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Supplementary Information

Rational design of a mesoporous silica-based cathode for efficient trapping of polysulfides in Li–S battery

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Experimental

Materials. Tetraethylorthosilicate (TEOS, 99%), $Ni(NO_3)_2 \cdot 6H_2O$ (98.5%), dodecylamine (DDA, 99%), pyrrole (99%), $FeCl_3 \cdot 6H_2O$ (99.7%), sublimed sulfur (99.95%), 1-Methyl-2-pyrrolidinone (NMP, 99.9%), ethanol (99.7%), bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, 99%), $LiNO_3$ (99%), polyvinylidene fluoride (PVDF, HSV900), 1, 3-dioxolane (DOL. 99%), dimethoxyethane (DME, 97%), super P carbon, were purchased from Sigma-Aldrich. Polyvinylpyrrolidone (PVP, K30, 99.8%) was purchased from Sinopharm Chemical Reagent Co. Ltd. All of these chemicals were used without additional purification.

Preparation of materials.

HMS and NiO/HMS. The classic mesoporous silica HMS was prepared referring to the reported protocol by Pinnavaia et al.[1] In a typical synthesis, 5 g TEOS was added to a solution of 1.2g DDA in 28 ml ethanol/water mixture (1/1, v/v) under vigorous stirring.

The substrate mixture was stirred at room temperature for 20 h in a closed vessel. The resulting precipitate was filtered, washed with water, and air dried at 60 ^{o}C to obtain the as-synthesized HMS. Finally, the surfactant was removed by calcination at 600 ^{o}C for 4 h in air with a heating rate of 2 ^{o}C/min. The synthesis procedure for NiO/HMS is identical to that for HMS described above except for the addition of 0.675 g $Ni(NO_3)_2 \cdot 6H_2O$ to the substrate mixture.

HMS/S and NiO/HMS/S composites. In the typical synthesis, HMS (or NiO/HMS) and sulfur with a mass ratio of 1:4 were mixed by grinding for 30 min. The obtained mixture was transferred to a sealed teflon-lined autoclave filled with argon atmosphere and heated at 155 ^{o}C for 12 h to obtain the HMS/S or NiO/HMS/S composites.

HMS/ppy/S and NiO/HMS/ppy/S composites. The composite materials were prepared according to the reported method by Jiang et al.[2] HMS/S or NiO/HMS/S (200 mg) was dispersed in 15 mL PVP aqueous solution (0.4 M) by stirring for 0.5 h. The obtained suspension was centrifuged, and the precipitant was washed with water to remove excess PVP. After stirring with pyrrole monomers (0.075 g) in 25 ml deionized water for 10 mins, $FeCl_3 \cdot 6H_2O$ (0.544 g) was added and continuous stirred for 12 h at 0 °C in dark. The black product was collected by centrifuging and washed with water and ethanol. Finally, the precipitate was dried at 60 °C in vacuum for 12 h to provide the final HMS/ppy/S or NiO/HMS/ppy/S product.

Preparation of Cathode. To prepare the electrode, PVDF was firstly dissolved in NMP (20 mg ml^{-1}) to obtain the binder solution. Active materials (HMS/S, HMS/ppy/S, or NiO/HMS/ppy/S) were mixed with super-P carbon and PVDF with weight ratio of 7:2:1. The slurry was coated on an Al foil and then dried in vacuum at 60 ^{o}C for 12 h to form the working electrode.

Electrochemical evaluation

Coin cell test. Electrochemical performances of electrodes were tested in CR 2032 coin cells under galvanostatic charge/discharge at room temperature using LANDHE (CT2001A, Wuhan LAND electronics Co., Ltd.) battery analyzers. Cells were assembled in an Ar-filled glove box using metallic lithium wafer as counter electrode. The electrolyte contained 1M LiTFSI in a binary solvent of DOL and DME (1:1 in volume) with 1 wt% $LiNO_3$ as electrolyte additive. The areal sulfur loading of each working electrode was 1 mg cm^{-2}, and the electrolyte to sulfur ratio was controlled at 0.02 ml electrolyte/1 mg sulfur. Celgard 2500 membrane was used as separator. Current density and specific capacity were calculated based on the mass of S active material.

CV test. Cyclic voltammetry (CV) study of the electrode was carried out on a CHI760E electrochemical work station (Shanghai Chenhua, China) in the voltage range of 1.7-2.8 V vs. Li/Li^+ at a scan rate of 0.1 mV s^{-1}.

EIS test. Electrochemical impedance spectroscopy (EIS) of the electrode was recorded by a CHI660E electrochemical work station with amplitude of 5 mV in the frequency range of 0.01 Hz-100 kHz.

Characterization. Powder X-ray diffraction was carried out on a Bruker D8 Advance X-ray diffractometer using CuKα (λ=1.54 Å) radiation. Nitrogen adsorption-desorption measurement was conducted on a Belsorp-mini(II) at liquid nitrogen temperature. The content of S was measured by a thermogravimetric analysis (TGA, NETZSCH TG 209 F3). SEM investigation of morphological features and elemental mapping analysis was carried out with a Hitachi SU-8220 instrument. The content of Ni was determined by using ICP-OES (PerkinElmer 8300).

Lithium polysulfide adsorption tests. A Li_2S_6 solution (4 mM) was prepared by dissolving sulfur and Li_2S (molar ratio = 5 : 1) in DOL and DME (1 : 1 by volume) in glove box. HMS or NiO/HMS as the adsorbent (50 mg) was added to 3 mL above Li_2S_6 solution, respectively. Digital images were recorded after absorption for 30 min. 2 mL of each supernatant after adsorption was transferred for Ultraviolet-visible (UV-vis) analysis using a TU-1900.

Computational method. The spin-polarized density functional theory (DFT) calculations are performed by the Vienna ab initio simulation package (VASP).[3,4] The Kohn–Sham orbitals were expanded in a plane wave basis set with a cutoff energy of 500 eV. The project-augmented wave (PAW) method[5] and Perdew-Burke-Ernzerhof (PBE)[6] functional were used to describe the interaction between the ionic core and valence electrons and the electron exchange correlation energy, respectively. The Brillouin zone was sampled by the 2×2×1 Monkhorst-Pack k-point mesh. 55 A vacuum distance of 14 Å was created to separate the adjacent mirror images. The amorphousness of SiO_2 was produced using the “melt-and-quench” technique. The details of this technique can be referenced to the previous paper.[7]

The binding energy (E_b) of the representative polysulfide, Li_2S_6, on the two substrates, i.e., the SiO_2 and NiO/SiO_2, was calculated by the following equation:

$$E_b = E_{\text{substrate+Li2S6}} - E_{\text{substrate}} - E_{\text{Li2S6}}$$

where $E_{\text{substrate+Li2S6}}$, $E_{\text{substrate}}$, and E_{Li2S6} is the energy of the substrate with adsorbed Li_2S_6 molecule, the energy of the clean substrate, and the energy of the isolated Li_2S_6 molecule.

Table S1. Textural properties of samples.

Samples	**S_{BET} ($m^2\ g^{-1}$)**	**V_{total} ($cm^3\ g^{-1}$)**
HMS	1025	1.02
NiO/HMS	880	0.77
NiO/HMS/S	23.7	0.026
NiO/HMS/ppy/S	8.5	0.025

Table S2. Electrochemical performances of some reported carbon/sulfur cathodes and our work in Li-S battery for comparison.

Sulfur host	**Current density**	**Cycle**	**Initial capacity (mAh g^{-1})**	**Final capacity (mAh g^{-1})**	**Ref.**
Hierarchically porous carbon	0.1 C	25	1305	469	[8]
Graphene	0.2 C	100	750	522	[9]
Carbon spheres	0.4 A g^{-1}	500	1180	650	[10]
Graphene foam/rGO	0.2 C	350	1000	645	[11]
3D copolymer graphene	50 mA g^{-1}	50	812.8	353	[12]
Carbon nanotube	0.25 C	100	933	680	[13]
CNT foam	0.1 C	100	1039	450	[14]
MWNTs/hollow porous carbon nanotubes	2 A g^{-1}	200	1274(0.5A g^{-1})	647	[15]
Hollow carbon nanofiber	0.2 C	150	1080	730	[16]
Porous carbon nanofiber/carbon nanotube	0.5 C	200	975	675	[17]
Graphene-based layered porous carbon	0.5 C	100	853	597	[18]
Mesoporous carbon/rGO	1 C	500	919	582	[19]
Mesoporous nitrogen-doped carbon	0.7 mA cm^{-2}	100	1100 (0.35 mA cm^{-2})	800	[20]
Nitrogen-doped aligned carbon nanotube/graphene	1 C	80	1152	880	[21]
g-C_3N_4@PCNF	100 mA g^{-1}	100	1026	700	[22]
N,S-codoped graphene sponge	0.5 C	200	925	670	[23]
NiO/HMS/ppy	0.2 C	100	1218	814	This work
NiO/HMS/ppy	0.2 C	300	1218	714	This work
NiO/HMS/ppy	0.5 C	300	1087	661	This work

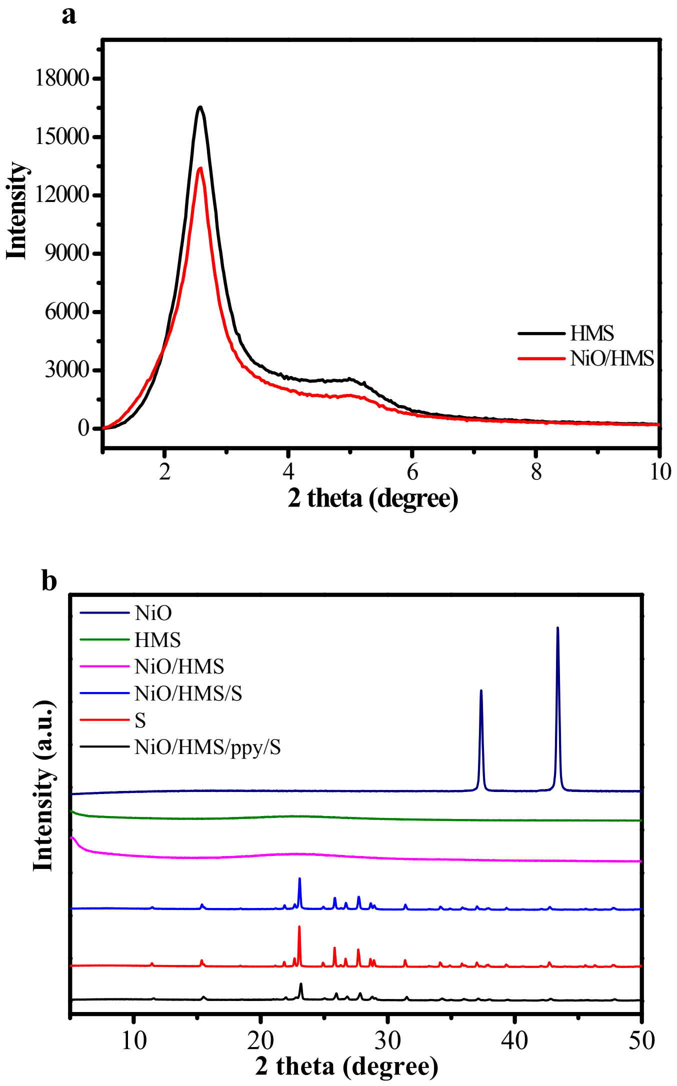

Figure S1. XRD patterns of samples.

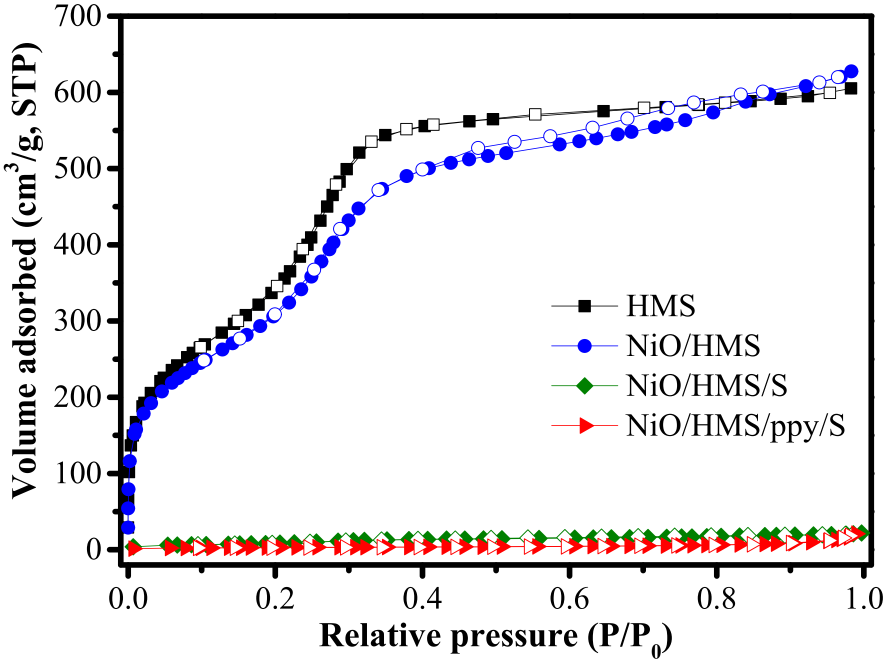

Figure S2. Nitrogen adsorption-desorption isotherms of samples.

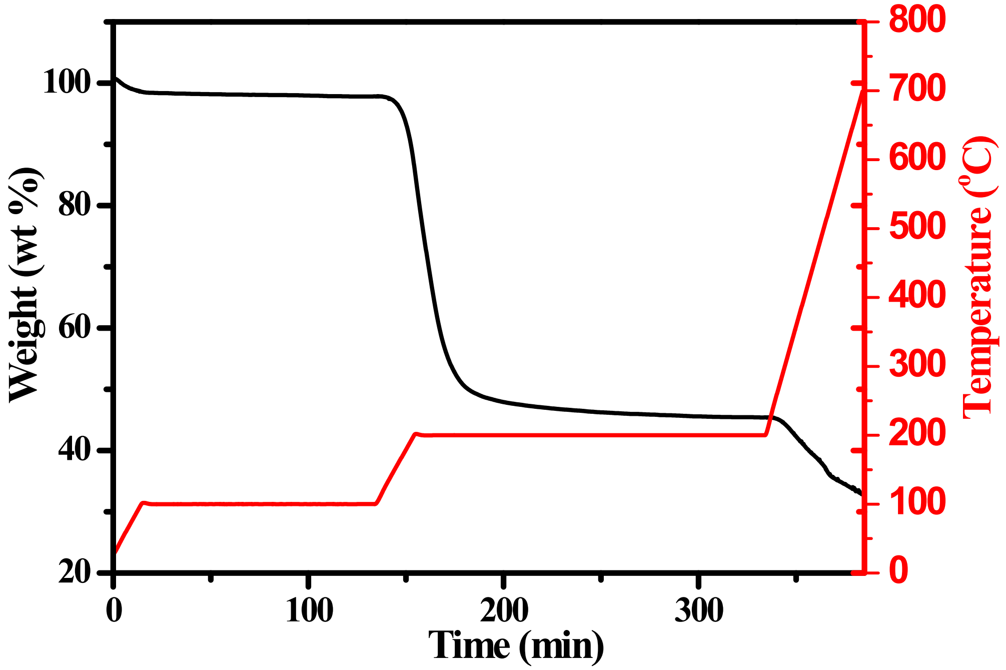

Figure S3. TGA diagram of NiO/HMS/ppy/S.

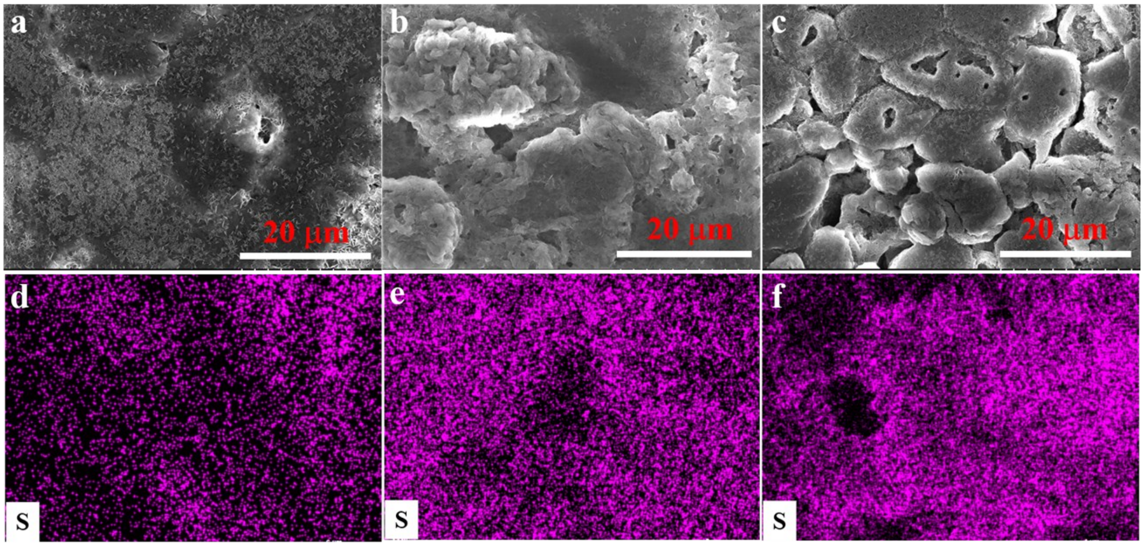

Figure S4. SEM pictures of the Li anodes paired with (a) NiO/HMS/ppy/S, (b) HMS/ppy/S and (c) HMS/S cathodes in cells after 300 cycles at 1.0 C; elemental mapping images of sulfur in Li anodes paired with (d) NiO/HMS/ppy/S, (e) HMS/ppy/S and (f) HMS/S cathodes in cells after 300 cycles at 1.0 C.

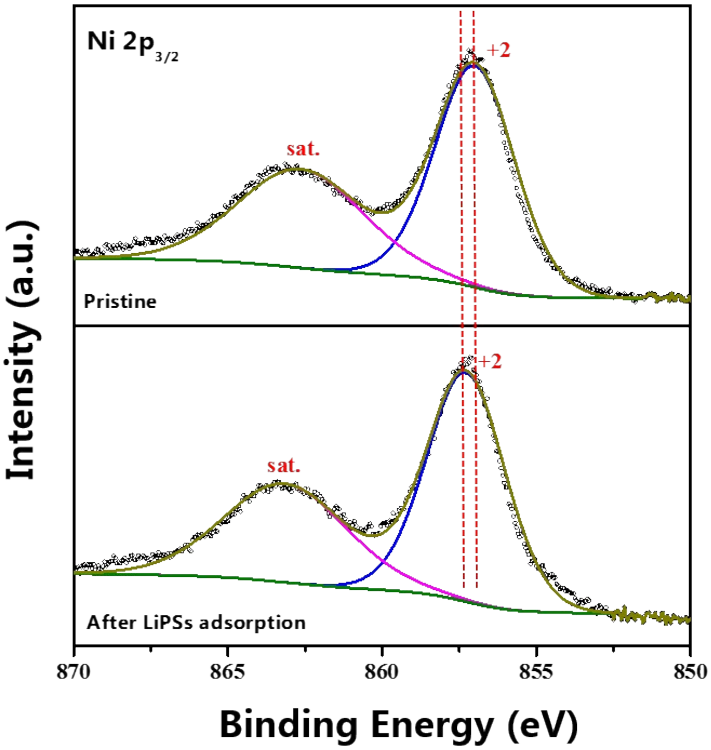

Figure S5. High-resolution XPS spectra of Ni $2p_{3/2}$ of the NiO/HMS before and after LiPSs adsorption.

Supplementary References

1. P. T. Tanev, T. J. Pinnavaia, Science, 1995, 267, 865-867.
2. H. Jiang, X. C. Liu, Y. Wu, Y. Shu, X. Gong, F. S. Ke, H. Deng, Angew. Chem. Int. Ed., 2018, 57, 3916-3921.
3. G. Kresse, D. Joubert, Phys. Rev. B: Condens. Matter Mater. Phys., 1999, 59, 758-1775.
4. G. Kresse, J. Furthm¨uller, Phys. Rev. B: Condens. Matter Mater. Phys., 1996, 54, 11169-11186.
5. P. E. Bl¨ochl, Phys. Rev. B: Condens. Matter Mater. Phys., 1994, 50, 17953-17979.
6. J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865-868.
7. H. H. Pham, L. W. Wang, Phys. Chem. Chem. Phys., 2015, 17(1), 541-550.
8. L. Yu, N. Brun, K. Sakaushi, J. Eckert, M. M. Titirici, Carbon, 2013, 61, 245−253.
9. H. Wang, Y. Yang, Y. Liang, J. T. Robinson, Y. Li, A. Jackson, Y. Cui, H. Dai, Nano Lett., 2011, 11, 2644−2647.
10. B. Zhang, X. Qin, G. R. Li, X. P. Gao, Energy Environ. Sci., 2010, 3(10), 1531-1537.
11. G. Hu, C. Xu, Z. Sun, S. Wang, H. M. Cheng, F. Li, W. Ren, Adv. Mater., 2016, 28(8), 1603-1609.
12. K. Shen, H. Mei, B. Li, J. Ding, S. Yang, Adv. Energy Mater., 2018, 8(4), 1701527.
13. J. Guo, Y. Xu, C. Wang, Nano Lett., 2011, 11, 4288−4294.
14. M. Li, R. Carter, A. Douglas, L. Oakes, C. L. Pint, ACS Nano, 2017, 11(5), 4877-4884.
15. Y. Zhao, W. Wu, J. Li, Z. Xu, L. Guan, Adv. Mater., 2014, 26(30), 5113-5118.
16. G. Zheng, Y. Yang, J. J. Cha, S. S. Hong, Y. Cui, Nano Lett., 2011, 11, 4462−4467.
17. Y. Z. Zhang, Z. Zhang, S. Liu, G. R. Li, X. P. Gao, ACS Appl. Mater. Interfaces, 2018, 10, 8749-8757.
18. X. Yang, L. Zhang, F. Zhang, Y. Huang, Y. Chen, ACS Nano, 2014, 8(5), 5208-5215.
19. W. Qian, Q. Gao, Z. Li, W. Tian, H. Zhang, Q. Zhang, ACS Appl. Mater. Interfaces, 2017, 9(34), 28366-28376.
20. J. Song, T. Xu, M. L. Gordin, P. Zhu, D. Lv, Y.B. Jiang, Y. Chen, Y. Duan, D. Wang, Adv. Funct. Mater., 2014, 24, 1243-1250.
21. C. Tang, Q. Zhang, M. Q. Zhao, J. Q. Huang, X. B. Cheng, G. L. Tian, H. J. Peng, F. Wei, Adv. Mater., 2014, 26(35), 6100-6105.
22. Z. Bian, T. Yuan, Y. Xu, Y. Pang, H. Yao, J. Li, J. Yang, S. Zheng, Carbon, 2019, 150, 216-223.
23. G. Zhou, E. Paek, G. S. Hwang, A. Manthiram, Nat. Commun., 2015, 6, 7760.