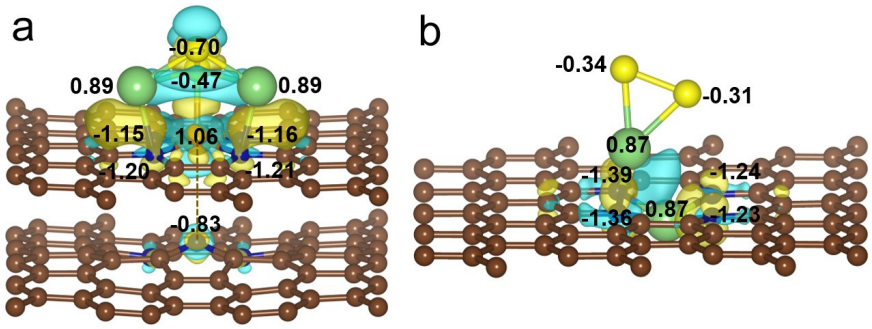

Fig. S22 Charge density difference plots of Li_2S_2 adsorbed on (a) Fe-NCNC and (b) NCNC with the isosurface value of 0.002 e $bohr^{-3}$. Cyan and yellow areas correspond to the respective charge depletion and accumulation.

Table S1. Fitting parameters of the Fe K-edge EXAFS curves for Fe-NCNC.

Path	R (Å)	N	ΔE_0 (eV)	σ^2 (10^{-3}Å^2)
Fe-N	1.98	5	6.3	9.4

R is the distance between absorber and backscatter atoms; N is the coordination number; ΔE_0 is the inner potential correction; σ^2 is the Debye-Waller factor to account for both thermal and structural disorder.

Note S1. Fractional coordinates of the compounds mentioned in DFT calculations (Fe-NCNC: a = 12.78 Å, b = 12.30 Å, c = 17.00 Å, α = β = γ = 90°; NCNC: a = 12.72 Å, b = 12.39 Å, c = 15.00 Å, α = β = γ = 90°).

Fe-NCNC

C	0.701337	12.280566	8.376767
C	2.828166	1.210541	8.402913
C	1.407328	1.217516	8.405344
C	3.537518	12.280283	8.363881
C	4.957399	12.279287	8.365343
C	7.092128	1.194674	8.414388
C	5.675583	1.195056	8.412841
C	7.810082	12.278942	8.366210
C	9.230065	12.280222	8.365411
C	11.360153	1.217024	8.406925
C	9.939148	1.210591	8.405208
C	12.066182	12.280332	8.377838
C	0.706975	2.456814	8.416887
C	2.861657	3.679028	8.378807
C	1.428150	3.689164	8.393206
C	3.543117	2.434305	8.407690
C	4.963176	2.416458	8.414728
C	7.098800	3.629496	8.351046
C	5.667761	3.629644	8.351454
C	7.803755	2.416409	8.415306
C	9.223699	2.434022	8.409492
C	11.338205	3.688967	8.394736
C	9.904700	3.678869	8.380286
C	12.059688	2.456568	8.417975
C	0.715258	4.920037	8.345555
C	2.924994	6.130320	8.201259
C	1.468620	6.131070	8.270211
C	3.635484	4.884736	8.268749
C	9.130949	4.884638	8.267576
C	11.298401	6.131021	8.270296
C	9.841707	6.130086	8.200562
C	12.051788	4.919902	8.346099
C	0.715679	7.343617	8.256509
C	2.864558	8.583653	8.199185
C	1.430106	8.574170	8.252123
C	3.637529	7.374588	8.111159
C	7.098480	8.636224	8.065820
C	5.669141	8.636310	8.066942
C	9.129517	7.374318	8.109935
C	11.336915	8.573887	8.251596
C	9.902769	8.583223	8.198216
C	12.051827	7.343703	8.256033
C	0.706962	9.806040	8.294368
C	2.828844	11.050344	8.311572
C	1.407468	11.044674	8.329456
C	3.544472	9.829410	8.230533
C	4.964506	9.845264	8.199916
C	7.092000	11.064108	8.290050
C	5.675238	11.064465	8.290152
C	7.803205	9.844994	8.199916
C	9.223149	9.829016	8.230431
C	11.359501	11.044625	8.330204
C	9.938202	11.050320	8.313051
C	12.059317	9.806040	8.294487
C	0.683173	0.055190	4.672008
C	2.802665	1.279163	4.661519
C	1.385700	1.290799	4.714831
C	3.513871	0.044182	4.558244
C	4.938404	0.012903	4.488170
C	7.077581	1.223961	4.501022
C	5.654326	1.224379	4.499815
C	7.793376	0.012325	4.490159
C	9.217806	0.043911	4.561678
C	11.345581	1.290405	4.718027
C	9.928474	1.278388	4.668098
C	12.048478	0.055055	4.675153
C	0.692773	2.541168	4.794323
C	2.896975	3.771229	4.893654
C	1.439872	3.769421	4.868902
C	3.525465	2.498105	4.733123
C	4.929852	2.435744	4.627468
C	7.067866	3.596569	4.809232
C	5.663197	3.596704	4.809385
C	7.801224	2.435449	4.630443
C	9.205394	2.497281	4.738155
C	11.289555	3.769224	4.870942
C	9.832964	3.770700	4.897105
C	12.037127	2.541119	4.796193
C	0.700136	4.984932	4.900675

C	2.910026	6.207097	4.897326
C	1.458880	6.199914	4.858464
C	3.693452	4.999052	5.046977
C	5.181885	4.854822	5.184609
C	7.549306	4.854699	5.183912
C	9.037304	4.998868	5.047827
C	11.271033	6.200159	4.858957
C	9.820297	6.206937	4.898295
C	12.029062	4.984944	4.900692
C	0.694716	7.415363	4.755410
C	2.816458	8.665965	4.626329
C	1.392308	8.652989	4.676275
C	3.588073	7.469126	4.683891
C	7.108873	8.605941	4.476814
C	5.622677	8.606076	4.476780
C	9.142722	7.469077	4.685778
C	11.338973	8.653284	4.676955
C	9.914913	8.665732	4.627825
C	12.036130	7.415424	4.755478
C	0.683225	9.885228	4.649653
C	2.807178	11.120061	4.565418
C	1.391337	11.120086	4.625513
C	3.523765	9.886371	4.540768
C	4.944949	9.865584	4.486742
C	7.076686	11.090185	4.461021
C	5.655157	11.090308	4.460715
C	7.786639	9.865154	4.486776
C	9.207772	9.886248	4.541465
C	11.340085	11.120418	4.630205
C	9.924334	11.120024	4.569345
C	12.048031	9.885375	4.650010
N	5.015252	4.827086	8.217902
N	7.750924	4.827172	8.217035
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N	7.803090	7.468732	4.548724
Fe	6.382021	6.084084	7.629753
C	-0.716318	12.280332	8.377838
C	1.407328	13.517516	8.405344
C	3.537518	-0.019717	8.363881
C	2.828166	13.510542	8.402913
C	7.810082	-0.021058	8.366210
C	7.092128	13.494675	8.414388
C	12.066182	-0.019668	8.377838
C	11.360153	13.517024	8.406925
C	13.483838	12.280566	8.376767
C	-0.722812	2.456568	8.417975
C	-0.730712	4.919902	8.346099
C	-0.730673	7.343703	8.256033
C	-0.723183	9.806040	8.294487
C	-0.734022	0.055055	4.675153
C	1.391337	-1.179915	4.625513
C	5.655157	-1.209692	4.460715
C	9.924334	-1.179976	4.569345
C	-0.745373	2.541119	4.796193
C	-0.753439	4.984944	4.900692
C	-0.746370	7.415424	4.755478
C	-0.734470	9.885375	4.650010
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C	7.793376	12.312325	4.490159
C	12.048478	12.355055	4.675153

NCNC

C	0.697345	0.003525	7.486710
C	2.812419	1.236306	7.486980
C	1.399987	1.241944	7.486845
C	3.516701	0.003487	7.486830
C	4.938482	0.003673	7.486905
C	7.056609	1.235017	7.486875
C	5.642142	1.235277	7.486860
C	7.760522	0.003525	7.486830
C	9.182227	0.003574	7.486770
C	11.298764	1.242192	7.486935
C	9.886027	1.236764	7.486890
C	12.001138	0.003587	7.486800
C	0.696481	2.487019	7.487010
C	2.827887	3.712748	7.486605
C	1.403842	3.726256	7.486890
C	3.522311	2.474887	7.486860
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C	7.089135	3.731040	7.487010
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C	9.176109	2.475060	7.486875
C	11.294377	3.726554	7.487040
C	9.870281	3.713157	7.486800

C	12.001979	2.486932	7.487055
C	0.705564	4.969187	7.486965
C	2.892136	6.199936	7.486815
C	1.460840	6.200097	7.486860
C	3.600424	4.921067	7.486680
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C	11.236503	6.200184	7.486650
C	9.804788	6.200146	7.486935
C	11.992427	4.969199	7.486725
C	0.705780	7.430920	7.486470
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C	1.404047	8.673540	7.486740
C	3.600668	7.478495	7.486815
C	7.089340	8.668894	7.486770
C	5.609048	8.668559	7.486785
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C	2.812703	11.163194	7.486860
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C	7.762345	9.928492	7.486770
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C	9.885848	-1.229306	7.486770
C	-0.717821	2.486932	7.487055
C	-0.727373	4.969199	7.486725
C	-0.727143	7.430895	7.486485
C	-0.717768	9.912815	7.486755
C	3.516960	12.395987	7.486830
C	7.760781	12.396025	7.486830
C	12.001398	12.396086	7.486800

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