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Supporting Information

High Performance Sulfur-doped Disordered Carbon Anode for Sodium Ion Batteries

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Experiment section

Preparation of DC-S and DC: All the sources of reagent were used without further purification. The sulfur doped carbon was synthesized by the following synthetic route. In a typical procedure, 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTCDA, 98%, Sahn Chemical Technology Co.,Ltd, China)and sulfur(99.9%,Sinopharm Chemical Reagent Co.,Ltd ,China)with the mass ratio of 1:1 were mixed thoroughly, followed by annealing at 500 ^{o}C for 4 hours in the atmosphere of Ar with a heating ramp of 2 ^{o}C min^{-1}, and the obtained sample was designated as DC-S. For comparison, NTCDA was directly annealed at 500 ^{o}C by the same method without sulfur, and the sample was designated as DC.

Materials characterization: The structure of obtained samples were determined by X-ray diffraction (XRD) using a PANalytical Multi-Purpose Diffractometer equipped a Cu K_{α} Radiation (λ=1.5406Å). Fourier transformed infrared (FTIR) spectra were recorded on a Bruker VERTEX 70 FTIR spectrometer. Raman spectra were collected on a Renishaw Invia spectrometer using Ar^{+} laser of 514.5 nm at room temperature. The elemental analysis measurements were carried out to collect the composition of the products with a Vario Micro cube elemental analyzer (EA). X-ray photoelectron spectroscopy (XPS) was carried out on an Axis Ultra DLD system (UK) with a monochromatic Al K_α X-ray source. The nitrogen adsorption and desorption isotherms were collected at 77 K using a Micromeritics ASAP 2020 analyzer and the apparent surface areas were calculated using the BET method. The pore size distributions (PSD) were determined by means of the Quench Solid State Density Functional Theory (QSDFT) method for nitrogen. The morphology of the products were characterized using field-emission scanning electron microscopy(FESEM, FEI, Sirion 200) coupled with an energy- dispersive X-ray (EDX, Oxford Instrument) spectrometer. Transmission electron microscopy (TEM) observations were carried out on a Tecnai G2 F30S-Twin microscope coupled with an EDX spectrometer. The electronic conductivity was measured based on the I-V curve of compressed pellets (diameter, 10 mm; mass, 0.2 g) with a thickness of 2.61 and 2.36 mm for DC-S and DC under the pressure of 18 MPa using electrochemistry workstation (Autolab, PGSTAT302N), respectively,

Electrochemical measurements: The working electrode was fabricated by mixing the as-obtained products with acetylene black and polyvinylidene difluoride (PVDF) in N-methyl-2-pyrrolidine (NMP) in a mass ratio of 70 : 20 : 10. The obtained slurry was pressed onto a copper foil, dried at 120 ^{o}C in vacuum for 24 h and cut into electrode films (diameter, ~11mm)with a mass loading of 1.0~1.2 mg cm^{-2}. CR2032 coin cells were assembled in an argon-filled glovebox. A sodium foil and Celgard 2400 membrane were used as counter electrode and separator, respectively. The electrolyte was composed of 1 M $NaPF_6$ in a mixture of ethylene carbonate (EC) and diethylcarbonate (DEC) (EC:DEC, 1:1 in volume) with the addition of 5 wt% fluoroethylene carbonate (FEC). Cyclic voltammogram (CV) measurements were performed on an electrochemistry workstation (Autolab, PGSTAT302N) at a scan rate of 0.1 mV s^{-1} at room temperature. Electrochemical impedance spectra (EIS) were also collected on an electrochemistry workstation (Autolab, PGSTAT302N) with the frequency rang form 100 KHz to 0.1 Hz. The galvanostatic charge/discharge tests with a cutoff voltage of 3.0-0.01 V (vs. Na^+/Na) at room temperature were measured with a Neware battery test system (Shenzhen, China).

1 Thermal analysis of the mixture of NTCDA and sulfur

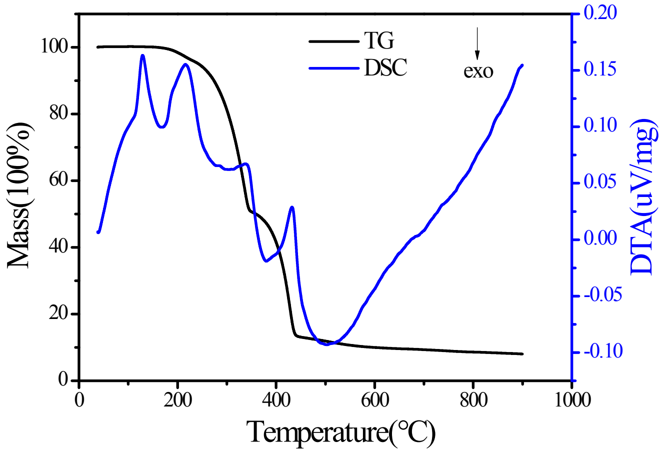

Figure S1 TG and DTA curves of the mixture of NTCDA and sulfur (mass/mass=1/1) in the temperature range of 40-900 ^{o}C with a heating rate of 10 ^{o}C min^{-1}in the Ar atmosphere.

In the TG curve, the mass change of mixture begins at 180 ^{o}C, and exhibits two significant mass loss in the temperature range of 250-340 ^{o}C and 380-420 ^{o}C. In the DTA curve, two endothermic peaks at 120 ^{o}C and 220 ^{o}C are owing to the melt of sulfur and the evaporation of moixure. Another endothermic peak at 340 ^{o}C can be attributed to the reaction between sulfur and pyrolyzed carbon. The peak at 440 ^{o}C is attributed to the boiling of molten sulfur. Based on the above analysis, the sulfurization temperature between sulfur and NTCDA is likely to be about 340 ^{o}C

2. **Elemental composition information of the NTCDA, DC and DC-S**

Table S1 Elemental composition information of the NTCDA, DC and DC-S

Sample	C(wt%)	H(wt%)	O(wt%)	S(wt%)
NTCDA	62.69	1.49	35.82	-
DC	79.00	2.47	18.53	-
DC-S	62.28	1.61	9.2	26.91

From Table S1, the weight contents of H and O of DC-S are lower than DC, suggesting that sulfur is favorable to dehydrogenation and deoxygenation. The lower content of oxygen-containing functional groups facilitates to reduce the irreversible reactions of sodium with functional groups in the initial charge and discharge process, thus improving the initial coulombic efficiency.[1]

3. Electronic conductivity of the as-prepared DC-S and DC

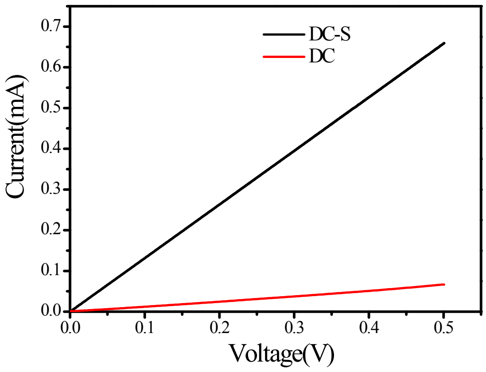

Figure S2 I-V curves of DC-S and DC

Based on the I-V analysis, the electronic conductivity of DC-S and DC is calculated to be 43.2 and 3.91 mS m^{-1}, respectively.

4. Nitrogen adsorption/desorption isotherms and the pore size distribution of the DC-S and DC

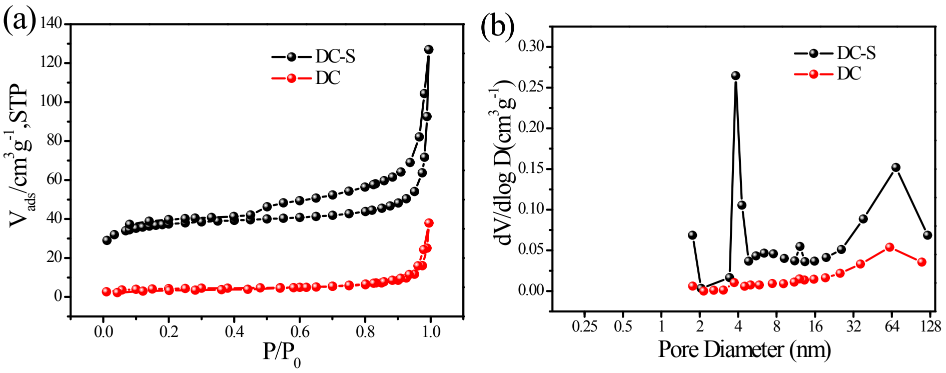

Figure S3. (a) Nitrogen adsorption and desorption isotherms and (b) pore size distribution of DC and DC-S.

Based on the nitrogen adsorption and desorption isotherms, the Brunauer-Emmett-Teller (BET) surface of DC-S and DC is calculated to be 117.3 and 14.8 m^2 g^{-1}, respectively.

5. Ex-situ Raman spectra of the DC-S electrode at fully charged and discharged state

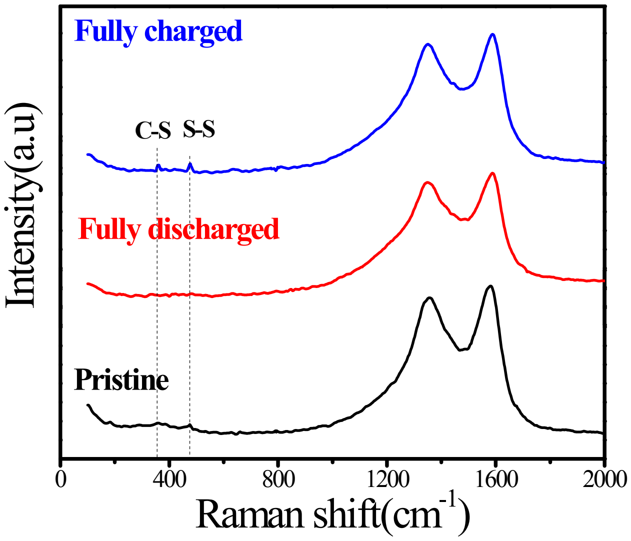

Figure S4. Raman spectra of DC-S electrode at fully discharged (0.01V)and fully charged (3.0 V) state.

6. SEM image of the DC-S electrode before and after cycling

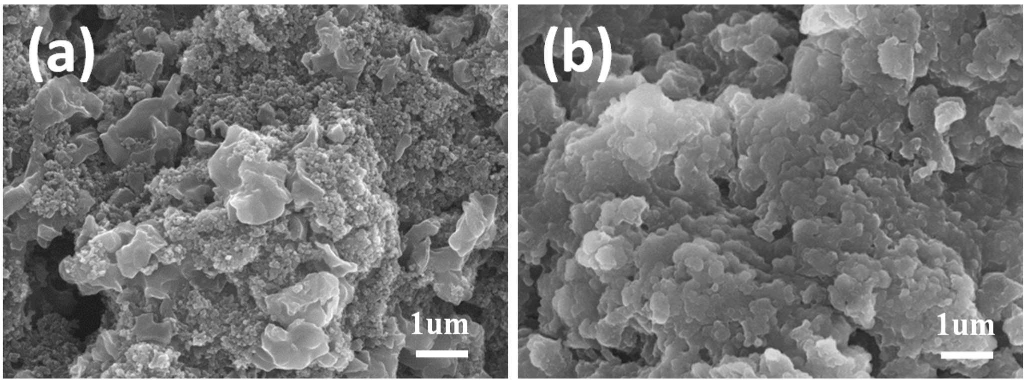

Figure S5 SEM image of DC-S of (a) before and (b) after 1000cycles at 1A g^{-1}

7. Electrochemical performances of the S-doped Carbon with different S contents.

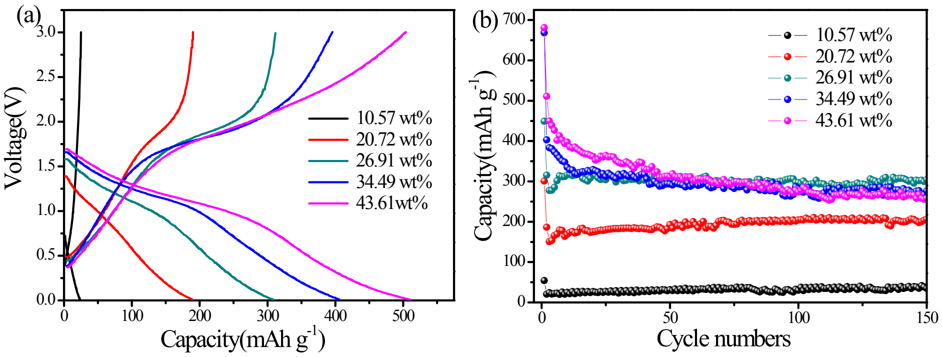

Figure S6 (a) Charge and discharge profiles of 2nd cycle and (b) cycling performances of sulfur doped disordered carbon with different sulfur contents at the current density of 1 A g^{-1}.

The electrochemical performances of the S doped carbon with different sulfur content(10.57, 20.72, 26.91, 34.49 and 43.61 wt%) were further evaluated. As shown in Figure S6, an increase of sulfur content leads to an increase of reversible capacity due to high theoretical capacity of the S electrode. However, there exists a trade-off between the sulfur content and cycling performance, and preservation of the sulfur content of to certain level is crucial for good electrochemical performance. The DC-S with S content of 26.91wt% exhibits an optimal cycling performance.

Reference

1 G. Q. Ning, X. L. Ma, X. Zhu, Y. M. Cao, Y. Z. Sun, C. L. Qi, Z. J. Fan, Y. F. Li, X. Zhang, X.Y. Lan, and J. S. Gao, *ACS Appl. Mater. Interfaces*, **2014**, *6*, 15950-15958.