Supporting Information

CoS2@C catalyzes polysulfide conversion to promote the rate and cycling performances of lithium-sulfur batteries

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Experimental Section

Synthesis of CoS_2@C

To prepare the NTC-Co nanowire precursors, 2.1 g of $CoCl_2$ $6H_2O$, 0.9 g of nitrilotriacetic acid (NTC), and 15 mL of 2-propanol were mixed with 45 mL of deionized (DI) water, and the resulting solution was stirred thoroughly. The mixture was then sealed in a Teflon-lined stainless steel autoclave (100 mL) and heated at 180 °C for 6 h. After cooling to room temperature, the pink NTC-Co nanowire precursors were collected by vacuum filtration and dried in a vacuum oven at 60 °C for 12 h.

Next, 0.45 g of the dried NTC-Co precursor was dispersed into 60 mL of deionized water, followed by the addition of 0.225 g of glucose. The resulting solution was transferred to a stainless steel autoclave and heated at 180 °C for 12 h. After centrifugation and washing with deionized water ten times, the mixture was freeze-dried for 24 hours. The Co@C was obtained by annealing at 600 °C for 2 h with a ramp rate of 1 °C min^{-1}.

Finally, 100 mg of the Co@C was placed downstream of a furnace, while pure sublimated sulfur (500 mg) was placed upstream of the furnace. The powders were annealed in argon at 400 °C for 1 hour to obtain CoS_2@C.

Visualized Adsorption of Li_2S_6

A molar ratio of 5:1 of S to Li_2S was dispersed in a 1, 2-dimethoxyethane/1, 3-dioxolane (DME/DOL) solution with a volumetric ratio of 1:1. The resulting mixture was stirred at 60 °C for 24 h, yielding a 0.005 mol L^{-1} Li_2S_6 solution. To perform a visual adsorption test, 10 mg of MWCNTs and CoS_2@C were separately added to the Li_2S_6 solution (1 mL). After 12 h, a final digital photograph was taken.

Assembly of Symmetric Cells

MWCNT and CoS_2@C were dispersed in ethanol at a mass ratio of 3:7, resulting in a uniform suspension after ultrasonic dispersion. This suspension was then dropped onto carbon paper (CP) and dried naturally at room temperature. The same method was used

to prepare MWCNT electrodes, with both electrodes having a mass loading of ≈ 0.5 mg cm^{-2}. To assemble a Li_2S_6 symmetric cell, Celgard 2400 was employed as the separator, while two identical electrodes were used as the electrodes in the symmetric cell. The electrolyte was composed of 40 μL of a DME/DOL solution (v/v=1:1), which contained 0.5 mol L^{-1} Li_2S_6, 2.0 wt% $LiNO_3$, and 1.0 mol L^{-1} lithium bis(trifluoromethanesulfonyl)imide (LiTFSI).

Nucleation of Li_2S

Initially, Li_2S and S were dissolved in a DME/DOL (v/v=1:1) electrolyte, which contained 1.0 M LiTFSI and 2.0 wt% $LiNO_3$, with a molar ratio of 1:7. After stirring at 60 °C for 24 hours, a Li_2S_8 electrolyte ([S]=0.25 M) was successfully prepared. For the experiment, CoS_2@C and MWCNT were dispersed in absolute ethanol based on a mass ratio of 3:7 before dropping the suspension into CP with a diameter of 10 mm. The mixture was then dried at 60 °C for 12 hours to create the CP-CoS_2@C/MWCNT electrodes. MWCNT electrodes were also prepared in the same way. The resulting mass loading of both electrodes was approximately 0.5 mg cm^{-2}. For nucleation of Li_2S, the 2032-type coin cell was utilized with Celgard 2400 being the separator. Lithium metal foil was used as the anode, and CP-CoS_2@C/MWCNT or CP-MWCNT electrodes as the working electrode. A Li_2S_8 electrolyte (20 μL) was used as a catholyte. The same composition of electrolyte without Li_2S_8 (20 μL) was applied to the anode. The cells were galvanostatically discharged at 0.112 mA until the voltage reached 2.06 V. The voltage was then maintained at 2.05 V to facilitate Li_2S nucleation. The tests were completed using a VMP3 multichannel electrochemical workstation (BioLogic, France).

Assembly of the Cells and Electrochemical Measurements

CoS_2@C and MWCNT were mixed at a mass ratio of 7:3. Additionally, the mass ratio of sublimated sulfur to the combined mass of the two powders was 7:3. First, sulfur was added to 20 mL of CS_2 and sonicated for 5 min. Subsequently, CoS_2@C and MWCNT were added and stirred at 45 °C for 12 h to allow for the volatilization of CS_2.

The resulting powders were heated at 155 °C for 12 h in a stainless-steel autoclave filled with Ar gas to obtain CoS_2@C/MWCNT/S. MWCNT/S was prepared using a similar procedure. To form a uniform suspension, electrode materials (CoS_2@C/MWCNT/S), polyvinylidene fluoride (PVDF), and Super P were dispersed in N-methyl-2-pyrrolidinone (NMP) at a weight ratio of 7:1:2 and coated on CP. The dried cathodes were punched into disks with a diameter of 13 mm. The thickness of the CoS2@C/MWCNT/S cathode is around 300 μm as shown in Fig.S13. The sulfur loading of the CoS2@C/MWCNT/S cathode is around 1 mg cm^{-2}. Electrochemical measurements were performed in a 2032-type coin cell, with a Li foil being used as the anode, Celgard 2400 as the separator, and the dried electrode as the cathode. The electrolyte was composed of 1.0 M LiTFSI and 2.0 wt % $LiNO_3$ in DME/DOL (v/v = 1:1) solution. The galvanostatic discharge/charge (GCD) tests were conducted in a voltage range between 1.7 and 2.8 V using a LANCT battery test system (Wuhan, China). The cyclic voltammetry (CV) measurements were carried out using a VMP3 multichannel electrochemical workstation (Biologic, France). The CV measurements were carried out in a voltage range of 1.7–2.8 V and at a scan rate of 0.1 mV s^{-1}.

Characterization of the Materials

The morphology and microstructure of all samples were characterized using scanning electron microscopy (SEM, SU70, Hitachi, Japan) and transmission electron microscopy (TEM, FEI, Tecnai TF20), respectively. X-ray diffraction (XRD, Rigaku D/max2600 with Cu Kα) was carried out in the range of 10−80 ° to detect the crystalline structure. Thermogravimetric analysis (TGA, Diamond 6300, Perkin Elmer, American) was conducted under an N2 atmosphere with a heating rate of 10 °C min^{-1}. The nitrogen adsorption/desorption isotherms were obtained on an ASAP 2010 accelerated surface area and porosimetry instrument (Micromeritics). X-ray photoelectron spectroscopy (XPS, Kratos AXIS SUPRA+ with a monochromatic Al Kα source) was used to evaluate the surface chemical states of samples.

Supplementary Figures and Tables

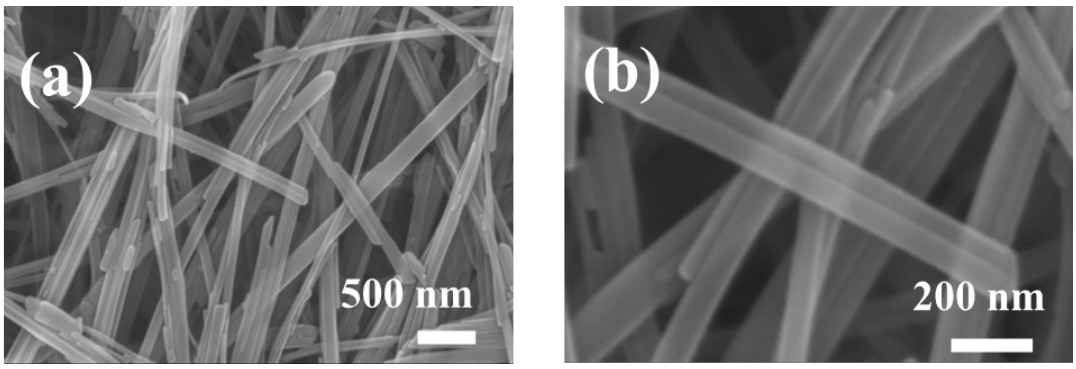

Fig. S1. (a, b) SEM images of NTC-Co fibers at different magnifications.

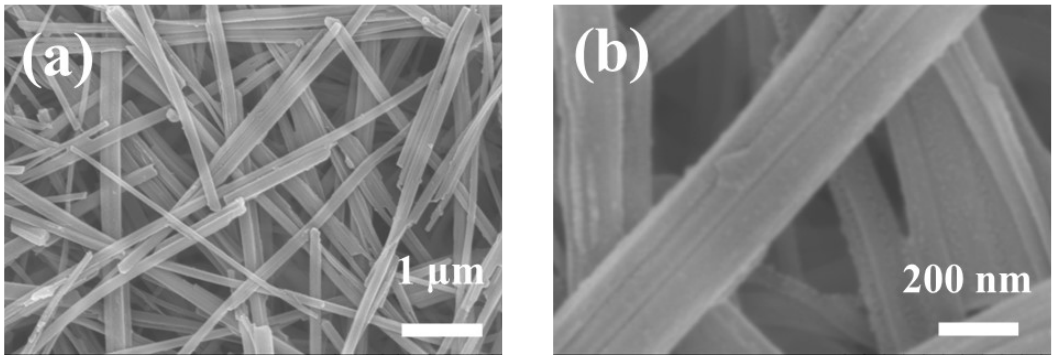

Fig. S2. (a, b) SEM images of 1D NTC-Co@glucose at different magnifications.

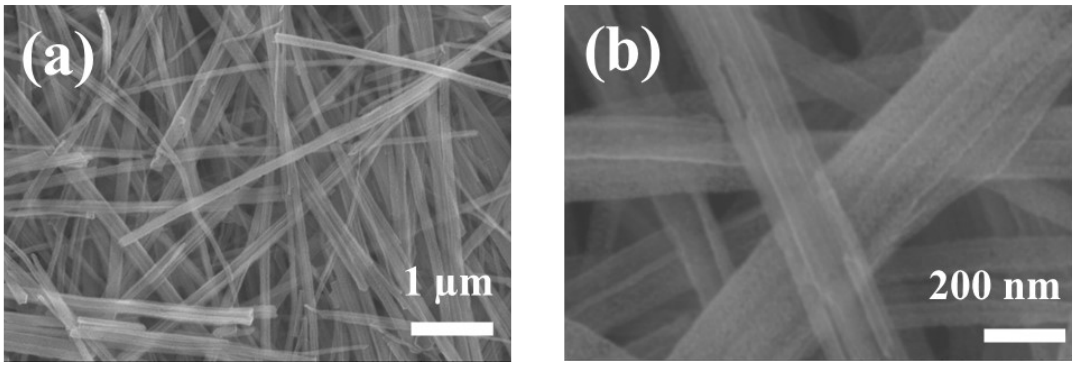

Fig. S3. (a, b) SEM images of Co@C fibers at different magnifications.

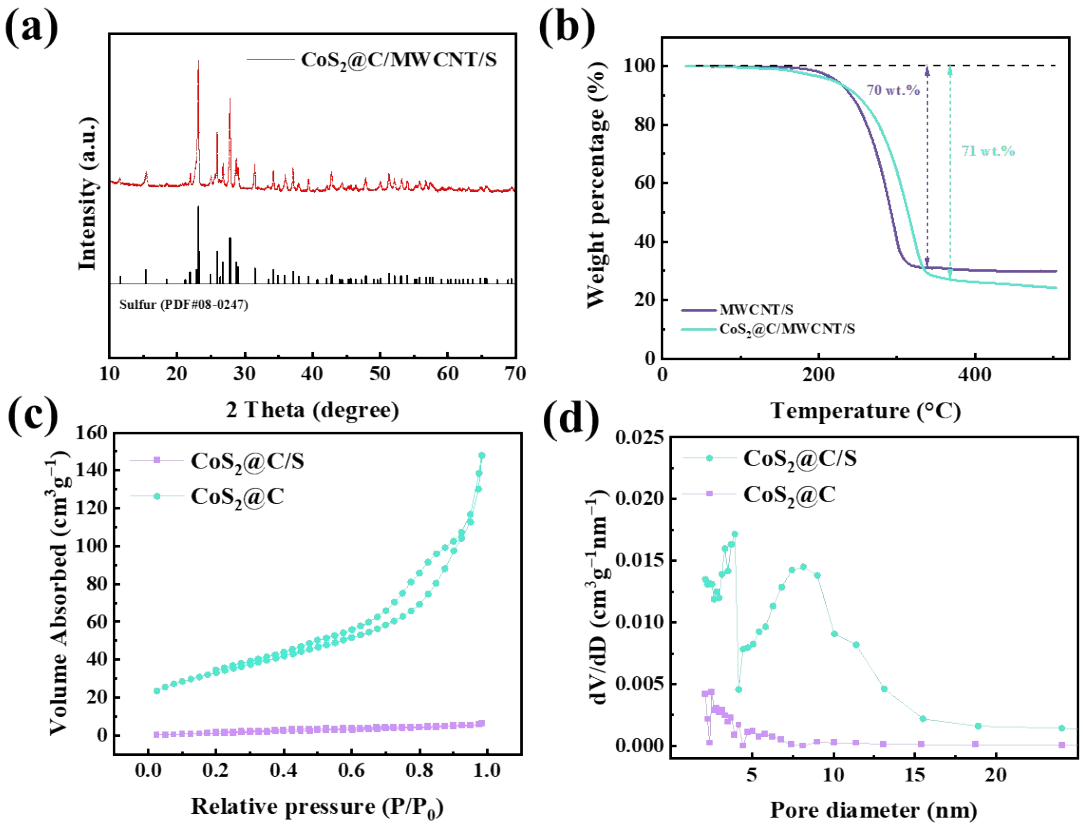

Fig. S4. (a) XRD pattern of CoS_2@C/MWCNT/S. (b) TGA curves of MWCNT/S and CoS_2@C/MWCNT/S in N_2 with a heating rate of 10 °C min^{-1}. (c) Isotherms of N_2 adsorption/desorption for MWCNT/S and CoS_2@C/MWCNT/S. (d) Pore size distribution of MWCNT/S and CoS_2@C/MWCNT/S.

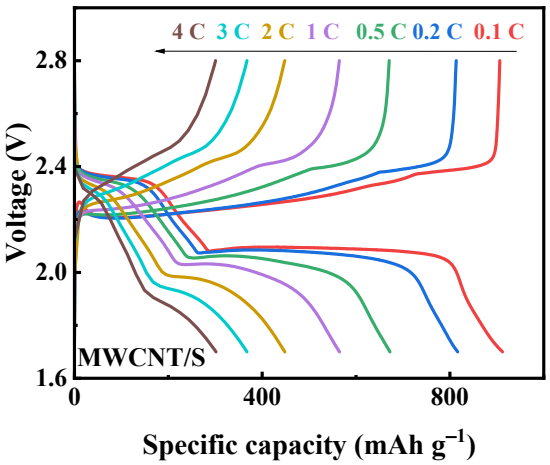

Fig. S5. GCD profiles of MWCNT/S cathodes with a sulfur loading of 1 mg cm^{-2} at different rates.

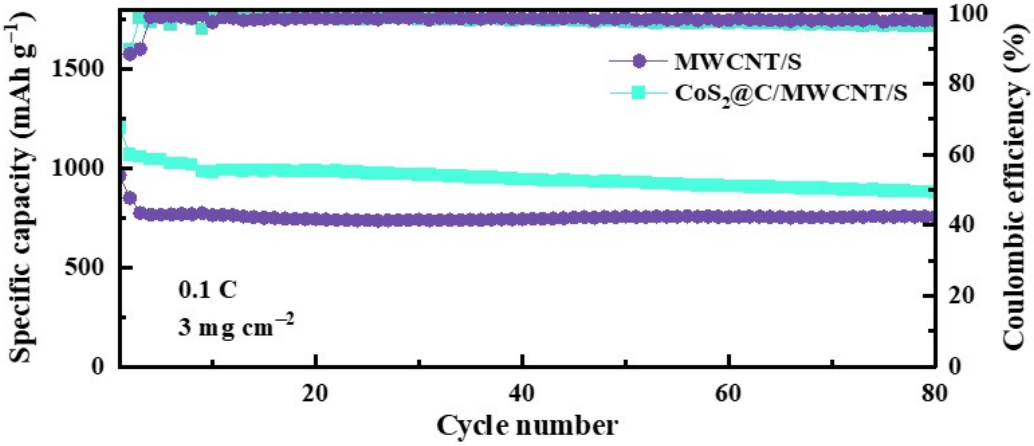

Fig. S6. Cycling performance of CoS_2@C/MWCNT/S and MWCNT/S with sulfur loading with 3 mg cm^{-2} at 0.1 C

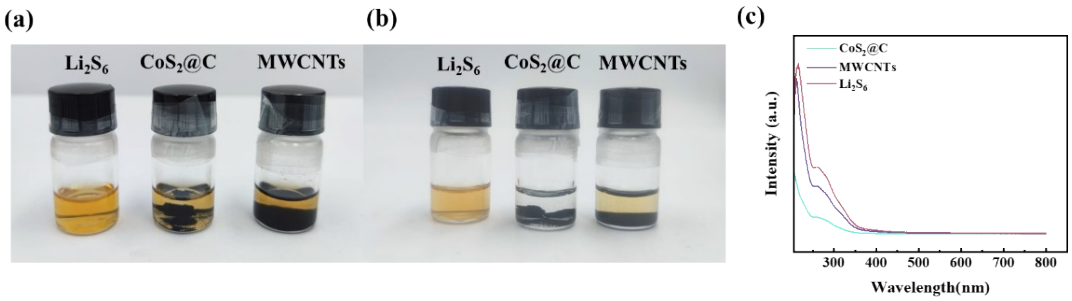

Fig. S7. (a, b) Visualized adsorption of Li2S6 by pristine CoS_2@C and MWCNTs. (c) UV–vis absorption spectra were measured for the Li_2S_6 solution before and after adsorption.

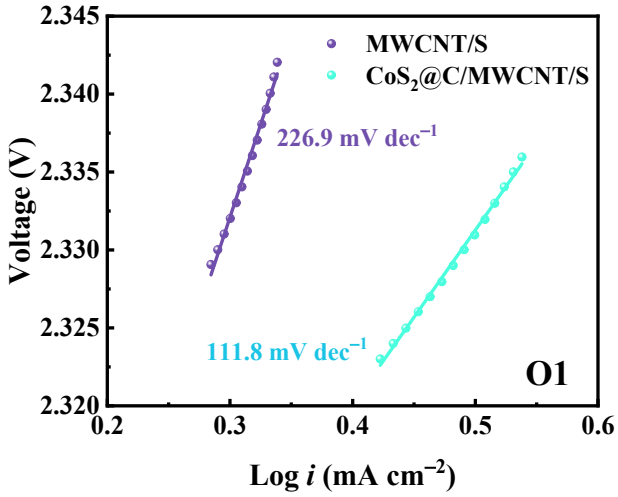

Fig. S8. Tafel plots corresponding to the oxidation of Li_2S.

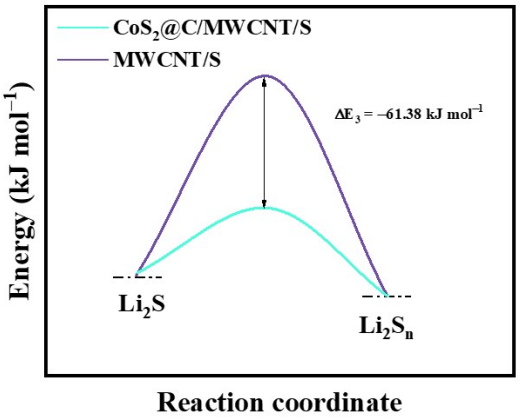

Fig. S9. Relative activation energies of Li_2S to Li_2S_n.

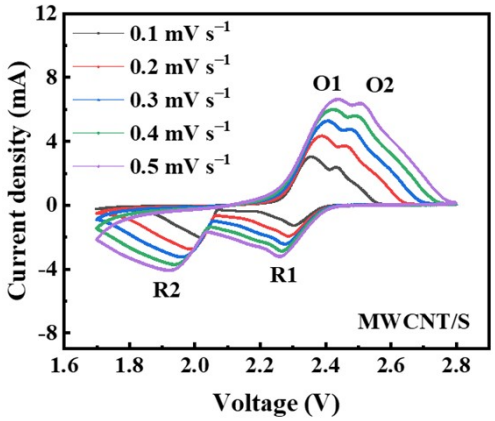

Fig. S10. CV curves of MWCNT/S cathodes at different scan rates.

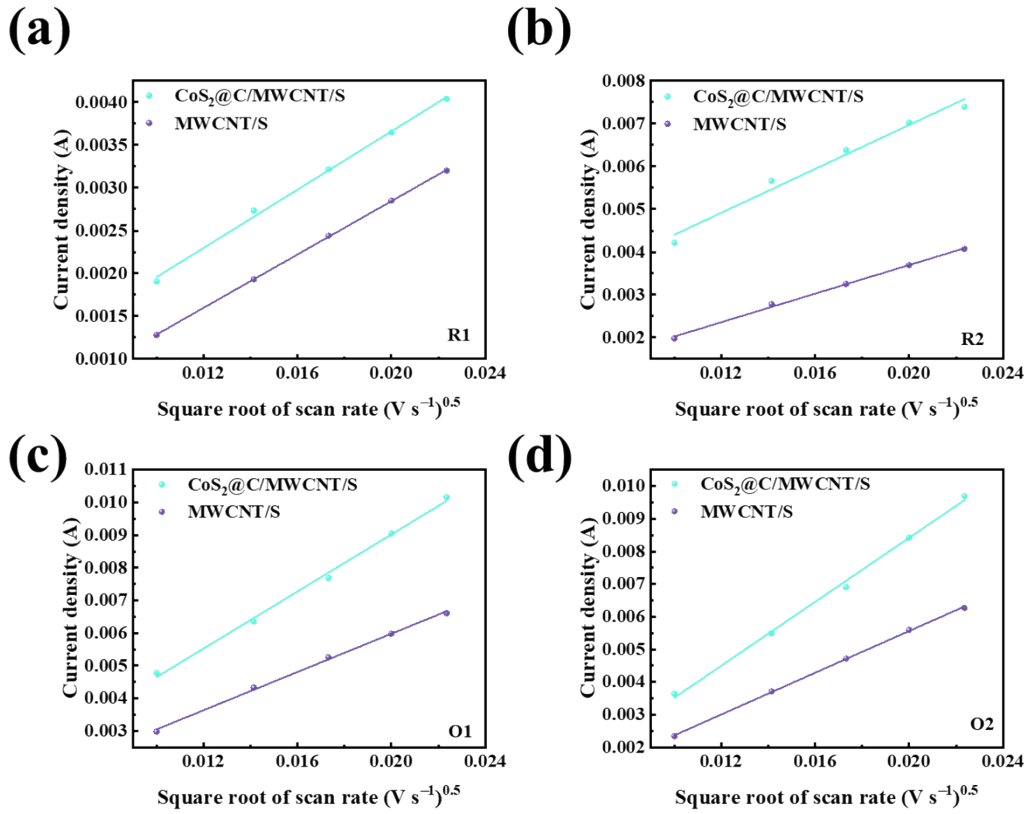

Fig. S11. Lithium-ion diffusion rate corresponding to the reductions and oxidations of (a) R1, (b) R2, (c) O1, and (d) O2.

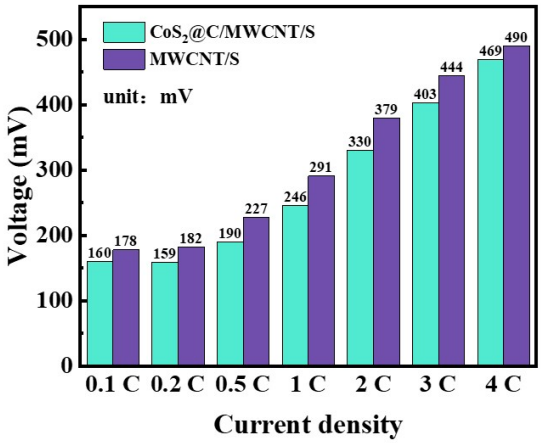

Fig. S12. Polarization voltage for CoS_2@C/MWCNT/S and MWCNT/S cathodes at different rates from 0.1 to 4 C.

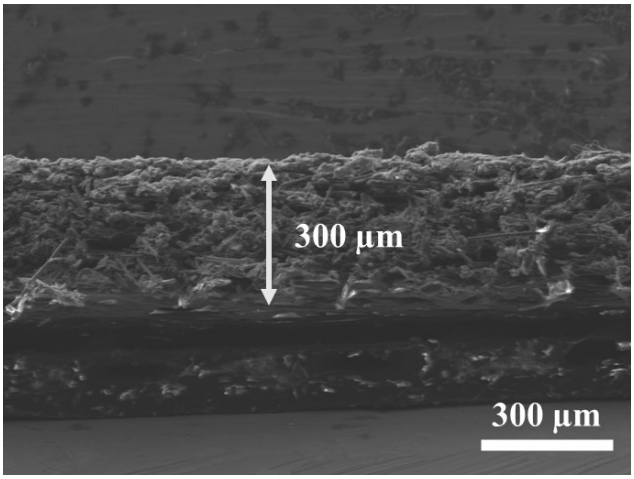

Fig. S13. Cross-sectional SEM image of the CoS_2@C/MWCNT/S cathode.