Supporting Information for

Bifunctional Hierarchical Porous Carbon Network Integrated with In-Situ Formed Ultrathin Graphene Shell for Stable Lithium-Sulfur Battery

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Figure S1. SEM image of porous GO film (containing nickel acetate).

Figure S2. Nitrogen adsorption-desorption isotherms of G-PG film and G-HPC film.
Figure S3. XRD patterns of pure sulfur, G-PG, G-HPC and G-HPC/S films.
Figure S4. TEM images of G-PG sample (a), G-HPC sample (b) and G-HPC/S sample (c). STEM image (d) of G-HPC/S sample and the corresponding elemental mapping of carbon (e) and sulfur (f).
Figure S5. TG curves of G-HPC film tested under air atmosphere and G-HPC/S tested under nitrogen atmosphere.

Figure S6. SEM image (a) and corresponding elemental carbon mapping (b) and sulfur mapping (c) of G-HPC/S electrode.
Figure S7. Nitrogen adsorption-desorption isotherms curves of G-HPC/S sample and G-PG/S sample.

Figure S8. CV curves of G-HPC/S cathode at a scan rate of 0.1 mV s\(^{-1}\).
Figure S9. (a) Low magnification and (b) high magnification SEM images of PG/S electrode.

Figure S10. TGA profile of G-PG/S electrode.
Figure S11. SEM images of the original (a) and artificially shaved (b) surface of porous GO films.

Figure S12. (a) The cross-section morphology of HPC electrode without graphene nano shell after shaving by a blade coater. Top-view SEM image (b) and slope-sectional SEM image (c) of HPC.
Figure S13. Nyquist plots of the HPC/S cathode after different cycles at the rate of 0.5 C.

Figure S14. Galvanostatic discharge/charge profiles of G-HPC/S cathode (a) and HPC/S cathode (b) at different cycles at 0.5 C.
Figure S15. SEM images of the surface (a) and along 45° cross-section (b) of G-HPC/S electrode cycled for 50 times at 0.5 C.

Figure S16. (a) SEM image of CNTs/graphene/S layer of G-HPC/S cathodes after 50 cycles at 0.5 C. (b) Top-view SEM image of multi CNTs/graphene/S layers of G-HPC/S cathodes after 50 cycles at 0.5 C and its corresponding carbon (c) and sulfur (d) mapping.
Figure S17. SEM images of the surface of Li counter electrode in the G-HPC/S cell (a) and HPC/S cell (b) after cycling for 50 times at 0.5 C.

Figure S18. Initial galvanostatic discharge profiles and 2nd discharge profiles after resting for 120 h of the HPC/S cell (a) and the G-HPC/S cell (b).
Table S1. Comparisons of sulfur loading, cyclic performances and rate performances in previously reported works and this work.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Sulfur loading (mg/cm²)</th>
<th>Cyclic performances</th>
<th>Rate performances</th>
<th>Notes</th>
<th>Reference</th>
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<tr>
<td>This work</td>
<td>3.6</td>
<td>3.015</td>
<td>~750 /200</td>
<td>0.5</td>
<td>764.7</td>
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<td>N-doped carbon foam</td>
<td>1.2</td>
<td>1.005</td>
<td>~800 /200</td>
<td>0.5</td>
<td>696</td>
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<td>hollow carbon foam</td>
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<td>-</td>
<td>653.5 /100</td>
<td>0.1</td>
<td>~180</td>
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<td>Fibrous Hybrid of Graphene</td>
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<td>~700 /50</td>
<td>~0.5</td>
<td>670</td>
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<td>graphene-sulfur</td>
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<td>~750 /100</td>
<td>0.2</td>
<td>581</td>
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<td>550 /100</td>
<td>0.05</td>
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<td>Free-Standing Carbon-Nanotube Paper</td>
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<td>0.38</td>
<td>700 /150</td>
<td>0.05</td>
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