Supporting Information

Long-Life and High-Areal-Capacity Li–S Batteries Enabled by a Light-Weight Polar Host with Intrinsic Polysulfide Adsorption

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Figure S1. Characterization of g-C$_3$N$_4$: a) XRD pattern; b) FTIR spectrum; c) XPS survey spectrum showing the C, N and O contributions; d) C 1s and (e) O 1s spectra. f) High-resolution XPS N 1s spectrum and g) EDS spectrum (inset: element atomic compositions) of the as-synthesized N-doped carbon (NdC).
Figure S2. (a) The EDS spectrum of g-C$_3$N$_4$ with the inset table showing the elemental composition in atomic ratio; (b) the low-magnification SEM image of g-C$_3$N$_4$, showing the bulk monolith architecture; (c-f) EDS mapping of the combined elements (c), C (d), N (e) and O (f) on the area in (b), respectively. The scale bars are 5 µm.
Figure S3. (a, c) Low- and (b, d) high-magnification SEM images of (a, b) as-synthesized NdC and (c, d) commercial Vulcan carbon™ (VC).
Figure S4. (a) Plot showing the variation of charge transfer onto \( S_2^{2-} \) anion clusters (per anion) upon interaction with the respective substrates, with respect to the number of \( \text{Li}_2\text{S}_2 \) as calculated by Bader charge analysis after full relaxation; (b-f) the most stable binding configurations of variable numbers of \( \text{Li}_2\text{S}_2 \) molecules on the respective substrates, as indicated on the top right (bottom panels for side views); Insets on top left of (b, c) are the 2D deformation charge distributions of the corresponding substrates without \( \text{Li}_2\text{S}_2 \) (red for accepting electrons, blue for donating electrons). Grey, blue, purple and yellow balls represent C, N, Li and S atoms, respectively.

The back-of-the-envelope calculation shown below demonstrates that the 53.5 at% of N sites are enough to adsorb all polysulfide for a 75wt% sulfur electrode.

Using the starting polysulfide \( \text{Li}_2\text{S}_8 \) as the representative and assuming one N site can adsorb one \( \text{Li}_2\text{S}_8 \) molecule and all N sites are accessible:

For 1g of g-C\textsubscript{3}N\textsubscript{4}/S75 composite containing 75 wt% of sulfur:

The number of N sites is: \( 1 \text{g} \times 25\% \times \frac{53.5\% \times 14 \text{g/mol} + 41.9\% \times 12 \text{g/mol} + 4.6\% \times 16 \text{g/mol}}{53.5\% \times 14 \text{g/mol} + 41.9\% \times 12 \text{g/mol} + 4.6\% \times 16 \text{g/mol}} = 0.010 \text{ mol}; \)

the number of \( \text{Li}_2\text{S}_8 \) molecule is: \( 1 \text{g} \times 75\% \times \frac{1}{8 \times 32 \text{g/mol}} = 0.003 \text{ mol}; \)

Since the number of N active sites are over 3 fold greater than the available \( \text{Li}_2\text{S}_8 \) molecules, it shows that the N concentration of 53.5 at% is sufficient for polysulfide absorption, given the dynamic nature of polysulfide creation and consumption as redox progresses.
Figure S5. TGA curve of the g-C$_3$N$_4$/S75 composite under a N$_2$ atmosphere, with a ramp rate of 10 °C/min.

Figure S6. (a) The voltage profile and (b) cycling performance of the electrodes made from g-C$_3$N$_4$ without sulfur at a rate of 83 mA g$^{-1}$. 
Figure S7. a) First-cycle voltage profiles and b) evolution of Coulombic efficiency (CE) of Li-S cathodes in LiNO$_3$-free electrolyte over 100 cycles. CE is calculated as the ratio of the discharge capacity of N$^{\text{th}}$ cycle over the charge capacity of N-1$^{\text{st}}$ cycle (the 1$^{\text{st}}$ cycle CE is not shown). Polysulfide shuttle in the first cycle leads to significant overcharge for NdC/S75 and VC/S75, but during following cycles the consequent anode passivation alleviates the shuttling problem. c) High-rate cycling performance of the g-$\text{C}_3\text{N}_4$/S75 electrode in LiNO$_3$-containing electrolyte at 1C for 1000 cycles.

Figure S8. a) Low-magnification and b) high-magnification SEM images of the g-$\text{C}_3\text{N}_4$/S75 electrode after 200 cycles at a C rate; fully discharged status.