In situ SiO$_2$ embedded into the graphene oxide to generate 3D hierarchical porous graphene laminates for high performance lithium-sulfur batteries

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1. Experimental section

1.1. Materials synthesis

All chemicals in experiment were of analytical grade and used as received.

Synthesis of 3D porous graphene laminates (GLs): Typically, a 50 ml GO (0.5 mg ml^{-1}) aqueous solution was modified with poly(diallyldimethyl ammonium chloride) (PDDA) or polyelectrolyte poly(sodium 4-styrenesulfonate) (PSS) (0.4 mg ml^{-1} in H$_2$O) under ultrasonication for 30 minutes. The samples were respectively labelled as PDDA-GO and PSS-GO. Secondly, 0.5 ml tetraethylorthosilicate (TEOS) (or NH$_3$ H$_2$O) was added into these modified GO aqueous solution under stirring for 10 minutes, respectively. Thirdly, PDDA-modified negatively charged GO solution was added dropwise into the PSS-modified negatively charged GO under vigorous stirring for 6 h. Then centrifuged and washed repeatedly with DI water and ethanol and dried at 60 ℃ for 12 h. Finally, the products were carbonized by heating sequentially in a tubular furnace at 800 ℃ for 2 h under Ar atmosphere; Silica was removed by immersing the composite in 10 wt % hydrofluoric acid solution under stirring for 24 h at room temperature.

Preparation of the C-S composite: The C-S composite was prepared via a facile melt-diffusion strategy. GO used here were produced by the modified Hummers method, as our previous report.[1] rGO was attained by heating at a heating rate of 10 K min^{-1} in a tubular furnace at 800 ℃ for 2 h under Ar atmosphere. Typically, carbon material (GLs or rGO) and sulfur with weight ratios of 1:4 were dissolved in 5 ml CS$_2$ to form a homogeneous solution under ultrasonic radiation. Subsequently, CS$_2$ was allowed to completely evaporate from the solution under magnetic stir to obtain the C-S composite. The final C-S product was placed in a crucible, then heated to 155 ℃ with a slow heating rate of 0.5 ℃ min^{-1} and kept at that temperature for 12 h in an argon environment. The products were denoted as GLs-S or rGO-S.

1.2. Materials Characterization

The structure and morphology of composites were characterized by X-ray diffraction (XRD, RIGAKU SCXmini), scanning electron microscope (SEM, JSM-6700F), and transmission electron microscope (TEM, Tecnai G2 F20). Thermal gravimetric analysis (TGA, NETZSCH STA449 C) tests were measured from 30 to 600 ℃ at a heating rate of 10 K min^{-1} in a N$_2$ environment to evaluate the weight content of sulfur in the composites. The nitrogen adsorption/desorption isotherms and the pore size distribution using the density functional theory (DFT) calculation were performed by an ASAP-2020 surface area analyzer.

1.3. Electrochemical measurements

The electrochemical tests were performed via CR2025 coin-type test cells which were fabricated in an argon-filled glove box using lithium metal as the counter electrode and a Celgard 2300 membrane. The cathode slurry was prepared by mixing 80 wt% C-S composite, 10 wt% conducting carbon (ketjen black, KB), and 10 wt% polyvinylidene fluoride (PVDF) in N-methyl-2-prrolidone (NMP) solvent dispersant. Positive electrodes were produced by pasting the slurry on Ni foam with an average sulfur loading of 1.1~1.3 mg cm^{-2}, then drying at 60 ℃ for 12 h. The electrolyte solution was 1 M lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) in a mixed solvent of 1,2-dimethoxy ethane (DME) and 1,3-dioxolane (DOL) (a volume ratio of 1 : 1) with 0.25 M lithium nitrate addictive (LiNO3). The charge-discharge performance of the cells was tested with LAND CT-2001A instrument. The cut-off potentials were 1.9 and 2.7 V at room temperature. Cyclic voltammetry (CV) tests were performed on a Zennium Electrochemical Workstation. The cut-off potentials were 1.9 and 2.7 V at room temperature.
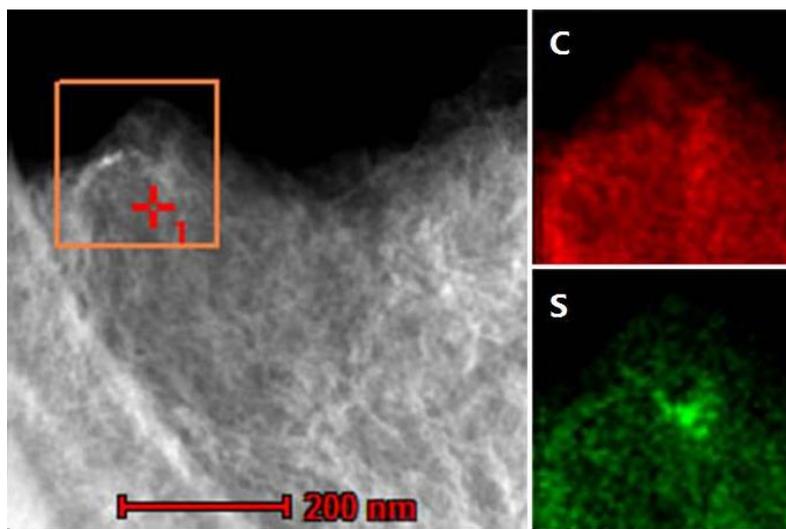
Fig. S1. Scanning transmission electron microscopy (STEM) image and the corresponding element mapping images of carbon and sulfur of the GLs-S composite.
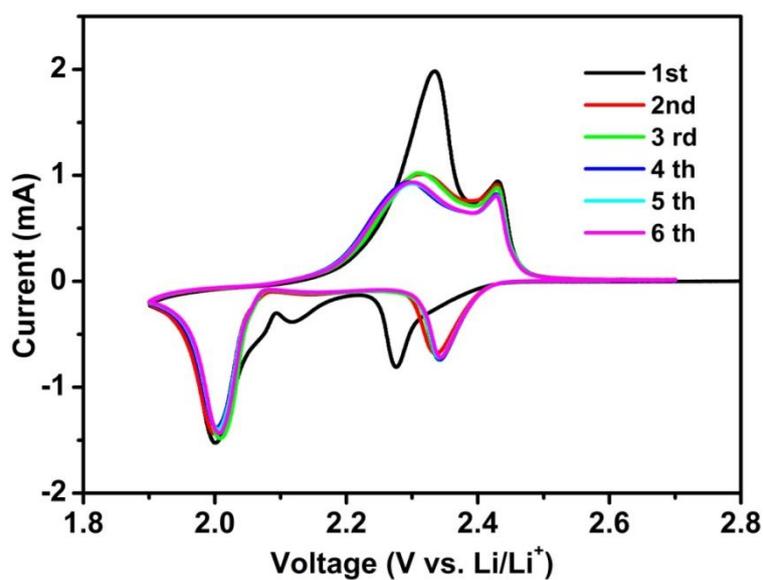
Fig. S2. CV curves of the GLs-S electrode at a scan rate of 0.1 mv s^{-1}.

Table 1 Textural characteristic of samples

samples	BET	Pore Volume
GLs	771 m^2 g^{-1}	1.53 cm^3 g^{-1}
rGO	252 m^2 g^{-1}	1.12 cm^3 g^{-1}
GLs-S	29 m^2 g^{-1}	0.1 cm^3 g^{-1}
rGO-S	29 m^2 g^{-1}	0.1 cm^3 g^{-1}

1.   C. Wan, W. Wu, C. Wu, J. Xu and L. Guan, *RSC Adv.*, 2015, **5**, 5102-5106.