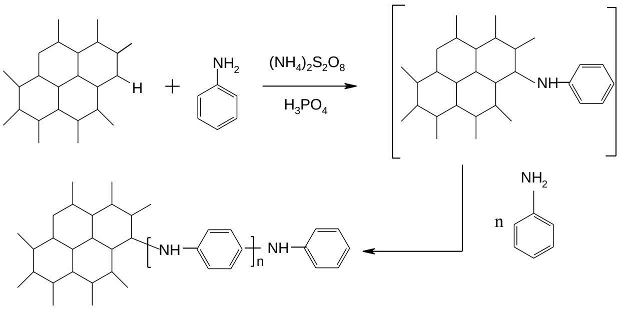
Supporting information

Preparation of the Composites

In a typical experiment, acetylene black (28.0g) was added into ethanol aqueous solution, and the whole mixture was ultrasonicated until a homogeneous black aqueous dispersion was obtained. Then aniline monomer (1.5g), phosphoric acid (2mL) and an aqueous solution of $(NH_4)_2S_2O_8$ (4.6 g dissolved in 200 mL distilled water) were added slowly to the above solution respectively. After stirring rapidly for 2.5 h, C-PANI was obtained. The mixture of $Na_2S \cdot 9H_2O$ (765.0g) and sublimed sulfur (408.0g) was added into distilled water (12L) at 50℃ to form Na_2S_x solution. Subsequently, hydrochloric acid solution (540 mL dissolved in 1L distilled water) and the above Na_2S_x solution were simultaneously added dropwise to the above C-PANI solution. Keep on stirring for 20 min when finished dropping, then the precipitate was filtered and washed repeatedly. The C-PANI-S composite was obtained.

The C-PANI-S composite (200.0g) was added into 2.5 wt.% PVP aqueous solution, and ultrasonicated till forming a homogeneous black aqueous solution. Then aniline monomer (18.6g), phosphoric acid (4mL) and an aqueous solution of $(NH_4)_2S_2O_8$ (57.0 g dissolved in 500 mL distilled water) were added slowly to the above solution respectively. After stirring rapidly for 30 min, the precipitate was filtered and washed repeatedly with distilled water and acetone until the washing solution became transparent and pH value was neutrality. The C-PANI-S@PANI composite was synthesized and dried in a vacuum oven at 50°C for 24 h for subsequent use.

The chemical equation of the synthesis of C-PANI was as follows.



Characterization of the Composites

The morphology of the composites was characterized by a field-emission scanning electron microscope (SEM, S4700) and a transmission electron microscope (TEM, JEM-2100). FTIR spectra were recorded using an FTIR spectrometer (Tensor 27, Bruker). X-ray diffraction (XRD) patterns were recorded with an automated HPC-2500 X-ray diffractometer (Gogaku). The percentage of C, H, N and S element was detected with organic elemental analysis instrument (varioElcube).

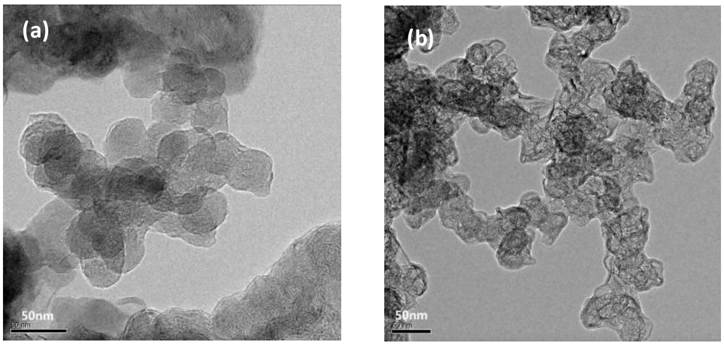


Fig. S1 SEM images of (a) acetylene black and (b) C-PANI particles.

Table 1 Elemental analysis of the C-PANI-S@PANI composite

Composite	Element weight percentage (%)			
	N	C	H	S
C-PANI-S	0.207	6.630	0.085	92.913
C-PANI-S@PANI	1.372	10.160	0.559	86.874

Electrochemical Measurements

The working cathode slurries were prepared by mixing 80 wt.% composite with 7 wt.% acetylene black, 5 wt.% CNTs and 8 wt.% LA binder using n-propyl alcohol as a dispersant. Then the slurries were coated onto Al foil current collector. The sulfur loading in each electrode was about 6 mg cm^{-2}. The electrodes were dried in a vacuum oven at 50℃ for 24 h. Subsequently, soft package lithium-sulfur batteries were assembled with Li foil as anode, 1 M LiTFSI in a mixed solvent of 1,3-dioxolane (DOL) and dimethyl ether (DME) (1:1 by volume) as the electrolyte. The galvanostatic charge/discharge tests were carried out at a current density of 0.2C using a LAND-CT2001A instrument (Wuhan, China). The cut-off potentials for the charge/discharge processes were 1.8 and 2.6 V (versus Li$^+$/Li).

Fig. S2 showed the initial discharge capacity of the C-PANI-S@PANI composite at the rate from 0.2C-5C. The initial discharge capacities were 1101 mAh g^{-1}, 1042 mAh g^{-1}, 982 mAh g^{-1}, 813 mAh g^{-1}, 673 mAh g^{-1}, 488 mAh g^{-1}, 392 mAh g^{-1} respectively at 0.2C, 0.5C, 1C, 2C, 3C, 4C and 5C.

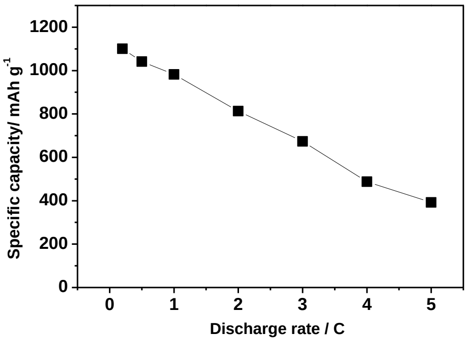


Fig. S2 Rate performance of the C-PANI-S@PANI composite.