Ultrathin dendrimer–graphene oxide composite film for stable cycling lithium–sulfur batteries

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Lithium–sulfur batteries (Li–S batteries) have attracted intense interest because of their high specific capacity and low cost, although they are still hindered by severe capacity loss upon cycling caused by the soluble lithium polysulfide intermediates. Although many structure innovations at the material and device levels have been explored for the ultimate goal of realizing long cycle life of Li–S batteries, it remains a major challenge to achieve stable cycling while avoiding energy and power density compromises caused by the introduction of significant dead weight/volume and increased electrochemical resistance. Here we introduce an ultrathin composite film consisting of naphthalimide-functionalized poly(amidoamine) dendrimers and graphene oxide nanosheets as a cycling stabilizer. Combining the dendrimer structure that can confine polysulfide intermediates chemically and physically together with the graphene oxide that renders the film robust and thin (<1% of the thickness of the active sulfur layer), the composite film is designed to enable stable cycling of sulfur cathodes without compromising the energy and power densities. Our sulfur electrodes coated with the composite film exhibit very good cycling stability, together with high sulfur content, large areal capacity, and improved power rate.

Significance

The promise of lithium–sulfur batteries for future electric transportation and stationary energy storage is being limited by their poor cycling stability. Previous approaches to improvement often involve incorporating additional components with significant dead weight or volume in battery structures. We develop an ultrathin functionalized dendrimer–graphene oxide composite film which can be applied to virtually any sulfur cathode to alleviate capacity fading over battery cycling without compromising the energy or power density of the entire battery. The design provides a new strategy for confining lithium polysulfide intermediates and thus stabilizing lithium–sulfur battery. It also brings a suitable platform for elucidating the underlying materials and surface chemistry.


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Successful decoration was confirmed by UV-vis spectroscopy (XPS) studies and density-functional theory (DFT) calculations suggest that the Li ions of LPS bind strongly to the \( O \) atoms in the amide groups of the dendrimer. The well-defined molecular structure of the dendrimer facilitates mechanistic investigation of LPS binding. X-ray photoelectron spectroscopy (EDX), which confirms the existence of the C, N, O, and S elements are identified by energy-dispersive X-ray spectroscopy (EDX). The atomic force microscopy (AFM) image shows that the thickness of the film is about 100 nm (Fig. 1D). We coated the Naph-Den–mGO slurry onto a prepared GO–S (SI Appendix, Fig. S3) electrode surface (Fig. 1E). As a proof of concept, the GO–S electrode material had a sulfur content of 65 wt % and the sulfur mass loading on the cathode was 1 mg cm\(^{-2}\). Fig. 1F shows the top view of the GO–S electrode coated with the Naph-Den–mGO film (Naph-Den–mGO/GO–S), where a thin surface layer is observed. C, N, O, and S elements are identified by energy-dispersive X-ray spectroscopy (EDX), which confirms the existence of the N-containing dendrimer in the surface layer (SI Appendix, Fig. S4). Fig. 1G shows the side view of the Naph-Den–mGO/GO–S electrode, where the Naph-Den–mGO layer can be clearly distinguished from the underlying GO–S layer. The Naph-Den–mGO film has a thickness of \( \sim 90 \) nm shown in the enlarged image, which is a negligible fraction (<1%) in volume compared with the active GO–S layer. The Naph-Den–mGO/GO–S electrode was evaluated in a coin cell with a Li metal anode. The cell was first discharged and recharged at various current rates (0.1–10 C), and then tested for consecutive long-term cycling at 1.0 and 2.0 C. Specific capacities of 1,472, 1,255, 1,083, and 943 mAh g\(^{-1}\) (based on sulfur mass) were observed at 0.1, 0.2, 0.5, and 1.0 \( C \) together with well-defined voltage profiles (Fig. 2A and B). Remarkably, reversible capacities of 785 and 530 mAh g\(^{-1}\) were obtained at high rates of 2.0 and 5.0 C (Fig. 2A and B). As a comparison, the GO–S cathode without the Naph-Den–mGO film exhibited comparable capacities at low rates but much lower capacities at high rates (Fig. 2B and SI Appendix, Fig. S5). At 5.0 \( C \) the specific capacity was already as low as 143 mAh g\(^{-1}\).

The cell was then cycled at 1.0 C with a starting capacity of 830 mAh g\(^{-1}\). After 560 cycles at 1.0 C, the Naph-Den–mGO/GO–S electrode retained a capacity of 757 mAh g\(^{-1}\), corresponding to an average capacity loss of 0.011% per cycle (Fig. 2C). After that the cell was further cycled for another 665 cycles at 2.0 C, during which the capacity dropped from 668 to 562 mAh g\(^{-1}\), giving an average capacity decay of 0.024% per cycle (Fig. 2C). Stable charging and discharging voltage profiles with well-defined voltage plateaus were recorded throughout the cycling process (SI Appendix, Fig. S6). In comparison, the GO–S cathode without the Naph-Den–mGO film showed inferior cycle life. The capacity decreased 0.054% per cycle at 1.0 C, and then 0.073% per cycle at 2.0 C (Fig. 2 C and D).

We further increased the sulfur content in the GO–S electrode material to 76 wt % (SI Appendix, Fig. S7) and the sulfur mass loading on the electrode to 2 mg cm\(^{-2}\). The Naph-Den–mGO/GO–S electrode still had better kinetics than the GO–S electrode as evidenced by the voltage profiles with flatter discharging plateaus (SI Appendix, Fig. S8), although both electrodes manifested compromised specific capacities and rate capabilities as...
the sulfur content and mass loading increased. Notably, the Naph-Den-mGO/GO–S electrode still exhibited excellent cycling stability. Starting from 727 mAh g$^{-1}$ at 1.0 C, the capacity remained 698 mAh g$^{-1}$ after 500 cycles, giving an average capacity loss as low as 0.008% per cycle (Fig. 3A). Importantly, the discharge voltage did not decay over the 500 cycles (Fig. 3B). Without the Naph-Den-mGO film, the GO–S electrode experienced much faster capacity decay (0.068% per cycle) accompanied by decreasing discharging voltages (Fig. 3A and C). Parallel testing demonstrated consistent electrochemical performance of the Naph-Den-mGO/GO–S cathodes. Capacity decay of about 0.01% per cycle over 1,000 discharging–recharging cycles can be realized (SI Appendix, Fig. S9). As sulfur mass loading further increased to 3.5 mg cm$^{-2}$, the Naph-Den-mGO/GO–S electrode was able to deliver a stable specific capacity of ∼1,000 mAh g$^{-1}$ at 0.2 C, corresponding to a high areal capacity of 3.5 mAh cm$^{-2}$ (SI Appendix, Fig. S10). At 0.5 C, 750 mAh g$^{-1}$ and 2.8 mAh cm$^{-2}$ could be achieved with negligible capacity fading over cycling (SI Appendix, Fig. S11). The Naph-Den–mGO film can also enhance cycling performance of other sulfur electrodes. Protected by the composite film, a carbon nanotube buckypaper electrode loaded with 6 mg cm$^{-2}$ of sulfur exhibited stable capacity of ∼750 mAh g$^{-1}$ at 0.5 C (SI Appendix, Fig. S12).

Electrochemical impedance spectroscopy (EIS) was performed for the Naph-Den-mGO/GO–S and GO–S electrodes before and after long-term cycling. The Nyquist plots are shown in Fig. 4A. Typically the depressed semicircle in the high-to medium-frequency region reflects charge transfer resistance ($R_t$) and the inclined line in the low-frequency region is related to mass transfer process (35, 36). The GO–S cathode had an initial $R_t$ of 25 Ω, which rose to 175 Ω after 1,275 discharging–charging cycles. Applying the Naph-Den–mGO film drastically suppresses the increase of charge transfer resistance over cycling. The $R_t$ of the Naph-Den–mGO/GO–S cathode only increased to 45 Ω from the initial 32 Ω over 1,275 cycles. The Naph-Den–mGO/GO–S electrode after long-term cycling was imaged with SEM. The surface of the cycled electrode remained smooth and clean without chunk precipitates (Fig. 4B). The EDX spectrum (SI Appendix, Fig. S13) revealed C, N, O, F, and S elements on the electrode surface, which indicated the robustness of the Naph-Den–mGO film. The side-view image of the cycled electrode further confirmed the integrity of the surface film over cycling (Fig. 4C). It was observed that the thickness of the film increased to 400 nm due to uptake of sulfur species during the cycling process. The elemental distributions of C and S in the vertical cross-section of the electrode are shown in Fig. 4D. It is clear that the sulfur species are well confined by the surface film. The electrochemical stability of the composite film was also verified by cyclic voltammetry (CV) measurements: In the potential window of 1.7–2.7 V vs. Li$^+$/Li (the operating voltage range of sulfur cathodes), the film showed no obvious redox peaks during repeated CV cycles (SI Appendix, Fig. S14).

To further examine the LPS-confining effect of the Naph-Den–mGO film, Li | GO–S and Li | Naph-Den–mGO/GO–S cells were disassembled after 250 cycles, and the used Li anodes were carefully analyzed with SEM and EDS. From the digital photos of the disassembled cells (SI Appendix, Fig. S15A and B), it is obvious that the separator of the cycled Li | GO–S cell contains a significant amount of LPS (yellow), whereas the separator of the cycled Li | Naph-Den–mGO/GO–S cell is almost free of LPS. Combined SEM imaging and EDS mapping (SI Appendix, Figs. S15–17) shows that the cycled Li anode paired with the GO–S cathode is composed of loosely packed small Li particles with a high amount of sulfur species, whereas that paired with the Naph-Den–mGO/GO–S cathode features densely packed, larger Li granules containing a much smaller amount of sulfur. These data, taken together, reveal that the shuttle effect has been substantially suppressed by deploying the Naph-Den–mGO interlayer.

The polysulfide-confining Naph-Den–mGO film promotes high electrochemical performance of sulfur cathodes. The composite film not only prevents LPS from diffusing away from the cathode and thus avoids active material loss and Coulombic efficiency decrease, but it also affords a uniform environment on the cathode surface for facile LPS redox conversion and thus ensures a high degree of utilization of active material and low electrochemical resistance throughout the long-term cycling process. As a result, the Naph-Den–mGO/GO–S electrode has a long cycle life with a capacity decay of <0.01% per cycle, which substantially outperforms any other sulfur cathode with interlayer protection (SI Appendix, Table S1). It is also arguably the best cycling stability among all sulfur cathodes reported to date (SI Appendix, Table S2). It is worth mentioning that our...
Naph-Den–mGO film is only 100 nm thick, its small volume and light weight allow for cycling stability enhancement without compromising the battery energy and power densities. This is difficult to achieve with previously reported interlayers that are usually thicker or heavier by at least one order of magnitude (SI Appendix, Fig. S18). With N- and O-containing functional groups embedded in its branched structure, the Naph-Den is expected to interact with LPS strongly. In a control experiment, we evaluated a GO–S electrode coated with an mGO film without the dendrimer component. The capacity fading over cycling (0.049% per cycle) was substantially faster than the Naph-Den–mGO/GO–S electrode, although slightly slower than the GO–S electrode without any film coated (SI Appendix, Fig. S19). It is thus clear that the Naph-Den is the central component of the composite film for confining polysulfides. The following part of the article will discuss the molecular origins of the binding between the Naph-Den and LPS.

Discussion

We first used XPS to probe the chemical interactions between Naph-Den and LPS using Li$_2$S$_2$ as a model compound. The S 2p core-level spectrum of Li$_2$S$_2$ exhibits two sets of doublets located at 163.1/164.3 eV and 161.4/162.6 eV (Fig. 5A), with binding energy splittings of 1.2 eV, which are attributed to the bridging and terminal sulfur ($S_{2n}^n$ and $S_{1}^1$) atoms, respectively. The spectral features agree well with previous results reported elsewhere (37). In the presence of Naph-Den, the S 2p doublets both shift to lower binding energy (Fig. 5A), indicating increased valence electron density on the S atoms upon interaction with Naph-Den. The binding energy of the N 1s electrons in the Naph-Den remains almost unchanged upon interaction with Li$_2$S$_2$ (Fig. 5B), which suggests a minor contribution from the N sites in the dendrimer structure for LPS binding. This is distinct from previous reports where N atoms in the carbon materials bind LPS strongly (14). The O 1s spectrum of Naph-Den exhibits two components at 531.8 and 533.5 eV (Fig. 5C), which could be due to the O atoms of the amide and imide groups in the Naph-Den structure. In the presence of Li$_2$S$_2$, the O 1s peak shifts to lower binding energy, indicating that the O atoms interact strongly with LPS. Further XPS studies reveal that the PAMAM dendrimer interacts with Li$_2$S$_2$ in a similar manner as the Naph-Den (SI Appendix, Fig. S20). It is thus likely that the O atoms of the amide groups in the PAMAM structure are the major interacting sites responsible for Naph-Den binding with LPS.

We then performed DFT calculations to examine the LPS binding mechanism. We modeled LPS with LiSSH to include S atoms representing both the terminal and bridging S atoms in LPS. Different from many previous reports based on binding energy ($\Delta E_B$) (14, 23), we focused on the binding free energy ($\Delta G_B$) to evaluate the interaction strength between LiSSH and different binding sites (BSite) and/or solvent molecules (Sol). $\Delta G_B$ is defined as follows:

$$\Delta G_B = G(\text{HSSLiSOL_BS}e_{\text{BSite}}) - G(\text{HSSLi}) - mG(\text{Sol}) - nG(\text{BSite}),$$

where HSSLiSOL_BS$e_{\text{BSite}}$ is the complex of LiSSH with $m$ solvent molecules and $n$ binding sites. The use of $\Delta G_B$ in place of $\Delta E_B$ brings the advantage of including both thermal and entropy corrections, which is important for accurate modeling of the interaction strength. For example, we calculated the $\Delta E_B$ of LiSSH to the 1,3-dioxolane (DOL) solvent molecule to be −20.7 kcal mol$^{-1}$ (SI Appendix, Fig. S21), in excellent agreement with previously reported values for similar systems (14, 38). However, taking entropy into consideration, $\Delta G_B$ for binding of LiSSH to DOL is −10.6 kcal mol$^{-1}$, which differs substantially from $\Delta E_B$. We found that $\Delta G_B$ for binding of LiSSH to another solvent molecule, dimethoxyethane (DME), is −20.6 kcal mol$^{-1}$, significantly more negative than that for DOL (Fig. 6A and B), suggesting that LiSSH prefers to be solvated by the chelating ligand DME. $\Delta G_B$ for binding of LiSSH to two DME molecules is −24.3 kcal mol$^{-1}$ (Fig. 6C), corresponding to $\Delta G$ of −3.7 kcal mol$^{-1}$ for HSSLi–DME to bind a second DME molecule. Therefore, LiSSH prefers to be solvated by two DME molecules in the battery electrolyte, consistent with previous reports on DME-solvated Li complexes in both solution (39) and crystals (40, 41).

Now we turn to the binding of LiSSH to Naph-Den. There are three sites in the Naph-Den molecular structure that can bind LPS, namely the O atoms in the amide groups (O1 site), the N atoms in the tertiary amine groups (N1 site), and the O atoms in the terminal imide groups (O2 site), as shown in SI Appendix, Fig. S22. SI Appendix, Fig. S23 shows that the binding between LiSSH and a functional group is hardly affected by other atoms beyond...
the functional group, and thus demonstrates the validity of our model. As shown in Fig. 6 D–F, ΔG_B values for binding of LiSSH to the N1, O1, and Ot sites in Naph-Den are −13.2, −19.0, and 17.3 kcal mol\(^{-1}\), respectively. All are smaller than that to DME, indicating that the three types of binding sites are unlikely to replace the DME ligand in HSSLi(DME). ΔG_B values for binding of LiSSH to the N1, O1, and Ot sites in the presence of one DME molecule are calculated to be −22.8, −27.0, and −24.5 kcal mol\(^{-1}\), respectively (Fig. 6 G–I). The ΔG_B values for binding of HSSLi(DME) to the N1, O1, and Ot sites can thus be derived to be −1.2, −6.4, and −3.9 kcal mol\(^{-1}\), respectively. Compared with the ΔG_B values for binding of HSSLi(DME) to a second DME molecule (−3.7 kcal mol\(^{-1}\)), our results suggest that it is thermodynamically favorable for the O1 site to replace a DME molecule in HSSLi(DME)\(_2\) (ΔG = −2.7 kcal mol\(^{-1}\)) and thus bind LPS. Our results also suggest that the N1 site is unlikely to bind the solvated LiSSH.

Considering that the samples for XPS study are under high vacuum condition in which the volatile organic solvents are likely to be removed from the samples, we include analysis of interactions

![Fig. 5](image1)

**Fig. 5.** XPS analysis of the interactions between Naph-Den and LPS. (A) S 2p core-level spectra of Li\(_2\)S\(_4\) before and after interacting with Naph-Den. (B) N 1s and (C) O 1s core-level spectra of Naph-Den before and after interacting with Li\(_2\)S\(_4\).

![Fig. 6](image2)

**Fig. 6.** DFT calculations of binding free energies (ΔG_B). Optimized geometries for the binding of LiSSH to (A) one DOL molecule, (B) one DME molecule, (C) two DME molecules, (D) N1 site, (E) O1 site, (F) Ot site, (G) N1 site and one DME molecule, (H) O1 site and one DME molecule, and (I) Ot site and one DME molecule, and corresponding binding free energies in kilocalorie per mole. Gray, white, red, blue, yellow, and purple balls represent C, H, O, N, S, and Li atoms, respectively.
between LiSSH and Naph-Den in the absence of solvent molecules. The calculated binding free energies suggest that the O1 site should still be the dominant binding sites for LPS (SI Appendix, Fig. S24 A–C). Based on the optimized structure for LiSSH binding to the O1 site of the Naph-Den, we further calculated the partial atomic charges for the S, O, and N atoms in the structure to correlate with the binding energy shifts measured by XPS (42, 43). As shown in SI Appendix, Fig. S24D, the Mulliken charges on the O atom of the Naph-Den O1 site and on the S atoms of the LiSSH all become more negative (with increased electron density) upon interaction, which well explains the experimentally observed red shifts of O 1s and S 2p binding energies in the XPS spectra. It is, therefore, confirmed that the O atoms of the amide groups in the Naph-Den structure are the dominant sites that bind LPS.

In summary, we have designed and developed an ultrathin dendrimer–GO composite film to mitigate the polysulfide shuttling problem and stabilize the cycling of Li-S batteries without compromising their energy and power densities. The dendrimer molecules provide strong affinity to polysulfides via specific chemical interactions between amide groups and Li ions. The graphene oxide nanosheets ensure mechanical robustness and low thickness. The resulting composite is a bifunctional binder.

Materials and Methods

Material synthesis, electrode preparation, materials characterization, electrochemical measurements, and computational methods are detailed in SI Appendix.

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Supporting Information Appendix for

An Ultrathin Dendrimer-Graphene Oxide Composite Film for Stable Cycling Lithium-Sulfur Batteries

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MATERIALS AND METHODS

Synthesis of Naph-Den and preparation of Naph-Den-mGO slurry

All chemicals and solvents were commercially available and used as obtained without further purification. Following a reported procedure (1) with modifications, a mixture of PAMAM G4 dendrimer (25 mg, 1.76 μmol) and 1,8-naphthalic anhydride (26.8 mg, 135 μmol) in DMF (1.5 mL) was stirred at 90 °C for 48 h in the dark under a nitrogen atmosphere. The crude Naph-Den product was purified by dialysis using a regenerated cellulose membrane with a molecular weight cutoff of 12–14 kDa in dimethyl sulfoxide (DMSO) for three days. The light yellow solution in the dialysis bag was dried under vacuum for four days to yield the Naph-Den as a light yellow brown semi-solid (40 mg, 85%): 1H NMR (400 MHz, CDCl3), δ 8.26 (br, 252H, naphthyl-H and amido-H, overlapped), 7.94 (br, 128H, naphthyl-H), 7.67 (br, 128H, naphthyl-H), 4.02 (br, 128H, CH2 adjacent to naphthyl unit), 2.90 (s, 256H, -CH2-CO-), 2.74 (s, 256H, -CH2-NH-CO-), 2.09 (br, 356H, -CH2-N-); λabs (DMSO) 330 nm. The Naph-Den-mGO slurry was prepared by vortex mixing a 6 mg mL⁻¹ mGO (prepared with a modified Hummers method in which 0.5 g KMnO4 for 1 g Graphite (2)) DMF suspension with a 6 mg mL⁻¹ Naph-Den DMF solution.

Fabrication of Naph-Den-mGO film protected cathode

The GO-S composite material was prepared by decomposing sodium polysulfide (NaSx) in the presence of GO (prepared with a modified Hummers method in which 4 g KMnO4 used for 1 g Graphite (3)) in a water/ethanol mixed solvent. The obtained GO-S was mixed with carbon black and polyvinylidene difluoride (PVDF) in a mass ratio of 80:10:10 in N-methylpyrrolidone (NMP) to make a slurry that was then casted onto a carbon-coated Al foil (MTI Corporation, USA) and dried at 50 °C in a vacuum oven for 2 h. The sulfur electrode film was compressed and punched into circular pellets with a diameter of 14 mm. 20 μL of the Naph-Den-mGO slurry (6 mg mL⁻¹) was then cast onto the sulfur cathode by doctor blading, followed by drying at 50 °C in a vacuum oven for another 2 h. The BP-S electrodes were prepared by immersing BP (NTL-12214, 45 gsm MWNT Blend, Nanotech Labs, Inc.) in a 0.04 g ml⁻¹ Sn/DMF solution followed by drying in a vacuum oven at 70 °C. The electrodes were then punched into circular...
disks with a diameter of 14 mm. After that, the electrode disks were sealed in a Teflon lined stainless steel autoclave and heated at 155 °C for 12h. The Naph-Den-mGO/BP-S electrodes were prepared by casting the Naph-Den-mGO slurry onto the BP-S electrodes following the same procedure as for preparing the Naph-Den-mGO/GO-S electrodes.

**Materials characterization**

$^1$H NMR spectra were recorded with an Agilent 400 MHz NMR instrument. Chemical shifts are reported as ppm from the internal reference tetramethylsilane (TMS). Absorption spectra were recorded with a Varian Cary 50 Bio UV-visible spectrophotometer. SEM imaging and EDX measurements were performed with a Hitachi SU8230 field emission SEM microscope. TEM images were taken on a JEM-1400 Plus TEM microscope. XPS measurements were performed with a PHI Versa Probe II with Al K$_\alpha$ radiation. The XPS samples were prepared by soaking material loaded silicon chips for 24 h in a 0.01 mol L$^{-1}$ Li$_2$S$_4$ solution prepared by dissolving stoichiometric amounts of elemental sulfur and lithium sulfide (Li$_2$S) in a mixed solvent of DME and DOL (1:1 by volume), followed by drying in an argon-filled glove box. The samples were then transferred into the XPS chamber without exposing to air, using an air-tight vessel.

**Electrochemical measurements**

CR2032 coin cells were assembled in an argon-filled glove box with the prepared sulfur electrodes as cathode, lithium disks as anode, and a porous membrane (Celgard 3501) as the separator. The electrolyte was lithium bis(trifluoromethane) sulphonimide (1.0 M) in a solvent mixture of DOL and DME (1:1 by volume) containing lithium nitrate (2 wt.%). Galvanostatic discharging and charging were performed on an Arbin BT-2143 battery analyzer at various rates (1 C = 1600 mA g$^{-1}$) in the potential window of 1.7-2.7 V vs Li$^+/\text{Li}$). The EIS data were recorded using a 760D electrochemistry workstation (CH Instruments) at 2.4 V over the frequency range of 100 kHz to 10 mHz. To assess the electrochemical stability of the Naph-Den-mGO film, the Naph-Den-mGO slurry was coated onto Al foil and then cut into electrode disks with a diameter of 14 mm. CR2032 coin cells were assembled using the Naph-Den-mGO electrode as cathode and Li foil as anode. CV data were recorded with the Arbin BT-2143 battery analyzer at a scan rate of 0.05 mV s$^{-1}$. 
**Computational details**

The DFT study was performed with the B3LYP functional (4, 5) implemented in Gaussian 09 Rev. D.01 (6). Dispersion interactions were considered with Grimme’s D3 correction (7). A pruned grid having 99 radial shells and 590 angular points per shell, called “ultrafine” grid in Gaussian 09, was used for the non-analytic integral evaluations. The 6-31G(d) basis set (8, 9) was used for the geometry optimization, Mulliken population analysis, and the vibrational frequency analysis required for free energy calculations. The calculated vibrational frequencies were used for the computation of molecular partition functions to evaluate thermal contributions to the free energy at 298.15 K by employing the ideal gas, rigid rotator, harmonic oscillator approximation (10). The 6-311+G(2df,p) basis set (11) was used in single-point calculations for refined energetics. The thermal contribution to the free energies from the frequency analysis was added to the refined energetics for all final composite free energies reported in the manuscript. In the calculation of binding free energies, the 1 M standard state was used for all species.
Figure S1 UV-Vis absorption spectra. Both the dendrimer (PAMAM) and its naphthalimide functionalized product Den-Naph (PAMAM-Naph) were measured in DMSO at a concentration of 0.5 mg mL\(^{-1}\).

Figure S2 \(^1\)H NMR spectrum of Den-Naph in DMSO-d6.
Figure S3  Morphology and elemental distribution of GO-S cathode material with 65 wt.% sulfur content. SEM images of GO-S at low (a) and high (b) magnification. (c, d, e) HAADF image and EDX maps of GO-S.

Figure S4  SEM and EDX analysis for sulfur electrodes. (a, b) SEM image and corresponding EDX spectrum of the GO-S electrode. (c, d) SEM image and corresponding EDX spectrum of the Naph-Den-mGO/GO-S electrode.
Figure S5 Representative discharging-charging voltage profiles of GO-S at different C rates.

Figure S6 Discharging and charging voltage profiles of the GO-S electrodes with and without the Naph-Den-mGO film at different stages of cycling stability test. The sulfur content in the GO-S composite is 65 wt.%, and the total sulfur loading on the electrode is 1 mg cm\(^{-2}\).

Figure S7 Morphology of the GO-S cathode material with 76 wt.\% sulfur content. SEM images of the GO-S at low (a) and high (b) magnification.
Figure S8 Electrochemical performance of the Naph-Den-mGO/GO-S electrode compared with the GO-S electrode. (a) Discharge capacities and (b) representative discharging-charging voltage profiles of the GO-S electrode at different C rates. (c) Discharge capacities and (d) representative discharging-charging voltage profiles of the Naph-Den-mGO/GO-S electrode at different C rates. The sulfur content in the GO-S composite is 76 wt.%, and the sulfur mass loading on the electrode is 2 mg cm$^{-2}$.

Figure S9 Parallel cycling stability test of the Naph-Den-mGO/GO-S electrodes. The sulfur content in the GO-S composite is 76 wt.%, and the sulfur mass loading on the electrode is 2 mg cm$^{-2}$.
Figure S10 Cycling performance of Naph-Den-mGO/GO-S electrode at 0.2 C. The sulfur content in the GO-S composite is 76 wt.%, and the sulfur mass loading on the electrode is 3.5 mg cm$^{-2}$.

Figure S11 Electrochemical performance of the Naph-Den-mGO/GO-S electrode with high sulfur mass loading. (a) Representative discharging-charging voltage profiles. (b) Discharging capacities at different C rates. (c) Cycling stability at 1.0 C and 0.5 C. The sulfur content in the GO-S composite is 76 wt.%, and the sulfur mass loading on the electrode is 3.5 mg cm$^{-2}$. 
Figure S12 SEM images and electrochemical performance of the Naph-Den-mGO/BP-S electrode. (a) Top-view and (b) cross-section SEM images of the Naph-Den-mGO/BP-S electrode. (c) Enlarged cross-section SEM image showing the Naph-Den-mGO film on the electrode surface. (d) Enlarged cross-section SEM image showing the carbon nanotubes coated with sulfur particles. (e) Cycling stability of the BP-S and Naph-Den-mGO/BP-S electrodes. (f) Discharging-charging voltage profiles of the Naph-Den-mGO/BP-S electrode.

Figure S13 SEM and EDX characterization of the Naph-Den-mGO/GO-S electrode after cycling (1275 cycles).
Figure S14. Cyclic voltammograms of the Naph-Den-mGO film in the Li-S battery electrolyte.

Figure S15. Postmortem analysis of the Li anodes paired with the GO-S and Naph-Den-mGO/GO-S cathodes in cells after 250 cycles. Photographs of the disassembled cells using (a) GO-S and (b) Naph-Den-mGO/GO-S as cathodes. SEM images and the corresponding EDS spectra and elemental maps of the cycled Li anodes paired with the (c) GO-S and (d) Naph-Den-mGO/GO-S cathodes.
Figure S16. Cross-section SEM images of the Li anodes paired with the (a, b) GO-S and (c, d) Naph-Den-mGO/GO-S cathodes after 250 cycles.

Figure S17. SEM-EDS analysis of the cross sections of the Li anodes paired with the (a) GO-S and (b) Naph-Den-mGO/GO-S cathodes after 250 cycles.
Figure S18 Figures of merit for Li-S battery cathode interlayers reported in the literature (Table S1). (a) Plot of cathode capacity loss upon cycling against interlayer thickness. (b) Plot of cathode capacity loss upon cycling against interlayer mass (percentage of sulfur active material). Our Naph-Den-mGO film outperforms any other interlayer reported to date.

Figure S19 Electrochemical performance of the mGO/GO-S electrode. (a) Cycling stability at 1.0 and 2.0 C rates. (b) Representative discharging-charging voltage profiles at different C rates. (c) The discharging-charging voltage profiles before and after cycling at 1.0 and 2.0 C. The sulfur content in the GO-S composite is 65 wt.%, and the total sulfur loading on the electrode is 1 mg cm\(^{-2}\).
Figure S20 XPS analysis of the interaction between lithium polysulfide and the unmodified dendrimer (PAMAM). (a) S 2p core level spectra of free Li$_2$S$_4$ and Li$_2$S$_4$ adsorbed on PAMAM. (b) N 1s and (c) O 1s core level spectra of the PAMAM before and after its interaction with Li$_2$S$_4$. 
Figure S21 Theoretical calculations of binding energy ($\Delta E_b$). Optimized geometries for the binding of LiSSH to (a) DOL, (b) DME, (c) two DME molecules, (d) N1 site, (e) O1 site, (f) Ot site, (g) N1 site and one DME molecule, (h) O1 site and one DME molecule, and (i) Ot site and one DME molecule, together with the corresponding binding energies in kcal/mol. Grey, white, red, blue, yellow, and purple balls represent C, H, O, N, S, and Li atoms, respectively.
Figure S22  Structure of the PAMAM G2 dendrimer and three possible binding sites for lithium polysulfides. Grey, white, red, and blue balls represent C, H, O, and N atoms, respectively.

Figure S23 Optimized geometries for the binding of LiSSH to the O1 sites. Models include (a) 1 bond, (b) 2 bonds, (c) 3 bonds, (d) 4 bonds, and (e) 5 bonds beyond the amide group. The calculated binding free energies and key bond lengths are shown in kcal/mol and Å. Grey, white, red, blue, yellow, and purple balls represent C, H, O, N, S, and Li atoms, respectively.
Figure S24 Theoretical calculations in the absence of solvent molecules. Optimized geometries for the binding of LiSSH to (a) N1 site, (b) O1 site, and (c) Ot site of Naph-Den, with the binding free energies in kcal mol$^{-1}$; Mulliken charges (d) before and (e) after LiSSH binding to the O1 site of Naph-Den. Grey, white, red, blue, yellow, and purple balls represent C, H, O, N, S, and Li atoms, respectively.
SUPPORTING TABLES

Table S1. Performance comparison with sulfur cathodes protected by different interlayers reported in the literature (green: average capacity decay <2% per 100 cycles; yellow: 2-10%; red: >10%).

<table>
<thead>
<tr>
<th>Interlayer</th>
<th>Sulfur loading (mg cm⁻²)</th>
<th>Interlayer thickness (µm)</th>
<th>Interlayer mass (mg cm⁻²)</th>
<th>Cycling stability</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naph-Den-mGO</td>
<td>2.0</td>
<td>0.1</td>
<td>~0.05</td>
<td>500</td>
<td>0.8%@1 C</td>
</tr>
<tr>
<td>TiO₂-CNT</td>
<td>0.8</td>
<td>35</td>
<td>0.5~0.6</td>
<td>500</td>
<td>5%@1 C</td>
</tr>
<tr>
<td>Carbon/MWCNT paper</td>
<td>1.8~2.7</td>
<td>~60</td>
<td>\</td>
<td>100</td>
<td>6.5%@1 C</td>
</tr>
<tr>
<td>GO-TiO₂</td>
<td>1.2</td>
<td>~3</td>
<td>0.15</td>
<td>250</td>
<td>7.2%@0.5 C</td>
</tr>
<tr>
<td>GO</td>
<td>1~1.2</td>
<td>0.75</td>
<td>0.29</td>
<td>400</td>
<td>8%@1 C</td>
</tr>
<tr>
<td>N,P co-doped graphene</td>
<td>2.1</td>
<td>\</td>
<td>1.0</td>
<td>500</td>
<td>9%@1 C</td>
</tr>
<tr>
<td>Graphene</td>
<td>3~4</td>
<td>20</td>
<td>1.3</td>
<td>300</td>
<td>10%@1 C</td>
</tr>
<tr>
<td>Carbon nanofibers</td>
<td>1.4</td>
<td>~280</td>
<td>4.2</td>
<td>100</td>
<td>10%@1 C</td>
</tr>
<tr>
<td>Ethylenediamine-functionalized rGO</td>
<td>3.6</td>
<td>0.1</td>
<td>0.54</td>
<td>200</td>
<td>10%@0.2 C</td>
</tr>
<tr>
<td>Microporous carbon paper</td>
<td>\</td>
<td>\</td>
<td>\</td>
<td>100</td>
<td>15%@1 C</td>
</tr>
<tr>
<td>Ni foam</td>
<td>\</td>
<td>~90</td>
<td>\</td>
<td>50</td>
<td>17%@0.2 C</td>
</tr>
<tr>
<td>GO/Nafion</td>
<td>1.2</td>
<td>0.13</td>
<td>0.0532</td>
<td>200</td>
<td>18%@0.5 C</td>
</tr>
<tr>
<td>SWCNT</td>
<td>1.5</td>
<td>~9</td>
<td>0.14</td>
<td>300</td>
<td>18%@0.2 C</td>
</tr>
<tr>
<td>GO</td>
<td>1~1.5</td>
<td>~6</td>
<td>0.12</td>
<td>100</td>
<td>23%@0.1 C</td>
</tr>
<tr>
<td>N doped graphene paper</td>
<td>1.06</td>
<td>~8</td>
<td>0.5</td>
<td>100</td>
<td>23%@0.2 C</td>
</tr>
<tr>
<td>rGO-carbon black</td>
<td>3</td>
<td>\</td>
<td>3</td>
<td>100</td>
<td>29%@0.2 C</td>
</tr>
<tr>
<td>Al₂O₃-activated carbon cloth</td>
<td>12</td>
<td>500</td>
<td>~2</td>
<td>40</td>
<td>\</td>
</tr>
<tr>
<td>MWCNT</td>
<td>\</td>
<td>40~50</td>
<td>0.6~0.8</td>
<td>100</td>
<td>38%@1 C</td>
</tr>
</tbody>
</table>
Table S2. Performance comparison with state-of-the-art high-performance sulfur cathodes reported in the literature (green: average capacity decay <2% per 100 cycles; yellow: 2-10%; red: >10%).

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Sulfur content in material</th>
<th>Sulfur loading on electrode (mg cm⁻²)</th>
<th>Cycling stability</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naph-Den-mGO/GO-S</td>
<td>65%</td>
<td>1.0</td>
<td>830</td>
<td>1.6%@1 C</td>
</tr>
<tr>
<td></td>
<td>76%</td>
<td>2.0</td>
<td>727</td>
<td>1%@1 C</td>
</tr>
<tr>
<td></td>
<td>76%</td>
<td>3.5</td>
<td>741</td>
<td>1.1%@0.5 C</td>
</tr>
<tr>
<td>Covalent bond glued sulfur nanosheets</td>
<td>83%</td>
<td>1.2</td>
<td>715</td>
<td>2.1%@0.625C</td>
</tr>
<tr>
<td>S-TiO₂ yolk-shell</td>
<td>71%</td>
<td>0.4-0.6</td>
<td>1030</td>
<td>3.3%@0.5 C</td>
</tr>
<tr>
<td>CoS₂-graphene/S</td>
<td>75%</td>
<td>0.4</td>
<td>1000</td>
<td>3.4%@2C</td>
</tr>
<tr>
<td>MnO₂ nanosheets/S</td>
<td>75%</td>
<td>0.7-1.0</td>
<td>870</td>
<td>3.6%@2C</td>
</tr>
<tr>
<td>Mesoporous carbon sphere-CNT/S</td>
<td>70%</td>
<td>5</td>
<td>1200</td>
<td>5%@0.2 C</td>
</tr>
<tr>
<td>Hollow carbon nanospheres/S</td>
<td>67%</td>
<td>\</td>
<td>842</td>
<td>5.3%@1C</td>
</tr>
<tr>
<td>Si/SiO₂@C-S</td>
<td>70%</td>
<td>3.1-3.5</td>
<td>890</td>
<td>6.3%@2C</td>
</tr>
<tr>
<td>TiO₂/S</td>
<td>60%</td>
<td>1.5-1.8</td>
<td>850</td>
<td>6%@2C</td>
</tr>
<tr>
<td>ethylenediamine-functionalized rGO/S</td>
<td>69%</td>
<td>/</td>
<td>700</td>
<td>7%@0.5C</td>
</tr>
<tr>
<td>S/Co-N-Graphitic carbon</td>
<td>70%</td>
<td>2.5</td>
<td>795</td>
<td>9%@1C</td>
</tr>
<tr>
<td>Graphene-S sandwich</td>
<td>70%</td>
<td>3~4</td>
<td>1000</td>
<td>10%@1C</td>
</tr>
<tr>
<td>Dual confined N-doped double-shelled hollow carbon spheres/S</td>
<td>63%</td>
<td>3.9</td>
<td>838</td>
<td>19%@0.5C</td>
</tr>
</tbody>
</table>

This work
SUPPORTING REFERENCES


