

Supplementary information

Cotton Cloth Templated In-situ Encapsulation of Sulfur into Carbon Fibers for Lithium-Sulfur Batteries

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Experimental Section

Materials Used

Sodium sulphate (Na_2SO_4 , anhydrous, Fisher Scientific), poly(acrylonitrile) (PAN), $M_w \sim 150,000 \text{ g mol}^{-1}$, Sigma-Aldrich), polystyrene ($M_w \sim 192,000 \text{ g mol}^{-1}$, Sigma-Aldrich) N, N-Dimethylformamide (DMF, ACS reagent, $\geq 99.8\%$ Fisher Scientific), iron (III) chloride (FeCl_3 , anhydrous, Merck), were used without further purification. Deionized water used in the experiment was doubly distilled before use.

Fabrication of S@C fibers

A cotton cloth was used as the template for the fabrication of S@C fibers. Prior to use, the cotton cloth was washed by acetone and DI water for several times and then dried overnight at $60 \text{ }^\circ\text{C}$ in vacuum oven. The cleaned cotton cloth was cut into square pieces of $2 \times 4 \text{ cm}$, immersed in $1 \text{ M Na}_2\text{SO}_4$ aqueous solution and stirred for 30 min to fully soak in the solution. Then, the cotton cloths were taken out of the solution, squeezed, and dried at $60 \text{ }^\circ\text{C}$ in a vacuum oven for 12 h. The Na_2SO_4 treated cotton cloths ($\text{Na}_2\text{SO}_4/\text{CC}$) were then dipped in 5 wt.% PAN/PS (90:10) in DMF solution. Afterward, the PAN/PS coated $\text{Na}_2\text{SO}_4/\text{CC}$ were heated at $900 \text{ }^\circ\text{C}$ for 2 h with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ under continues flow of nitrogen in a horizontal tube furnace to obtain $\text{Na}_2\text{S@carbon}$ ($\text{Na}_2\text{S@C}$) cloth. The product was immersed in 0.6 M FeCl_3 aqueous solution for 12 h to form S@C fibers. Finally, the obtained S@C was washed several times with DI water and dried at $60 \text{ }^\circ\text{C}$ overnight.

Materials characterization

The scanning electron microscope (SEM, ZEISS EVO 50), field emission SEM equipped with energy-dispersive X-ray spectroscopy (EDS) elemental mapping (JEOL JSM 7800F Prime),

X-ray diffractometer (Rigaku Ultima IV diffractometer with Cu K α radiation of $\lambda = 0.154$ nm) and Raman spectrometer (Horiba, France) were employed for the morphological and structural characterization of the as-prepared materials. Differential scanning calorimeter (DSC, TA Q2000 DSC instrument) was used to characterize the in-situ synthesized sulfur. Thermogravimetric analysis was conducted with TGA-4000 Perkin Elmer at a heating rate of 10 °C min^{-1} under continuous nitrogen flow to measure the amount of sulfur present in the as-synthesized material.

Preparation of sulfur cathode and cell assembly

S@C electrodes were prepared from a slurry composed of the as-synthesized S@C fibers, Super P and PVDF in a weight ratio of 70:20:10. Using a doctor blade, the slurry was pasted onto a carbon cloth, which is obtained by the thermal annealing of a cotton cloth at 800 °C under nitrogen environment. The slurry pasted carbon cloth was dried at 60 °C for 24 h in a vacuum oven, then punched to obtain electrodes of 10 mm diameter and were compacted by a roll press. The areal sulfur loading of the electrodes was ~ 2 mg cm^{-2} . For comparison, bare S cathodes of similar areal sulfur loadings was also prepared by same slurry coating method using bare sulfur instead of S@C, mixed with super P and PVDF. To evaluate the electrochemical performance, LSB cells were assembled in CR2016 coin-type test cells in an inert atmosphere glove box with S@C cathode or bare sulfur cathode as working electrode, lithium foil as counter and reference electrode and Whatman glass fiber paper as separator. The electrolyte was supplied by TOB New Energy, China, which was consisting of 1 M lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) in a mixed solvent of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 in volume) with 1% lithium nitrate (LiNO_3). A controlled amount of electrolyte with maintaining ~ 15 $\mu\text{L}_{(\text{electrolyte})}$ $\text{mg}^{-1}_{(\text{sulfur})}$ electrolyte/sulfur (E/S) ratio was placed on the cathode facing the

anode side and $\sim 14 \mu\text{L cm}^{-2}$ electrolyte was placed on two sides of the Whatman glass fiber separator equally.

Electrochemical Measurements

The cyclic voltammetry (CV) was conducted at a scan rate of 0.1 mV s^{-1} in the voltage window of 1.7 to 2.8 V (vs. Li/Li⁺). The galvanostatic cycling at different C-rates (1C = 1675 mA g^{-1} , based on the mass of sulfur in the electrode) were performed in the potential range of 1.7 to 2.8V (vs. Li/Li⁺). All the electrochemical tests were performed with BioLogic BCS-810 electrochemical workstation under ambient temperature conditions.

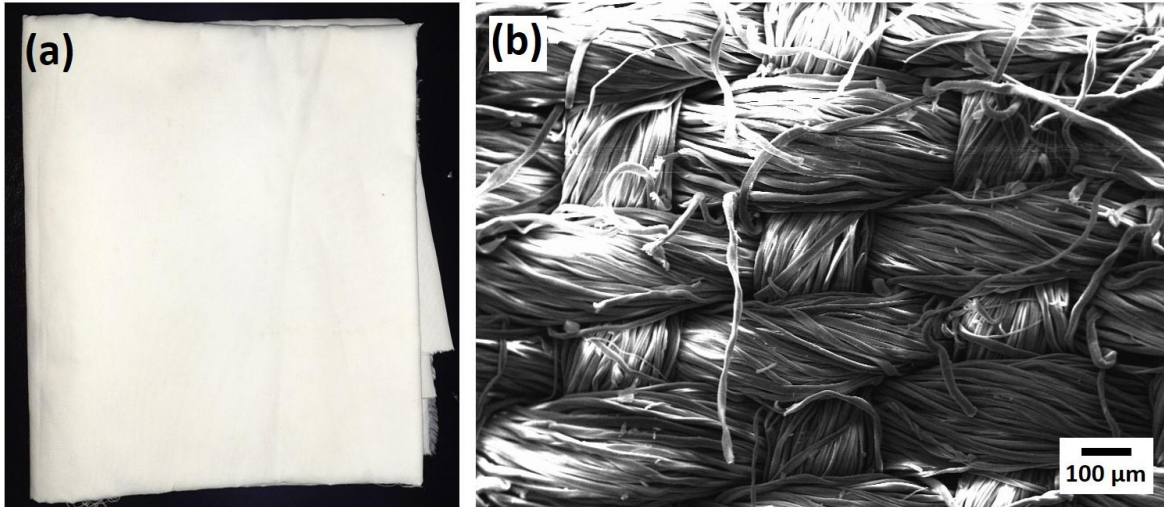


Fig. S1 (a) Digital photograph and (b) SEM image of the cotton cloth.

Fig. S1 shows the digital photograph and SEM image of the cotton cloth used throughout the experiment. As displayed clearly, the cotton cloth exhibits a woven structure consisting of bundle of interweaved cotton fibers. The diameter of single cotton fiber ranges from ~ 10 to $15 \mu\text{m}$.

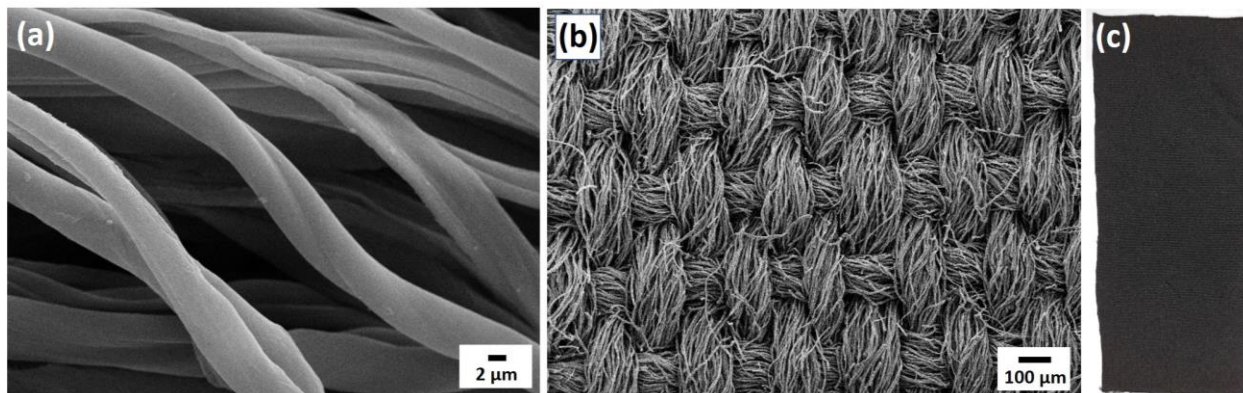


Fig. S2 (a) High magnification, (b) low magnification SEM images and (c) digital photograph of a piece of cotton derived carbon fiber cloth obtained by annealing cotton cloth at 900 °C under nitrogen atmosphere.

Fig. S2 shows the SEM images and digital photographs of a piece of carbon cloth derived by the carbonization of cotton cloth during high temperature thermal annealing process. The low magnification image in fig. S2b clearly represent that the overall morphology retaining a woven structure after the annealing. However, the fiber diameter decreased to ~ 4 to $7 \mu\text{m}$ as clearly observed in fig. S2a.

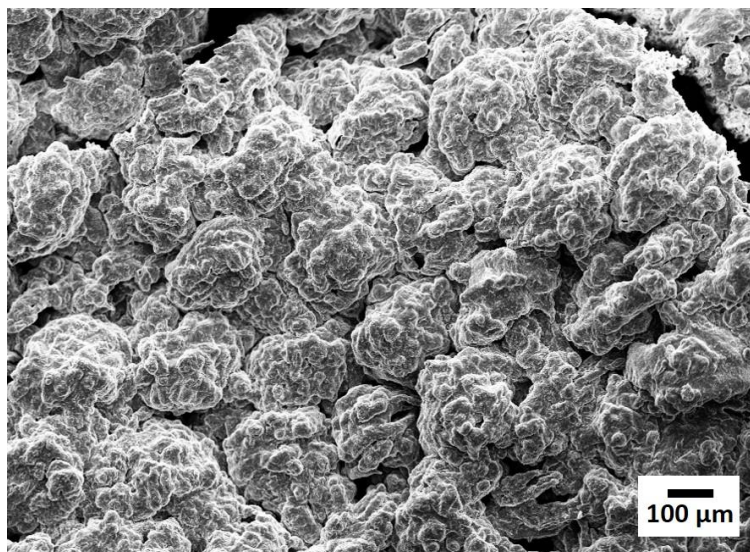


Fig. S3 Morphology of Na_2SO_4 treated cotton cloth after annealing at $900\text{ }^\circ\text{C}$ under nitrogen.

Fig. S3 demonstrates that the fibrous structure of cotton collapses after the thermal annealing of Na_2SO_4 treated cotton cloth.

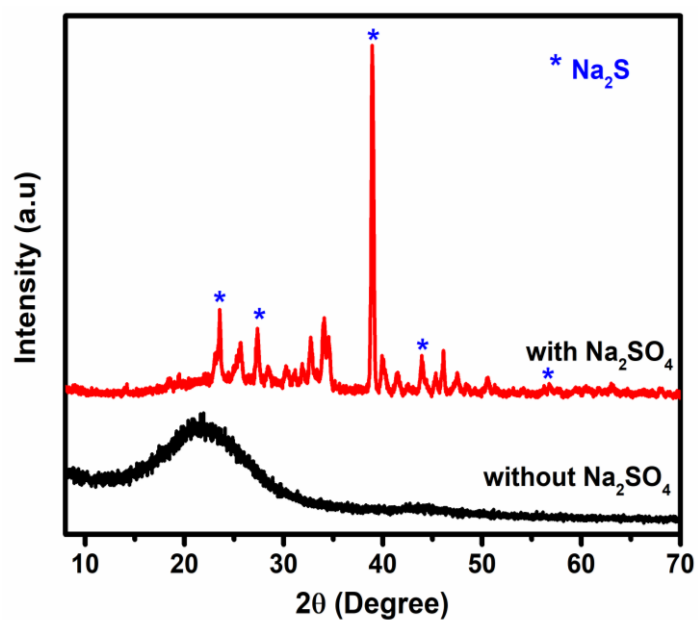


Fig. S4 XRD pattern of annealed cotton cloth (without Na_2SO_4 treatment) displaying the crystalline planes of partially graphitized carbon, and annealed $\text{Na}_2\text{SO}_4/\text{CC}$ (with Na_2SO_4) displaying the characteristic crystalline planes of Na_2S .

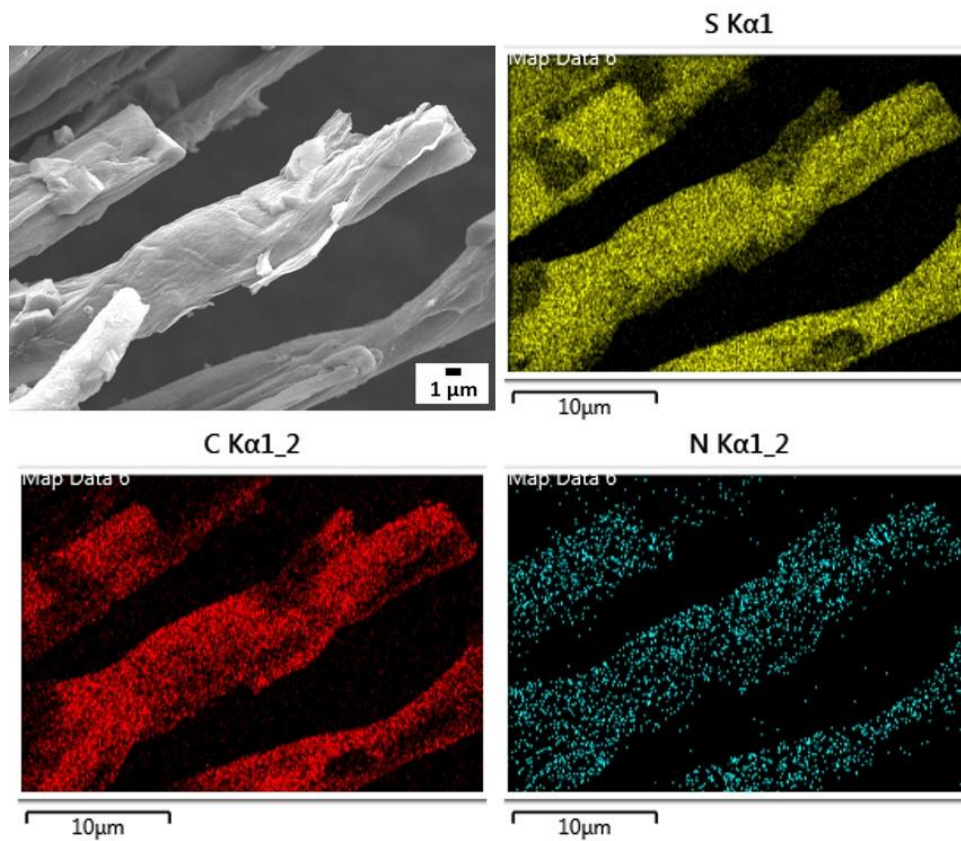


Fig. S5 FESEM image and corresponding energy-dispersive spectrometer (EDS) mapping images of sulfur (S), carbon (C) and nitrogen (N) present in the S@C fibers.

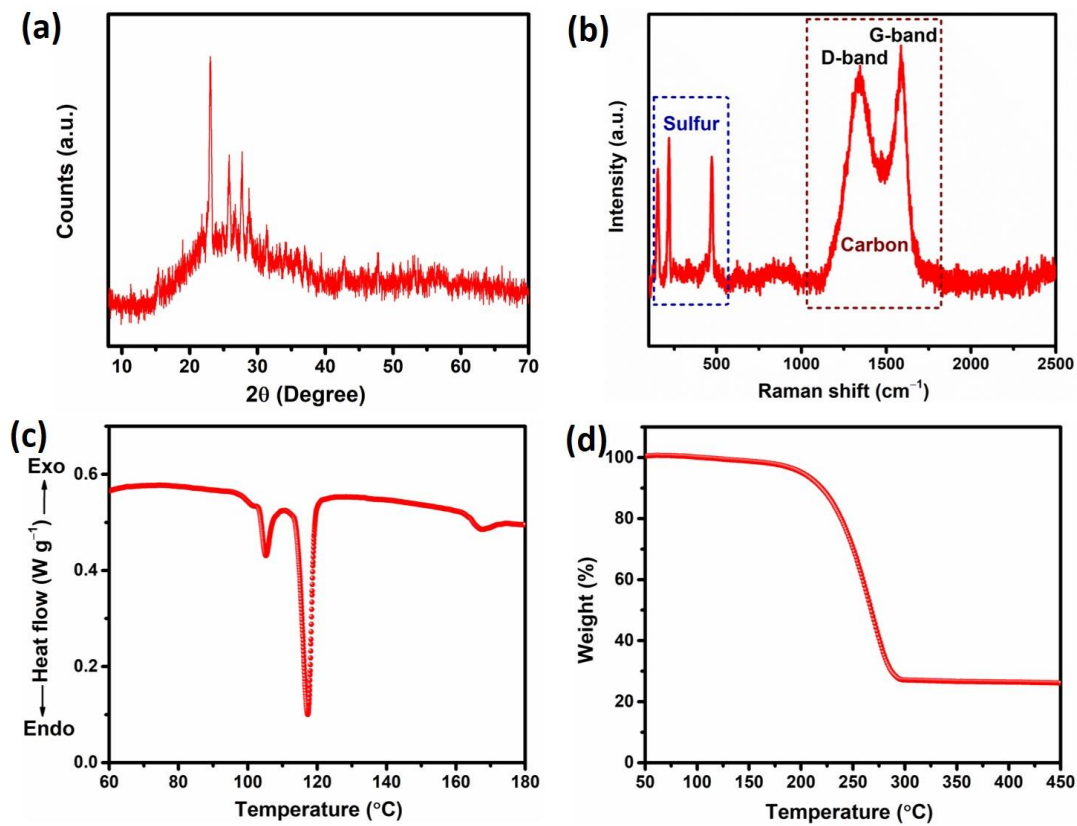


Fig. S6 (a) XRD pattern, (b) Raman spectrum, (c) DSC and (d) TGA curve of S@C fibers.



Fig. S7 Digital photograph of the electrical resistance measurement of the S@C fiber cloth by a digital multimeter.

To roughly examine the electrical resistance of the of S@C fibers, the DC resistance of the as obtained S@C fiber cloth was measured by a digital multimeter. The size of the tested S@C fiber cloth was about $1.8 \text{ cm} \times 1.2 \text{ cm} \times 250 \text{ }\mu\text{m}$. This shows the S@C fibers have low contact resistance even at a high sulfur loading of $\sim 71\%$.

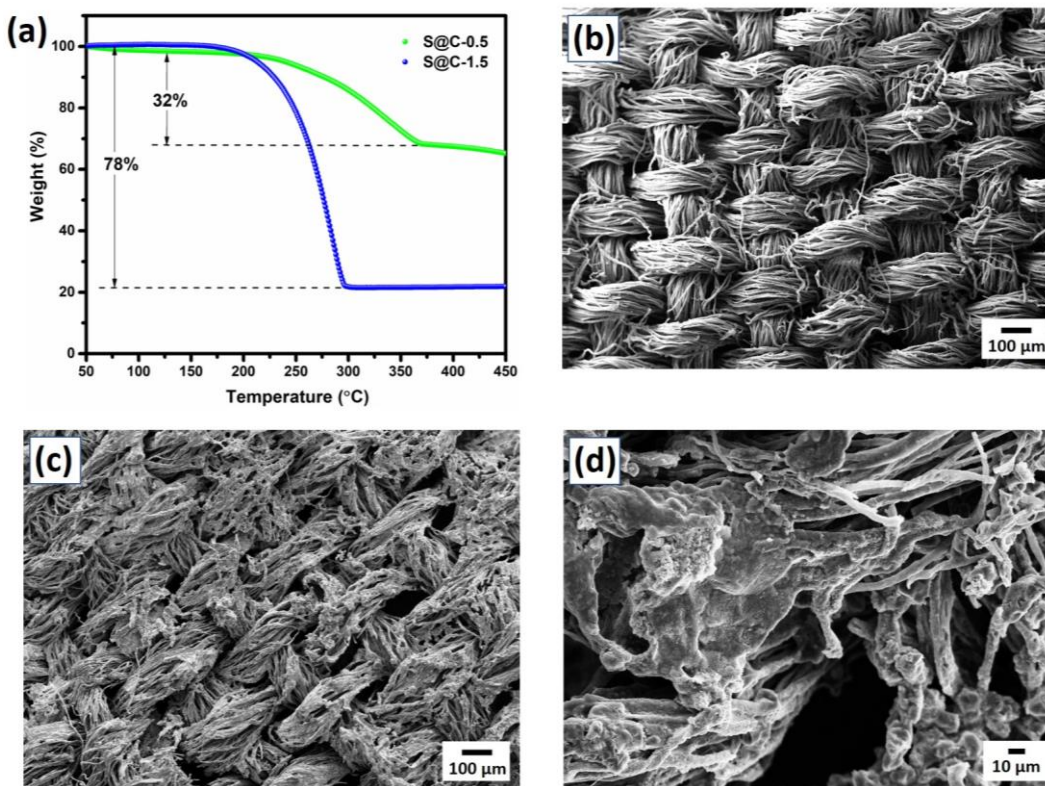


Fig. S8 (a) The TGA curve of S@C fibers fabricated from the Na_2SO_4 treated cotton cloth prepared with 0.5M (S@C-0.5) and 1.5M Na_2SO_4 aqueous solution (S@C-1.5). SEM image of (b) S@C-0.5 and (c) S@C-1.5. (d) High magnification SEM image of S@C-1.5.

Since the variation of Na_2SO_4 concentration plays a critical role for the synthesis and loading of sulfur in S@C, the cotton fabrics were also treated with 0.5M and 1.5M Na_2SO_4 aqueous solutions to prepare $\text{Na}_2\text{SO}_4/\text{CC}$ -0.5 and $\text{Na}_2\text{SO}_4/\text{CC}$ -1.5, respectively. They were further used for the fabrication of S@C fibers following a similar method to that of the $\text{Na}_2\text{SO}_4/\text{CC}$ prepared with 1M Na_2SO_4 . The TGA curve (Fig. S8a) showed that the S@C fabricated from $\text{Na}_2\text{SO}_4/\text{CC}$ -0.5M (S@C-0.5) exhibited a sulfur content of only ~32%, whereas that with $\text{Na}_2\text{SO}_4/\text{CC}$ -1.5 (S@C-1.5) exhibited ~78% sulfur content. It indicates that the sulfur content in S@C increases with increase in the concentration of Na_2SO_4 , however, the increase in the sulfur content become limited above 1M concentration of Na_2SO_4 (~71%). Moreover, at higher

concentration of Na_2SO_4 , the fibrous structure of S@C ruptures due to the excess Na_2SO_4 that react with the carbon present in the shell. This was confirmed by the morphological analysis of both the samples (S@C-0.5 and S@C-1.5) by SEM. The S@C-0.5 showed a well-maintained woven structure with the individual S@C-0.5 fibers retaining the fibrous morphology (Fig. S8b). However, the S@C-1.5 showed the partial collapse of fibrous morphology at various regions (Fig. S8c and d). Such collapse of fibrous morphology would be unable to retain the sulfur as the core.

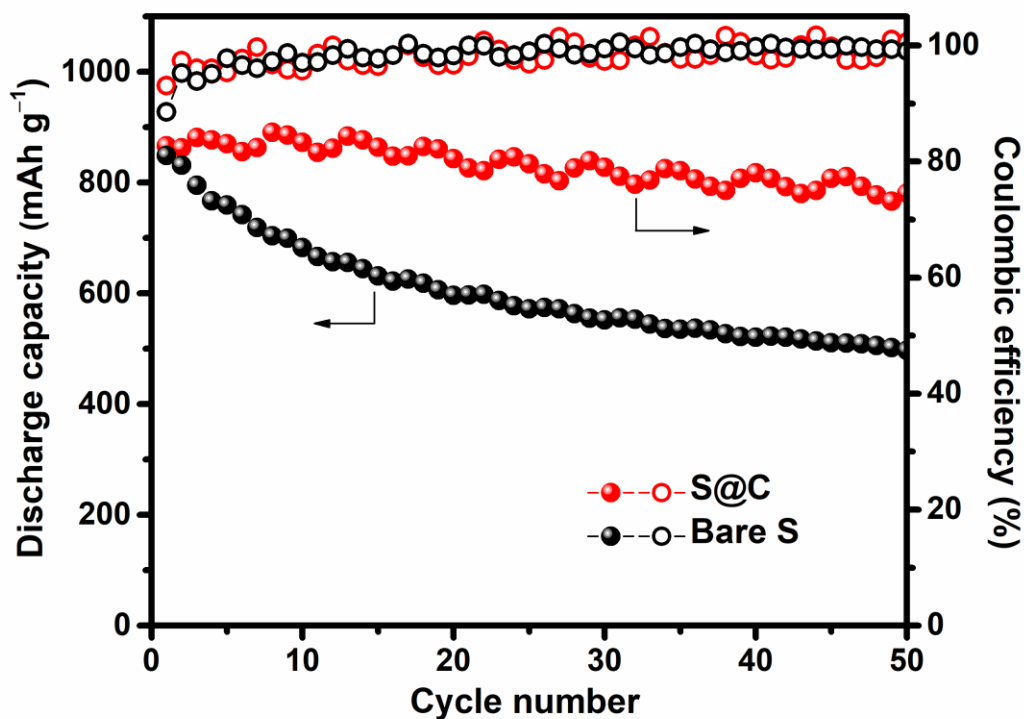


Fig. S9 Cycling performance at 0.2 C-rate of the S@C electrode and bare sulfur electrode with Celgard 2400 separator.

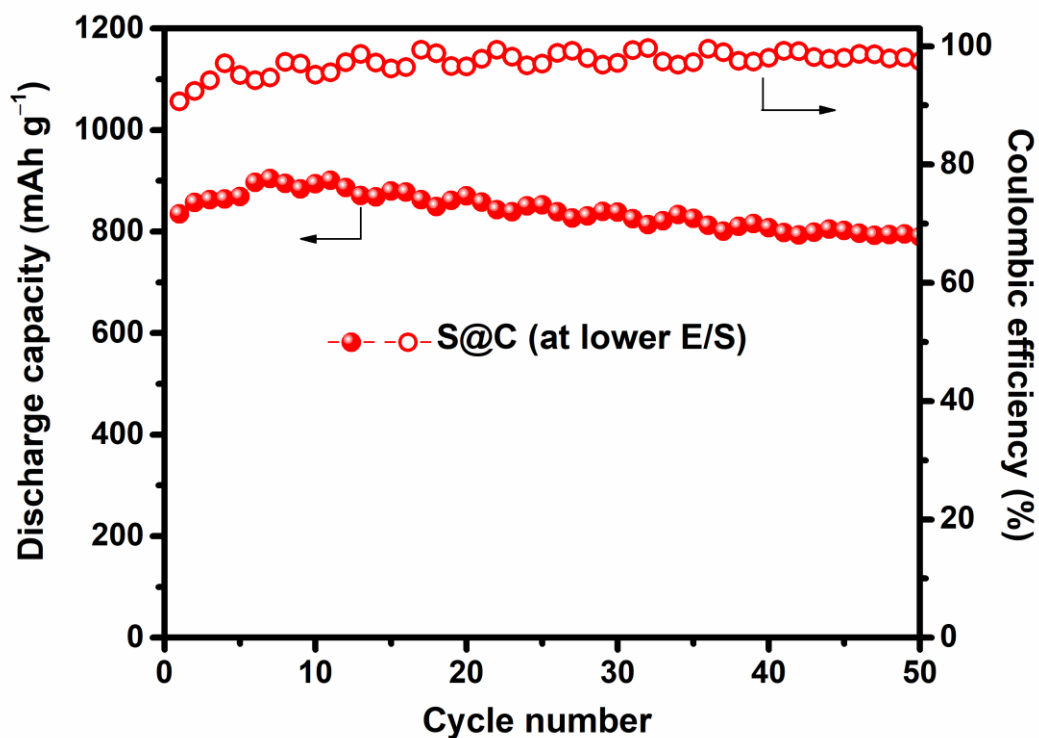


Fig. S10 Cycling performance at 0.2 C-rate of the S@C electrode at low E/S ratio.

To test the electrochemical performance of S@C electrode at lower E/S ratio, a lower amount of electrolyte with maintaining $\sim 3 \mu\text{L}_{(\text{electrolyte})} \text{mg}^{-1}_{(\text{sulfur})}$ electrolyte/sulfur (E/S) ratio was placed on the S@C cathode facing the anode side and $\sim 5 \mu\text{L cm}^{-2}$ electrolyte was placed on the Celgard 2400 separator. Even at such low E/S ratio, the S@C electrode displayed a promising electrochemical performance with a discharge capacity retention of 94.5% of its initial capacity after 50 cycles as shown in Fig. S10.

Table S1. Comparison of LSB performance with some reported biomass derived carbon-sulfur hybrids.

Cathode (Source of biomass carbon)	Sulfur content (%)	Sulfur loading (mg cm ⁻²)	Specific discharge capacity (mAh g _{sulfur} ⁻¹)		Capacity retention (%)	C-rate	Ref.
			Initial	After cycling			
OPC/S (Peony shell)	71.5	1.6	792.2	458.6 (200 cycle)	57.9	0.2	S1
S/MCS-20-60 (Chitosan)	60	N/A	969	642 (100 cycle)	Ca. 66.2	0.2	S2
C-hemp-S (Hemp fiber)	N/A	3	874	Ca. 594 (100 cycle)	68	0.1	S3
OPWC/S (Onion peel)	52.5	N/A	798	630 (100 cycles)	Ca. 78.9	0.1	S4
BPC/S (Bamboo stem)	47.6	1.5 – 2.1	893.64	453.3 (100 cycles)	49.6	0.1	S5
S/ONPC (Coffee grounds)	47.6	Ca. 2	1150	613 (100 cycles)	Ca. 53.3	0.2	S6
BCF/S (Bamboo sticks)	60	1.5	1014	447 (200 cycles)	40	0.2	S7
S@C (Cotton cloth)	71	Ca. 2	844.6	439.7 (100 cycle)	Ca. 52.06	0.2	This work

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