

Electronic Supplementary Information for

N-doped Branched Carbon Nanofibers @S as Cathode for Lithium-Sulfur Batteries

Yongsheng Zhou,^{*,a} Yu Qin^a, Yingchun Zhu,^{b,d} and Bingshe Xu^c

^a College of Chemistry and Materials Engineering, Anhui Science and Technology University, Bengbu, 233030, P. R. China;

^b Key Laboratory of Inorganic Coating Materials CAS, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, 200050, P. R. China;

^c Key Laboratory of Interface Science and Engineering in Advanced Materials, Ministry of Education, Taiyuan University of Technology, Taiyuan, 030024, P. R. China;

^d

Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

*Corresponding author. E-mail: yszhou1981@gmail.com.

Experimental section

Preparation of NBCNF@S

60 mg sulfur powder was dispersed in 20 ml 0.1 M sodium polysulfide (Na-poly-S) solution in a 40 ml glass vial with a PET cap. The vial was closed, hand shaken and sonicated at 40 °C for 30 min. The Ni(NO₃)₂ and PAN powder were placed in a graphite crucible enclosed within a graphite susceptor using an induction furnace, heated up to the reaction temperature with a flow of Ar (1000 sccm), NH₃ (100 sccm) and C₂H₄ (100 sccm). C₂H₄ was allowed to bubble through the vial. The temperature of the susceptor was heated to 1000 °C. After growth for 15 min, the C₂H₄ and NH₃ flow was stopped and the chamber was cooled down to room temperature. During the cooling process, the system was purged with Ar to prevent a backflow of air from the exhaust line.

The obtained product was washed three times by replacing the liquid products with distilled water and HCl, allowing soluble components to diffuse out of the product for at least 2 h. The washed product was freeze dried to remove the liquid component. The resulting product was cut into discs with a razor blade. Prior to use as a cathode, the discs were dried in a vacuum oven at 90 °C for 1 h and directly transferred to an argon filled glove box.

Preparation of CNF@S

Commercial CNFs were mixed with sulfur (Aldrich, with a purity of >99.995%) in a mass ratio of 1:2 and heated to 155 °C for 10 h in a closed glass container under air atmosphere. This facilitated sulfur diffusion into the carbon scaffold to obtain the CNF@S composite.

Characterization

The products were characterized by scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HRTEM, JEM-2010). N₂ sorption analysis was conducted on an ASAP2020 accelerated surface area and porosimetry instrument (Micromeritics), equipped with automated surface area, at 77 K using BarrettEmmettTeller (BET) calculations for the surface area. The pore size distribution (PSD) plot was recorded from the adsorption branch of the isotherm based on the density functional theory (DFT) model. X-ray powder diffraction (XRD) pattern of the sample was recorded using a D/max-3C diffractometer equipped with Cu-K α X-ray source. Thermogravimetric analysis (TGA) was conducted in a simultaneous DSC-TGA analyzer (NETZSCH-409PC), and the samples were heated from room temperature to 600 °C with a heating rate of 5 °C/min under a continuous flow of N₂ gas. Ultraviolet/visible absorption spectra were obtained on a Lambda 750 UV-Visible Spectrophotometer. Raman spectra were measured using a Renishaw inVia Raman spectrometer system (Gloucestershire, UK) equipped with a Leica DML Bmicroscope (Wetzlar, Germany) and a 17 mW at 633 nm Renishaw helium neon laser source. XPS measurements were carried out on a Kratos XSAM-800 spectrometer with an Mg K α radiation source.

Electrochemical measurements

The electrochemical properties of the samples were measured using CR2025-type coin cell with lithium metal as the counter electrode. The working electrodes were composed of 90 wt% of the active material and 10 wt% of the binder (poly(vinylidene difluoride), PVDF), which were mixed with 1-methyl-2-pyrrolidinone (NMP) to form a homogeneous slurry. The well-mixed slurry was then spread onto an aluminum foil and dried at 55 °C in a vacuum oven for 12 h. The loading amount of the active sulfur cathode was 1.2 mg cm⁻² in each electrode. The electrodes were assembled into 2025-type coin cells in an argon-filled glove box with the Celgard 2300

microporous polypropylene membrane as the separator. The electrolyte was prepared in an argon-filled glovebox as reported in the literature, i.e., 1 M LiTFSI and 1 wt% LiNO₃ in 1, 3-dioxolane and 1, 2-dimethoxyethane (volume ratio 1:1). Coin cells were tested on a Scribner 580 battery cyclers. Cyclic voltammetry (CV) curves were collected by a CHI600E electrochemical working station at a scan rate of 0.1 mV s⁻¹ at room temperature. The discharge/charge tests were performed between 1.4 V and 2.8 V on a Land CT2001A battery test system (Wuhan, China). Rates were calculated per mass sulfur in the cathode and the loading was 80 wt% sulfur per electrode. Rate capability was tested after precycling at 0.1 C for five cycles. Each C-rate, 0.1, 0.25, 0.5, 1 and 2 C (1 C=1680 mA h g⁻¹) were tested for 5 cycles followed by returning to 0.1 C. Stability tests were run at 0.1 C. All the electrochemical experiments were conducted at ambient temperature. The specific capacities here are specified as mA h g⁻¹ on the basis of the mass of sulfur.

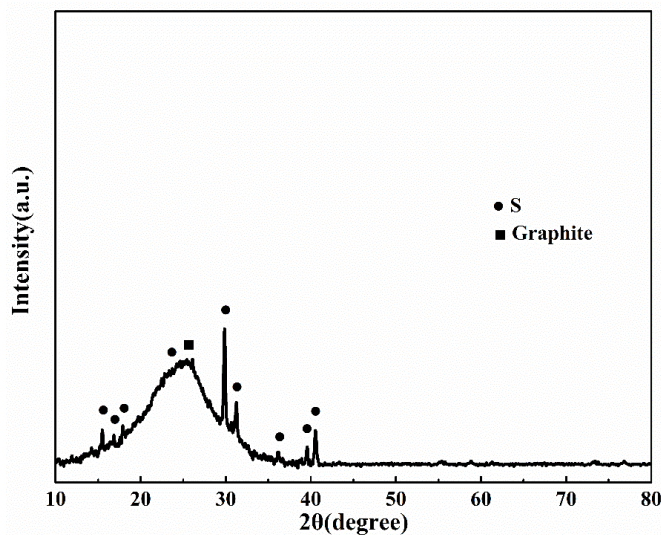


Figure S1. XRD of NBCNF@S.

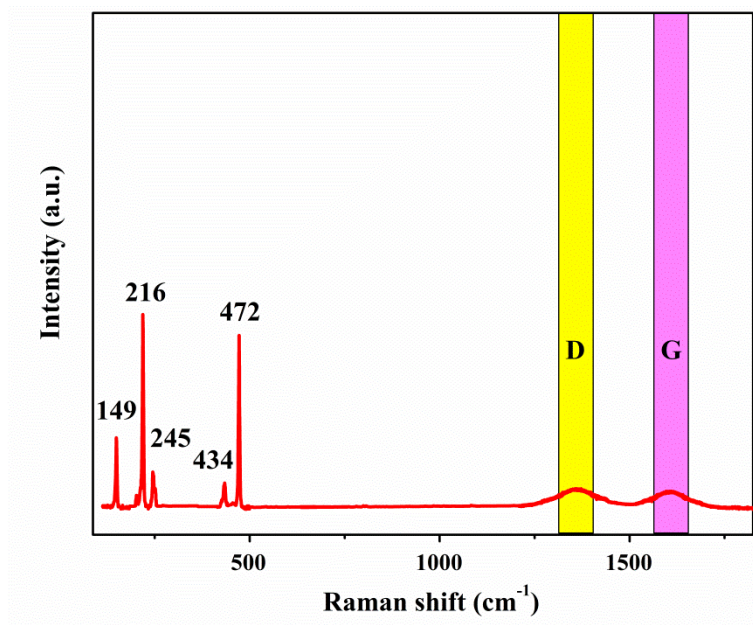


Figure S2. Raman spectra of the NBCNF@S.

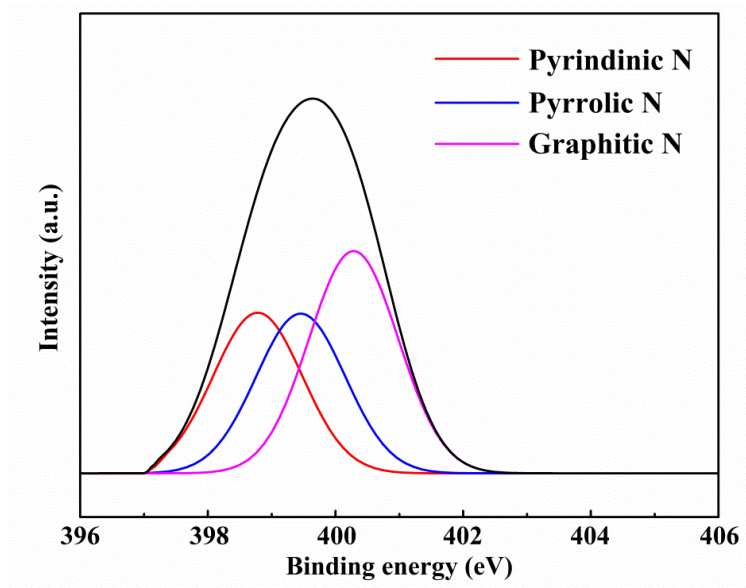


Figure S3. High-resolution XPS N1s spectrum of NBCNF@S.

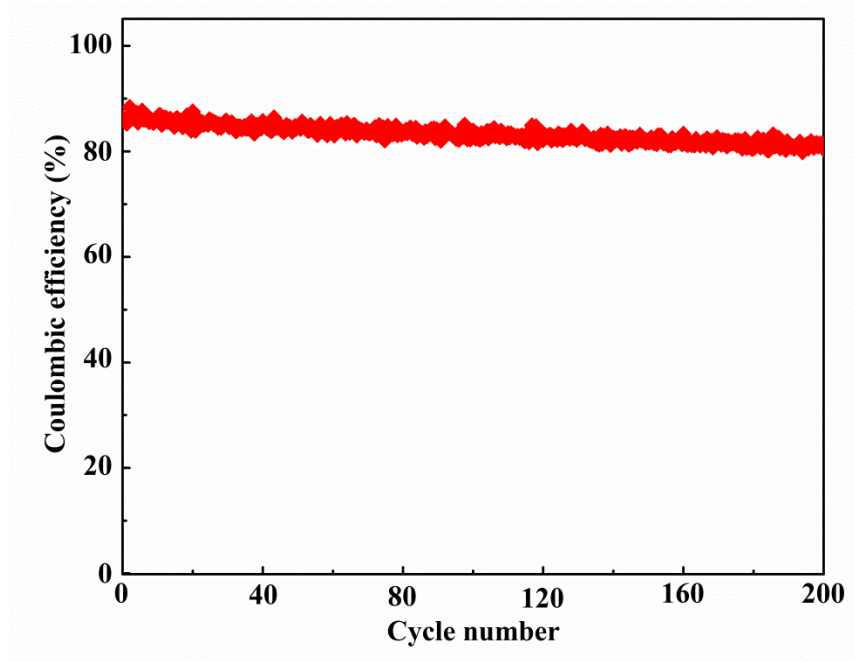


Figure S4. Coulombic efficiency of CNF@S cathodes cycling at 0.1 C.

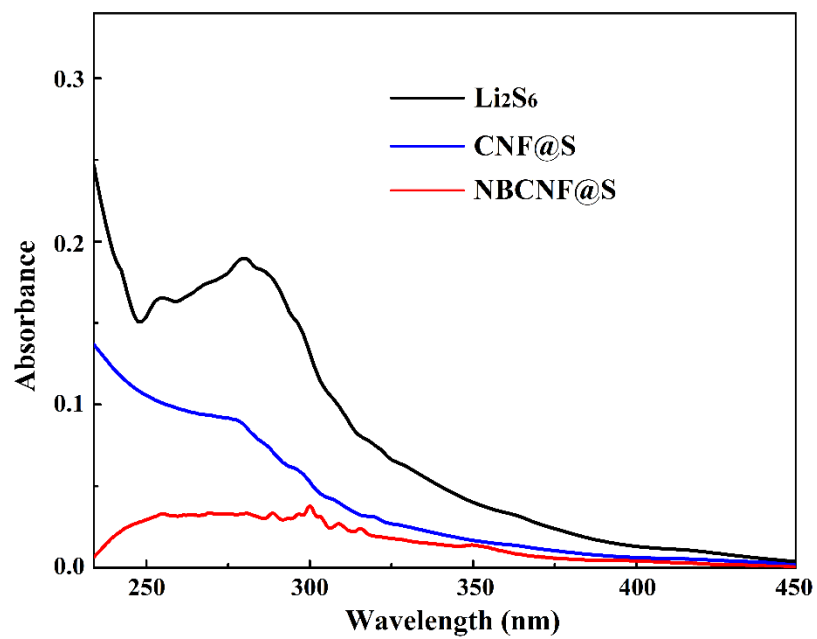


Figure S5. Ultraviolet–visible absorption spectra of Li_2S_6 solution without or with addition of CNF@S or NBCNF@S composites.

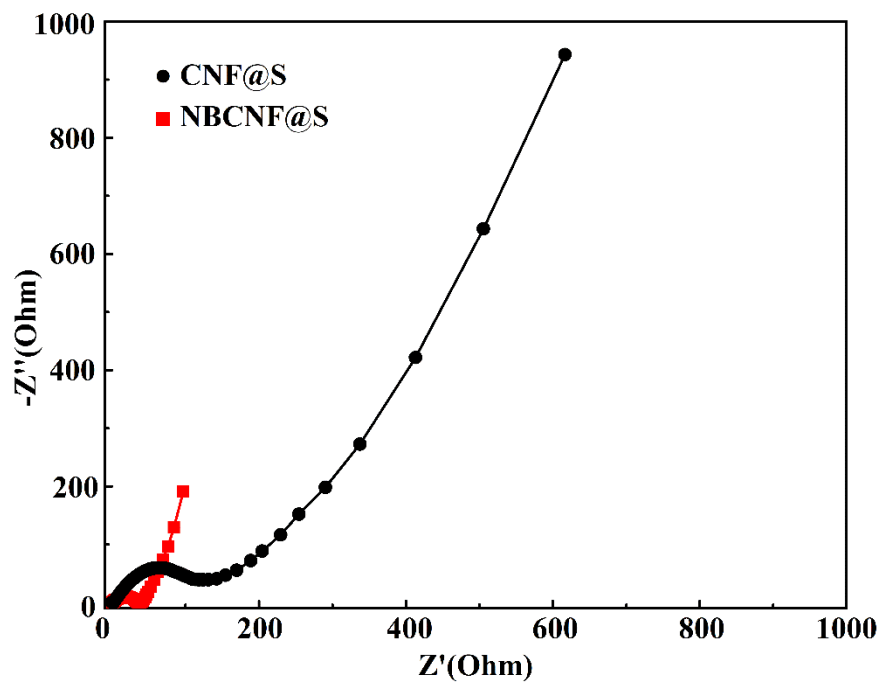


Figure S6. Nyquist plots for the CNF@S and NBCNF@S cells.

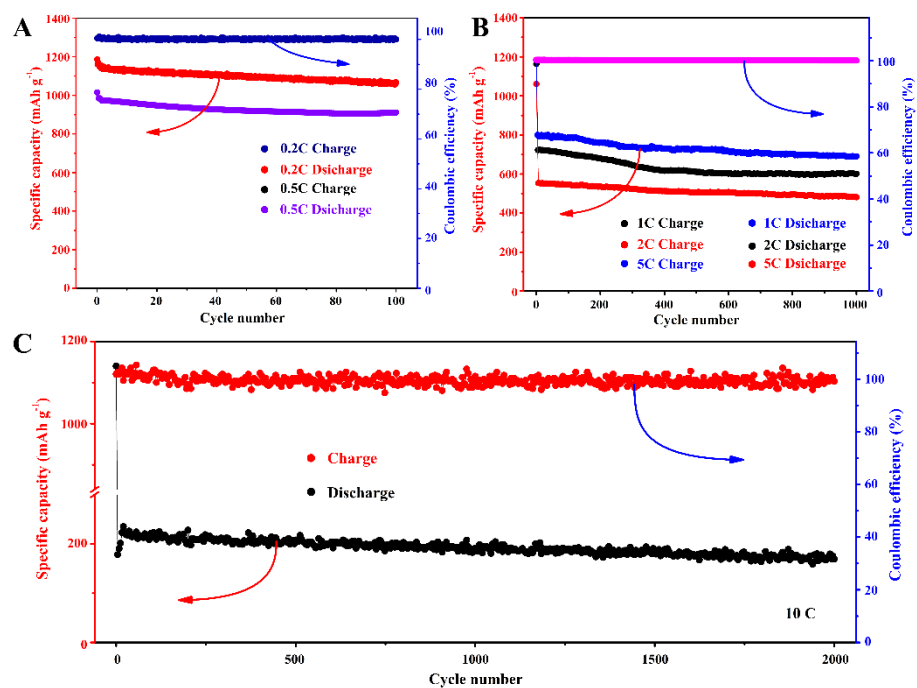


Figure S7. (A) Cycling performances and Coulombic efficiencies of the NBCNF@S at 0.2, and 0.5 C rates. (B) Cycling performances and Coulombic efficiencies of NBCNF@S at 1, 2, and 5 C rates. (C) Cycling performances and Coulombic efficiencies of NBCNF@S at 10 C rates.

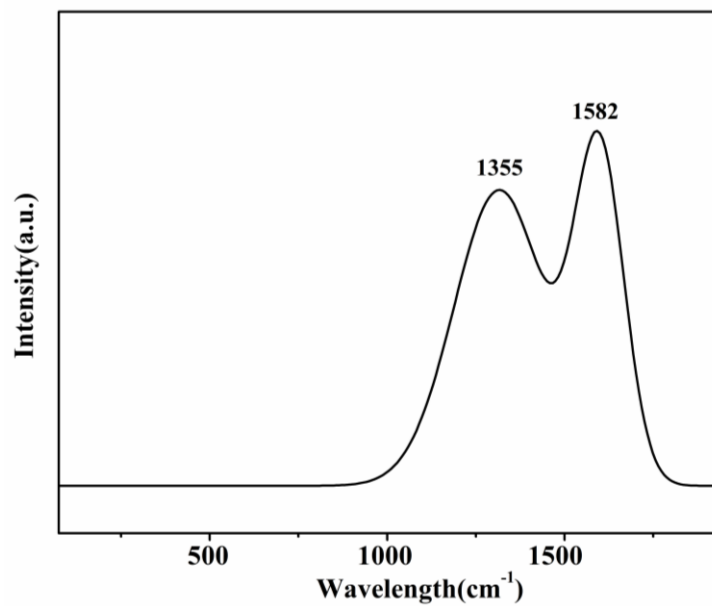


Figure S8. Ex-situ Raman spectrum of CNF@S composites electrode after 1000 cycles.

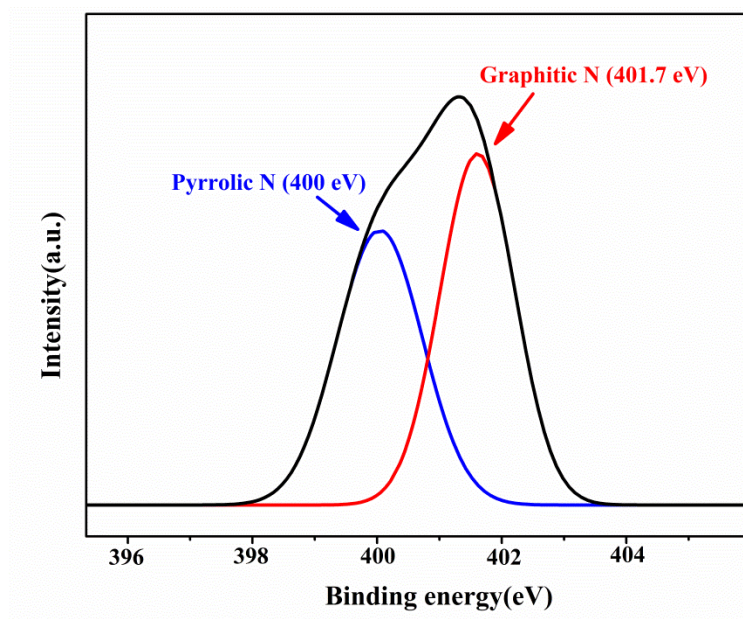


Figure S9. XPS of N 1s of the electrode after discharge down to 2.0 V.

Table S1 | Different oxides and sulfides employed in cathodes for lithium-sulfur batteries.

Materials	Electrochemical performance (initial capacity [mAh g^{-1}] and cycles)	References
CoP@C	1237.6 (1142.3 after 100 cycles)	1
(ZIF-8(C))@CMK-3	1597.2 (596 after 300 cycles)	2
HDNi@g-C ₃ N ₄	1271.6 (673.63 after 500 cycles)	3
mono-MBene/CNT	12.73 mAh cm^{-2} (11.07 mAh cm^{-2} after 120 cycles)	4
P-Mn ₃ O _{4-x}	843.1 (784 after 250 cycles)	5
CoP-HNC	800 (784 after 1000 cycles)	6
NOMCs	530.9 (430 after 200 cycles)	7
G-NHMC/S	1322 (~ 1000 cycles)	8
Our work	1280 mAh g^{-1} (1039 mAh g^{-1} after 200 cycles)	

References

- Xinhang Liu, Lirong Zhang, Xinzhi Ma, Huiqing Lu, Lu Li, Xitian Zhang, Lili Wu. *Chem. Eng. J.* **2023**, 454, 140460.
- Qianqian Liu, Xiaomian Wang, Yinghui Wei, Junjie Liu, Miao Cheng, Lu Wang, Yabing Li, Jianfeng Wu, Tao Wei, Jing Hu, Yun Ling, Bo Liu, Wanfei Li. *J. Alloys Compd.* **2023**, 934, 167861.
- Wen-Wu Liu, Sheng-Tao Niu, Zhi-Qiang Xu, Rong Zou, Chong-Yang Cui, Yi-Xiao Lei, Xiao-Bo Zhang, Fen Ran. *Appl. Surface Sci.* **2023**, 609, 155327.
- Z. F. Li, Q. H. Zeng, Y. Yu, Y. Liu, A. Q. Chen, J. Z. Guan, H. H. Wang, W. Liu, X. Liu, X. F. Liu, L. Y. Zhang. *Chem. Eng. J.* **2023**, 452, 139366.
- Tao Liu, Jing Li, Hongtao Cui, Yuanyuan Liu, Kaihua Liu, Huiying Wei, Meiri Wang. *J. Energy Chem.* **2023**, 76, 339-348.

6. H. Y. Zhang, S. S. Xin, J. Li, H. T. Cui, Y. Y. Liu, Y. Z. Yang, M. R. Wang. *Nano Energy* **2021**, 85, 106011.
7. R. G. Cheng, Y. X. Guan, Y. M. Luo, C. C. Zhang, Y. P. Xia, S. Wei, M. M. Zhao, Q. Lin, H. Li, S. Y. Zheng, F. Rosei, L. X. Sun, F. Xu, H. G. Pan. *J. Mater. Sci. Technol.* **2022**, 101, 155-164.
8. Y. Yan, P. Zhang, Z. H. Qu, M.M. Tong, S. Zhao, Z. W. Li, M. K. Li, Z. Q. Lin. *Nano Lett.* **2020**, 20, 10, 7662–7669.