Electronic Supplementary Information

Fabrication of Mesoporous Li_2S-C Nanofibers for High Performance Li/Li_2S Cells cathode

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Experimental sections

Materials synthesis: In this work, commercial lithium sulfide powder (Li_2S, Alfa Aesar, 99.9%), commercial sulfur (S, Sigma-aldrich), Polyvinylpyrrolidone (PVP, k90, M_w=130,000) and absolute ethanol (J&K Scientfic, 99.5%) were used without further purification. The Li_2S-C nanofibers composite was obtained according to the following three steps. First, the precursor gels for electrospinning was prepared. In a typical procedure, 7.5 mmol Li_2S powder and 12 mmol sulfur powder were in turn added into 10 ml absolute ethanol and stirred to form a brown solution in an argon-filled vacuum glove-box. 300 mg PVP was then added into this brown solution and stirred for overnight. Finally, the bottle with the precursor gels was sealed and transferred to a simple organic glass glove-box with dry air. After this step, when the humidity in glove-box decreased to below 5%, the nanofibers were spun by electrospinning under a flow of nitrogen. During the electrospinning, the high voltage was adjusted to about 7~8 kV and the distance between needle tip and aluminum foil collector was about 15cm. Finally, the as-spun Li_2S_3-PVP fibers were calcined at 350 ^oC for 3h and subsequent 600 ^oC for 1h in a tubular furnace under argon atmosphere to obtain final Li_2S-C nanofiber composite.

Materials Characterization: The morphology and structure of samples were characterized by scanning electron microcopy (SEM), Transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS), respectively. SEM was measured on a Quanta 400 FEG field-emission scanning electron microscope. TEM was measured on a Tecnai G2 F20 S-Twin field-emission transmission electron microscope. XRD was collected on a Bruker D8. XPS was conducted with Thermo Scientific ESCALAB 250Xi. The Brunauer-Emmett-Teller

(BET) surface area and pore diameter distribution were analyzed on Micrometrics (ASAP 2020 HD88).

Calculation of Li_2S content in Li_2S-C NFs

Considering the uniform distribution of PVP and Li_2S_3 in the as-fabricated Li_2S_3-PVP NFs, and pure Li_2S crystalline phase in annealed Li_2S-C NFs, the Li_2S content in the composite NFs can be evaluated according the following formula:

$$Li_2S\ \text{wt.}\% = \frac{m_{Li_2S_3-PVP} \times \frac{m_{S-Li_2S}}{m_S}}{m_{Li_2S-C}} \times 100\%$$

Where *m* indicate the mass, the subscripts *Li_2S_3-PVP, S-Li_2S, S and Li_2S-C* represent as-fabricated NFs before annealed, Li_2S represents the solid powder used to prepared the electrospinning gel, and Li_2S-C represents the NFs after annealed.

Table S1 the mass change of NFs before and after annealed (600 ^oC)

	Li_2S_3-PVP (mg)	**Li_2S-C (mg)**	**Li_2S wt. %**
Exp 1	266.8	112.7	72.6
Exp 2	224.8	96	71.8

According to the above results of Exp 1 and Exp 2, the Li_2S content in the Li_2S-C NFs was estimated to be 72.2 wt. % (average value).

Electrochemical measurements: The electrochemical measurements were carried out using Land CT2001A with lithium metal as the counter and reference electrodes at room temperature. The electrode consists of active materials (Li_2S-C NFs), conductive reagent (Super P carbon black) and polymer binder (PVDF) by a weight ratio of approximately 83:7:10. The loaded slurry on each electrode was about 1.5 mg/cm^2. The electrolyte was LiTFSI (1 M in DOL/DME) containing $LiNO_3$ (1 wt. %). The Li/Li_2S cells were assembled in an Ar-filled glove-box. The cells were first charged up to 3.2V and subsequently discharged to 1.7 V at a current density of 0.025 C (1 C=1166 mA

g^{-1}). After the initial charge/discharge, the cells were cycled between 1.7 V and 2.8 V at a current density of 0.5 C. The rate performance was evaluated at a current density of 0.025C, 0.2C, 0.5C, 1C, and 2C, respectively. Cyclic voltammogram and electrochemical impedance spectra were carried out to investigate the electrode reaction processes and the initial activation process. The cells were firstly swept with the scanning range from open circuit voltage to 3.2 V and then were cycled between 1.7 V and 2.8 V at a rate of 0.025 mV s^{-1}. The electrochemical impedance spectra were performed in the frequency range from 0.01 Hz to 100 kHz.

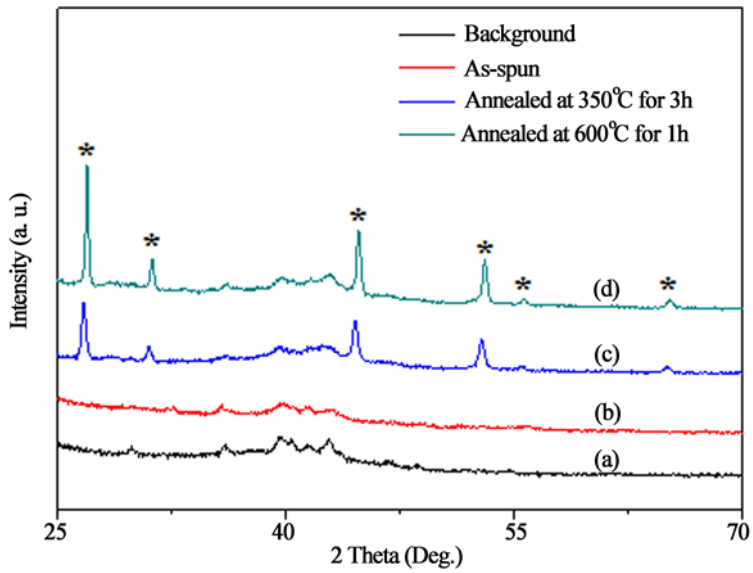

Figure S1 XRD patterns for as-spun and annealed samples, respectively.

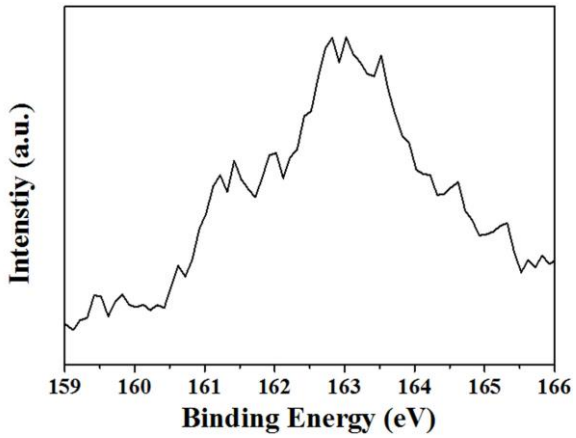

Figure S2 S 2p XPS spectra of the as-spun Li_2S_3-C NFs

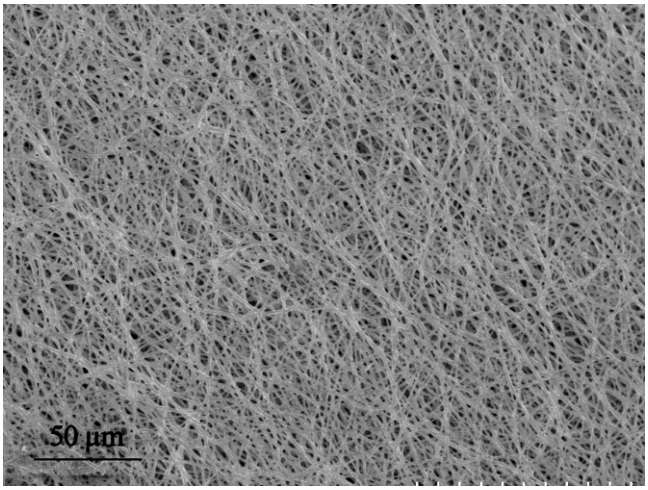

Figure S3 SEM image of as-spun Li_2S_3-PVP composites.

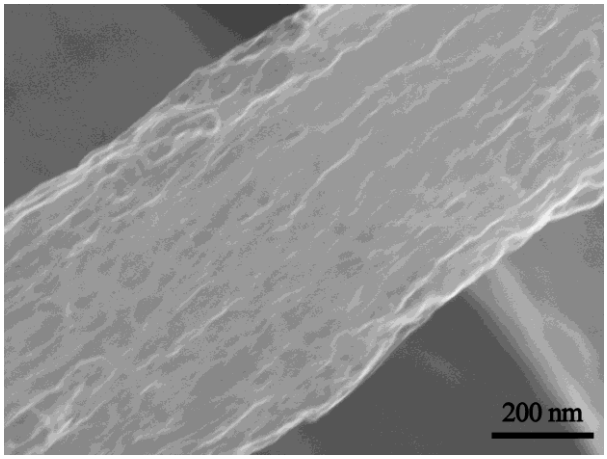

Figure S4 SEM image of a Carbon fiber with the absence of Li_2S.

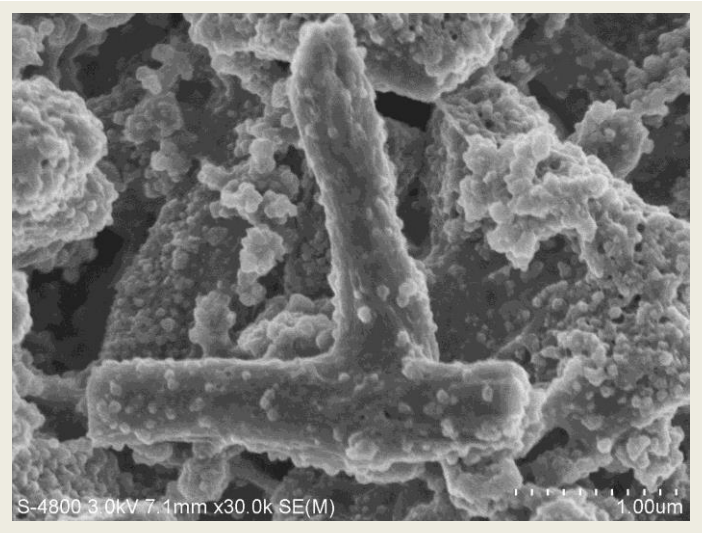

Figure S5 The SEM image of Li_2S-C NFs after CV scan for 5cycles

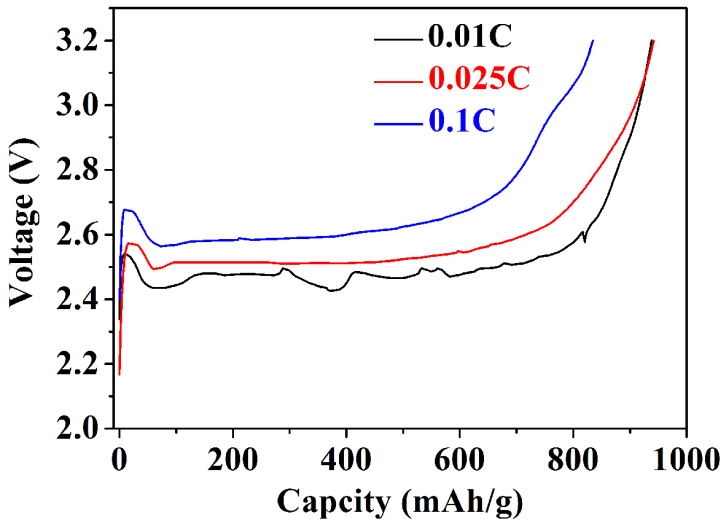

Figure S6 Initial charge curves at a rate of 0.01C, 0.025C and 0.1C, respectively.