

Supporting Information

A general phase transfer strategy to achieve sulfur encapsulated carbon for advanced lithium-sulfur battery

Xuliang Fan, Yangfan Zhang, Jing Li, Kang Yang, Zhongxin Liang, Yaoguang Chen, Cunyuan Zhao, Zishou Zhang*, Kancheng Mai*

Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, Key Laboratory of High Performance Polymer-based Composites of Guangdong Province, Materials Science Institute, School of Chemistry, Sun Yat-sen University. Guangzhou 510275 (China)

E-mail: zhazish@mail.sysu.edu.cn; cesmkc@mail.sysu.edu.cn.

EXPERIMENTAL PROCEDURES

Fabrication of SWNT@S, MWNT@S, and YP80@S. SWNT (Nanjing XFNANO. Materials Tech Co., Ltd) and sulfur particles (Beijing Deke Daojin Science and Technology Co., Ltd.), at a serial of mass ratio of 4:6, 3:7 and 2:8, were added to acetone and dispersed with ultrasonication treatment for approximately 30 min. The resultant homogeneous suspension was poured into a vessel to allow solution to volatilize, thus producing a free-standing SWNT@S film. A SWNT film, MWNT@S (MWNT from NANOCYLTM NC7000 series) film at a mass ratio of 4:6 and YP80@S (YP80 from Kuraray Chemical Co., Ltd) powders at a mass ratio of 3:6 were fabricated following the same procedure. The YP80@S powders were further kept at 200 °C for 2h under argon flow in a tube furnace to remove sulfur aggregation on the surface of YP80.

Material Characterization. The morphology and microstructure were characterized by a field-emission scanning electron microscope (SEM; Hitachi S-4800, Japan) at 10kV, a

transmission electron microscopy (TEM; JEM-2010HR, Japan) at 200kV and a Barrett-Emmett-Teller (BET, ASAP2060) system, respectively. The X-ray diffraction was conducted by a Bruker D8 Advance diffractometer with Cu K α radiation at room temperature. The X-ray photoelectron spectroscopy (XPS) was performed by an ESCALAB 250 instrument. Before mechanical testing, all specimens were kept at 25 °C and 50 % relative humidity for 5 days. Mechanical properties were measured by a Hounsfield THE 10K-S testing machine according to ASTM D 638. Five specimens were tested for all the samples and the average results were recorded. Thermo-gravimetric (TG) analysis was performed on a TG209 F1 instrument with a temperature range of 30-700°C at a heating rate of 10 °C/min in N₂ atmosphere. The conductivity was determined by with a physical property measurement system (ST2253) according to a four-probe method. The repeated bending was achieved in a programmable motorized precision translation stage (NL03STA-150).

Electrochemical Measurements. SWNT@S and MWNT@S films with area of 0.6*0.6 cm² were used as working electrodes. A slurry of YP80@S, conductive black carbon and polyvinylidene fluoride (PVDF) at a mass ratio of 8:1:1 in N-methyl-pyrrolidinone (NMP) was coated on an aluminum foil and dried in vacuum at 60 °C for 24 h. The derived film was cut into 12 mm-diameter rounds for YP80@S working electrodes. The 2032-typed coin cell was assembled with Lithium metals as anode, Celgard 2400 polypropylene membranes as separator, and 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 0.1M LiNO₃ in mixture solution of 1,3-dioxolane and 1,2-dimethoxyethane (DOL/DME, 1:1, v/v) as electrolyte. The

electrolyte was added in the coin cell with 40 μ L/mg (sulfur). For assembly of pouch cell, SWNT@S with area of 2*3 cm² and lithium metal foil were stacked with polypropylene based separator (Celgard 2400), follow by sealed them inside aluminum-lined battery pouch, with 1.0 M LiTFSI and 0.1M LiNO₃ in DOL/DME (1:1, v/v) as electrolyte. All coin cells and pouch cells were assembled in an Ar-filled glove box, where the concentration of the oxygen and water were limited below 0.1 ppm. These cells were held at room temperature for 12h before testing. The rate and cycle performance of electrodes were tested in a Land battery test system (Wuhan Land Electronic Co., China) at the voltage range of 1.7-2.8V. The cyclic voltammetrys (CV), electrochemical impedance spectroscopy (EIS) and linear sweep voltammograms (LSV) were performed in an electrochemical workstation (CHI 760E). The EIS measurements were tested with an amplitude of 5mV and a frequency between 0.01Hz and 100kHz at the open circuit potential.

Computational Details. Density functional theory calculations were carried out using Generalized-Gradient Approximation (GGA) with Dmol3^{1, 2} code of Material studios package. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional³ with long-range dispersion correction (Grimme)⁴ was implemented. The Brillouin zone integration was performed by 1*1*1 Monkhorst-Pack K-points grid⁵ during the geometry relaxation. An all-electron double numerical basis set including polarization function (DNP basis set) was employed. For geometry optimization, the convergence threshold was set to be 1.0 $\times 10^{-5}$ Hartree for energy, 2.0 $\times 10^{-3}$ Hartree $\cdot\text{\AA}^{-1}$ for force, 5.0 $\times 10^{-3}$ $\text{\AA}$ for displacement. To calculate the absorption energy, we set up 1D model

in the supercells, including a single-wall carbon nanotube as substrate, a S₈ molecule as adsorbate and a vacuum region about 15Å to prevent the interaction between each cells. Meanwhile, for S₈ absorption systems, we also set up two independent S₈ molecules in the supercells, including one S₈ molecule as substrate and another S₈ molecule as adsorbate. Two kinds of single-wall CNT, named CNT1(8,8) and CNT2(14,0) with the similar tube diameter (~11Å), was applied in this system. Besides, three different configurations of S₈ interaction were considered. To further study these adsorption behavior, CNT with stone-wales defect were replaced with pure CNT in these systems. Two defect CNT is named CNT1_{defect} and CNT2_{defect}, respectively. The adsorption between defect CNT and S₈ molecule was also shown in figure S1.

The absorption energy is defined as:

$$E_{ads} = E_{total} - (E_{substrate} + E_{adsorbate})$$

Where E_{total} is the total energy of the system (CNT/S₈ & S₈/S₈), E_{adsorbate} is the energy of the S₈ adsorbate, E_{substrate} is the energy of CNT or S₈ substrate, respectively. According to this definition, the negative values of E_{ads} show an exothermic process. Moreover, larger negative values of E_{ads} imply stronger interaction between the substrate and adsorbate⁶⁻⁸.

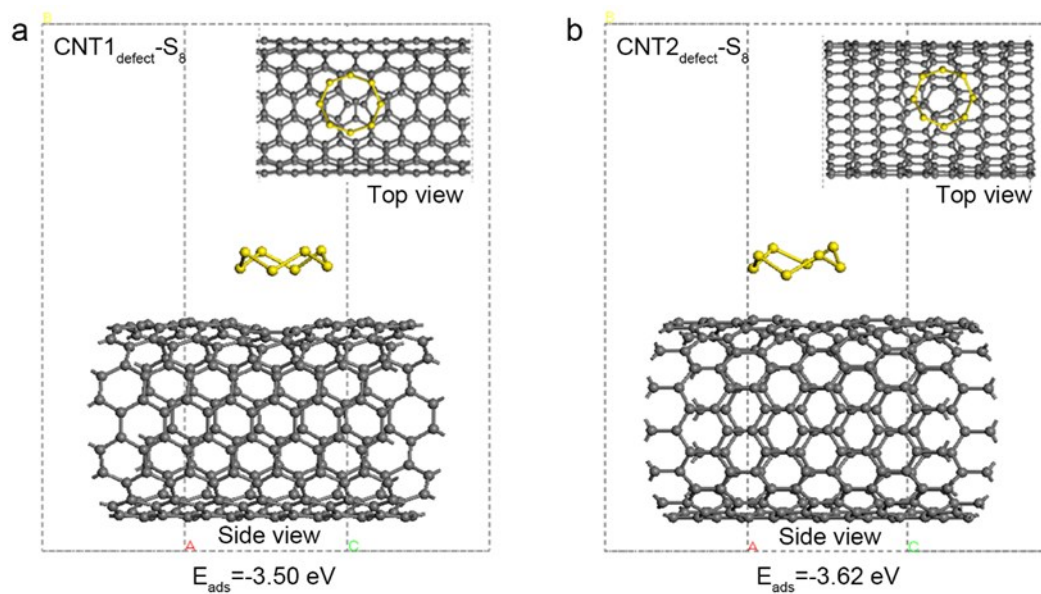


Figure S1. (a) $\text{CNT1}_{\text{defect}}-\text{S}_8$ and (b) $\text{CNT2}_{\text{defect}}-\text{S}_8$ consisting of 224 C plus a S_8 adsorbate.

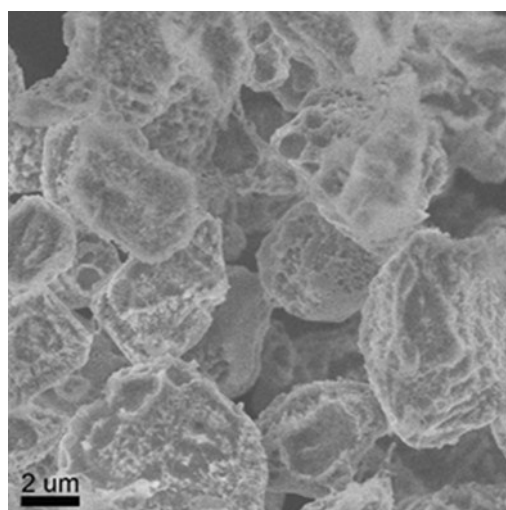


Figure S2. SEM image of sulfur aggregation prepared in the same experimental procedure, only without addition of SWNT.

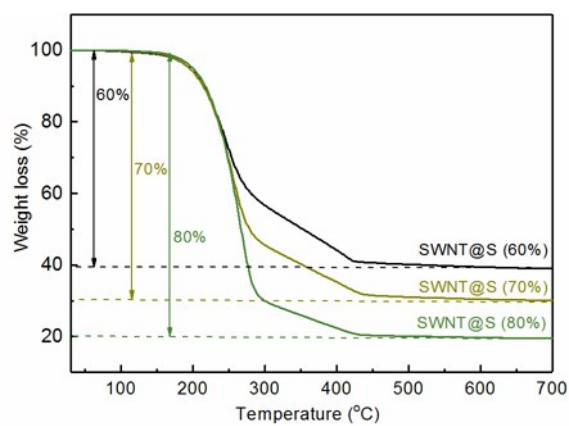


Figure S3. Thermal gravimetric analysis of SWNT@S film with the sulfur content of 60%, 70% and 80%.

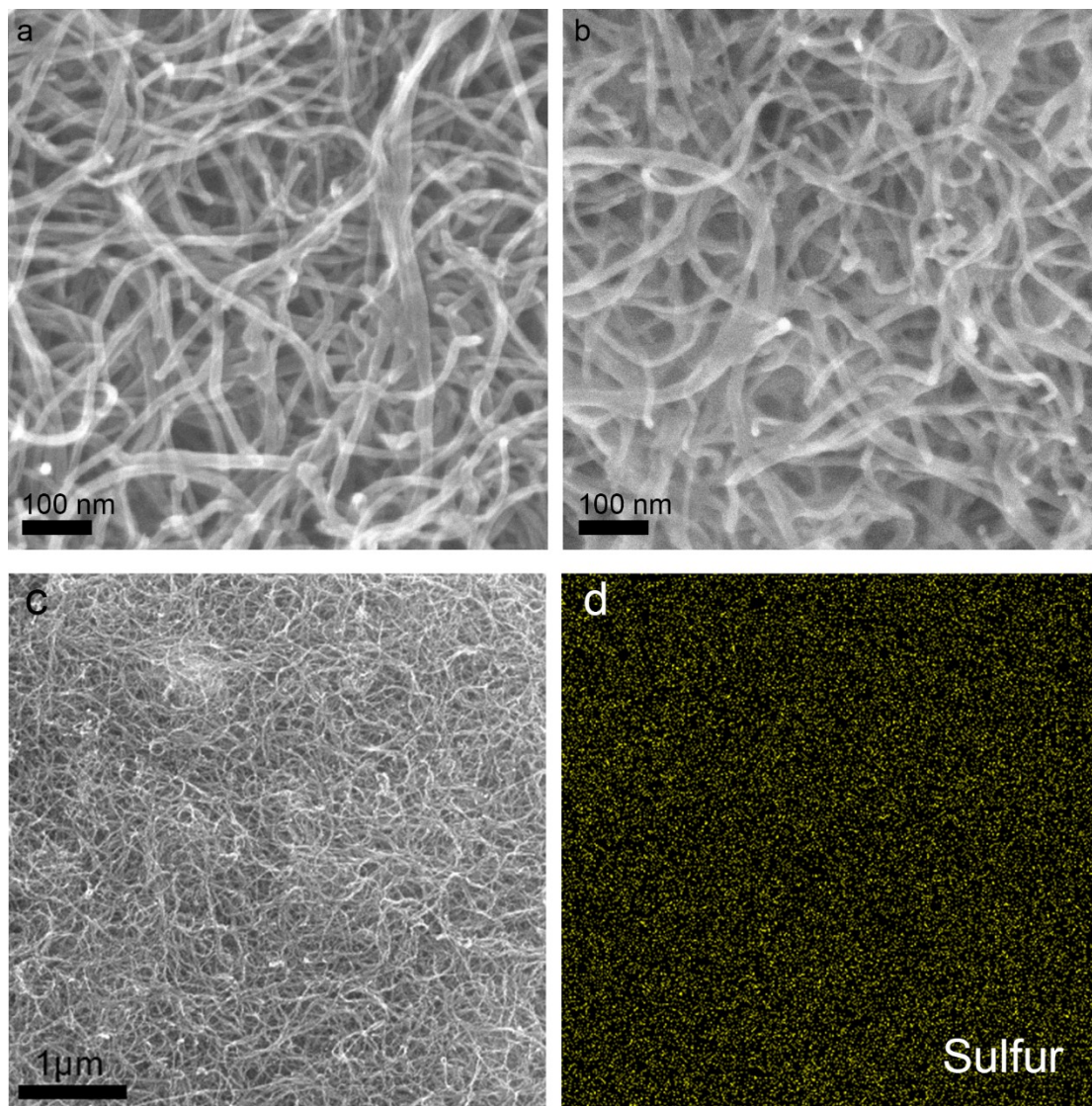


Figure S4. SEM image of (a) MWNT film (b) MWNT@S film. (c) Morphology and (d) corresponding EDS sulfur mapping of MWNT@S film.

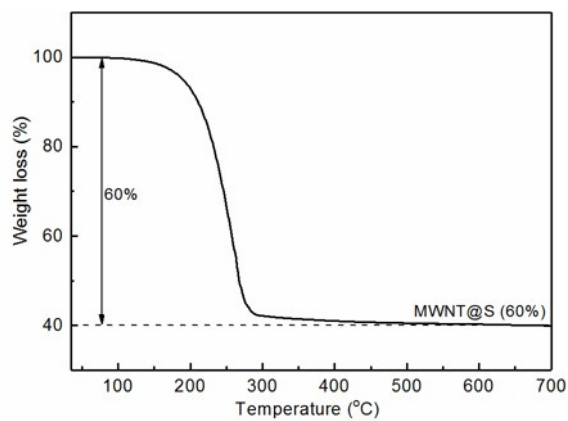


Figure S5. Thermal gravimetric analysis of MWNT@S film with the sulfur content of 60%.

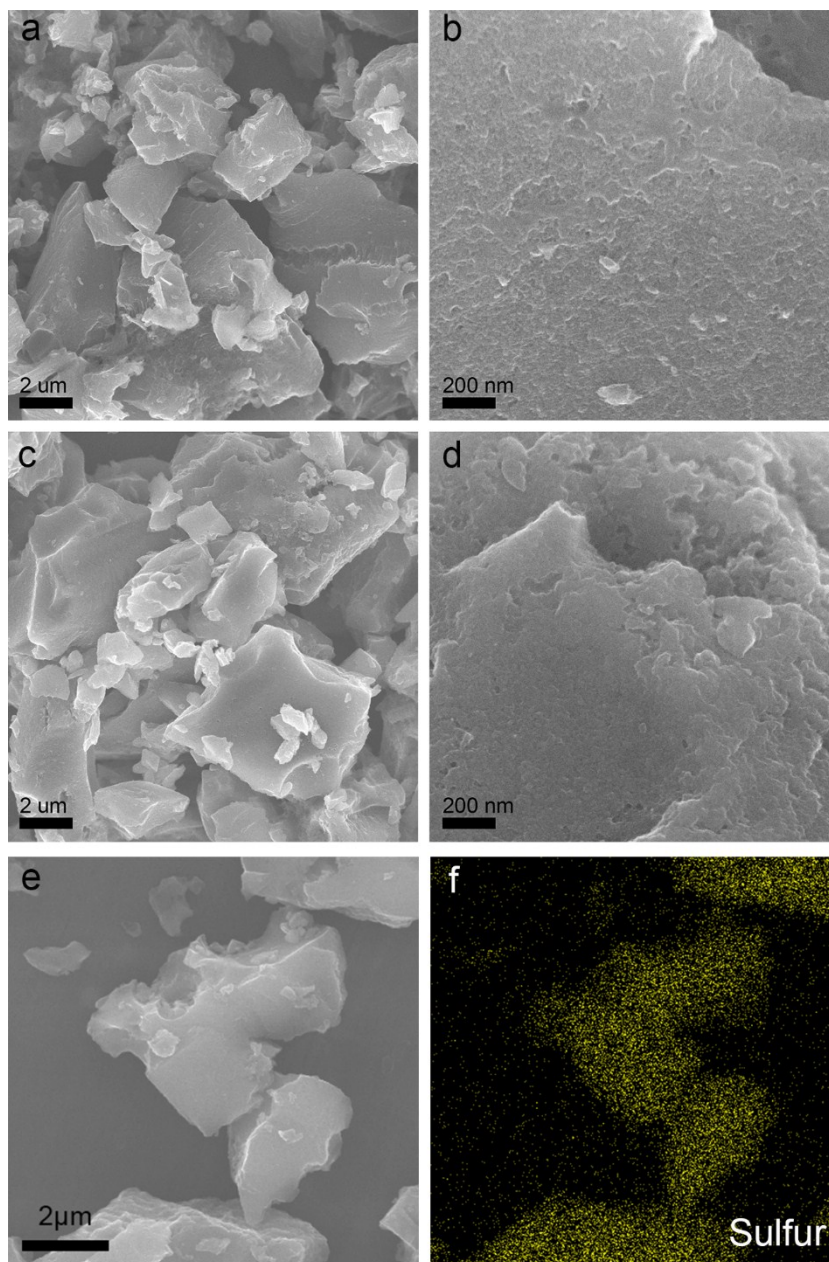


Figure S6. (a) Low-resolution and (b) high-resolution SEM image of YP80 particles. (c) Low-resolution and (d) high-resolution SEM image of YP80@S particles. (e) Morphology and (f) corresponding EDS sulfur mapping of YP80@S particles.

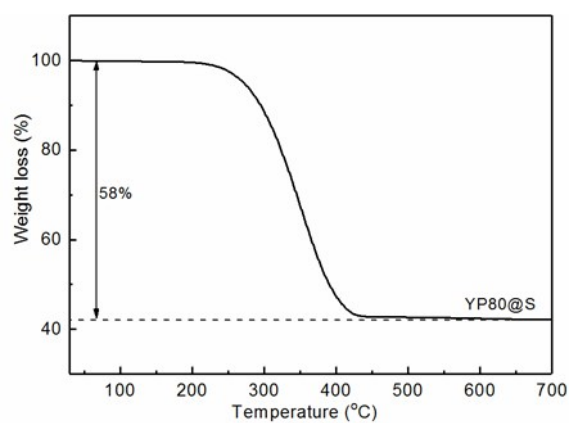


Figure S7. Thermal gravimetric analysis of YP80@S with dissolution-recrystallization strategy.

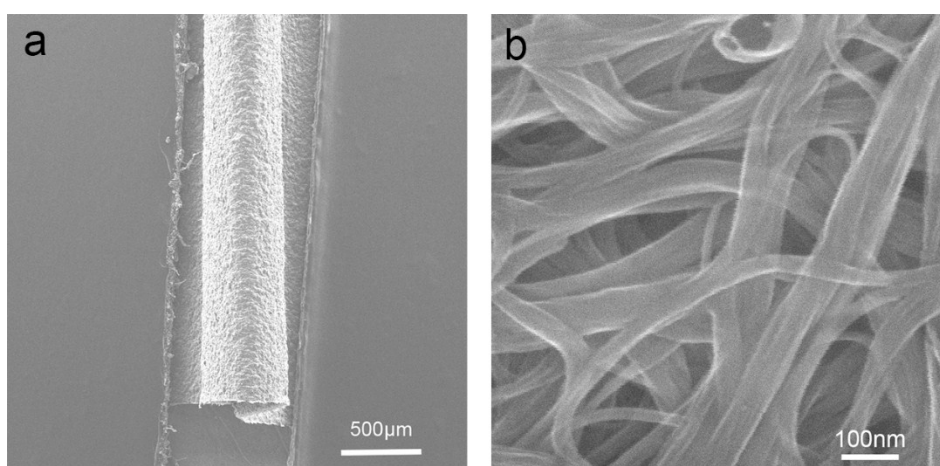


Figure S8. SEM images of SWNT@70%S at bending state.

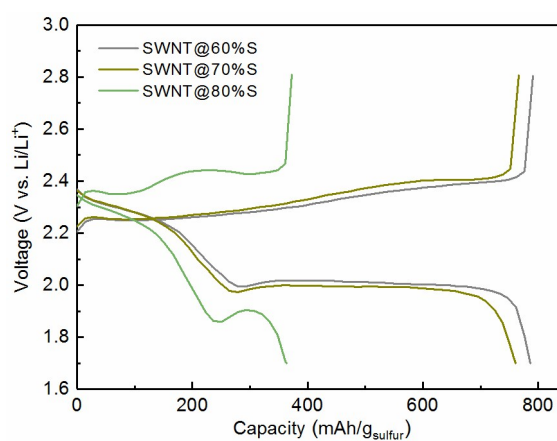


Figure S9. Charge-discharge profiles of SWNT@60%S, SWNT@70%S and SWNT@80%S at 2C.

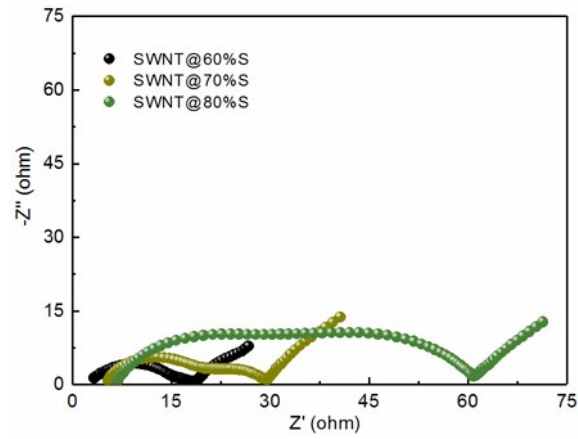


Figure S10. Impedance spectra of SWNT@60%S, SWNT@70%S and SWNT@80%S after 5 cycles at 0.2C.

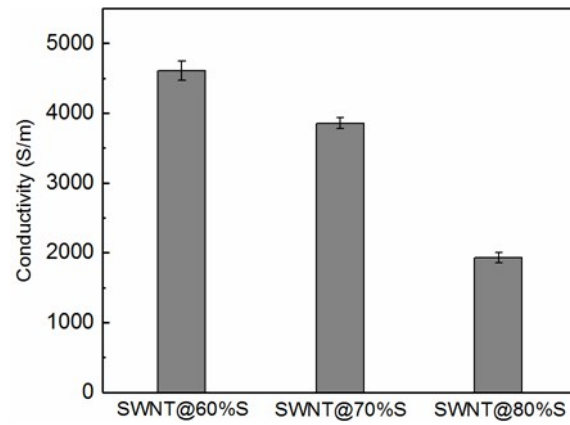


Figure S11. Conductivity of SWNT@60%S, SWNT@70%S and SWNT@80%S.

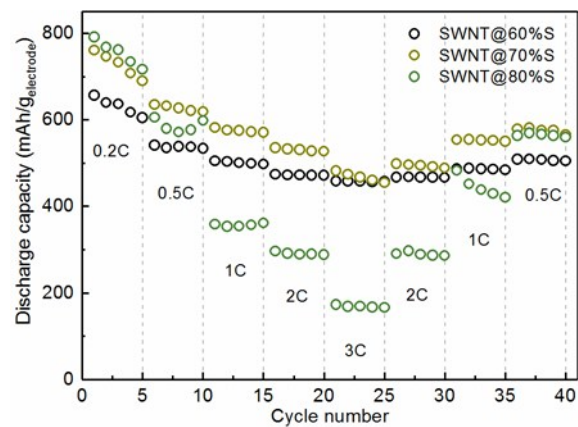


Figure S12. Comparison on the rate performance of SWNT@60%S, SWNT@70%S and SWNT@80%S calculated based on the total mass of electrodes.

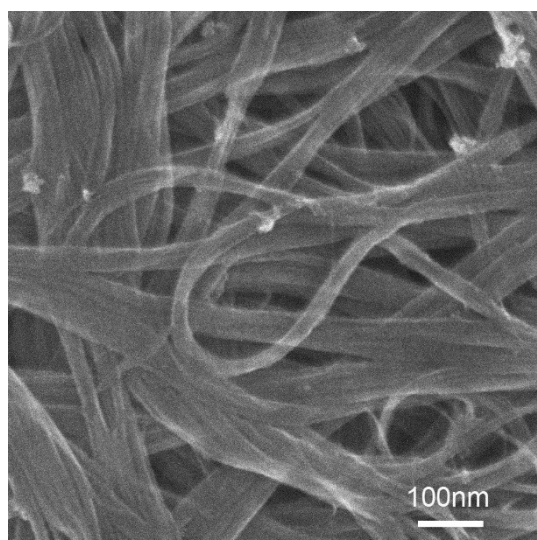


Figure S13 SEM image of SWNT@70%S after 400 cycles.

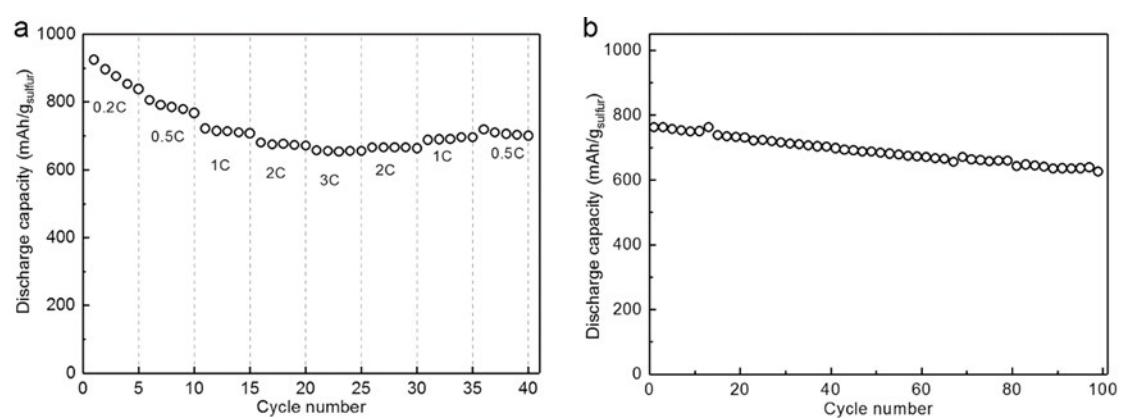


Figure S14. (a) Rate performance and (b) cyclic performance at 1 C of MWNT@S.

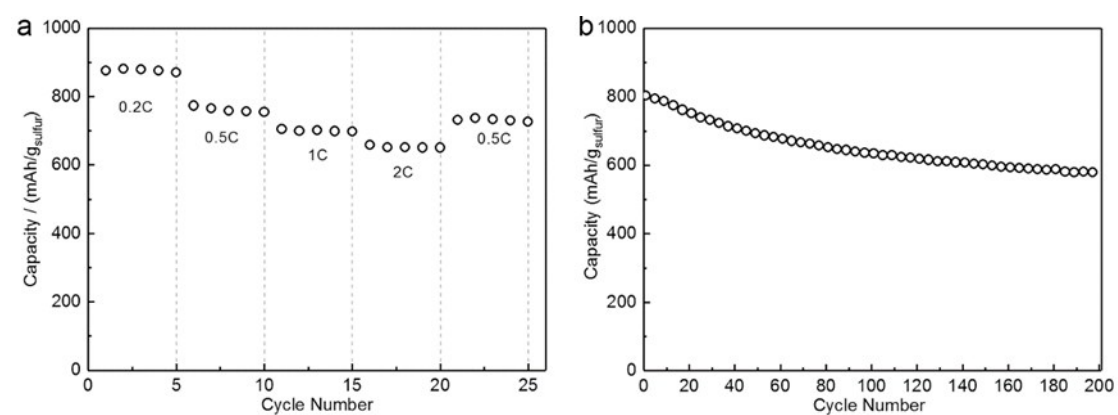


Figure S15. (a) Rate performance and (b) cyclic performance at 0.5 C of YP80@S.

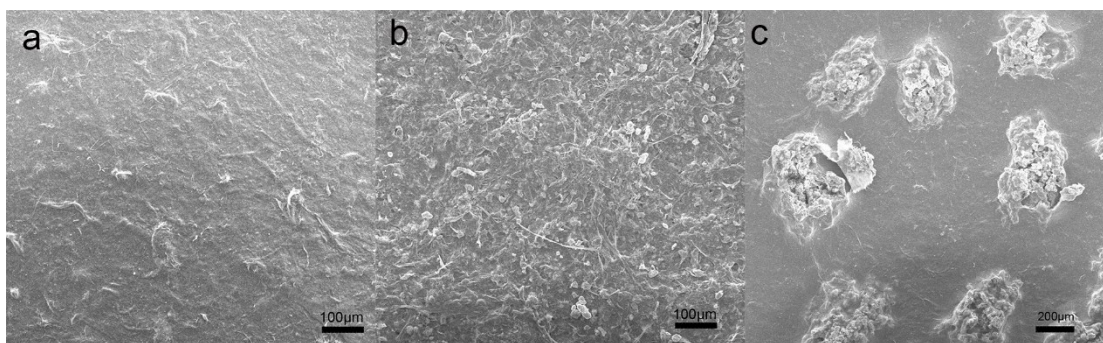


Figure S16. SEM images for SWNT@70%S fabricated with acetone (a), deionized water (b) and tetrahydrofuran (c)

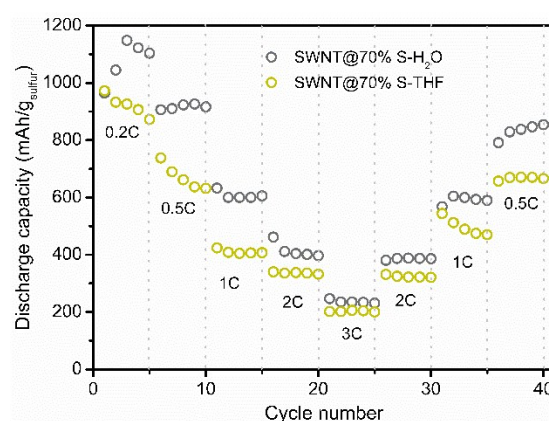


Figure S17. Rate capability of SWNT@70%S-H₂O and SWNT@70%S-THF in different current densities.

From the Figure S14 and S15, we can find obvious sulfur particles and serious aggregation in the SWNT@70%S-H₂O and SWNT@70%S-THF. Owing to the nonuniform distribution of sulfur, both of the electrodes show poor capacities in different current densities compared to the SWNT@70%S fabricated with acetone.

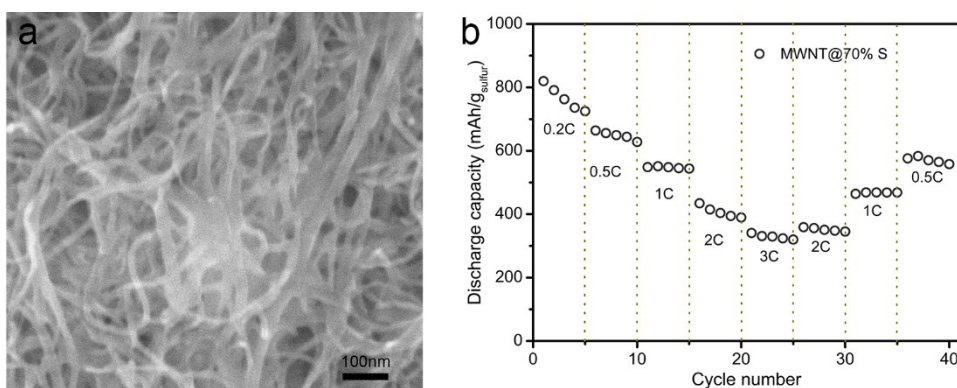


Figure S18. (a) SEM image for MWNT@70%S. (b) Rate capability of MWNT@70%S in different current densities.

The specific surface area of MWNT is only 206.2 m²/g which is much less than SWNT. From the SEM images, we could find the obvious aggregation of sulfur in MWNT@70%S owing to the low surface area which could not accommodate high sulfur dosage. Moreover, the sulfur aggregation also leads to inferior electrochemical performance due to the difficult diffusions of electron and lithium ion in the interior of sulfur aggregation.

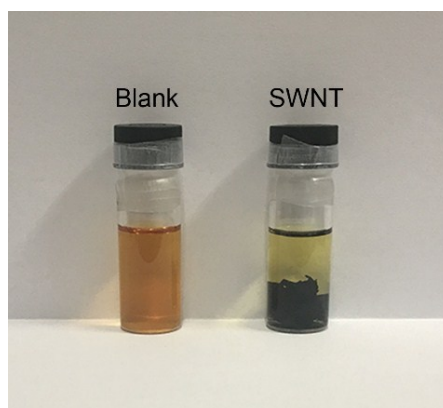


Figure S19. Visualized adsorption of Li₂S₄ on SWNT.

The fabrication of Li₂S₄ solution could be found in previous literature⁹. It can be seen that the color of Li₂S₄ solution mixed with SWNT film become light compared with the original Li₂S₄ solution, indicating the adsorption between SWNT and Li₂S₄.

References

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