Electronic supplementary information

Sulfur-amine Chemistry Based Synthesis of Multi-walled Carbon Nanotube-Sulfur Composites for High Performance Li-S Batteries

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I. Experimental Details.

Chemicals.

Multi-walled carbon nanotubes (MWNT, ⩾98%, Nanjing JC nano Tech Co., Ltd), sublimed sulfur (99.9%, Aldrich), aniline ($C_6H_5NH_2$, ⩾99%, Alfa Aesar), ethylene diamine anhydrous (EDA, analytical grade), ammonium persulfate ($(NH_4)_2S_2O_8$, analytical grade), carbon disulfide (CS_2, analytical grade), hydrochloric acid (HCl, analytical grade) and absolute ethyl alcohol were purchased from Sinopharm chemical reagent Co., Ltd. lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) with 1,3-dioxolane (DOL) and dimethoxyethane (DME) (Novolyte technologies Co., Ltd., Suzhou) were used as purchased without treatment.

Synthesis of MWNT-S composite.

Sublimed sulfur was added into 10 mL of EDA and formed dark red S-EDA precursor solution. Secondly, MWNT was dispersed in 140 mL of 0.1 M HCl solution under ultrasonication (130W, Sonics & Materials, Inc. USA) for 10 minutes. Thirdly, S-EDA precursor solution was added into the MWNT dispersion solution dropwise with a speed of ~ 3 mL min^{-1} under vigorous stirring. The

mixture solution was further stirred for 10 minutes under airtight condition. Then the mixture was filtered and rinsed with deionized water and alcohol several times. Finally, the MWNT-S composite was obtained after drying at 60 ℃ for 12 hours.

Synthesis of MWNT-S-TT composite by thermal treatment.

For a comparison, thermal treatment sample (the mass ratio of MWNT to sulfur is 1:4) was synthesized. Sulfur and MWNT were mixed by ball-milling for 6 hours. Then the mixture was annealed at 155℃ for 6 hours under Ar protection. The final product is named as MWNT-S-TT.

Synthesis of MWNT-S@PANI composite.

In a parallel experiment of preparing MWNT-S composite (M_{MWNT}=0.50 g, M_S=2.0 g), we added HCl solution into the fresh obtained MWNT-S mixture solution until pH<7. Then, 0.45 g aniline monomer ($C_6H_5NH_2$) was added directly into the mixture solution with continuous stirring. Meanwhile, $(NH_4)_2S_2O_8$ with equal mole of aniline dissolving in 5 mL 2 M HCl solution was used as oxidizer and added into the MWNT-S mixture solution with speed of ～0.5 mL min^{-1}. After 12 hours, the product was filtered and washed with diluted HCl, alcohol and deionized water, respectively. After filtration, the final deposits were dried under 60 ℃ for 12 hours to get polyaniline (PANI) coated MWNT-S composite (this product is labeled as MWNT-S@PANI).

The coin batteries assembling and testing.

To prepare the working electrodes, the composites were mixed with acetylene black and LA132 (aqueous binder, Chengdu Indigo Power Sources Co., Ltd) in a weight ratio of 7:2:1 with water as a dispersant. The pastes were coated on aluminum foil and dried at 60 °C for 12 hours. The electrochemical performances of the composite were tested in a coil cell (type CR2025) assembled in an argon-filled glove box with moisture and oxygen contents below 1 ppm. The cathode was

separated from the lithium anode by a separator (Celgard 2400). The electrolyte was 1 M LiTFSI in a mixed solvent of DME and DOL at a volume ratio of 1:1. The cells were tested with Neware battery test system (Shenzhen Neware technology Co., Ltd) under cut-off voltage of 1.5–2.8 V. Charging rate 0.25C = 418 mA g^{-1}. Cyclic voltammograms (CV) were recorded with a coin cell using a CHI 660C electrochemical workstation (CHI Instruments, Inc., USA) at a scan rate of 0.1 mV s^{-1}. Electrochemical Impedance Spectroscopy (EIS) of these batteries was test from 100 kHz to 0.1Hz.

Material Characterizations.

The samples were characterized using scanning electron microscope (Hitachi S-4800) coupled with an energy dispersive X-ray spectrometer (EDX), X-ray diffractometer (XRD, Diffraktometer D500/501, Siemens), Fourier transform infrared spectrometer (FTIR, Thermal scientific Nicolet 6700). Thermogravimetric analysis (TG analysis, EXSTAR6200) was carried out at heating rate of 5 ℃ min^{-1} under argon atmosphere,

II. Supporting Figures

Figure S1. The photo of the EDA solution and EDA-S complex.

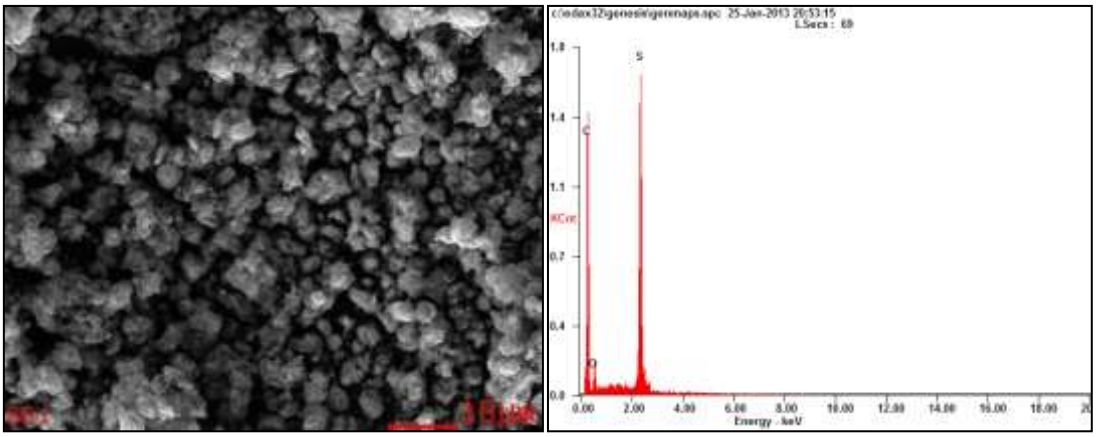

Figure S2. The EDX of MWNT-S composites.

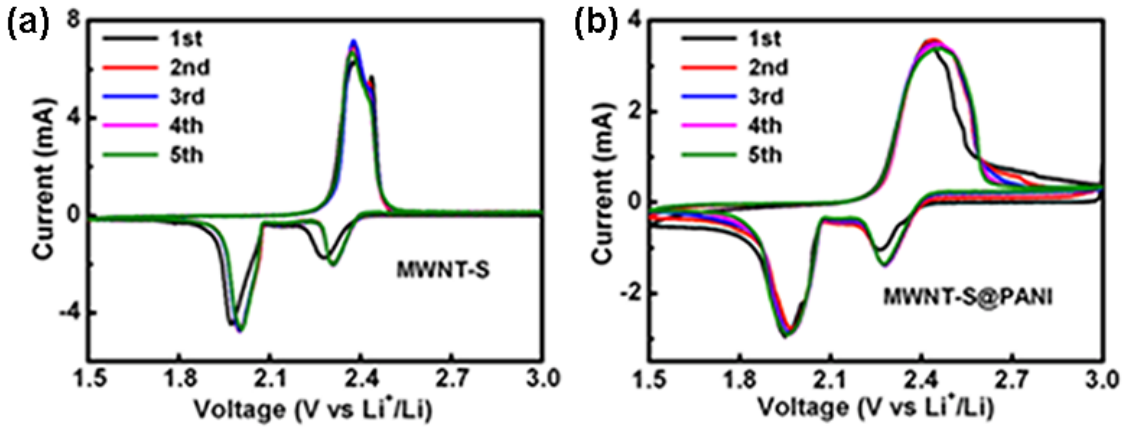

Figure S3. The cyclic voltammograms (CV) curves of (a) MWNT-S and (b) MWNT-S@PANI composites.

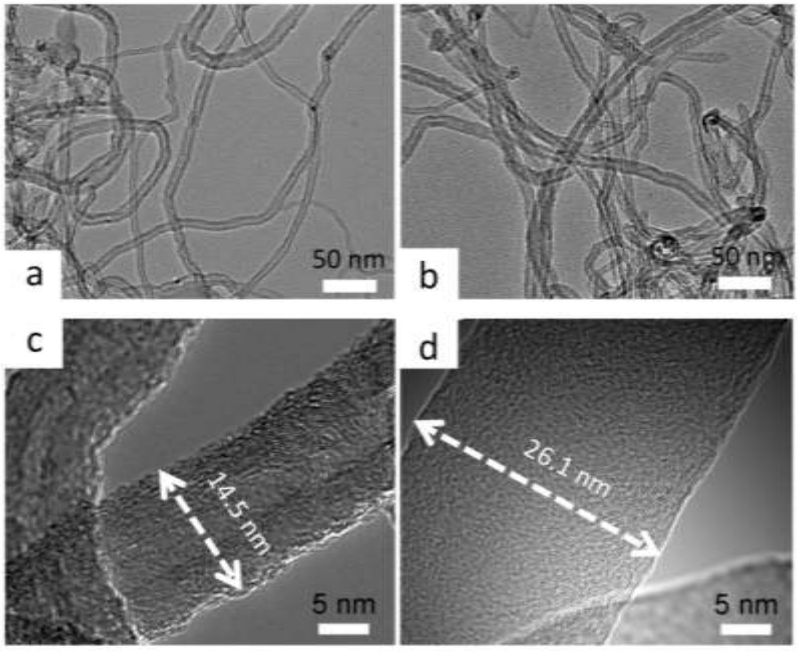

Figure S4. Transmission electron micrographs of MWNT (a and c) and MWNT-S composites (b and d).