

Supporting Information

Three-Dimensional CNT/Graphene-Li₂S Aerogel as Freestanding Cathode for High-Performance Li-S Batteries

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Experimental Section

1. Synthesis of graphene oxide (GO) and acidization of CNTs.

Graphene oxides were synthesized from natural flake graphite with the reported Hummers' method. Multi-walled carbon nanotubes (MWCNTs, Shenzhen New materials Co., Ltd. Product) were treated in a mixture of concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ (3:1) in a water bath at 80 °C for 2.5 h, followed by washing with deionized (DI) water until the pH was 7.0. The acidified MWCNTs were obtained upon vacuum drying at 60 °C.

2. Synthesis of 3DCG and 3DG.

The 3DCG was prepared by solvothermal reduction-assembly of homogeneous GO/CNTs suspension. 60 mg CNTs were added to GO aqueous dispersion (3 mg mL^{-1}) in 30 mL DI water and 30 mL ethanol. The mixture was intensively ultra-sonicated using an ultrasonication probe (1000 W) for 30 min to form a uniform suspension. Then the solution was sealed in a 100 mL Teflon-lined stainless steel autoclave at 180 °C for 20 h. After the autoclave cooled down to room temperature, the black hydrogel was fully immersed in water to exchange the ethanol absorbed inside the hydrogel. This step was then repeated 10 times. Finally, the 3DCG aerogel was obtained after removing the remaining water by freeze-drying.

3. Synthesis of 3DG- Li_2S and 3DCG- Li_2S .

Lithium sulfide (Li_2S , 99.98% trace metals basis) and anhydrous ethanol ($\geq 99.5\%$) were purchased from Sigma-Aldrich. A liquid infiltration-evaporation method was used for the synthesis of 3DG- Li_2S and 3DCG- Li_2S in a glove box. 75 mg Li_2S was added to 5 mL anhydrous ethanol to obtain a 15 mg mL^{-1} solution. Water in ethanol reacted with Li_2S to form LiOH , and precipitated in ethanol. The supernatant was pale yellow. The above 3DG and 3DCG aerogels were cut, compressed, and shaped into discs. To reduce the size of Li_2S heterogeneously nucleated on 3DG and 3DCG, we added ethanol- Li_2S solution into 3DG and 3DCG very slowly and periodically, the solvent evaporation is sufficiently rapid, which increases the nucleation rate and minimize the time available for Li_2S grain growth. Furthermore, the sample was exposed to vacuum to increase solvent infiltration and ensure the uniform distribution of Li_2S nanoparticles within the 3DG and 3DCG discs. Several infiltration/vacuum drying cycles were performed to ensure the particle-to-particle uniformity of the samples and the sufficient loading of Li_2S . Finally, the 3DG- Li_2S and 3DCG- Li_2S were then put into an autoclave in glove box and heated at 260 °C for 30 min to form Li_2S nanoparticles in the 3DG and 3DCG network. The obtained 3DG- Li_2S and 3DCG- Li_2S were used directly as cathode electrode in coin cells. The component ratio of the composite was determined by comparing the weights of the 3DG- Li_2S and 3DCG- Li_2S before and after loading Li_2S .

4. Characterizations

The crystalline structure of the obtained samples was characterized by X-ray diffraction (XRD Rigaku D/MAX-rA diffractometer) using $\text{Cu K}\alpha$ radiation after the

samples were tightly sealed using Kapton tape. The morphology investigation was performed by scanning electron microscope (SEM, JSM-7000F, JEOL) with an energy dispersive X-ray spectrometer (EDS) and transmission electron microscope (TEM, Tecnai F20 at 200 kV). Oxygen peaks originating from the unavoidable oxidation of samples in air were removed from the EDS spectra.

5. Electrochemical measurements

3DG-Li₂S and 3DCG-Li₂S discs were used as electrodes and the Li₂S mass loading of the cathode was 4 mg cm⁻². Coin-type (CR2025) cells were assembled in an argon-filled MBraun glove box with oxygen and water content below 0.5 ppm using lithium metal as anode. Celgard 2400 was used as separator. 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (v/v=1:1) (Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd) with 0.2 M lithium nitrate (LiNO₃) as an additive was employed as electrolyte. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were conducted by CHI 660D electrochemical workstation (CHI instrument). CV measurements were performed at a scan rate of 0.1 mV s⁻¹ in the voltage range from 1.5 to 3.6 V at the first cycle and 1.5 to 3 V in subsequent cycles. EIS tests were conducted at an open-circuit potential in the frequency range between 100 kHz and 0.01 Hz. Galvanostatic charge-discharge cycles were tested by LAND CT2001A instrument (Wuhan Jinnuo Electronic Co. Ltd.) at various C rates between 1.5 V and 3 V (vs. Li⁺/Li) at the room temperature (1.5 V to 3.6 for the first cycle). In

this work, 1C corresponds to a current density value of 1166 mA g⁻¹ and specific capacity values were calculated on the basis of Li₂S mass.

7. Computational Methods

The atomic configurations and binding energies were calculated using DFT within the Perdew–Berke–Ernzerh of generalized gradient approximation (GGA-PBE), as implemented in the Dmol3 package. The double numerical plus polarization (DNP) basis sets with effective core potential were employed to describe atomic potentials. The graphene sheet was modeled using a 5 × 5 supercell, and the CNT was modeled in (10, 10) orientation and 10 nm in length. Different initial binding configurations between graphene, CNT and Li₂S were tried to obtain optimized binding configurations with the lowest energy. Self-consistent field calculations were carried out until the SCF tolerance is below 1×10⁻⁶.

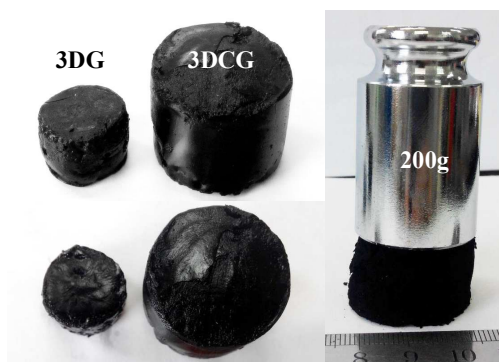


Fig. S1 Photographs of the 3DG and 3DCG hydrogels after the hydrothermal reaction.

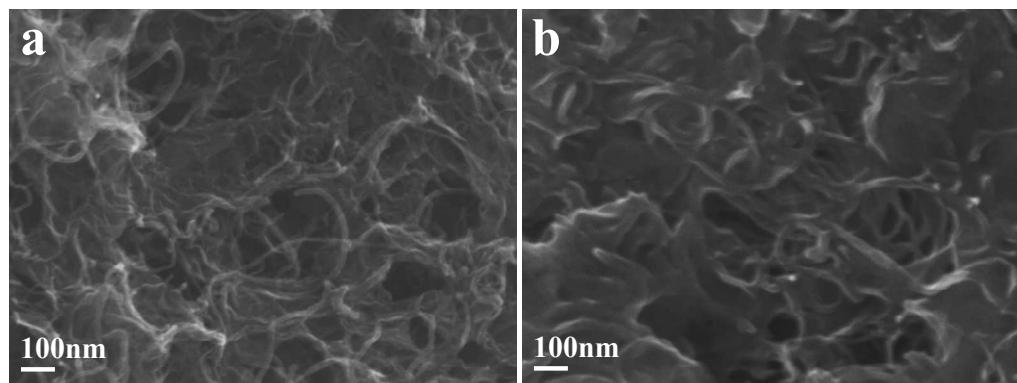


Fig. S2 High-magnification SEM images of (a) 3DCG and (b) 3DCG-Li₂S.

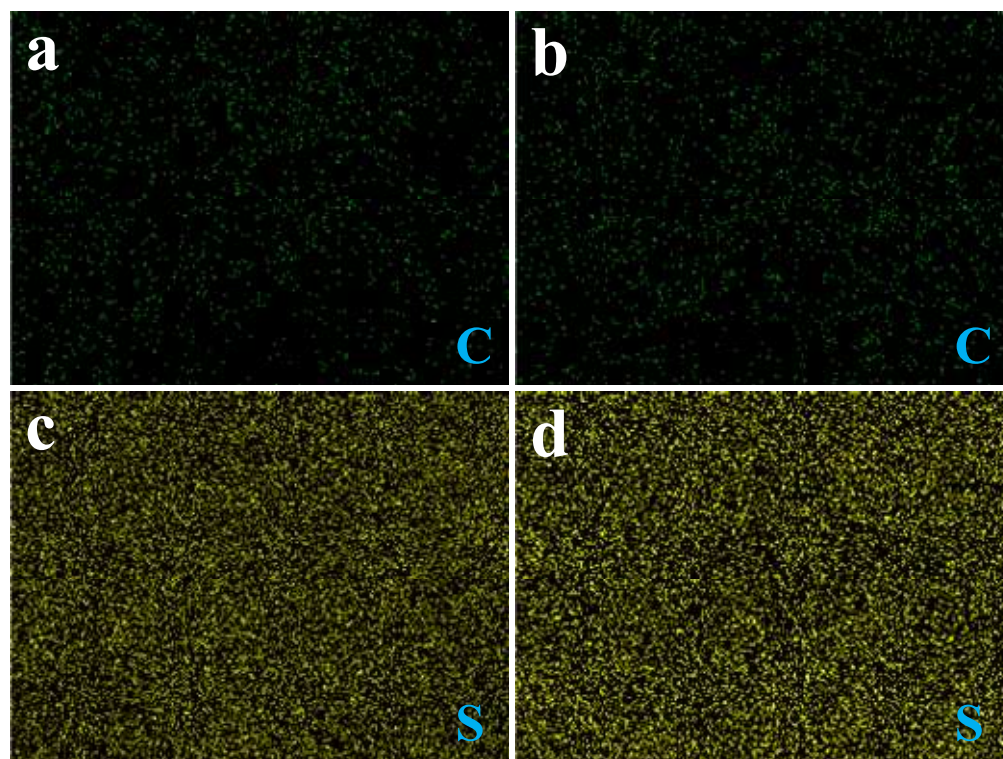


Fig. S3 The elemental maps of carbon and sulfur in the 3DG-Li₂S (left) and 3DCG-Li₂S (right) composite.

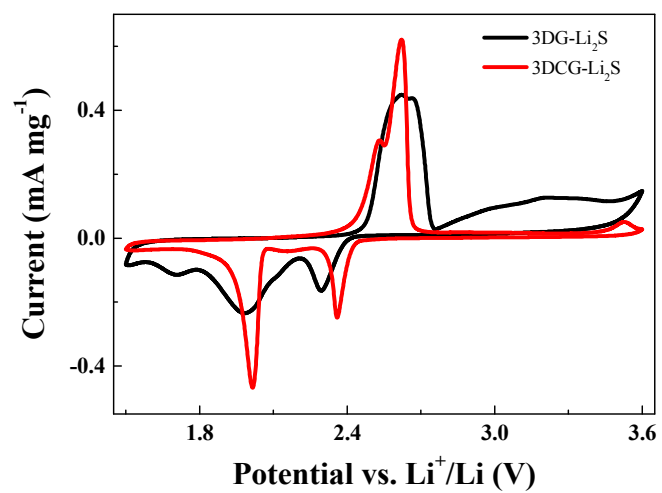


Fig. S4 CVs of the 3DG-Li₂S and 3DCG-Li₂S electrodes in the first cycle.

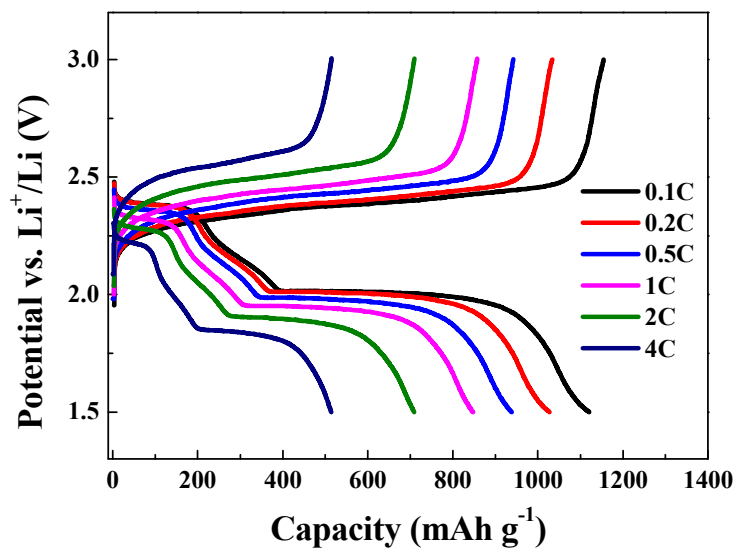


Fig. S5 The charge-discharge profiles of 3DCG-Li₂S at various C rates.

Table S1. A survey of electrochemical properties of Li₂S-C composites.

Electrode description	Binder free/ Free-standing	Li ₂ S content in composite/electrode (wt%)	Capacity basis on Li ₂ S (mAh g ⁻¹)	Capacity basis on electrode materials (mAh g ⁻¹)
3DCG-Li ₂ S (This work)	Y/Y	81.4/81.4	1123.6 mAh g ⁻¹ (0.1C), 1026.1 mAh g ⁻¹ (0.2C), 938.2 mAh g ⁻¹ (0.5C), 847.4 mAh g ⁻¹ (1C), 709 mAh g ⁻¹ (2C), 514 mAh g ⁻¹ (4C).	914.6 mAh g ⁻¹ (0.1C), 835.2 mAh g ⁻¹ (0.2C), 763.7 mAh g ⁻¹ (0.5C), 689.8 mAh g ⁻¹ (1C), 577.1 mAh g ⁻¹ (2C), 418.4 mAh g ⁻¹ (4C).
3D nano-Li ₂ S/rGO paper (Ref.1)	Y/Y	60/60	1119 mAh g ⁻¹ (0.1C), 708 mAh g ⁻¹ (3C), 597 mAh g ⁻¹ (7C).	671.4 mAh g ⁻¹ (0.1C), 424.8 mAh g ⁻¹ (3C), 358.2 mAh g ⁻¹ (7C).
3D Li ₂ S-Doped Graphene (Ref. 2)	Y/Y	55/55	1000 mAh g ⁻¹ (0.1C), 487 mAh g ⁻¹ (2C).	550.0 mAh g ⁻¹ (0.1C), 267.9 mAh g ⁻¹ (2C).
graphene-Li ₂ S-C composite (Ref. 3)	N/N	55/47	900 mAh g ⁻¹ (0.1C), 670 mAh g ⁻¹ (2C).	423.0 mAh g ⁻¹ (0.1C), 314.9 mAh g ⁻¹ (2C).
Li ₂ S particle-C shell (Ref.4)	N/N	61/52	1100 mAh g ⁻¹ (0.1C), 200 mAh g ⁻¹ (5C).	572.0 mAh g ⁻¹ (0.1C), 104.0 mAh g ⁻¹ (5C).
Li ₂ S-graphene composite (Ref. 5)	N/N	94/47	650 mAh g ⁻¹ (0.05C), 450 mAh g ⁻¹ (0.5C).	305.5 mAh g ⁻¹ (0.05C), 211.5 mAh g ⁻¹ (0.5C).
Li ₂ S-CNT (Ref. 6)	N/N	90/45	700 mAh g ⁻¹ (0.05C), 500 mAh g ⁻¹ (0.5C).	315.0 mAh g ⁻¹ (0.05C), 235.0 mAh g ⁻¹ (0.5C).
Li ₂ S@C composites (Ref. 7)	N/N	77.5/46.5	971 mAh g ⁻¹ (0.1 A g ⁻¹), 598 mAh g ⁻¹ (1 A g ⁻¹).	451.5 mAh g ⁻¹ (0.1 A g ⁻¹), 281.1 mAh g ⁻¹ (1 A g ⁻¹).
Li ₂ S-PPy composite (Ref. 8)	N/N	86/51.6	785 mAh g ⁻¹ (0.2C), 560 mAh g ⁻¹ (2C).	405.1 mAh g ⁻¹ (0.2C), 289.0 mAh g ⁻¹ (2C).
Li ₂ S@TiS ₂ (Ref. 9)	N/N	78/40	750 mAh g ⁻¹ (0.2C), 560 mAh g ⁻¹ (2C).	300 mAh g ⁻¹ (0.2C), 224 mAh g ⁻¹ (2C).
exfoliated graphene-Li ₂ S (Ref. 10)	N/N	53/42.4	1119 mAh g ⁻¹ (0.1C), 565 mAh g ⁻¹ (2C).	474.5 mAh g ⁻¹ (0.1C), 239.6 mAh g ⁻¹ (2C).
Li ₂ S-graphene oxide (Ref. 11)	N/N	76/53.2	782 mAh g ⁻¹ (0.2C), 640 mAh g ⁻¹ (2C).	416.0 mAh g ⁻¹ (0.2C), 340.5 mAh g ⁻¹ (2C).
C-Li ₂ S composite (Ref.12)	N/N	75/64	1100 mAh g ⁻¹ (0.05C), 200 mAh g ⁻¹ (5C).	640 mAh g ⁻¹ (0.05C), 128 mAh g ⁻¹ (5C).
C-Li ₂ S nanocomposite	N/N	73/62	1082 mAh g ⁻¹ (0.05C), 853.3 mAh g ⁻¹ (0.5C).	670.8 mAh g ⁻¹ (0.05C), 529 mAh g ⁻¹ (0.5C).

(Ref.13)				
Li ₂ S@C spheres (Ref.14)	N/N	90/54	972 mAh g ⁻¹ (0.2C), 570 mAh g ⁻¹ (2C).	524.9 mAh g ⁻¹ (0.2C), 307.8 mAh g ⁻¹ (2C).
Micrometer-Sized Li ₂ S Particles (Ref. 15)	N/N	100/40	800 mAh g ⁻¹ (0.05C), 620 mAh g ⁻¹ (0.125C).	320.0 mAh g ⁻¹ (0.05C), 248.0 mAh g ⁻¹ (0.125C).

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