

Electronic Supplementary Information (ESI)

## A Highly Dense Graphene-Sulfur Assembly: A Promising Cathode for Compact Li-S Batteries

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### Experimental Section

**Materials synthesis:** Graphene oxide (GO) and H<sub>2</sub>S were prepared following our previous work. Typically, H<sub>2</sub>S was bubbled into a GO aqueous dispersion at 70 °C while stirring for 1 h to realize an appropriate reduction of GO. The obtained dispersion was dried at 70 °C for 12 h to accelerate the self-assembly of rGO/S sheets. A black cylindrical hydrogel was obtained and separated from the water. Note that the reaction time and the reduction degree of GO are the critical parameter for the morphology and microstructure of the obtained products. The reaction time is optimized to accelerate the formation of 3D assembly. For preparing the rGO/S hybrid with different densities, evaporation-induced drying (EID) and freeze-drying were respectively used for the preparation of HDGS and LDGS. The EID used here is vacuum drying at room temperature for 24 h to obtain HDGS. The evaporation of water exerts a “pulling force” (capillary compression forces) on the graphene sheets and results in the shrinkage of the 3D network. This method does not damage the intrinsic microstructure of the 3D hydrogel but introduces a high density. The final hard monolith and non-compact carbon foam were used for further electrochemical measurements and no further heat treatment was needed.

**Characterization:** SEM and TEM and STEM observations were performed using Hitachi S-4800 (Hitachi, Japan) and JEM-2100F (JEOL, Japan) instruments, respectively. XRD measurements were conducted at room temperature with a Bruker D-8 diffractometer (Cu K $\alpha$  radiation,  $\lambda=0.154056$  nm). Nitrogen adsorption was measured using a BEL mini-instrument, and the specific surface areas were obtained by Brunauer-Emmett-Teller (BET) analysis of the adsorption isotherms. Thermogravimetric analysis (TG, Rigaku, Japan) was performed in a N<sub>2</sub> atmosphere at a heating rate of 5 °C/min to 500 °C to calculate the fraction of sulfur in the hybrid. To measure the precise content of sulfur in both HDGS and LDGS, elemental analysis was conducted by the consumption method using a Vario Micro cube (Elementar, Germany). Differential scanning calorimetry (DSC) was carried out using a DSC 8270 (Rigaku, Japan) with a heating rate of 5 °C/min from RT to 450 °C under a N<sub>2</sub> flow. XRM was performed using a Versa XRM-500

desktop system with a microfocus tube whose acceleration voltage could be adjusted from 30 to 160 kV. X-ray photoelectron spectroscopy (XPS) analyses were conducted with a Physical Electronics PHI5802 instrument using a magnesium anode (monochromatic  $K\alpha$  X-rays at 1253.6 eV) as the source. Raman spectra were recorded using a multi-wavelength micro-Raman spectroscope (JY HR800) using 532 nm incident radiation and a 50 $\times$  aperture. The thickness of the electrode was measured by digimatic microeter (Mitutoyo).

**Electrochemical performance measurement:** The LDGS and HDGS cathodes were prepared by mixing 80 wt % HDGS or LDGS, 10 wt % conductive carbon black with 10 wt % PVDF in NMP to form a slurry, which was stirred for 5 h and was then coated onto a carbon-coated Al foil and vacuum-dried at 50 °C for 24 h. The foil was then cut into a circular pallet with a diameter of 10 mm and used as the cathode. The electrolyte was 1.0 M lithium bis-trifluoromethanesulphonylimide (LiTFSI) dissolved in 1, 3-dioxolane and 1, 2-dimethoxyethane (DOL: DME, 1:1 volume). A 2032 coin cell was assembled to use as a test cell that was examined in an Ar-filled glovebox (MBraun). The gravimetric capacity is based on the mass of sulfur in HDGS and the volumetric capacity is based on the volume of the whole electrode (graphene, sulfur, binder PVDF and additive carbon black). The density of the electrode was calculated by the ratio of the mass to the volume of the pallet, the thickness of the pallet was measured by the micrometer and SEM. The volumetric capacity of the electrode was calculated by the ratio of the gravimetric capacity based on the mass of whole electrode to the density of the whole electrode. In a typical case, the mass of HDGS electrode which contains HDGS, PVDF and carbon black is 1.8 mg, and its thickness (Al foil is not included) is 21.4  $\mu\text{m}$ . Thus, the density of the HDGS electrode is calculated to be 1.07  $\text{g cm}^{-3}$ . The density of LDGS electrode is calculated to be 0.38  $\text{g cm}^{-3}$  by the same method. The gravimetric capacity of HDGS is 753.5  $\text{mAh g}^{-1}$  (based on sulfur), and the gravimetric capacity of the whole electrode is 192.9  $\text{mAh g}^{-1}$  ( $753.5 \times 0.32 \times 0.8$ , where 0.32 is the sulfur content in HDGS, and 0.8 is the HDGS content in whole electrode). Thus the volumetric capacity is calculated to be 206.4  $\text{mAh cm}^{-3}$ .

CV curves were obtained using an Autolab workstation at a scan rate of 0.1  $\text{mV s}^{-1}$  in the potential range 1.5-3.0 V (vs.  $\text{Li}^+/\text{Li}$ ) and electrochemical impedance spectroscopy (EIS) was also conducted using an Autolab workstation with a frequency range of 0.01-10<sup>5</sup> Hz. A LAND galvanostatic charge-discharge instrument was used to perform the cycle and rate performance tests. The current densities for the cell are based on the mass of sulfur in the hybrid. The binder and current collector-free slice of HDGS, which is prepared by cutting the formed HDGS with a thickness of less than 100  $\mu\text{m}$ , is also being investigating as a model electrode for future applications.

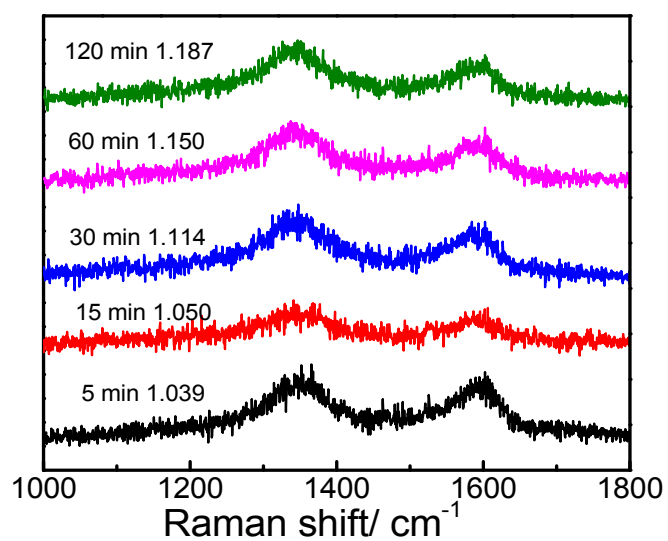


Fig S1. Raman spectra of HDGS with different reaction periods. The increased  $I_D/I_G$  ratio is indicative of the increased reduction degree.



Fig S2. Schematic illustration of the formation of HDGS of “Shiu mai” structure, composed of a graphene skin and sulfur stuffing.

Table S1. Elemental analysis results of HDGS

Sample (wt %)	C	S	O	H
HDGS-1h	52.78	32.73	14.37	0.62
HRGOS <sup>1</sup>	48.93	40.49	10.13	0.45

Table S2. Specific surface area and pore volume of different samples

Samples	HDGS-monolith	LDGS	HDG	LDG
$S_{\text{BET}}$ [ $\text{m}^2 \text{g}^{-1}$ ]	1.1	49.3	432.1	258.7
$V_{\text{total}}$ [ $\text{cm}^3 \text{g}^{-1}$ ]	0.0059	0.23	0.49	0.42

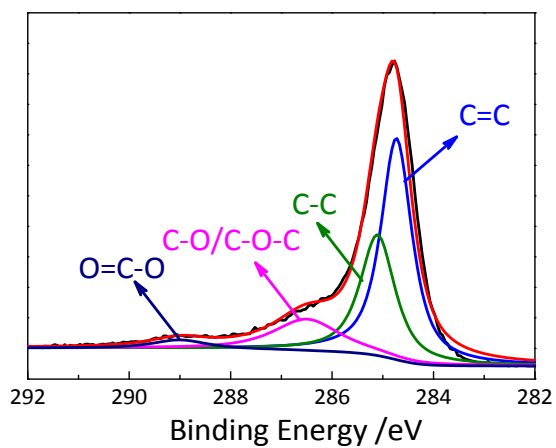


Fig S3 XPS analysis of HDGS

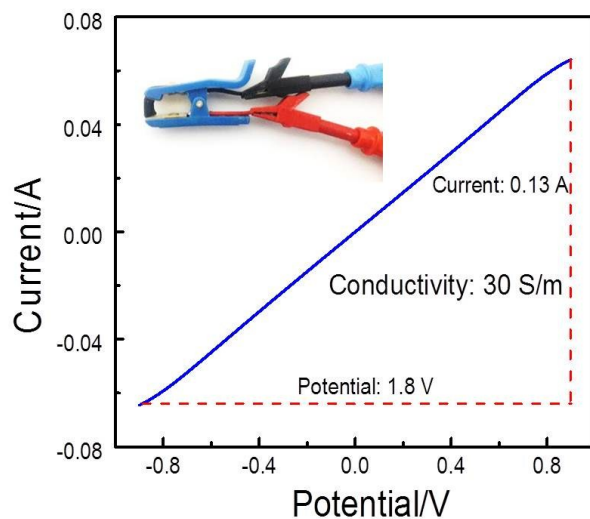


Fig S4. Room temperature I-V curve of HDGS: the inset shows the measurement apparatus for conductivity test.

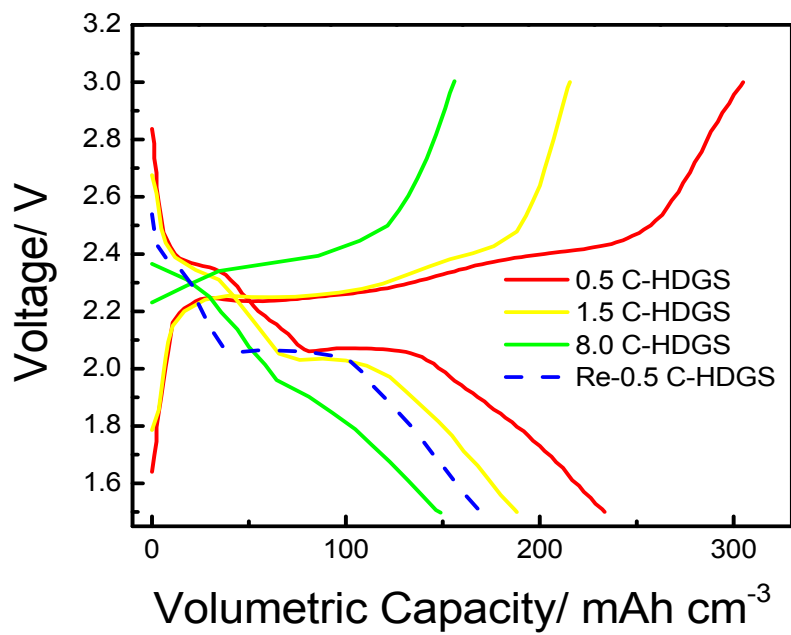


Fig S5. Charge-Discharge curves of HDGS at 0.5, 1.5, 8.0 and 0.5 C, respectively.

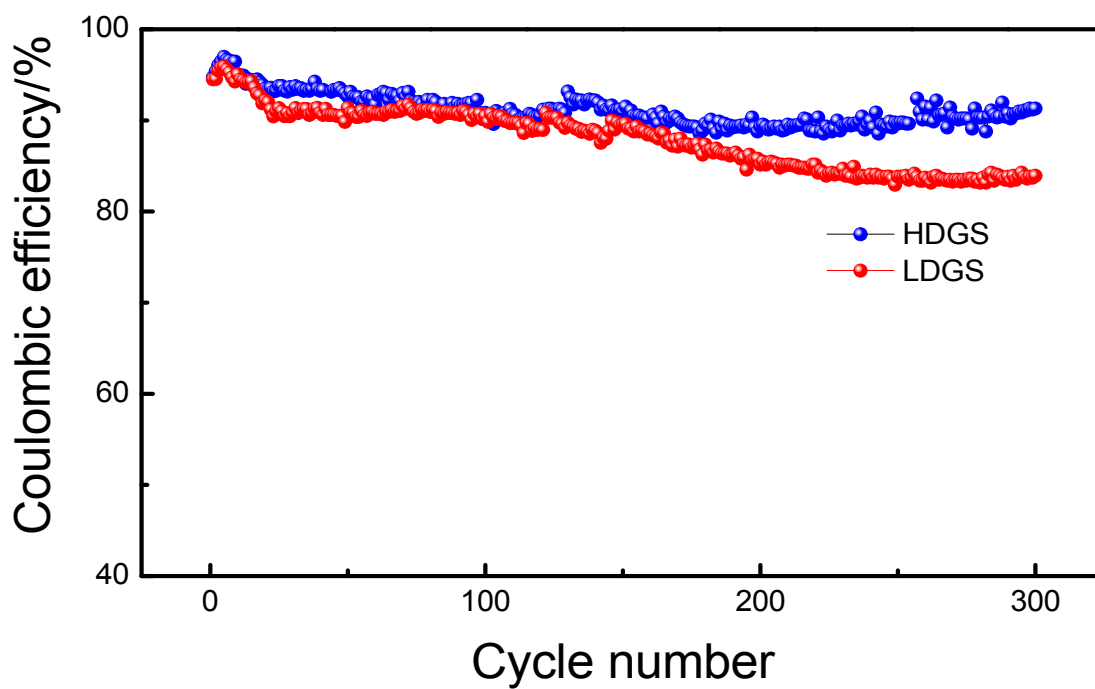


Fig. S6. The Coulombic efficiencies of LDGS and HDGS at 0.8 C

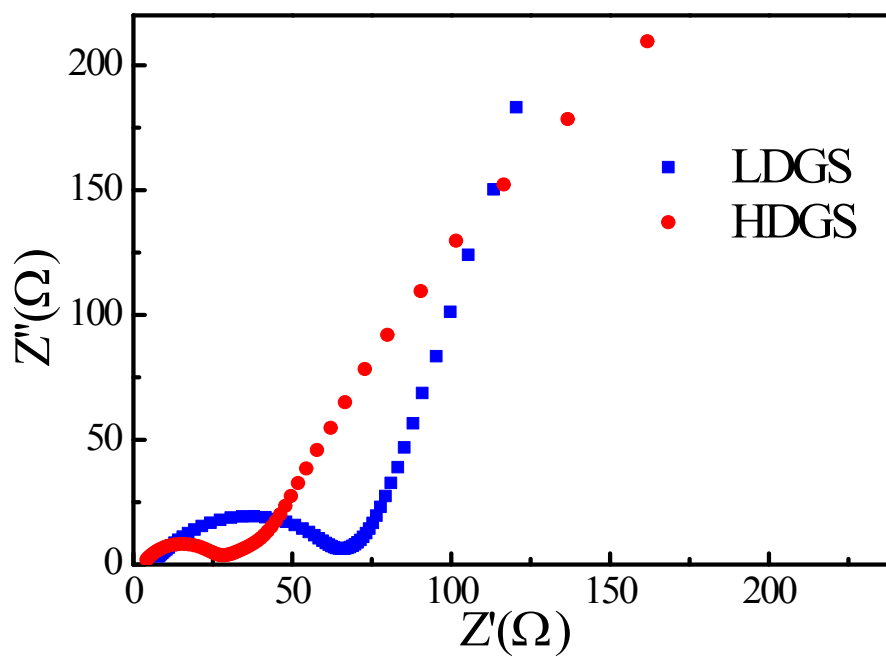


Fig. S7. Electrochemical impedance spectroscopy (EIS) of HDGS and LDGS

1. C. Zhang, W. Lv, W. G. Zhang, X. Y. Zheng, M. B. Wu, W. Wei, Y. Tao, Z. J. Li and Q. Yang, *Adv Energy Mater*, 2014, 4, 1301565.