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1. Introduction

To meet the increasing demand for electric vehicles and portable electronics, it is necessary to develop advanced highenergy-density batteries with high security.¹⁻³ Due to its low cost, high theoretical capacity (1672 mA h g^{-1}) and high energy density (2600 W h k g^{-1}), sulfur has been widely investigated as the most promising cathode.⁴⁻⁹ Unfortunately, some problems have hindered the practical applications of lithium–sulfur (Li–S) batteries. As for the cathode side, the insulating nature of sulfur and its discharge products lead to low sulfur utilization.

Graphene-nanoscroll-based Janus bifunctional separators suppress lithium dendrites and polysulfides shuttling synchronously in highperformance lithium-sulfur batteries[†]

Zhigang Zhang, ^(b) ^a Yanfeng Dong, ^(b) ^{bc} Yuefeng Gu, ^(b) ^{ad} Pengfei Lu, ^b Fangfang Xue, ^(b) ^a Yangtao Fan, ^a Zhicheng Zhu, ^a Jun Lin, ^a Qiuhong Li ^(b) ^{*ad} and Zhong-Shuai Wu ^(b) ^b

Li sulfur (Li-S) battery is regarded as one of the most promising candidates for next-generation rechargeable batteries. However, some challenging obstacles such as uncontrolled dendrites of Li metal anode and polysulfides shuttling in the sulfur cathode substantially impede the practical application. In this work, we propose a versatile strategy of fabricating graphene nanoscroll (GNS) based bifunctional Janus polypropylene (Janus PP) separators for inhibiting lithium dendrites and suppressing polysulfides shuttling toward high-performance Li-S batteries. On the anode side of the separator, nitrogen-doped GNS (NGNS) were used to protect the lithium metal. The highly uniform NGNS nanostructure facilitated electrolyte penetration and homogenous Li⁺ flux, thus fundamentally prompting lithiation/delithiation kinetics and inhibiting the growth of Li dendrites. Due to these properties, the Li symmetrical cell with NGNS-modified PP separator (NGNS-PP) delivers an ultralow voltage hysteresis of 36 mV at 6.0 mA cm^{-2} after 12 000 h (65.5 mV at 10 mA cm^{-2} after 3400 h). On the cathode side, GNS-wrapped Co_3O_4 nanoparticles (Co₃O₄@GNS) used as an interlayer on the PP separator, acting as a wonderful physical blocking and chemical catalytic layer to sufficiently mitigate the "shuttle effects" of lithium polysulfides. As a result, with the Janus PP separator, Li–S cells obtained a stable capacity of 805 mA h g^{-1} after 800 cycles (a capacity decay of 0.018% per cycle at 1.0C). Therefore, this proposed strategy of GNS-based Janus separators will pave a new way to rationally construct durable and efficient Li-S batteries.

The soluble polysulfide intermediates $(Li_2S_x, 4 \le x \le 8)$ in the electrolyte will trigger a serious shuttle effect and fast capacity decay of batteries. With regards to the anode side, the huge volume change of Li metal and fragile solid electrolyte interphase (SEI) during the plating/stripping process results in Li pulverization and the generation of dead Li, thus deteriorating the cycling stability of Li–S batteries. The Li dendrites and the generated inactive-Li may pierce the separator and thus cause short circuit and safety hazards.^{10,11} Therefore, it is crucial to simultaneously inhibit the polysulfide shuttle and lithium dendrites for the design of Li–S batteries.

Until now, various efforts have been developed to overcome these issues. As for anodes, many strategies have been conducted to regulate Li nucleation and restrict Li dendrites, which includes constructing framework/substrate with lithiophilic surface to control the flux of Li ions, strengthening SEI films and building-up artificial interphase between the electrode and electrolyte to protect Li metal.¹²⁻¹⁶ Besides, more strategies such as solid electrolytes, functional electrolyte additives and modified separator membranes are also efficient to alleviate the dendrite growth.¹⁷⁻²² For cathodes, different carbon materials

[&]quot;Pen-Tung Sah Institute of Micro-Nano Science and Technology, Xiamen University, Xiamen 361005, China. E-mail: liqiuhong@xmu.edu.cn

^bState Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

^cDepartment of Chemistry, College of Sciences, Northeastern Univer sity, Shenyang 110819, China

^dSchool of Electronic Science and Engineering, Xiamen University, Xiamen 361005, China

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such as porous carbon, carbon nanotubes (CNTs) and graphene have been applied as the skeleton of the sulfur cathode.²³⁻²⁵ Many metal compounds (oxides, sulfides and nitrides) possessing strong adsorptive properties could be used to enhance the conversion rate of polysulfides and accelerate the reaction kinetics of Li-S batteries.²⁶⁻³¹ The separators offer channels for the diffusion of both Li⁺ and polysulfides in the Li-S battery. The "shuttle effects" associated with the dissolution of polysulfide intermediates could affect the cycling life directly. Therefore, forming a functional membrane in cell design is a promising way to suppress parasitic reactions and extend the cycling lifetime.³²⁻³⁴ The modification of functional separator membrane based on the principles of permeability and electrical interaction has been widely studied. Owning to the flux of ions related to the membrane thickness, two-dimensional (2D) materials have attracted extensive attention. The functional membranes with 2D materials such as graphene and MXene have been investigated.³⁵⁻⁴⁰ However, the diffusion of Li⁺ could also be hindered owing to the excessive accumulation of adsorptive materials.41 The high interface impedance is caused by an additional physical barrier or insufficient contact, the parasitic reaction between Li and excessive electrolyte may influence the cycling performance and coulombic efficiency.^{42,43} Therefore, introducing multi-functional integration that can inhibit both lithium dendrites and the shuttle effect will significantly improve the performance of Li-S batteries.

Graphene nanoscrolls (GNSs), as scrolled graphene nanosheets, well inherit the advantages of graphene nanosheets.³⁷⁻³⁹ Meanwhile, GNSs also possess the unique features of fast electron transfer and Li⁺ ion diffusion kinetics. Here, functional GNS-based Janus separators were constructed for Li-S batteries, especially, on the anode side of the Janus separator, nitrogendoped nanoscrolls (NGNS) were used to suppress Li dendrites due to uniform Li-ion flux enabled by the strong interaction between Li ions and pyridinic N. On the cathode side of the Janus separator, GNS-wrapped Co₃O₄ nanoparticles (Co₃O₄@-GNS) were used as an interlayer on the separator, which acted as a wonderful blocking layer to hinder the "shuttle effects".44,45 For the cathode, we prepared the CoS₂@GNS framework as the S/polysulfides host. The unique GNS framework is beneficial for electrolyte penetration and fast Li⁺ ion diffusion kinetics, and the interconnected CoS2@GNS framework guarantees high S loading. CoS₂ nanoparticles were used as an active electrocatalyst to promote the conversion kinetics of the polysulfides. The Li metal with the NGNS-PP separator displays the extremely stable properties in symmetric cells up to 5000 h at 10 mA cm $^{-2}$. As a result, the cathode with the Janus PP separator manifests a high specific capacity of 1155 mA h g^{-1} after 200 cycles at 0.2C, and long-term cycling stability with a low decay rate of 0.018% per cycle over 800 cycles at 1C.

2. Experimental section

2.1 Synthesis of GNS-based precursors

The GNS-based precursors were fabricated according to our previous works.⁴⁶⁻⁴⁸

In order to obtain precursors with specific functions, Co₃O₄ nanoparticles of different sizes were synthesized. The surface of the as-synthesized Co₃O₄ nanoparticles was further modified using a surfactant. A scrolling structure was obtained after placing the material in liquid nitrogen for cold quenching. Then, the completely frozen solid composite material was treated by vacuum freeze-drying and then reduced by thermal treatment at 400 °C in argon atmosphere to obtain Co₃O₄(a)-GNS. CoS2@GNS was synthesized by the following process. The as-obtained Co3O4@GONS powder and sulfur powder were loaded in two combustion boats. With the temperature increasing, the solid sulfur transformed into a gas state and totally immersed the Co₃O₄@GONS powder. Finally, CoS₂@-GNS was obtained through a high-temperature reaction. The pure GONS precursor was prepared by the same method. The NGNS powder was obtained by thermal treatment of GONS at 500 °C in ammonia atmosphere.49,50

2.2 Fabrication of the functional Janus PP separator

The manufacturing process of the Janus PP separator is shown in Fig. S1.† The modified separators were prepared by vacuum filtration on the routine PP membranes. The as-prepared NGNS powder was dissolved in a deionized water/ethanol mixture followed by ultrasonication for 30 min to obtain stable and homogeneous NGNS aqueous suspension (0.1 mg mL⁻¹). The surface area mass loading of NGNS was estimated to be ~0.1 mg cm⁻². For comparison, the other functional separators (RG-PP and NG-PP) were prepared according to the same strategy. The Janus PP separator was prepared with Co₃O₄@GNS and NGNS suspension. Co₃O₄@GNS suspension was filtered on the other side of the PP membrane according to the same process. After drying, the Co₃O₄@GNS interlayer (0.05 mg cm⁻²) and NGNS (0.05 mg cm⁻²) with a thickness of 5 µm was attached to the routine PP separator.

The same Co_3O_4 @GNS suspension was filtered on the PP membrane as the control sample (Co-PP) (Fig. S4†). The obtained separators were then dried in a vacuum at 60 °C.

2.3 Fabrication of CoS₂@GNS/S cathode

The cathode material was synthesized by a traditional meltdiffusion method. The CoS_2 @GNS powder was immersed in the sulfur-containing carbon disulfide (CS₂) solution (200 mg mL⁻¹), and heated at 155 °C for 15 h in an argon atmosphere (CoS₂@GNS/S denoted as CSG/S). The cathode was fabricated with the homogeneous slurry *via* a ball-milling approach (mass ratio: 70% CSG/S, 20% Super P, and 10% PVDF) onto Al foil and dried at 60 °C for 6 h in a vacuum environment.

2.4 Theoretical calculations

The first-principle calculations were conducted using the VASP package. Firstly, the optimum geometries of graphene, Co_3O_4 and CoS_2 substrate models were calculated using the generalized gradient approximation (GGA) method in the Perdew-Burke-Enzerhof (PBE) level. The effective core potentials were considered when tackling the electron-ion interactions in the whole system. The minimum allowed energy change between

the two adjacent iterative steps was set to 1×10^{-5} eV, the force and displacement tolerances were set to 0.004 Ha Å⁻¹ and 0.005 Å, respectively. After that, the adsorbing simulations of Li₂S₆ on different substrate models were carried out with the same level and the same parameter setting. The adsorption energy (E_{int}) was defined by subtracting the energies of Li₂S₆ (E_1) and the substrate models (E_2) from the energy of their composites (E_{tot}): $E_{int} = E_{tot} - (E_1 + E_2)$.

Besides, the optimum geometries of pyridinic N (pN), pyrrolic N and graphitic N in graphene substrate models were calculated with the GGA method at the PBE level. To understand the interaction strength between Li ions and different substrates, the binding energy (E_b) was defined as $E_b = E_{total} - E_{sub} - E_{Li}$, where E_{total} is the total energy of the whole adsorbed system, E_{sub} is the energy of the substrate materials and E_{Li} is the energy of the Li atom in a Li crystal.

3. Results and discussion

The mass loading of NGNS on the PP membrane was 0.1 mg cm⁻² (Fig. 1a). The thickness of the NGNS layer was 10 μ m in the cross-sectional SEM image (Fig. 1b). As shown in Fig. 1c and S5,† the NGNSs formed into a perfect three-dimensional (3D) cross-linked GNS network. The diameter of NGNSs was about 80–100 nm (Fig. 1d). The hollow structure of NGNS can also be observed in the TEM image (Fig. 1e). On the basis of previous reports, the addition of surfactants can effectively increase the content of functional groups of graphene oxide (GO).⁵¹⁻⁵⁴ Therefore, more functional groups will produce more defect sites during the process of high-temperature reduction, and it is more conducive to the nitrogen doping of GO. Moreover, XPS

analysis further confirmed that the content of pyridinic N (pN) in NGNS was much higher than that of NG (Fig. S6[†]). Ultimately, more pN and carboxylic groups were obtained in the NGNS. In NGNS, the content of nitrogen (14.78 at%) was much higher than the NG (11.63 at%) (Fig. S7 and Table S1[†]). The residual carboxylic group of NGNS (3.15%) was also much higher than that of NG (1.48%) (Fig. 1f-h). Fig. 1g exhibits the O1s XPS spectra of NGNS. It showed a strong peak of -COOH compared to NG (Fig. S7d[†]). It is reported that the strong interaction between Li and pN has been attested.34,42 The pN exhibited relatively larger binding energies of -3.72 eV compared with the pyrrolic N (-3.03 eV) and graphitic N (-0.56 eV). The pyridine N site is the preferred site for Li adsorption, leading to the uniform dispersion of Li ions and affinity of the electrolyte (Fig. 1i and S8[†]). NGNS could be used as a framework to form the stable SEI layer and restrain the growth of Li dendrites.55 In addition, the contact angle of the electrolyte on NGNS-PP (9°) is much lower than that on the PP separator (35°) (Fig. S9[†]). Compared with the PP separator, NGNS-PP could absorb the electrolyte quickly (Movie S1[†]). Due to the excellent adsorption and capillarity of NGNS materials, the electrolyte could be well withheld by the NGNS-PP membrane. This allows the electrolyte to be distributed more evenly and mitigates the formation of dead lithium due to the side effects of excess electrolyte.

In order to study the effect of the functional membrane on LMBs, different modified materials such as RGO, NG and NGNS were filtered on the PP separators. The coulombic efficiency (CE) is an important factor to analyze the applicability of the separators. As shown in Fig. 2a, the cell with NGNS-PP separator could keep 800 cycles with CE of 99.5%, which is much longer than the cells with NG-PP (398 cycles with the CE of 90.5%) and RG-PP



Fig. 1 Structural characterizations of NGNS-PP. (a) Digital photos of the pure PP membrane and NGNS-modified PP membrane (NGNS-PP). (b) Side-view SEM image of NGNS-PP; (c and d) SEM images of NGNS with different magnifications. (e) TEM image of NGNS. (f and g) High-resolution XPS spectra (N 1s and O 1s) of NGNS. (h) Comparison of different element contents. (i) The calculated adsorption energy between a Liion and the functional groups on NGNS.



Fig. 2 Electrochemical performance of asymmetric and symmetric Li metal cells with different functional separators. (a) Coulombic efficiency comparison of Li–Cu cells with different separators at current density and capacity of 1 mA cm⁻² and 1 mA h cm⁻². (b) Voltage–time curves during Li nucleation at 0.50 mA cm⁻² with different separators. (c) Relative Li nucleation overpotentials at different current densities. (d) Voltage profiles of Li–Li cells with different separators at current density and capacity of 3 mA cm⁻² and 1 mA h cm⁻². (e) Cycling stability of Li/Li symmetric cell with NGNS-PP at a high current density of 6 mA cm⁻² with areal-capacity of 3 mA h cm⁻². (f) Li plating/stripping behavior of Li/Li symmetric cell with NGNS-PP at various current densities from 0.5 to 20 mA cm⁻². (g) Cycling stability of Li/Li symmetric cells with a Janus PP separator and other reported works recently.

(260 cycles with CE of 81%). To further evaluate the lithiophilicity of the different separators, Li nucleation overpotentials were tested. As shown in Fig. 2b, the PP, RG-PP, NG-PP and NGNS-PP separators showed their corresponding nucleation overpotentials of 26.5, 21.2, 17.6 and 12.5 mV, respectively, demonstrating the lowest nucleation energy barrier of NGNS-PP. In addition, the nucleation overpotential of PP, RG-PP and NG-PP enlarged 5.27, 4.85 and 3.26 times, respectively, as the densities ranged from 0.05 to 1.00 mA cm⁻². In contrast, the nucleation overpotential of NGNS-PP enlarges merely 2.23 times, revealing the best steady nucleation overpotential (Fig. 2c).

The functional separators also played an excellent role in symmetric cells. As shown in Fig. 2d, the voltage plateaus of cells with PP and RG-PP separators increased rapidly with the increase of the cycle number. After cycling for only 200 h, the voltage profile of the PP separator oscillated dramatically, and the cell with the RG-PP separator could stably cycle for about 300 h (42 mV). Furthermore, the cell with NG-PP separator displayed a lower over-potential of 25 mV. More specifically, the voltage plateaus subsequently increased after 500 h. In contrast, after introducing the NGNS-PP separator, the cell delivered stable flat voltage plateaus over 2000 h with a low over-potential (20 mV), indicating that Li dendrites were efficiently inhibited by the NGNS-PP interlayer. As shown in Fig. 2e, with the help of NGNS-PP membrane, the cell demonstrated a remarkably stable overpotential of 36 mV over 12 000 h at 6 mA cm⁻² with of 3 mA h cm⁻². The cells with NGNS-PP displayed good rate

capability under increasing current densities up from 0.5 to 20 mA cm⁻² (0.25 to 10 mA h cm⁻²) (Fig. 2f). The excellent rate performance was much better than that of the Li//Li symmetric cell with NG-PP separator (Fig. S10[†]). The voltage-time curves of the Li//Li symmetric cell with NGNS-PP at 10 mA cm⁻² are shown in Fig. 2g. The overpotential was gradually maintained at 62.5 mV after 50 cycles. Stable cycling with stable hysteresis could still be attained. After 3400 h, the over-potential was still stabilized at 65.5 mV, and the voltage remained stable at 85 mV without obvious polarization voltage even after 5000 h (Fig. S11[†]). The mass loading of NGNS would also affect the voltage plateaus in the Li//Li cell (Fig. S12†). The cell with NGNS-PP (0.1 mg cm^{-2}) delivered the most stable flat voltage plateaus over 500 h with a low over-potential. Moreover, the Li//Li cell with the NGNS-PP separator revealed better cycling stability than that reported in previous studies (Fig. 2h).55-62

The cycled Li foil with a routine PP separator displayed a rough surface (Fig. 3a1). As shown in Fig. 3b1, the Li foil with NG-PP exhibited a lot of shedding materials. Besides, the cycled Li foil with NGNS-PP showed a metallic luster and an intact surface. SEM images were used to further investigate the influence of the functional membrane on plating/stripping behaviors. As shown in Fig. 3a(2-4), the pulverization and corrosion of Li metal could be confirmed due to the adverse reaction of electrolytes.^{59,63} When the NG-PP membrane was applied in the cell, pulverization and collapse were dramatically limited after the cycles. However, there were still some cracks on



Fig. 3 Optical photos of cycled Li foils with different separators (a1, b1 and c1). Top-view and side-view SEM images for the cycled Li-metal electrodes with (a2–a4) PP separator, (b2–b4) NG-PP separator and (c2–c4) NGNS-PP separator, respectively.

the surface of the Li metal (Fig. 3b(2-4)). In contrast, the NGNS-PP embellished Li anode remained smooth without obvious dendrites after Li stripping/plating (Fig. 3c(2-4)). This significant variation further confirmed the suppression effect of the NGNS-PP membrane on Li dendrites.

To apply the excellent protection property of N-GNS against lithium metal in the Li-S batteries, we further constructed a Janus-PP separator. On the anode side of the separator, NGNS was used to protect the lithium metal. On the cathode side of the separator, Co₃O₄@GNS was used as an interlayer on the PP separator, which can act as a wonderful blocking layer to mitigate the "shuttle effects". To further unravel the intrinsic interfacial modulation essence of different Co-based compounds for Li-S chemistry, a first-principle calculation based on DFT was performed. Fig. S13† shows the optimized adsorption configurations of Li_2S_6 on graphene (001) (0.56 eV), CoS₂ (001) (1.27 eV) and Co₃O₄ (001) (3.87 eV). Obviously, Co₃O₄ had the strongest adsorbability for Li₂S₆. The adsorption capability of Co₃O₄@GNS with polysulfide was also experimentally evaluated in Fig. S14.† In the cathode, we prepared GNSwrapped CoS₂ nanoparticles (CoS₂@GNS) frameworks as S/ polysulfides host. The unique CoS2@GNS framework was beneficial to electrolyte penetration and fast reaction kinetics.

Fig. 4a schematically illustrates the working process in a typical Li–S battery. The polysulfide intermediates from the S cathode could react with Li metal directly, which could lead to the irreversible loss of active materials and surface passivation of the Li metal anode.^{64–66} The persistent side effects could lead to the passivation of Li metal and the sluggish kinetics of the electrochemical reaction. In contrast, the polysulfide intermediates could be anchored by the Co_3O_4 @GNS membrane. After introducing the Janus PP membrane, the shuttle effect and growth of Li dendrites could be simultaneously inhibited. The SEM and corresponding EDX elemental mapping images are shown in Fig. 4b and c. The NGNS and Co₃O₄@GNS were evenly distributed on both sides of the Janus PP separator. The particle size of Co₃O₄ in Co₃O₄@GNS is uniform (Fig. 4e). The Co₃O₄ particles were wrapped around by a thin GNS structure. Fig. 4f and S15[†] showed the morphology of CoS₂@GNSs. The GNS structure remained unchanged during the reaction process. TEM images further proved that CoS₂ nanoparticles are tightly covered by graphene (Fig. S16[†]). Through TEM, these particles were confirmed to be distributed homogeneously, which could endow enough active sites during the electrochemical reaction process. After sulfur loading, SEM images of CoS2@GNS/S are shown in Fig. 4g. As shown in Fig. S16,† sulfur is uniformly dispersed in the GNS structure. The diameter of the CoS₂@GNS/ S composite varied from 300 to 400 nm (Fig. S17[†]). The sulfur content in CoS2@GNS/S was calculated to be about 78 wt% by TG studies (Fig. S18[†]).

GCD profiles with different separators are shown in Fig. 5a. It is distinct that the CSG/S-Janus PP shows a much lower polarization value (115 mV) than those of CSG/S–Co PP (150 mV), CSG/S (165 mV) and GNS/S cathode (320 mV). The significantly reduced polarizations in CSG/S-Janus PP could be attributed to the enhanced interfacial kinetics and fast Li⁺/e⁻ transportation caused by the functional Janus PP separator.^{35,67} Cyclic voltammetry (CV) investigations were performed to analyze the reaction kinetics (Fig. 5b). Compared to GNS/S and CoS₂@GNS cathodes with Co-PP or regular PP separators, the CSG/S-Janus PP exhibited high anodic and cathodic peaks, owing to the inhibited shuttle effect and higher utilization of active sulfur



Fig. 4 Characterization of the Janus interlayer. (a) Schematic illustrations of Li–S cell prototypes without (left) and with interlayers (right). (b and c) SEM images and corresponding EDX elemental mapping images of the Janus PP separator, (d and e) SEM images of $Co_3O_4@GNS$, SEM images of $Co_2@GNS$ (f) and $CoS_2@GNS$ (g).

species. This conclusion was in accordance with the polarization voltage during the charge and discharge process. Fig. S19[†] shows the CV curves of the CSG/S-Janus PP cathode at 0.1 mV s^{-1} . The CV curves of CSG/S-Janus PP from 0.1 to 5 mV s^{-1} are shown in Fig. 5c. The stable peak current and potential indicate superb redox reversibility and stability. The electrochemical impedance spectroscopy (EIS) of Li-S cells with different separators was further investigated to verify the reaction kinetics. The CSG/S-Janus PP cathode exhibited the lowest chargetransfer resistance (R_{ct}) of 64.5 Ω (Fig. 5d). Moreover, the charge-transfer resistance (R_{ct}) value of CSG/S-Janus PP was significantly reduced to 25 Ω after 50 cycles (Fig. S20[†]). The decrease in the R_{ct} value indicates good interfacial engineering between the Janus PP separator and sulfur anode in the cell. The GNS-based interlayer with excellent electrical conductivity and unique cross-linked network structure could serve as a current collector to enhance the electric conductivity and provides a stable channel for ionic transmission. Besides that, the polysulfides dissolved in the electrolyte would be effectively absorbed by Co₃O₄ nanoparticles in the GNS structure. The shuttling effect could be inhibited by the Janus PP membrane.

The cycling performances of the S cathodes with different separators at 0.2 C are shown in Fig. 5e. The CSG/S cathode with Janus PP displayed the best cycling stability. The initial capacity of CSG/S-Janus PP was 1325 mA h g^{-1} and it was then maintained at 1155 mA h g^{-1} after 200 cycles (retention of 87.1%).

The representative GCD curves of CSG/S-Janus PP are shown in Fig. S21.[†] In contrast, the capacities of the CSG/S cathode with bare PP separator and Co3O4@GNS-modified PP (Co-PP) were 904 and 985 mA h g^{-1} . The GNS/S cathode with the PP separator depicts the lowest capacity of 304 mA h g^{-1} after 100 cycles. The rate capability of the CSG/S-Janus PP cathode under various current rates is shown in Fig. 5f and g. In details, the specific capacities at 0.2, 0.5, 1.0, 2.0, 5.0 and 10 C were 1150, 1085, 1015, 840, 610 and 304 mA h g^{-1} , respectively. Besides, the rate capabilities of CSG/S-Co PP and CSG/S cathodes with routine PP separators declined seriously at high current rates (Fig. S22[†]). It is suggested that the functional PP membrane is beneficial for kinetically promoting the reaction. As shown in Fig. 5h, the CSG/S-Janus PP exhibited an initial capacity of 950 mA h $\rm g^{-1}$ and maintained it at 805 mA h $\rm g^{-1}$ after 800 cycles at 1.0 C (retention of 84.7%). Additionally, the structural integrity of the Li anode after long-term cycling was investigated (Fig. S23[†]). Therefore, the Janus PP separator could substantially enhance the performance by suppressing the shuttling effect of polysulfide and inhibiting the lithium dendrites.

The excellent performance of the Li–S battery was ascribed to the rational construct of the Janus PP separator. Firstly, the NGNS interlayer could improve the diffusion of lithium ions effectively and thus inhibit the growth of dendrites. The NGNS interlayer could be used as the internal current collector and reduce the charge-transfer resistance. Secondly, the unique



Fig. 5 (a) GCD profiles of the cathodes with different separators at a current density of 0.1C (b) voltage profiles at 0.1C based on different separators. (c) The CV curves of the CGS/S-Janus PP electrode were measured at different scan rates (d) EIS profiles of pristine and cycled for 50 cycles of Li–S cells with different separators (e) cycling performance of the Li–S batteries with different separators tested at 0.2C (f) rate capability of CGS/S-Janus PP cycled at different current densities from 0.05C to 10C (g) GCD profiles of CGS/S-Janus PP tested at different current densities. (h) Long-life cycling stability and corresponding coulombic efficiency of CGS/S-Janus PP were obtained at the current density of 1C.



Fig. 6 (a) Schematic of Janus PP separator for Li–S battery. (b) Photograph of LED lamps with the pattern of "XMU" lighted by two serially-connected Li–S batteries.

network structure of NGNS could suppress the deformation of lithium metal effectively. Thirdly, the adsorption and capillarity of NGNS allows the electrolyte to be distributed more evenly and thus relieve the formation of dead lithium due to the side effects of excess electrolyte. Besides, the Co_3O_4 @GNS interlayer could restrain the shuttling effect with both physical blocking and chemical interactions, thus maximally improving the

electrochemical properties (Fig. 6a). In addition, two seriallyconnected Li–S coin cells with CSG/S-Janus PP could light up an LED sign with "XMU" letters (Fig. 6b).

4. Conclusions

In summary, we propose a functional Janus-PP separator for Li-S batteries. The NGNS interlayer could improve the diffusion of lithium ions and reduce the charge-transfer resistance. Due to the super lithiophilicity and adsorption, the NGNS could relieve the formation of dead lithium and inhibit the lithium dendrites. The symmetric Li//Li cells with the NGNS-PP separator exhibited excellent cycling stability (12 000 h at 6 mA cm⁻²) and good rate performance (low overpotential of 80 mV at 10 mA cm⁻²). Further, the electrochemical properties of Li-S cells could be improved with the Janus-PP separator. Benefiting from the structural uniqueness and chemical protection of the Co₃O₄@GNS interlayer described above, the Li-S batteries achieved exceptional improvements in cycling and rate performance. The CSG/S-Janus PP displayed long-term cycling stability with a low decay rate of 0.018% per cycle over 800 cycles at 1C. Therefore, we envision that the strategy can be a versatile orientation for simultaneously inhibiting the shuttle effect and growth of lithium dendrites towards advanced Li-S batteries.

Conflicts of interest

The authors declare no conflicts of interest.

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References

- C. Fang, J. Li, M. Zhang, Y. Zhang, F. Yang, J. Z. Lee, M. H. Lee, J. Alvarado, M. A. Schroeder, Y. Yang, B. Lu, N. Williams, M. Ceja, L. Yang, M. Cai, J. Gu, K. Xu, X. Wang and Y. S. Meng, *Nature*, 2019, 572, 511–515.
- 2 Y. J. Liu, X. Y. Tao, Y. Wang, C. Jiang, C. Ma, O. W. Sheng,G. X. lu and X. W. Lou, *Science*, 2022, 375, 739–745.
- 3 T. Lei, W. Chen, W. Lv, J. Huang, J. Zhu, J. Chu, C. Yan,
 C. Wu, Y. Yan, W. He, J. Xiong, Y. Li, C. Yan,
 J. B. Goodenough and X. Duan, *Joule*, 2018, 2, 2091–2104.
- 4 Y. Liu, D. Lin, Y. Li, G. Chen, A. Pei, O. Nix, Y. Li and Y. Cui, *Nat. Commun.*, 2018, **9**, 3656.
- 5 C. Yan, X. B. Cheng, Y. Tian, X. Chen, X. Q. Zhang, W. J. Li,
 J. Q. Huang and Q. Zhang, *Adv. Mater.*, 2018, 30, 1707629.
- 6 X. B. Cheng, M. Q. Zhao, C. Chen, A. Pentecost, K. Maleski, T. Mathis, X. Q. Zhang, Q. Zhang, J. Jiang and Y. Gogotsi, *Nat. Commun.*, 2017, 8, 336.
- 7 Q. Pang, A. Shyamsunder, B. Narayanan, C. Y. Kwok, L. A. Curtiss and L. F. Nazar, *Nat. Energy*, 2018, **3**, 783–791.
- 8 P. Albertus, S. Babinec, S. Litzelman and A. Newman, *Nat. Energy*, 2017, **3**, 16–21.
- 9 Z. Li, B. Y. Guan, J. Zhang and X. W. Lou, Joule, 2017, 1, 576–587.
- 10 R. Zhang, S. Wen, N. Wang, K. Qin, E. Liu, C. Shi and N. Zhao, *Adv. Energy Mater.*, 2018, 8, 1800914.
- 11 B. Horstmann, J. Shi, R. Amine, M. Werres, X. He, H. Jia, F. Hausen, I. Cekic-Laskovic, S. Wiemers-Meyer, J. Lopez, D. Galvez-Aranda, F. Baakes, D. Bresser, C.-C. Su, Y. Xu, W. Xu, P. Jakes, R.-A. Eichel, E. Figgemeier, U. Krewer, J. M. Seminario, P. B. Balbuena, C. Wang, S. Passerini, Y. Shao-Horn, M. Winter, K. Amine, R. Kostecki and A. Latz, *Energy Environ. Sci.*, 2021, **10**, 1037.
- 12 B. Liu, J.-G. Zhang and W. Xu, Joule, 2018, 2, 833-845.
- 13 L. Ma, J. Cui, S. Yao, X. Liu, Y. Luo, X. Shen and J.-K. Kim, Energy Storage Mater., 2020, 27, 522–554.
- 14 D. Lin, Y. Liu, Z. Liang, H. W. Lee, J. Sun, H. Wang, K. Yan, J. Xie and Y. Cui, *Nat. Nanotechnol.*, 2016, **11**, 626–632.
- 15 G. Zheng, S. W. Lee, Z. Liang, H. W. Lee, K. Yan, H. Yao, H. Wang, W. Li, S. Chu and Y. Cui, *Nat. Nanotechnol.*, 2014, 9, 618–623.

- 16 L. Liu, Y. X. Yin, J. Y. Li, S. H. Wang, Y. G. Guo and L. J. Wan, *Adv. Mater.*, 2018, **30**, 1706216.
- 17 Y. J. Gong, J. W. Heo, H. Lee, H. Kim, J. Cho, S. Pyo, H. Yun, H. Kim, S. Y. Park, J. Yoo and Y. S. Kim, *Adv. Energy Mater.*, 2020, **10**, 2001479.
- 18 C. Y. Wang, Z. J. Zheng, Y.-Q. Feng, H. Ye, F.-F. Cao and Z. P. Guo, *Nano Energy*, 2020, 74, 104817.
- 19 Y. Xu, T. Li, L. Wang and Y. Kang, *Adv. Mater.*, 2019, **31**, 1901662.
- 20 H. Duan, Y. X. Yin, X. X. Zeng, J. Y. Li, J. L. Shi, Y. Shi, R. Wen, Y.-G. Guo and L.-J. Wan, *Energy Storage Mater.*, 2018, **10**, 85– 91.
- 21 R. Mukherjee, A. V. Thomas, D. Datta, E. Singh, J. Li,
 O. Eksik, V. B. Shenoy and N. Koratkar, *Nat. Commun.*, 2014, 5, 3710.
- 22 L. Jiao, S. Wu, Y. Tao, W. Lv, C. Zhang, G. Ling and Q.-H. Yang, *Energy Storage Mater.*, 2019, 23, 112–136.
- 23 S. Liu, J. Li, X. Yan, Q. Su, Y. Lu, J. Qiu, Z. Wang, X. Lin, J. Huang, R. Liu, B. Zheng, L. Chen, R. Fu and D. Wu, *Adv. Mater.*, 2018, **30**, 1706895.
- 24 J. H. Kim, Y. H. Lee, S. J. Cho, J. G. Gwon, H. J. Cho, M. Jang, S. Y. Lee and S. Y. Lee, *Energy Environ. Sci.*, 2019, **12**, 177–186.
- 25 E. Cha, M. D. Patel, J. Park, J. Hwang, V. Prasad, K. Cho and W. Choi, *Nat. Nanotechnol.*, 2018, **13**, 337–344.
- 26 Y. Gao, Q. Guo, Q. Zhang, Y. Cui and Z. Zheng, *Adv. Energy Mater.*, 2020, **11**, 2002580.
- 27 Y. Mao, G. Li, Y. Guo, Z. Li, C. Liang, X. Peng and Z. Lin, *Nat. Commun.*, 2017, **8**, 14628.
- 28 K. Chen, J. Cao, Q. Lu, Q. Wang, M. Yao, M. Han, Z. Niu and J. Chen, *Nano Res.*, 2018, **11**, 1345–1357.
- 29 Z. Sun, J. Zhang, L. Yin, G. Hu, R. Fang, H. M. Cheng and F. Li, *Nat. Commun.*, 2017, **8**, 14627.
- 30 R. Fang, G. Li, S. Zhao, L. Yin, K. Du, P. Hou, S. Wang, H.-M. Cheng, C. Liu and F. Li, *Nano Energy*, 2017, 42, 205– 214.
- 31 H. Shi, X. Zhao, Z.-S. Wu, Y. Dong, P. Lu, J. Chen, W. Ren, H.-M. Cheng and X. Bao, *Nano Energy*, 2019, **60**, 743–751.
- 32 J. Y. Wei, X. Q. Zhang, L. P. Hou, P. Shi, B. Q. Li, Y. Xiao,
 C. Yan, H. Yuan and J. Q. Huang, *Adv. Mater.*, 2020, 32, 2003012.
- 33 S. Li, J. Lin, Y. Ding, P. Xu, X. Guo, W. Xiong, D. Y. Wu, Q. Dong, J. Chen and L. Zhang, *ACS Nano*, 2021, **15**, 13803.
- 34 P. Xiong, F. Zhang, X. Zhang, Y. Liu, Y. Wu, S. Wang, J. Safaei, B. Sun, R. Ma, Z. Liu, Y. Bando, T. Sasaki, X. Wang, J. Zhu and G. Wang, *Nat. Commun.*, 2021, **12**, 4184.
- 35 Y. Dong, P. Lu, H. Shi, J. Qin, J. Chen, W. Ren, H.-M. Cheng and Z.-S. Wu, *J. Energy Chem.*, 2019, **36**, 64–73.
- 36 Y. Dong, S. Zheng, J. Qin, X. Zhao, H. Shi, X. Wang, J. Chen and Z. S. Wu, ACS Nano, 2018, 12, 2381–2388.
- 37 Y. Xu, H. Yan, T. Li, Y. Liu, J. Luo, W. Li, X. Cui, L. Chen, Q. Yue and Y. Kang, *Energy Storage Mater.*, 2021, 36, 108–114.
- 38 J. Zhao, G. Zhou, K. Yan, J. Xie, Y. Li, L. Liao, Y. Jin, K. Liu, P. C. Hsu, J. Wang, H. M. Cheng and Y. Cui, *Nat. Nanotechnol.*, 2017, **12**, 993–999.
- 39 H. Tian, Z. W. Seh, K. Yan, Z. Fu, P. Tang, Y. Lu, R. Zhang, D. Legut, Y. Cui and Q. Zhang, *Adv. Energy Mater.*, 2017, 7, 1602528.

- 40 Y. Dong, P. Lu, Y. Ding, H. Shi, X. Feng and Z. S. Wu, *SusMat*, 2021, **1**, 393–412.
- 41 Y. K. Huang, R. Pan, D. Rehnlund, Z. Wang and L. Nyholm, *Adv. Energy Mater.*, 2021, **11**, 2003674.
- 42 X. Chen, X. R. Chen, T. Z. Hou, B. Q. Li, X. B. Cheng, R. Zhang and Q. Zhang, *Sci. Adv.*, 2019, 5, 7728.
- 43 Y. Fang, Y. Zeng, Q. Jin, X. F. Lu, D. Luan, X. Zhang and X. W. D. Lou, *Angew. Chem., Int. Ed.*, 2021, **60**, 8515–8520.
- 44 Z. Chang, H. Dou, B. Ding, J. Wang, Y. Wang, X. Hao and D. R. MacFarlane, *J. Mater. Chem. A.*, 2017, 5, 250–257.
- 45 C.-Y. Fan, S.-Y. Liu, H.-H. Li, Y.-H. Shi, H.-C. Wang, H.-F. Wang, H.-Z. Sun, X.-L. Wu and J.-P. Zhang, *J. Mater. Chem. A.*, 2017, 5, 11255–11262.
- 46 J. Zhao, W. Pei S Fau Ren, L. Ren W Fau Gao, H. M. Gao,
 L. Fau -Cheng and H. M. Cheng, ACS Nano, 2010, 4, 2045.
- 47 Z. Zhang, J. Zhao, J. Zhou, Y. Zhao, X. Tang and S. Zhuo, Energy Storage Mater., 2017, 8, 35-41.
- 48 Z. Zhang, J. Lin, J. Hao, F. Xue, Y. Gu, Z. Zhu and Q. Li, *Carbon*, 2021, **181**, 69–78.
- 49 W. Zhang, C. Xu, C. Ma, G. Li, Y. Wang, K. Zhang, F. Li, C. Liu, H. M. Cheng, Y. Du, N. Tang and W. Ren, *Adv. Mater.*, 2017, **29**, 1701677.
- 50 X. Li, H. Wang, J. T. Robinson, H. Sanchez, G. Diankov and H. Dai, *J. Am. Chem. Soc.*, 2009, **131**, 15939–15944.
- 51 J. Kim, L. J. Cote, F. Kim, W. Yuan, K. R. Shull and J. Huang, J. Am. Chem. Soc., 2010, 132, 8180.
- 52 H. Xu and K. S. Suslick, J. Am. Chem. Soc., 2011, 133, 9148– 9151.
- 53 M. C. Hsiao, S. H. Liao, M. Y. Yen, P. I. Liu, N. W. Pu, C. A. Wang and C. C. Ma, *ACS Appl. Mater. Interfaces*, 2010, 2, 3092–3099.
- 54 X. Cai, Q. Zhang, S. Wang, J. Peng, Y. Zhang, H. Ma, J. Li and M. Zhai, *J. Mater. Sci.*, 2014, **49**, 5667–5675.

- 55 R. Zhang, X. R. Chen, X. Chen, X. B. Cheng, X. Q. Zhang,
 C. Yan and Q. Zhang, *Angew. Chem., Int. Ed.*, 2017, 56, 7764–7768.
- 56 J. Cai, J. Jin, Z. Fan, C. Li, Z. Shi, J. Sun and Z. Liu, Adv. Mater., 2020, 32, 2005967.
- 57 K. Wen, X. Tan, T. Chen, S. Chen and S. Zhang, *Energy Storage Mater.*, 2020, **32**, 55–64.
- 58 H. Yang, A. Naveed, Q. Li, C. Guo, J. Chen, J. Lei, J. Yang, Y. Nuli and J. Wang, *Energy Storage Mater.*, 2018, **15**, 299– 307.
- 59 T. Liu, J. Ge, Y. Xu, L.-P. Lv, W. Sun and Y. Wang, *Energy Storage Mater.*, 2020, **32**, 261–271.
- 60 Y. He, Z. Chang, S. Wu, Y. Qiao, S. Bai, K. Jiang, P. He and H. Zhou, *Adv. Energy Mater.*, 2018, 8, 157.
- 61 M. Chen, J. Zheng, O. Sheng, C. Jin, H. Yuan, T. Liu, Y. Liu, Y. Wang, J. Nai and X. Tao, *J. Mater. Chem. A.*, 2019, 7, 18267– 18274.
- 62 L. Lin, J. Wang, R. Li, C. Wang, C. Zhang, J. Yang and Y. Qian, Energy Storage Mater., 2020, 26, 112–118.
- 63 H. Chen, Y. Yang, D. T. Boyle, Y. K. Jeong, R. Xu, L. S. de Vasconcelos, Z. Huang, H. Wang, H. Wang, W. Huang, H. Li, J. Wang, H. Gu, R. Matsumoto, K. Motohashi, Y. Nakayama, K. Zhao and Y. Cui, *Nat. Energy*, 2021, 6, 790.
- 64 Z. Ye, Y. Jiang, L. Li, F. Wu and R. Chen, *Adv. Mater.*, 2020, 32, 2002168.
- 65 S. Li, D. Leng, W. Li, L. Qie, Z. Dong, Z. Cheng and Z. Fan, *Energy Storage Mater.*, 2020, 27, 279–296.
- 66 L. Luo, S. H. Chung, H. Yaghoobnejad Asl and A. Manthiram, *Adv. Mater.*, 2018, **30**, 804149.
- 67 C. Shang, L. Cao, M. Yang, Z. Wang, M. Li, G. Zhou, X. Wang and Z. Lu, *Energy Storage Mater.*, 2019, **18**, 375–381.