Graphitic Carbon Nitride: Preparation, Properties and Applications in Energy Storage

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Abstract

Graphitic carbon nitride (g-C₃N₄) has received much attention in recent years due to its unique optical and electrochemical properties. In this review, preparation, properties and some applications of g-C₃N₄ in energy storage are summarized. In order to improve the specific surface area of g-C₃N₄, hard and soft template, template-free and exfoliation methods are usually used. The properties of g-C₃N₄ including stability, optical, photoelectrochemical and electrochemical properties are introduced. Some applications in photocatalysis, electrocatalysis and Li-based batteries are also analyzed. Finally, the outlook of g-C₃N₄ is also provided.

Keywords: g-C₃N₄; Synthesis; Properties; Applications.

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1. Introduction

The growing population and rising consumption of fossil fuels continuously increase the people’s awareness in energy requirement and environment damage. At present, the large demand of fossil fuels has caused environmental damages. Therefore, certain solutions need to be raised to promote sustainable energy storage technologies towards urgent energy demands. Novel nanomaterials are considered as the efficient way to address the problems.[1] Various kinds of nanomaterials with special properties have been prepared and used for energy conversion and storage. Nanostructured carbon nitrides (CNs) are promising in terms of a variety of applications. CNs can be synthesized by the pyrolysis of nitrogen rich precursors. Depending on the degree of condensation, the resulting materials are called melon (linear polymers of connected tri-s-triazines via secondary nitrogen) or graphitic carbon nitrides (g-C₃N₄, 2D sheets of tri-s-triazine connected via tertiary amines). g-C₃N₄ is considered to be the most stable allotrope of various CN structures because of its favorable intriguing properties such as high hardness, facile preparation, unique structure and chemical stability.[1-7] Two structures have been proposed as the basic building block of g-C₃N₄.[8] One is composed of condensed s-triazine units (ring of C₃N₃) with a periodic array of single carbon vacancies; the other is composed of condensed tri-s-triazine (triring of C₆N₇) subunits connected through planar tertiary amino groups with larger periodic vacancies in the lattice.[8] The second one is the most stable local connection pattern.[9,10] Therefore, tri-s-triazine is widely accepted as the basic unit for the g-C₃N₄. As a result, g-C₃N₄ has a great potential in energy conversion and storage as well as environmental applications,[11] such as photocatalysis,[12,13] fuel cells,[14,15] CO₂ capture,[16,17] and battery catalysis.[18,19]

G-C₃N₄ is a visible-light-response material (2.7 eV bandgap), and the energy position of conduction band (CB) and valence band (VB) is at -1.1 and 1.6 eV vs. normal hydrogen electrode (NHE), respectively. In addition, g-C₃N₄ has very high resistance to heat, strong acid, as well as strong alkaline solution. g-C₃N₄ contains carbon and nitrogen elements only and it can be synthesized from the facile pyrolysis of nitrogen-rich precursors, such as melamine,[20,21] urea,[22,23] thiourea,[24,25] and cyanamide.[26,27] It has been reported that the choice of precursor and different pyrolysis temperatures have great influences on the electronic structure and bandgap of g-C₃N₄, which will further influence its potential applications in many fields.[25-30] Recently, some significant advances have been made regarding the research of g-C₃N₄. Therefore, an article which can summarize the synthesis of g-C₃N₄-based materials and their potential

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applications in energy storage is necessary.

This review article focuses on recent progress in the properties, synthesis and potential applications of g-C₃N₄ and g-C₃N₄-based nanocomposites in energy storage and conversion, such as photocatalytic hydrogen evolution, oxygen reduction reaction (ORR), and Li-based battery. Eventually, some concluding remarks and perspectives on current situations of the g-C₃N₄-related studies are presented, which are aimed to improve the understanding as well as promote the applications of g-C₃N₄-based nanocomposites. Therefore, this review gives a brief summary of synthesis, properties and applications of g-C₃N₄ and its composites.

2. Preparation of g-C₃N₄ materials

g-C₃N₄ contains C and N elements only and it is a stable polymer semiconductor. At present, many nitrogen-rich organic precursors (such as urea, melamine, dicyandiamide, thiourea and cyanamide) are used for preparing g-C₃N₄. However, carbon nitride materials prepared by direct condensation of these precursors are with bulk structures, which have low specific surface areas. For practical applications as catalysts, it is necessary to introduce well-controlled porous structures in the bulk g-C₃N₄. Researchers have designed several different methods to obtain porous g-C₃N₄.

2.1 Hard and soft-template method

“Templating” essentially involves the replication of one structure into another under the structural inversion. A template, in its most general definition, is a structure-directing agent. Template method therefore is a versatile technique for the preparation of nanostructured or porous materials, as the size and shape of the resulting pore structures can be easily tuned by the appropriate template.[28]

The hard templates are used to fabricate porous structures and design hierarchical pore architectures in g-C₃N₄.[4,29,30] Silica templates are used as the typical structure directing agent to control the nanostructures. Groenewolt et al.[31] reported on synthesis of novel g-C₃N₄ nanoparticles with different diameters by employing different pore size mesoporous silica matrices. Afterwards, many researches on mesoporous g-C₃N₄ materials prepared by silica-based hard templates have been reported. Highly ordered mesoporous g-C₃N₄ with tunable pore diameters was synthesized by using aminoguanidine hydrochloride as precursor and SBA-15 as hard templates.[32] Fukasawa et al.[33] used uniform-sized silica nanospheres as templates to synthesize ordered porous g-C₃N₄. Xu et al.[34] employed guanidinium chloride as precursors to synthesize mesoporous g-C₃N₄ by a nanocasting method. The as-prepared g-C₃N₄ samples possessed two types of pores and high specific surface areas. Park et al.[35] prepared 2-dimensional (2D) and 3-dimensional (3D) mesostructured g-C₃N₄ via the incipient wetness process with mesoporous silica as a hard template. These materials exhibit open pores and large specific surface area. Notably, in the hard-template approach, the removal of the template is necessary to obtain the desired g-C₃N₄ structure. This process usually involves aqueous NH₄HF₂ or HF, which may cause damages to the environment.

Fig. 1 Schematic illustration of the synthesis of ordered porous g-C₃N₄ by using close-packed silica nanospheres (SNSs) as the primary template. Reproduced with permission.[33] (Copyright © 2010, John Wiley and Sons)

By contrast, the soft-template method is greener, since the soft template can be removed by calcination. In the soft-template method, the mesopores of g-C₃N₄ are achieved by amphiphilic surfactant molecules driven by the natural tendency of reducing interfacial energy.[1] Therefore, the properties of organic templates are vital for the mesostructures of g-C₃N₄ materials and the templates are called structure directing agents. The soft-template process can fabricate g-C₃N₄ with different morphologies by changing the soft templates as well as simplify the preparation of g-C₃N₄. Many researchers have used different surfactants such as P123, Triton X-100, Brij30 and Brij58 or liquids as soft templates to prepare g-C₃N₄ with different morphologies and specific surface areas. For example, Yan et al.[36] used Pluronic P123 as soft-templates to prepare g-C₃N₄ with worm-like pore, which possessed high BET surface. Yang et al.[37] prepared mesoporous g-C₃N₄ by a soft template of Triton X-100. The hydrophobic groups of this template can form bubbles during the synthesis of mesoporous g-C₃N₄. In the preparation of 3D porous sulfur/graphene@g-C₃N₄ (S/GCN) hybrid sponge, oil emulsion droplets were used to form pores, and 3D interlinked S/GCN sponge structure through the hydrothermal process was achieved.[38]

(Fig. 2) presents two representative synthesis routes for ordered mesoporous materials, which are suitable for the preparation of g-C₃N₄.[39]

The hard-template method has the advantage that the copies of the template structure can be achieved easily. A variety of inorganic nanostructures can be used as templates for the synthesis of organic replicas.[28] The soft-template method is more environmental-friendly. However, the improper choice of template and pyrolysis can result in unsuccessful synthesis of g-C₃N₄, since the template materials will be decomposed before the formation of g-C₃N₄. Moreover, the template will leave carbon residue in the final products, which could decrease the nitrogen content and lower its catalytic activity.[1]
2.2 Template-free method
Han et al.\textsuperscript{[38]} prepared porous g-C\textsubscript{3}N\textsubscript{4} by a facile thermal-treatment of dicyandiamide. The prepared porous g-C\textsubscript{3}N\textsubscript{4} achieved a high BET surface area (201-209 m\textsuperscript{2} g\textsuperscript{-1}) and large pore volume (0.50-0.52 m\textsuperscript{3} g\textsuperscript{-1}). Tahir et al.\textsuperscript{[39]} prepared g-C\textsubscript{3}N\textsubscript{4} nanofibers (GCNNFs) by a facile template-free method. Melamine reacted with ethanol first and then was annealed at 450 °C for 2 hours to get GCNNFs, which exhibited 1D structure with a high specific surface area. Graphene modified porous g-C\textsubscript{3}N\textsubscript{4} (porous g-C\textsubscript{3}N\textsubscript{4}/graphene) was also synthesized by the thermal calcinations.\textsuperscript{[40]} In this method, the polymerization process was carried out at different temperatures, and the porous g-C\textsubscript{3}N\textsubscript{4} was obtained at high calcination temperatures.

3. Properties of g-C\textsubscript{3}N\textsubscript{4} materials
3.1 Stability
3.1.1 Thermal stability
According to the research of Yan et al.,\textsuperscript{[21]} g-C\textsubscript{3}N\textsubscript{4} started to decompose at the temperature of 600 °C. Fig. 6 shows the thermogravimetric-differential scanning calorimetry analysis of melamine and g-C\textsubscript{3}N\textsubscript{4}. It was clear that g-C\textsubscript{3}N\textsubscript{4} started to decompose when the temperature reached 750 °C. The thermal stability of g-C\textsubscript{3}N\textsubscript{4} is one of the highest among inorganic materials. The thermal stability of g-C\textsubscript{3}N\textsubscript{4} is affected by different preparation methods and the choice of precursors.\textsuperscript{[6,42-46]}

For both the hard-template and soft-template methods, the complete removal of the template may require complicated post-treatments and be very challenging. Therefore, it is necessary to develop a template-free method. Such template-free method does have the advantage that it is one-step processes. Any template synthesis and removal thus can be avoided, and no waste is produced. The choice of precursor is vital for the template-free method, so the research focus mostly concentrates on the kinds of precursor as well as the changes of thermal treatment.
was achieved via soft-chemical method. It found out that the samples stayed stable at temperatures up to 550 °C, suggesting a stable construction from heptazine-base units in the materials. Komatsu et al.\cite{42} prepared g-C$_3$N$_4$ by polycondensation/pyrolysis of several tris-s-triazine derivatives, which were prepared from melamine and thiocyanates. Thermogravimetry shows that all the samples exhibited high heat-resistance over 600 °C, and the heat resistance of g-C$_3$N$_4$ tended to decrease with an increase in the nitrogen content. According to the report of Shi et al.,\cite{47} g-C$_3$N$_4$ was synthesized by directly heating guanidine hydrochloride at different temperatures in air. Based on TG-DSC curve, the weight of g-C$_3$N$_4$ decreased rapidly between 600 and 700 °C, and decomposed totally at 700 °C. Yuan et al.\cite{45} reported a high-yield synthesis of g-C$_3$N$_4$ by heating melamine powders under vacuum at temperatures between 450 and 650 °C. The samples obtained at 550-650 °C did not start to decompose until 640 °C. The high thermal stability of g-C$_3$N$_4$ features its various applications, as a heterogeneous organic catalyst, at operating temperature below 500 °C. High thermal stability also allows its easy removal by simply increasing the calcination temperature beyond 600 °C, thus favoring its utilization as confinement templates, structuring agents or nitrogen sources for synthesizing a refined carbon nanostructure or metal nitride nanostructures with continuously adjustable compositions.

3.1.2 Chemical stability
Besides, g-C$_3$N$_4$ also exhibits a great chemical stability. g-C$_3$N$_4$ possesses optimized van der Waals interactions between the layers, as a result, it is insoluble in most solvents, such as water, acid and many organic solvents.\cite{48,49}

However, treating g-C$_3$N$_4$ in molten alkali metal hydroxides or KMnO$_4$ results in a hydrolysis of its structure. However, treating g-C$_3$N$_4$ in concentrated acids leads to a colloidal dispersion. According to the report of Zhang et al.,\cite{50} acids
did not chemically disintegrate g-C\textsubscript{3}N\textsubscript{4}. When treated in the concentrated-acid solvents at room temperature, g-C\textsubscript{3}N\textsubscript{4} formed some dispersed nanosheets without destroying their layer structure.

### 3.2 Optical and photoelectrochemical properties

g-C\textsubscript{3}N\textsubscript{4} possesses certain decisive optical properties, which have been studied by means of experimental characterizations and theoretical calculations. g-C\textsubscript{3}N\textsubscript{4} has been used in various photochemistry-related areas, such as ultraviolet-visible absorption, photoluminescence and electrochemiluminescence.

As an inorganic semiconductor, g-C\textsubscript{3}N\textsubscript{4} has a typical absorption bandgap adsorption at \(\sim 420\) nm (Fig. 7).\textsuperscript{[51]} In fact, this medium bandgap can be confirmed by the yellow color of g-C\textsubscript{3}N\textsubscript{4}, and the results are in consistence with previous reports.\textsuperscript{[52,53]} It is also worth noting that some modification strategies can affect the absorption edge of g-C\textsubscript{3}N\textsubscript{4}, such as Fe, S, B doping\textsuperscript{[54,55]} and copolymerization by barbituric acid.\textsuperscript{[56]}

![Fig. 7 (a) Diffuse reflectance absorption spectrum and photoluminescence (PL) spectrum (inset) under 420 nm excitation, and (b) time-resolved PL spectrum monitored at 525 nm under 420 nm excitation at 298 K for bulk g-C\textsubscript{3}N\textsubscript{4} (black) and mpg-C\textsubscript{3}N\textsubscript{4} (red). (c) Periodic on/off photocurrent \(I_{ph}\) response of mpg-C\textsubscript{3}N\textsubscript{4} electrode in 0.5 M Na\textsubscript{2}SO\textsubscript{4} under zero bias in a standard two electrode photoelectrochemical cell. Reproduced with permission \textsuperscript{[52]} (Copyright © 2009, American Chemical Society)](image)

In the report of Tahir \textit{et al.},\textsuperscript{[39]} they researched the optical properties of bulk g-C\textsubscript{3}N\textsubscript{4} (GCN) and g-C\textsubscript{3}N\textsubscript{4} nanofibers (GCNNFs). GCN has a bandgap at 2.67 eV, while GCNNF has a bandgap at 2.80 eV. The slight blue shift by 0.13 eV is due to the more perfect packing, electronic coupling and quantum confinement effect that shift conduction and valence band edges\textsuperscript{[39]} Meanwhile, PL intensity of GCN is higher than that of GCNNF, which indicates the slow recombination rate of photogenerated electrons and holes. The decrease of PL intensity is caused by the defects in the crystal structure that reduces the strength of fluorescence peaks. These defects are the recombination centers for electrons and holes generated during photocatalysis. Therefore, a decrease in the number of defects in GCNNF ultimately increases its photocatalytic performance.

g-C\textsubscript{3}N\textsubscript{4} has been employed in photovoltaic conversion systems (photoelectrochemical cells etc.) because of its favorable electronic band structure.\textsuperscript{[57]} Besides, in photoelectrochemical cells, g-C\textsubscript{3}N\textsubscript{4}’s band gap can be adjusted by changing its morphology or doping. Also, photoelectrochemical cells can operate stably in O\textsubscript{2} due to the excellent chemical and thermal stability of g-C\textsubscript{3}N\textsubscript{4}.

### 3.3 Electrochemical properties

g-C\textsubscript{3}N\textsubscript{4} can be used as electrocatalysts for various electrocatalytic reactions, such as oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER).\textsuperscript{[58,59]} g-C\textsubscript{3}N\textsubscript{4} can provide a higher electrocatalytic activity than pure carbon\textsuperscript{[60]} which makes it become more attractive towards electrocatalysis. This is because g-C\textsubscript{3}N\textsubscript{4} possesses pyridinic N atoms, which can accept electrons and serve as reaction active sites.\textsuperscript{[49,61]} However, the performance and applications of g-C\textsubscript{3}N\textsubscript{4} in electrochemical reactions are restricted by its poor conductivity and electron transportation. Zheng \textit{et al.}\textsuperscript{[62]} theoretically revealed that the low ORR catalytic activity of pure g-C\textsubscript{3}N\textsubscript{4} is through an unfavorable 2e\textsuperscript{-} pathway. While in the g-C\textsubscript{3}N\textsubscript{4}@carbon composite, a nearly 100% of selectivity for 4e-ORR pathway could be achieved in alkaline aqueous solutions. Recently, it has been demonstrated that the electrocatalytic activities of g-C\textsubscript{3}N\textsubscript{4} can be significantly enhanced by coupling with other conductive supports to improve electron transfer. As a result, tremendous efforts have been made to explore more strategies to achieve new-generation g-C\textsubscript{3}N\textsubscript{4}-based electrocatalysts with higher conductivity and electrochemical performance.

### 4. Energy storage of g-C\textsubscript{3}N\textsubscript{4}

#### 4.1 Photocatalytic hydrogen production

Hydrogen has been regarded as a clean energy source without consuming fossil fuels. Photocatalytic water splitting by employing semiconductor photocatalysts and solar energy is a promising approach to generate hydrogen energy. The choice of photocatalyst is vital for achieving ideal hydrogen production performance. Various kinds of photocatalysts have been explored in hydrogen evolution
reaction (HER), such as metal oxides,[63,64] metal nitrides,[65] metal sulfides[66] and metal phosphides[67] or their mixed solid solutions.[68,69] Besides these materials, g-C$_3$N$_4$ has been considered as an efficient photocatalyst because of its structural and electronic properties.[48] g-C$_3$N$_4$ possesses an appropriate bandgap and high specific surface area, therefore, it can promote the utilization of visible light and increase the electron transport, which will then promotes the photocatalytic hydrogen production.[70,71]

Maeda et al.[72] studied the performance of g-C$_3$N$_4$ as a nonmetallic photocatalyst for HER and OER under both ultraviolet (UV) and visible light. It indicated that g-C$_3$N$_4$ catalyst exhibited favorable performance for HER and oxygen evolution reaction (OER) due to a proper electron donor or acceptor. Zhang et al.[73] used a facile one-step synthesis process to prepare g-C$_3$N$_4$ as photocatalysts. The porous structure with increased specific surface area and pore volume helped g-C$_3$N$_4$ achieve a better hydrogen production activity.

However, the photocatalytic efficiency of pristine g-C$_3$N$_4$ is still not satisfactory. As a result, many researchers have employed other strategies to promote its photocatalytic properties. For example, g-C$_3$N$_4$ could be complexed with other electron-rich nanocomposites.[74] For example, g-C$_3$N$_4$ was complexed with nitrogen-doped graphene to catalyze HER.[60] This hybrid catalyst exhibited desirable HER activities due to its intrinsic chemical and electronic coupling. She et al.[75] confirmed that a small amount of α-Fe$_2$O$_3$ nanosheets formed 2D hybrid with g-C$_3$N$_4$, which exhibited an all-solid-state Z-scheme junction. The hybrid achieved a high H$_2$ evolution rate because the Z-scheme junction could suppress the recombination of electron-hole pairs as well as promote the overall water splitting without any sacrificial donor. Hou et al.[76] successfully constructed MoS$_2$/g-C$_3$N$_4$ nanojunctions, which exhibited enhanced photocatalytic HER activities under visible light compared with bare MoS$_2$ and g-C$_3$N$_4$. Besides, they also found that other layered transition metal dichalcogenides (for example, WS$_2$) promoted HER rates after complexed with g-C$_3$N$_4$. Besides, noble metal Pt is also a good choice of cocatalyst, however the high cost greatly limits its application. Li et al.[22] anchored isolated single Pt atoms on g-C$_3$N$_4$ with a high dispersion and stability to form a co-catalyst. It was found that Pt-CN remarkably enhanced the photocatalytic hydrogen evolution activity as well as achieved the maximum utilization of Pt atoms to reduce the cost.

On the other hand, doping selected heteroatoms is an efficient way to modify its electronic properties.[56,77] Some non-metallic elements, such as boron (B), fluorine (F), phosphor (P) and sulfur (S) are often introduced into g-C$_3$N$_4$ to modify its electronic structure and improve its photocatalytic activity.[1] Using P doping and thermal exfoliation, Ran et al.[78] successfully prepared porous P-doped g-C$_3$N$_4$ nanosheets. This photocatalyst showed a high visible-light photocatalytic hydrogen production rate. After P doping, the intrinsic bandgap of g-C$_3$N$_4$ was narrowed from 2.98 to 2.66 eV, and the empty midgap states (−0.16 V vs. SHE) induced by P doping was favorable for promoting the visible light absorption of P doped g-C$_3$N$_4$ nanosheets (PCN). In another paper, P doped g-C$_3$N$_4$ was prepared by a thermally induced copolymerization method.[79] The HER rate of P doped g-C$_3$N$_4$ reached 50.6 mmol h$^{-1}$, because P atoms changed the electronic structure of g-C$_3$N$_4$ and suppressed the recombination of charge carriers. Lan et al.[13] synthesized Br doped g-C$_3$N$_4$ for hydrogen evolution. By doping Br, the CNU-Br$_0.1$ showed more than two times higher HER rates than pure CNU sample. Some metallic elements also introduced free electrons to g-C$_3$N$_4$ to modify its electronic structure as well as provide organic-metal hybrid. Thang et al.[80] investigated cobalt (II) phosphate hydroxide co-doped g-C$_3$N$_4$ (Co-P/C$_3$N$_4$) for the hydrogen production. Results showed that the hydrogen production rate of Co-P/C$_3$N$_4$ was 14 times higher than g-C$_3$N$_4$. Combining doped g-C$_3$N$_4$ with other photocatalyst can further promote their photocatalytic activity. Chen et al.[81] prepared a novel photocatalyst of Co-g-C$_3$N$_4$/MoS$_2$ by coupling Co-doped g-C$_3$N$_4$ and MoS$_2$ nanosheets. The photocatalytic activity of the catalyst was better than g-C$_3$N$_4$/MoS$_2$ and Co-g-C$_3$N$_4$, which was mainly due to the formation of a 2D heterojunction, promoted charge carrier transport, suppressed recombination of charge carriers, and increased light absorption.[81]

<table>
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<th>Materials</th>
<th>Application</th>
<th>HER rate</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-C$_3$N$_4$ powder/Pt</td>
<td>water reduction</td>
<td>7.3 μmol h$^{-1}$</td>
<td>[73]</td>
</tr>
<tr>
<td>porous g-C$_3$N$_4$</td>
<td>water splitting</td>
<td>0.25 μmol h$^{-1}$</td>
<td>[74]</td>
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<tr>
<td>α-Fe$_2$O$_3$/g-C$_3$N$_4$</td>
<td>water splitting</td>
<td>3×10$^4$ μmol g$^{-1}$ h$^{-1}$</td>
<td>[76]</td>
</tr>
<tr>
<td>MoS$_2$/g-CN</td>
<td>water splitting</td>
<td>20.6 mmol h$^{-1}$</td>
<td>[77]</td>
</tr>
<tr>
<td>Pt-CN</td>
<td>water splitting</td>
<td>300 μmol h$^{-1}$</td>
<td>[22]</td>
</tr>
<tr>
<td>P doped g-C$_3$N$_4$</td>
<td>water splitting</td>
<td>1596 μmol g$^{-1}$ h$^{-1}$</td>
<td>[79]</td>
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<tr>
<td>P doped g-C$_3$N$_4$</td>
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<td>50.6 μmol h$^{-1}$</td>
<td>[80]</td>
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<tr>
<td>Br-modified g-C$_3$N$_4$</td>
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<td>48 μmol h$^{-1}$</td>
<td>[13]</td>
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<tr>
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<td>386.8 μmol g$^{-1}$</td>
<td>[81]</td>
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<tr>
<td>Co-g-C$_3$N$_4$/MoS$_2$</td>
<td>water reduction/photodegradation of RhB</td>
<td>5411 μmol g$^{-1}$ h$^{-1}$</td>
<td>[82]</td>
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### 4.2 Oxygen reduction reactions in fuel cells

Fuel cells attract great interest for offering cleaner and more sustainable energy. At present, the practical applications of fuel cells are restricted by the high cost of Pt catalyst and the sluggish kinetics of ORR.[14,82] Nitrogen-containing carbon materials, such as g-C$_3$N$_4$, are worthy investigating because they provide sufficient active sites for ORR.[18,84] However, the electrocatalytic performance of g-C$_3$N$_4$ is restricted by its poor electron transfer. To solve this problem, one strategy
is to use conductive carbon materials as support to improve the electron accumulation, thus to enhance the electrocatalytic performance. Lyth et al.\textsuperscript{[58]} used g-C\textsubscript{3}N\textsubscript{4} as a catalyst for oxygen reduction, and they found out that although the electrocatalytic activity of g-C\textsubscript{3}N\textsubscript{4} was better than pure carbon, the current densities were pretty low, which possibly was due to its low surface area. It was found that the current densities increased by mixing C\textsubscript{3}N\textsubscript{4} with carbon black.

Yang et al.\textsuperscript{[85]} fabricated graphene-based C\textsubscript{3}N\textsubscript{4} (G-CN) nanosheets by nanocasting. The G-CN nanosheets possessed a high nitrogen content and a high specific surface area and showed promoted electrical conductivities.\textsuperscript{[85]} As a result, the G-CN nanosheets exhibited excellent electrocatalytic activity for ORR. Macroporous g-C\textsubscript{3}N\textsubscript{4}/C was prepared by using silica microspheres as hard templates.\textsuperscript{[14]} This hybrid catalyst exhibited outstanding activities towards ORR in fuel cells, and was comparable with commercial Pt/C.\textsuperscript{[14]} Liu et al.\textsuperscript{[15]} doped Co into g-C\textsubscript{3}N\textsubscript{4} polymer and supported it on graphene as a catalyst for ORR in alkaline fuel cells (Fig. 8). The experimental results showed that ORR catalyzed by Co-g-C\textsubscript{3}N\textsubscript{4} mainly occurred in a four-electron pathway. The high ORR activity was attributed to the sufficient Co-N\textsubscript{x} active sites and fast electron transport.\textsuperscript{[15]}

Apart from carbon-based materials, some metals are also investigated to complex with g-C\textsubscript{3}N\textsubscript{4} to achieve a better ORR performance. For example, Kundu et al.\textsuperscript{[59]} reported a facile synthesis of porous gold aerogel supported on carbon nitride (Au-aerogel-C\textsubscript{3}N\textsubscript{4}). Results showed that four-electron ORR process was dominant at the catalysts in both alkaline and acidic media, and the excellent ORR performance was due to the synergistic effects between porous Au-aerogel-C\textsubscript{3}N\textsubscript{4}. Zheng et al.\textsuperscript{[86]} designed and synthesized a series of g-C\textsubscript{3}N\textsubscript{4} coordinated transition metals as catalysts for oxygen electrode reactions. After theoretical calculation and experimental measurements of a Co-g-C\textsubscript{3}N\textsubscript{4} catalyst, it was found that the high ORR activity was ascribed to the Co-N\textsubscript{2} coordination.\textsuperscript{[86]}

It can be seen that g-C\textsubscript{3}N\textsubscript{4} shows promising activity towards photocatalytic hydrogen evolution. Especially, when combined with conductive supports (such as mesoporous carbon or graphene), g-C\textsubscript{3}N\textsubscript{4} can exhibit highly efficient ORR activity, which will be beneficial for the development of fuel cells. Although g-C\textsubscript{3}N\textsubscript{4} has a great potential in various applications, the correlations between the g-C\textsubscript{3}N\textsubscript{4} structure and its catalytic activity are still not clear. Current research basically focuses on the performance rather than the mechanism. For future studies, powerful theoretical calculation is needed to understand the physicochemical properties of carbon nitride and to clarify the relationship of nanostructure and catalytic kinetics. Besides, in current research, the combination of g-C\textsubscript{3}N\textsubscript{4} and other materials has achieved promising performances, but the inherit mechanism is still needed to be found out.

4.3 Li-based battery

Because of the relatively high specific energy and good stability, some Li-based batteries, such as Li-ion battery, Li-O\textsubscript{2} battery and Li-S battery have attracted tremendous interests for their potential applications in electric vehicles. However, the practical applications of these batteries are restricted by the sluggish kinetics of the reactions on the electrodes. In order to solve this problem, efficient catalyst should be developed and employed. g-C\textsubscript{3}N\textsubscript{4} may provide more active sites for the electrode reactions due to its high nitrogen content.\textsuperscript{[87,88]} Still, g-C\textsubscript{3}N\textsubscript{4} is limited by the low electronic conductivity. Therefore, some electronic conductive materials should be used to increase electrons accumulated on g-C\textsubscript{3}N\textsubscript{4} surface.\textsuperscript{[87]}

Hou et al.\textsuperscript{[89]} prepared a N-doped graphene/porous g-C\textsubscript{3}N\textsubscript{4} nanosheets supporting layered-MoS\textsubscript{2} hybrid as Li-ion battery anodes. MoS\textsubscript{2} nanosheets were dispersed uniformly on the matrix to form a multilayered structure.\textsuperscript{[89]} The hybrid catalyst shows excellent cycling stability, high rate capability and large capacity due to the special structure. Yin et al.\textsuperscript{[90]} anchored SnS\textsubscript{2} on g-C3N4 nanosheets to synthesize a composite electrode for Li-ion batteries. The large surface area provided more active sites and promoted the charge transfer. Besides, the synergistic effect between g-C\textsubscript{3}N\textsubscript{4} nanosheets and SnS\textsubscript{2} lowered the charge-transfer resistance, which was in favor of the alloying reaction between metallic Sn and Li\textsuperscript{+}. As a result, the catalyst delivered a high discharge capacity with a high coulombic efficiency of over 99.9\%, and it also achieved a high specific capacity retention rate. g-C\textsubscript{3}N\textsubscript{4}@carbon papers

![Fig. 8](image_url)
(GCN@CP) were prepared via a facile in situ method to improve the electronic conductivity of g-C3N4 and obtained a high nitrogen content. When employed as cathodes for Li-O2 batteries, GCN@CP exhibited favorable electrocatalytic performance toward ORR and OER in nonaqueous electrolytes, showing good rate capability and cyclic stability. In another paper, Luo et al. synthesized a free-standing graphene@g-C3N4 (G@CN) composite cathode for Li-O2 batteries. During the reaction process, g-C3N4 nanosheets acted as electrocatalysts while graphene nanosheets accommodated Li2O2 and improved the electron transfer. As a result, the G@CN electrocatalyst showed a favorable cyclic stability with a high round-trip efficiency. Zhao et al. synthesized single-atom Pt catalyst supported on holey ultrathin g-C3N4 nanosheets (Pt-CNHS) to serve as cathode in Li-O2 battery (Fig. 9). Li-O2 batteries utilizing Pt-CNHS showed much higher discharge specific capacities than those with pure CNHS.

![Fig. 9 Schematic illustration of the synthesis and reaction mechanism of Pt-CNHS. Reproduced with permission (Copyright@2019, Elsevier Ltd.)](image)

The assembled batteries using Pt-CNHS as catalyst could deliver a 17059.5 mAh g⁻¹ discharge capacity, while that of pure CNHS was only 5890.1 mAh g⁻¹. CNHS with porous structure promoted the mass transport and electrolyte wetting, as well as accommodated Li2O2. Single-atom Pt was also in favor of the efficient interfacial mass transfer due to its high electrical conductivity. Meng et al. used g-C3N4 nanosheets as a sulfur anchoring material in Li-S batteries. The as-prepared g-C3N4 nanosheets possessed a high nitrogen (N) content of 56 wt% and a high specific surface area of 209.8 m² g⁻¹, which were in favor of the loading of lithium polysulfides. As a result, the GCN/S delivered good electrochemical performances at the initial and 750th cycle. 3D light-weight and porous C3N4 nanosheets@reduced graphene oxide (PCN@rGO) network was prepared to solve the shuttle effect in Li-S batteries. The PCN@rGO network anchored polysulfides by strong chemical adsorption as well as promoted electron and mass transfer. As a result, the PCN@rGO-S cathode showed superior rate capability and ultra-long cycling stability. Zhang et al. synthesized a 3D porous sulfur/graphene@g-C3N4 (S/GCN) hybrid sponge and applied it as a free-standing cathode for Li-S batteries. The N-sites in GCN provided a large amount of adhesion sites for polysulfides, achieving a “physical-chemical” dual-confinement for polysulfides. Moreover, the porous 3D graphene frameworks promoted electron/Li⁺ transport and maintained good structure integrity. By using a microemulsion encapsulation method, S/GCN cathodes achieved a sulfur loading up to 82 wt%. Therefore, the S/GCN delivered a high specific capacity and excellent rate capability as well as alleviated anode corrosion issues.

5. Summary and outlook

In summary, this review presents an overview of g-C3N4 and g-C3N4-based materials, focusing on the synthesis methods, properties and applications in energy storage. The unique properties and wide applications prove that g-C3N4 is promising for efficient energy storage. Therefore, the research of g-C3N4-based composite for energy storage and conversion will continue to accelerate in the near future.
g-C$_3$N$_4$ unique structure and catalytic activity is still not clear. There are still many opportunities for further research efforts. Accordingly, more studies are needed to figure out the structural and electronic properties of g-C$_3$N$_4$.

As g-C$_3$N$_4$ related research develops, an urgent and realistic question is raised: what else can we continue to work on g-C$_3$N$_4$-based material presently? After reviewing the research works in the past, we believe that the following problems should be solved in the future studies: (1) New synthesis process for g-C$_3$N$_4$ should be proposed. As we introduced in this review, g-C$_3$N$_4$ is commonly prepared from the condensation of nitrogen rich precursors, which can be polymerized into various mediates. In order to improve the catalytic activity of g-C$_3$N$_4$, exploiting new methods to prepare the g-C$_3$N$_4$ with a higher crystalline quality is of great importance. (2) A more comprehensive understanding of the reaction mechanism is necessary for promoting the design and performance of g-C$_3$N$_4$ based catalysts. The charge carrier transfer mechanism, the thermodynamics and kinetics of surface reactions are worth studying. In order to realize the understanding of mechanism, some powerful tools, such as in-situ characterization techniques and theoretical calculation may be of great importance. (3) Apart from the research of sole g-C$_3$N$_4$, combining it with other novel catalysts may be a path towards more efficient energy storage strategies. It’s important that researchers should try to design a g-C$_3$N$_4$ based composite rather than simply find one. Therefore, the understanding of g-C$_3$N$_4$ and other novel materials is vital for the new catalyst. In a word, there are enormous opportunities regarding g-C$_3$N$_4$ and g-C$_3$N$_4$-based materials, but this may require the unremitting efforts of worldwide researchers.

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Supporting information
Not applicable

Conflict of interest
There are no conflicts to declare.

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