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Supporting Information

Shuttle Confinement of Lithium Polysulfides in Borocarbonitride

Nanotubes with Enhanced Performance for Lithium–Sulfur Batteries

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Experimental Section

Preparation of BCN nanotubes (BCNNTs): All chemicals were analytic grade and used without any purification. For the synthesis of BCNNTs, urea (5.5 g), PEG-2000 (1.0 g), and boric acid (0.15 g) were dissolved in 100 mL water under stirring. After stirring, the precursor materials were obtained by dried at 100 °C for 24 h. In order to get the BCNNTs materials, the dried precursor materials were then heated to 900 °C for 4 h in Ar atmosphere.

Preparation of BCNNTs/S : The BCNNTs/S composites were prepared using a conventional melt–infiltration method. In a typical procedure, BCNNTs and sulfur BCNNTs and sulfur are mixed in a ratio of 3:7. The mixture was heated at 155 °C for 12 h in Ar atmosphere. The product was collected after cooling to room temperature to generate the BCNNTs/S composites. The sulfur content of ~64 wt% was determined by TGA measurements.

Adsorption test of lithium polysulfides: The BCNNTs materials were dried under vacuum at 60 °C overnight before the adsorption test. Li_2S_6 was prepared by the chemical reaction of sulfur and Li_2S at a molar ratio of 5:1 in the DOL/DME solution (1:1 by volume). The solution was stirred under Ar atmosphere at 50 °C for 24 h to produce Li_2S_6 solution. The BCNNTs materials (10 mg) were then added into the Li_2S_6 solution (5 mL) for the lithium polysulfides adsorption test.

Materials Characterization

The morphology and microstructure of the samples were characterized by scanning electron microscope (SEM, Hitachi S-4800). Energy-dispersive spectroscopy (EDS)

elemental scans were performed on the same instrument equipped with detector (7593-H, Horiba). Transmission electron microscopy (TEM) and corresponding high resolution images were obtained using a Philips Tecnai 20U-Twin microscope at an acceleration voltage of 200 kV. X-ray diffraction (XRD) spectra were collected by a Bruker diffractometer (D8 Advance) with Cu K α radiation, $\lambda = 1.5418$ Å. Thermogravimetric analysis (TGA) was performed on Perkin-Elmer, TG7, under N₂ flow with heating rate of 5 °C min⁻¹. The room-temperature Raman spectra were measured with 532 nm photons from an Ar⁺ laser (Horiba Jobin Yvon). The surface area was determined by Brunauer-Emmett-Teller (BET) measurements with an ASAP 2020 sorptometer. X-ray photoelectron spectra (XPS) were acquired on the Thermo ESCALAB 250 with Al K α radiation (1486.8 eV) as the excitation source.

Electrochemical measurements

The electrochemical performances of the samples were investigated in CR2032-type coin cells, which were assembled in an argon-filled glove box (Mikrouna, Super 1220/750/900). The working electrodes were made of active material (80 wt %, BCNNTs/S or pure sulfur), conducting carbon (10 wt %) and polyvinylidene fluoride (PVDF) binder (10 wt %). These materials were mixed in N-Methyl pyrrolidone (NMP) and pasted on aluminum foil. The as-prepared electrodes were dried at 60 °C for 24 h in vacuum. The mass loadings of sulfur in the electrodes are 1.2, 3.1, 5.3 mg cm⁻¹ with a diameter of 12 mm. For regular cells, lithium metal was used as the anode, Celgard 2400 as the separator, 1.0 M LiTFSI with 2 wt% LiNO₃ in DOL/DME (1:1, by volume) as the electrolyte. The cycling and rate performances (0.2 C–5 C, 1 C = 1672 mAh g⁻¹)

were recorded on a NEWARE battery measurement system with a cut-off voltage of 1.6–2.8 V (vs. Li/Li⁺) at room temperature. The gravimetric capacity was counted by sulfur. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using a CHI660D electrochemical workstation (Shanghai CH Instruments Co., China). CV curves were recorded in 1.6–2.8 V (vs. Li/Li⁺) at different scan rates. EIS were tested at the frequency ranging from 0.01 Hz to 100 kHz. For comparison, the cells of BCNNTs (without sulfur loading) were also prepared and tested by the same procedures.

First-Principles Calculations.

The present calculations employed the Vienna ab initio Simulation Package $(VASP)^{1,2}$ implementation of density functional theory (DFT) in conjunction with the projector-augmented-wave (PAW) formalism³. Thus the B $2s^22p^1$, C $2s^22p^2$ and N $2s^22p^3$ were treated as valence electrons. The exchange correlation potential was described by the Perdew-Burke-Ernzerhof (PBE) form within the generalized gradient approximation (GGA) functional ⁴. The kinetic cutoff for plane-waves was set to 400 eV, total energy and force on each atom convergence criterion were set to be 10^{-4} eV and 0.05 eV/Å, respectively. For structural optimizations and charge density calculations, the Monkhorst-Pack scheme *k*-point grids were $2\times 2\times 1$ and $1\times 1\times 1$, respectively.

The stability of Li_2S_4 and Li_2S_6 adsorption geometries were evaluated using the adsorption energy (E_{ads}), which is defined as:

$$E_{\text{ads}} = E_{\text{tot}} - E_{\text{substrate}} - E_{\text{Li}_2\text{S}_4/\text{Li}_2\text{S}_6}$$

where E_{tot} and $E_{\text{substrate}}$ are the total energies of BCN substrate with and without Li₂S₄ and Li₂S₆. $E_{\text{Li}_2\text{S}_4/\text{Li}_2\text{S}_6}$ is the energy of a Li₂S₄ or Li₂S₆ molecule. Hence, a negative value of E_{ads} represents an exothermic process and stable adsorption.

RESULTS



Fig. S1. EDX spectrum and corresponding element mapping images of BCNNTs.



Fig. S2. EDX spectrum and corresponding element mapping images of BCNNTs/S.



Fig. S3. CV curves of BCNNTs/S electrode in the first three cycles at 0.1 mV s⁻¹.



Fig. S4. Electrochemical performance of BCNNTs (without sulfur loading) electrodes

at 1.6–2.8 V.



Fig. S5. (a) SEM and (b) TEM images of BCNNTs/S after cycling.



Fig. S6. CV curves of the pure sulfur electrode at varied scan rates $(0.1-1.0 \text{ mV s}^{-1})$.



Fig. S7. XPS survey spectra of the as-prepared BCNNTs.



Fig. S8. XPS survey spectra (a) and S 2p (b) of BCNNTs/S.



Fig. S9. XPS survey spectra (a), Li 1s (b) and S 2p (c) of the BCNNTs/S electrode after

the first discharge.



Fig. S10. Schematic structure model of the pristine graphene and BCNNTs.

Electrode	$R_{e}\left(\Omega ight)$	$R_{ct}\left(\Omega ight)$
Pure S	4.7	94.8
BCNNTs/S	1.9	43.4
BCNNTs	1.1	25.8

 Table S1 Impedance parameters calculated according to the equivalent circuits

Table S2. The electrochemical performance of BCNNTs/S in this work compared

with other carbon-based hosts for Li-S batteries. (1 C = 1672 mA g^{-1}).

	Electrochemical performance					High-loading performance		
Sulfur host	Sulfur loading (mg cm ⁻²)	Current density (C)/ cycles (n)	Capacity (mAh g ⁻¹)/ average decay rate	Current density (C)/ cycles (n)	Capacity (mAh g ⁻¹)/ average decay rate	Sulfur loading (mg cm ⁻²)	Capacity (mAh g ⁻¹)/ cycles	Ref.
Borocarbonitride nanotubes	1.2	0.2/200	852.5/0.15%	1.0/1000	619.6/0.041%	5.3	643.4/100	This work
N,B rich carbon layer	0.9-1.2	0.2/200	783.8/0.18%	1.0/250	588/0.08%	1.7	390/200	5
B,O co-doped multi- walled carbon nanotubes	0.69-1.15	0.06/100	937/0.34%	1.1/10	221	-	-	6
Nitrogen-doped carbon	0.8-1.0	0.18/180	706/0.21%	0.5/400	511/0.11%	3	529/180	7
3D boron-doped graphene aerogel	0.135-	0.2/200	810/0.19%	2.0/200	601/0.16%	-	-	8
N, B co-doped graphene nanoribbons	2.0	0.2/300	740/0.08%	1.0/10	750	-	-	9
B-doped porous carbon	-	0.25/80	900/0.38%	1.0/10	800	-	-	10
B-doped porous carbon	1.5	0.1/100	703/0.12%	0.5/100	500/0.23%			11
B-doped porous carbon spheres/graphene	1.0	0.2/80	694/0.16%	0.5/500	577/0.05%	-	-	12
B-doped microporous carbon	1.0	0.2/20	700	2.0/500	561.8/0.056%	-	-	13
Core-shell carbon fibers	-	0.2/5	1200	0.5/300	660/0.12%	-	-	14
Hollow Nitrogen- Doped Carbon Nanospheres	1.2	0.2/5	1173	1.0/800	600/0.045%	3.6	540/150	15
Double-shelled nanocages	3.0	0.1/100	653/0.36%	0.5/100	491/0.34%	-	-	16
Hierarchical Carbon Nanotubes	0.8-1.0	0.3/100	618.5/0.23%	1.0/150	558/0.13%	-	-	17
Porphyrin-Derived Graphene-Based Nanosheets	1.0	0.5/300	798/0.1%	1.0/1000	613/0.042%	5.7	796/250	18

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