Supporting Information for Stable High Performance Li-S Battery with a Polysulfide Ions Blocking Layer

S1 *Detail of the experiment*.

Preparation of CBO: 1 g of carbon black was first mixed with 14 g of $Na_2S_2O_4$ and dispersed in 400 ml of deionized water (Millipore, 18.2 MΩcm).The pH value was adjusted to 1 by adding H_2SO_4. The aqueous solution was slowly stirred for 3 days at 35 ^oC and then centrifuged 3~5 times. The obtained product was dried at 80 ^oC for 10 hours in the air.

Synthesis of CBO: S: 100 mg of CBO and 1400 mg of $Na_2S_2O_3$ was first dispersed in 400 ml of deionized water and then sonicated for 2 hours. 560 μL of H_2SO_4 was first dispersed in 300 mL of H_2O and then slowly added into the CBO/$Na_2S_2O_3$ solution. Finally, the precipitate was filtered and washed with deionized water several times to eliminate salts and impurities. After filtration, the precipitate was dried at 50 ^oC for 10 hours. The CB:S composite was obtained through the same progress.

Fabrication of CBO:S cathode and the coating of PIBL: The obtained CBO:S was mixed with the CBO and polyvinylidene difluoride (PVDF) at a weight ratio of 8:1:1 and then dispersed in N-methyl-2-pyrrolidinone (NMP) by sonication for 20 min. The solution was loaded onto an Al foil and then put in a drying oven in the air for 10 hours. As received PEDOT: PSS solution (Heraeus AI 4083, solid content: 1.3~1.7%) was first mixed with ethanol (1:1 vol%) and dripped on the electrode with a pipette. The amount of the PEDOT: PSS/ethanol solution was 12, 24, and 40 μL for different

electrodes (The area of the electrode was ~1.76 cm^2) and the weight of the PEDOT: PSS polymer for every electrode was obtained by weighting the electrode before and after the polymer coating.

Electro-chemical test: For electro-chemical test, 2032 type coin cells were fabricated using lithium foil as the counter electrode and the electrolyte was lithium bis-rifluoromethanesulfony-imide (0.8M, Sigma-Aldrich) and $LiNO_3$ (0.2 M, Sigma-Aldrich) in 1,2-dimethoxyethane and 1,3-DOL (1:1 vol%, Sigma-Aldrich). Porous polypropylene separator (Celgard 2400, Inc., USA) was used between the cathode and anode. The process was finished in a glove box filled with Ar. The cells were cycled from 1.8 to 3.0 V versus Li^+/Li. Specific discharge/charge capacities were calculated based on the mass of S. The test of cycle performance was finished using a MACCOR 4000 battery testing system and the CV test was carried out with a CHI 660D electrochemical work station. All the electrochemical measurements were obtained at a room temperature.

Characterization: SEM was measured on a Philips XL30 FEG scanning electron microscope. XRD was collected on a XRD Philips X'Pert. TGA measurement was performed using a TGA Q50.

S2 IR spectra of carbon black before (CB) and after (CBO) functionalization

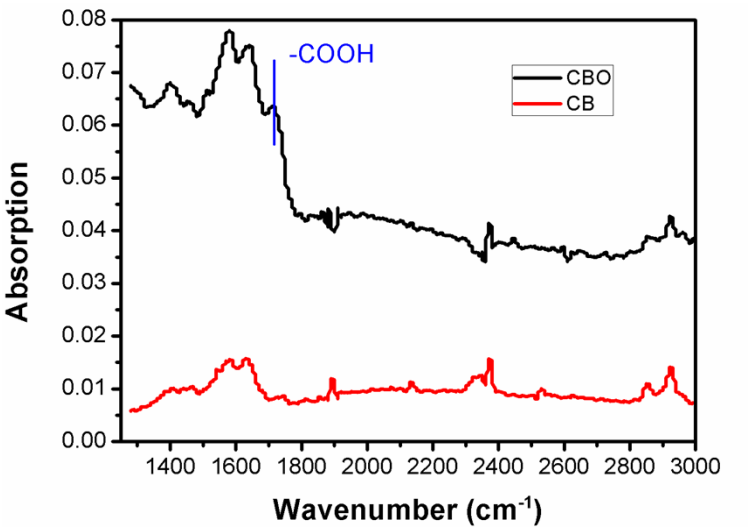


Figure S1 IR spectra of carbon black before (CB) and after (CBO) functionalization.

S3 Capacity of the cathode with CB:S and CBO:S as the active material

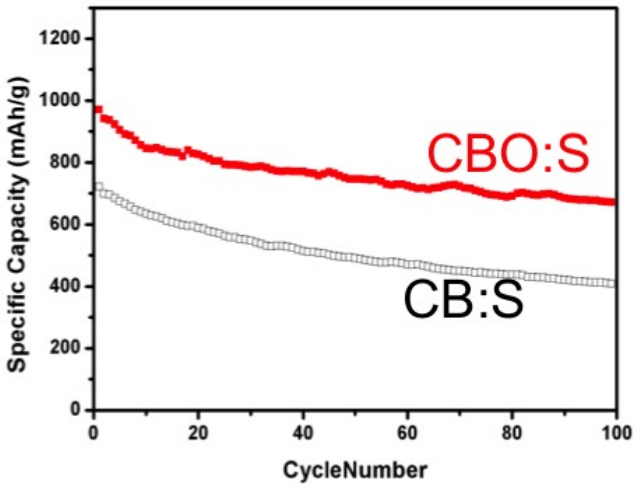


Figure S2 Capacity and cycle stability of the cathodes with CB:S and CBO:S as active materials.

As shown in figure S2, CB:S cathodes shown a similar cycle stability as the CBO:S cathode. However, the latter shown a much higher capacity than the former throughout the 100 cycles.

S4 Cycle stability of the cathodes with different thickness of PIBL

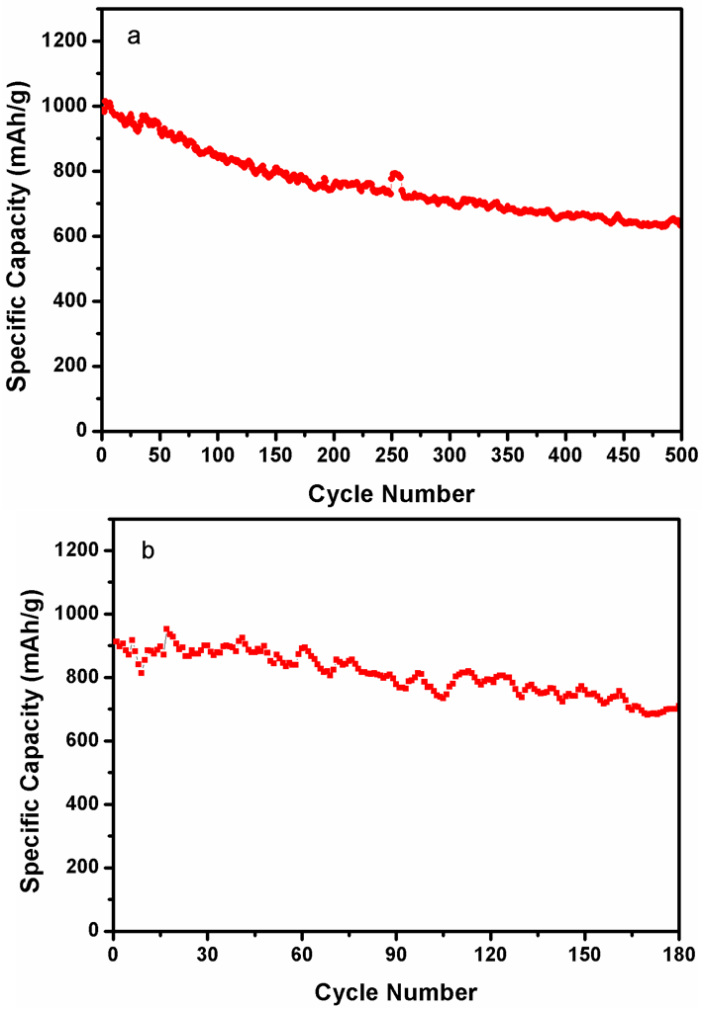


Figure S3 Specific cycle stability of the CBO:S cathodes with PIBLs of different thicknesses. The amount of the PEDOT: PSS PIBL used is about (a) 0.07and (b) 0.25 mg/cm^2.

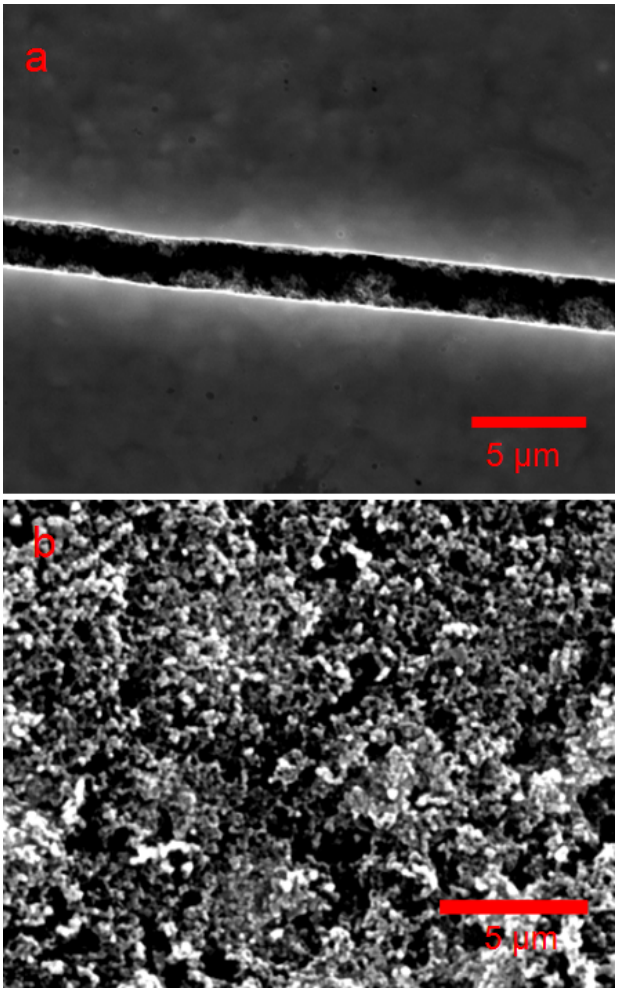
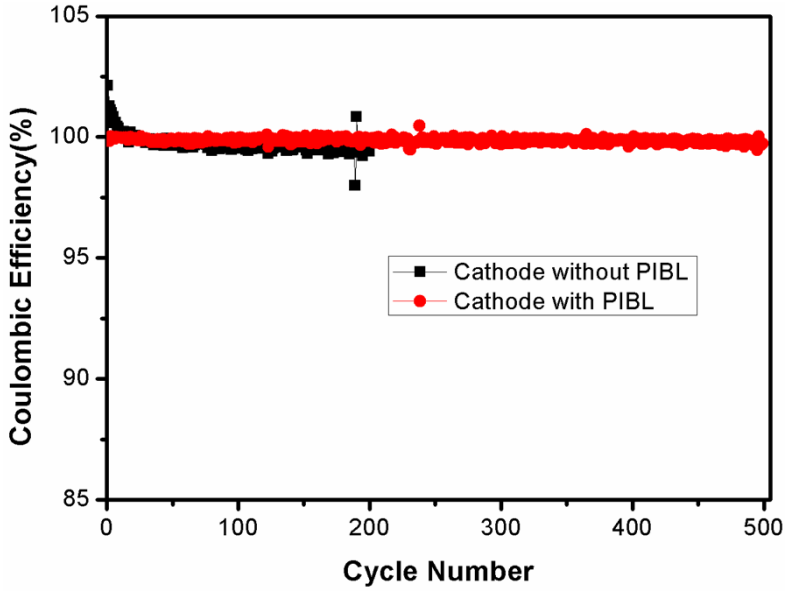


Figure S4 SEM images of the top view of the S cathode coated with (a) 0.25 and (b) 0.07mg/cm^2.

S5, Coulomb efficiency of the coin cells with $LiNO_3$ in the electrolyte



S6 Cycle stability performance and coulomb efficiency of the coin cells without $LiNO_3$ in the electrolyte.

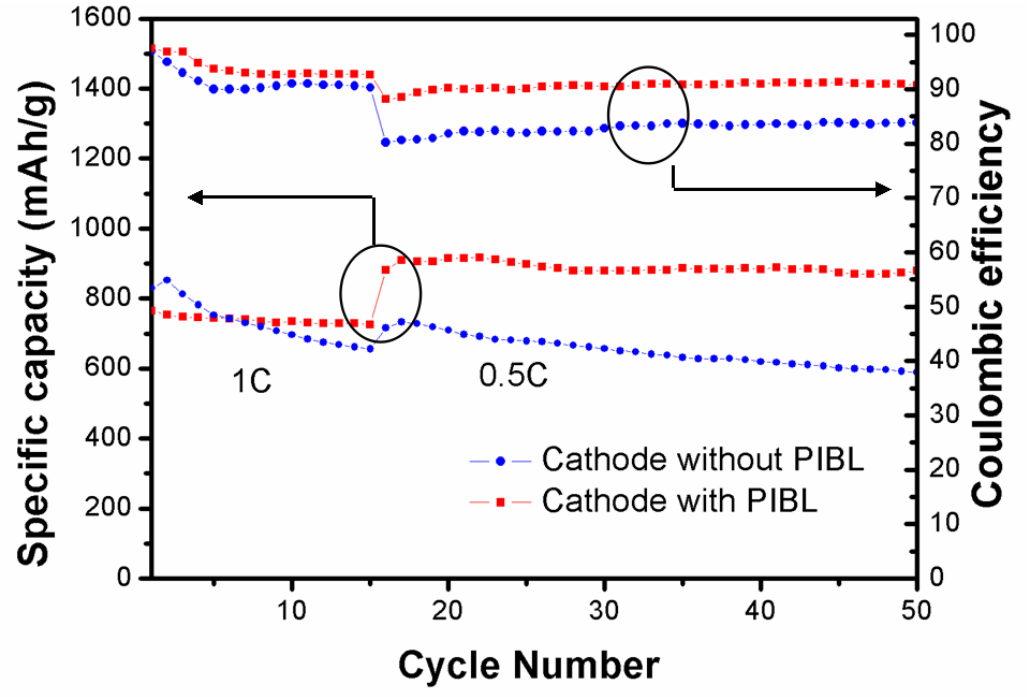


Figure S6 Cycle stability and coulomb efficiency of the cathode with and without the PIBL at 0.5 C and 1 C. The electrolyte was lithium bis(rifluoromethanesulfony)imide (1M) in 1,2-DME and 1,3-DOL (1:1 vol%).The cells were cycled from 1.8 to 3.0 V versus Li^+/Li.

S7 The electrochemical impedance spectroscopy for cathodes with and without PIBL.

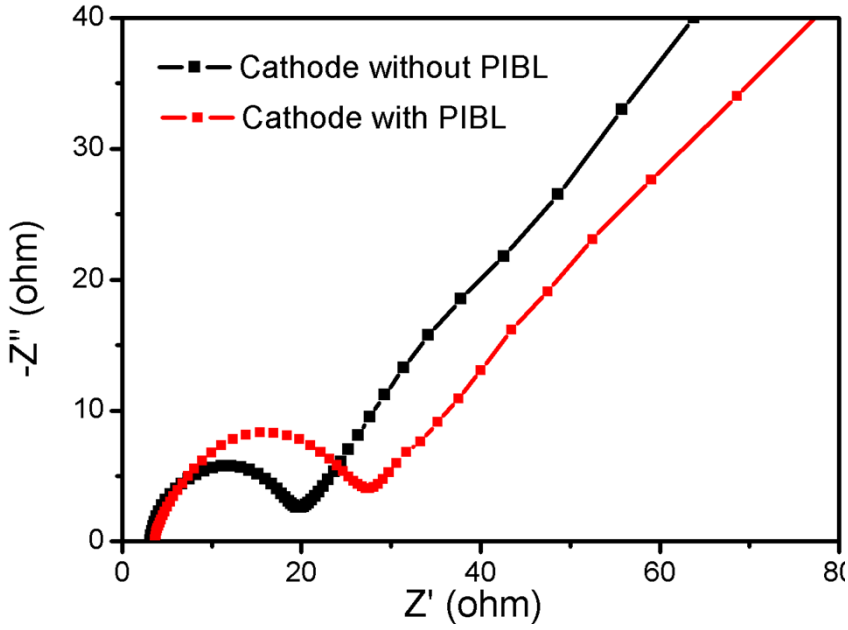


Figure S7 Electrochemical impedance spectroscopy of cathodes with and without PIBL before cycling.

As is shown in figure S7, the charge-transfer resistance of the cell with PIBL is larger than that of the one without PIBL, which is consistent with the observation that the cell without the PIBL shows a slightly higher initial capacity at 3350 mA/g (2C), while the one with the PIBL could retain a much higher capacity at low current rating after cycling.