Carbon-Nitride-Based Materials for Advanced Lithium–Sulfur Batteries

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HIGHLIGHTS

• The recent advances in CₓNᵧ-based materials including the optimized g-C₃N₄, g-C₃N₄-based composites, and other novel CₓNᵧ materials are summarized.

• The applications of CₓNᵧ-based materials in Li–S batteries are systematically discussed with a focus on the structure–activity relationship.

• The perspectives on the rational design of advanced CₓNᵧ-based materials for high-performance Li–S batteries are provided.

ABSTRACT Lithium–sulfur (Li–S) batteries are promising candidates for next-generation energy storage systems owing to their high energy density and low cost. However, critical challenges including severe shuttling of lithium polysulfides (LiPSs) and sluggish redox kinetics limit the practical application of Li–S batteries. Carbon nitrides (CₓNᵧ), represented by graphitic carbon nitride (g-C₃N₄), provide new opportunities for overcoming these challenges. With a graphene-like structure and high pyridinic-N content, g-C₃N₄ can effectively immobilize LiPSs and enhance the redox kinetics of S species. In addition, its structure and properties including electronic conductivity and catalytic activity can be regulated by simple methods that facilitate its application in Li–S batteries. Here, the recent progress of applying CₓNᵧ-based materials including the optimized g-C₃N₄, g-CₓNᵧ-based composites, and other novel CₓNᵧ materials is systematically reviewed in Li–S batteries, with a focus on the structure–activity relationship. The limitations of existing CₓNᵧ-based materials are identified, and the perspectives on the rational design of advanced CₓNᵧ-based materials are provided for high-performance Li–S batteries.

KEYWORDS Lithium–sulfur batteries; Carbon nitride; Polysulfide conversion; Shuttle effect; Anode protection
1 Introduction

The continuously increasing demands for sustainable energy and severe environmental crisis have boosted the development of various advanced energy technologies around the world, with the purpose of efficient utilization and storage of renewable energy [1, 2]. High energy density and economical rechargeable batteries are the key components of these advanced energy technologies [3–5]. Operated based on lithium ion (Li-ion) intercalation chemistry, Li-ion batteries have enjoyed great success in powering commercial portable electronics and electric vehicles [6]. However, the limited capacity of electrode materials and their high cost hinder the penetration of traditional Li-ion batteries in large-scale emerging fields. Therefore, it is increasingly important to develop electrochemical energy storage devices with higher energy density and lower cost [7–9].

Lithium–sulfur (Li–S) batteries are considered one of the most promising energy storage systems beyond Li-ion batteries due to their high energy density and low cost [10]. Typically, Li–S batteries consist of elemental sulfur (S8) cathodes and Li anodes, as shown in Fig. 1a. Based on the multi-electron conversion mechanism between S8 and Li metals (S8 + 16Li ↔ 8Li2S) [11, 12], Li–S batteries deliver high theoretical specific capacity of 1675 mAh g−1 and specific energy of 2,600 Wh kg−1, which is 2–5 times that of Li-ion batteries [13]. The widely accepted reaction mechanism of Li–S batteries is shown in Fig. 1c. During the discharge process, solid S8 is firstly reduced to soluble lithium polysulfides (LiPSs, usually denoted as Li2Sn, 2 < n ≤ 8) in a first discharge plateau at around 2.35 V and then continues to be reduced to solid lithium sulfide (Li2S) in a second discharge plateau at around 2.1 V. Due to the involved solid–solid conversion between Li2S2 and Li2S, the corresponding reaction kinetics performs sluggish. During the subsequent charge process, Li2S is reconverted to LiPSs and finally to S8, forming a reversible cycle [14].

Due to inherent properties of the Li–S reaction, the commercial applications of Li–S batteries are limited by three main obstacles (Fig. 1a). (i) The insulating and insoluble nature of S8 and Li2S limits their utilization efficiency and redox kinetics [15–17], especially for the deposition of solid Li2S, which is considered to be the rate-limiting step of the whole discharge process due to the sluggish kinetics in the solid–solid conversion from Li2S2 to Li2S, resulting in low capacity and low rate performance of Li–S batteries; (ii) long-chain LiPSs intermediates are soluble in organic electrolyte, which leads to their shuttling to the Li anode and thus low coulombic efficiency, high self-discharge, and passivation of the Li anode surface with the continuous reaction with LiPSs [13, 18]; (iii) due to the density difference between S8 and Li2S, the cathode encounters a large volume change (∼80%) during the discharge and charge process [19, 20], leading to irreversible damage of the electrode structure and rapid capacity fading; (iv) due to the uneven Li deposition, the generated Li dendrites may pierce the separator, resulting in internal short circuiting and even explosion [13].

S composite cathodes [21–24] and functional interlayers/separators [25–28] based on advanced materials could mitigate these obstacles and achieve high-performance Li–S batteries. Adsorption by a large surface area and abundant active sites could effectively immobilize LiPSs, and high catalytic activity could enhance the reaction kinetics [29–31]. Moreover, highly conductive, interconnected, and flexible structure could promote the utilization of the

![Fig. 1 Schematic illustration of a the challenging issues in common Li–S batteries and b the improved performance for modified Li–S batteries with the introduced CxNy additive in different components. c Typical discharge/charge voltage profiles of Li–S batteries](https://doi.org/10.1007/s40820-022-00954-x)
insulating active materials (S₈ and Li₂S) and mitigate the impact of volume expansion [32–34]. Carbon nitride (CₓNᵧ) is a kind of ordered semiconductor material with strong absorption capability, high catalytic activity, excellent stability, low cost, and environment friendliness, rendering it a promising additive for Li–S batteries [35, 36]. As shown in Fig. 1b, represented by graphitic carbon nitride (g-C₃N₄), its high N content provides abundant active sites for LiPSs’ immobilization. Moreover, the heptazine units of g-C₃N₄ contain high levels of pyridinic N, which can provide lone pair electrons to promote electrochemical reactions [37, 38]. Besides, the high N content of g-C₃N₄ endows it with good capability to homogenize Li ion deposition with the strong affinity between Li and N atoms, and the stable g-C₃N₄ coating on Li anode can physically inhibit the growth of Li dendrites and guarantee the fast transport for Li ions [39, 40]. Although the original g-C₃N₄ bulk shows limited electronic conductivity and surface area [34, 41, 42], these properties can be improved by regulating its structure and properties with simple methods. With various precursors and synthesis conditions, g-C₃N₄ could be synthesized with different C/N ratios, surface area, porosity, nanostructure shapes, and morphologies [43–46].

In this review, we present recent advances in CₓNᵧ-based materials applied in Li–S batteries, including the optimized g-C₃N₄, g-C₃N₄-based composite materials, and other novel CₓNᵧ materials. We systematically summarized their synthetic methods, structures, properties, and effects on Li–S batteries, with a focus on the structure–activity relationship. Based on an extensive analysis of literature, we identified the limitations of existing CₓNᵧ-based materials and provided our perspective on the rational design of advanced CₓNᵧ-based materials for high-performance Li–S batteries.

2 Basics of Representative Carbon Nitride: g-C₃N₄

CₓNᵧ material, represented by g-C₃N₄, was firstly reported in the nineteenth century [37]. Due to its unique structure and properties, g-C₃N₄ has been widely applied in various fields ever since, such as photocatalysis [47], carbon dioxide capture [48, 49], and energy storage, for example, Li–S batteries [35].

2.1 Structures and Properties

Common g-C₃N₄ exhibits a graphene-like nanosheet structure. In the lamellas, tri-s-triazine rings as basic units [37] are composed of sp² hybrid conjugated C and N atoms and further connected by hydrogen bonds between NH and/or NH₂ groups on ring edges [50, 51], as shown in Fig. 2a-b. The connection of multiple basic units constructs angstrom pore structure in the lamellas with a diameter of around 3 Å, which is larger than that of Li⁺ and smaller than that of soluble LiPSs [52], leading to the restricted “shuttle effect”. Between these lamellas, there exists a weak van der Waals force (Fig. 2c) [53], which provides a stronger interlamellar binding ability and smaller stacking distance (0.319 nm) compared to that of graphite (0.335 nm) [54].

g-C₃N₄ has high stability and flexibility, which attribute to its intra- and inter-lamella structure. The aromatic heterocyclic ring in the lamella of g-C₃N₄ ensures its high thermal stability. g-C₃N₄ can withstand a high temperature of around 600 °C in the air without obvious degradation observed [51]. The strong inter-lamellar binding ensures its high chemical stability. g-C₃N₄ is insoluble in most acid/alkali water solutions or organic solutions [55, 56]. Moreover, g-C₃N₄ shows high flexibility, which is conducive to alleviating the volume change of electrodes during the charge and discharge process [57].

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Fig. 2  a Tri-s-triazine unit of g-C₃N₄, b Plane repeats and c π–π stacking structure of g-C₃N₄ [37]. Copyright 2021, Wiley–VCH
More importantly, g-C₃N₄ performs strong LiPSs adsorption capability due to its high N content (60.87 wt%, in theory) and various types of N-site, including bridged N, graphitic N, and pyridinic N. The strong interaction between N and Li [35, 36] effectively immobilizes LiPSs and further accelerates the redox reaction of S species, improving the rate capability of Li–S batteries [58]. The adsorption performances of pristine carbon, N-doped carbon, and g-C₃N₄ to LiPSs were compared by the first-principles calculation [35]. Figure 3a-c displays the 2D deformation charge distribution of various substrates (red for receiving electron and blue for giving electron) and the most stable adsorption configurations of Li₂S₂ molecules on their surfaces. The pristine carbon shows evenly distributed positive charges on each C site and adsorbs Li₂S₂ without special binding bonds, while both N-doped carbon and g-C₃N₄ perform negative charges on the N sites and adsorb Li₂S₂ by forming a Li-N bond with the average distance between g-C₃N₄ and Li₂S₂ as short as 2.06 Å. In addition, as shown in Fig. 3d, g-C₃N₄ shows higher binding energy for Li₂S₂, confirming that g-C₃N₄ can provide rich active sites (pyridinic N) for the adsorption of LiPSs with high intrinsic polarity.

Besides, the high N content of g-C₃N₄ endows it with high affinity with Li ions, which can ensure the uniform deposition of Li ions [40]. Moreover, the shear modulus of the g-C₃N₄ layer is about 21.6 Gpa, which is higher than that of

![Image](https://doi.org/10.1007/s40820-022-00954-x)
Li metal (~4.9 Gpa), thus physically inhibiting the growth of Li dendrites [39].

2.2 Synthesis Methods and Applications in Li–S Batteries

The synthesis methods of g-C₃N₄ reported mainly include the direct condensation method and template method. By heating the nitrogen-containing precursor such as melamine at a certain temperature, direct condensation is a simple and commonly applied method to fabricate 2D g-C₃N₄ nanosheet. With this method, the properties of g-C₃N₄ such as specific surface area could be easily regulated by changing the types of precursor and heating temperature. Different precursors lead to different reaction processes and different by-products, which affect the structure of g-C₃N₄. For example, the evolution of NH₃ gas during the calcination of melamine (g-C₃N₄ precursor) could lead to a g-C₃N₄ product with a porous structure [59]. Heating temperature mainly affects the reaction rate. An excessive temperature would lead to the collapse of g-C₃N₄ structure. Li et al. prepared g-C₃N₄ using cyanuric acid (TTCA) as the precursor [60]. The g-C₃N₄ product shows a porous structure with high specific surface area and high N doping content (up to 56.87 wt%), which facilitate the fast ion transfer and LiPSs immobilization. Furthermore, Yao et al. systematically studied the effect of precursors [43] and pyrolysis temperature [61] on the properties of g-C₃N₄. Among the g-C₃N₄ materials prepared with different precursors, including urea, melamine, thiourea, and dicyandiamide, urea-based g-C₃N₄ shows the highest specific surface area (~93 m² g⁻¹). For the pyrolysis temperature, g-C₃N₄ synthesized at 550 °C shows the highest specific surface area with a rich mesoporous lamellar structure. These results were later reconfirmed by Versaci et al. [44]. In addition, they further proved that g-C₃N₄ prepared at 550 °C with urea had a high content of -NH₂ group, which was conducive to the immobilization of soluble LiPSs.

Based on the direct condensation mechanism, the template method is introduced to fabricate g-C₃N₄ with 3D secondary structures such as hollow or core–shell structures, which could not only provide high surface area but also accommodate the volume change during cycling. The template and reaction temperature selected are important, which affect the structure and properties of the product. Silica is a common template applied. A hollow g-C₃N₄ material was prepared using mesoporous silica as a template and further constructed into an S@C₃N₄ composite cathode with a core–shell structure [62]. In addition, Han et al. used silica microspheres as a hard template and investigated the effect of calcination temperature on the structure of the synthesized hollow g-C₃N₄ microspheres [45]. With calcination temperatures set as 600, 700, and 800 °C, the synthesis procedure is shown in Fig. 3e. According to the SEM images of as-prepared g-C₃N₄ (Fig. 3f-h), the thickness of the shell decreases, and the microsphere structure collapses as the temperature increases from 600 to 800 °C. This could be related to the excessively decompose of the precursors at high temperatures. As a result, the cell with g-C₃N₄ prepared in 600 °C as the S host exhibited a low capacity fading rate of 0.076% per cycle after 500 cycles at 0.5C.

Generally, g-C₃N₄ is applied as an additive to the S cathode. Li et al. fabricated composite cathodes with g-C₃N₄ and S, which exhibited a high capacity of 1200 mAh g⁻¹ at 0.2C and maintained a high capacity of 800 mAh g⁻¹ after 100 cycles with the coulombic efficiency above 99.5% [60]. Yet some studies also use g-C₃N₄ to construct multifunctional layers on the cathode or separator to limit the diffusion of LiPSs. Li et al. coated a layer of g-C₃N₄ on the surface of the S cathode (S-C₃N₄) by the spraying method [63]. This unique design has the following advantages: (1) the g-C₃N₄ layer has a strong chemical adsorption capability for LiPSs, which can limit LiPSs shuttling and alleviate the self-discharge phenomenon; (2) spraying technology ensures the uniformity of the coating, and it is easy to large-scale production with the controlled thickness. Therefore, the cell with an S-C₃N₄ composite cathode displayed a high capacity of 630 mAh g⁻¹ at 5C. Similarly, Xie et al. coated ultra-thin g-C₃N₄ nanosheets on the commercial polypropylene (PP) separator (g-C₃N₄ separator) by using the vacuum filtration technology [64], which effectively prevents LiPSs from diffusing across the separator but allows lithium ions to pass freely (Fig. 3i-j). Moreover, the LiPSs permeation test also showed the strong restriction effect of g-C₃N₄ for LiPSs diffusion (Fig. 3k-l). Thus, the cell with a g-C₃N₄ separator performed a high capacity of 829 mAh g⁻¹ after 200 cycles at 0.2C.

3 Optimization of g-C₃N₄

With various synthesis methods, g-C₃N₄ could perform different microstructures with enhanced specific surface area. Beyond this, the LiPSs absorption capability, catalytic activity, and electron conductivity of g-C₃N₄ could be further improved via defect engineering and heteroatom
doping. Defect engineering plays an important role in adjusting the atomic distribution and surface properties of nanomaterials and has widespread application in various fields including hydrogen evolution reaction [65], oxygen evolution reaction [66], and carbon dioxide reduction reaction [67]. Heteroatom doping is also an effective method to regulate the polarity of carbon materials, and various heteroatoms including nonmetal atoms and metal-single atoms have been studied extensively [68–70]. In particular, the introduction of metal single atoms with unsaturated coordination environments, unique electronic structures, and high surface free energy could significantly enhance the catalytic activity of the materials [71–73]. In recent years, defect engineering and heteroatom doping have attracted more and more attention in Li–S systems due to their significant potential in inhibiting LiPSs shuttling and promoting the redox chemistry [74–77].

3.1 Defect Engineering

With a certain proportion of N defects, g-C₃N₄ materials show enhanced adsorption and catalytic performance of LiPSs. Huang et al. prepared ultrafine spindle g-C₃N₄ (sCN) with N defects by K treatment (Fig. 4a) [58]. Compared with the original g-C₃N₄, the sCN performs spindle-like morphology (Fig. 4b) and an obvious different molecular structure with a large number of defects manifested as N vacancies or cyano groups (Fig. 4c–d). The introduction of N defects increases the polarity of sCN, which leads to 2–3 times increased LiPSs binding energy compared with that of the original g-C₃N₄. Therefore, the Li–S cell with sCN modified separator delivered a high initial capacity of 637 mAh g⁻¹ at 5C and a low capacity fading rate of 0.05% per cycle after 500 cycles. Besides, various g-C₃N₄ materials with different defect structures, concentrations, and preparation methods have been reported, which obviously improve the performance of Li–S batteries [78, 79]. However, excessive N defects could destroy the structure of g-C₃N₄ and thus decrease its electron transport and LiPSs adsorption capability. According to Du et al. [46] (Fig. 4e), as the N content decreases from the original 60% (GCN-60%N) to 6% (GCN-6%N), the content of defect increases, which leads to an increased LiPSs adsorption capability of the material. It is worth noting that when the nitrogen content continues to drop below 6%, the adsorption capability of the material (GCN-2%N) for LiPSs begins to decrease. This could be related to the destruction of the material.

![Fig. 4](https://example.com/fig4.png)

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**Fig. 4** a Schematic illustration of the preparation process of sCN/PDA/PP separator. b TEM images of sCN. c Adsorption energies for Li₅S₅, Li₅S₆, Li₃S₄, Li₂S₆ and LiS₈ on pristine CN, the cyano group of sCN and the N vacancy of sCN. d The stable adsorption models of Li₅S₅ or Li₅S₆ on the cyano group of sCN and the N vacancy of sCN [58]. Copyright 2021, Wiley–VCH. e UV–Vis spectra of a bare Li₂S₈ solution and Li₂S₈ solutions with different GCN materials after aging for 24 h; the inset is the corresponding optical photograph. f Cycling performance of cells with different GCN/S cathodes at 0.5C [46]. Copyright 2020, American Chemical Society
structure, which is also reflected in the performance of Li–S batteries. The cell with optimized GCN-6%N/S composite cathode displayed a high initial capacity of 852.2 mAh g⁻¹ at 0.5C and retained a reversible capacity of 532.4 mAh g⁻¹ after 300 cycles (Fig. 4f).

3.2 Heteroatoms Doping

Heteroatom-doped g-C₃N₄, including nonmetal atom- and metal single-atom-doped materials, are reported to be applied in Li–S batteries with enhanced cycling performance and distinct working mechanisms.

Nonmetal atom doping, such as N, S, O, P, and B, enhances the electronic conductivity and the LiPSs absorption capability of g-C₃N₄. Liu et al. [80] prepared O-doped g-C₃N₄ nanosheets (OCN) by one-step self-supported solid-state pyrolysis (OSSP) technique with urea as the precursor and glucose as the oxygen source (Fig. 5a). The introduction of O atoms into g-C₃N₄ promotes the chemical interactions with LiPSs by forming Li–O bonds. Thus, the cell with OCN/S composite cathode performed a high capacity of 447.3 mAh g⁻¹ after 500 cycles at 0.5C with the capacity fading rate of 0.1% per cycle (Fig. 5b). Zhang et al. prepared P-doped g-C₃N₄ (PCN), which was used as the S host to enhance the performance of Li–S batteries [83]. According to density functional theory (DFT) calculation results [83, 84], both OCN and PCN have higher conductivity and stronger adsorption capability for LiPSs compared with original g-C₃N₄, which is conducive to improving the S utilization efficiency. In addition to O and P, B-doped g-C₃N₄ nanosheets (BCN) were prepared by a one-pot thermal condensation method and used as functional separator coating for Li–S batteries [81]. As shown in Fig. 5c, in the heat treatment process, the g-C₃N₄ bulk

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**Fig. 5** a Schematic illustration of the preparation process and structure of OCN. b Cycling performance of cells with g-C₃N₄ and OCN-900 as sulfur hosts at 0.5 C [80]. Copyright 2015, American Chemical Society. c Schematic illustration of the preparation process and structure of BCN. d STEM image of BCN. e Charge–discharge voltage profiles of cells with different modified separators [81]. Copyright 2020, Elsevier. f Adsorption energies for Li₂S₄, Li₂S₆ and Li₂S₈ on g-C₃N₄, B-g-C₃N₄, O-g-C₃N₄, P-g-C₃N₄ and S-g-C₃N₄. g Differential charge densities of Li₂S₄ adsorbed on g-C₃N₄, B-g-C₃N₄, O-g-C₃N₄, P-g-C₃N₄ and S-g-C₃N₄ [82]. Copyright 2021, Elsevier
was exfoliated to g-C₃N₄ nanosheets due to the blowing erosion caused by the decomposition of ammonium chloride. At the same time, B atoms were successfully doped into g-C₃N₄ matrix with N-B-N bonds. The TEM images in Fig. 5d show that BCN performs the wrinkled and irregular lamellar structure. The low polarization overpotential and high capacity of Li–S cells with BCN-coated separator at 0.5C (Fig. 5e) suggest the improvement of S utilization efficiency and redox kinetic.

Yanmsang et al. investigated the adsorption capabilities and mechanisms of g-C₃N₄-doped with different heteroatoms (B, O, P and S) for LiPSs on the molecular level by DFT calculations [82]. As shown in Fig. 5f-g, the B-doped g-C₃N₄ (B-g-C₃N₄) shows the strongest adsorption capability for LiPSs among investigated g-C₃N₄ materials. The result can be attributed to the lower capability of B atoms to attract electrons than C atoms, resulting in more negative charge accumulation around pyridinic N atoms and thus facilitating charge transfer between g-C₃N₄ and LiPSs.

Metal single-atom doping, such as Fe, Co, and Ni, also improves the adsorption and electrical conductivity of g-C₃N₄ [85–87]. In addition, the metal atoms as electropositive active sites could directly interact with LiPSs, which largely improves the catalytic activity of doped g-C₃N₄ for LiPSs redox reactions [86]. Fe atom-doped g-C₃N₄ (Fe-N₂/CN) material with a hierarchical porous lamellar structure was successfully prepared by Qiu et al. (Fig. 6a-b) [85]. The uniform pyridinic N sites of g-C₃N₄ control the coordination structure of Fe-NC. As shown in Fig. 6c, a large number of independent Fe atoms with the size of about 2 Å are evenly distributed in obtained g-C₃N₄. According to the X-ray absorption near-side structure spectra (XANES) and Fourier transform of Fe K-edge extended X-ray absorption fine structure (EXAFS) spectra of Fe-N₂/CN (Fig. 6d-g), Fe atoms on g-C₃N₄ are positively charged and coordinated with two N atoms through N–Fe–N bond. These Fe-N₂ unsaturated sites show not only stronger LiPSs adsorption capability with higher binding energy (Fig. 6h-i) but also higher catalytic activity for Li₂S decomposition with a lower energy barrier (Fig. 6j). Therefore, the cell with Fe-N₂/CN@S composite cathode exhibited a low capacity fading rate of only 0.011% per cycle after 2000 cycles at 2C (Fig. 6k). Co atom-doped g-C₃N₄ (Co@C₃N₄) material was also reported with a similar working mechanism in Li–S batteries [87]. The formation of Co-S bonds effectively immobilizes LiPSs.

Chen et al. compared the adsorption and electrocatalytic capability of single-metal-atom-doped g-C₃N₄ (M-C₃N₄, where M = Fe, Co, or Ni) for LiPSs [86]. According to DFT calculation results, the metal atoms’ doping can enhance the conductivity of g-C₃N₄, among which Fe-C₃N₄ and Co-C₃N₄ show semi-metallic properties, while Ni-C₃N₄ exhibits metallic properties. Moreover, as shown in Fig. 6l, Ni-C₃N₄ shows the strongest interaction with Li₂S₆ and leads to the largest response current when applied in Li–S batteries (Fig. 6m). In addition, Li₂S decomposition presents the lowest energy barrier on the surface of the Ni-C₃N₄ substrate (Fig. 6n), suggesting that Ni-C₃N₄ can promote solid–liquid conversion. Therefore, the cell with a Ni-C₃N₄/C-modified separator performed a high capacity of 893 mAh g⁻¹ after 300 cycles at 0.5 A g⁻¹ with a capacity retention of 89.4%, showing good cycling stability and high S utilization efficiency (Fig. 6o).

To summarize, defect engineering and heteroatom doping are effective methods to regulate the adsorption capability and catalytic activity of g-C₃N₄. The performances of Li–S cells with optimized g-C₃N₄ materials are compared and listed in Table 1. However, excessive defects and heteroatoms could destroy the structure of g-C₃N₄. An in-depth understanding of the doping- and defect-structure–activity relationship still remains a grand challenge.

### 4 Design of g-C₃N₄-Based Composites

Although g-C₃N₄ has made remarkable progress in Li–S systems, it is difficult for pristine g-C₃N₄ to enable practical performance in Li–S batteries, owing to its intrinsic properties, including poor conductivity and low electrocatalytic activity. To explore novel g-C₃N₄-based materials with satisfying physical/chemical properties, g-C₃N₄ has been incorporated with other functional materials, such as conductive carbon materials, metal nanoparticles, and polar compounds. And the final g-C₃N₄-based composites exhibit various advantages, such as strong LiPSs immobilization, rapid Li-ion transfer, and accelerated conversion of S species.

#### 4.1 Conductive Carbon/g-C₃N₄ Composites

Various conductive carbon materials were applied in g-C₃N₄-based composite materials, including carbon
Fig. 6  a TEM image and b corresponding EDS mappings and c HAADF-STEM image of Fe-N₂/CN. d Fe K-edge XANES spectra and e Fourier transformation of Fe K-edge EXAFS spectra of Fe-N₂/CN, Fe foil, and Fe₂O₃. f Fe k-space EXAFS curve and corresponding fitting curve, and g Fe r-space EXAFS curve and corresponding fitting curve of Fe-N₂/CN. h Optimized structures and binding energies of Li₂S₆ adsorbed on Fe-N₂/CN and CN surfaces. i UV–vis spectra of Li₂S₆ solution with CN and Fe-N₂/CN. j Decomposition energy barriers of Li₂S on Fe-N₂/CN and CN surfaces. k Cycling performance of cells with CN@S and Fe-N₂/CN@S cathodes at 2C [85]. Copyright 2020, American Chemical Society. l Differential charge densities of Li₂S₆ adsorbed on g-C₃N₄, Fe-C₃N₄, Co-C₃N₄ and Ni-C₃N₄. m CV curves of symmetric cells with g-C₃N₄/C, Fe-C₃N₄/C, Co-C₃N₄/C and Ni-C₃N₄/C modified separators. n Decomposition barriers of Li₂S on C₃N₄, Fe-C₃N₄, Co-C₃N₄ and Ni-C₃N₄. o Cycling performance of cells with g-C₃N₄/C, Fe-C₃N₄/C, Co-C₃N₄/C and Ni-C₃N₄/C modified separators at 0.5 A g⁻¹ [86]. Copyright 2019, Elsevier

Table 1  Comparison of performances of Li–S cells with optimized g-C₃N₄ materials

| Materials | S loading (mg cm⁻²) | S content (wt%) | Current rate (C) | Capacity (mAh g⁻¹)/cycle number | Capacity decay rate (%) | References |
|-----------|---------------------|----------------|-----------------|---------------------------------|------------------------|------------|
| Defective g-C₃N₄/CNTs | – | 58.6 | 1 | 567/500 | 0.066 | [78] |
| Defective g-C₃N₄/PDA | 2 | 62.3 | 5 | 476/500 | 0.05 | [58] |
| O-g-C₃N₄ | – | 39.2 | 0.5 | 447/500 | 0.1 | [80] |
| B-g-C₃N₄ | – | – | 1 | 553/500 | 0.09 | [81] |
| F-g-C₃N₄ | 1.5 | 0.2 | ~0.3 | 882/100 | 0.34 | [83] |
| Ni-g-C₃N₄/crystalline carbon | 2.8 | – | ~0.3 | 893/300 | 0.035 | [86] |
| Co@C₃N₄ | 2 | – | ~0.448 | 1160/200 | 0.086 | [87] |
| Fe-g-C₃N₄ | 1.3–1.5 | 48.7 | 2 | 620/2000 | 0.011 | [85] |
nanotubes (CNTs), porous carbon material, graphene, and carbon cloth. The combination of g-C\textsubscript{3}N\textsubscript{4} with conductive carbon materials could effectively improve the electronic conductivity of composite materials, which is critical for its application in Li–S batteries. In addition to this, different carbon materials could also provide various other benefits due to their specific structures and properties. For example, a large specific surface area of carbon materials could suppress LiPSs diffusion.

### 4.1.1 CNTs Constructed Conductive Networks

With the characteristic 1D structure and excellent electronic conductivity, CNTs could construct a conductive network and achieve fast electron conduction. By the high-temperature-assisted self-assembly method, Wang et al. directly synthesized g-C\textsubscript{3}N\textsubscript{4} on the CNTs (Fig. 7a) [33]. Through hydrogen bonds, cyanic acid and melamine not only construct the triazine structure of g-C\textsubscript{3}N\textsubscript{4} but also connect together with the CNTs. After heating treatment, the supramolecular structure can be further transformed into the final g-C\textsubscript{3}N\textsubscript{4}/CNTs composite. The obtained g-C\textsubscript{3}N\textsubscript{4}/CNTs composite shows a network structure with uniform coverage of the g-C\textsubscript{3}N\textsubscript{4} layer. With largely improved conductivity and high LiPSs adsorption capability, the Li–S cell with g-C\textsubscript{3}N\textsubscript{4}/CNTs/S composite cathode displayed a high-capacity retention of 77.1% after 200 cycles at 1C at a 5 mg cm\(^{-2}\). Chen et al. [89] and Yao et al. [90] prepared g-C\textsubscript{3}N\textsubscript{4}/CNTs composite-based membranes and separately applied them as shielding layer and self-supported cathode. Profited from the strong LiPSs adsorption capability of g-C\textsubscript{3}N\textsubscript{4} and good
conductivity network of CNTs, the shuttle effect is largely inhibited, and S utilization efficiency is obviously improved.

### 4.1.2 Highly Conductive Graphene

Graphene is one of the most widely used materials to combine with g-\(\text{C}_3\text{N}_4\). It processes a similar 2D honeycomb structure with g-\(\text{C}_3\text{N}_4\) yet provides a much higher electronic conductivity even compared with CNTs. The obtained graphene/g-\(\text{C}_3\text{N}_4\) composite shows increased conductivity than the original g-\(\text{C}_3\text{N}_4\), which further leads to an enhanced cell performance when applied in Li–S systems. Based on the cohesion action between g-\(\text{C}_3\text{N}_4\) precursor (melamine) and graphene oxide (GO), Nazar et al. synthesized a hybrid material (NG-CN) with high conductivity (Fig. 7b) [42]. And they subsequently coupled NG-CN with cellulose and citric acid (CMC-CA) to construct a stable composite cathode material (NG-CN/CMC-CA/S) with high S loading. The cell with NG-CN/CMC-CA/S composite cathode exhibited a high areal capacity of 14.7 mAh cm\(^{-2}\) with a sulfur loading of 14.9 mg cm\(^{-2}\), indicating the high S utilization efficiency (Fig. 7c). Besides, Dai et al. coated a 2D-layered composite material composed of graphene and g-\(\text{C}_3\text{N}_4\) (C\(_3\text{N}_4\)/GS) on the S cathode surface [91]. Graphene as the upper collector accelerates the electron transfer in the cathode, and the strong adsorption capability of g-\(\text{C}_3\text{N}_4\) inhibits the LiPSs diffusion. In addition, Guo et al. prepared a 3D porous S/graphene/g-\(\text{C}_3\text{N}_4\) composite (S/GCN) with high conductivity and high stability by a microemulsion-assisted assembly method [32]. As shown in Fig. 7d, the internal oil emulsion dissolved sublimed S and acted as a soft template to create pores in the composite material, and the hydrophilic GCN tightly packed around the oil emulsion, thus forming a crosslinked 3D network structure. As the emulsion evaporates, the S attached evenly to the GCN walls and was eventually encased into the composite. The obtained S/GCN performs a cylindrical shape with graphene closely stacked with g-\(\text{C}_3\text{N}_4\) nanosheets (Fig. 7e-f). The abundant N atoms and porous cross-linking network in GCN effectively limit the LiPSs dissolution and diffusion into the electrolyte. In addition, the 3D interconnected graphene network facilitates rapid electron transfer and maintains the integrity of the electrode structure, thus ensuring the long-term cycling stability of Li–S cells. The cell with S/GCN composite cathode displayed a high capacity of 612 mAh g\(^{-1}\) at 10C and maintained 974 mAh g\(^{-1}\) after 800 cycles at 0.5 A g\(^{-1}\) with a high capacity retention of 86% (Fig. 7g). Furthermore, by constructing heterostructures, the graphene/g-\(\text{C}_3\text{N}_4\) composite could further achieve high electrocatalytic activity. Wang et al. used a phenyl modification strategy to construct g-\(\text{C}_3\text{N}_4\)/carbon heterostructures in situ on graphene sheets and coated them on the Celgard separator (G@g-\(\text{C}_3\text{N}_4\)/C) to inhibit the shuttle effect of LiPSs [92]. The g-\(\text{C}_3\text{N}_4\)/C heterostructure exhibits a unique electron distribution, showing a strong adsorption capability of LiPSs and high electrocatalytic activity for redox reactions. Therefore, the cell with G@g-\(\text{C}_3\text{N}_4\)/C coating revealed a low capacity fading rate of 0.050% per cycle after 800 cycles at 1 C.

### 4.1.3 Porous Carbon Materials Facilitated LiPSs Adsorption and Stable Structure

Porous carbon materials provide not only outstanding electronic conductivity but also controllable porosity and high specific surface area, which could facilitate the LiPSs adsorption. Qiu et al. reported g-\(\text{C}_3\text{N}_4\) nanodots embedded MOF-derived N, S co-doped hollow porous carbon shells (CN@NSHPC) through a dual-solvent strategy [93]. Adsorption experiments show that the adsorption capability of CN@NSHPC composite for LiPSs is significantly higher than that of pristine g-\(\text{C}_3\text{N}_4\) and NSHPC. Therefore, the cell using CN@NSHPC/S composite cathode displayed a low capacity fading rate of only 0.048% per cycle after 500 cycles at 1C, showing good cycling stability. Besides, the porous carbon/g-\(\text{C}_3\text{N}_4\) composite was also applied to construct the core–shell structure with S\(_8\) (Fig. 7h) [88]. As a shell, porous carbon/g-\(\text{C}_3\text{N}_4\) composite provides high LiPSs adsorption, high electronic and ionic conductivity, and also enough space to alleviate the volume change of cathode during cycling [20]. The TEM images in Fig. 7i-j show that the g-\(\text{C}_3\text{N}_4\)/C composite performs a hollow spherical structure; after S loading, the cavity is filled to form a typical core–shell structure (S@g-\(\text{C}_3\text{N}_4\)/C). The porous g-\(\text{C}_3\text{N}_4\)/C shell promotes rapid electron transport and acts as a physical barrier in combination with chemisorption (abundant N atoms in g-\(\text{C}_3\text{N}_4\)) to synergistically inhibit LiPSs diffusion. Beyond that, Mandal et al. designed a double-shell
structure, which is composed of a hollow mesoporous carbon (HCS) inner layer and a g-C_3N_4 outer layer [94]. The inner HCS layer provides high electron conductivity, high physical adsorption of LiPSs, and large spaces to mitigate the volume change of the electrode. The outer g-C_3N_4 shell can chemically anchor the LiPSs by forming Li-N bonds. Thus, the cell with HCS@g-C_3N_4/S composite cathode delivered a low capacity fading rate of 0.049% per cycle after 500 cycles at 1C.

4.1.4 Carbon Cloth Constructed Independent Electrode

The carbon cloth (CC) combined with g-C_3N_4 can not only enhance the electron conductivity of composites and can be used as an independent free-standing electrode. Without any current collector or binders, the energy density of batteries could be enhanced. Liu et al. prepared a g-C_3N_4/CC composite by in situ growing g-C_3N_4 nanosheets on the surface of 3D CC with abundant pores and used it as the S host [95]. Benefited from the strong LiPSs adsorption capability of g-C_3N_4 and the 3D conductive network of CC, the g-C_3N_4/CC composite cathode displayed good cycle stability with a high capacity of 892 mAh g⁻¹ after 250 cycles at 0.2 C. Zheng et al. loaded poly (3, 4-ethylene dioxythiophene) (PEDOT) conductive polymer and g-C_3N_4 on commercial CC, and combined with S to form a free-standing, flexible cathode [41]. As shown in Fig. 7 k, g-C_3N_4/CC is synthesized by annealing CC with g-C_3N_4 precursor (urea) at high temperature, and S is introduced into g-C_3N_4/CC by sulfur–amine chemistry method. In order to further inhibit the LiPSs diffusion and improve the overall electrical conductivity of the electrode, PEDOT conductive polymer (CP) was introduced into the composite cathode by pressure impregnation, forming the S@CP/g-C_3N_4/CC. Thus, the cell with S@CP/g-C_3N_4/CC cathode exhibits a reversible capacity of 516.9 mAh g⁻¹ after 500 cycles at 1C.

4.2 Metal Nanoparticles/g-C_3N_4 Composites

The introduction of metal nanoparticles into g-C_3N_4 could improve the electrical conductivity and adsorption/catalytic active sites of composites and further enhance the performance of Li–S batteries. Zhang et al. prepared Ag nanoparticles modified defective g-C_3N_4 (Ag-CN_x) by the magnesium thermal reduction and "silver mirror" reaction [96]. The TEM image (Fig. 8a) shows that Ag particles are evenly distributed on the defective g-C_3N_4 nanosheets without agglomeration. As shown in Fig. 8b-c, the cell with Ag-CN_x modified separator shows the lowest energy barrier of the nucleation and dissolution reaction of Li_2S. Thus, the modified cell exhibits outstanding cycling stability over 550 cycles at 2C. The Co nanoparticle-modified g-C_3N_4 composites also show high catalytic activity for LiPSs redox reactions, which were reported as functional materials for modified cathodes [98] and separators [99].

Compared with the strategy using a single kind of metal nanoparticles, the synergistic interaction between different kinds of metal nanoparticles can enhance the adsorption capability and electrocatalysis of g-C_3N_4 to LiPSs more effectively. Guo et al. prepared an electrocatalyst composed of a highly conductive N-deficient g-C_3N_4 (ND-C_3N_4) and a very small amount of hollow PdNi alloy nanospheres (PdNi@ND-C_3N_4) by using the galvanic substitution effect [97]. As shown in Fig. 8d, in the designed PdNi@ND-C_3N_4 composite, the PdNi alloy and introduced N vacancies exhibit strong chemisorption capability to LiPSs and high catalytic activity for their redox conversion. Moreover, the pyrrole ring of g-C_3N_4 provides a mediator for the rapid transfer of Li-ion with high lithiophilicity. In situ Fourier transform infrared spectroscopy (FT-IR) revealed the state changes of S species on the PdNi@ND-C_3N_4 surface during the charge and discharge process, as shown in Fig. 8e-f. When discharged to 2.3 V, soluble LiPSs were detected. The characteristic peak at 1073 cm⁻¹ is related to the stretching vibration of asymmetric C-N bonds. The interaction between Li in LiPSs and electron-rich pyrrole rings in PdNi@ND-C_3N_4 causes the vibration of C-N bonds. With the increase of discharge depth, the strength of the C-N bond becomes weaker, indicating the conversion of soluble LiPSs to insoluble Li_2S. When the discharge voltage reaches 2.0 V, the characteristic peak of the C-N bond disappears, indicating the completed conversion to Li_2S at the cooperative catalytic interface of PdNi@ND-C_3N_4. In the charging process, the characteristic peak of the C-N bond appears first and then disappears, which demonstrates the Li_2S is oxidized to soluble LiPSs and finally to S. The DFT calculation results in Fig. 8g-h show that compared with g-C_3N_4 materials combining one single-metal Pd, the reduction of S species and decomposition of Li_2S at the surface of PdNi@ND-C_3N_4 showed a much lower Gibbs free energy change, indicating
the synergistic catalysis of PdNi@ND-C3N4. Thus, the cell with PdNi@ND-C3N4/S composite cathode delivers a high discharge capacity of 989 mAh g\(^{-1}\) after 500 cycles at 1C (Fig. 8i); increasing the sulfur loading to 6.0 mg cm\(^{-2}\), the cell exhibits a low capacity fading rate of only 0.025% per cycle, suggesting the excellent cycling stability. Fe/Co-based g-C3N4/carbon composite material (Fe/Co-C3N4/C) shows similar synergistic catalysis [100]. With high conductivity, large specific surface area, and high catalytic activity, the cell with Fe/Co-C3N4/C/S composite cathode shows much enhanced electrochemical performance compared with that of C3N4/C/S cathode.

### 4.3 Polar Compounds/g-C\(_3\)N\(_4\) Composites

Polar compound, such as transition metal compound, is another representative material to composite with g-C\(_3\)N\(_4\) due to their adsorption capability and catalytic activity. The strongly polar sites of polar compounds could interact with LiPSs and lower the energy barrier of their following reactions. Deng et al. uniformly dispersed lamellar CoS onto g-C\(_3\)N\(_4\) nanosheets and then compounded them with conductive carbon (Ketjen black, KB) to prepare an ultra-thin multifunctional separator coating (CoS@g-C\(_3\)N\(_4\)/KB, ~2.1 μm) [103]. The Li-N bond and the Lewis acid–base interaction
between CoS and LiPSs inhibit the shuttle effect. Metal oxide-based g-C₃N₄ composites, including TiO₂/g-C₃N₄ [104] and Fe₃O₄/t-C₃N₄ [105], are also applied in Li–S batteries to improve S utilization and capacity retention.

In addition to their own adsorption and catalytic capabilities, some compounds can also form heterostructures by composing with g-C₃N₄, which would further improve their catalytic performance for redox conversion of S species. On the interfaces of heterostructures, electrons can be rearranged to modify the active sites, and the synergy of different active sites can promote reaction kinetics. By combing bimetallic phosphide CoFeP with g-C₃N₄ nanotube (t-CN), a Mott–Schottky heterojunction catalyst (CoFeP@CN) was prepared by Cabot et al. [101]. The tubular morphology of t-CN was maintained with CoFeP nanocrystals uniform distributed on the surface (Fig. 9a-b). As an n-type semiconductor, g-C₃N₄ has a work function of about 4.4 eV and a band gap of 2.6 eV, while the work function of CoFeP is about 4.8 eV (Fig. 9c). When they contact, the difference in Fermi energy levels drives electrons from g-C₃N₄ to CoFeP until their work functions reach equilibrium at the interface (Fig. 9d). In equilibrium, the electron band of g-C₃N₄ at the interface is bent upward, forming a Mott–Schottky heterostructure. CoFeP@CN has suitable electronic structure and

Fig. 9  a Schematic illustration of the preparation process of CoFeP@CN composite. b TEM image of CoFeP@CN. Energy band diagrams of CoFeP and g-C₃N₄ before c and after d Schottky contact formation. e Gibbs free energies of the reduction reactions of Li₂S₆, Li₂S₄, Li₂S₂ and Li₂S on t-CN, CoFeP and CoFeP@CN, respectively. f Cycling performance of the cell with S@CoFeP@CN cathode at 3C [101]. Copyright 2021, Wiley–VCH. g SEM image and h HRTEM image of MoS₂/g-C₃N₄. i Cycling performance of the cell with MoS₂/g-C₃N₄/S cathode at 2C, 4C and 8C. j Discharge voltage profiles showing the self-discharge behavior of MoS₂/g-C₃N₄/S cathode [59]. Copyright 2019, Elsevier. k Schematic illustration of interaction mechanism of OTC/C₃N₄ and LiPSs [102]. Copyright 2021, Elsevier. l Schematic illustration of multifunctional ion-sieve composed of g-C₃N₄, BN, and graphene [52]. Copyright 2019, American Chemical Society
charge rearrangement characteristics, which can accelerate the redox conversion of S species. Compared with CoFeP and t-CN, CoFeP@CN shows the lowest Gibbs free energy change, suggesting that CoFeP@CN heterojunction catalyst can promote the nucleation of Li2S (Fig. 9e). Moreover, the tubular shape of CoFeP@CN facilitates the diffusion of Li ions, alleviates volume changes of S cathode, and provides rich adsorption sites to effectively capture soluble LiPSs. Thus, the cell with S@CoFeP@CN composite cathode outputted a high capacity of 606 mAh g⁻¹ after 700 cycles at 3C with a low capacity fading rate of 0.014% per cycle and a high coulombic efficiency of 99.6% (Fig. 9f). Chen et al. prepared another heterojunction composite MoS2/g-C3N4, with MoS2 nanosheets growing in situ on porous g-C3N4 nanosheets [59]. TEM images in Fig. 9g-h show that the MoS2/g-C3N4 composite has a lamellar and porous structure with a pore size of 5–20 nm. With strong chemical polarity, high porosity, and heterostructure, MoS2@g-C3N4 can effectively restrict the LiPSs diffusion and accelerate the redox conversion of S species. The cell with S/MoS2@g-C3N4 composite cathode delivered a high capacity retention of 88.47% after 400 cycles at 8C (Fig. 9i) and low self-discharge behavior of 0.026% per hour after 10 days (Fig. 9j), indicating the good rate capability and cycling stability.

With polar compounds/g-C3N4 composites, electrodes and separators with special structures were constructed, which further improved the performance of Li–S batteries. Huang et al. designed a sandwich cathode material (Fig. 9k), in which S was embedded between layered g-C3N4 and Ti3O7-Ti3C2 (OTC) [102]. The strong adsorption of g-C3N4 and Lewis acid–base interaction of the OTC heterojunction can immobilize LiPSs effectively. Furthermore, g-C3N4 and OTC simultaneously adsorb Li and S atoms in LiPSs, which can promote the cleavage of long-chain LiPSs and thus accelerate the reduction kinetics. The cell with such OTC/S@g-C3N4 cathode outputted a high discharge capacity of 750 mAh g⁻¹ after 2000 cycles at 0.5C, showing outstanding cycling stability and high S utilization efficiency. Moreover, Dong et al. designed a multifunctional ion sieve composed of three kinds of 2D nanosheets, including g-C3N4, boron nitride (BN), and graphene (BN/graphene-C3N4), and used it as a separator coating [52]. As shown in Fig. 9l, the g-C3N4 overlaps with the graphene sheet to form a sandwich structure in which the BN sheet is vertically embedded. In the g-C3N4 monomer, there are ordered channels with a size of 3 Å, which can effectively prevent the LiPSs shutting but allow free diffuse of Li ions; BN as a good electrocatalyst can accelerate the redox reaction of S species. The conductive network of graphene can promote the electron transport. Therefore, the cell with BN/graphene-g-C3N4 coating displayed a low capacity fading rate of 0.01% per cycle after 500 cycles at 1C with a high sulfur loading of 6 mg cm⁻², suggesting the high S utilization efficiency.

The construction of g-C3N4-based composites offers new possibilities for g-C3N4 as additives in high-performance Li–S batteries. With different materials, the composites could realize the balance of various properties including catalytic activity and conductivity. The performances of Li–S cells with g-C3N4-based composites are compared and listed in Table 2. However, we note that most of the polar compounds were not combined with g-C3N4 alone but with conductive carbon materials at the same time [106]. Since the polar compounds applied show low conductivity as well as g-C3N4, carbon materials are required to construct a conductive network which enables the better catalytic performance of the materials. This leads to a notable issue of the increasing weight of inactive material in Li–S batteries.

5 Other CxNy Materials

With different C/N ratios, carbon nitride (CxNy), other than g-C3N4, shows different molecular configurations, which endows them with different physicochemical characteristics and electronic properties.

The regulation of the C/N ratio could change the coordination environment of N, which further leads to enhanced catalytic performance. Yu et al. reported a covalent organic framework (COF)-like C3N4 material, C3N4, with a C/N ratio of 4:1 connected with pyrazine, and subsequently prepared ultra-small colloidal C3N quantum dots (C3NQDs) with the average size of 2.2 nm (Fig. 10a) [112]. Pyrazine N atoms and carbonyl groups at the edge of C3NQDs show preferential adsorption capability to LiPSs with significantly higher binding energy compared with that of the N sites in the C3NQDs plane (Fig. 10b). The electrochemical performance further confirmed the excellent catalytic capability of C3NQDs for LiPSs redox reactions (Fig. 10c-d). Compared with that on pristine carbon paper (CP), the Li2S precipitation and decomposition on C3NQDs/CP perform higher capacity contributions and an earlier peak current response.
Therefore, the Li–S cell with C4NQDs@CNTs modified separator exhibited excellent cycling stability with a low capacity fading rate of 0.061% per cycle after 800 cycles at 1C (Fig. 10e). Besides, the LiPSs adsorption on 2D C2N nanosheets was investigated by Wang et al. [113]. Unlike g-C3N4, C2N is connected by one N atom and two C atoms with higher structural stability. The original graphene C-ring structure is surrounded by six N atoms in C2N, each of which has a suspended bond. The size of the hole formed in the middle is smaller than that of long-chain LiPSs, which could physically inhibit the shuttle effect. In addition, C2N shows highly negative Gibbs free energy for Li-C2N and strong adsorption capability for Li2S. Its high LiPSs adsorption capability was also confirmed by Zhang et al. using first-principles calculations [114]. Comparing four nonmetallic layered materials (graphene, BN, C2N, and C3N4), C3N4 and C2N exhibit stronger LiPSs adsorption capability through the

| Materials | S loading (mg cm⁻²) | S content (wt%) | Current rate (C) | Capacity (mAh g⁻¹)/cycle number | Capacity decay rate (%) | References |
|-----------|---------------------|-----------------|------------------|-----------------------------------|------------------------|------------|
| g-C3N4/Graphene oxide | – | – | ~ 0.197 | 700/300 | 0.037 | [107] |
| N-doped graphene-g-C3N4/cellulose-citric acid | 2.0 | 65.45 | 0.05 | – | – | [42] |
| g-C3N4@N, S co-doped hollow porous carbon shell | 1.7–2.0 | – | 1 | 445/500 | 0.048 | [93] |
| PEDOT@g-C3N4@CC | 4.7 | – | 1 | 517/500 | – | [41] |
| g-C3N4@porous carbon nanofiber | 1.2 | – | 0.6 | 466/500 | 0.056 | [108] |
| 3D Graphene oxide-g-C3N4 sponge | 4 | 73 | ~ 0.3 | 974/800 | 0.017 | [32] |
| g-C3N4/carbon nanotubes | 1 | 64 | 1 | 584/500 | 0.08 | [33] |
| Reduced graphene oxide/g-C3N4/carbon nanotubes | 1.5 | 56.64 | 1 | 620/500 | 0.03 | [34] |
| Hollow porous carbon nanosphere/g-C3N4 | 1 | 51.62 | 1 | 719/500 | 0.049 | [94] |
| Hierarchical porous carbon/g-C3N4 | 1.0–1.2 | 51.6 | 1 | 757/250 | 0.024 | [109] |
| g-C3N4/carbon spheres | 1.2 | 46.9 | 1 | 636/400 | 0.09 | [88] |
| g-C3N4/carbon nanotubes | 4.74 | – | 0.5 | 633/300 | 0.092 | [90] |
| g-C3N4/carbon cloth | 2.5 | – | 0.2 | 892/250 | – | [95] |
| g-C3N4/carbon fiber paper | 2.21–2.66 | 45.06 | – | –/400 | 0.068 | [110] |
| Reduced graphene oxide/g-C3N4/carbon fiber paper | 1.62–1.89 | 45 | 1 | –/800 | 0.056 | [111] |
| g-C3N4/graphene oxide | 0.9–1.1 | 45.81 | 1 | 612/1000 | – | [91] |
| graphene@g-C3N4/C | 1.0 | 80 | 1 | 464/800 | 0.050 | [92] |
| g-C3N4/carbon nanotubes | 1.4 | 57.6 | 1 | –/500 | 0.03 | [89] |
| Co-g-C3N4 | 1.31 | 51.2 | 1 | 740/300 | 0.03 | [98] |
| Ag-defective g-C3N4 | 1.3 | 53.3 | 2 | 652/550 | 0.053 | [96] |
| Co-CNTs/defective g-C3N4 | – | – | 1 | –/1000 | 0.04 | [99] |
| PdNi@ND-C3N4 | 2 | 55.6 | 1 | 989/500 | 0.027 | [97] |
| Fe/Co-C3N4/C | 1.8 | 47.6 | 0.2 | 749/135 | 0.156 | [100] |
| TiO2/g-C3N4 | 3.1 | 59.6 | 0.5 | 540/500 | 0.063 | [104] |
| OTC/C3N4 | 1.2 | – | 0.5 | 750/2000 | 0.022 | [102] |
| CoFe@CN | 1.0 | – | 3 | 606/700 | 0.014 | [101] |
| MoS2/g-C3N4 | 1.5 | 59.1 | 2 | 521/400 | 0.049 | [59] |
| CoS@g-C3N4/KB | 1.5 | 68.4 | 1 | 572/500 | 0.030 | [103] |
| Fe3O4/t-C3N4 | 0.8–1.0 | – | 2 | 658/1000 | 0.020 | [105] |
| BN/graphene-C3N4 | 6.0 | 70 | 1 | 603/500 | 0.01 | [32] |
interfacial interactions and inhibit the dissolution of LiPSs into the electrolyte.

It is worth noting that, in addition to the adsorption and catalytic capability, the electron conductivity of the materials can also be regulated with different C/N ratios. Zhang et al. designed a new 2D carbon nitride, C$_5$N, by introducing the vacancy defects into monolayer C$_3$N and studied its adsorption capability for LiPSs [115]. After the introduction of $V_C + V_N$ vacancy defects in C$_3$N and the optimization of the full structure, the new configuration is composed of 5 carbon nitrogen ring-8 carbon nitrogen ring-5 carbon ring. The electronic band structure and state density (DOS) reveal that the Fermi level of C$_5$N is below the maximum value of the valence band and its band gap structure is similar to that of Cu metal, indicating that C$_5$N has good electrical conductivity and metallic properties. Besides, it also shows an adsorption capability of both LiPSs and Li$_2$S. Comparing 10 kinds of N-containing 2D materials (C$_5$N$_6$, C$_5$N$_4$, BN, CTF, C$_2$N$_6$S$_3$, g-C$_3$N$_4$, p-C$_3$N$_4$, C$_3$N$_5$, S-N$_2$S, and T-N$_2$S), Chen et al. found that the C$_9$N$_4$ and C$_2$N$_6$S$_3$ perform good electronic conductivity and strong adsorption for LiPSs [116]. With increased electronic conductivity of C$_x$N$_y$, the LiPSs adsorbed can directly lose/gain electrons to be oxidized/reduced, which avoids the loss of LiPSs and improve the rate capability of Li–S batteries.

However, other than g-C$_3$N$_4$, most of the C$_x$N$_y$ materials used in Li–S batteries have only been reported in simulation. Future experimental studies will benefit the understanding and application of these materials.

6 Summary and Outlook

To date, C$_x$N$_y$ materials, represented by g-C$_3$N$_4$, have been widely applied in Li–S batteries as additives to enhance electrochemical performance due to their strong LiPSs adsorption capability and high tunability in composition and structure, which leads to controllable properties. With the advancing studies on C$_x$N$_y$-based materials, the structure–activity relationship is gradually revealed. The changes in the chemical composition, for example, the regulation of the C/N ratio and the introduction of heteroatoms, could modulate the coordination structure of catalytic active sites and the electronic structure of the material, leading to increased catalytic capability and electronic conductivity. The construction of various structures, such as porous nanosheet structure, spindle-like structure, and hollow
spherical structure, could lead to high specific surface area and increasingly exposure of active sites, which also enhance the adsorption and electrocatalytic capability of CxNy materials and further improve the rate performance of Li–S batteries. Besides, the hollow or core–shell structure could also accommodate the volume change during cycling and increase the cycle life of Li–S batteries. However, the understanding of the structure–activity relationship of CxNy is still limited. In-depth understandings, such as the effects of doping and defect structures on the catalytic and conductive performance, are critical for the development of CxNy-based materials for advanced Li–S batteries.

At this stage, Li–S batteries are developing toward practicality. The demonstration for practical specific energy and stability dominates the future development direction of Li–S batteries. Based on the understanding of CxNy-based materials and Li–S chemistry, we identified the existing limitations and provided our perspective on future rational design of advanced CxNy-based materials for high-performance Li–S batteries:

1. As an inactive material, CxNy should be added at low amounts to increase the overall energy density of the Li–S cell. According to some reported works [35, 45], g-C3N4 added as S host accounts for about 15% of the total cathode weight. The reduction of CxNy content requires an increase in their specific surface area, which means an increased in the adsorption capability, and therefore, a similar function could be realized with a smaller amount of CxNy materials. Different preparation methods, such as the hard template method and stripping-assisted method, can be used to obtain the g-C3N4 with controllable morphology and high specific surface area;

2. The electronic conductivity of g-C3N4, which limits the rate performance of Li–S batteries, should be increased. Although improved by numerous reported methods, the conductivity of g-C3N4 is still unsatisfactory. The effect of heteroatom doping and defect treatment on the conductivity of g-C3N4 appears limited; the additional carbon material introduced in the form of g-C3N4/carbon composite increases the amount of inactive materials. Besides these methods, the electronic conductivity of the materials could also be increased by regulating the C/N ratios. Synthesizing novel CxNy materials with higher electron conductivity and studying their adsorption and electrocatalytic effect on LiPSs could be prospective directions in Li–S systems.

3. The catalytic mechanism of CxNy-based materials should be systematically studied. Although most of the CxNy-based materials are proposed with a working mechanism, the reaction mechanism of S8 with CxNy-based materials is still unclear. Since the conversion process of LiPSs is quite complex, it is necessary to combine advanced in situ characterization techniques such as cryo-electron microscopy, in situ Raman, and XRD to monitor the electronic structure and morphology changes of intermediates on CxNy-based materials under various conditions in real time. By comparing series of materials in parallel, the structure–activity relationship can be revealed, which is critical for further material design.

4. The enhancement of Li anode stability with CxNy-based materials worthy more attention. The growth of dendrite limits the cycling life of Li anode. Besides, the soluble LiPSs lead to the passivation of Li anode in Li–S batteries. g-C3N4 has high shear modulus and good affinity with Li ions, and thus, it is promising in promoting the uniform deposition of Li ions and inhibiting the growth of Li dendrites [39, 40]. However, relevant studies are very limited. With more effort on this topic, an enhancement of Li anode stability with CxNy-based material is expected.

Looking into the future, there are infinite opportunities and challenges for the vigorous development of CxNy-based materials. With further efforts, it is expected that CxNy-based materials will promote the practical application of high energy density and long-life Li–S batteries.

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