

## Supporting information

### **A carbon sandwich electrode with graphene filling coated by N-doped porous carbon layers for lithium-sulfur batteries**

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**The calculating method of volumetric capacity:**

The gravimetric capacity is based on the mass of sulfur in N-CS while the volumetric capacity was based on the volume of the whole electrode (including N-CS, sulfur, binder PVDF and additive carbon black). The density of the electrode was calculated as the ratio of the mass to the volume of the pallet, the thickness of the pallet was measured by the micrometer and SEM. The diameter of the pallet is 12 mm. The volumetric capacity of the electrode was calculated as the ratio of the gravimetric capacity based on the mass of whole electrode to the density of the whole electrode. In a typical case, the mass of N-CS/S-60 electrode which contains N-CS/S, PVDF and carbon black is 2.6 mg, and its thickness (Al foil is not included) is 39.6  $\mu\text{m}$ . Thus, the density of the N-CS/S-60 electrode is calculated to be 0.58  $\text{g cm}^{-3}$ . The gravimetric capacity of N-CS/S-60 is 1256  $\text{mAh g}^{-1}$  (based on sulfur), and the gravimetric capacity of the whole electrode is 602.9  $\text{mAh g}^{-1}$  ( $1256 \times 0.6 \times 0.8$ , where 0.6 is the sulfur content in N-CS, and 0.8 is the N-CS/S-60 content in whole electrode). Thus the volumetric capacity is calculated to be 349.7  $\text{mAh cm}^{-3}$ .

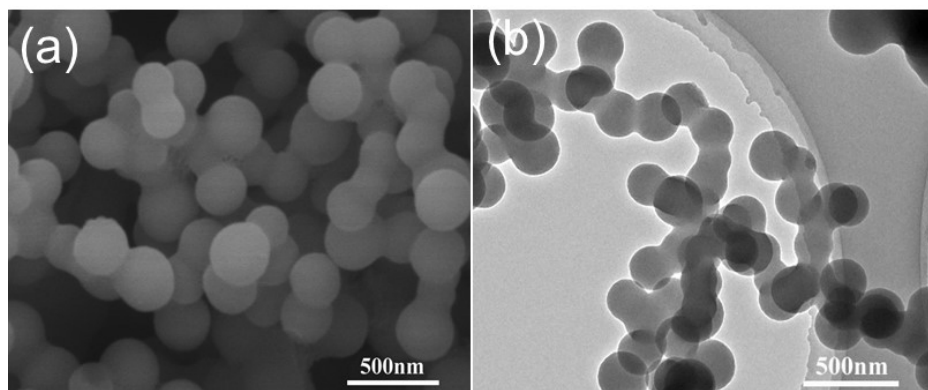


Fig. S1 SEM images of pure carbon spheres (CS) without adding graphene and pyrrole.

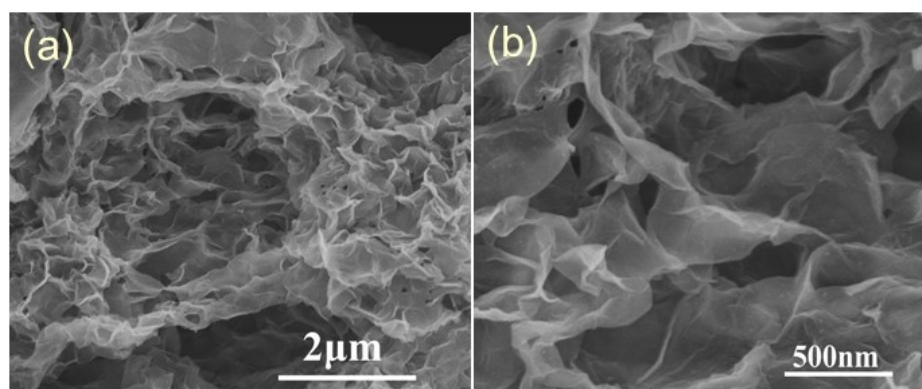


Fig. S2 SEM images of graphene sheets after hydrothermal reaction at 180 °C for 12h.

**Table S1** Pore properties of N-CS and N-CS/S hybrid

Sample	BET total surface area ( $\text{m}^2 \text{g}^{-1}$ )	Total pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	Average pore size (nm)
N-CS	2677.4	1.82	2.72
N-CS/S-60	246.3	0.24	2.89
N-CS/S-70	172.3	0.18	2.96

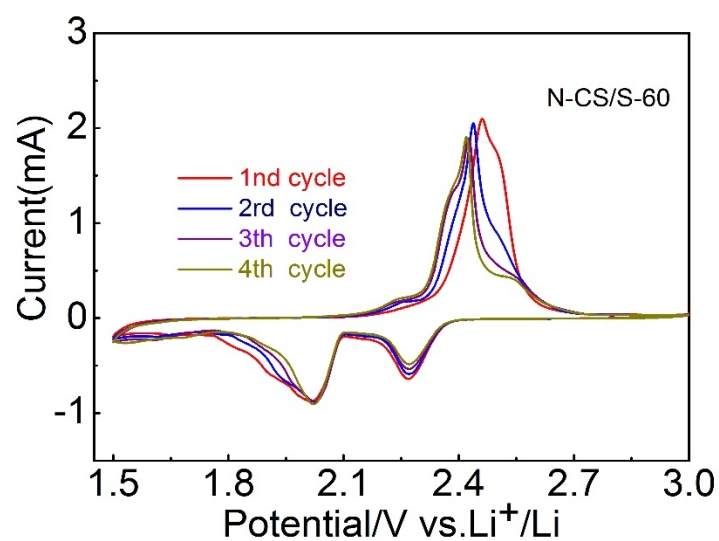


Fig. S3 Cyclic voltammograms of N-CS/S-60 hybrid at a scan rate of  $0.1 \text{mV s}^{-1}$ .

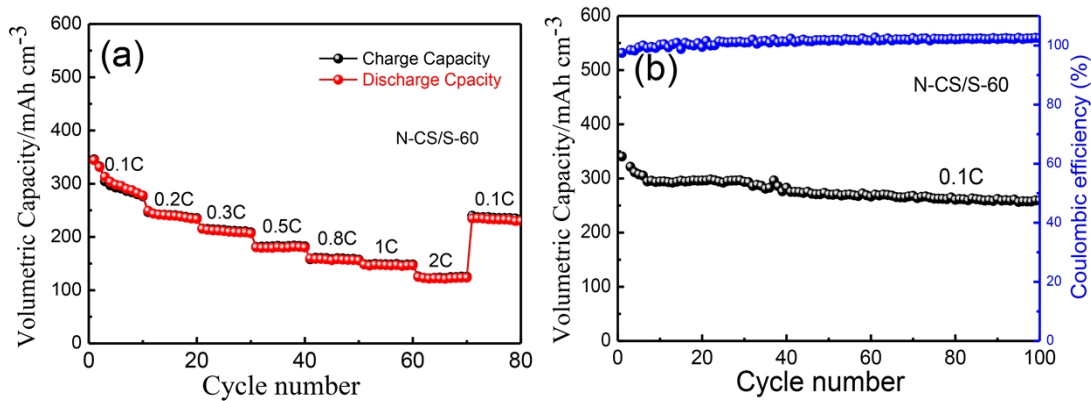


Fig. S4 Volumetric capacity of N-CS/S-60 hybrid cathode at different discharge rates (a) and 0.1C (b).

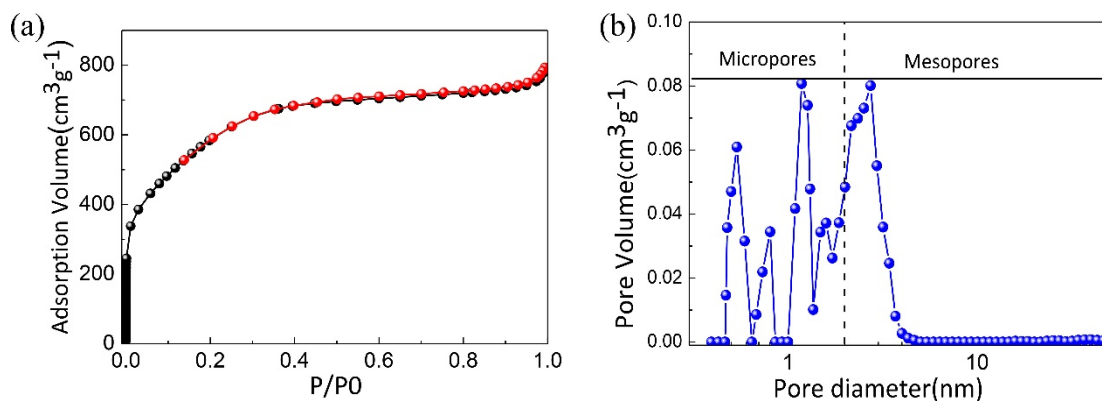


Fig. S5 The adsorption-desorption isotherms (a) and pore size distribution of porous carbon spheres. The porous carbon sphere exhibits a specific surface area of 2157.8 m<sup>2</sup> g<sup>-1</sup> by BET method and a total pore volume of 1.17 cm<sup>3</sup> g<sup>-1</sup> with a broad pore size distribution by the Density Functional Theory (DFT) method.

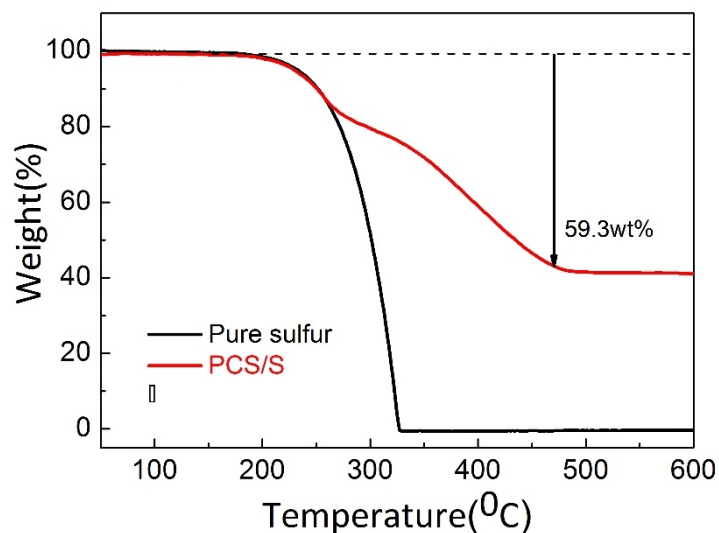


Fig. S6 TG curves of the pure sulfur and the prepared porous carbon sphere /sulfur hybrid in  $N_2$  with a heat rate of  $5\text{ }^\circ\text{C min}^{-1}$ , indicating a sulfur content of 59.3 wt%.

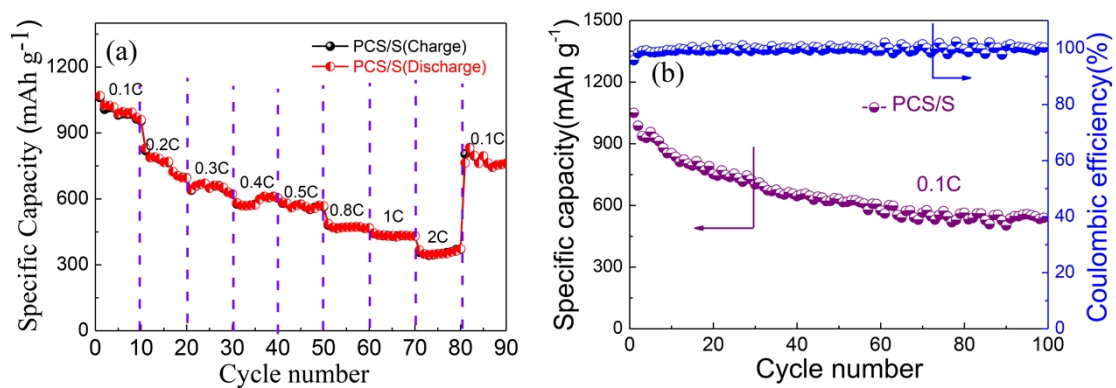


Fig. S7 Electrochemical characterization of porous carbon spheres/sulfur (PCS/S) hybrid in a lithium sulfur battery. (a) Rate performance of PCS/S hybrid at different discharge rates and (b) Cycling performance at 0.1C.

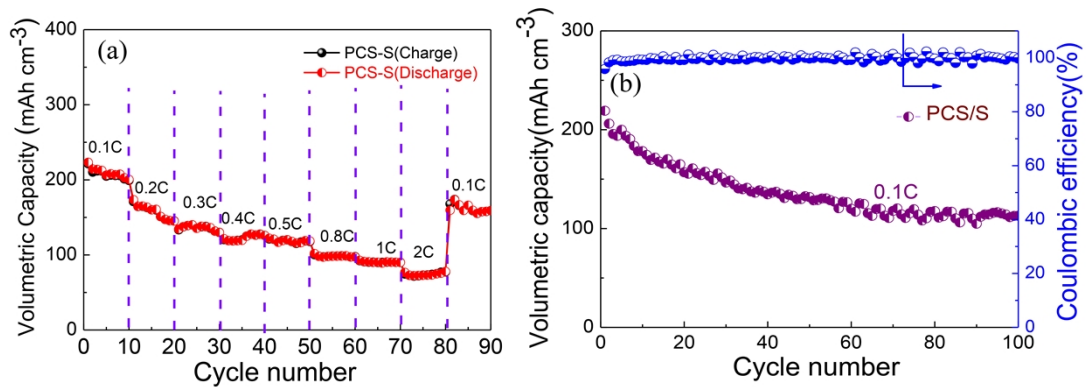


Fig. S8 Volumetric capacity profiles of the reference sample, porous carbon spheres/S (PCS/S) hybrid. (a) At different discharge rates and (b) cycling profile at 0.1C for 100 cycles. The packing density of the PCS/S cathode is 0.44 g cm<sup>-3</sup> and the volumetric capacity of the PCS/S hybrid was stable at 113 mAh cm<sup>-3</sup> at 0.1C after 100 cycles.