

## Supporting Information

### Synergistic Electrocatalysis of Polysulfides by a Nanostructured VS<sub>4</sub>-Carbon Nanofibers Functional Separator for High-Performance Lithium-Sulfur Batteries

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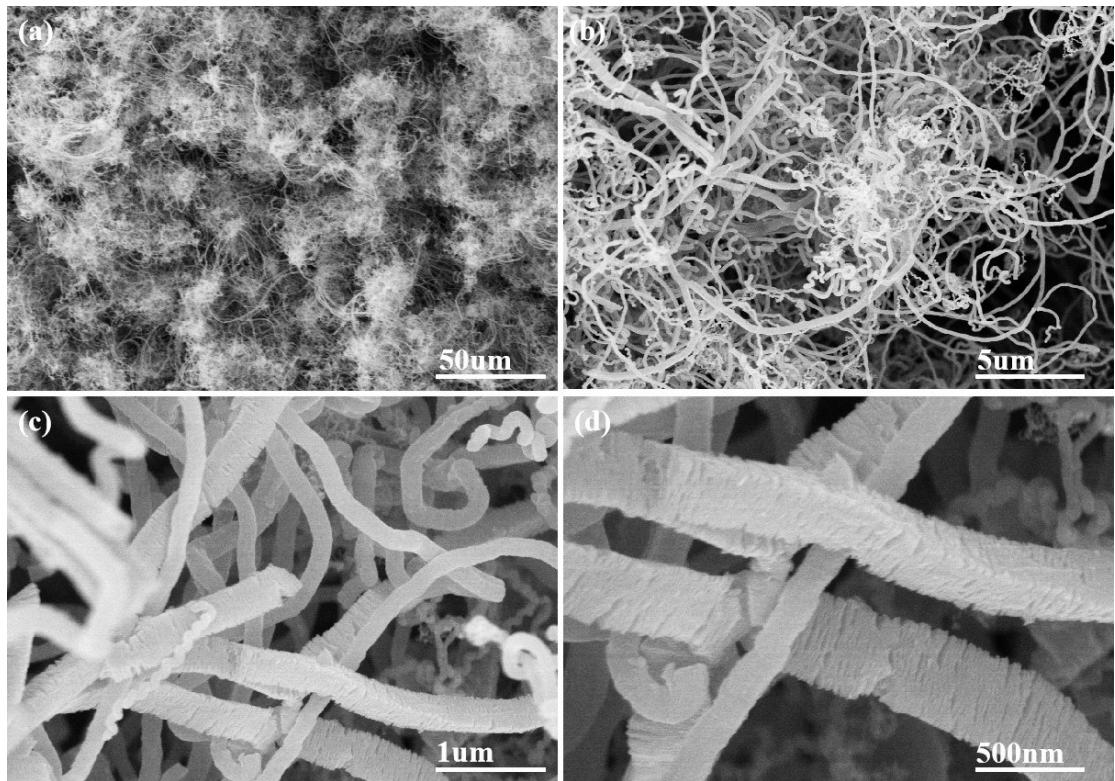
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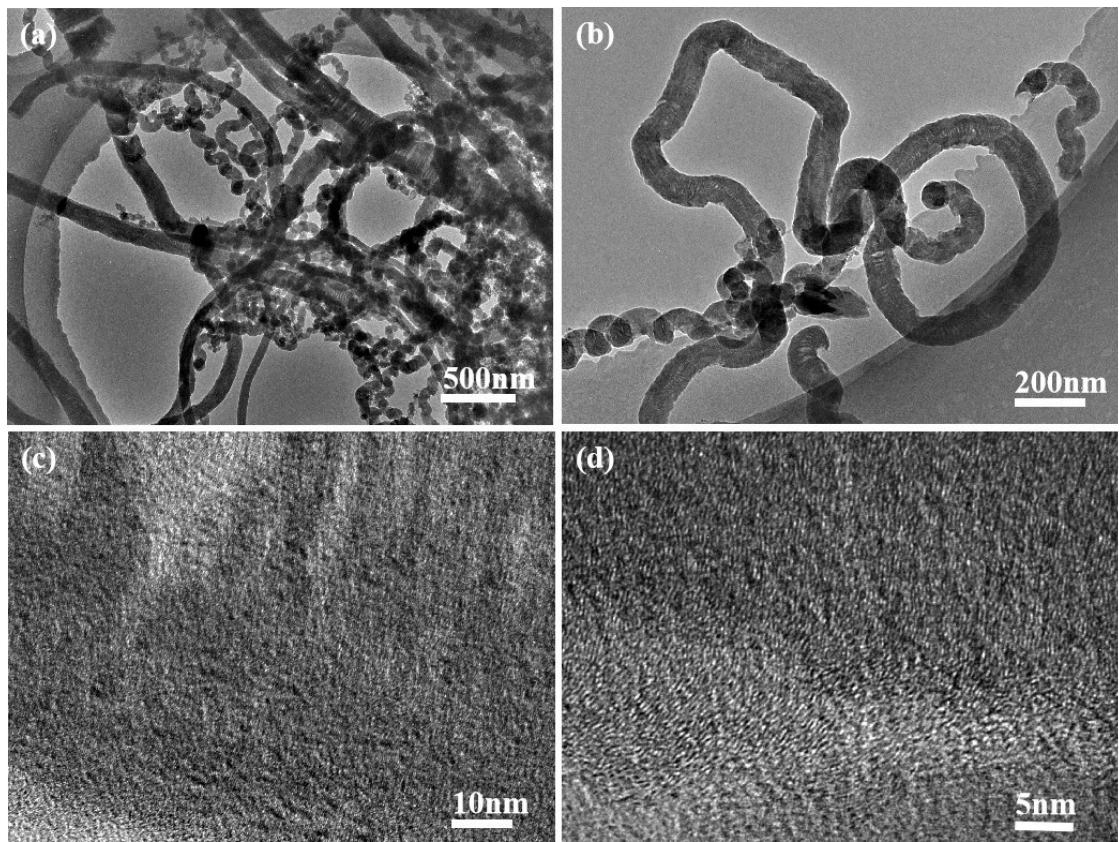
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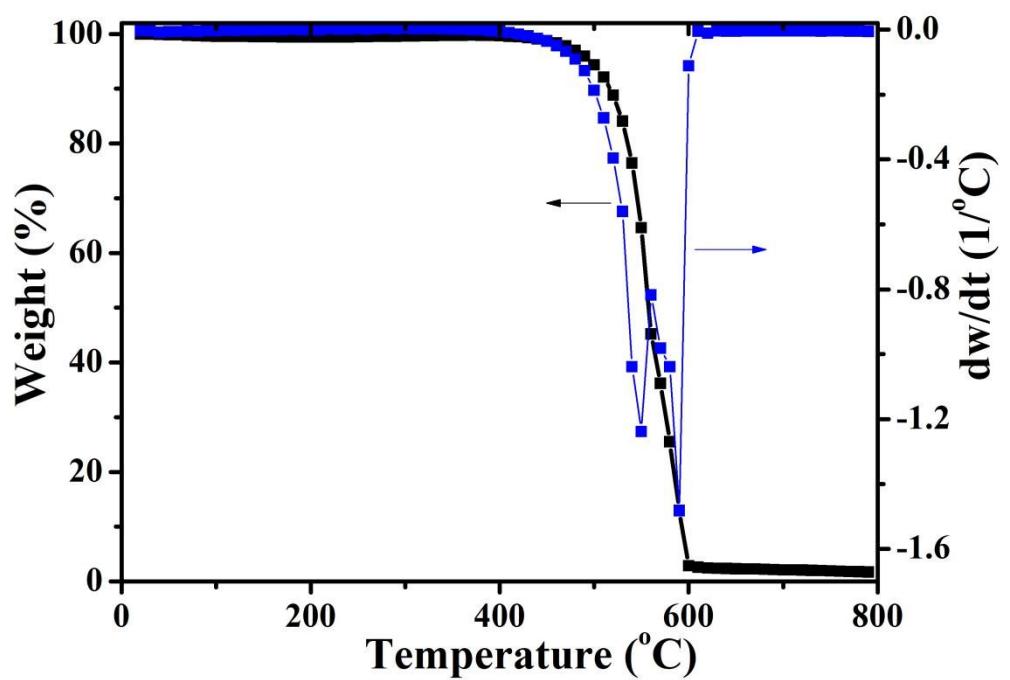
**Figure S1.** Optical images of the sample (a) before and (b) after CVD treatment.



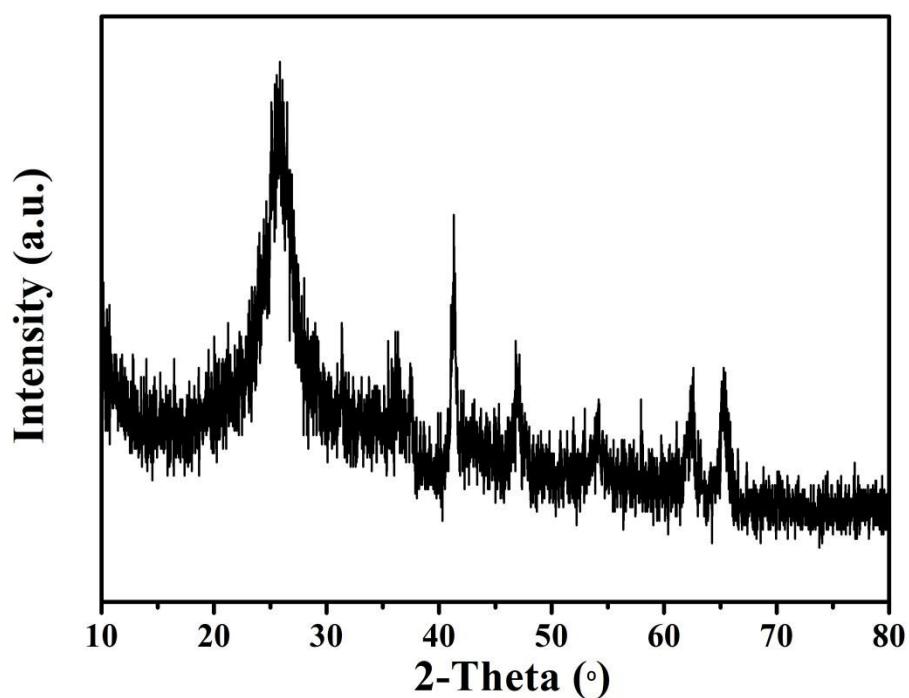
**Figure S2.** SEM images of the defect-rich CNFs



**Figure S3.** (a-b) TEM and (c-d) HRTEM images of the defect-rich CNFs



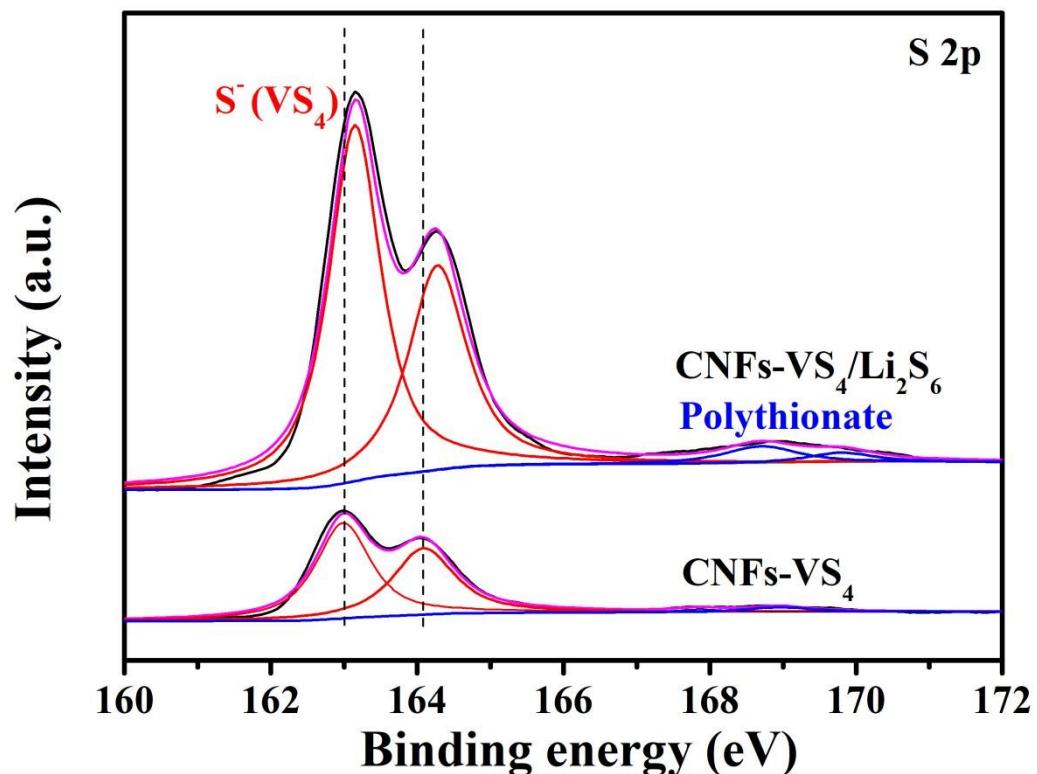
**Figure S4.**TG curve of the defect-rich CNFs thermal-treated at 800  $^{\circ}$ Cin air atmosphereat a heating rate of 10 $^{\circ}$ C/min.



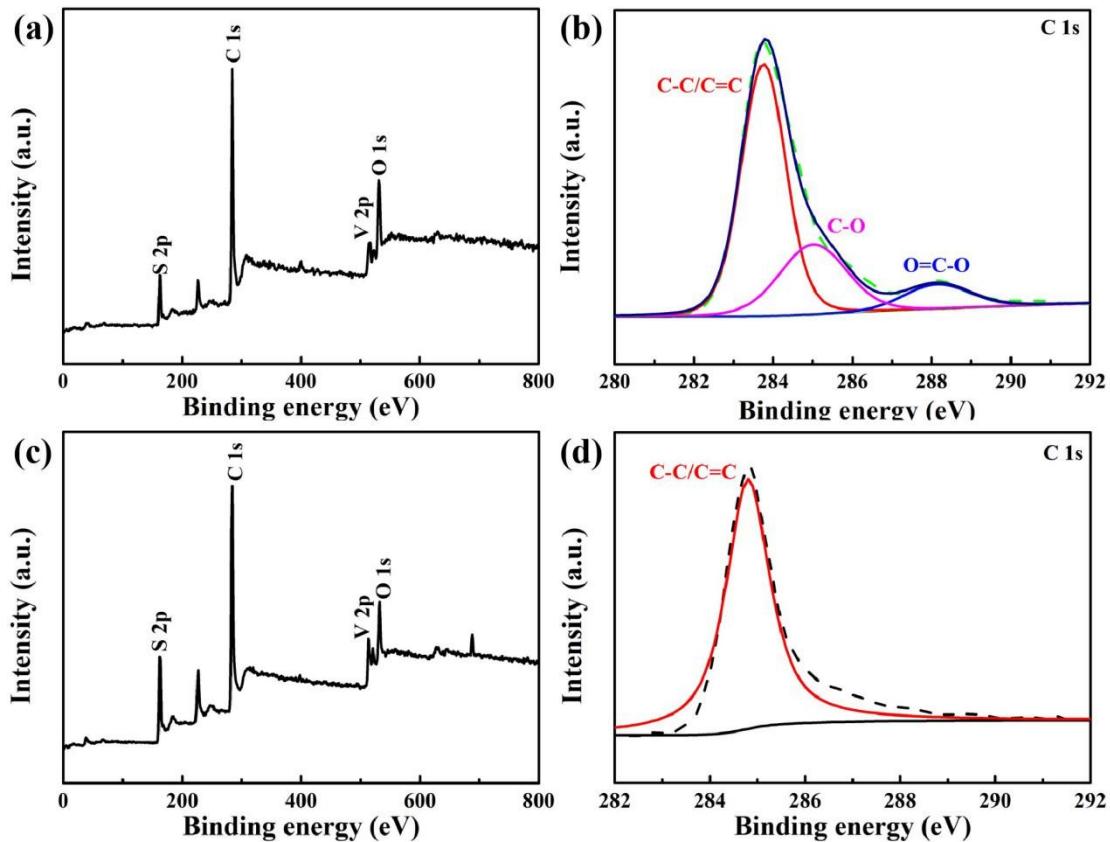
**Figure S5.** XRD pattern of the CNFs-VS<sub>x</sub> hybrid synthesized in water solution

**Table S1.** Comparison of the BET surface area of the CNFs

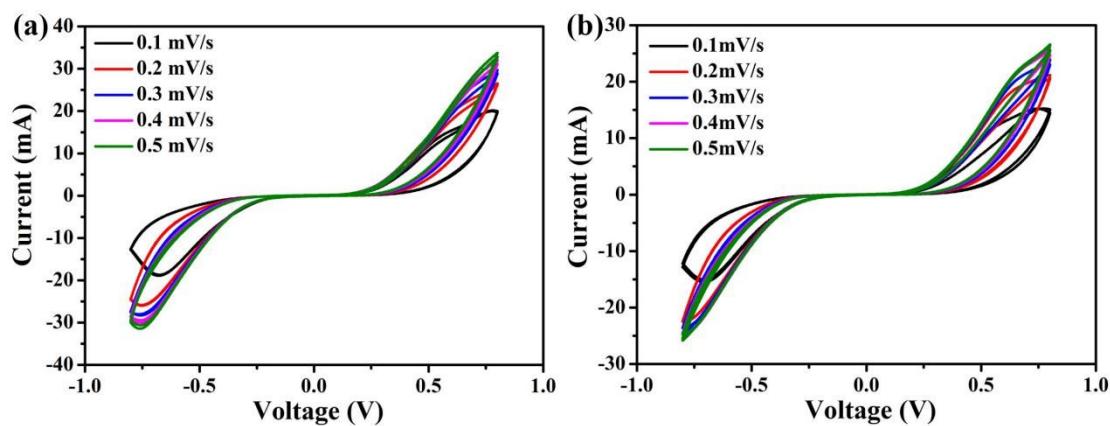
Reference	Specific surface area/m <sup>2</sup> g <sup>-1</sup>	Total pore volume/cm <sup>3</sup> g <sup>-1</sup>
S1	20.354	0.083
S2	19.95	-
S3	249.53	0.36
S4	34.9	-
S5	0.32	-
S6	41.9	0.17
S7	25.3-43.8	-
This work	239	0.31



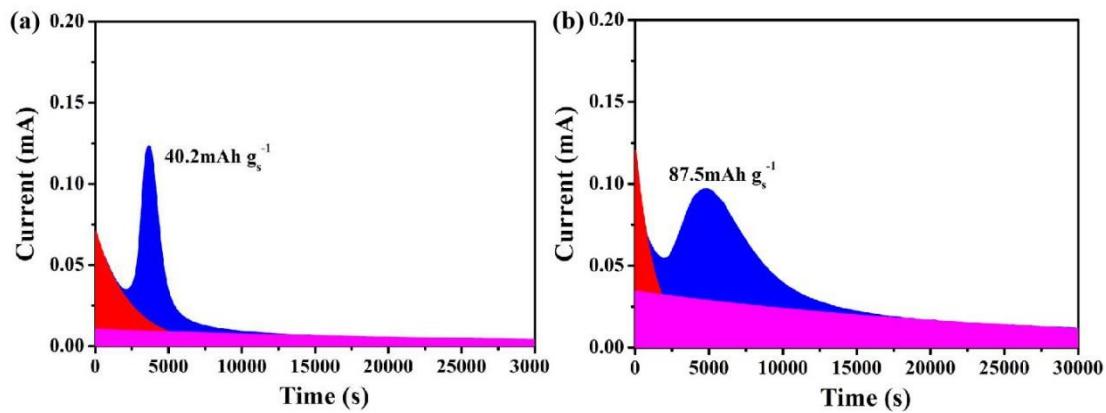
**Figure S6.** S 2p XPS spectrum of CNFs-VS<sub>4</sub> composite before and after adsorption of Li<sub>2</sub>S<sub>6</sub>.



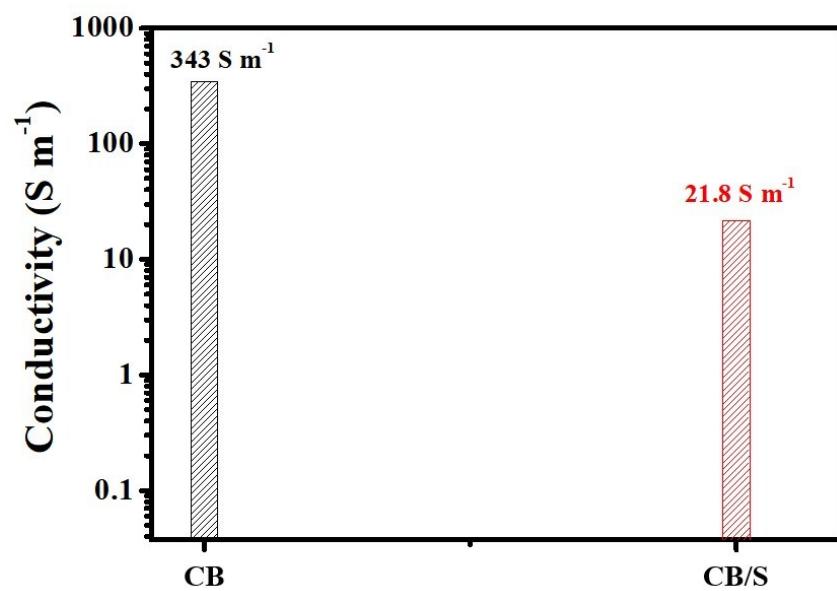
**Figure S7.** (a) XPS spectra and (b) C 1s spectrum of the pristine CNFs-VS<sub>4</sub> hybrids, (c) XPS spectra and (d) C 1s spectrum of CNFs-VS<sub>4</sub> hybrids after adsorption of Li<sub>2</sub>S<sub>6</sub>.



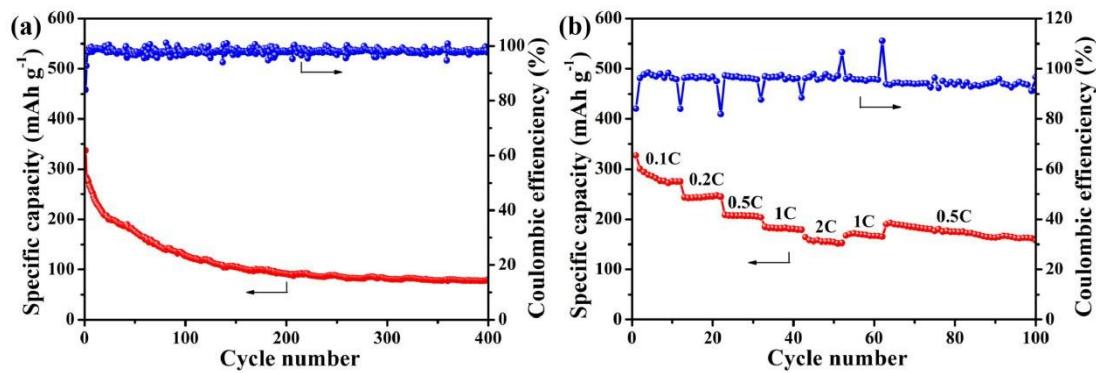
**Figure S8.** CV curves of symmetric dummy cells employing CNFs-VS<sub>4</sub> and CNFs functional separators at various scan rates.



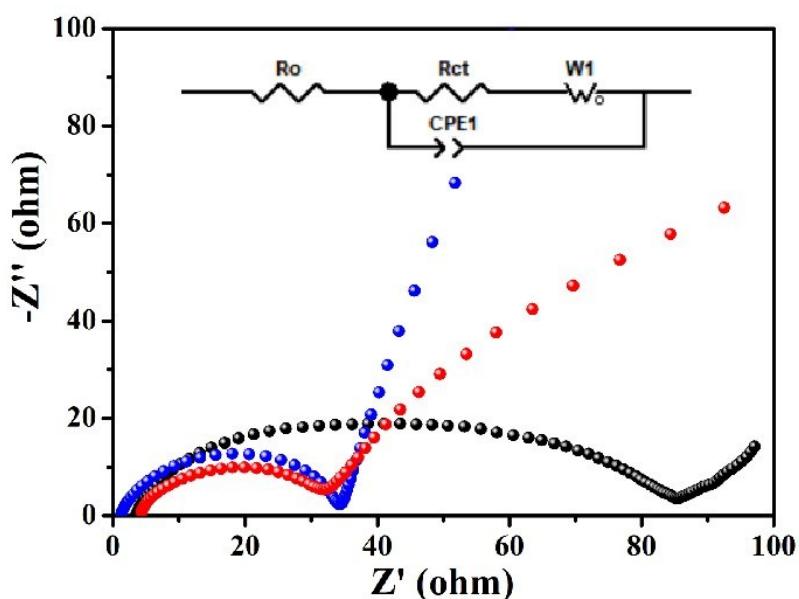
**Figure S9.** The curve of  $\text{Li}_2\text{S}$  precipitation experiments of CNFs and CNFs-VS<sub>4</sub> electrodes.



**Figure S10.** Comparative conductivity of CB and 80wt% CB/S cathode.



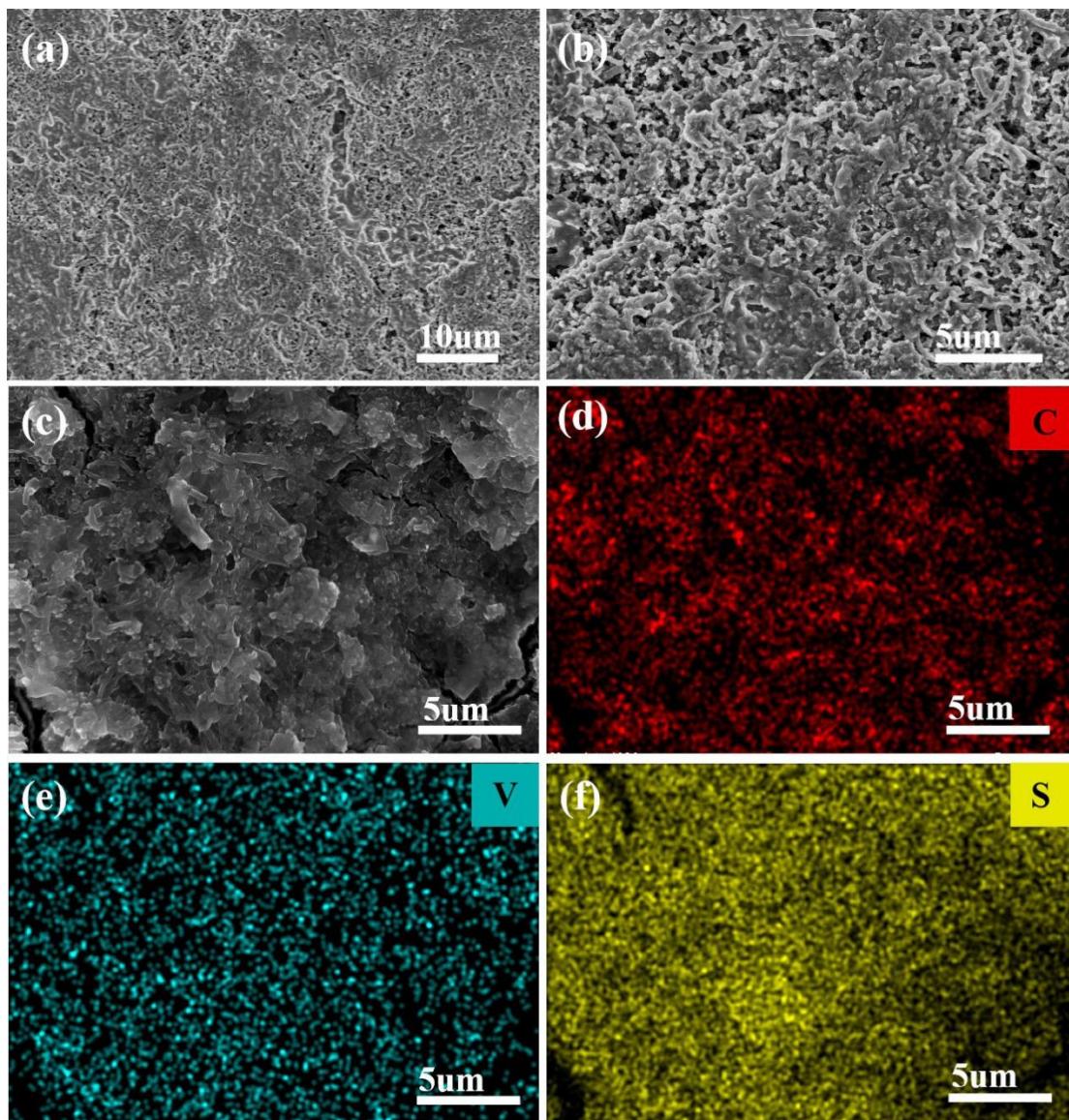
**Figure S11.** (a) Cyclic (at 0.2C) and rate performance of the CB/S cathode based on the pristine separator.  
(b) Cyclic (at 0.2C) and rate performance of the CB/S cathode based on the functionalized separator.



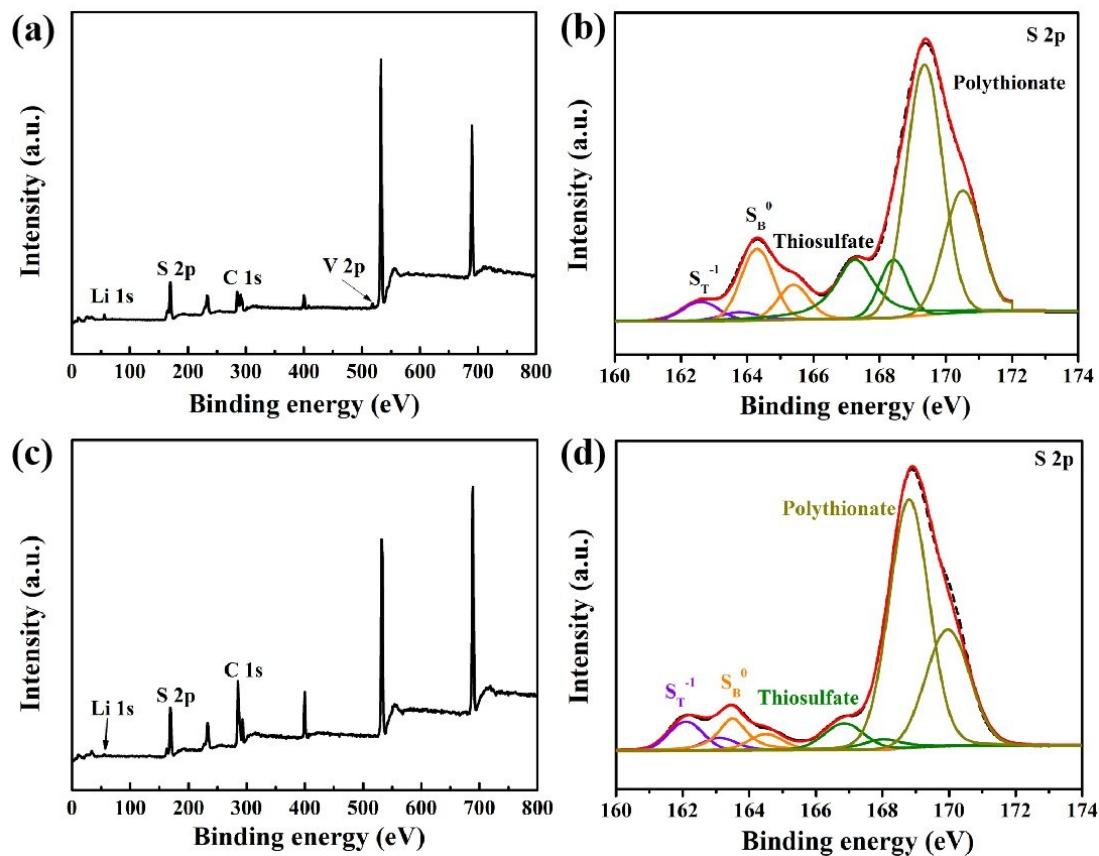
**Figure S12.** EIS curves of the fresh cell with (black) Cathode+PP, (blue) Cathode+CNFs-VS<sub>4</sub> functional separator, (red) Cathode/CNFs-VS<sub>4</sub>+PP.

**Table S2.** The impedance parameters simulated from the equivalent circuit fitting of different cells

Sample	$R_o(\Omega)$	$R_{ct}(\Omega)$
Cathode+PP	1.90	83.34
Cathode+CNFs-VS <sub>4</sub> functional separator	1.09	33.97
Cathode/CNFs-VS <sub>4</sub> +PP	3.77	30.64



**Figure S13.** (a-c) SEM images and corresponding (d) C, (e) V (f) S elemental mapping images of CNFs-VS<sub>4</sub> functional separator after cycling.



**Figure S14.** (a) XPS spectra and (b) S 2p spectrum of CNFs-VS<sub>4</sub> functional separator after cycling, (c) XPS spectra and (d) S 2p spectrum of CB/S cathode after cycling.

## **Reference**

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