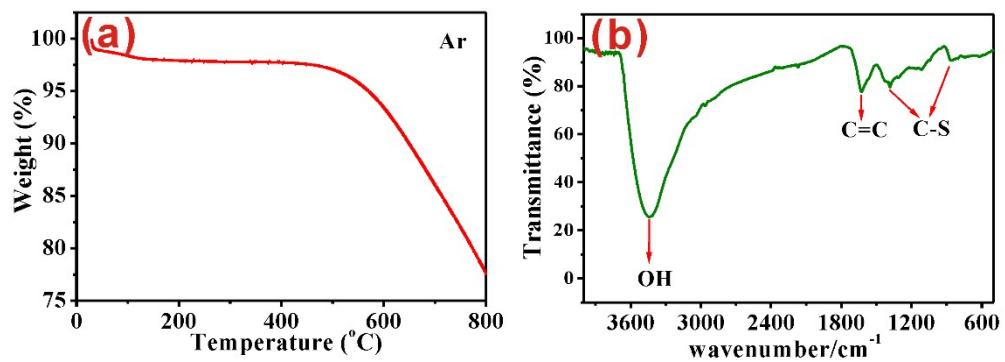


# **Untying thioether bond structures enabled by “voltage-scissors” for stable room temperature sodium-sulfur batteries**

Kejun Chen<sup>a,b</sup>, HuangJingWei Li<sup>b</sup>, Yan Xu<sup>a</sup>, Kang Liu<sup>b</sup>, Hongmei Li<sup>b</sup>, Xiaowen Xu<sup>b</sup>,  
Xiaoqing Qiu<sup>a\*</sup>, Min Liu<sup>b\*</sup>

<sup>a</sup>College of Chemistry and Chemical Engineering, Central South University, Changsha 41083, PR  
China

<sup>b</sup>Institute of Super-microstructure and Ultrafast Process in Advanced Materials, State Key  
Laboratory of Powder Metallurgy, School of Physical Science and Electronics, Central South  
University



IR bands $\text{cm}^{-1}$	Assignment
3440	OH stretching vibrations
1630	C=C asymmetric vibrations <sup>1</sup>
1385	C-S wagging vibrations <sup>2</sup>
850	C-S stretching vibrations <sup>3</sup>

Figure S1. (a) TGA of sulfur-doped microporous carbon in Ar with a temperature rise rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ , (b) FT-IR spectra of sulfur-doped microporous carbon.

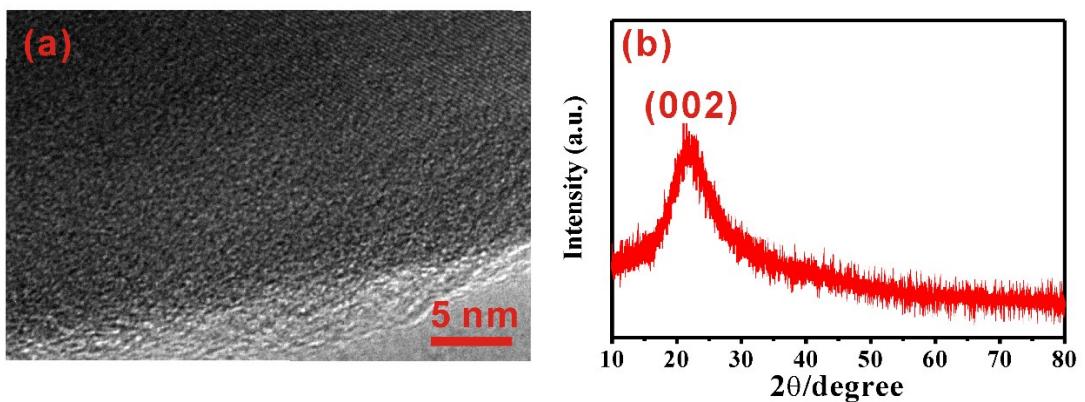


Figure S2. (a)The HRTEM images of SC, (b) XRD pattern of sulfur-doped microporous carbon.

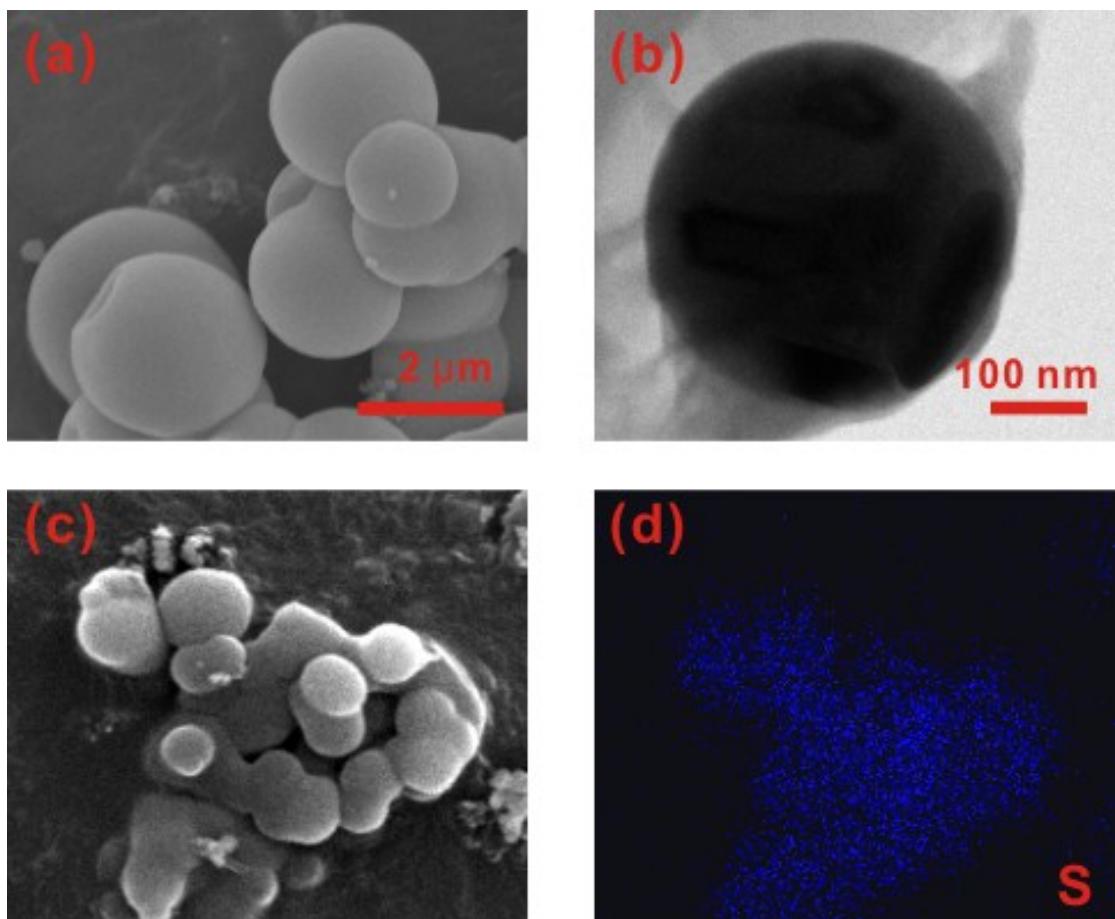


Figure S3. The morphology and structural characterization of SC: (a) SEM image, (b) TEM image, (c) elemental mapping for sulfur element and (d) the distribution of sulfur in the carbon

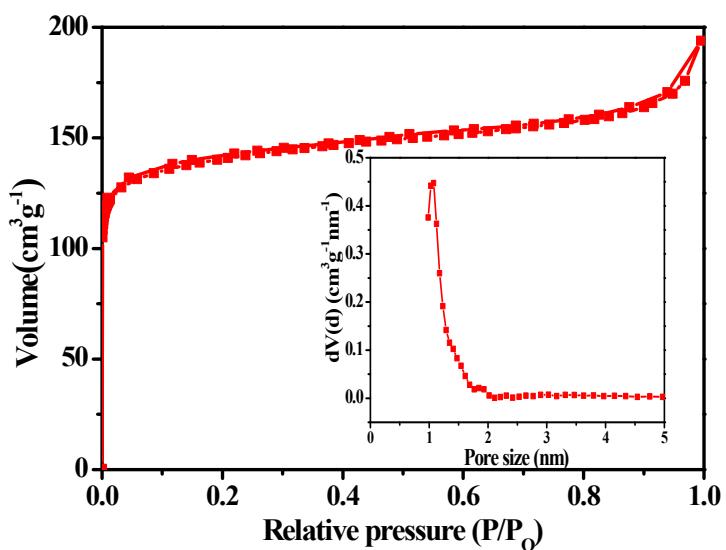


Figure S4. The nitrogen absorption/ desorption isotherms and the pore size distribution plot (inset) calculated by DFT method.

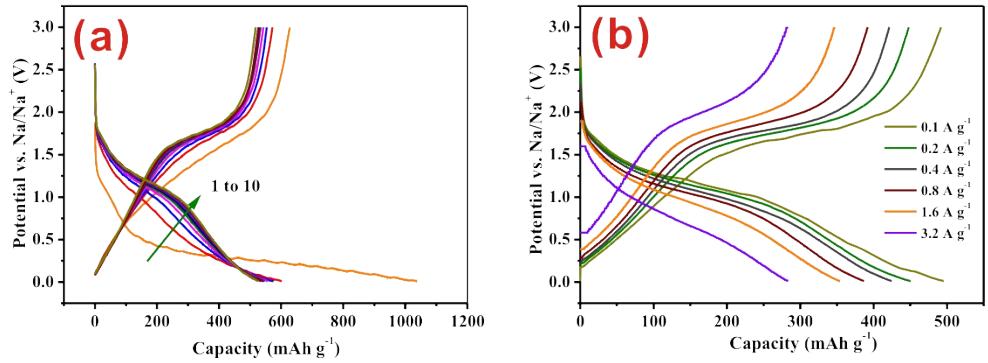


Figure S5. Discharge/charge curves of sulfur doped carbon: (a) at  $0.1 \text{ A g}^{-1}$  in the initial 10 cycle and (b) at different current densities ranging from  $0.1 \text{ A g}^{-1}$  to  $3.2 \text{ A g}^{-1}$ .

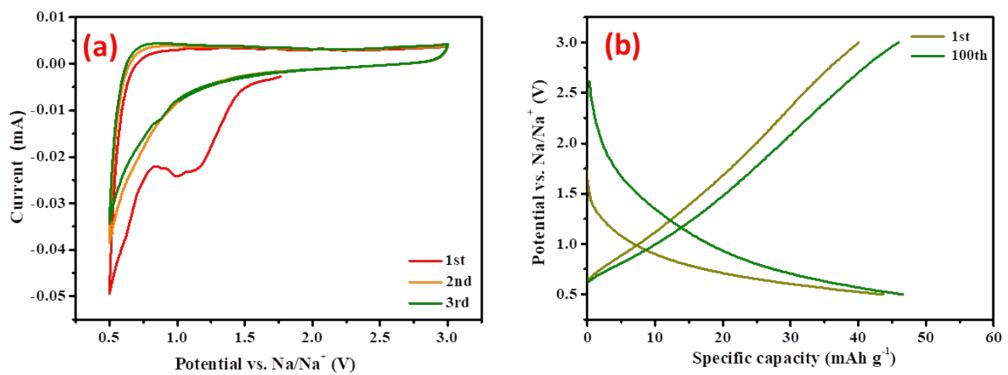


Figure S6. (a) The CV profiles of the unactivated SC, (b) electrochemical discharge/charge voltage profiles of the new cell at different cycles in the voltage windows of 0.5~3.0 V at 0.1 A g<sup>-1</sup>.

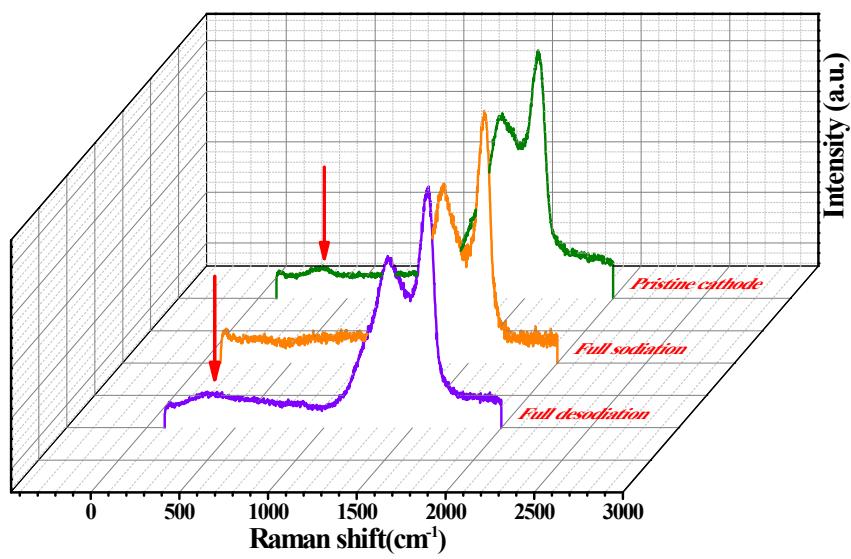


Figure S7. The ex-situ Raman spectra of SC at the different states during the first cycle.

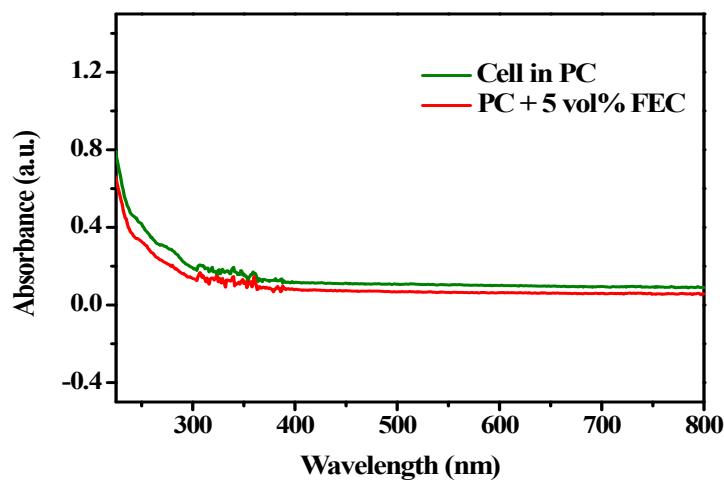


Figure S8. Ultraviolet-vis spectra of the electrolyte and cathodes solutions cycled in the propylene carbonate electrolyte after 100 cycles at  $0.1 \text{ A g}^{-1}$ .

Table S1. Comparison of electrolyte, loading content and performance with results from the previous RT Na-S batteries.

Ref	Electrolyte	Loading (wt%)	Current density	Capacity	Cycle No
4	1M NaClO <sub>4</sub> +EC/DEC +SiO <sub>2</sub> -IL-ClO <sub>4</sub>	47	78.7mA g <sup>-1</sup> (0.1 C)	282 mA g <sup>-1</sup> <sub>total</sub>	100
5	0.8M NaClO <sub>4</sub> +EC/DEC	31.42	220mA g <sup>-1</sup> (1C)	153 mA g <sup>-1</sup> <sub>total</sub>	500
6	1M NaClO <sub>4</sub> +EC/PC	40	67 mA g <sup>-1</sup> (0.1C)	400 mA g <sup>-1</sup> <sub>total</sub>	20
7	1M NaPF <sub>6</sub> +EC/DEC	41	68.7mA g <sup>-1</sup> (0.1C)	257 mA g <sup>-1</sup> <sub>total</sub>	200
8	1M NaClO <sub>4</sub> +EC/DEC	18	100 mA g <sup>-1</sup>	417 mA g <sup>-1</sup> <sub>total</sub>	100
9	1M NaPF <sub>6</sub> + NaNO <sub>3</sub> + TEGDME	35	586 mA g <sup>-1</sup> (1C)	306 mA g <sup>-1</sup> <sub>sulfur</sub>	1500
10	1M NaClO <sub>4</sub> +EC/DEC+F EC	59.4	100 mA g <sup>-1</sup>	292 mA g <sup>-1</sup> <sub>sulfur</sub>	200
this work	1M NaClO <sub>4</sub> +PC+FEC	21.5	100 mA g <sup>-1</sup>	500 mA g <sup>-1</sup> <sub>total</sub>	100
this work	1M NaClO <sub>4</sub> +PC+FEC -	21.5	1000 mA g <sup>-1</sup>	330 mA g <sup>-1</sup> <sub>total</sub>	800

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