Nitrogen-doped nanoarray-modified 3D hierarchical graphene as a cofunction host for high-performance flexible Li-S battery

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Abstract
Lithium-sulfur (Li-S) batteries with high energy density are promising candidates for next-generation energy storage systems. Practical application of Li-S batteries is hindered by shuttle effect of polysulfides and Li dendrites growth. Herein, a self-supporting cofunction host is constructed with 3D hierarchical graphene modified by N-doped nanoarrays, for both Li anode and S cathode to improve their performances simultaneously. Attributed to high conductivity, strong affinity, and optimized Li-ion transport pathway of N-doped nanoarrays, cofunction host provide excellent Li and S load, which facilitates uniform Li deposition and enhanced S conversion. Particularly, an extra graphene barrier is specialized for S cathode to inhibit the shuttle effect. As a result, Li anode shows long cycle life with outstanding Li-plating behavior, and S cathode shows high capacity and ultrahigh capacity retention with good immobilization of polysulfides. More importantly, the integrated Li-S battery shows long cycle stability and good flexibility, which is important for future application.

KEYWORDS
cofunction host, flexible Li-S batteries, hierarchical nanoarrays structure, Li anodes, S cathodes

1 | INTRODUCTION

The rapid development of portable, flexible, implantable, and wearable electronics creates a growing demand for corresponding flexible energy-storage systems.1-3 To satisfy the commercial needs, flexible energy-storage systems should meet several criteria, such as safety, low cost, high energy density, and long cyclic life.4 However, conventional lithium-ion batteries with LiCoO2 and graphite cannot meet the growing requirements owing to their inherent low energy density.5 So, the exploration of high energy-density storage technologies is urgently required.
Lithium-sulfur (Li-S) battery is one of the prospective candidates for the next-generation flexible energy-storage technology. Li-S batteries offer a high theoretical capacity of 1675 mAh/g and a high theoretical energy density of 2600 Wh/kg, which are three to five times higher than the conventional Li-ion batteries. Moreover, elemental S also possess several interesting features like earth abundant, low cost, environment friendly, and easy large-scale production. On the other hand, the Li metal anode shows the highest theoretical specific capacity (3860 mAh/g), light weight, and lowest electrochemical potential (−3.04 V vs standard hydrogen electrode). With so many attractive advantages, Li-S batteries are super-promising in flexible energy-storage systems. But the practical application of Li-S batteries still faces some key challenges on both Li anode and S cathode. First, the uncontrolled Li dendrites growth and infinite relative volume change during cycling destroy the Li anode, resulting in severe safety issues and poor cycle life. Second, S cathode suffers from the poor electronic conductivity of elemental S and its insoluble discharging products, large volume variation (over 80%), and the “shuttle effect” of long-chain polysulfides (Li2Sn, 4 ≤ n ≤ 8) that lead to rapid capacity decay, self-discharge, and low coulombic efficiency (CE). Thus, development of a flexible Li-S system with high performances for both Li anode and S cathode can provide fascinating opportunity to flexible systems for future commercialization.

To overcome challenges in Li-S batteries, various methods have been thoroughly explored for Li anode or S cathode separately, with little attention to the cofunction hosts for both Li and S. For Li anode, there are some strategies to improve the cycling performance, including the design of stable artificial solid electrolyte interphase (SEI), rational engineering of interfacial layer, the use of vertically aligned channels, the introduction of 3D scaffolds as the current collectors, and so on. 3D porous scaffolds are the current research hotspot in Li anode for improving the Li plating/stripping behavior by accommodating volume change and reducing current density. For S cathode, carbon-based materials with excellent conductivity, such as CNT and graphene, are the most popular hosts to promote conversion reactions and enhance S utilization. To inhibit shuttle effect, it is highly necessary to increase the adsorption by polar substrates such as heteroatom N/P, Co/V/Ni metal compound, and so on. With higher binding energy, polar hosts can inhibit the diffusion of polysulfides and accelerate the redox kinetics. Recently, biomass-derived novel carbons (BDNCs) have attracted much attention for great potential applications in Li-S batteries.

Despite tremendous research in Li-S batteries, practical application especially the flexible Li-S batteries cannot meet the realistic requirements with only improvement of single electrode. So, the cofunction hosts are prospective with simultaneous promotion for both Li anode and S cathode. Luckily, there are various similarities in the design of structures and properties, such as highly conductive skeleton to effectively host active materials and uniformly polar surface to improve the performances, which makes it possible to use the same material to improve performances simultaneously. Therefore, to build an approach of cofunction hosts for Li anode and S cathode simultaneously, a rational design of 3D hierarchical skeleton is highly desired.

Herein, we designed and fabricated a 3D, freestanding, and hierarchical porous reduced graphene oxide with N-doped nanoarrays (3DRGO/NC) as the cofunction host for Li anode and S cathode. The 3D freestanding porous RGO forms the main skeleton structure to hold the Li metal and elemental S, and heteroatom N doping can lower the Li nucleation overpotential and immobilize the polysulfides. More importantly, the well-aligned nanoarrays can effectively confine Li-ions flux and provide an optimized ion-diffusion pathway for better Li plating/stripping behavior and enhanced S utilization/conversion. Particularly, an ultrathin graphene barrier layer was built on RGO with N-doped nanoarrays (3DRGO/NC-BL), which can effectively retain intermediate polysulfides staying in the cathode through physical confinement. As a result, the 3DRGO/NC exhibits high initial discharge capacity of 1185 mAh/g with excellent CE and presents a long stability up to 500 cycles with high reversible specific capacity of 927 mAh/g. Most importantly, a flexible battery is demonstrated with excellent performance in flat, bent, and even rolled states by combining 3DRGO/NC@Li anode and 3DRGO/NC-BL@S cathode, which provides a promising strategy for flexible energy-storage devices.

2 RESULTS AND DISCUSSION

2.1 Fabrication and characterization

The procedure of fabricating the Li anode and S cathode is schematically illustrated in Figure 1. We prepared the 3D porous reduced graphene oxide with polyaniline (PANI) nanoarrays (3DRGO/PANI, Figure 1B) and reduced graphene oxide with PANI nanoarrays and block layer (3DRGO/PANI-BL, Figure 1C) by a series of...
treatment to GO solution (Figure 1A). The detailed preparation process is shown in Figure S1. The freestanding flexible porous N-doped 3DRGO/NC (Figure 1D) and 3DRGO/NC-BL (Figure 1E) were then fabricated through controllable carbonization via a three-step pyrolysis process. The structures of 3DRGO skeleton and N-doped nanoarrays did not show any obvious change after three-step pyrolysis.39 Finally, 3DRGO/NC@Li (Figure 1F) anode was fabricated by electroplating Li, and 3DRGO/NC-BL@S (Figure 1G) cathode was fabricated by a typical melt-diffusion strategy, respectively.

The morphology and structure of 3DRGO/NC and 3DRGO/NC-BL were characterized by scanning electron microscopy (SEM). As shown in the Figure 2, the cross-section and surface morphologies of 3DRGO/NC and 3DRGO/NC-BL both reveal that graphene sheets are tangled and interwoven, forming a 3D hierarchical interconnected configuration. Abundant porous spaces exist in both films, favoring the active material and ionic transport through electrode-electrolyte interfaces. Furthermore, the unique architecture can substantially accommodate the volume variation induced by charge/discharge reactions, thus ensuring structural stability during cycling. Compared with the porous side, the barrier layer of 3DRGO/NC-BL prepared with extra GO solution shows a more compact and flatter surface, which is beneficial to entrap polysulfides on the cathode for the physical blockage. The porous side surface morphology of 3DRGO/NC-BL displays almost identical structure to the porous side of 3DRGO/NC (Figure S2), indicating the difference between two films is only the barrier layer. The surface morphologies of 3DRGO/NC in high magnification of the porous side and barrier layer display the vertical nanoarrays structure (Figure 1C, F, Figure S3b and S3c) compared with smooth surface of 3DRGO (Figure S3a) without the growth of PANI. The aligned nanoarrays supply an optimal pathway for ion diffusion.

Raman spectroscopy (Figure 2G) of both the films mainly exhibits two peaks of the D-band (1354 cm$^{-1}$) and G-band (1581 cm$^{-1}$), which respectively originated from the structural and partially disordered structures of graphene and the vibrations of sp²-hybridized carbon domains.40,41 The intensity ratio of D-band to G-band ($I_D/I_G$) reflects the structural imperfection of graphitic sp² domains, and a certain degree of $I_D/I_G < 1.0$ guarantees high-quality electrical conductivity.36,42 The values of $I_D/I_G$ for 3DRGO/NC and two sides of 3DRGO/NC-BL are 0.92, 0.90 (porous side), and 0.88 (barrier layer), respectively. The $I_D/I_G$ value of the barrier layer slightly decreases because the barrier layer has more compact and ordered conjugated structure. The overall range of X-ray photoelectron spectra (XPS) of 3DRGO/NC and
3DRGO/NC-BL clearly revealed high N content (9.7% and 9.4%) in both films (Figure S4a). High-resolution N 1s second spectrum (Figure 2H and Figure S4b) shows the presence of pyridinic-N (N6, 398.5 ± 0.2 eV), pyrrolic-N (N5, 400.7 ± 0.1 eV), and quaternary-N (NQ, 401.6 ± 0.2 eV) in the 3DRGO/NC and 3DRGO/NC-BL, and confirms the N is doped into the graphene framework rather than as residue or impurities. The uniform distribution of N element can be proved in elemental mapping (Figure 2I), which will be beneficial to the homogeneous Li nucleation and S loading. The exact EDX elemental mapping corresponding to the SEM images of 3DRGO and 3DRGO/NC are also provided in Figure S5.

2.2 Morphology of Li metal deposition

To investigate the Li plating behavior on the 3DRGO, 3DRGO/NC, and 3DRGO/NC-BL, we assembled coin cells with the 3DRGO, 3DRGO/NC, and 3DRGO/NC-BL as the working electrodes, and the Li foil as the counter electrode. The importance of N-doped carbon nanoarrays for Li nucleation can be clearly clarified by SEM after plating 0.2 mA h/cm² Li on the 3DRGO and 3DRGO/NC at 1 mA/cm² (Figure S6). After Li deposition, 3DRGO/NC exhibits a smooth and flat surface without obvious growth of Li dendrites or concentrated metallic Li (Figure S6c and S6d). Such a uniform nucleation can be attributed to well-distributed N-containing nanoarrays in the 3DRGO/NC. The strong interaction between N-doped functional group and Li can initiate uniform nucleation of Li ions with lower nucleation overpotential. For comparison, the 3DRGO shows an uneven rugged surface with high concentration of metallic Li (Figure S6a and S6b). The Li deposited on the 3DRGO is agglomerated with clearly “small hill” structure showing the uneven nucleation of Li. When plating 1 mAh/cm² on the three types current collectors at 1 mA/cm², there exist more
obvious differences on the morphology as shown in Figure 3. The surface morphologies of 3DRGO/NC are quite smooth and flat without Li dendrites or “bulk” Li (Figure 3D,E), and there is no concentrated deposition of metallic Li as seen in the cross-section morphology, demonstrating the homogenous deposition of Li throughout the 3DRGO/NC. The superdeposition appearances benefit from the uniform growth of Li on the 3DRGO/NC, for the reduced local current density from large surface area of 3D porous skeleton and regularly Li-ions confinement through vertically aligned channels produced by evenly N-doped carbon nanoarrays.24,25 However, “bulk” Li and Li dendrites are clearly observed on the surface of 3DRGO and 3DRGO/NC-BL (Figure 3A,B,G,H), Li bulk on the top surface can also be easily observed through the cross-section morphology (Figure 3C,I). Although 3DRGO and 3DRGO/NC show almost the same morphologies, the reasons may be different from each other. For 3DRGO, the cause is the uneven nucleation and growth of Li for high nucleation overpotential on bare carbon materials and concentration of Li-ions to the Li nucleation position, which then gradually grows into “bulk” Li. For 3DRGO/NC-BL, the main problem comes from the barrier layer for Li-ions nucleate directly on the barrier layer. Without the help of 3D porous structure, uneven deposition behavior of Li is unavoidable. With increased capacity to 4 mAh/cm², the similar morphologies appear. 3DRGO/NC still shows the smooth flat surface without “bulk” Li or Li dendrites, and even distribution of Li deposition (Figure 57d-f). The surfaces of 3DRGO and 3DRGO/NC-BL have many discontinuous, even isolated, Li bulks with loose porous morphology or Li dendrites; bigger and thicker Li bulks appear on the top surface by cross-section SEM (Figure S7a-c, S7g-i, Supporting Information).

2.3 | Electrochemical performance of Li anode

The electrochemical performances of three different current collectors have been investigated as shown in Figure 3.
Before the tests, we get the 3DRGO@Li, 3DRGO/NC@Li, and 3DRGO/NC-BL@Li electrodes by plating 3 mAh/cm\(^2\) on the 3DRGO, 3DRGO/NC, and 3DRGO/NC-BL at 1 mA/cm\(^2\). Galvanostatic cycling stability is investigated by symmetrical Li\(|3\)DRGO@Li, Li|3DRGO/NC@Li and Li|3DRGO/NC-BL@Li batteries with Li foil as the counter electrode. Figure 4A shows the voltage profiles of three types of symmetrical batteries with capacity of 1 mAh/cm\(^2\) at 1 mA/cm\(^2\). The 3DRGO/NC@Li displays a smooth and stable voltage profile with a low overpotential of 20 mV and long cycle life of 500 hours (about 250 cycles). With the help of N-doped nanoarrays, 3DRGO/NC has much faster Li\(^+\) transport and maintain a low mass-transfer overpotential in a long-term repeating stripping/plating of Li metal. By comparison, 3DRGO@Li and 3DRGO/NC-BL@Li show gradually increasing voltage profile with the overpotential up to 100 mV and short lifespan, indicating the unstable charge/discharge process and short cycle life. The fluctuant voltage profile is due to the instability of fragile Li/electrolyte interface and inevitable Li dendrite growth on 3DRGO@Li and 3DRGO/NC-BL@Li during the
repeated cycling process. When the current density increased to 2 and 5 mA/cm² with 1 mAh/cm² area capacity, the voltage hysteresis of both three electrodes go larger, but the 3DRGO/NC@Li still shows the best cycling performance and longest lifespan compared with the other two electrodes (Figure S8a and S8b). Excellent cycle stability of 3DRGO/NC@Li is better reflected in the galvanostatic rate test as shown in Figure 4B. The rate performance is tested under an areal capacity of 1 mAh/cm² with current density 0.5, 1, 2, 5, 10 mA/cm², and then decreased to 1 mA/cm² again. The profile of 3DRGO/NC@Li shows a perfect rate performance without fluctuation even at the 10 mA/cm² current density, and much smaller voltage hysteresis. But 3DRGO@Li and 3DRGO/NC-BL@Li exhibit obvious oscillation especially when the current density reaches 10 mA/cm², which really makes a difference. More importantly, when the current density returns to 1 mA/cm², 3DRGO/NC@Li electrode still presents a very excellent curve and can continue to cycle many laps without continuous overpotential increase. In strong contrast, the profiles of 3DRGO@Li and 3DRGO/NC-BL@Li get more and more sharp companied with gradually increased voltage hysteresis, indicating higher charge transfer resistance due to the unstable Li/electrolyte interface and Li dendrite.

Coulombic efficiency (CE) is a critical factor to measure the utilization of Li and evaluate the performance of current collector. CE of three different current collectors have been investigated with a capacity of 1 mAh/cm² at 0.5 mA/cm² and 1 mA/cm² as shown in Figure 4C and Figure 5A, respectively. 3DRGO/NC@Li electrode can maintain high CE above 98% with long lifespan of 300 cycles at 0.5 mA/cm², demonstrating excellent Li accommodation performance and high utilization without production of “dead Li.” However, the CE of 3DRGO and 3DRGO/NC-BL decreases to 90% around 100 cycles due to the “dead Li” and Li dendrite. The CE at 1 mA/cm² has a similar trend showing the best performance of 3DRGO/NC. Figure 4D shows the voltage profiles of plating Li on 3DRGO and 3DRGO/NC electrodes at 0.5 mA/cm². Such a high CE and long-cycle performances are superior to that of most reported 3D Li anodes with N-doped materials (Table S1). Nucleation overpotential defined as the voltage gap between the lowest shape corner and later platform is the key point towards the difficulty of Li nucleation on current collector. 3DRGO/NC has tiny nucleation overpotential about 14 mV much smaller than 3DRGO (24 mV) for the lithiophilicity of N heteroatoms decreases the charge transfer resistance. Figure 4E shows the typical charge-discharge profiles of the 3DRGO/NC, with a cycling capacity of 1 mA h/cm² at 0.5 mA/cm², indicating good consistency to the CE.

2.4 | Electrochemical performance of S cathode

The N-doped carbon materials for S cathode are highly investigated in previously works. The electron-rich N heteroatoms can form Li−N bond via strong dipole-dipole electrostatic interaction and enhanced inductive and conjugative effect, which significantly improves the interaction between the hosts and the lithium polysulfides. Thus, we focused on the influence of graphene barrier layer. Based on 3DRGO/NC and 3DRGO/NC-BL, Li-S batteries with three different configurations are designed to study the roles of barrier layer by using Li foil as the anode. As shown in Figure 5A, cell A used 3DRGO/NC@S with two porous sides as cathode, whereas cells B and C used 3DRGO/NC-BL@S with one porous side and one barrier layer as battery cathode. In cell B, the porous side in contact with the separator, whereas the barrier layer is in contact with the separator in cell C. The S contents in the electrodes were 55.7 and 57.1 wt % for the 3DRGO/NC@S and 3DRGO/NC-BL@S (Figure S10a), respectively. Both 3DRGO/NC@S and 3DRGO/NC-BL@S films were freestanding and highly conductive, and can be cut into slices of desired size to directly serve as cathodes for Li-S batteries, where neither insulating binder nor conducting additive is needed. Figure 5B shows an S element cross-section mapping of the 3DRGO/NC-BL, which proves sulfur is distributed uniformly in the cathode. Figure 5C and Figure 5D, respectively show the 1st to 11th cyclic voltammetry (CV) curves of cells C and A in the voltage range of 1.5 to 3.0 V with a constant scan rate of 0.1 mV/s. Figure 5C shows two peaks during reduction in the cathodes. The peak located at about 2.3 V involves the reduction of elemental S8 to Li polysulfides (Li2Sx, 4 < X < 8), and the peak located at about 2.03 V corresponds to the reduction of Li polysulfides to Li2S2 and eventually to Li2S. Meanwhile, one anodic peak at about 2.45 V can be observed during charging corresponding to the conversion of Li sulfides to polysulfides and further to S8.48 Notably, the measured CV curves are similar in shape, suggesting high reversibility. The integral areas of peaks increased gradually from the first to fifth cycles, demonstrating the effective suppression of polysulfide shuttle effect. The CV curves from cell A (Figure S10b) show a low reduction potential with significantly decreased integral areas, suggesting a sluggish kinetic process. The superior properties of cell C can be ascribed to the effectively decreased dissolution of polysulfides species, thereby promoting active material utilization and capacity retention.

The galvanostatic charge-discharge behavior of cells A and C was evaluated at 0.5 C for 500 cycles within a
The charge-discharge profiles of cell C consist of two plateaus (Figure 5D) even after 500 cycles, corresponding to the reduction of elemental sulfur to long-chain Li polysulfides at 2.3-2.4 V and the formation of short-chain Li$_2$S$_2$/Li$_2$S at 2.1 V. The plateaus of cell C are flat and stable with relatively low polarization, which suggests a kinetically efficient reaction process with a barrier layer. By contrast, discharge potential decreases and charge potential increases with increased voltage hysteresis for cell A (Figure S10c), indicating high polarization and slow redox reaction kinetics with inferior reversibility. These results are consistent with the CV measurements. The EIS spectra are presented in Figure S11. Cell C shows the smallest middle-frequency semicircle and highest slope of line in the low-frequency regions, indicating decreased polarization and charge transfer resistance and increased reaction kinetics.

The rate capabilities of batteries with and without barrier layer are also investigated at various current densities, with the results presented in Figure 5E. The C rates specified in this study are based on the mass and theoretical capacity of S (1C = 1675 mA/g). Cell C shows excellent rate capability in contrast with cells A and B at the gradually changed current densities. Cell C exhibits a reversible discharge capacity of 1185 mAh/g at 0.1 C, which gradually decreases to 1025, 891, 765, 695, and 634 mAh/g as the specific current increased to 0.2, 0.5, 1, 2, and 5 C, respectively. When the current rate is switched back to 0.1 C, the capacity can recover to 1077 mAh/g, indicating the good stability and reliability of the developed graphene barrier layer to prevent polysulfide shuttling of the cathode material at various current rates. The increase in discharge capacity during the first four cycles is due to the reutilization of the sulfur core in the cathode during cell cycling, demonstrating the assistance
of the effective graphene barrier layer to enhance conductivity and active material utilization. Cyclic stability was investigated at a current density of 0.5 C, as shown in Figure 5F. Cell C delivers a high capacity of almost 920 mAh/g, with an ultrahigh cyclic capacity retention of 99.94% per cycle for 500 cycles. By comparison, cells A and B electrodes are only able to demonstrate capacity retention of 99.89% and 99.90% per cycle after 500 cycles, indicating an increased degree of Li polysulfides dissolution into the electrolyte. Notably, the CE of cell C is stabilized at a high value of 92.6%, whereas the efficiencies of cell A and cell B are 89.3% and 89.1%, respectively. This superiority is ascribed to the introduction of the barrier layer between active S and separator, which can effectively suppress the diffusion of polysulfides into the electrolyte and mitigate the shuttle phenomenon, thereby enhancing the utilization of $S_8$ and improving cycle life and efficiency. As shown in the Table S2, the performances of 3DRGO/NC-BL@S are highly competitive among other reported S cathodes in the literature.

Based on above discussion, we conclude the schematic for plating behavior of Li on the 3DRGO/NC and the inhibition of polysulfide shuttle effect by 3DRGO/NC-BL with dual chemical and physical interaction (Figure 6). For 3DRGO, Li metal shows obviously uneven deposition due to the inhomogeneous distribution of electric field and Li ion flux (Figure S12). For the 3DRGO/NC, Li metal gets an excellent deposition due to the heteroatom N doping and aligned nanoarrays synergistic effect. At the nucleation stage, heteroatom N reduce the Li nucleation resistance compared with the bare carbon materials for strong chemical interplay, so the uniform distribution of N-doping can lead to the evenly nucleation of Li metal. Especially, good movement of Li-ion flux can be achieved by the inherent physical confinement of nanoarrays structure with shorter Li$^+$ diffusion pathway and faster Li$^+$ transport. And 3D skeleton and nanoarrays structure can offer large surface area to reduce the local current density, bringing the decrease of mass transfer resistance at the growth stage. However, with only N-doped adsorption, the effect of 3DRGO/NC on inhibiting the polysulfide shuttling is not obvious. For 3DRGO/NC-BL, the synergistic effects of heteroatom N-doped and barrier layer have a stronger and better inhibition to polysulfides shuttle than only N-doped of 3DRGO/NC. N-doped functional group provides superior adsorption of soluble polysulfide as the chemical interconnection between N and polysulfides. The graphene barrier layer provides a strong physical confinement to block polysulfides migration. Nevertheless, the introduction of barrier layer is detrimental to the deposition behavior of Li, which is proved to result in the appearance of “bulk” Li and occurrence of the uneven Li deposition morphology.

2.5 | Cycling stability and flexibility of Li-S full battery

To further prove the integrated performance of both electrodes, full Li-S coin cell is assembled with 3DRGO/NC@Li anode (~100% excess) and 3DRGO/NC-BL@S...
cathode. By comparison, full Li-S coin cell with 3DRGO@Li anode (~100% excess) and 3DRGO/NC@S cathode is also assembled. Figure 7A shows the cycle performances of two different coin cells. Li-S cell with 3DRGO/NC@Li and 3DRGO/NC-BL@S shows an excellent performance with a high capacity about 810 mAh/g, and a high capacity retention of 99.92% per cycle for 400 cycles. However, the capacity of another Li-S cell with 3DRGO@Li and 3DRGO/NC@S is only 630 mAh/g, and the capacity retention is 99.85% per cycle. The two different results demonstrate prominent performance of integrated Li-S full cell with our designed electrode. A prototype of a soft-pack, large-area (about 8 cm²) flexible Li-S battery is assembled to demonstrate the application of 3DRGO/NC@Li anode and 3DRGO/NC-BL@S cathode in flexible devices. A structural representation of the flexible Li-S battery is shown in Figure S13. The fully flexible battery delivered a stable open-circuit voltage of 3.0 V (Figure S14a and S14b). The rate performance of the large-area flexible device is also investigated (Figure 7B). Large-area flexible device delivers an initial capacity of 863 mAh/g at 0.1 C and retains a capacity of 480 mAh/g at 0.5 C for 200 cycles. This trend is very similar to the button-type cell. Cyclic stability is investigated at a current density of 0.5 C when the bending radius of flexible battery was 1.25 cm. The flexible device based on 3DRGO/NC@Li and 3DRGO/NC-BL@S retains almost 82.6% of its initial capacity after 200 cycles with no obviously decrease of CE. To show the stability of both electrodes, mechanical deformation tests are conducted. The soft-pack Li-S battery prototype can light up 25 blue light-emitting diodes (LEDs) under flat, bent, and even rolled states.

**FIGURE 7** A, Capacity retention and CE of two different Li-S coin cells over 400 cycles at 0.5C. B, Rate capability of flexible Li-S soft-pack battery. C, Capacity retention of the flexible battery over 200 cycles at 0.5 C at the bending radius of 1.25 cm. D-F, Experimental demonstration showing that the prototype of soft-pack battery can light up 25 green LEDs under flat, D, bent, E, and even rolled states, F
rolled states (Figure 7D–7F). Apparently, no difference in dimming or brightness is observed when the battery is rolled into a circular shape and then unfurled to its original shape (Video S1). Dynamic bending test through a mechanical system is conducted during LED illumination. Video S2 shows no reduction of light intensity even when the device was bent through a distance of 3 cm during dynamic bending test. As a result, the Li-S full battery coupled with 3DRGO/NC@Li anode and 3DRGO/NC-BL@S cathode is highly suitable for flexible and wearable energy systems and is highly competitive with other full-cell configurations in the literature, as shown in Table S3.

3 | CONCLUSION

In summary, we have designed and fabricated a 3D porous cofunction host through N-doped nanoarrays modified hierarchical graphene for Li metal and elemental S. With structure design and morphology optimization, the performances of Li-S battery are improved due to chemical interactions and physical effects. Chemical interactions are derived from the strong effects of homogeneously distributed heteroatoms N to metallic Li and polysulfides. Physical effects come from the confinement of nanoarrays to Li-ion flux and the block of barrier layer to polysulfides. Attributed to the wonderful synergistic effects, significant improvements have been achieved as the cofunction host for both Li anode and S cathode. 3DRGO/NC shows smooth and flat Li deposition behavior with low nucleation overpotential, ultralong cycle lifespan, high coulombic efficiency and excellent rate performance. 3DRGO/NC-BL@S cathode exhibits a high-specific capacity, good rate performance, and good cyclability. What is more, a further successful demonstration of full flexible device also indicates the practical application of this type of materials in flexible electronic devices. Therefore, this material displays a great potential application in the development of flexible energy storage system.

3.1 | Experimental section

3.1.1 | Preparation of 3DRGO/NC and 3DRGO/NC-BL film

The 3D RGO/NC was prepared by vacuum-assisted filtrated method, which was described in detail in our previous work. The 3D RGO/NC-BL was prepared by a two-step vacuum-assisted filtration method. An extra barrier layer was formed by 5 mL of 0.25 mg/mL GO solution filtrated on the one side of RGO/NC. The two sides of the film were prepared with barrier layer named porous side and barrier layer, respectively. The detailed preparation process is shown in the Supporting Information.

3.1.2 | Preparation of S cathode

The composite films were soaked in 50 mg/mL S/CS₂ solution for 2 hours. The films and sulfur mixture were sealed in a weighing bottle and annealed at 155°C for 6 hours. Then, the product was heated at 200°C for 10 minutes under argon atmosphere in a tube to remove redundant sulfur outside. The freestanding films mixed with sulfur were named 3DRGO/NC@S and 3DRGO/NC-BL@S.

3.1.3 | Li metal anode test

Electrochemical measurements were carried out using CR2032-type coin cells assembled in an argon-filled glove box. Lithium metal foil (15 mm in diameter) was used as counter and reference electrodes, and polypropylene film (Celgard 2400, 16 mm in diameter) as separator. The freestanding films 3DRGO, 3DRGO/NC, and 3DRGO/NC-BL were cut into round slices (11 mm in diameter) of electrode as the working electrode. The organic electrolytes comprised 40 μL solutions of lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) in a mixed solvent of 1,3-dioxolane and 1,2-dimethoxyethane with a volume ratio of 1:1 and 0.1 mol/L LiNO₃ as an additive. Electrochemical Li plating at a current density of 1 mA/cm² was performed with area capacity of 0.2, 1, 2 mA/cm² to study the deposited behavior. For the symmetrical cell test, 3 mA/cm² of Li was first plated onto the current collectors at 1 mA/cm², then the cells were cycled at the current density of 1, 2, 5 mA cm⁻² for 1 mA cm⁻² in each half cycle. The rate performances were recorded at different current rates (0.5, 1, 2, 5, 10 mA/cm² then return to 1 mA/cm²). Before the CE test, the cells were precycled at 0-1 V (vs Li/Li⁺) at 50 μA for five cycles for cell aging and activation. The coulombic efficiencies were recorded by employing 1 mAh/cm² cutoff capacities and a charge limit of 1 V for the cells at different current rates (0.5, 1 mA/cm²). All tests were performed using LAND2001 cycler.

3.1.4 | S cathode test

The Li-S full cells were prepared by using 3DRGO/NC@S and 3DRGO/NC-BL@S as cathode with commercial Li
foils as anode. The types of electrolyte and separator were the same. The electrolyte addition is about 30 μL/mg. CV measurements were performed using a potentiostatic electrochemical workstation (VMP3, Bio-Logic, France) in the voltage range of 1.5 V to 3.0 V with a constant scan rate of 0.1 mV/s. The galvanostatic charge/discharge was performed by LAND2001 cycler within the voltage range of 1.5 to 3.0 V (vs Li/Li⁺) at 0.5C. The rate performances were performed by LAND2001 cycler within the voltage range of 1.5 to 3.0 V (vs Li/Li⁺) at 0.1, 0.2, 0.5, 1.0, 2.0, and 5.0 C and then back to 0.1C.

3.1.5 | Li-S coin cell

3DRGO@Li and 3DRGO/NC@Li can be obtained by electroplating or molten Li infusion with about 100% Li excess. The Li-S coin cells were coupled with 3DRGO/NC@Li and 3DRGO/NC-BL@S or 3DRGO@Li and 3DRGO/NC@S. The types of electrolyte and separator were the same. The electrolyte addition is about 30 μL/mg.

3.1.6 | Flexible Li-S full battery

The flexible Li-S battery was assembled by laminating the anode, separator, cathode, and current collector together and packaging in laminated Al-plastic film. First, the three sides of the laminated Al-plastic film were sealed. Then, the electrolyte (as received from DoDoChem) was injected into the battery bag before the battery was placed in a vacuum environment for several minutes. After the electrolyte was fully absorbed, the battery was sealed using a vacuum sealing machine. Finally, a man-made pressing device was used to shape the wave-like structure. Stress pressure was set to 2 MPa and maintained for 5 minutes.

3.1.7 | Instrumentation

Raman spectra were performed on a confocal Raman spectrometer (Renishaw inVia plus, UK) with an excitation wavelength of 514 nm. X-ray photoelectron spectroscopy (ESCALAB250Xi) was used to evaluate elemental composition and different nitrogen doping configurations. TGA measurements were performed using Diamond TG/DTA by Perkin-Elmer Inc. at a heating rate of 5°C/min in Ar atmosphere. The temperature range was set from room temperature to 800°C. The element mapping test and morphologies of electrode films with and without the barrier layer were investigated by field-emission SEM (Hitachi SU8220, Japan). For evaluating electrochemical performance, CV measurements were performed using a potentiostatic electrochemical workstation (VMP3, Bio-Logic, France). Bending test of the battery was conducted using a man-made bending device. The rate performance and stability characterization of coin-type battery and flexible device were performed on a LAND2001 cycler.

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Additional supporting information may be found online in the Supporting Information section at the end of this article.

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