

Supporting Information

Local Charge Rearrangement to Boost Chemical Adsorption and Catalytic Conversion of Polysulfides for High-performance Lithium–Sulfur Batteries

Tongkun Zhao,^{a,b} Junwu Chen,^a Menglei Yuan,^{a,b} Kaiqing Dai,^c Jingxian Zhang,^{a,b} Shuwei Li,^a Hongyan He,^a Zhanjun Liu^d and Guangjin Zhang^{a,b,*}

^aCAS Key Laboratory of Green Process Engineering, State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China.

^bCenter of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

^cSchool of Mechanical and Electrical Engineering, Central South University, Changsha 410083, Hunan, China

^dCAS Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China

*To whom correspondence should be addressed. Email: zhanggj@ipe.ac.cn.

1. Experimental Section

1.1. Materials and Chemicals

Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 98%), 1,3,5-benzenetricarboxylic acid (H_3BTC , 99%), N,N-dimethylformamide (DMF, 99%), dicyandiamide (DCD, 99%) were all supplied by Aladdin Reagent Co., Ltd. Methanol anhydrous (CH_3OH , 99%) was purchased from Sinopharm Chemical Reagent Co. Ltd. All these reagents were used without any further purification.

1.2. Preparation of Bi-MOF

The Bi-MOF was synthesized via a solvothermal method. Typically, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (200 mg) and H_3BTC (1000 mg) were dissolved in a mixture of DMF (64 mL) and CH_3OH (16 mL) with continuous stirring. Then, the transparent mixture was transferred into a Teflon lined steel reactor (100 mL). After sealed, the reactor was heated at 120 °C for 24 h. Afterwards, the obtained precipitates were collected by centrifugation and washed several times with CH_3OH . Finally, the obtained product was named Bi-MOF after drying at 80 °C.

1.3. Preparation of Bi-NC and NC

The as-synthesized Bi-MOF (200 mg) and DCD (300 mg) were first put in two porcelain boats. After porcelain boats were placed at two separate positions in the tube furnace, the samples were carbonized at 900 °C for 2 h with a heating rate of 2 °C min^{-1} under flowing Ar to yield Bi-NC. For comparison, NC was prepared by the similar procedures except for increasing the carbonization temperature to 1000 °C.

1.4. Preparation of Bi-NC/S and NC/S Composites

The as-synthesized Bi-NC was mixed with sublimed sulfur in a weight ratio of 3:7 and heated under 155 °C for 12 h to attain the Bi-NC/S composites. Using the identical method, the NC/S composite was also obtained.

1.5. Material Characterization

The morphologies of samples were characterized by scanning electron microscopy (SEM, JSM-7800F Prime) and transmission electron microscopy (TEM, JEM-2100F). X-ray diffraction (XRD) patterns were recorded on an X-ray powder diffractometer (Bruker AXS D advance) equipped with Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm). The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Kratos, AXIS-HS monochromatized Al $K\alpha$ cathode source at 75–150 W. Raman spectra were recorded with a Renishaw Raman Test system ($\lambda = 532$ nm). The N_2 adsorption–desorption experiments were carried out on a

Quantachrome SI-MP Instrument and the specific surface area was determined by the Brunauer-Emmett-Teller method. Thermogravimetric analysis (TGA) was conducted on a Netzsch, STA 449F3 instrument with a heating rate of 10 °C min⁻¹.

1.6. Visualized Adsorption of Polysulfides

Li₂S₆ was selected as a prototype of polysulfides. Li₂S₆ solution (10 mM) was prepared by mixing the Li₂S and sulfur with a molar ratio of 1:5 in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (v/v = 1/1) under vigorous stirring at 60 °C for 24 h. Then, 10 mg of Bi-NC and NC were added separately into the as-prepared Li₂S₆ solution. The digital photographs were taken after 20min, 2, 4, and 8 h of adsorption with repetitive shaking and standing.

1.7. Assembly and Measurements of Symmetric Cells

The Bi-NC (or NC) was mixed with N-lauryl acrylate (LA133) binder in a mass ratio of 9:1 in alcohol to form a uniform slurry. Then the slurry was coated on Al foil and dried at 60 °C for 12 h to obtain the working electrodes. The loading of active material (Bi-NC or NC) was controlled at about 0.5 mg cm⁻². Two identical working electrodes were assembled into a CR2032 coin cell with Celgard 2400 polypropylene separator and 40 μL of Li₂S₆ electrolyte. The Li₂S₆ electrolyte was Li₂S₆ (0.2 M) in a mixed solvent of DOL/DME (v/v = 1/1) with bis(trifluoromethanesulfonyl)imide lithium (LiTFSI, 1.0 M) and LiNO₃ (1.0 wt%). Cyclic voltammetry (CV) of symmetric cells was performed from -0.8 V to 0.8 V at the scan rates of 3 and 50 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was performed in the frequency range of 0.1 Hz to 10 kHz. Both CV and EIS were conducted on a CHI 760E workstation.

1.8. Measurements for the Li₂S Deposition

The above working electrodes were assembled into a CR2032 coin cell with Celgard 2400 polypropylene separator and Li foil as the anode. 20 μL of Li₂S₈ catholyte was dropped onto working electrodes, while 20 μL of blank electrolyte without Li₂S₈ was added in the anode side. The Li₂S₈ catholyte was Li₂S₈ (0.2 M) in tetraglyme solvent with LiTFSI (1.0 M). The assembled cells were galvanostatically discharged at 0.112 mA to 2.06 V, and subsequently kept potentiostatically discharged at 2.05 V until the current was below 0.01 mA. The capacity of deposited Li₂S was calculated according to Faraday's law.

1.9. Measurements for the Li₂S Dissolution

The cells identical to those in the tests of Li₂S nucleation were employed for the tests of Li₂S dissolution. The fresh cells were firstly galvanostatically discharged at 0.10 mA to 1.80 V, and

subsequently galvanostatically discharged at 0.01 mA to 1.80 V for full transformation of S species into solid Li_2S . Then the cells were potentiostatically charged at 2.40 V for the dissolution of Li_2S into polysulfides until the current was below 0.01 mA.

1.10. Assembly and Measurements of Li–S Cells

The Bi-NC/S (or NC/S) composite was mixed with super P and LA133 binder in a mass ratio of 8:1:1 in alcohol to form a homogeneous slurry. Then the slurry was coated on Al foil and dried at 60 °C for 12 h to obtain sulfur cathodes. The areal loading of sulfur was controlled at about 1.2–1.6 mg cm^{-2} . The sulfur cathodes with high areal loadings of 3.7 and 7.0 mg cm^{-2} were also prepared to investigate the practicability of Bi-NC/S composite. CR2032 coin cells were assembled employing the as-prepared sulfur cathode, Celgard 2400 polypropylene separator, and Li foil as the anode. The electrolyte was LiTFSI (1.0 M) in a mixed solvent of DOL/DME (v/v = 1/1) with LiNO_3 (2.0 wt%). For consistency, the ratio of electrolyte to sulfur was kept at 15 $\mu\text{L mg}^{-1}$ for the low areal loadings, while the lower E/S ratios were employed for the high areal loadings. The galvanostatic charge/discharge tests of the coin cells were measured using a LAND CT2001A battery tester within a voltage window of 1.7–2.8 V. CV tests were conducted between 1.7 and 2.8 V. EIS was performed by applying an AC amplitude of 5 mV over a frequency range from 0.01 Hz to 100 kHz.

1.11. Theoretical Calculation.

All calculations were performed using density functional theory (DFT) method implemented in Vienna ab initio simulation package (VASP). The projector augmented wave (PAW) method was used to describe electron-ion interactions. The gradient-corrected Perdew-Burke-Ernzerh (GGA-PBE) functional was adopted to describe electron exchange and correlation energy. The cutoff energy for plane-wave basis set was set as 520 eV, and the total energy convergence was set to be lower than 1×10^{-6} eV, with the force convergence set at 0.02 eV/Å for geometric optimization. The first Brillouin zone was sampled with $2 \times 2 \times 1$ Gamma-centered k-points grids. The DFT-D3 empirical correction method was employed to describe van der Waals interactions.

2. Supporting Figures

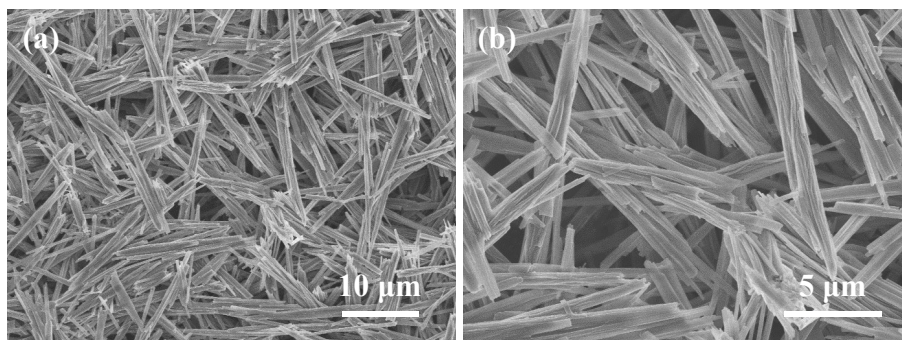


Fig. S1. (a,b) SEM images of Bi-MOF with different magnifications.

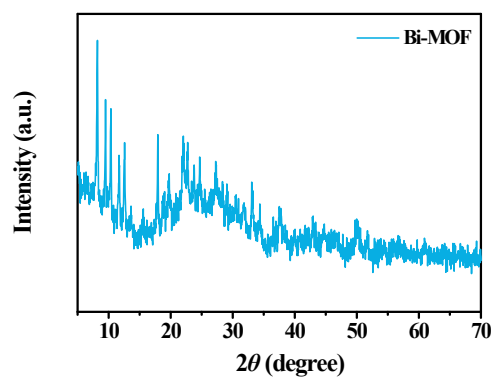


Fig. S2. XRD pattern of Bi-MOF.

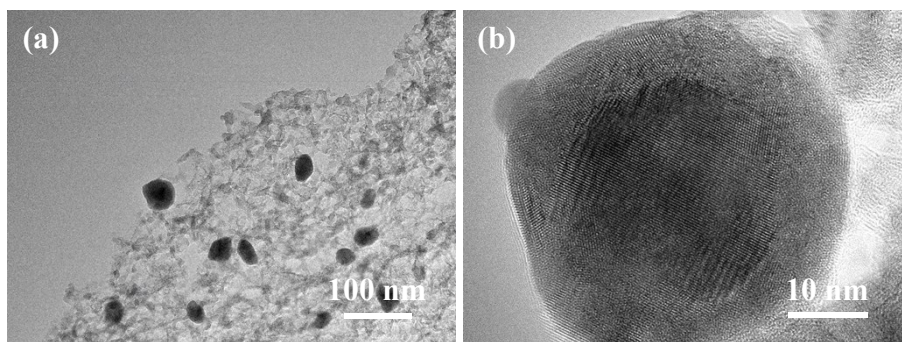


Fig. S3. (a,b) TEM images of Bi-NC with different magnifications.

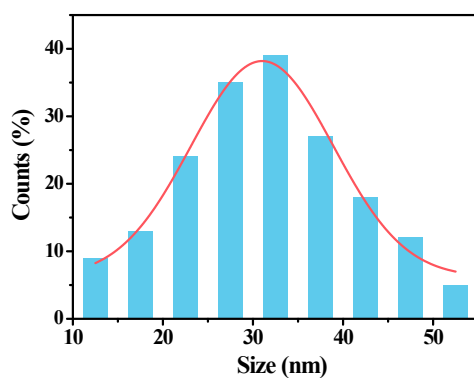


Fig. S4. Statistical analysis of the sizes of Bi nanoparticles collected from the TEM observation.

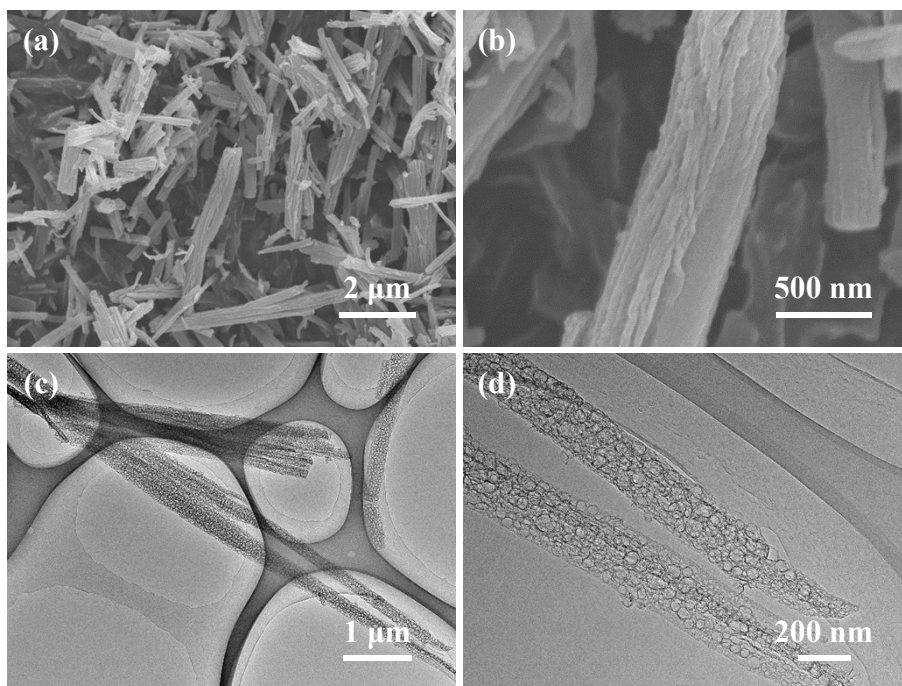


Fig. S5. (a,b) SEM and (c,d) TEM images of NC with different magnifications.

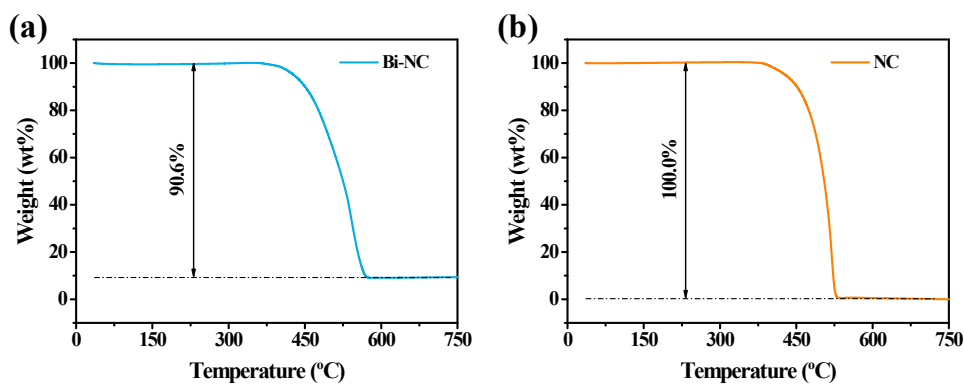


Fig. S6. TGA curves of (a) Bi-NC and (b) NC in flowing air. The Bi content in Bi-NC could be quantitatively calculated through the following equation:

$$\text{Bi (wt\%)} = \frac{2 \times \text{atomic weight of Bi}}{\text{molecular weight of Bi}_2\text{O}_3} \times \frac{\text{weight of Bi}_2\text{O}_3}{\text{weight of Bi - NC}} \times 100\% = \frac{417.96}{465.96} \times 9.4\% = 8.43 \text{ wt\%}$$

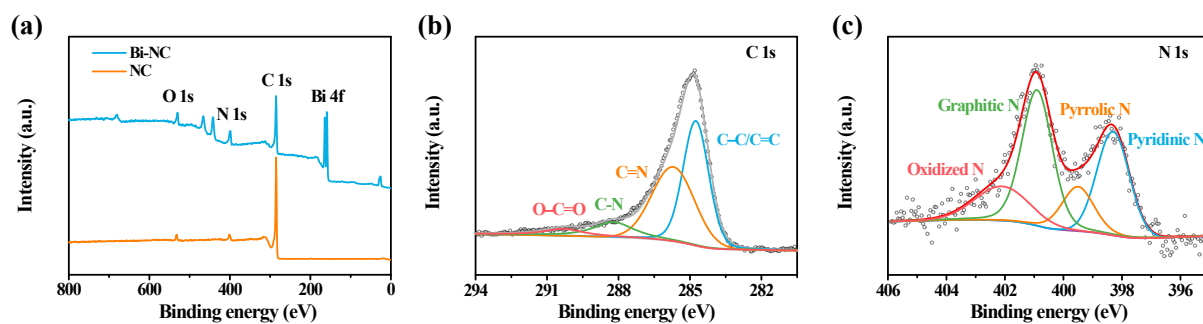


Fig. S7. (a) XPS survey spectra of Bi-NC and NC; (b) C 1s XPS spectrum of Bi-NC; (c) N 1s XPS spectrum of the mixture of commercial Bi nanoparticles and NC showing almost the same peaks as that of NC in 402.1 (oxidized N), 400.9 (graphitic N), 399.5 (pyrrolic N), and 398.3 eV (pyridinic N).

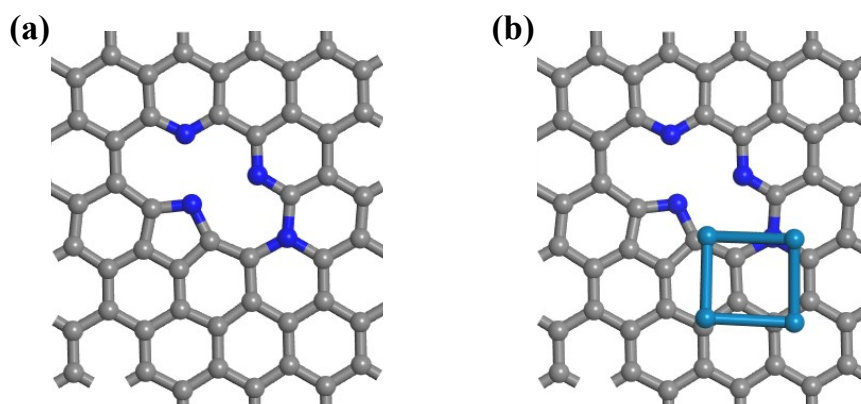


Fig. S8. Optimized geometrical configurations of (a) NC and (b) Bi-NC.

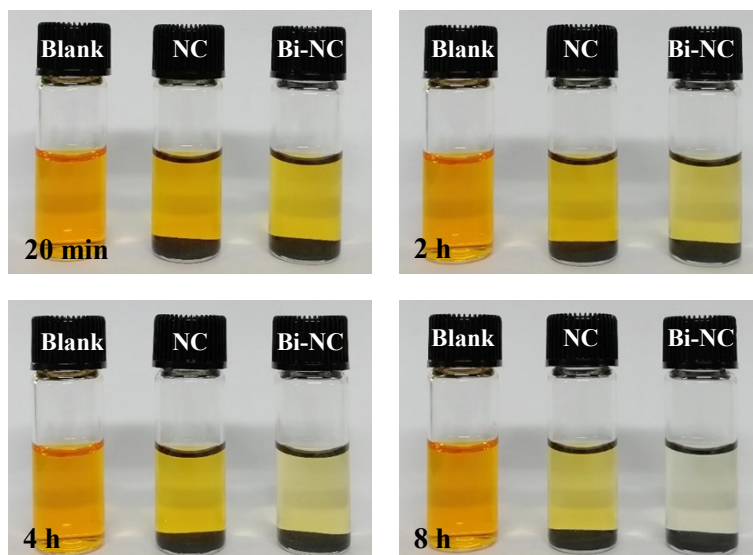


Fig. S9. The digital photographs of Li_2S_6 solution adsorbed by various samples for different times after repetitive shaking and standing.

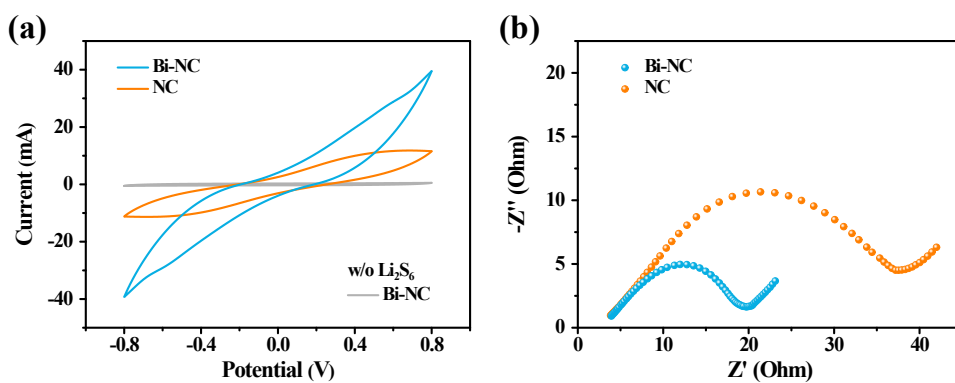


Fig. S10. (a) CV curves at 50 mV s^{-1} and (b) EIS spectra of Li_2S_6 symmetric cells with Bi-NC and NC electrodes.

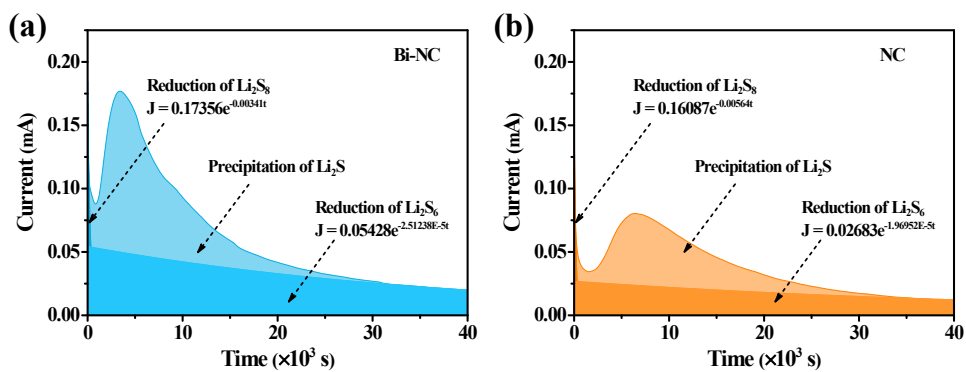


Fig. S11. Fitting of current vs. time for potentiostatic discharge at 2.05 V with (a) Bi-NC and (b) NC electrodes.

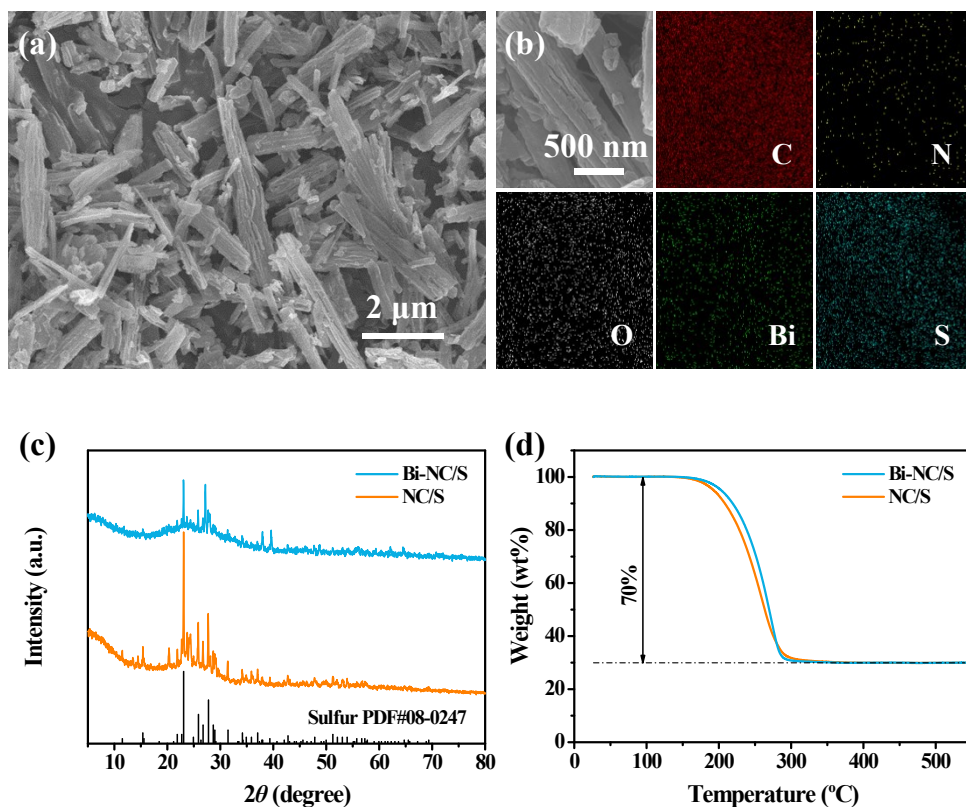


Fig. S12. (a) SEM image and (b) elemental mapping images of Bi-NC/S; (c) XRD patterns and (d) TGA curves of Bi-NC/S and NC/S composites.

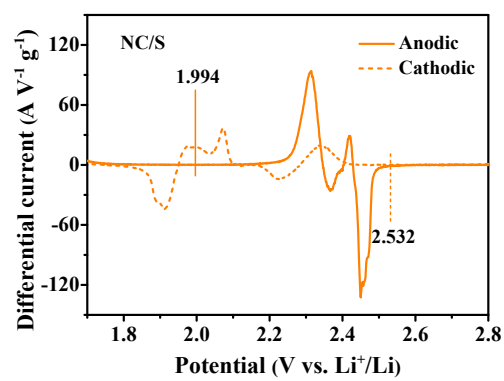


Fig. S13. Differential CV curves of NC/S electrode.

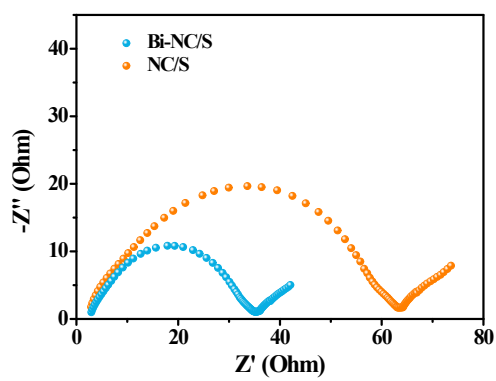


Fig. S14. EIS spectra of Bi-NC/S and NC/S cathodes.

Table S1. The elemental contents of Bi-NC determined by XPS analysis.

Elements	C	N	O	Bi
Content (at.%)	75.45	14.13	7.39	3.03

Table S2. Comparison of electrochemical performances between Bi-NC/S electrode and other sulfur electrodes in reported works.

Sulfur cathodes	Sulfur content	Rate capability	Long cycling stability	Ref.
Bi-NC/S	70 wt%	779 mAh g ⁻¹ at 5 C	811 mAh g ⁻¹ after 500 cycles at 1 C	This work
CNT@TiO _{2-x} -S	70 wt%	399 mAh g ⁻¹ at 5 C	590 mAh g ⁻¹ after 500 cycles at 1 C	1
Co/N-PCNF@S	62 wt%	672 mAh g ⁻¹ at 3 C	728 mAh g ⁻¹ after 200 cycles at 1 C	2
g-C ₃ N ₄ @HPC/S	65 wt%	410 mAh g ⁻¹ at 2 C	757 mAh g ⁻¹ after 250 cycles at 1 C	3
S@NHSC	70 wt%	516 mAh g ⁻¹ at 2 C	598 mAh g ⁻¹ after 500 cycles at 1 C	4
PPy@S/GAVD	65 wt%	409 mAh g ⁻¹ at 5 C	698 mAh g ⁻¹ after 500 cycles at 0.5 C	5
HCS-5-S	66 wt%	301 mAh g ⁻¹ at 2 C	528 mAh g ⁻¹ after 300 cycles at 0.5 C	6
BOC@CNT/S	69 wt%	636 mAh g ⁻¹ at 5 C	794 mAh g ⁻¹ after 500 cycles at 1 C	7
CMK-3/S-Te-1	63 wt%	646 mAh g ⁻¹ at 1.5 C	727 mAh g ⁻¹ after 200 cycles at 0.2 C	8
S/(T-PPy)@SnO ₂	65 wt%	384 mAh g ⁻¹ at 5 C	543 mAh g ⁻¹ after 500 cycles at 1 C	9
S/ZCCDN	70 wt%	548 mAh g ⁻¹ at 2 C	739 mAh g ⁻¹ after 500 cycles at 0.5 C	10

References

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