## **Supporting Information**

# An *in-situ* confinement strategy to porous poly(3, 4ethylenedioxythiophene)/sulfur composites for lithium–sulfur batteries

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## **1 Experimental Section**

### 1.1 Preparation of PEDOT/S composites

## Synthesis of DBEDOT:

DBEDOT was synthesized high yield *via* the common bromination method.<sup>1,2</sup> Typically, 14.0 g 3,4-ethylenedioxythiophene (EDOT) was dissolved in solvent mixture of 300 mL chloroform and 150 mL acetic acid. 6.0 g *N*-bromosuccinimide was added to the mixture slowly at 0–5 °C. The mixture stirred for 8 h at room temperature and quenched with de-ionized water. The organic layer was separated, and the water layer was extracted with chloroform. The combined chloroform extract was neutralized with 5% sodium bicarbonate solution, washed with distilled de-ionized water, and dried with anhydrous magnesium sulfate. Solvent remaining from the filtered mixture was evaporated until little solvent was left. Then, the remaining solvent was fully evaporated using a vacuum pump. The light yellow powder was recrystallized from ethanol to produce a white needle-like crystal.

*Synthesis of SBA-15:* For the synthesis of SBA-15 with short pore length, Pluronic P123 (2 g) was dissolved in 60 mL of 2 M HCl at 38 °C. Then tetraethylorthosilicate (TEOS) (4.2 g) was added to the solution with vigorous stirring. The mixture was stirred for 6 min and remained quiescent for 24 h. The mixture was transferred to an autoclave and subsequently heated at 100 °C for another 24 h. The as-prepared SBA-15 was collected by filtration, dried and calcined at 550 °C in air.<sup>3</sup>



Fig. S1 (a) SEM image and (b) small angle XRD pattern of SBA-15.



Fig. S2 SEM image and corresponding EDS mapping of elemental C, O and S.



Fig. S3 (a, b) SEM images and (c, d) TEM images of PEDOT/S composite.



**Fig. S4** (a, b) SEM images of residual PEDOT (The elemental sulfur in the PEDOT/S composite was dissolved by chloroform).



Fig. S5 TG curves of PEDOT/S and pPEDOT/S composites.



**Fig. S6** The equivalent circuit.  $R_e$ : resistance of electrolyte;  $R_{ct}/CPE_2$ : charge-transfer resistance;  $R_1/CPE_2$ : finite diffusion resistance in a thin layer.

#### **Reference:**

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- S3. X. L. Ji, K. T. Lee and L. F. Nazar, Nat. Mater., 2009, 8, 500.