Electronic Supplementary Information

Sulfur-Infiltrated Graphene-Backboned Mesoporous Carbon Nanosheets with Conductive Polymer Coating for Long-life Lithium-Sulfur Batteries

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Experimental details

Fabrication of graphene-backboned mesoporous carbon (GC) nanosheets: Graphite oxide (GO) was prepared via a modified Hummers' method reported elsewhere.¹ Graphene-based mesoporous silica (G-mSiO₂) nanosheets were fabricated by the hydrolysis of tetraethylorthosilicate (TEOS) on GO in the presence of CTAB and NaOH.² They were employed as the template for nanocasting of GC nanosheets. Typically, 230 mg of G-mSiO₂ was immersed in ethanol solution of sucrose (758 mg in 100 mL) for 5 h under stirring at 100 °C. After annealing at 700 °C for 1 h in N₂, GC nanosheets were obtained by etching out the silica in carbon-filled G-mSiO₂ nanosheets. The content of graphene in GC is ca. 35.2 wt.%, as measured by the difference in sample weight before and after loading mesoporous carbon.

Preparation of sulfur-infiltrated graphene-backboned mesoporous carbon (GCS) nanosheets: GCS nanosheets were synthesized by heating the mixture of sulfur powder and GC sample in an Ar-filled container at 155 °C for 12 h. For comparison, graphene-sulfur (GS) composite was also prepared following the similar procedure except that thermal reduced graphene sheets were used.

PPy nanocoating of GCS nanosheets: Aqueous solution of ammonium peroxydisulfate (APS, 4.38 M, 10 mL) was dropwisely added into the mixture of pyrrole (60 μ L), concentrate hydrochloric acid (120 μ L, 37 %) and the suspension of GCS nanosheets (160 mg) in distilled water (100 mL) and ethanol (2 mL) at room temperature. After constant stirring for 6 h, the precipitate was harvested by several rinsing-filtration cycles with distilled water and drying at 50 °C, yielding GCS@PPy nanosheets. For comparison, the composites consisting of graphene-sulfur composite with (GS@PPy, 62 wt.% S) or without PPy coating (GS, 64 wt.% S) and PPy-coated mesoporous carbon-sulfur composite (CS@PPy, 65 wt.% S) were also

prepared following the similar procedure without the introduction of graphene, mesoporous carbon or pyrrole.

The sulfur content (W_s) in GCS@PPy sample is 64 wt.%, as characterized by TGA analysis conducted in N_2 flow. The content of PPy (W_{PPy}) in this sample is measured to be 11 wt.% by the difference in sample weight before and after PPy coating. Therefore, the content of graphene (W_G) and mesoporous carbon (W_c) in GCS@PPy sample can be calculated by following equations:

 $W_G = 35.2 \text{ wt.}\% \times (1 - W_s - W_{PPy}) = 8.8 \text{ wt.}\%$

$$W_C = 1 - W_s - W_{PPv} - W_G = 16.2$$
 wt. %.

Material characterization: The morphology and microstructure of the samples was characterized with field-emission scanning electron microscopy (FESEM, QUANTA 450) and transmission electron microscopy (TEM, FEI TF30). Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2400 type X-ray spectrometer (Cu K α , $\lambda = 1.5406$ Å). The Raman analysis was carried out on RENISHAW inVia Raman microscope. The surface characteristics of the samples were investigated using a Nicolet-20DXB Fourier transform infrared spectrometer (FTIR). The weight ratio of sulfur in the samples was measured by thermogravimetric analysis (TGA, Shimadzu, DRG-60) in N₂ flow. The textural properties of the samples were measured by Micrometrics ASAP 2020 surface area and porosity analyzer at 77 K.

Electrochemical measurement: The electrochemical measurements were conducted using CR2026 coin cells with pure lithium foil as the counter and reference electrode at room temperature. The working electrode consists of a test material (e.g., GS, GCS or GCS@PPy nanosheets), carbon black (Super-P-Li) and polyvinylidene difluoride (PVDF) in a weight ratio of 7:2:1. The electrolyte used is 1.0 M lithium bistrifluoromethanesulfonylimide (LiTFSI) in 1, 3-dioxolane (DOL) and 1, 2-dimethoxyethane (DME) (1:1 by volume) with 1.0 wt. % LiNO₃ additive. Cell assembly was carried out in an Ar-filled glovebox with concentrations of moisture and oxygen below 1.0 ppm. The galvanostatic charge/discharge tests were performed using a LAND CT2001A electrochemical workstation at different current densities within a cut-off voltage window of 1.5-3.0 V. The specific capacity is calculated based on the mass of the sulfur. The average loading amount of the sulfur on the electrodes is ca. 0.4-0.6 mg cm⁻². Cyclic voltammetry (CV) study was conducted using a CHI

660A electrochemical workstation between 1.5-3.0 V at a scan rate of 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was performed using a CHI660A electrochemistry workstation by applying AC amplitude of 5 mV over the frequency range from 0.01 to 10^5 Hz.

- 1. H. Hu, Z. Zhao, Q. Zhou, Y. Gogotsi and J. Qiu, *Carbon*, 2012, **50**, 3267.
- 2. S. Yang, X. Feng, L. Wang, K. Tang, J. Maier and K. Müllen, Angew. Chem. Int. Ed., 2010, 49, 4795.



Figure S1. (a) SEM and (b) TEM image of GC nanosheets.



Figure S2. N_2 adsorption/desorption isotherms of GC sample. The corresponding pore size distribution is shown as the inset.



Figure S3. TGA curves of GCS@PPy sample.



Figure S4. XPS full scan of GCS@PPy sample.



Figure S5. Electrochemical impedance spectroscopy of GCS@PPy and CS@PPy electrodes



Figure S6. Optical photos of the separators detached from the cells using GCS@PPy, GCS and GS electrodes. The cells were discharged to 2.0 V before disassembly.



Figure S7. (a) SEM and (b) TEM image of GCS@PPy electrode after deep cycling; (c) elemental mapping showing the homogenous distribution of carbon, sulfur and nitrogen in the sample.