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A lightweight multifunctional interlayer of sulfur–nitrogen dual-doped graphene for ultrafast, long-life lithium–sulfur batteries

A lightweight multifunctional interlayer of sulfur–nitrogen dual-doped graphene enables the Li-S battery to deliver an excellent rate performance.

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1. Introduction

Rechargeable batteries with a high energy/power density and long-lasting cycling performance are highly sought after for electric vehicles and large-scale electrochemical energy storage systems.^{1,2} Owing to their advantages of low cost, natural abundance, eco-friendliness, and high theoretical capacity and energy density, lithium–sulfur (Li–S) batteries are a promising candidate for the next-generation battery systems.¹⁻⁴ However, upon discharging/charging, the intermediate lithium polysulfides (LiPSs, Li_2S_n , $2 \le n \le 8$) could dissolve in the electrolyte and diffuse to the anode side to be reduced and then shuttle back to the cathode, which is known as the "shuttle effect" and causes self-discharge, low coulombic efficiency, and active material loss.¹⁻³ As such, shuttling is one major hurdle—along with a low sulfur utilization ratio, high volume expansion, and lithium anode degradation—that limits the practical use of Li–S batteries.⁴

A lightweight multifunctional interlayer of sulfurnitrogen dual-doped graphene for ultrafast, longlife lithium-sulfur batteries†

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Lithium–sulfur batteries are a promising candidate for next-generation battery systems owing to their low cost and high theoretical capacity and energy density. However, the notorious shuttle effect of the intermediate polysulfides as well as low conductivity of sulfur greatly limits their practical applications. Here, we introduce a new design that uses a porous-CNT/S cathode (PCNT–S) coupled with a lightweight multifunctional porous sulfur–nitrogen dual-doped graphene (SNGE) interlayer. It is confirmed that the introduced SNGE has outstanding conductivity, high ability to trap polysulfides, ability to modulate Li_2S_2/Li_2S growth, and the functionality to protect separator integrity. With such rich functionalities, the SNGE interlayer enables the PCNT–S cathode to deliver a reversible specific capacity of ~1460 mA h g⁻¹ at 0.25C and a much higher rate performance, up to 40C, with a capacity retention of 130 mA h g⁻¹. Critically, these cathodes exhibited ultrahigh cyclability when cycled at 8C for 1000 cycles, exhibiting a capacity degradation rate of 0.01% per cycle. To the best of our knowledge, such a low capacity degradation rate beyond 5C in the cathodes of advanced Li–S batteries has been reported only rarely. These results impressively revealed the outstanding high-power output performance of the Li–S batteries.

Research studies on addressing these issues have mostly focused on impregnating sulfur into various carbon matrixes,5-7 carbon materials doped with nitrogen⁸⁻¹⁰ or S, N co-doped carbon materials.¹¹⁻¹⁵ Although these approaches do improve cyclability and capacity, the improvement in performance produced by only adjusting the matrixes to carry sulfur is often limited. Among the proposed concepts for suppressing the shuttle effect, introducing an interlayer between the cathode and separator might be an ideal strategy because the interlayer could intercept the migrating LiPSs and reuse the trapped active material.^{1,2} Recently, various carbon-based interlayers or ion selective membranes have been developed,¹⁶⁻²⁶ including microporous carbon paper,¹⁶ microporous carbon nanofiber,17 mesoporous carbon interlayers,18 hierarchical carbonized paper,19 carbonized eggshell membranes,20 Fe₃C-carbon layers,²¹ and graphene class materials.²²⁻²⁵ More recently, we developed a lightweight, chemically selective TiO₂/ graphene interlayer.27 The as-obtained Li-S battery exhibited a high reversible specific capacity and excellent cycling stability at a relatively high rate (3C). Despite these significant successes, however, the high-power performance of Li-S batteries with interlayers is still far from satisfactory. To meet the requirements for the use of these batteries in electric vehicles, it remains an urgent task to further improve the performance of Li-S batteries at high rates, especially beyond 5C.10,28

To improve the high-power output performance of Li–S batteries with the interlayer approach, three interlayer



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attributes must be optimized: first, the whole interlayer should have excellent electronic conductivity.1,16-20 As such, some functional materials used to suppress the shuttle effect (e.g. FeC₃,²¹ thiocarbohydrazide,²⁴ TiO₂²⁷ and Al₂O₃,²⁹) should be avoided in the interlayer because they have poor electronic conductivity or are too easily destroyed at high current densities. Second, the ability of the interlayer to trap LiPS ions must be further improved because LiPS shuttling between the cathode and anode will become more prevalent at higher rates of discharge/charge cycling.30,31 Third, the hasty conversion and accumulation of Li2S2/Li2S crystals could cause volume changes and cracks of the cathode in Li-S batteries; so, the cathode structure must be made as resilient as possible.³²⁻³⁴ Considering the fact that the interlayer is close to the cathode, it may be an interesting strategy to give the interlayer some special functionalities, such as modulating Li₂S₂/Li₂S growth and protecting the cathode's structural integrity.^{1,4,32,34-36} To the best of our knowledge, this strategy involving the interlayer having such rich functionalities has not been yet been proposed.

In the present study, after considering the three attributes described above, we introduce a new design that uses a porous-CNT/S cathode (PCNT-S) coupled with a lightweight porous sulfur-nitrogen dual-doped graphene (SNGE) interlayer, whose introduced porous SNGE has excellent electric conductivity and can efficiently trap LiPS ions. Although there were a few reports involving the functionalized graphene containing sulfur and nitrogen atoms as interlayer materials, our work has a significant difference as well as additional benefits: (1) the introduced SNGE has obviously high conductivity compared with the graphene grafted with thiocarbohydrazide reported by Xing et al.24 because of avoiding any additional materials with poor electronic conductivity in our case. (2) The abundant pore structure coupled with the high heteroatom doping concentration endows the SNGE with abundant chemical adsorption sites, which is favorable for trapping the migrating LiPSs and suppressing the shuttling of LiPSs; (3) as an exhilarating discovery, it is first confirmed that the SNGE in the Li-S batteries can modulate Li₂S₂/Li₂S growth and protect the separator's integrity. With its outstanding properties, the SNGE interlayer enable the PCNT-S cathode to deliver a reversible specific capacity of \sim 1460 mA h g⁻¹ at 0.25C and a much higher rate performance, up to 40C, with a capacity retention of 130 mA h g^{-1} . Critically, these cathodes exhibited ultrahigh cyclability when cycled at 8C for 1000 cycles, exhibiting a capacity degradation rate of 0.01% per cycle. To the best of our knowledge, such a low capacity degradation rate at beyond 5C in the cathodes of advanced Li-S batteries has been reported only rarely.

2. Results and discussion

Fig. 1a shows a schematic of the cell configuration. Compared with a conventional Li–S battery, our electrode design introduces a special SNGE interlayer inserted between the cathode and separator. The preparation of this modified cathode can be broadly divided into two steps, as shown by the photographs in Fig. S1.† In the first step, a conventional sulfur cathode with a host material of porous CNTs (PCNTs) was prepared (Fig. S2†).



Fig. 1 Schematic of the electrode configuration for the Li–S battery with the SNGE interlayer; (a) photograph (b) and cross-sectional SEM image (c) of the cathode with the SNGE interlayer; the inset are photographs of the PCNT–S@SNGE cathode and the as-made Li–S cell.

The PCNTs were obtained via a high-temperature reaction between the crude CNTs and a nebulized water stream, as we previously reported.5 In the second step, using a facile coating method, the lightweight SNGE film was deposited onto the as-made PCNT-S cathode; the obtained cathode is named PCNT-S@SNGE. Fig. 1b and c and S3[†] show a photograph and scanning electron microscopy (SEM) images of typical crosssection and top-view of the PCNT-S@SNGE cathode sheet. The SNGE film, which has a macroscopically smooth surface, perfectly covers and adheres to the PCNT-S layer. The measured thicknesses of the SNGE film and PCNT–S layer were ${\sim}4\,\mu\text{m}$ and 32 µm, respectively. The weight of the coating film was determined by weighing the electrode with and without the double coating,²⁷ about 6 wt% weight occupation of the integrated cathode (without including the aluminum foil), lighter than most of the reported free-standing interlayers.16-20,27 In our experiments, we prepared SNGE by annealing graphene oxide (GO) and thiourea at high temperature in argon. For comparison, we performed nitrogen doping, sulfur doping and pyrolysis of GO under similar synthetic conditions by changing the doping precursors, as detailed in the Experimental section. The obtained materials and the corresponding coated cathodes are named NGE, SGE, rGO, PCNT-S@NGE, PCNT-S@SGE, and PCNT-S@rGO, respectively, based on the net PCNT-S cathode. Fig. S4-S8[†] show SEM images, transmission electron micrographs (TEM), and the corresponding elemental maps for the SNGE, NGE, SGE, and rGO cathodes, respectively; these figures suggest that the heteroatoms (e.g., S or N) were uniformly

introduced into the carbon skeletons of the SNGE, NGE, and SGE, respectively.^{11,37,38}

X-ray photoelectron spectroscopy (XPS) analysis was conducted to investigate the chemical nature of the elements in the SNGE. The XPS spectra in Fig. 2a show a dominant C1s peak (284.5 eV), an O1s peak (532.0 eV), a N1s peak (400.5 eV), and two S peaks (164.5 eV, 228.2 eV) for the SNGE, which further confirms the presence of elemental S and N in the SNGE.32,33 The nitrogen and sulfur contents in SNGE were determined to be 6.01 and 1.15 at%, respectively, and its nitrogen content is far higher than that of the NGE (2.22 at%), as summarized in Table S1,† suggesting that more polar sites were introduced into the graphene framework in the SNGE than in the other cathodes.9,32 Interestingly, using thiourea as the precursor, providing N for the SNGE, gave a lower nitrogen content than urea did for the NGE (36.8% of thiourea versus 46.7% of urea), while the nitrogen content is higher in the SNGE than in the NGE. This result also indicates that S doping can facilitate the infiltration of nitrogen into the carbon skeletons, leading to higher nitrogen doping concentration.41,42 Fig. S9b† shows the high-resolution spectra of C1s of SNGE, which can be deconvoluted into several single peaks corresponding to C-C, C-N, C–O, C–S, and C=O bonds.^{6,33,37–40} Compared to that of the GO (Fig. 2b), the peak corresponding to the sp² carbon of the SNGE becomes narrower and the intensity of peaks corresponding to C-O and C=O is reduced. These results suggest that the oxygen-



Fig. 2 The XPS survey of SNGE and rGO (a); the high-resolution spectra of C1s for SNGE and GO (b), N1s (c), and S2p (d) for SNGE; N₂ adsorption–desorption isotherms curves (e) and pore size distributions of rGO and SNGE (f).

containing functional groups were removed and that N and S atoms were incorporated into the graphene sheets.¹¹ The high-resolution spectra of N1s in the SNGE (Fig. 2c) show that the SNGE only contains pyridinic N (398.2 eV) and pyrrolic N (400.6 eV), while the NGE contains pyridinic N, pyrrolic N, and dominant graphitic N (Fig. S9d[†]).^{42,43} Considering that pyrrolic N species could be converted to graphitic N sites above 800 °C, as demonstrated in previous reports, we predict that the quaternary N in the SNGE may have disappeared because introducing sulfur makes the material more polarizable due to its lone-pair electrons; as such, N doping was preferable so as to avoid the defects induced by sulfur doping and leading to the formation of pyridinic N and pyrrolic N.11,12,41,42,44 The S2p spectra of the SNGE (Fig. 2d) can be deconvoluted into peaks corresponding to S-S, S-C, and S-O bonds, as well as sulfate species.^{6,11,12} A higher content of sulfate species appeared in the SNGE than in the SGE (Fig. S9d[†]). A previous report predicted that sulfur-containing functional groups could act as adsorption sites for sulfur species; as such, the enhanced introduction of sulfate species may play a positive role in improving the performance of the sulfur cathode.45 Additionally, Raman spectra (Fig. S10[†]) also show that introducing the synergistic effect of N and S co-doping can increase defects and facilitate the doping reaction.11,37,38

Fig. 2e and f show the microstructural analysis of the SNGE, and Table S2[†] summarizes information on the pore structures of the four graphene materials. The SNGE had a greater specific surface area (239.11 m² g⁻¹) and pore volume (0.38 cm³ g⁻¹). The isotherm adsorption–desorption curve at $P/P_0 < 0.1$ in Fig. S11b[†] also verifies that the SNGE had a larger micropore volume than the rGO, and the microstructural information on NGE, and SGE is revealed in Fig. S11c–f.^{†6,17} Interestingly, micropores with a diameter of 0.54 nm were introduced into the SNGE and SGE, and the SNGE had a higher proportion of these micropores, which may have been caused by the etching of the carbon framework by SO_x (x = 2, 3) during pyrolysis, and the higher proportion of micropores in the SNGE over the SGE may have been caused by the difference in the sulfur content for thiourea and benzyl sulfide: 42.1% and 26%, respectively.

To explore the practical application of the SNGE in Li-S batteries, we designed two kinds of configurations containing the SNGE and S (with an areal sulfur loading of 0.54 mg cm^{-2}), as detailed in the Experimental sections. In the first configuration, the SNGE only acts as a conductive scaffold in the S cathode and the mass ratio of the SNGE and S is controlled to be 5 : 5. The obtained battery is defined as SNGE-S-5 : 5. In another configuration, the SNGE plays dual roles including a conductive scaffold and interlayer material. The mass ratio of the conductive scaffold, S and interlayer is controlled to be 3:5:2 and the corresponding battery is defined as SNGE-S@SNGE-3:5:2. EIS measurements verified the superior conductivity of SNGE-S@SNGE-3:5:2 to the SNGE-S-5: 5 cathode.^{17,19,20,22} From Fig. 3b, it is also found that the SNGE-S@SNGE-3:5:2 has a more superior cycling stability to SNGE-S-5 : 5. The rate capabilities and the corresponding galvanostatic charge-discharge profiles for the two batteries at various current densities from 0.5 to 2C are shown in Fig. S12.† Compared with the SNGE-S-5:5, the SNGE-S@SNGE-3:5:2 exhibits



Fig. 3 (a) Nyquist curves from EIS measurements; (b) cycling performance and their corresponding galvanostatic discharge-charge profiles at 2C; (c) cycling performance of SNGE-S-5: 5 and SNGE-S@SNGE-3: 5: 2 cathodes at 5C; (d) cycling performance of SNGE-S@SNGE-3: 5: 2 cathode at elevated rate of 8C.

a much higher capacity at various rates, with specific capacities of 877, 695, and 620 mA h g^{-1} at 0.5, 1, and 2C, respectively. And the galvanostatic discharge-charge profiles in Fig. S12b and c† indicate that the SNGE-S@SNGE-3:5:2 cathode is of higher sulfur utilization and collection efficiency and lower polarization, in accordance with the CV curves (Fig. S12d†) and the EIS measurements. The improved performance after using an interlayer might be due to that employing SNGE as the interlayer renders deeper reduction of the long chain LiPSs and higher utilization of sulfur than the case where SNGE acts as a conductive scaffold.^{17,19,20,27,28} Furthermore, the cycling performance at elevated rates of 5C and 8C was also conducted (Fig. 3c and d), and the galvanostatic discharge-charge profiles are shown in Fig. S13.† The SNGE-S@SNGE-3 : 5 : 2 delivered a capacity of 356 mA h g^{-1} stably over 950 cycles at 5C. The performance is far superior to that of the SNGE-S-5:5. Additionally, it is seen that the SNGE-S@SNGE-3 : 5 : 2 could retain \sim 330 mA h g⁻¹ capacity over 200 cycles at 8C. All these results also strongly suggest that introducing SNGE as interlayer materials should be an important feature for advanced Li-S batteries. Although some investigations involving sulfur-nitrogen dual-doped carbon materials as the conductive scaffold applied in the cathode have been reported,12,24 to our knowledge, the research into the SNGE as an interlayer material in Li-S batteries has been reported rarely.

To further improve the battery performance with the SNGE interlayer approach, a C/S cathode composite employing PCNTs as a conductive scaffold that we reported previously was prepared.²⁷ First, we used cyclic voltammetry (CV) to evaluate the electrochemical properties of the as-obtained Li–S batteries, studying the kinetic processes of the PCNT–S@SNGE cathode *versus* the lithium anode. As shown in the first four CV plots in Fig. 4a, the cathodic scan of the PCNT–S@SNGE cathode exhibits two pronounced peaks at ~2.34 V (*vs.* Li⁺/Li) and 2.03 V, corresponding to the transition from elemental sulfur (S₈) to

long-chain LiPSs (Li_2S_x , 4 < x < 8) and further reduction of loworder LiPSs to Li₂S₂ and Li₂S, respectively.^{5,6,20,31,39} The anodic scan had a prominent peak at ~2.35 V and a weak shoulder peak at \sim 2.40 V, which are associated with oxidation reactions of short-chain polysulfides to S₈/Li₂S₈.^{5,6,20,31} We ascribe the variation in anodic peaks between the first and second cycles to the rearrangement of active sulfur to more energetically stable sites.5,27 The almost identical CV plots for the PCNT-S@SNGE cathode in the subsequent three cycles (Fig. 4a) suggests that the electrode has high electrochemical stability and operates with low polarization.^{15,20,31,35} Fig. 4b shows the second cycles of the CV plots of the five cathodes. The PCNT-S@SNGE cathode exhibited a collection coefficient (the ratio of the area of the peak associated with the formation of Li_2S at ~ 2.0 V to that of the peak of the formation of LiPSs at ~ 2.4 V) of 2.75, greater than those of the other four cathodes (2.5, 2.34, 2.3, and 2.2 for PCNT-S@NGE, PCNT-S@SGE, PCNT-S@rGO and PCNT-S cathodes, respectively, shown in Fig. S14[†]). This result suggests that the SNGE film helped to effectively inhibit the shuttle effect and enhance the reduction of LiPSs.27

Fig. S15[†] compares the first four cycles of the CV plots of the five cathodes; among the five cathodes, the most stable curve is



Fig. 4 (a) The first four cycles of cyclic voltammetry curves of the PCNT–S@SNGE cathode; (b) the second cycle of cyclic voltammetry curves of PCNT–S and those with an interlayer of rGO, SGE, NGE, and SNGE; (c) Nyquist plots of the five cathodes; (d) rate performance of the five cathodes at various current densities; (e) galvanostatic charge–discharge profiles of the PCNT–S@SNGE cathode at a rate of 0.25–5C; (f) galvanostatic charge–discharge profiles of the five cathodes at a rate of 0.5C.

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that of the PCNT-S@SNGE cathode, which further suggests that the interaction between the carbon matrix and sulfur species introduced by the polar sites is greater in the PCNT-S@SNGE cathode than in the other four.35 The Nyquist plots in Fig. 4c, derived from electrochemical impedance spectroscopy (EIS), indicate that introducing the SNGE interlayer can decrease the charge transfer of the cathode.11,39,46 The minimized offset between the reduction and oxidation peaks with the sharpest cathodic and anodic peaks among the five cathodes for the PCNT-S@SNGE cathode also suggests that the active materials are confined in an environment that is highly accessible to ions and charge carriers.^{6,12} All these results strongly confirm that introducing the SNGE interlayer can improve the electronic and ionic conductivity, decrease the potential polarization of the cathode, and suppress the shuttling of LiPSs. Considering the SNGE's morphology and structure, we speculate that the excellent rate capability of the PCNT-S@SNGE cathode comes from their hierarchical porous structure, as well as the introduction of increased polar active species that physically intercept and chemically anchor the LiPSs, which may accommodate the volume change and provide additional electron/Li⁺-ion pathways and continuous electrolyte channels for the sulfur cathodes, confining the active materials in a highly ion/charge accessible environment.9,12,17,19,39

Fig. 4d shows the rate performance of the PCNT-S@SNGE cathode. This cathode exhibited remarkably improved specific capacity at various current densities up to 40C (1C = 1675 mA h g⁻¹): \sim 1460, \sim 1030, \sim 910, 800, 740, and 675 mA h g⁻¹ at 0.25C, 0.5C, 1C, 2C, 3C, and 5C, respectively, based on sulfur mass. Also, at elevated rates from 10C to 40C, the cathode preserved specific capacities of 600, 488, 400, 220, and 130 mA h g^{-1} , respectively, which are comparable to those reported in the literature.17,20,35 After operating at a high rate of 40C and abruptly changing the current density back to 0.25C, the cathode exhibited a reversible capacity of 925 mA h g^{-1} . As far as we know, charge-discharge cycling at such a high rate of 40C has rarely been reported. This excellent rate performance suggests that the PCNT-S@SNGE cathode has a highly stable structure that can tolerate varied high-current charge-discharge cycling.10,32,35,40

Fig. 4e and S16[†] show the galvanostatic charge-discharge profiles for various rates. As the rate increased, the polarization increased a little, indicating favorable kinetics and good electrolyte accessibility of the discharged/charged products, owing to the high electronic conductivity of the SNGE interlayer with the hierarchical porous structure.1 We also studied a blank SNGE electrode without sulfur loading (Fig. S17[†]). The absence of the typical features of a Li-S battery verifies that capacity from intercalation/de-intercalation of Li⁺ is negligible with a discharge cutoff voltage of 1 V, which further suggests that the SNGE interlayer contributes to the improved capacity retention and rate performance of the sulfur cathode by intercepting the LiPSs shuttling and by increasing conductivity.12,17,39,46 Additionally, it has been reported that insulating discharge products Li₂S₂/Li₂S, which could block electron/Li⁺-ion pathways and electrolyte channels, are more inclined to transform and aggregate upon charging/discharging at a high rate with a lower discharge cut-off voltage.^{17,30–33,36,46} Here, by incorporating the SNGE interlayer, even solid sulfur species could be reactivated or reused to participate in the electrochemical reaction, as the plateaus illustrated (Fig. S16†),^{5,39} the sulfur cathode could operate at elevated rates of 10C up to 40C with a cutoff voltage of 1 V. In striking contrast, the electrochemical reactions stagnated in the PCNT–S, PCNT–S@rGO, PCNT–S@SGE, and PCNT–S@NGE cathodes at 20C, 30C, and 40C, respectively. The galvanostatic charge–discharge profiles at 0.5C of the five cathodes (Fig. 4f) also show that the PCNT–S@SNGE cathode exhibits increased usage of the sulfur material, sufficient reduction of the intermediate polysulfides to Li_2S_2/Li_2S , and effective utilization of sulfur, agreeing with the collection coefficient from the CV plots.^{27,37}

Comprehensive cycling performance at high rates was further evaluated. As illustrated in Fig. 5a, compared with the other four cathodes, the PCNT–S@SNGE exhibited the highest capacity retention and more stable performance, from an initial capacity of 770 mA h g⁻¹ to 612 mA h g⁻¹ over 250 charge– discharge cycles at 2C, with a decay rate of 0.08%, which is comparable to previous reports.^{4,10,27,35,39} The EIS spectra in Fig. S18† also provides more information on the cycling performance among the five cathode systems. Before cycling and after 250 cycles, the PCNT–S@SNGE exhibited a lower charge-transfer resistance (R_{ct}) than the other four cathodes. Moreover, the minimal variation in R_{ct} before and after cycling indicates that the PCNT–S@SNGE cathode had superior structure stability and that the dissolution of LiPSs was effectively suppressed.^{40,47}

We also performed prolonged cycling performance measurements at elevated rates for the PCNT–S@SNGE cathode (areal sulfur loading of 0.56 mg cm⁻²). As shown in Fig. 5b, after over 1000 charge–discharge cycles at 8C, the PCNT–S@SNGE cathode retained a capacity of 326 mA h g⁻¹, based on the second discharge capacity of 360 mA h g⁻¹ (441 mA h g⁻¹ for the first discharge), and exhibited a decay rate of 0.01%, among the



Fig. 5 (a) Cycling performance of the five electrodes at a rate of 2C; (b) prolonged cycling performance of the PCNT–S@SNGE cathode at a rate of 8C over 1000 cycles.

best, with a coulombic efficiency well above 96%, indicating a stable long-term cycle life with an effectively suppressed shuttle effect.^{20,27,39,48} To our knowledge, charge–discharge cycling at a high rate of 8C for 1000 cycles has never been reported, suggesting that our PCNT–S@SNGE cell has great potential for long-term use with a high power output. Fig. S19† shows the 2nd and 1010th charge–discharge profiles at 8C. Interestingly, as the number of cycles increased up to the 1010th cycle, the discharge voltage plateau recovered and the potential hysteresis (ΔV) between the charging and discharging profiles decreased, suggesting a slow capacity decay with an increasing cycle number.¹⁰ A similar phenomenon also appeared in the measurements of cycling stability at 10C (Fig. S20†).

Considering the slow redox kinetics of polysulfide intermediates and the fast electron/ion transport at such a high rate, the two maintained discharge plateaus imply that including the SNGE interlayer produced smooth pathways that allowed electron/ion/electrolyte access to the sulfur species and the stable structure of the cathode, maintaining the electrochemical behaviors fractionally and integrally during a prolonged life of over 1000 cycles.^{17,31,32,34-37} In contrast, for the cathode with the rGO interlayer (Fig. S21†), the first plateau almost vanished, and the discharge plateau corresponding to the conversion of shortchain polysulfides to $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ faded with an increasing cycle number, leading to fast capacity decay, which was ascribed to severe migration of polysulfides and accumulation of irreversible $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ that could block Li^+ transport and increase the cathode resistance (Fig. S21c†).^{17,20,30,32,36,43}

To further improve the energy density of the PCNT-S@SNGE, the electrochemical measurements of the PCNT-S@SNGE cathodes with an increased sulfur content up to 91% in the PCNT-S composites were also conducted. As shown in Fig. S22a,† these PCNT-S@SNGE cathodes with areal sulfur loadings of 0.94, 1.45 and 2.1 mg cm⁻² could deliver 1168, 1123, and 1025 mA h g⁻¹ at 0.05C, respectively. Moreover, the long-term cycling stability of the PCNT-S@SNGE cathode with an areal sulfur loading of 2.1 mg cm^{-2} was also tested at 1C and 2C (Fig. S22c⁺). After 250 cycles, the discharge capacity of the cells approached 495 mA h g^{-1} and 368 mA h g^{-1} at 1C and 2C, with capacity degradation rates of 0.09% and 0.01% per cycle, respectively. The notable cycling performance at 2C with such sulfur loading is comparable to that of the previous reports.4,31,48 In addition, the practical high-power application of the PCNT-S@SNGE cathode was also evaluated. As shown in Fig. S23,† with three half-cells consisting of 2.6 mg elemental sulfur assembled in series, the battery pack could drive 60 green and red indicators of LED modules (a nominal voltage of 12 V and a nominal power of 3 W; the inset is the circuit diagram), meaning that the instantaneous current and power of the device was 379 A g⁻¹ and 2692 W g⁻¹, respectively, superior to those in previous reports.31 The results impressively revealed the outstanding high-power output performance of this Li-S cell.

To further understand why the SNGE showed improved performance, we disassembled cells of the five cathodes (after discharging at 2C) inside a glovebox, and soaked the cathodes in a mixture of 1,3-dioxolane/1,2-dimethoxyethane (DOL/DME, 1 : 1 vol) solution (Fig. S24a[†]).

The UV-vis absorption of the solutions obtained from soaking the cathodes was then measured (Fig. 6a). The sharp peak at 280 nm was attributed to S_8^{2-} and S_6^{2-} species, while the shoulder peak at 310 nm was attributed to S_6^{2-} or S_4^{2-} species.49,50 The PCNT-S@SNGE cathode exhibited optimal suppression of LiPS dissolution. High-resolution XPS spectra of the Li 1s for the cycled PCNT-S@SNGE electrode (Fig. S24b[†]) verified the presence of chemical interaction of the SNGE with sulfur species, supporting the recovery of the discharge plateau in Fig. S19 and S20b[†] and the CV plots in Fig. S15.^{†12,51} We further studied how well the four net interlayer materials could absorb LiPSs, with SNGE immersed in the solution of LiPSs (the preparation of the adopted LiPS solution is shown in Fig. S25⁺). After letting the SNGE stand in solution for 12 h and then sonicating and centrifuging it to separate the residue, we further analyzed the filtered solution by UV-vis absorption measurements. As illustrated in Fig. S25b,† the typical peaks of the polysulfide solution located at 260, 280, and 300 nm are attributed to S_6^{2-} species;^{11,43} the intensity of these characteristic absorption peaks decreased after absorption, and the SNGE exhibited the best adsorption performance among the four cathodes. The high-resolution XPS spectra of Li1s (Fig. S26[†]) for the residue also confirmed the chemical interaction between the



Fig. 6 (a) Comparison of the UV-vis absorption spectra of the five cathodes after 250 cycles; (b) typical photographs of PCNT-S (1) and PCNT-S@SNGE (2) electrodes in a mixture of DOL/DME (1 : 1, vol); (c) XRD patterns of Li_2S for the cycled electrodes of PCNT-S, PCNT-S@rGO, and PCNT-S@SNGE at 15C; (d) SEM image of cycled PCNT-S@SNGE at 15C; SEM images of separators collected from cycled cell with PCNT-S (e) and PCNT-S@SNGE (f) both at a rate of 15C.

LiPSs and the SNGE.^{12,51} It is believed that introduction of polar sites has been enhanced because of the synergistic effect between N and S doping, especially the added N atoms, and the hierarchical structure may have improved the excellent immobilization of polysulfides chemically and physically, respectively.^{9,12,17,37}

Furthermore, we characterized the disassembled PCNT-S, PCNT-S@rGO, and PCNT-S@SNGE cathodes by using SEM and XRD. Fig. S27[†] shows the SEM images and XRD patterns of the cycled cathodes (discharged state) at a current density of 15C. The SEM images of the PCNT-S@SNGE (Fig. 6d) show that the discharge products were uniformly deposited and distributed, in accordance with the XPS measurement verifying a higher density of electrochemically active sites for SNGE.43 While the PCNT-S cathode appeared porous with agglomerated discharge products (Fig. S27a[†]), which suggests that the interior of the cathode layer was hardly utilized for the formation of Li₂S₂/ Li₂S.^{32,36} The X-ray diffraction (XRD) patterns of Li₂S (Fig. 6c) further verify that, with the help of the SNGE interlayer, the Li₂S was distributed uniformly, while the peaks corresponding to the (111), (200), and (220) lattice planes of Li₂S strengthened for the cycled PCNT-S and PCNT-S@rGO cathodes (Fig. S27[†]), agreeing with the SEM images.^{6,9,32,36,43,51} We believe that incorporating the SNGE interlayer further inhibited the permeation of LiPSs, both physically and chemically, and encouraged the uniformly modulated Li2S distribution, ensuring sufficient paths for electron/Li⁺-ion transport and channels for electrolyte immersion to electrochemical reaction, and the stably integral structure was achieved with a greatly relieved volume change, contributing to the excellent long-term cycle performance of the PCNT-S@SNGE cathode.^{6,10,17,32,34-36,43} Moreover, the uniformly distributed Li2S2/Li2S could facilitate the adsorption of soluble LiPSs, and the polysulfides in the cathode region could assist in converting and reusing the precipitated Li2S2/Li2S during cycling, which also benefited the stable long-term cycling performance.19,33,52

The separator is an essential part of an electrochemical cell, playing the vital role of preventing an internal short-circuit and maintaining the diffusion pathway for ions.² As such, an intact separator is greatly important for maintaining the cell's performance (Fig. S28[†] shows a photograph of the separator). A separator close to a cathode is considered to experience volume change because of the conversion of solid Li2S2 to Li2S, but there are few studies on this issue. Fig. 6e and f show SEM images of separators collected from a cycled cell at a rate of 15C for the PCNT-S and PCNT-S@SNGE, revealing that the separator can be well preserved by incorporating an SNGE interlayer, making it distinctly superior to the uncoated PCNT-S cathode. Fig. S29-S31[†] show more SEM images of the separators for the cycled PCNT-S, PCNT-S@rGO, and PCNT-S@SNGE cathodes at various current densities; we attribute the serious damage to the separators for the cathodes without an interlayer here to their greater tendency to form Li₂S/Li₂S₂ at elevated rates,³⁶ which could result in volume expansion of the electrode and would increase the true current density,32 leading to damage of the separator at high rates. In other words, after introducing the SNGE interlayer, deposition and distribution of solid products

could be reduced and uniformly modulated, leading to a reduction in the volume expansion of the electrode;^{6,9,12} additionally, superiorly conductive SNGE interlayer ensured smooth transition of charge in the electrode.^{9,12,43,53} All of these factors contributed to protecting the separator from a puncture and scald and better maintained its integrity, compared with the cases of PCNT–S and PCNT–S@rGO.

Based on the UV-vis absorption measurements, XRD of the cathodes, and the XPS spectra of the Li1s peak given above, we believe that the effectively suppressed dissolution and reduction of soluble LiPSs, and the uniformly modulated insoluble Li₂S/Li₂S₂ by polar sites in the SNGE interlayer, both contributed to the remission of volume expansion, greatly reducing the mechanical damage to the separators.8,35 Furthermore, without the aggregation of solid Li₂S/Li₂S₂ as the cycle number increased, the true current density was well accommodated, producing a more homogeneous thermal distribution, which could decrease the scalding of the separator and improve the cell's cycling performance.^{17,30,32,53} The photograph of the separators in Fig. S28† also suggests that the PCNT-S@SNGE cathode better maintained the macroscopic structure of the separator. From another perspective, because the SNGE interlayer protects the separator, it is ensured that the Li-S battery can stably operate for a long term at ultrahigh rates, even at a discharge cutoff voltage of 1 V.

3. Conclusions

In summary, we developed a lightweight multifunctional interlayer composed of SNGE by a simple, green, scalable approach. Using an SNGE film as an interlayer enabled the PCNT-S cathode to deliver a reversible specific capacity of \sim 1460 mA h g⁻¹ at 0.25C with a much higher rate performance of up to 40C with a capacity retention of 130 mA h g^{-1} . More impressively, these cathodes cycled at 8C for 1000 cycles, exhibited ultrahigh cyclability, with a capacity degradation rate of 0.01% per cycle. To the best of our knowledge, such a low capacity degradation rate in cathodes of advanced Li-S batteries has been reported only rarely. We verified that this excellent performance comes from the SNGE endowed with some special functionalities, such as its outstanding conductivity, high ability to trap polysulfides, ability to modulate Li2S2/Li2S growth, and its protection of the separator integrity. These encouraging properties of the multifunctional SNGE interlayer might enable Li-S batteries to be used in electric vehicles and other large-scale electrochemical energy storage systems.

4. Experimental sections

4.1 Synthesis of porous CNTs

The porous CNTs were prepared by a water stream etching method as reported in our previous reports.^{5,27} Briefly, the water was first nebulized to create a mist of droplets. The droplets formed were then passed into a quartz tube of raw commercial CNTs using an Ar carrier gas when the desired temperature of 850 °C is reached. After the water etching, the water steams were

turned off, and the furnace was cooled to room temperature under an argon flow.

4.2 Synthesis of CNT-S composites

The PCNT–S composites were prepared following a meltdiffusion strategy. In a typical procedure, the PCNT and sulfur (high purity sulfur, 99.99% metal basis, Aladdin) were mixed according to the design of the target composite. Then the powder was ground and heated in an oven at 160 °C for 12 h, followed by another 12 h at 180 °C in the air. Sulfur ratios were adjusted to produce composites with different sulfur contents.

4.3 Synthesis of reduced graphene oxide (rGO), S-doped GE (SGE), N-doped GE (NGE), and N,S dual-doped GE (SNGE)

Graphene oxide (GO) was purchased from a commercial corporation. Sulfur-doped graphene (SGE) was synthesized by directly annealing graphene oxide (GO) and benzyl disulfide (BDS) in argon. The annealing treatment was carried out in a tube furnace with high purity argon as the protective ambient. The detailed procedure is as follows: GO and BDS were first ultrasonically dispersed in ethanol for about 30 min. The resulting suspension was spread onto an evaporating dish and dried, forming a uniform solid mixture. The mixture was placed into a quartz tube with an argon atmosphere and annealed at 900 °C. After that, the sample was cooled to room temperature under ambient Ar and collected from the quartz tube to obtain SGE.

Similar to the synthesis of S-doped GE, N-doped GE (NGE) was prepared by replacing benzyl disulfide (BDS) with urea as the nitrogen precursor, directly annealing graphene oxide (GO) and urea in argon at 900 $^{\circ}$ C to obtain N-doped GE (NGE).

Similarly to synthesis of S-doped GE, N,S dual-doped GE (SNGE) was prepared by directly annealing graphene oxide (GO) and thiourea in argon at 900 $^{\circ}$ C. The GO without any dopant addition was treated at 900 $^{\circ}$ C in argon, and reduced graphene oxide (rGO) was obtained.

4.4 Synthesis of SNGE-S-5 : 5 and SNGE-S@SNGE-3 : 5 : 2 cathodes

(1) The SNGE-S composite was prepared following a meltdiffusion strategy. In a typical procedure, the SNGE and sulfur (high purity sulfur, 99.99% metal basis, Aladdin) were mixed. Subsequently, the mixture was heated in an oven at 160 °C for 12 h, followed by another 12 h at 180 °C. The sulfur content of the SNGE-S composite was controlled to be ~50%. Then the 90 wt% SNGE-S composite, 5 wt% conductive agent and 5 wt% polyvinylidene difluoride (PVDF) were mixed in NMP to form a slurry. Subsequently, the slurry was pasted onto an aluminum foil and dried at 60 °C overnight. The obtained cathode was defined as SNGE-S : 5.

(2) The SNGE–S@SNGE-3:5:2 cathode was prepared following procedures similar to that of SNGE–S-5:5 cathode, while the mass ratio of SNGE conductive scaffold, S and SNGE interlayer was controlled to be 3:5:2, and the SNGE interlayer

was pasted onto the sulfur cathode following the procedure shown in Fig. S1.†

4.5 Synthesis of the interlayer coated PCNT-S cathodes

The cathode for Li–S batteries was prepared by mixing 85 wt% PCNT–S composite materials, 10 wt% conductive agent and 5 wt% polyvinylidene difluoride (PVDF) in NMP to form a slurry. Subsequently, the slurry was pasted onto an aluminum foil and dried at 60 °C overnight. After drying, the interlayer slurry was then pasted onto the PCNT–S cathode following the procedure shown in Fig. S1[†] to produce PCNT–S@rGO, PCNT–S@SGE, PCNT–S@NGE, and PCNT–S@SNGE cathodes. The sulfur cathode was compressed and cut into circular pellets with a diameter of 14 mm and used as a cathode, and the sulfur loading of the cathodes was determined to be 0.56 mg cm⁻².

4.6 Electrochemical characterization

Electrochemical experiments were performed via CR2025 cointype test cells assembled in an argon-filled glovebox with lithium metal as the counter and reference electrodes at room temperature. A Celgard 2400 membrane was used as the separator to isolate electrons. The electrolyte was 1 M bis(trifluoromethane) sulfonimide lithium salt (LiTFSI) with 1% LiNO3 dissolved in a mixture of 1,3-dioxolane (DOL) and dimethoxyethane (DME) (1:1 by volume). The discharge/charge measurements were conducted using a CT2001A battery test system (LAND Electronic Co.). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed on a CHI660D electrochemical workstation. The scan rate for CV measurements was set to be 0.1 mV s⁻¹, and the DC voltage was kept at open-circuit voltage and an AC voltage of 5 mV in amplitude was applied with a frequency of 200 kHz to 20 mHz in EIS measurements.

4.7 Structural characterization

X-ray photoelectron spectroscopy (XPS) measurements were carried out with an ultrahigh vacuum setup, equipped with a monochromatic Al KR X-ray source and a high resolution Gammadata-Scienta SES 2002 analyzer. X-ray diffraction patterns (XRD) were obtained with a D/MAX-2400 diffractometer using Cu K α radiation (40 kV, 100 mA, $\lambda = 1.54056$ Å). The nitrogen adsorption/desorption data were recorded at the liquid nitrogen temperature (77 K) using a Micromeritics ASAP 2020 M apparatus. The samples were degassed at 200 °C under vacuum for 3 h prior to the measurement. Pore size distribution (PSD) was derived from the adsorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) model. Total pore volumes were calculated from the amount adsorbed at a relative pressure (P/P_0) of 0.99. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation. Scanning electron microscope (SEM) images were obtained with a JSM-6700F fieldemission scan electron microscope. Thermogravimetric analysis (TGA) was carried out with a STA449 F3 Jupiter thermogravimetric analyzer (NETZSCH), at a heating rate of 10 $^{\circ}$ C min⁻¹ in a nitrogen atmosphere. UV-vis absorption spectroscopy was used to characterize the polysulfide species and their contents

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in the electrolyte after the cells completed a certain number of cycles.

Conflict of interest

The authors declare no competing financial interest.

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