

## **Supporting Information**

### **Efficient synthesis of graphene nanoscrolls for fabricating sulfur-loaded cathode and flexible hybrid interlayer towards high-performance Li-S batteries**

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## **Part I: Experimental Section**

### **Material Synthesis**

In this work, graphene and graphene oxides (GO) are purchased from Tanfeng Tech. Inc (Suzhou, China). Other reagents are analytical grade without further purification and purchased from Chengdu Kelong Chemical Reagents Corporation.

***Synthesis of the graphene nanoscroll (GNS).*** In a typical synthesis, GO were firstly added into DI water by ultrasonically treating for 1 h to obtain a brown homogeneous single-layer GO suspension with a concentration of 0.5 or 1.0 g L<sup>-1</sup>. N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O solution (85%) was then added into the obtained GO dispersions (the weight ratio of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O to GO is about 15:1), and kept at 60 °C for 20 min. After that, the mixture was transferred into plastic tubes to continue heating up to 80 °C, followed by putting them into liquid nitrogen immediately. The completely frozen solids were placed into lyophilizer, and kept at around -50 °C and under ~ 1 Pa vacuum. After freeze-drying, samples were transferred to a vacuum oven and dried at 50 °C for 12 h. Finally, the dried samples were sealed into alundum tube and heated to 1000 °C at the rate of 5 °C/min and kept at 1000 °C for 2 h, under the atmosphere of the mixture of H<sub>2</sub> (5%) and Ar. After cooling to room temperature, GNS was obtained.

***Preparation of the S@GNS composite cathode material.*** Typically, the obtained GNS and sublimed sulfur powder were mixed together in a mortar gently, and then transferred to a sealed Teflon-lined autoclave, heated at 155 °C for 15 h under argon atmosphere, followed by heating up to 200 °C for another 1.5 h to remove the redundant sulfur on the external surface of the GNS. After the thermal treatment, the S@GNS was collected. For comparison, commercial graphene was also used as a host matrix for sulfur loading, and the graphene sheets-supported sulfur composite (Gs-S) was prepared in the same procedure as described in the synthesis of S@GNS composite.

***Fabrication of the free-standing GNS/MnO<sub>2</sub> nanowires hybrid interlayer (GNSM).*** MnO<sub>2</sub> nanowires were prepared according to a previously reported hydrothermal method.<sup>1</sup> Firstly, the as-prepared MnO<sub>2</sub> nanowires were ultrasonically dispersed into ethanol to form a suspension. At the same time, the GNS (the weight ratio of GNS to

MnO<sub>2</sub> nanowires is 4:1) was also homogeneously dispersed into ethanol by ultrasonicatio to get another suspension. Afterward, the MnO<sub>2</sub> nanowires suspension was slowly added into the GNS suspension drop by drop under vigorous stirring at room temperature until a homogeneous mixed solution was obtained. A flexible and free-standing GNS/MnO<sub>2</sub> nanowires hybrid film was then assembled and collected after the mixed solution was subjected to vacuum filtration, room-temperature drying, and peeling off. Finally, the obtained film was then punched into wafers (14 mm; average weight: ~1.5 mg), which were directly used as the free-standing GNSM hybrid interlayers in subsequent cell assembly process.

### **Characterization**

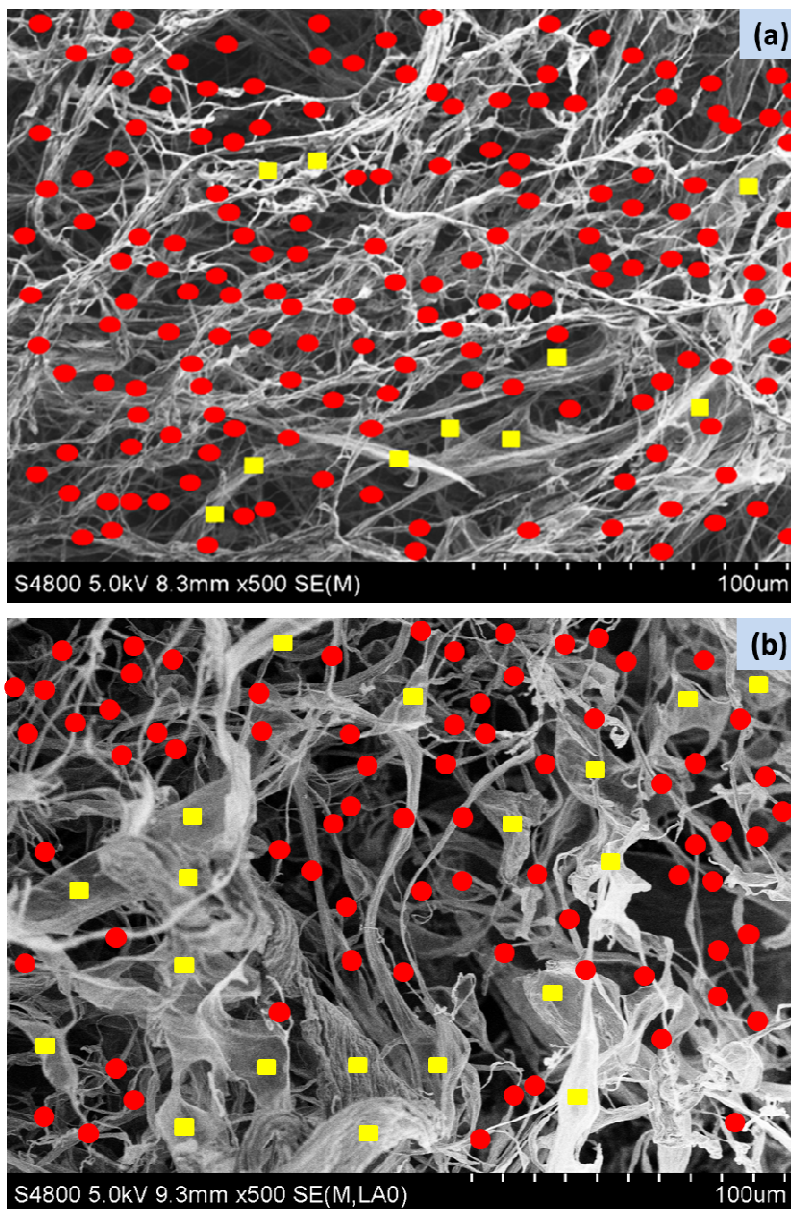
The microstructure and morphology of samples were characterized by field-emission scanning electron microscopy (FESEM, Hitachi S-4800) equipped with energy dispersive spectroscopy (EDS) and Transmission electron microscope (TEM, JEOL JEM-2100F). The crystalline structure of materials were detected by a X-ray diffraction (XRD) using a Bruker DX-1000 diffractometer (Cu K<sub>α</sub> radiation) in the range of 5° to 50° at a scan rate of 0.06° s<sup>-1</sup>. The content of sulfur in the composite was analyzed by thermogravimetric analysis (TGA) using a simultaneous TGA/DSC-2 instrument (METTLER TOLEDO, USA) in the temperature range of 50–600 °C at a heating rate of 10 °C min<sup>-1</sup> under the protection of inert gas . N<sub>2</sub> adsorption/desorption measurements were conducted with a Tristar II 3020 instrument at liquid nitrogen temperature. The specific surface area was calculated using the multipoint Brunauer-Emmett-Teller (BET) method, and the pore size distribution was computed using the Barrett-Joyner-Halenda (BJH) method. The electrical conductivity of the film was measured at room temperature using a ST-2258A digital four-point probe test system (Suzhou Jingge Electronic Co., Ltd).

### **Electrochemical measurements**

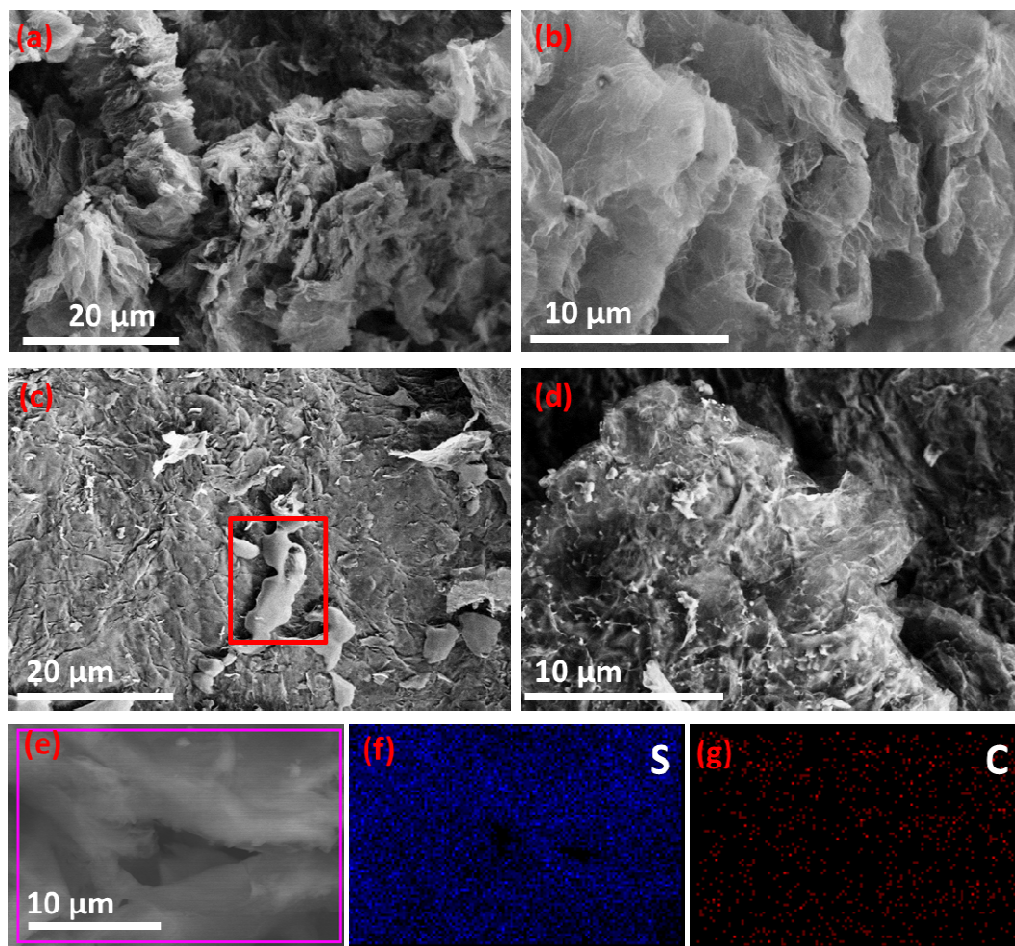
The electrochemical measurements were performed using CR2032 coin-type cells. Working electrodes were prepared by coating homogeneous slurries composed of as-synthesized S@GNS (80 wt%), super P (10 wt%) and polyvinylidene fluoride

binder (10 wt%), which were dispersed in N-methyl-2-pyrrolidone onto pure Al foil. After drying at 60°C for 24 h in a vacuum oven, the coated Al foil was punched into disks with a diameter of 12 mm. The typical mass loading of sulfur is about 1.2 mg cm<sup>-2</sup>. The disk as the working electrode was assembled into cells in an Ar-filled glovebox, using lithium metal as the counter/reference electrode, Celgard 2400 membrane as the separator. 1.0 M lithium bis(trifluoromethanesulfonate)imide (LiTFSI, 99.95%, Alfa Aesar) dissolved in a mixed solvent of 1, 3-dioxolane (DOL) and 1, 2-dimethoxyethane (DME) (1:1 by volume) with 0.1 M LiNiO<sub>3</sub> additive were employed as the electrolyte. The amounts of electrolyte in a single cell with and without interlayer are about 45 and 35 μl respectively. Galvanostatic charge/discharge tests were performed by a multi-channel battery test system (Neware CT-3008W, China) within the potential range of 1.5–2.8 V (vs. Li/Li<sup>+</sup>) at different current rates. All specific capacity values of the electrodes were calculated on the basis of sulfur weight (1C = 1675 mAh g<sup>-1</sup>). Cyclic voltammetry (CV) measurement was conducted using a PARSTAT multichannel electrochemical workstation (Princeton Applied Research, USA) at a scan rate of 0.1 mV s<sup>-1</sup>. Electrochemical impedance spectroscopy (EIS) was carried out over a frequency range of 100 kHz to 10 MHz with an applied amplitude of 5 mV.

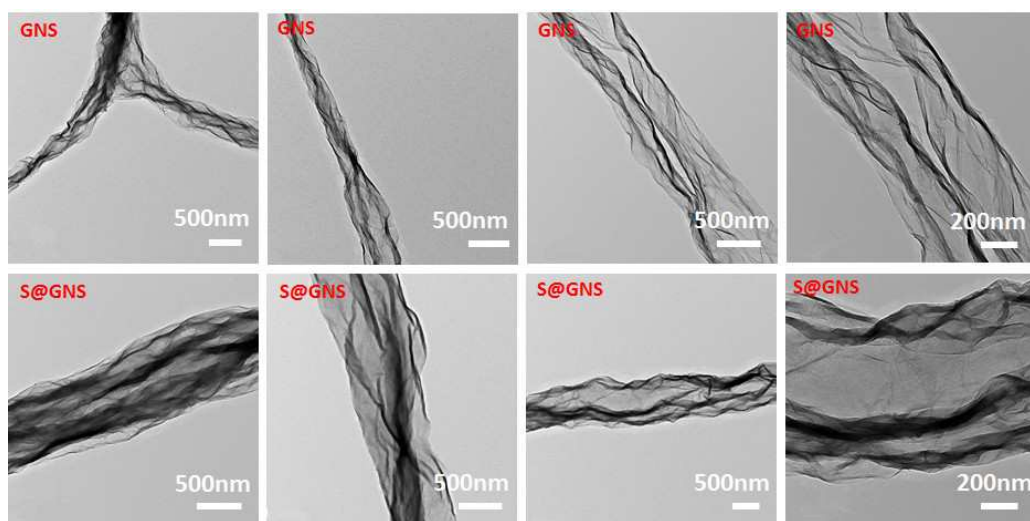
## Part II: Supporting Figures



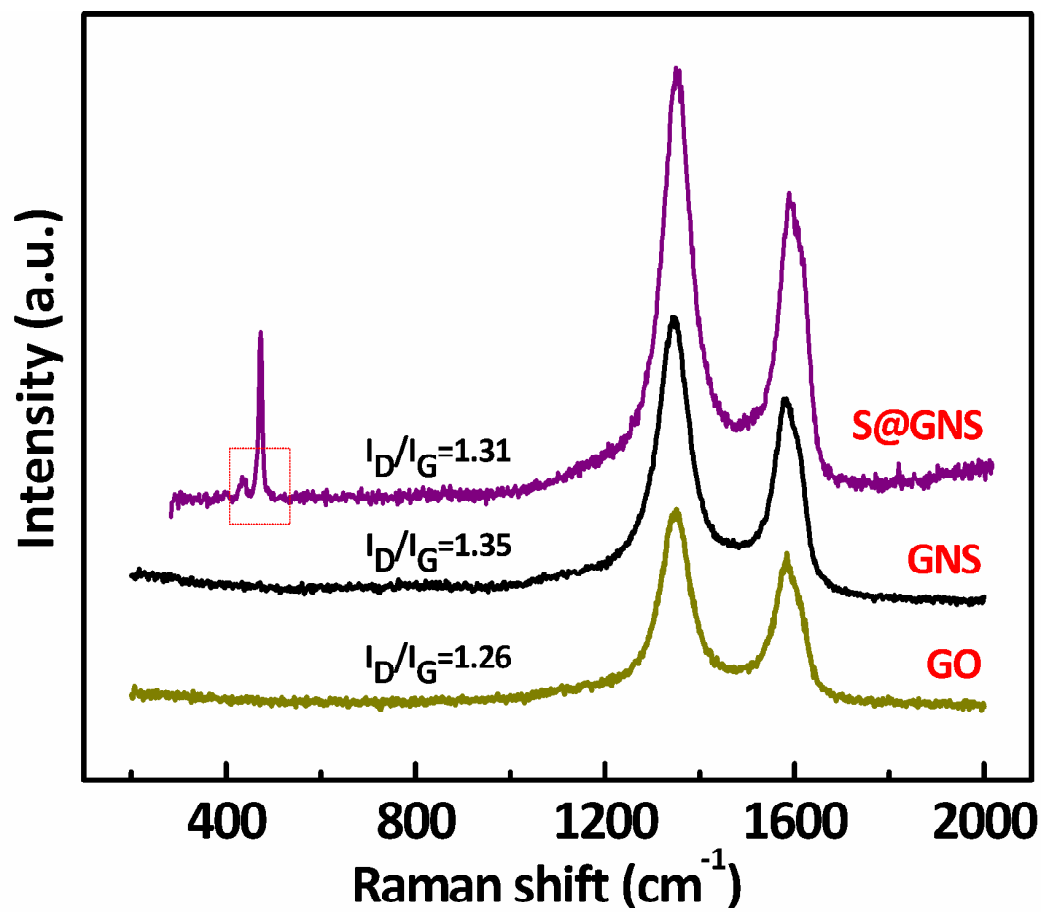
**Figure S1.** Typical FESEM image for the assessment of the efficiency to transform GO to GNS at the concentration of (a) 0.5 and (b) 1.0 g L<sup>-1</sup>. The red dots indicate graphene scrolls, and the yellow dots indicate unrolled graphene sheets. According to Gao's report <sup>2</sup>, the yield of the GNS can be calculated through counting the number of scrolls and sheets, as obtained by  $160 / (160+10) \times 100\% \approx 94\%$  for (a) and  $74 / (74+19) \times 100\% \approx 79\%$  for (b), respectively.



**Figure S2.** FESEM images of Gs (a, b) and Gs-S (c-e); Elemental mapping results of (f) sulfur and (g) carbon

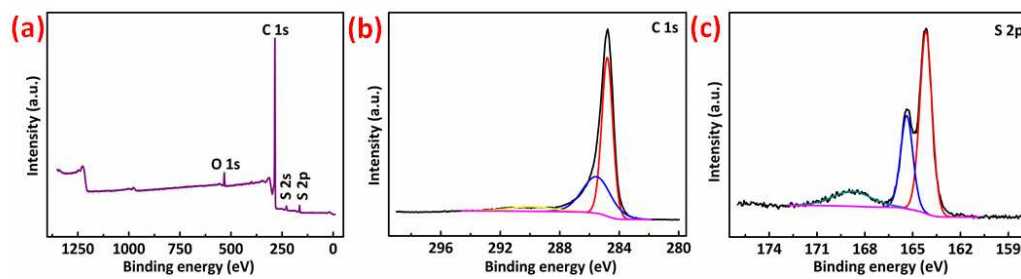


**Figure S3** TEM images of GNS and S@GNS

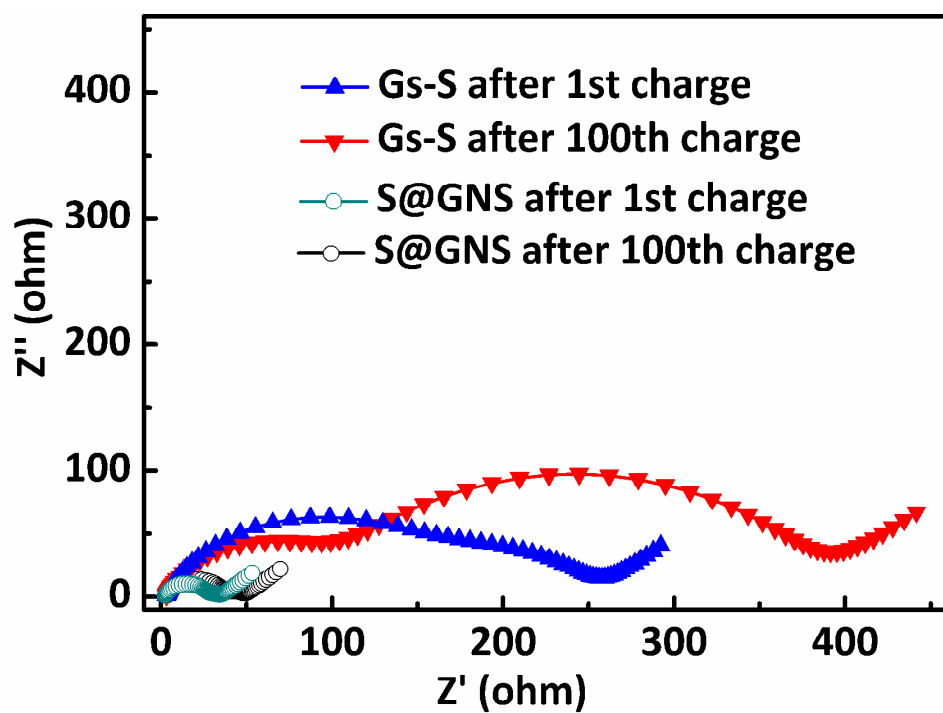


**Figure S4** Raman spectrum of GO, GNS and S@GNS.

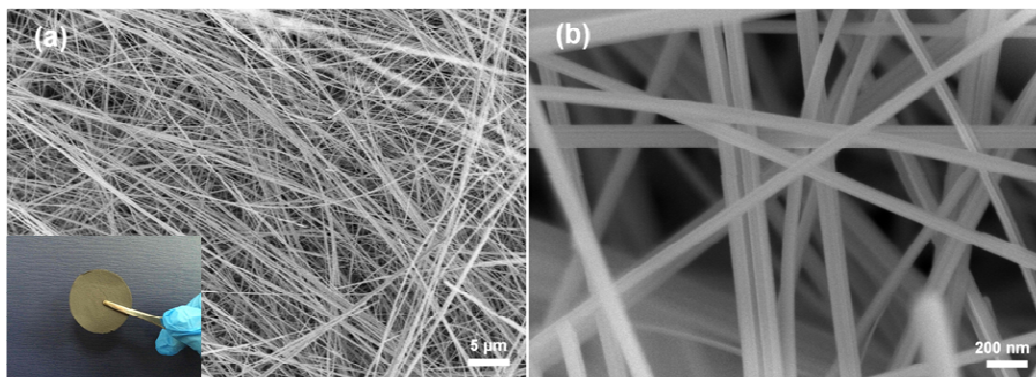




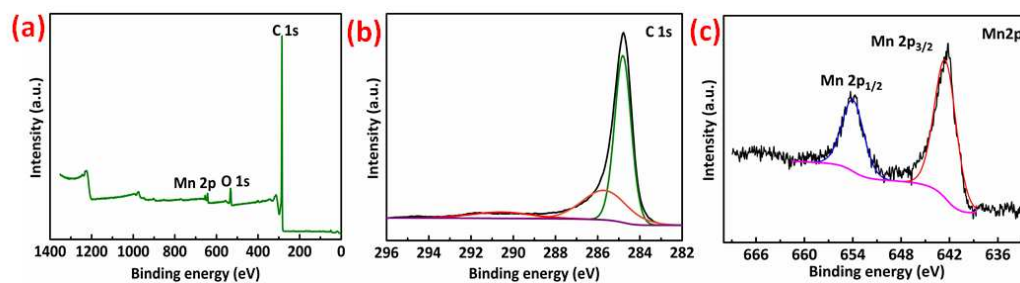
**Figure S5.** XPS spectrum of S@GNS: (a) survey scan and high resolution spectra of (b) C 1s and (c) S 2p.



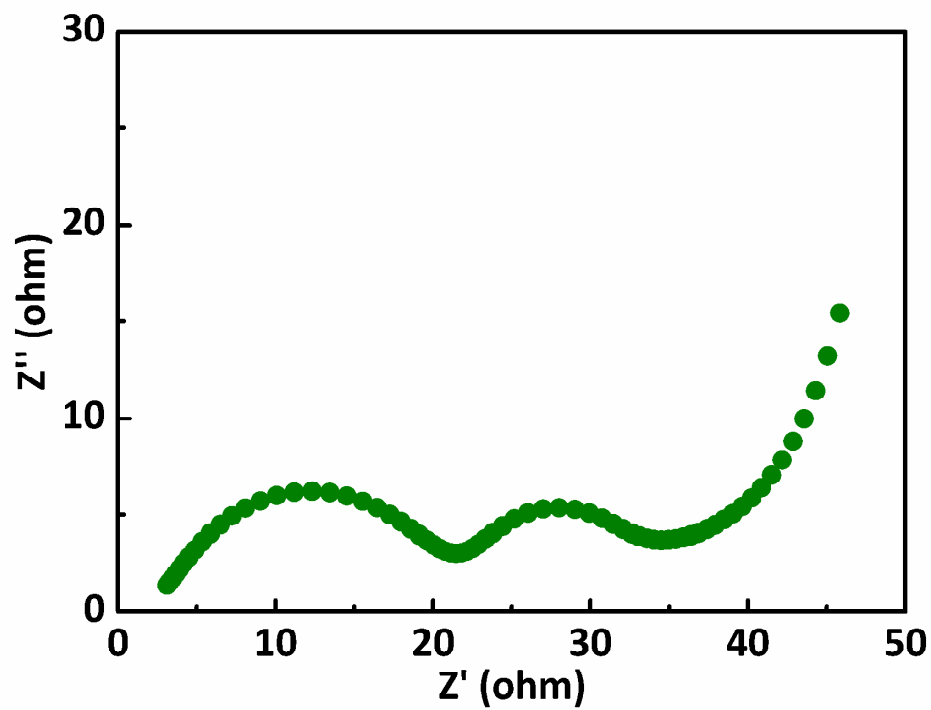
**Figure S6.** Nyquist plots of S@GNS and Gs-S after the first and 100th cycles.



**Figure S7.** FESEM images of as-synthesized MnO<sub>2</sub> nanowires (a, b); Inset in (a) shows the photo of a pure MnO<sub>2</sub> nanowires interlayer.



**Figure S8.** XPS spectra of GNSM: (a) survey scan and high-resolution spectra of (b) C 1s and (c) Mn 2p.



**Figure S9.** Electrochemical impedance spectra (EIS) plot of cell with GNSM interlayer after cycling.

**Table S1.** Comparison of the electrochemical performances of previously reported interlayer-engaged Li-S batteries with our work.

Interlayer materials	Cycling performance			Rate capability	Ref.
	Cycle number	Capacity remaining (mAhg <sup>-1</sup> )	Capacity retention (%)	Rate capacity (mAhg <sup>-1</sup> )	
MWCNTs	100	804 (1C)	~60	-	3
Carbonized polymer fibers	100	897 (0.1C)	73	416 (2C)	4
Carbonized polymer/carbon black	100	1000 (1C)	~85	846 (3C)	5
Carbonized PF resin/SiO <sub>2</sub>	200	1015 (0.2C)	~72	350 (4C)	6
Fe <sub>3</sub> C/carbon nanofibers	100	893 (0.2 A g <sup>-1</sup> )	76	600 (2 A g <sup>-1</sup> )	7
Carbonized Kimwipes	100	824 (2C)	71	824 (2C)	8
Carbonized eggshell membrane	100	1000 (0.1C)	0.25 (decay ratio, %)	-	9
CNT-loaded glass fibers	230	802.8 (0.2C)	72.2	853 (2C)	10
<b>GNS/MnO<sub>2</sub> NWs</b>	<b>400</b>	<b>545 (4C)</b>	<b>0.08 (decay ratio, %)</b>	<b>704 (4C)</b>	<b>This work</b>

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