

Supplementary Information

Traditional Chinese medicine residue-derived micropore-riched porous carbon frameworks as efficient sulfur hosts for high-performance lithium-sulfur batteries

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1 The synthesis of MRNCFs

The roots of *acanthopanax senticosus* were boiled for 2h at ordinary pressure and the liquid was extracted. Subsequently, the residues were dried 24 h at 80 °C. After smashing, 500mg of residue powder, 500 mg of urea and 80 mL deionized water were placed in a 100-ml Teflon-lined stainless autoclave, successively. Then the autoclave was sealed and undergone a heat treatment of 180 °C in an oven for 12 h. When autoclave cooled to room temperature naturally, dark brown precipitate was filtered and dried at 80°C overnight. The obtained hydrochar was immersed in KOH solution with the mass ratio of KOH to hydrochar (2:1). After standing for 12 h, homogeneous mixture was dried at 80 °C and then transformed to tube furnace. Under N₂ atmosphere, the mixture was activated at 800°C and maintained 1h with a heating rate of 5°C min⁻¹. The extra KOH was removed by 1M HCl. After washing with deionized water and drying at 80°C overnight, MRNCFs-2 was obtained. Meanwhile, MRNCFs-1 and MRNCFs-3 were synthesized by the same method but with the mass ratio of KOH to hydrochar (1:1 and 3:1), respectively.

2 The synthesis of S@MRNCFs and rGO/S@MRNCFs

The obtained MRNCFs was mixed with sulfur with the mass ratio of 4/1 (S / MRNCFs) and grinded for 30 min. Then the mixture was heated at 155°C for 12 h in a Teflon-lined stain-less steel autoclave. After cooling to room temperature, S@MRNCFs was prepared. The ζ-potential of S@MRNCFs(-44.3mV) was changed by 0.5 wt.% polydiallyldimethylammonium chloride (PDDA) aqueous solution containing 40 mM NaCl and 20 mM tris(hydroxymethyl)aminomethane solution. S@MRNCFs was dispersed into above solution and stirred 2h and then free PDDA was removed by washing and centrifugation. 100mg functionalized S@MRNCFs (43.8 mV) was dispersed into 100ml deionized water and 20ml graphene oxide suspension (1 mg ml⁻¹, -42.6 mV) was added and stirred for 12 h. Then 14mg hydrazine (80 wt.%) was added into the above suspension and stirred 12 h at 58°C. After washing by deionized water and dried overnight, reduced graphene oxide coated S@MRNCFs (rGO/S@MRNCFs) was obtained.

3 Characterizations

The scanning electron microscopy (SEM) images and the energy-dispersive spectrometry (EDS) images were obtained using FEI Quanta FEG 250, and the transmission electron microscopy (TEM) tests were carried by a FEI Talos 200F. The N₂ adsorption/desorption experiments were performed on ASAP 2460 at -196 °C. The surface area was obtained by the Brunauer–Emmett–Teller (BET) method and the micropore size distribution was calculated by DFT model. X-ray diffraction (XRD) curves were obtained by a Rigaku Ultimate IV at 10° min⁻¹. Raman spectroscopy was detected by a LabRAM HR Evolution Raman spectrometer with 532 nm laser. X-ray photoelectron spectroscopy (XPS) was obtained using Al Kα radiation (1486.6 eV) as the excitation source by Thermo ESCALAB 250XI.

4 Electrochemical measurements

The sulfur cathode was synthesized by mixing (80wt%) sulfur/carbon composite, (10wt%) PVDF and (10wt%) carbon black (SP) and using N-methyl-2- pyrrolidone (NMP) as solvent. The mixture was stirred for 12h to form a slurry and then the uniform slurry was coated onto an Al foil, dried in a vacuum oven at 60°C overnight, and the foil was sliced to a diameter of 12 mm and an average areal S loading below 0.65 mg cm⁻². For evaluating electrochemical performances, 2025-type coin cells were

assembled in a argon-filled glovebox and Celgard 2400 film as the separator to separate sulfur cathode and lithium metal anode. For each cell, 50 Ml electrolyte of 1.0M lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) in 1, 3-dioxolane (DOL) and 1, 2-dimethoxyethane (DME) (1:1 by volume) with 1 wt % LiNO₃ as additive was added in. Cyclic Voltametric (CV) curves were gotten at a scan rate of 0.1 mV s⁻¹ and electrochemical impedance spectra (EIS) were measured in the frequency range of 100kHz to 10mHz using a CHI660E electrochemical workstation. To test the cycle and rate performance, galvanostatic discharge/charge tests were performed out using LANDTE CT2001A battery test system with a potential range from 1.7 to 2.8 V.

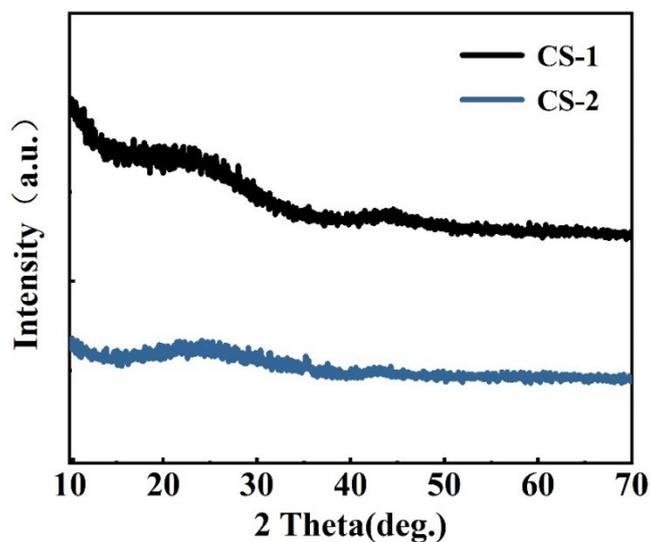


Fig. S1 XRD patterns of CS-1 and CS-2.

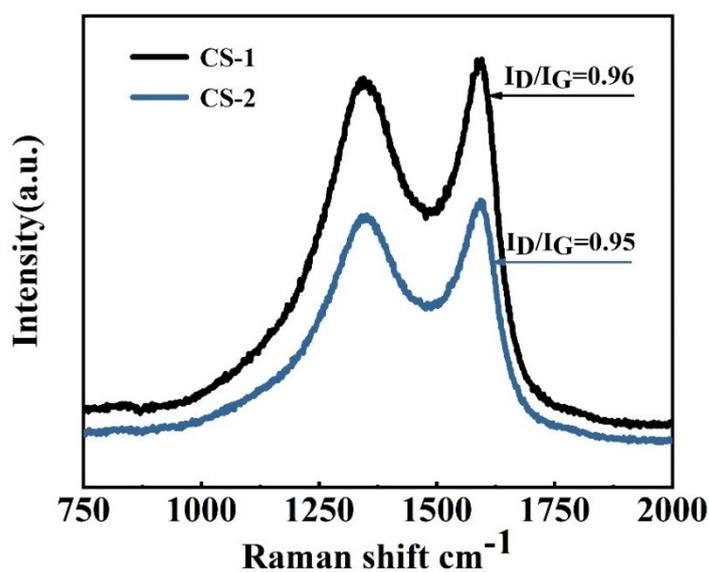


Fig. S2 Raman spectra of CS-1 and CS-2.

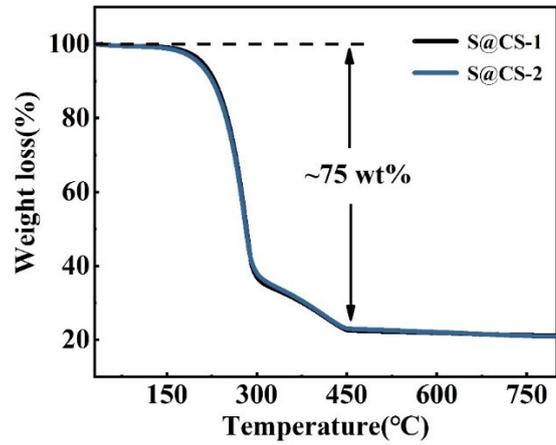


Fig. S3 Thermogravimetric analyses of S@CS-1 and S@CS-2.

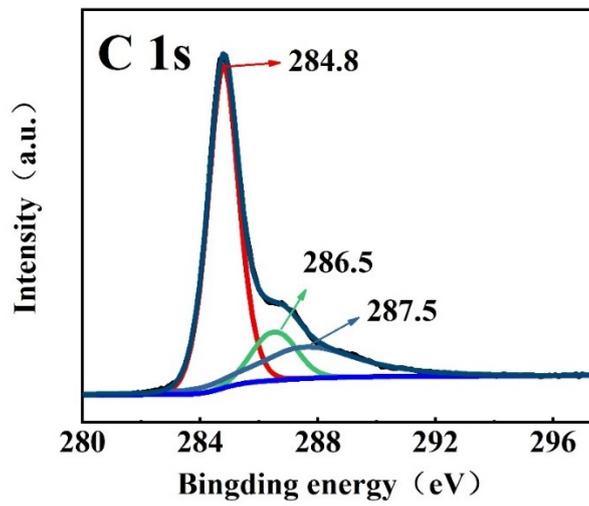


Fig. S4 The high resolution XPS of C 1s peak of MRNCFs.

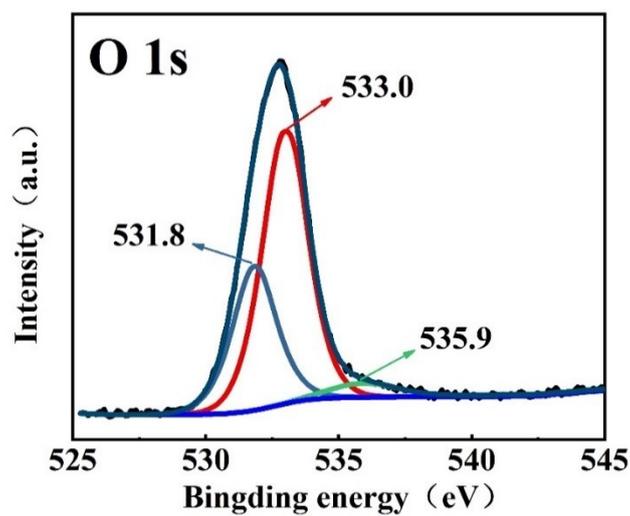


Fig. S5 The high resolution XPS of O 1s peak of MRNCFs.

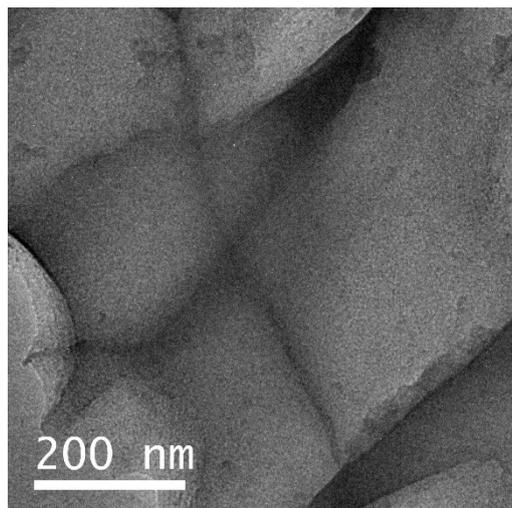


Fig. S6 TEM image of the MRNCFs

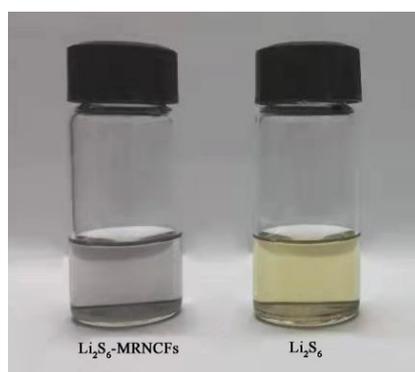


Fig. S7 Adsorption experiments of the Li_2S_6 solution before and after the addition of MRNCFs

Table S1

Textural properties of samples

	S_{BET}^a (m^2g^{-1})	V_{total}^b (cm^3g^{-1})	V_{micro}^c (cm^3g^{-1})
MRNCFs	1415.84	0.7690	0.7148
CS-1	1052.16	0.5545	0.4967
CS-2	1058.99	0.5594	0.4960

a BET specific surface area;

b Total pore volume;

c Microporous volume.

Table S2

Comparison of Li-S battery performance of various carbonaceous materials.

	Initial specific capacity (mAh g^{-1})	S_{BET}^a ($\text{m}^2 \text{g}^{-1}$)	V_{total}^b ($\text{cm}^3 \text{g}^{-1}$)	V_{micro}^c ($\text{m}^2 \text{g}^{-1}$)	Micropore volume/Total volume (%)	S content (%)	Ref.
Green tea	712 (0.1C)	2015	0.727	-	-	68	[1]
Carbon microfiber mesh	550 (0.5C)	581	0.3	-	-	-	[2]
bamboo	540 (~0.48C)	798.1	0.38	-	-	50	[3]
Kapok carbon fibers	537 (~0.3C)	282.38	0.1574	-	-	93.2	[4]
Mandarin peels	~100(0.5)	1077	0.57	0.41	72	50	[5]
Shrimp shell	455 (~0.6C)	1735	0.853	0.643	75.4	63	[6]
Almond shell	300 (0.48C)	967	0.49	0.44	89.8	60	[7]
Olive stones	350 (~0.6C)	587	0.333	0.23	69	80	[8]
This work	590.5 (0.5C)	1415.84	0.769	0.715	93	75	

References

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