

## Supporting Information for

# Smaller Sulfur Molecules Promise Better Lithium-Sulfur Batteries

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## Detailed Methods

**Preparation of CNT@MPC.** All the reagents used in the experiment were of analytical grade purity and were used as received. Multi-walled CNTs (40 – 60 nm in diameter and 5 – 15  $\mu\text{m}$  in length, Shenzhen Nanotech Port Co. Ltd.) were firstly refluxed in 6 M  $\text{HNO}_3$  solution for 12 h to remove impurities and to make them more dispersible in water. In a typical synthesis, 20 mg of the pretreated CNTs were ultrasonically dispersed in 10 ml of aqueous solution containing 800 mg of D-glucose (Sinopharm Chemical Reagent Co., Ltd.) and 2 mg of sodium dodecyl sulfate (SDS, Sinopharm Chemical Reagent Co., Ltd.) for 4 h, to form a homogenous black suspension. The suspension was then sealed in a 40 mL autoclave with a Teflon linear and was heated at 190  $^{\circ}\text{C}$  for 15 h to yield a dark brown precursor. After the hydrothermal reaction, a uniform carbon precursor layer was formed on the CNTs. The precursor was collected by centrifugation, washed with de-ionized water for four times, and then dried at 60  $^{\circ}\text{C}$  overnight. The dried precursor was calcined under



argon at 800 °C for 2 h, with a heating rate of 5 °C/min and a flow rate of 50 mL min<sup>-1</sup>, to obtain the CNT@MPC composite (Fig. S2b). From the XRD patterns (Fig. S3), one can see significant weakenings in the intensities of all characteristic peaks of CNTs after carbon coating (curves a1 to a2), and the intensity of D band has surpassed the intensity of G band in the Raman spectra (Fig. S7a, curves b1 to b2), suggesting the amorphous nature of the MPC layer.

**Synthesis of S/(CNT@MPC) and S/CB.** Sulfur (Aldrich, with a purity of >99.995%) and CNT@MPC were thoroughly mixed according to a mass ratio of  $m_S:m_C = 40:60$  in a quartz mortar for 1 h to yield a black mixture. The mixture was then sealed in a glass container and heated at 155 °C. At this temperature, the liquid sulfur has the lowest viscosity, and a substantial ring scission of cyclo-S<sub>8</sub> could take place<sup>1,2</sup>. Therefore, chain-like sulfur molecules could migrate into the carbon micropores. Once the sulfur molecules diffuse into the carbon micropores, they could not go back to S<sub>8</sub> rings due to the space confinement of carbon micropores, but maintain as small S<sub>2-4</sub> molecules. A slow heating rate of 0.5 °C min<sup>-1</sup> above 115 °C (the melting point of sulfur) and a long heating-time of 20 hours was applied to ensure a complete migration of sulfur into CNT@MPC to obtain S/(CNT@MPC)<sup>3</sup>. After heating, there is no bulk sulfur in the mixture (Fig. S2d). S/CB was prepared by mixing sulfur and carbon black with the same sulfur-carbon ratio.

**Structural Characterization.** Elemental analysis was conducted on an elementary analyzer (Flash EA 1112) to obtain the sulfur content in S/(CNT@MPC). XRD measurements were carried out using a Philips PW3710 with filtered Cu K $\alpha$  radiation (Rigaku D/max-2500,  $\lambda = 1.5405$  Å). Raman spectra were obtained using a Digilab FTS3500 (Bio-Rad) with a laser wavelength of 514.5 nm. SEM (6701F, operating at 10 kV), TEM (Tecnai F20), HRTEM (Tecnai F20), and EDX elemental mapping (Tecnai F20) were employed to visualize the morphologies, sizes, structures, and elemental compositions of the products. To observe the existence of sulfur in carbon channels, ABF imaging was performed using a JEOL 2100F (JEOL, Tokyo, Japan) scanning transmission electron microscope (STEM), which was operated at 200 keV with a CEOS hexapole Cs corrector (CEOS GmbH, Heidelberg, Germany) to cope



with the probe forming objective spherical aberration. XPS analysis was conducted on an ESCALab220i-XL electron spectrometer (VG Scientific) using 300W AlK $\alpha$  radiation. The base pressure was about  $3\times 10^{-9}$  mbar, and the binding energies were referenced to C1s line at 284.8 eV from adventitious carbon. The nitrogen absorption and desorption isotherms were obtained at 77.3 K with a Nova 2000e surface area pore size analyzer.

**Theoretical Calculation.** Before the theoretical calculations, XPS measurements were performed to investigate the valences of the elements in S/(CNT@MPC) (Fig. S5). Sulfur and carbon are two main elements of the composite. Besides, there is also some oxygen, which corresponds well with the EDX finding (Fig. S5a). The C1s spectra, the O1 spectra and the S2p spectra have respectively revealed the valance states of 0, -2, and 0 for C, O, and S in S/(CNT@MPC) (Fig. S5b-d). Moreover, the S2p spectra of sulfur do not vary much before and after heating, indicating no significant valance change of sulfur during the sulfur loading process (Fig S5d, e). Since sulfur does not form any bonds with other atoms during the preparation of S/(CNT@MPC), the theoretical calculations are implemented with the covalent radius (the bonding radius) of sulfur (ca. 0.103 nm) as the radius of a sulfur atom<sup>4</sup>.

Theoretical calculations were performed by using the dispersion-corrected density functional theory (DFT-D) provided by the DMol3 code<sup>5-7</sup>. The standard parameter set of Grimme was employed without any parameter optimization. The atomic orbitals were represented by a double-numeric-quality basis set with d-polarization functions (DNP). All of the calculations were all-electron ones and were conducted with an extra-fine mesh. A self-consistent field procedure was used with a convergence criterion of  $10^{-5}$  au on the energy and electron density.

**Electrochemical Measurements.** Electrochemical measurements were performed with Swagelok-type cells assembled in an argon-filled glovebox. For preparing working electrodes, a mixture of active material, super-P acetylene black, and poly-(vinyl difluoride) at a weight ratio of 80:10:10 was pasted on an Al foil. The sulfur cathode had a diameter of 1 mm and an active material load of about 1 mg cm<sup>-2</sup>. Lithium foil was used as the anode. A glyme-based electrolyte and a carbonate-based

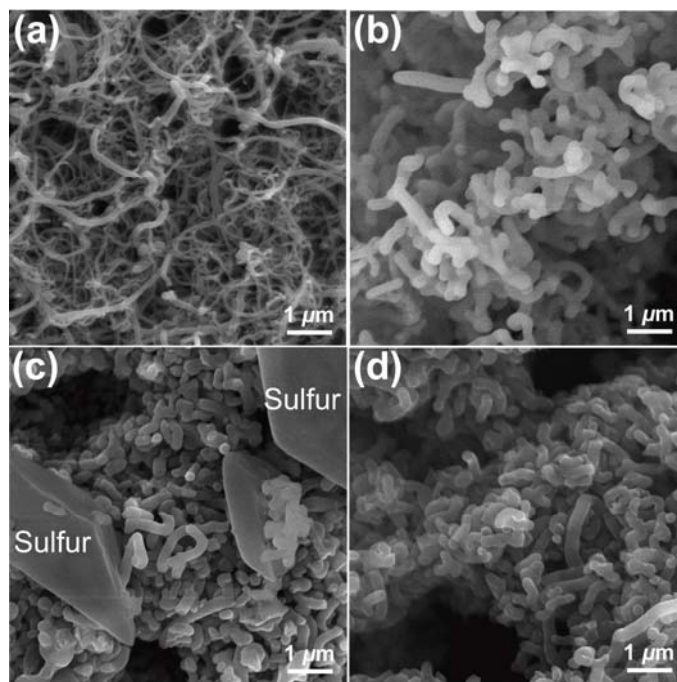


electrolyte were used. A glass fiber (GF/D) from Whatman was used as a separator. Two electrolytes were employed in the electrochemical measurements. A glyme-based electrolyte consisted of 0.5 M lithium bis-(trifluoromethanesulfonyl)-imide in tetra (ethylene glycol) dimethyl ether (Novolyte Technologies) was employed to study the electrochemical behaviors of S/(CNT@MPC) and S/CB, and their abilities in preventing polysulfide dissolution and shuttling. Another carbonate-based electrolyte of 1 M LiPF<sub>6</sub> in ethylene carbonate / dimethyl carbonate (1:1 in wt-%) (Zhangjiagang Guotai Huarong New Chemical Materials Co., Ltd.) was used to investigate the cycling and rate performances of S/(CNT@MPC) and S/CB. GDC cycling of the assembled cells was carried out using an Arbin BT2000 system in the voltage range of 1-3 V (vs Li<sup>+</sup>/Li). CV measurements were performed on an Autolab PG302N with a scan rate of 0.05 mV s<sup>-1</sup> in the potential range of 1-3 V (vs Li<sup>+</sup>/Li).

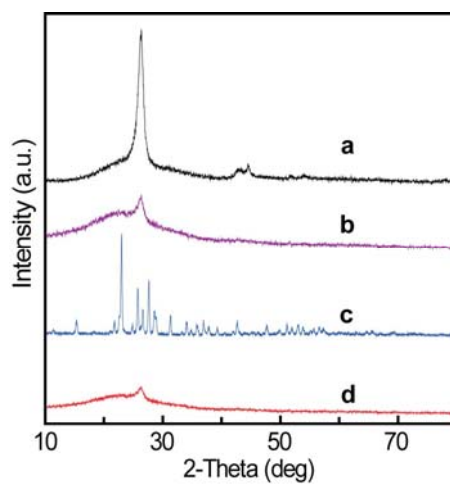


**Figure S1.** Schematic illustration showing the preparation process of S/(CNT@MPC).



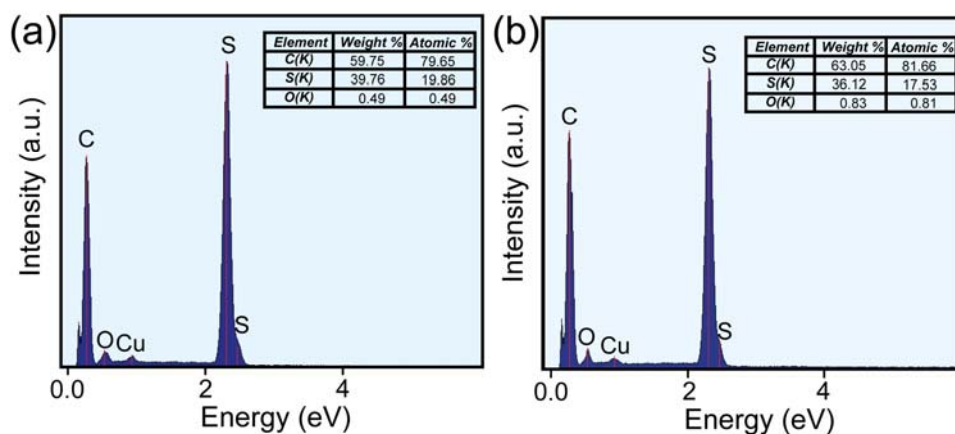


**Figure S2.** SEM images showing the preparation process. (a) CNTs, (b) CNT@MPC, (c) mixture of S and CNT@MPC, and (d) S/(CNT@MPC).

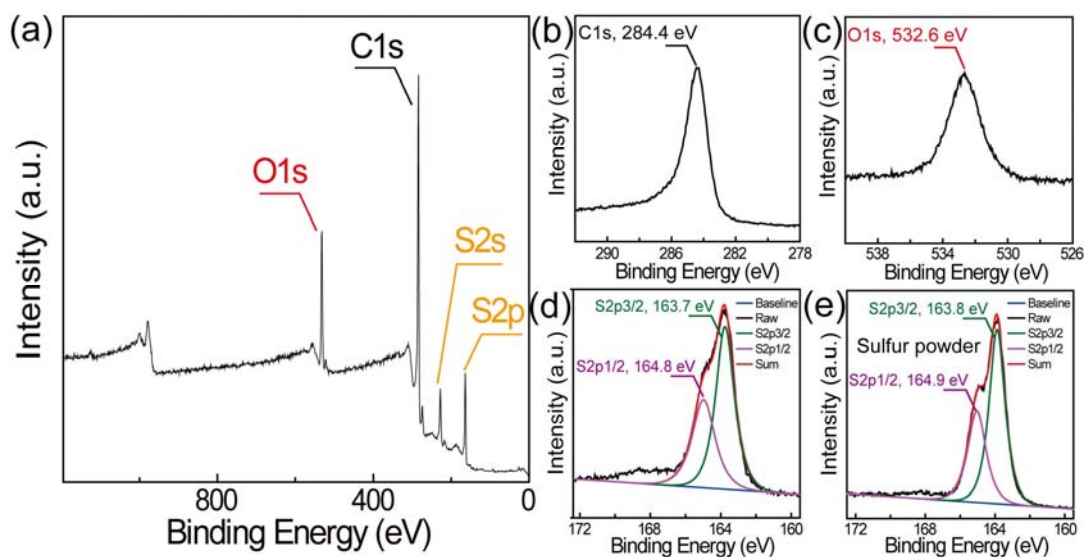


**Figure S3.** XRD characterizations. (a) multi-walled CNTs, (b) CNT@MPC, (c) mixture of S and CNT@MPC, and (d) S/(CNT@MPC).



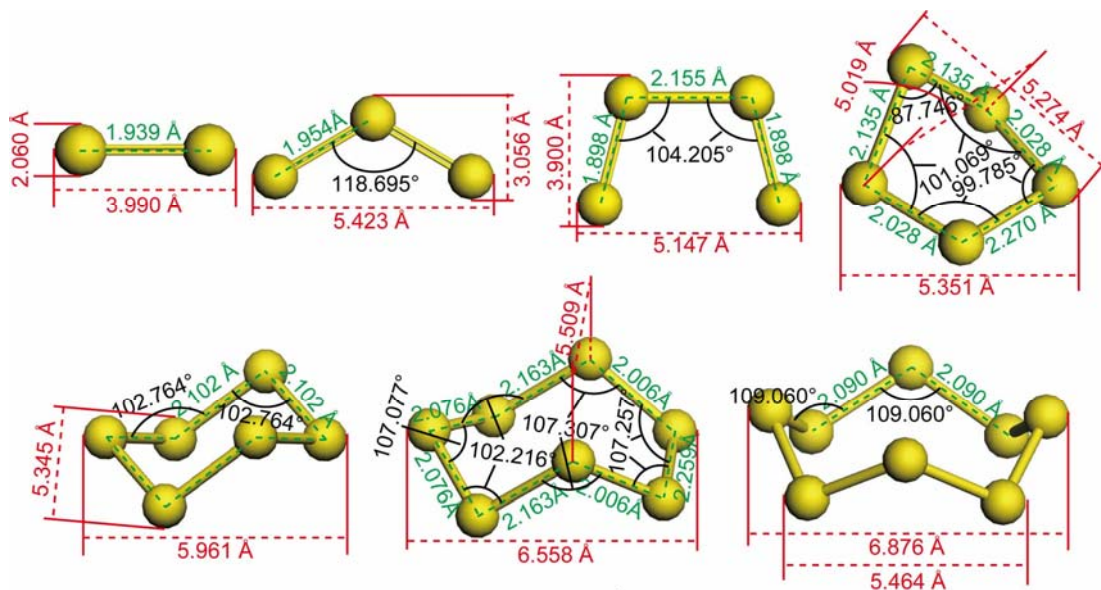


**Figure S4.** EDX patterns of S/(CNT@MPC). (a) before cycling, (b) after 200 cycles at 0.1 C in carbonate-based electrolyte.

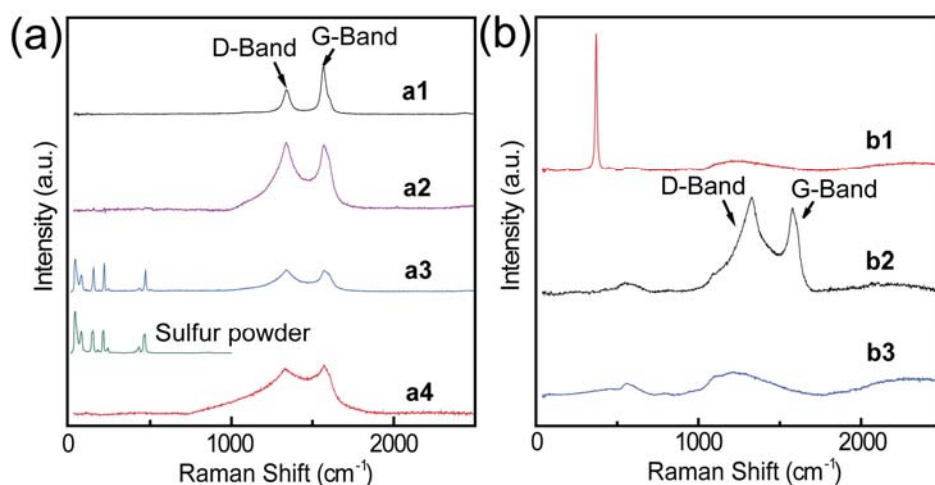


**Figure S5.** XPS spectra of S/(CNT@MPC) and sulfur powder. (a) full spectra, (b) C1s spectra, (c) O1 spectra, and (d) S2p spectra of S/(CNT@MPC). (e) XPS S2p spectra of sulfur powder.



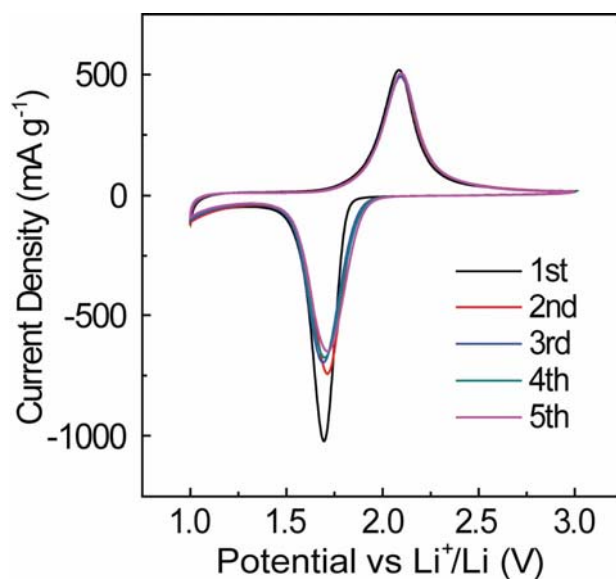


**Figure S6.** Theoretical calculation results of sulfur allotropes from  $S_2$  to  $S_8$ .

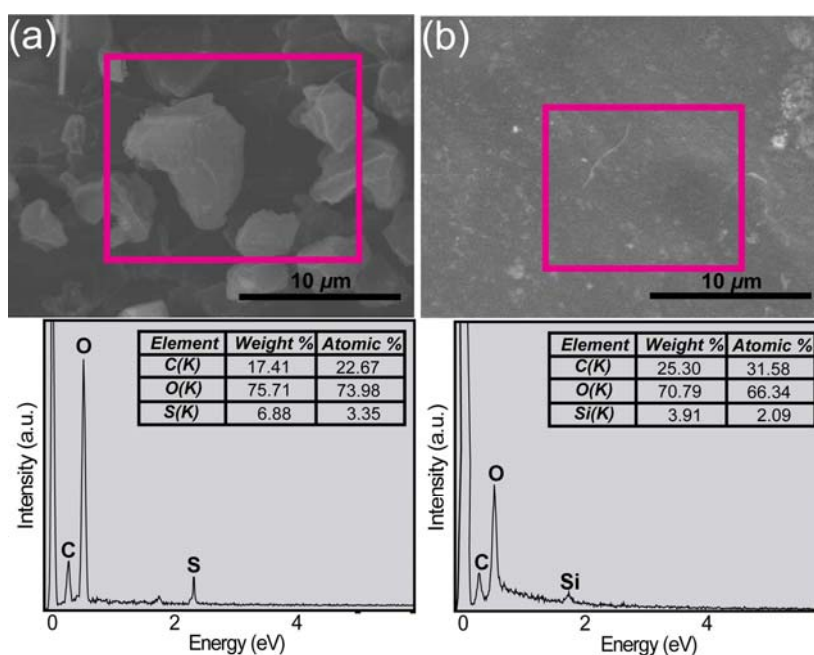


**Figure S7.** Raman characterizations. (a) Raman spectra of a1, multi-walled CNTs, a2, CNT@MPC, a3, mixture of S and CNT@MPC, and a4, S/(CNT@MPC), the green line shows the Raman spectrum of sulfur powder. (b) Raman spectra of b1,  $Li_2S$  powder, b2,  $Li_2S/(CNT@MPC)$  after 1st discharge to 1 V, and b3, glass holder used to seal  $Li_2S$  powder and  $Li_2S/(CNT@MPC)$ .





**Figure S8.** The first five cycling voltammograms of S/(CNT@MPC) obtained in glyme-based electrolyte at  $0.05 \text{ mV s}^{-1}$ .



**Figure S9.** Surface morphologies and corresponding EDX characterization results of lithium anodes cycled in glyme-based electrolyte. (a) after 1 GDC cycle with S/CB cathode, (b) after 50 GDC cycles with S/(CNT@MPC) cathode.



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