

Supporting Information

Vastly Restraining Polysulfide Shuttle by Designing a Dual Adsorption Structure of Bismuth Encapsulated into Carbon Nanotubes Cavity

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Experimental section

Preparation of PNTs and SPNTs

The chemical reagents are commercial analytical reagents without further purification in this work. PNTs and SPNTs are referred to the previously reported literatures.^{1, 2}

Synthesis of the cowpea-like CNTs@Bi composites

The cowpea-like CNTs@Bi composites were prepared by a facial method. The bismuth neodecanoate (1.0 g) and SPNTs (100 mg) were added in 10 mL ethanol, then the suspension was mechanically stirred for 10 h at room temperature. After centrifugation, the residual liquid was wiped off with a napkin. After drying at 80 °C for 12 h, the CNTs@Bi composites were obtained by calcining at 550, 650, 750 and 850 °C.

Based on calcination temperatures (550, 650, 750 and 850 °C), the products are noted as BNT1, BNT2, BNT3 and BNT4, respectively.

Synthesis of the CNTs@Bi/S composites with encapsulated structure

BNT3 (50mg) was dispersed in deionized water (10mL) containing ethanediamine (120uL) and stirring for 6h at 75°C. Then, the suspension was added in 50 mL deionized water with Na₂S₂O₃ (1.5g), and after ultrasonication for 1.5h, the concentrated hydrochloric acid (2mL, 12M) was added in the mixture solution. After 1h, the precursor was attained by suction filtration, washing with distilled water, and drying at 60 °C for 12h. Finally, the CNTs@Bi/S composite was harvested by fusing and infiltrating at 155 °C (1 °C min⁻¹) for 12 h in N₂ in a sealed container, and the samples were marked as BNTS3. Meanwhile, the samples obtained by using BNT2 and BNT4 as sulfur hosts were marked as BNTS2 and BNTS4, respectively.

Adsorption tests

To understand the adsorption experiment of LIPs, on the one hand, the cathode material after cycling 200 cycles at 1C was disassembled in the glove box filled with N₂, and the pole pieces are placed in a bottle containing the electrolyte. On the other hand, S and Li₂S (5:1 by molar ratio) were mixed and stirred in 1,3-dioxolane (DOL)/dimethoxymethane (DME) (1 : 1 in volume) for 48h in the glove box filled with N₂, resulting in the formation of the brownish yellow Li₂S₆ solution (0.1 M). Then, 15 mg BNT3 was added into the above Li₂S₆ solution (2 mL).

Materials characterization

Powder X-ray diffraction (XRD) patterns were provided by Bruker D8 using filtered Cu K α radiation. The morphologies of samples were characterized by a field emission scanning electron microscope (FESEM Hitachi S-4800), and the detailed structure information and composition were studied by high resolution transmission electron microscope (HRTEM JEM 2100). Thermogravimetric analysis (TGA) of carbon component was conducted on Netzsch STA 449C instrument in air at a heating rate of 10 °C min⁻¹ from 30 to 850 °C, and thermogravimetric analysis (TGA) of sulfur component was tested on Japan – Hitachi STA7300 instrument in N₂ at a heating rate of 10 °C min⁻¹ from 30 to 600 °C.

Electrochemical characterization

The anodes for LIBs were prepared by mixing as-synthesized active materials (70 wt%), conductive carbon black (super P, 20 wt%) and polyvinylidene fluoride (PVDF, 10 wt%) in a solution of N-methyl-2-pyrrolidone (NMP) to form a slurry. Then the mixture was uniformly pasted onto a Cu foil, and then dried at 110 °C for 12 h under vacuum. The cathodes for Li-S batteries were fabricated by mixing 80 wt% active material, 10 wt% carbon black (acetylene black), and 10 wt% polyvinylidene difluoride in N-methyl-2-pyrrolidone forming a homogeneous slurry. Afterwards, the obtained slurry was coated onto a carbon-coated Al foil, and dried at 60 °C for 12 h under vacuum. Li foil was used as the counter electrodes of LIBs and Li-S batteries, and the separator was Celgard 2400 membrane. In an Ar-filled glovebox, LIBs were assembled by using LiPF₆ (1 M) in ethylene carbonate/diethyl carbonate (EC/DEC, 1 : 1 vol) as the electrolyte.

Under the same conditions, the Li-S batteries were fabricated using a 1.0 M solution of LiTFSI in 1,3-dioxalane (DOL)/ dimethylether (DME) (1:1 by volume) with 2 wt% LiNO₃ as the electrolyte. The cell tests were carried out in the voltage window of 0.01–3.0 V (LIBs) and 1.7–2.8 V (Li–S batteries) by using a Land CT2001A battery testing instrument. Cyclic voltammetry (CV) curves were tested by CHI1040c electrochemical workstations.

The formation mechanism of Bi and chemical reaction route during the calcination

According to reported literature, the Bi³⁺ species will be transformed into bismuth oxide at about 350 °C in the N₂ atmosphere and subsequently began to reduce into liquid metallic Bi above 400 °C.³ In addition, the TG curves of the polymer nanotubes (SPNTs) and precursor consisted of bismuth neodecanoate and SPNTs were tested in N₂ atmosphere and shown in Fig. 1. The mass loss from 28 to 120 °C is attributed to the evaporation of adsorptive water. The pyrolysis of the polymer is located from 120 to 430 °C and the carbonation process is placed from 430 to 530 °C. Meanwhile, Bi³⁺ combines with oxygen to form bismuth oxide following the principle of proximity in the heating process. Subsequently, with the formation of carbon above 430 °C, Bi³⁺ can be reduced Bi by carbon shown in equation 1.

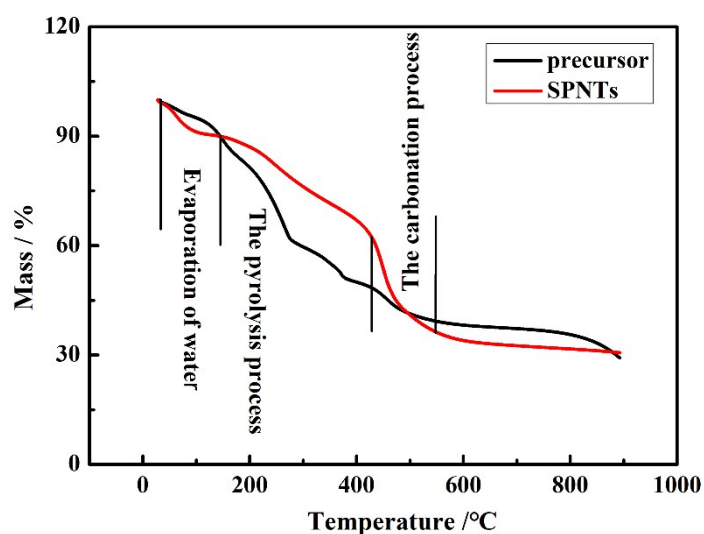
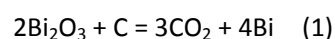


Fig. S1 TG curves of SPNTs and the precursor

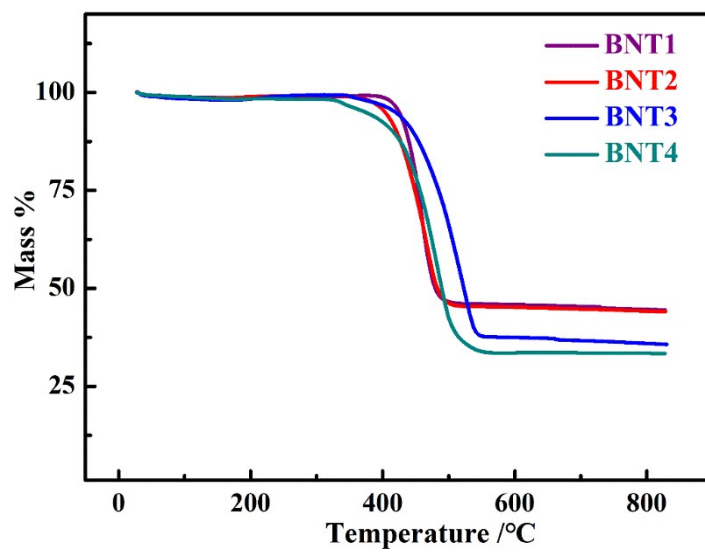


Fig. S2 TGA curves of BNT1, BNT2, BNT3 and BNT4 in air.

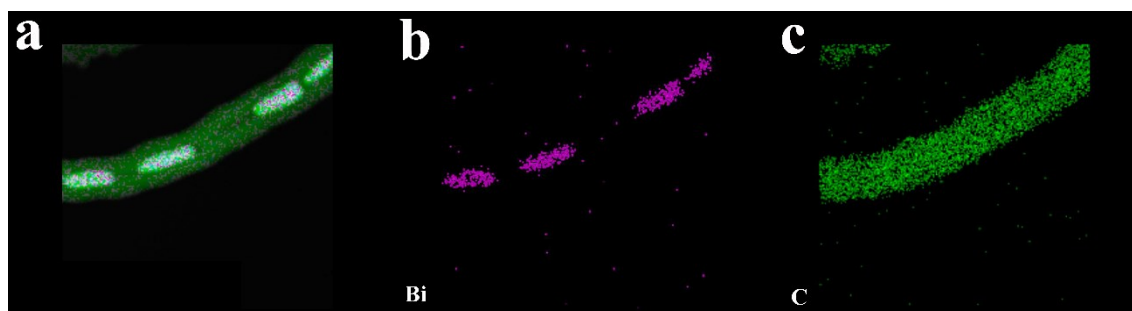


Fig. S3 EDS-elemental mapping images of BNT3.

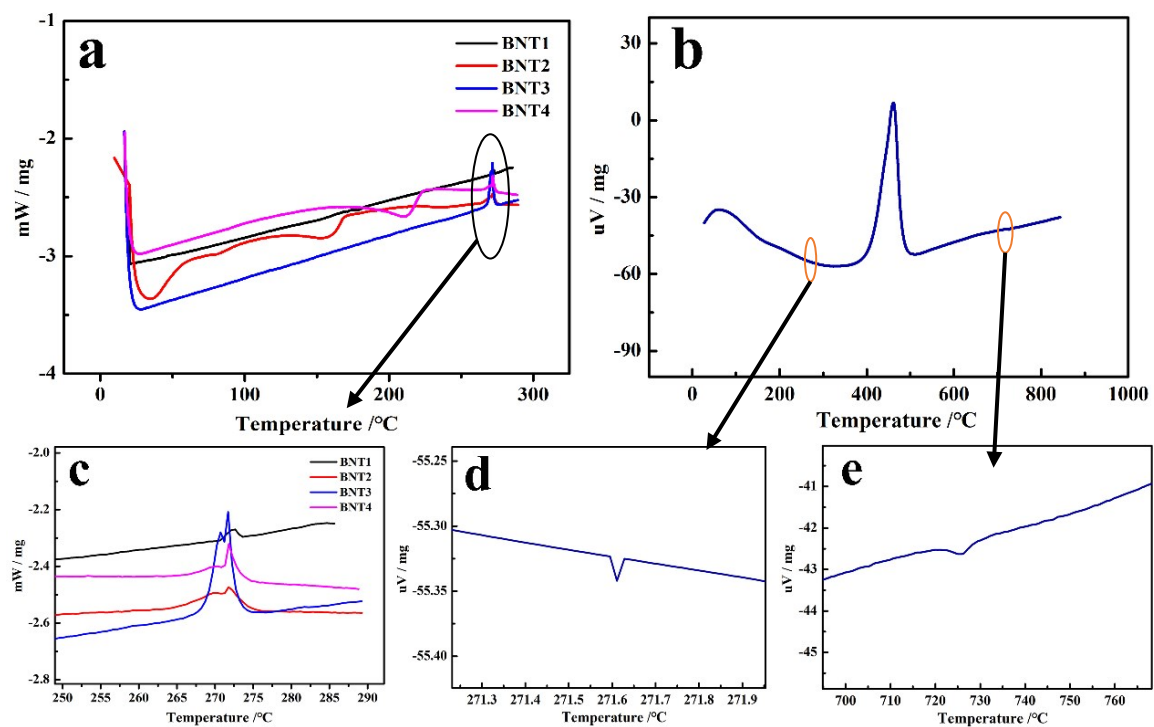


Fig. S4 The DSC curves of BNT1, BNT2, BNT3 and BNT4 (a) and their amplified image (c), the DTA curve of BNT1 (b) and its amplified image (d and e).

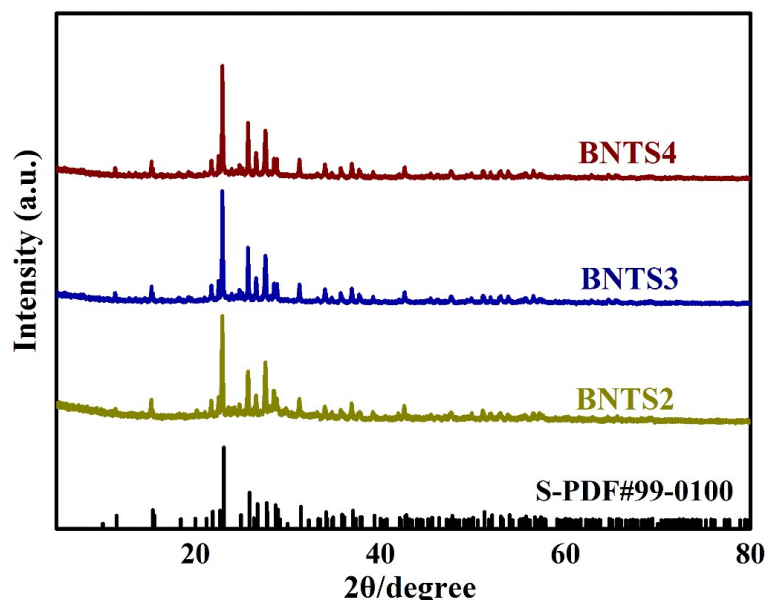


Fig. S5 XRD patterns of BNTS2, BNTS3 and BNTS4.

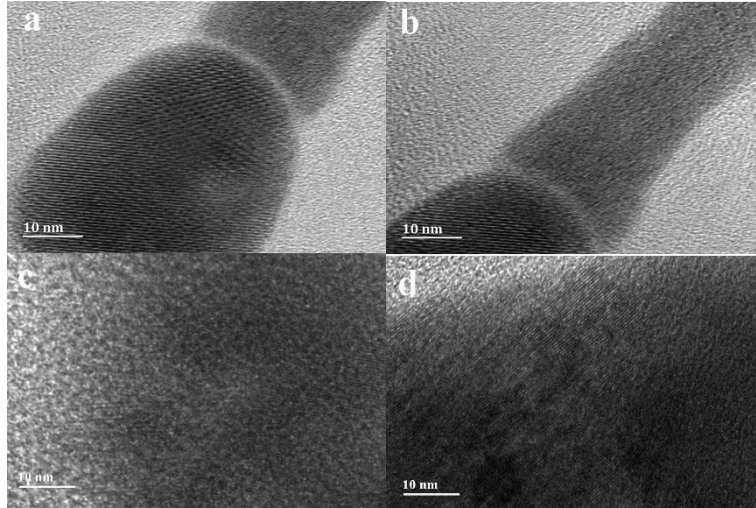


Fig. S6 HRTEM images of BNTS2 (a, b), BNTS3(c) and BNTS4(d).

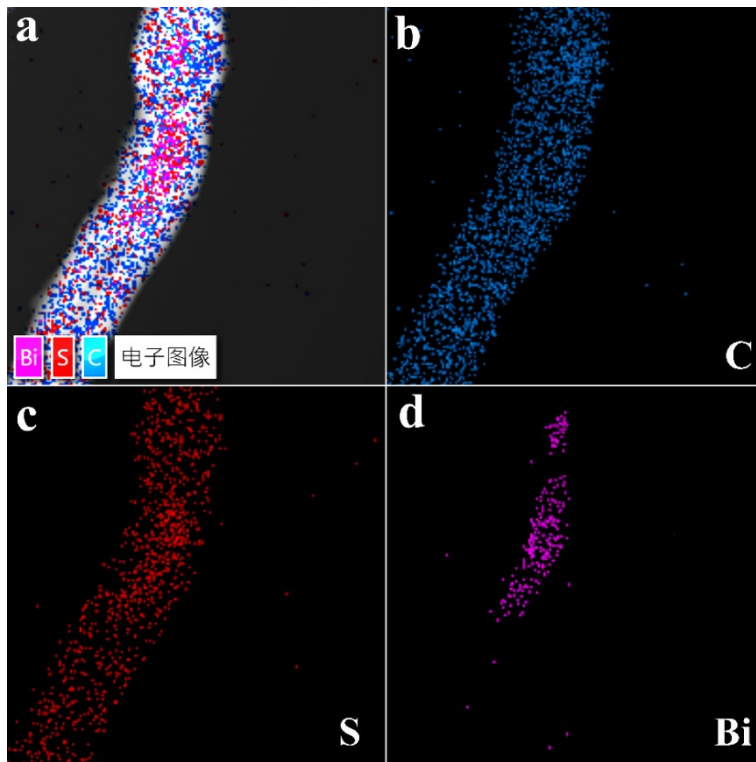


Fig. S7 EDS-elemental mapping images of BNTS3.

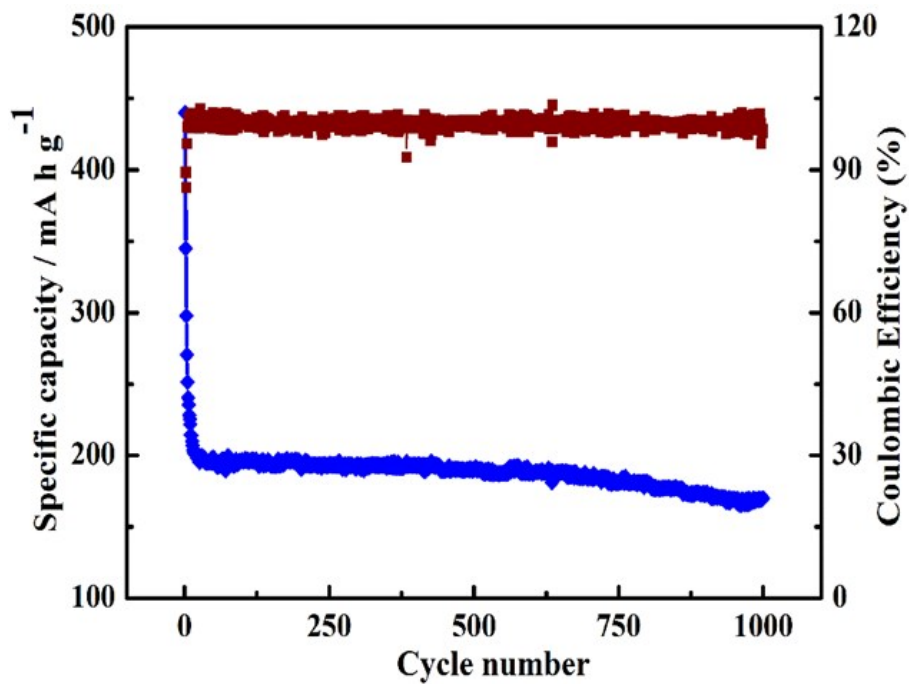


Fig. S8 Cycle performance of BNT3 over 0.01-3.0 V at 5 A g⁻¹

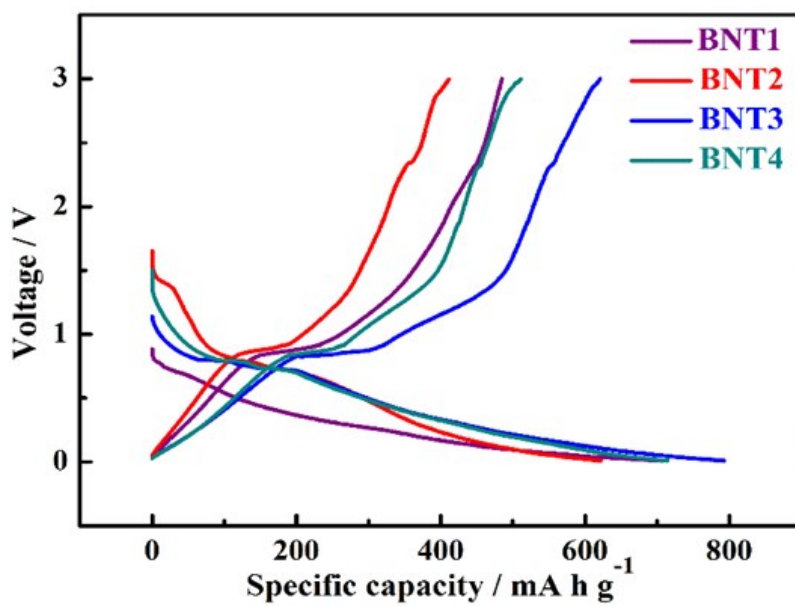


Fig. S9 First cycle charge-discharge profiles of BNT1, BNT2, BNT3 and BNT4 over the voltage range of 0.01-3.0 V at 0.1 A g⁻¹.

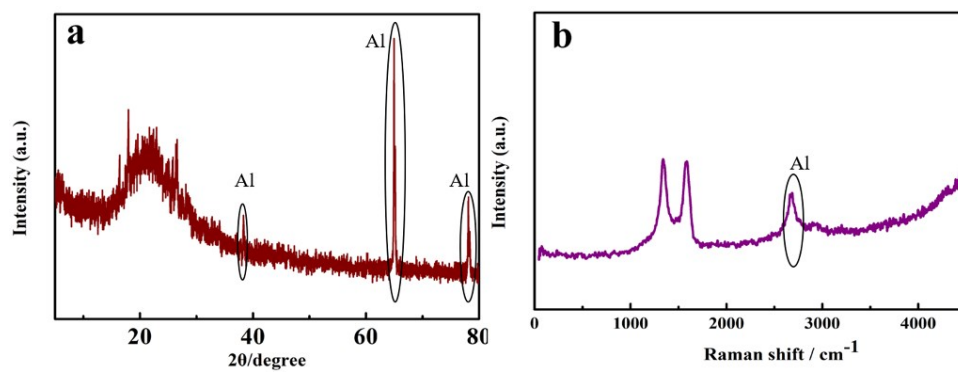


Fig. S10 XRD pattern(a) and Raman(b) of BNTS3 after 500 cycles at 2C

References

1. Y. Tang, L. Liu, X. Wang, H. Zhou and D. Jia, *RSC Adv.*, 2014, **4**, 44852-44857.
2. F. Murgia, L. Monconduit, L. Stievano and R. Berthelot, *Electrochim. Acta*, 2016, **209**, 730-736.
3. H. Yuan, Y. Jin, X. Chen, J. Lan, Y. Yu and X. Yang, *ACS Sustainable Chem. Eng.*, 2019, **7**, 6033-6042.