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Abstract

Graphitic carbon nitride (g-C3N4), as a new type of polymeric semiconductor, has been regarded as a promising photoelectrode material for efficient photoelectrochemical (PEC) water splitting for hydrogen production due to its suitable band structure for water splitting reaction, certain range of visible-light absorption, non-toxicity, low cost, and good stability. However, there are many obstacles impeding the further application of g-C3N4 material in PEC water splitting, such as its wide band gap, low electrical conductivity, high recombination rate of photogenerated electrons/holes, and the difficulty in fabrication of high-quality g-C3N4 films on substrates. In this view, we summarize the novel bottom-up technology for achieving the high-quality g-C3N4 films. Moreover, the modification strategies of enhancement on PEC performance of g-C3N4 film photoelectrodes, including functional groups introducing, heteroelements doping, and composite films designing, have been discussed in detail. At last, the key challenges and possible solutions for future development on g-C3N4-based PEC water splitting are concluded.

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Abstract: Graphitic carbon nitride (g-C₃N₄), as a new type of polymeric semiconductor, has been regarded as a promising photoelectrode material for efficient photoelectrochemical (PEC) water splitting for hydrogen production due to its suitable band structure for water splitting reaction, certain range of visible-light absorption, non-toxicity, low cost, and good stability. However, there are many obstacles impeding the further application of g-C₃N₄ material in PEC water splitting, such as its wide band gap, low electrical conductivity, high recombination rate of photogenerated electrons/holes, and the difficulty in fabrication of high-quality g-C₃N₄ films on substrates. In this view, we summarize the novel bottom-up technology for achieving the high-quality g-C₃N₄ films. Moreover, the modification strategies of enhancement on PEC performance of g-C₃N₄ film photoelectrodes, including functional groups introducing, heteroelements doping, and composite films designing, have been discussed in detail. At last, the key challenges and possible solutions for future development on g-C₃N₄-based PEC water splitting are concluded.

Keywords: Graphitic carbon nitride; Film; Photoelectrochemistry.

1. Background and Incentives

In the past few decades, an unprecedented amount of energy has been consumed due to the rapid industrialization and population expansion. This energy demand is, however, still increasing at a continuously accelerated speed. To be specific, it is estimated that the global energy demand will be doubled by 2050 [1, 2]. To make this scenario even worse, the present worldwide energy supply is mainly from fossil fuels, such as coal, oil, and natural gas [3], which have a limited reserve and can thus cause energy depletion in the near future. Meanwhile, the exploitation, transportation, and

utilization of these fossil fuels are inevitably accompanied with the release of various toxic and/or green-house gases, including carbon-dioxide and nitrogen/sulfur oxides. These will collaboratively result in both energy crisis and environmental deterioration, which will finally impose a significant threaten to the sustainable development of society and even the survival of mankind [4].

Therefore, the harvest and utilization of more environment-friendly and renewable energies (so-called new energies) to replace the conventional fossil fuels have been regarded as the most fundamental, promising, and effective solution to tackle these issues. With the fast advance of science and technology, various types of new energies, such as solar energy [5], wind energy [6], wave energy [7], and hydrogen energy [8], have been wildly investigated and utilized. Among the various alternative new types of energy, hydrogen energy, that is, the chemical energy stored in hydrogen gas, has been regarded as a very promising candidate due to its emission-free characteristics and relatively high energy density ($\sim 140 \text{ MJ kg}^{-1}$) [9]. Most of the hydrogen gas, however, is produced by steam reforming of methane in industry, which is energy-intensive, CO_2 -emitting, and low-efficient [10]. Besides, the as-produced hydrogen gas always contains CO, which is poisonous to many catalysts and is hard to be completely removed, making such hydrogen gas unsuitable to be directly used for the state-of-the-art fuel cells and greatly limiting its applications. Alternatively, high-purity hydrogen gas can be produced by electrically splitting water. However, the water electrolysis always consumes a large amount of electricity. Specifically, in the actual water electrolysis process, an approximately 5 kWh of electricity is required for the production of hydrogen gas of per cubic meter at one standard atmospheric pressure. In this case, a huge amount of electricity consumption may appear with the implementation of large-scale hydrogen generation from water electrolysis. Consequently, the more “green” and “sustainable” strategy to produce hydrogen gas at high purity is essential for the long-term development of

hydrogen energy.

Since the discovery of hydrogen generation using a TiO_2 photoelectrode under ultraviolet (UV) light radiation in 1972 [11], the photoelectrochemical (PEC) water splitting, which is able to directly split water into hydrogen gas and oxygen gas by utilizing the inexhaustible solar energy as the driving force, has become a research hotspot in materials science and new energy fields. Superior to the methane steam reformation process, the PEC water splitting can produce hydrogen gas at a higher purity, free of any CO or other impurities. Moreover, the PEC water splitting also behaves an inimitable advantage of lower electric energy consumption compared with electrochemical water electrolysis process. Therefore, the PEC water splitting for hydrogen generation shows a very great potential for solving both energy and environment crisis [12-16].

In a PEC water splitting system, the photoelectrode material is the core component, which plays an essential role by absorbing incident light and generating photogenerated electrons/holes to drive the water splitting reaction. So the structural and chemical characteristics of these materials fundamentally determine the actual water splitting pathway and the associated energy conversion efficiency. Up to now, a diverse range of materials have been utilized as photoelectrode materials for PEC water splitting, including oxides [17-22], sulfides [23-26], nitrides [27-29], and others.

To achieve an efficient utilization of solar energy, the photoelectrode materials should be able to absorb the visible light, which constitutes a large fraction (*ca.* 43%) in the solar spectrum [3]. However, the traditional photoelectrode materials, such as TiO_2 , meet a bottleneck to match such absorption requirements due to their extremely wide band gaps (3.0-3.2 eV). In order to absorb as much visible light as possible, the semiconducting materials with narrower band gaps have been developed for PEC water splitting, which are mainly based on the highly toxic and unstable CdS and CdSe materials, making them hard to be practically deployed at a large scale [30-32]. On the

basis of these considerations, seeking non-toxic, stable, and visible-light-driven photoelectrode materials has been a prerequisite and hotspot for future research on PEC water splitting.

Very recently, graphitic carbon nitride ($g\text{-C}_3\text{N}_4$), a new type of polymeric semiconducting material, has triggered a worldwide interest as the next generation photoelectrode material for PEC water splitting, due to its suitable band structure, a certain range of visible-light absorption, non-toxicity, low cost, and high stability [33, 34]. $g\text{-C}_3\text{N}_4$ has a layered structure that resembles graphite. In each layer, the structural units are triazine (C_3N_3) (**Figure 1a**) and tri-*s*-triazine/heptazine (C_6N_7) rings (**Figure 1b**). The latter is regarded as the most energetically stable structure at the ambient condition, and thus it has been the mostly accepted building block of $g\text{-C}_3\text{N}_4$ [35, 36].

For real application of $g\text{-C}_3\text{N}_4$ materials in PEC water splitting, acquiring $g\text{-C}_3\text{N}_4$ with film form instead of bulky or powdery structures is essential. During the PEC water splitting process, the photogenerated electrons (or holes) need to be gathered by conductive substrates, and transmitted to the opposite electrode *via* the outer circuit afterwards. However, the considerably large 3-dimensional (3D) sizes of bulk $g\text{-C}_3\text{N}_4$ will cause excessive consumptions/recombination of carriers, while those large interspaces among the $g\text{-C}_3\text{N}_4$ powder will block the transfer of carriers. Thus, this process is obviously impossible to proceed for those $g\text{-C}_3\text{N}_4$ materials with bulky and powdery structures.

Figure 1 (1.5-column). Structure illustration of g-C₃N₄ in (a) triazine and (b) tri-s-triazine/heptazine.

Up to now, hundreds of articles related to g-C₃N₄ films for PEC water splitting have been published. However, to the best of our knowledge, there have not been any comprehensive reviews available on this hot research topic except for one recent published mini-review [37]. This scenario thus makes it very necessary and urgent to provide a critical and comprehensive review to discuss the application of g-C₃N₄ films on PEC water splitting photoelectrodes in detail.

Herein, we focus on the latest advances in g-C₃N₄ films for PEC water splitting. Firstly, the principles of g-C₃N₄-based PEC water splitting, and the feasibility and challenge of g-C₃N₄ for PEC water splitting will be discussed. Subsequently, we will comprehensively summarize the different types of the g-C₃N₄ films as the PEC water splitting photoelectrodes according to their fabrication pathways and the modification methods of enhancement on PEC performance. Next, the g-C₃N₄-based composite films and their application in PEC water splitting will be presented. Lastly, we conclude with the key challenges and opportunities in the future development of g-C₃N₄-based films for PEC water splitting. We hope that this review will offer a valuable insight for g-C₃N₄-based PEC water splitting.

2. Principle, Feasibility and Challenge of g-C₃N₄ as Photoelectrode Materials

2.1. Principle of PEC Water Splitting on a g-C₃N₄-based Photoanode

A typical PEC water splitting reaction takes place in a PEC water splitting cell, which has at least one photoelectrode for harvesting incident light [38-41]. **Figure 2a** shows the structural diagram of g-C₃N₄-based PEC water splitting cell, which is composed of a g-C₃N₄-based photoanode and a counter electrode (cathode). These electrodes are usually immersed in an electrolyte (*e.g.* aqueous solution of Na₂SO₄), and connected by an outer circuit.

Figure 2 (2-column). Schematic illustration of (a) a PEC water splitting cell using a g-C₃N₄-based photoanode as the working electrode, and (b) fractional steps of g-C₃N₄-based PEC water splitting process.

In the PEC water splitting process, the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) simultaneously happen on the surfaces of g-C₃N₄-based photoanode and cathode, respectively (**Figure 2a**). Specifically, when the incident light irradiates the photoanode, the electrons in the valence band (VB) of g-C₃N₄ are excited to the conduction band (CB) to form photogenerated electrons, leaving positively charged holes in the VB (**step 1 in Figure 2b**). Subsequently, the photogenerated electrons transport from the photoanode to the cathode through the outer circuit (**step 2 in Figure 2b**), and then reduce the protons dissolved in the electrolyte and generate hydrogen gas (HER, **step 3 in Figure 2b**), as described in eq.1 [9]:

where, E_{red}^0 is H₂ evolution potential [0 V vs. normal hydrogen electrode (NHE) at pH=0].

At the meantime, the holes left in the VB of g-C₃N₄ migrate from inside the photoanode to the surface (**step 4 in Figure 2b**), and oxidize water to produce oxygen gas (OER, **step 5 in Figure 2b**), as described in eq.2 [9]:

where, E_{ox}^0 is O₂ evolution potential (1.23 V vs. NHE at pH=0).

Apart from the ones that are respectively involved in the electrode reactions, the rest of the photogenerated electrons and holes, which fail to reach the photoelectrode surface in their migration process, will be recombined and neutralized (**step 6 in Figure 2b**).

2.2. Feasibility and Challenge of g-C₃N₄ for PEC Water Splitting

As an emerging photoelectrode material, g-C₃N₄ exhibits a series of outstanding features, such as its suitable energy band structure for water splitting reaction, visible-light absorption at a certain wavelength range, non-toxicity, low price, and high stability. To be specific, firstly, the edge of CB for g-C₃N₄ is about -1.11 eV vs. NHE, lower than the H₂ evolution potential. Meanwhile, its VB edge locates at approximately 1.57 eV vs. NHE, higher than the O₂ evolution potential [42]. In this case, when g-C₃N₄ is excited by the incident light, it can produce the photogenerated electrons and holes with sufficient energy to drive the HER and OER on the surface of photoanodes and cathodes, respectively. Secondly, g-C₃N₄ has a visible-light-absorption up to 450 nm, resulting from its band gap (E_g) of *ca.* 2.7 eV [43]. This is a significant advantage compared with the traditional photoelectrode materials (*e.g.* TiO₂) because the latter can only absorb the ultraviolet (UV) light. Thirdly, g-C₃N₄ consists of earth-abundant elements of carbon and nitrogen, and does not consist of any toxic and rare elements. Fourthly, g-C₃N₄ can endure a high temperature up to 600 °C in air [44] and is stable in acid, alkali, and organic solvents [45]. Lastly, g-C₃N₄ can be obtained through a very

simple thermal polymerization from a diverse range of low-cost and nitrogen-rich precursors, such as melamine, urea, thiourea, and dicyandiamide [46, 47].

Apart from these, g-C₃N₄ nanosheets can also be obtained by exfoliating the bulky g-C₃N₄. This provides additional opportunity to utilize the advantages of 2-dimensional (2D) nanostructure. Furthermore, the surface chemistry of g-C₃N₄ can be easily modified at the molecular level, due to its polymeric nature, which further facilitates the performance improvement by heteroelement doping or composition designing [48, 49]. Owing to these desirable characteristics of g-C₃N₄, it has been regarded as one of the most promising photoelectrode materials for PEC water splitting.

In spite of these advantages, there are still a number of issues that impedes the further improvements of g-C₃N₄-based PEC water splitting. On the one hand, the difficulty in the fabrication of g-C₃N₄ films on substrates is the main issue. As above-mentioned, for hydrogen generation from PEC water splitting, deposition of semiconducting materials onto substrates to form photoelectrodes in a film-structure is essential [50-58]. However, the g-C₃N₄ materials, which are often obtained through the thermal polymerization of various precursors (*e.g.* melamine, urea, or thiourea), are normally bulky monolith or powders [33-36, 45-49, 59-66]. To make things even worse, g-C₃N₄ is hard to be dispersed or dissolved in almost all the common solvents, making it very difficult to form a stable and homogeneous slurry to be made into a film with high quality (*i.e.*, uniform, continuous, and good substrate adhesion) through the conventional methods, such as silk-screen printing, spin coating, and doctor blade. This significantly hinders the transport of photogenerated electrons, leading to poor PEC water splitting performance. On the other hand, some drawbacks in the intrinsic properties of g-C₃N₄ are also hindering the achievement of efficient PEC water splitting. For instance, although g-C₃N₄ shows the visible-light absorption, its maximal absorption wavelength of ~450 nm is still insufficient for an efficient solar light harvesting. Besides,

the low electrical conductivity and high recombination rate of photogenerated electrons/holes are still the obstacles that must be overcome in order to obtain a satisfactory PEC efficiency [67, 68].

In the recent years, significant breakthroughs in enhancing the performance of g-C₃N₄-based photoelectrodes for PEC water splitting have been achieved, including the novel bottom-up methods of preparing g-C₃N₄ films, introducing functional groups, doping heteroatoms, and constructing g-C₃N₄-based composite films, *etc.* Regarding the bottom-up technologies, g-C₃N₄ films can be in-situ deposited onto various substrates, usually resulting in a more homogeneous microstructure and intimate contact with substrates than those obtained by the conventional methods. Besides, modifying g-C₃N₄ films by functional groups or heteroatoms and constructing g-C₃N₄-based composite films can not only improve the absorption in the visible light region but also increase the electronic conductivity of g-C₃N₄ and suppress the recombination of photogenerated electrons and holes. All of these are very important for the enhancement on g-C₃N₄-based PEC water splitting performance. In the following sections, we will introduce the representative works and provide a summary of g-C₃N₄-based films as the key components in PEC water splitting process.

3. g-C₃N₄ Films and Their PEC Water Splitting Performance

3.1. Fabrication, Structure, and Performance of g-C₃N₄ Films

For an efficient PEC water splitting process based on a g-C₃N₄ photoelectrode, a high-quality g-C₃N₄ film on the substrate plays an essential role [69]. The g-C₃N₄ films that are obtained through the conventional top-down methods, however, usually show unsatisfactory PEC performances. Normally in these processes, the bulky g-C₃N₄ materials are prepared by thermal polymerization, with subsequent treatments to form particles or nanosheets by grinding or exfoliation, respectively.

Finally, the g-C₃N₄ films are prepared on different substrates by the conventional filming technologies, such as silk-screen printing [70], spin coating [71], drop casting [72], dip casting [73], doctor blade [74], sol process [75], vacuum filtration [76], and electrophoretic deposition [77].

As aforementioned, due to the poor dispersibility/solubility of g-C₃N₄ in most solvents, it is very difficult to fabricate the uniform and stable slurry or sol, frequently resulting in large g-C₃N₄ aggregations and cracks in both the film and the interface between film and substrate. As a result, the g-C₃N₄ photoelectrodes exhibit the drawbacks of inhomogeneous microstructure and weak contact with substrates. Therefore, such top-down-prepared g-C₃N₄ film photoelectrodes often show a low PEC performance and a limited photocurrent density that is only several microampere per square centimeter [70-77], as summarized in the **Table 1**.

Table 1. The PEC water splitting performance of g-C₃N₄ film photoelectrodes prepared by the top-down route.

Fabrication method	g-C ₃ N ₄ form	Photocurrent density (μA cm ⁻²)	Potential (V)	Electrolyte	Light source	Ref.
silk-screen printing	nanosheets	0.92	1.5 vs. Ag/AgCl	0.1 M Na ₂ SO ₃	visible light	[70]
spin coating	particles	8.3	0.6 vs. Ag/AgCl	0.2 M Na ₂ SO ₄	30 W visible LED	[71]
drop casting	particles	0.75	0.8 vs. Ag/AgCl	0.1 M KCl	visible light	[72]
dip casting	nanoplates and nanorods	3 (nanoplates) 4 (nanorods)	N/A	0.1 M Na ₂ SO ₄	visible light	[73]
doctor blade	nanosheets	0.2	1.2 vs. SCE*	0.05 M Na ₂ SO ₄	visible light (λ>420 nm)	[74]
sol process	particles	8	-0.2 vs. Ag/AgCl	N/A	visible light (λ>420 nm)	[75]
vacuum filtration	nanosheets	0.5	0.0 vs. SCE	0.5 M Na ₂ SO ₄	solar simulator	[76]
electrophoretic deposition	particles	1	0.0 vs. Ag/AgCl	1 M KOH	50 W white LED (λ>410 nm)	[77]

* SCE is saturated calomel electrode.

In order to improve the PEC water splitting performance, novel bottom-up approaches have been developed to fabricate g-C₃N₄ films, including the thermal vapor condensation [78-82], microcontact-printing-assisted access [83], solvothermal route [84, 85], and direct growth [86, 87]. Different from the g-C₃N₄ films prepared by the conventional top-down routes, the g-C₃N₄ films obtained from the bottom-up approaches can be free of large g-C₃N₄ particles aggregations and cracks, resulting in a uniform microstructure, continuous coverage, and intimate contact with the substrate. This thus greatly facilitates the charge transfer, usually resulting in a better PEC water splitting performance. In this section, the synthesis, structure, and performance of g-C₃N₄ films prepared by these bottom-up pathways will be illustrated in detail.

Thermal Vapor Condensation (TVC). The TVC method is a typical bottom-up route, in which a transformation from solid precursors to precursor vapors and then to the solid g-C₃N₄ is carried out to deposit g-C₃N₄ films on substrates. According to the different deposition procedures, TVC can be categorized into two types: the one-step and two-step TVC. In a one-step TVC procedure, the substrate is placed on top of a container that is filled with the nitrogen-rich precursors (**Figure 3a**). When the container is heated to a temperature that is higher than the sublimation point of precursors (~80-300 °C), the precursors vapor is generated, which then condenses on the substrate after reaching saturation in the container. When the temperature further increases to 550-600 °C, the precursors, which has condensed on the substrate, are thermal polymerized to form a g-C₃N₄ film on the substrate [78]. In contrast to the direct formation of the g-C₃N₄ film in the one-step TVC, the two-step TVC includes two deposition procedures in sequence (**Figure 3b**). In the first deposition, g-C₃N₄ is deposited on the inner wall of the reactor. Subsequently, a substrate is placed in the reactor; and g-C₃N₄ is vaporized and deposited again to form the g-C₃N₄ film on the surface of substrates in the second deposition [79].

Figure 3 (2-column). Schematic illustration of (a) one-step TVC [78], (b) two-step TVC [79], (c) microcontact-printing-assisted access [83], (d) solvothermal route [84], and (e) direct growth [87] procedure for deposition of g-C₃N₄ films on substrates. Reprinted from refs. [78, 79, 83, 84, 87] with permission, respectively.

In the TVC approach to fabricate g-C₃N₄ films, the frequently used precursors to prepare bulky g-C₃N₄, such as melamine [78, 80, 81], cyanamide [80], dicyanamide [79], thiourea [82], and urea [82], can also be utilized. Moreover, a wide variety of materials can be used as substrates for the g-C₃N₄ films, including fluorine-doped tin oxide conducting glass (FTO) [78-82], indium-doped tin oxide conducting glass (ITO) [78], quartz glass [78], and silicon slice [78]. By tuning the preparation parameters, the morphology and microstructure of the films can be easily modified, from compact particle films (**Figure 3a and b**) [78], nanorod films (**Figure 3c and d**) [78] to framework structures (**Figure 3e and f**) [82].

Figure 4 (2-column). SEM surface images of a compact particle $\text{g-C}_3\text{N}_4$ film obtained from TVC procedure in (a) low- and (b) high-magnification. The inset in b shows the digital photo of the compact particle film. Atomic force microscope (AFM) images of (c) surface and (d) three dimensional morphologies for a $\text{g-C}_3\text{N}_4$ nanorod film prepared by TVC technology. Reprinted from refs. [78] with permission. SEM surface images of (e) top view and (f) cross-sectional view for a framework $\text{g-C}_3\text{N}_4$ film deposited through TVC process. Reprinted from ref. [82] with permission. SEM images of (g) cross-sectional view of a $\text{g-C}_3\text{N}_4$ film prepared by microcontact-printing-assisted access and (h) a flexible $\text{g-C}_3\text{N}_4$ film detached from its substrate. Reprinted from ref. [83] with permission. SEM images of a $\text{g-C}_3\text{N}_4$ film obtained from solvothermal route (i, j) before and (k, l) after post-annealing. Reprinted from ref. [84] with permission. SEM surface images of (m) a nanorod and (n) a porous $\text{g-C}_3\text{N}_4$ film prepared by direct growth. Reprinted from refs. [86] with permission. SEM surface images of a compact $\text{g-C}_3\text{N}_4$ film obtained from direct growth in (o) low- and (p) high-magnification. The inset in p shows

the results of elemental analysis. Reprinted from refs. [87] with permission.

The g-C₃N₄ films prepared by TVC method can be utilized as the photoanodes in the PEC water splitting cells, and show significant performance enhancement. Specifically, the photocurrent densities (63-120 $\mu\text{A cm}^{-2}$) are not only higher than that generated by the photoanodes obtained from top-down approach (less than 10 $\mu\text{A cm}^{-2}$), but also show the greater advantage than the photoanodes prepared by other bottom-up approaches (3.5-30 $\mu\text{A cm}^{-2}$) (**Table 2**). Especially, the highest photocurrent density of 120 $\mu\text{A cm}^{-2}$ at 1.55 V *vs.* reversible hydrogen electrode (RHE) is generated by the g-C₃N₄ photoanode [78]. Based on the above discussion, TVC has been regarded as a very convenient, versatile, and effective strategy to fabricate g-C₃N₄ films.

Table 2. The performance of PEC water splitting cells based on the g-C₃N₄ film photoelectrodes prepared by the bottom-up approach.

Fabrication method	Photocurrent density ($\mu\text{A cm}^{-2}$)	Potential (V)	Electrolyte	Light source	Ref.
TVC	120	1.55 <i>vs.</i> RHE	0.1 M Na ₂ SO ₃ and 0.01 M Na ₂ S	solar simulator (AM 1.5 ^{**})	[78]
	63	1.23 <i>vs.</i> RHE	0.1 M Na ₂ SO ₄	solar simulator (AM 1.5)	[89]
	100	1.23 <i>vs.</i> RHE	0.1 M Na ₂ SO ₄ , 0.1 M Na ₂ SO ₃ and 0.01 M Na ₂ S	solar simulator (AM 1.5)	[80]
	75	1.23 <i>vs.</i> RHE	0.1 M Na ₂ SO ₄ , 0.1 M Na ₂ SO ₃ and 0.01 M Na ₂ S	solar simulator	[81]
	89	1.10 <i>vs.</i> RHE	0.1 M Na ₂ SO ₄	solar simulator (AM 1.5)	[82]
microcontact- printing-assisted access	30	1.23 <i>vs.</i> RHE	0.1 M Na ₂ SO ₄	solar simulator (AM 1.5)	[83]
solvothermal route	3.5	1.23 <i>vs.</i> RHE	0.2 M Na ₂ SO ₄	visible light ($\lambda > 420$ nm)	[84]
	10	1.23 <i>vs.</i> RHE	0.5 M Na ₂ SO ₄	solar simulator (AM 1.5)	[85]

direct growth	22	0.5 vs. RHE	0.1 M Na ₂ SO ₄	visible light ($\lambda > 420$ nm)	[87]
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* AM 1.5 is the 1.5 air mass, and the incident intensity is 100 mW cm⁻².

Microcontact-Printing-Assisted Access. A unique template-assisted method has been developed to deposit g-C₃N₄ films onto glasses or FTO substrates, which is similar to the microcontact-printing technology that is widely employed in electronic industry. Consequently, this method is named as microcontact-printing-assisted access (**Figure 3c**) [83]. In this method, an anodic aluminum oxide (AAO), an aqueous cyanamide solution, and two pieces of FTO (or glass slide) are used as the template, precursor, and substrates, respectively. Specifically, the cyanamide solution is infiltrated into the AAO membrane, and then the AAO is placed between two substrates. At a high temperature of 550 °C, the cyanamide inside AAO is released and turned into vapor, which diffuses upward and downward simultaneously along each channel. Finally, the cyanamide vapor reaches the substrates and thermally polymerizes to form the g-C₃N₄ films.

The g-C₃N₄ films obtained from the microcontact-printing-assisted access possess a series of unique features: 1) the thickness of the g-C₃N₄ film can be easily controlled by changing the concentration of the aqueous cyanamide solution; 2) the films on the upper and lower substrates almost show the same quality, because the precursor is released from both sides of the channels of AAO and then condenses and polymerizes on both substrates; 3) the obtained g-C₃N₄ film can partially inherit the periodic structure from AAO, which provides the possibility of fabricating an array of g-C₃N₄ nanorods (**Figure 4g**); 4) flexible and self-supporting g-C₃N₄ films can be easily obtained upon removal of substrates, making this method especially feasible for flexible devices (**Figure 4h**). Moreover, the g-C₃N₄ photoanode obtained from this technology shows a basic satisfactory performance, and its photocurrent density can reach ~30 $\mu\text{A cm}^{-2}$ at 1.23 V vs. RHE

(Table 2).

Solvothermal Route. The solvothermal route has been developed to prepare g-C₃N₄ films, and it usually includes two consecutive steps: solvothermal procedure and subsequent annealing treatment (**Figure 3d**) [84, 85]. In the solvothermal step, the growth of g-C₃N₄ film follows the Stranski-Krastanov mode. It begins with the 2D layer-by-layer mode (shorter than 12 h), and then transits to a 3D micro-spheres stacking manner. After this solvothermal step (*e.g.* 180 °C/24 h), the g-C₃N₄ film, which is composed of interconnected secondary microspheres (2-3 μm) with primary nanoparticles of about a few nanometers, is obtained (**Figure 4i and j**). The solvothermal treatment itself, however, can hardly provide sufficient kinetic energy to form a complete tri-s-triazine structure. As a result, a post-annealing treatment at 550 °C is necessary to improve the crystallinity of the g-C₃N₄ film for this method. Interestingly, after this annealing, the interfaces of microspheres and nanoparticles become indistinct, indicating that a thermal cross-linking and polymerization sequentially take place (**Figure 4k and l**).

Using the solvothermal method, g-C₃N₄ films can be formed on various substrates, such as FTO [84, 85], glass [85], and TiO₂ [85]. In addition, by changing the treatment time, precursor concentration, and post-annealing temperature, the thickness and density of the g-C₃N₄ films can be controlled. Importantly, a covalent bond can be formed between the molecular precursors and the substrate surface during the solvothermal process, which results in a strong and intimate interfacial contact between them. In consequence, the adhesion between the g-C₃N₄ film and substrate can be enhanced, so does transportation of photogenerated electrons from the g-C₃N₄ film to the substrate. In spite of the aforementioned advantages, the photoanodes obtained from this solvothermal route, however, do not show the satisfactory results in the PEC water splitting measurement. The poor photocurrent densities of 3.5-10 μA cm⁻² at 1.23 V *vs.* RHE are produced (**Table 2**) [84, 85]. The

low PEC performance could be caused by the rich surface defects of g-C₃N₄ particles in film [84].

Direct Growth. In the above-mentioned methods, such as TVC, the solid precursor is not in direct contact with the substrate. In the reaction, the solid precursors are firstly gasified, diffuses to the substrate, and then thermally polymerizes to form the g-C₃N₄ film on the substrate. In contrast, a direct growth process can directly transform the precursors to films without the participation of precursor vapor. In the direct growth method, the solid precursors are contacted with the substrates and directly transformed into the g-C₃N₄ film on substrates by thermal polymerization (**Figure 3e**) [86].

In this method, the g-C₃N₄ films can be grown onto different substrates, ranging from frequently-used FTO, glass slides, to metal oxide films (TiO₂ and ZnO). Importantly, the morphology of g-C₃N₄ films can be adjusted to various structures, including nanorod arrays (**Figure 4m**) [86], porous films (**Figure 4n**) [86], or dense films (**Figure 4o and p**) [87]. So the direct growth route provides not only an easy and feasible strategy for the fabrication of g-C₃N₄ films, but also a promising way for the preparation of g-C₃N₄-based heterofilms. In the PEC water splitting performance test, the photoanode based on the film prepared by direct growth show a photocurrent density of 22 $\mu\text{A cm}^{-2}$ at 0.5 V *vs.* RHE.

Obviously, the bottom-up route can provide the convenient, versatile, and efficient fabrication strategies of g-C₃N₄ films. More importantly, the photoanodes based on the g-C₃N₄ films obtained from the bottom-up technology show greater superiority than that of the top-down approach, in terms of 1) the better uniformity of the films grown on substrates [82]; 2) the more intimate contact between films and substrates [84]; and 3) the more facile morphology control for enhancing the PEC water splitting performance [79, 84, 86]. Hence, the photoanodes from bottom-up technology display an enhanced PEC water splitting performance.

3.2. Enhancement Strategies for PEC Water Splitting Performance of g-C₃N₄ Films

As above-mentioned, except for the difficulty in g-C₃N₄ film preparation (*i.e.* for achieving high-quality g-C₃N₄ films, the mature top-down methods are usually unserviceable, and the promising bottom-up approaches are still in their infancy stage), the intrinsic shortcomings of g-C₃N₄, such as the limited visible-light absorption range, low electrical conductivity, and high recombination rate of photogenerated electrons/holes, are also prevent the material from achieving a high-efficiency PEC water splitting. The breakthrough in these bottlenecks will significantly improve the performance of g-C₃N₄ films for PEC water splitting. Next, we will introduce some typical and effective ways for enhancing the PEC performance of g-C₃N₄ films, including introduction of functional groups [80, 88], and heteroelement doping [89-91].

Introduction of Functional Groups. Modification of g-C₃N₄ films by functional groups, the typical molecular modification of materials, has been regarded as a promising route to enhance its PEC water splitting performance. Recently, the sp² C has been introduced into g-C₃N₄ films through the copolymerization of 2, 6-diaminopyridine (26D) and melamine, to mediate the electronic structure of g-C₃N₄ for more excellent optic and electrical properties [80]. In this process, 26D as the source of sp² C was added into the precursor of g-C₃N₄ films. The successful integration of sp² C into g-C₃N₄ films lead to the increased C/N ratio in modified g-C₃N₄ films with the increment of weight ratio of 26D in co-monomer (**Figure 5a**). Importantly, it was found that the sp² C can enhance the optical properties of g-C₃N₄ films as well as reduce the resistance of charge separation and transport (**Figure 5b, c**). As a result, the highest photocurrent density of 0.1 mA cm⁻² at 1.23 V *vs.* RHE was achieved by the g-C₃N₄ film with 5% weight ratio of 26D (**Figure 5d**).

Figure 5 (1.5-column). (a) C/N atom ratio, (b) UV-vis absorption spectra, (c) EIS plots at 1.23 V vs. RHE in the dark and light, and (d) light-chopped linear sweep voltammetry (LSV) curves of the pristine and 26D modified g-C₃N₄ films with different weight ratios. CMD1, CMD5, and CMD10 refer to the modified g-C₃N₄ films with 1, 5, and 10 % weight ratio of 26D, respectively. Reprinted from refs. [80] with permission.

Moreover, the sp² C has also been added introduced into g-C₃N₄ films to improve the optical and electrical properties by the phenyl-modified approach [88]. Interestingly, the molten sulfur, which was used as a solvent at high temperature, can bring a more effective integration of sp² C into the g-C₃N₄ framework, resulting in an extended light absorption, a facile exciton separation, and an improved conductivity. Consequently, g-C₃N₄ film photoanode obtained from the precursor with 600 mg sulfur behaves the highest photocurrent density of about 60 $\mu\text{A cm}^{-2}$, which is 20.7 times than that of the g-C₃N₄ film photoanodes without sulfur in its precursor (2.9 $\mu\text{A cm}^{-2}$).

Heteroatoms Doping. Doping of additional atoms into the g-C₃N₄ matrix has been considered as an effective strategy to regulate its physicochemical properties, including extending visible light absorption scope, suppressing the recombination of photogenerated electrons/holes, *etc.* Up to now,

both metallic (*e.g.* K, Co, Fe) [92-95] and nonmetallic elements (*e.g.* N, O, P, B) [96-99] have been introduced into g-C₃N₄ as dopants, but most of products are still agglomerates, powders, and nanosheets. Recently, the elemental doping technology has been successfully combined with the bottom-up approach to fabricate the doped g-C₃N₄ films with an enhanced PEC water splitting performance.

Figure 6 (2-column). (a) Kubelka-Munk function vs. energy plots, (b) UV-vis absorbance spectrum, (c) transient photocurrent densities vs. time plots under AM 1.5 illumination at 0.26 V vs. Ag/AgCl of g-C₃N₄ film photoelectrodes with different Ni doping amount. Reprinted from refs. [89] with permission. (d) UV-vis absorbance spectrum, (e) Nyquist plots, and (f) transient photocurrent densities vs. time plots under visible light ($\lambda > 420$ nm) at 1.0 V vs. SCE for g-C₃N₄ film photoelectrodes with different Ag doping amount. Reprinted from refs. [90] with permission.

Ni, as a frequently-used metallic dopant, has been homogeneously dispersed throughout g-C₃N₄ film in the direct growth process [89]. Importantly, the doped Ni ions could affect the electronic structure of g-C₃N₄, resulting in a conspicuous decrease in band gap from 2.54 to 1.70 eV with the increased Ni doping amount from 0 to 5 wt.% (**Figure 6a**), corresponding to a remarkable red-shift

in its absorption spectra (**Figure 6b**). Besides, the doped Ni ions can also facilitate the OER by means of promoting the formation of hydroperoxide ($-\text{OOH}$) species (key intermediates in the OER). The optimal PEC performance was owned by the 3 wt.% Ni doped $\text{g-C}_3\text{N}_4$ film. The photocurrent density achieved $69.8 \mu\text{A cm}^{-2}$ at 0.26 V vs. Ag/AgCl (**Figure 6c**).

Apart from Ni, Ag has also been introduced into the $\text{g-C}_3\text{N}_4$ film. Similar to Ni, the Ag species in the matrix of the $\text{g-C}_3\text{N}_4$ film can also enhance the visible light harvesting (**Figure 6d**). Besides, the Ag-doped $\text{g-C}_3\text{N}_4$ films show the stronger ability of exciton separation and charge transfer compared with pristine $\text{g-C}_3\text{N}_4$ film (**Figure 6e**). In consequence, the Ag-doped $\text{g-C}_3\text{N}_4$ film photoanodes show higher photocurrent densities than the pristine $\text{g-C}_3\text{N}_4$ photoanode (**Figure 6f**) [90].

Figure 7 (2-column). (a) Top views of super-cell 3×3 pristine $\text{g-C}_3\text{N}_4$ (left) and BCN-0.6 with two C substituted by B at corner (middle) and bay (right) sites in a lattice with constants of $a=b=21.04 \text{ \AA}$, $c=20.0 \text{ \AA}$, and $\alpha=\beta=90^\circ$,

$\gamma=120^\circ$ by DFT optimizations. The green, blue, and pink colors represent C, N, and B atoms, respectively. The XPS spectra of (b) C 1s, (c) N 1s and (d) B 1s for B doping g-C₃N₄ films. (e) UV-vis absorption spectrum, (f) Nyquist plots, and (g) light chopped LSV curves under AM 1.5 illumination of B doping g-C₃N₄ film photoanodes. The inset in e is the Kubelka-Munk function vs. energy plots. Reprinted from refs. [91] with permission.

Nonmetallic elements (*e.g.* B) can also be incorporated into the g-C₃N₄ films to improve PEC ability through a typical TVC process using a mixture of melamine and boric acid as the precursor. [91]. The B atoms embedded into g-C₃N₄ matrix substitute the C atoms in the bay sites, resulting in the formation of C-B bonds (**Figure 7a-d**). This compositional change brings a significant influence on the electronic structure of the g-C₃N₄ films. As a result, the band gap of B-doped g-C₃N₄ films decreased from 2.77 to 2.60 eV with the increase of boric acid added amount in precursor from 0 to 0.8 g, corresponding to a remarkable enhancement on visible light absorption spectra (**Figure 7e**). Meanwhile, the recombination of photogenerated electrons and holes is suppressed, and charge transfer process is accelerated (**Figure 7f**). Consequently, the photoanode with boric acid added amount of 0.6 g in precursor produced the highest photocurrent density of 55 $\mu\text{A cm}^{-2}$ at 1.23 V vs. RHE (**Figure 6g**).

In a word, the introduction of functional groups or heteroelements into g-C₃N₄ films based on the novel bottom-up route can not only obtain high-quality g-C₃N₄ films, but also enhance the PEC water splitting performance.

4. g-C₃N₄-based Composite Films and Their PEC Water Splitting Performance

As aforementioned, the pristine g-C₃N₄ films usually do not possess satisfactory PEC performance, due to their intrinsic drawbacks, such as insufficient visible-light absorption, low electrical conductivity, and high recombination rate of photogenerated electrons and holes.

Although introducing functional groups or heteroatoms into g-C₃N₄ films can improve the PEC performance, the destruction of g-C₃N₄ structure and formation of defect could bring a number of negative effects, such as photogenerated electrons being captured and then recombined at the defects in g-C₃N₄ films.

Recently, compositing g-C₃N₄ with a secondary semiconductor to form a composite film has been intensively studied, due to its abilities of suppressing the recombination and enhancing the visible-light absorption, resulting in the enhancement on PEC water splitting performance. Importantly, the introduced secondary semiconductor materials normally do not affect the molecular structure and the properties of g-C₃N₄, therefore, the advantages of g-C₃N₄ can be successfully kept. Up to now, a series of semiconducting materials have been coupled with g-C₃N₄, including the wide band-gap metal oxides, metal sulfides, *p*-type semiconductor, and so on. In this section, this new strategy of constructing g-C₃N₄-based composite films will be discussed.

4.1. Principles of g-C₃N₄-based Heterojunctions

In a g-C₃N₄-based composite film, g-C₃N₄ and a secondary semiconducting material are coupled to form heterojunctions, which play a key role in improving the PEC water splitting performance. According to the separation mechanism of photogenerated electron and holes, the g-C₃N₄-based composites can be categorized into four classifications: type I, type II, type III, and Z-scheme heterojunction [3, 100].

Figure 8 (1.5-column). Schematic energy band diagram of (a) type I, (b) type II, (c) type III, and (d) Z-scheme heterojunction constructed by $g\text{-C}_3\text{N}_4$ and a secondary semiconductor material.

In a type I heterojunction, both VB and CB of the secondary semiconductor are within band gap region of $g\text{-C}_3\text{N}_4$, thereby building a straddling band alignment (**Figure 8a**). As a result, all the photogenerated electrons and holes are transferred in a single direction towards the secondary semiconductor in this structure, thereby all charges are accumulated in the secondary semiconductor. Obviously, in this case, the photogenerated electrons and holes can hardly be thoroughly separated and the recombination is inevitable [3]. In the type II heterojunction, the band edge potentials of $g\text{-C}_3\text{N}_4$ and the secondary semiconductor are staggered (**Figure 8b**). Consequently, the photogenerated electrons are transferred from the CB of $g\text{-C}_3\text{N}_4$ to the CB of the secondary semiconductor, while the holes migrate towards the opposite direction. This double-charge transfer mechanism significantly improves the separation rate of excitons, leading to the inhibited recombination of the photogenerated electrons/holes [101, 102]. In the type III heterojunction, the VB and CB of $g\text{-C}_3\text{N}_4$ and the secondary semiconductor do not overlap with each other (**Figure 8c**),

which does not affect the separation of photogenerated electrons and holes. At last, a new type of heterostructure, named Z-scheme heterojunction, has been reported in recently [103-105]. In the Z-scheme heterojunction, the photogenerated electrons in the CB of the secondary semiconductor are directly transferred to the VB of g-C₃N₄, thus leading to the efficient separation of the photogenerated electrons in the CB of g-C₃N₄ and the holes in the secondary semiconductor (**Figure 8d**). Based on the above discussions, only the type II and Z-scheme g-C₃N₄-based heterojunctions are effective in separating the photogenerated electrons and holes, thus desirable in the construction of a g-C₃N₄-based film.

Other than the improved separation and suppressed recombination, composing g-C₃N₄ with the secondary semiconductors can also modify the material's visible-light adsorption behavior, bringing a more effective utilization for solar energy. In the following sections, we will summarize the progress of g-C₃N₄-based composite films for PEC water splitting.

4.2. g-C₃N₄-based Type II Heterojunction Composite Films

As above-mentioned, the type II heterojunction, constituted by g-C₃N₄ and a secondary semiconductor, not only enhances the visible light absorption but also suppresses the recombination of photogenerated electrons/holes. Therefore, a series of semiconducting materials, including wide band-gap metal oxides (*e.g.* TiO₂, SnO₂), metal sulfides (*e.g.* CdS), and ternary oxides (*e.g.* BiVO₄), have been introduced into the g-C₃N₄ films to forming the g-C₃N₄-based type II heterojunction to achieve an improved PEC water splitting performance.

Firstly, wide band-gap metal oxides, such as TiO₂ and SnO₂, are the most extensively studied photoanode materials for PEC water splitting, due to their good physicochemical stability, low cost, and facile fabrication [106-109]. Nevertheless, their extremely wide band gap of ~3.2-3.4 eV usually results in a poor visible-light absorption ability, which hinders the further enhancement of

their PEC performance. However, the band edge positions of TiO_2 and SnO_2 are considered quite suitable to be coupled with $\text{g-C}_3\text{N}_4$ to form composite films with type II heterojunctions [71, 110, 111], leading to a much enhanced PEC water splitting performance compared with the pristine TiO_2 , SnO_2 , and $\text{g-C}_3\text{N}_4$ films.

Generally, the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ and $\text{SnO}_2/\text{g-C}_3\text{N}_4$ composite films can be fabricated by the top-down approach using the pre-prepared composite powders as the starting materials (**Figure 9a** and **e**). Importantly, the composite films show more excellent optic and electrical properties than the pristine TiO_2 , SnO_2 , and $\text{g-C}_3\text{N}_4$ films, including the strong absorption in the visible range (**Figure 9b** and **f**), and the accelerated separation and transfer of photogenerated charge (**Figure 9c** and **g**). As a result, the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ and $\text{SnO}_2/\text{g-C}_3\text{N}_4$ film photoanodes show higher photocurrent densities than the pristine TiO_2 , SnO_2 , and $\text{g-C}_3\text{N}_4$ photoanodes, respectively (**Figure 10d** and **h**) [71, 111].

Figure 9 (2-column). (a) TEM image of TC-8 sample. (b) UV-vis absorption spectra of TiO_2 , $\text{g-C}_3\text{N}_4$, and $\text{TiO}_2/\text{g-C}_3\text{N}_4$ heterojunctions. (c) Photoluminescence (PL) spectra of TiO_2 , $\text{g-C}_3\text{N}_4$, and TC-1 and TC-2 heterojunctions. (d) Transient photocurrent densities vs. time plots of $\text{TiO}_2/\text{g-C}_3\text{N}_4$ composite film photoanodes. Reprinted from refs. [110] with permission. (e) TEM image of SCN-45.1 sample. (f) UV-vis absorption spectra of

SnO₂, g-C₃N₄, and SnO₂/g-C₃N₄ heterojunctions. (g) Nyquist plots for g-C₃N₄, SnO₂, SCN-27.4, and SCN-45.1 samples. (h) Transient photocurrent densities vs. time plots of SnO₂/g-C₃N₄ composite films. Reprinted from Ref. [71] with permission. Here, TC-1, 2, 4, and 8 are the TiO₂/g-C₃N₄ heterojunction samples with different mass ratios of TiO₂ to g-C₃N₄ at 1:1, 1:2, 1:4, and 1:8, respectively. SCN5.3, 13.4, 24.7, and 45.1 refer the represent SnO₂/g-C₃N₄ heterojunction samples with different percentage content of SnO₂ in the composite at 5.3, 13.4, 24.7, and 45.1%, respectively.

Except for the wide band-gap metal oxides, metal sulfides have also been coupled with g-C₃N₄ to form the type II heterojunctions. Compared with metal oxides, the metal sulfides generally possess a narrower band gap and higher charge mobility, resulting in a stronger visible light absorption and more efficient charge separation [112-114].

Figure 10 (2-column). (a) UV-vis absorption spectra of g-C₃N₄ and CdS/g-C₃N₄ composite films. (b) PL spectra of g-C₃N₄ and CdS/g-C₃N₄ composite films. (c) Transient photocurrent densities vs. time plots of g-C₃N₄, CdS, and CdS/g-C₃N₄ composite films. (d) IPCE spectra of g-C₃N₄ and CdS/g-C₃N₄ composite films. Reprinted from ref. [115] with permission. (e) Schematic illustration of the formation process of the CdS/g-C₃N₄ composite films by a two-step (an electrophoretic deposition and a subsequent in-situ chemical bath deposition). (f) LVS curves of

g-C₃N₄, CdS, and CdS/g-C₃N₄ composite film photonodes. Herein, a, b, c, d, and e represent the g-C₃N₄, CdS-1h/g-C₃N₄, CdS-2h/g-C₃N₄, CdS-3h/g-C₃N₄, CdS film photonodes, and h refer to the reaction time in chemical bath deposition. Reprinted from ref. [116] with permission.

To obtain CdS/g-C₃N₄ composite films, a powdery composite of CdS and g-C₃N₄ was prepared by a facile hydrothermal route, and then the CdS/g-C₃N₄ composite films were fabricated by the conventional top-down approach [115]. This CdS/g-C₃N₄ composite film exhibited a stronger optical absorption than the pristine g-C₃N₄ film in the wavelength range of 430-550 nm (**Figure 10a**) and a more efficient separation of photogenerated electrons and holes (**Figure 10b**). Consequently, this CdS/g-C₃N₄ composite film photoanode shows a much higher photocurrent density (100 $\mu\text{A cm}^{-2}$) than CdS (17 $\mu\text{A cm}^{-2}$) and g-C₃N₄ (3.5 $\mu\text{A cm}^{-2}$) film, respectively (**Figure 10c**). In addition, this CdS/g-C₃N₄ composite film photoanode also possesses a higher incident photon-to-current efficiency (IPCE) with the maximum value of 27 % than the pristine g-C₃N₄ photoanodes (maximum value of 1.2 %) (**Figure 10d**).

In other related research, a two-step procedure, including an electrophoretic deposition of g-C₃N₄ onto FTO substrate and a subsequent in-situ chemical bath deposition of CdS onto g-C₃N₄/FTO was carried to fabricate the CdS/g-C₃N₄ composite films (**Figure 10e**) [116]. Finally, the CdS/g-C₃N₄ composite film photoanode obtained in optimum condition exhibited a maximum photocurrent density of 6.5 mA cm^{-2} at 0.2 V vs. Ag/AgCl under visible light illumination ($\lambda > 420$ nm) (**Figure 10f**).

Apart from metal oxides and sulfides, BiVO₄, a type of ternary oxide, has also been used to composite with g-C₃N₄ due to its good photocatalytic ability under visible light, suitable band edge position for water splitting, and high chemical stability [117,118]. The potentials of VB and CB for BiVO₄ are 2.80 and 0.27 eV, respectively, which is appropriate to form the type II heterojunction

with g-C₃N₄ [119-121].

For example, a BiVO₄/g-C₃N₄ composite film was fabricated by an electrospinning with post-annealing method (**Figure 11a** and **b**) [122]. Due to the enhancement of BiVO₄/g-C₃N₄ heterojunctions on visible light absorption and accelerated separation of excitons, this BiVO₄/g-C₃N₄ composite film showed an improved PEC water splitting performance. The photocurrent density of BiVO₄/g-C₃N₄ composite film photoanode reached 0.44 mA cm⁻² at the bias of 1.23 V *vs.* RHE, which is much higher than that of pristine g-C₃N₄ (0.15×10⁻³ mA cm⁻²) and BiVO₄ (0.30×10⁻¹ mA cm⁻²) film photoanodes, respectively (**Figure 11c**).

Figure 11 (2-column). (a) Schematic illustration of fabrication process of BiVO₄/g-C₃N₄ composite film by an electrospinning with post-annealing. (b) HR-TEM image of BiVO₄/g-C₃N₄ composites. The inset in b is the HR-TEM image of g-C₃N₄ nanosheets. (c) LSV curves of BiVO₄/g-C₃N₄, BiVO₄, and g-C₃N₄ film photoanodes under visible light illumination. The inset in d is a magnification of LSV curve for the pristine g-C₃N₄ film photoanode. Reprinted from ref. [122] with permission. (d) Schematic illustration of the exfoliation and acidification process for fabricating composite films of BiVO₄ and ultrathin g-C₃N₄ nanosheets. (e) HR-TEM image of BiVO₄/g-C₃N₄ core-shell structure heterojunction. (g) LSV curves of g-C₃N₄ nanosheets @ BiVO₄, BiVO₄, BiVO₄/bulk g-C₃N₄, BiVO₄/FeOOH, and BiVO₄/CoPi photoanodes under visible light illumination.

Reprinted from ref. [123] with permission.

The g-C₃N₄ nanosheets@BiVO₄ composite material with a rationally designed core-shell structure was also reported, which was fabricated by a simple impregnation method (**Figure 11d**) [123]. Different from the structure of BiVO₄ nanoparticles adhered to g-C₃N₄ nanosheets reported in ref. 122, the impregnation method provides a novel core-shell structure of g-C₃N₄ nanosheets@BiVO₄ (**Figure 11e**). As a result, this composite film showed a high photocurrent density of 3.12 mA cm⁻² at 1.23 V *vs.* RHE under visible light irradiation (**Figure 11f**). Noticeably, the BiVO₄/g-C₃N₄ composite films with this heterojunction structure also possessed a higher photocurrent density in comparison with ref. 122. This could be caused by a more compact contact between g-C₃N₄ and BiVO₄ in core-shell structure, resulting in a faster separation of photogenerated electron/hole pairs.

4.3. g-C₃N₄-based Z-scheme Heterojunction Composite Films

Although the g-C₃N₄-based composite films with type II heterojunctions can increase the separation efficiency and reduce the recombination possibility of the photogenerated electron/hole pairs, a major shortcoming, however, is the poor reduction/oxidation ability of the system [3, 103]. This is mainly caused by the jumping of the photogenerated electrons from the CB of g-C₃N₄ to the less negative CB of the secondary semiconductor; and the transfer of the holes from the VB of the secondary semiconductor to the less positive VB of g-C₃N₄, leading to the weakened reduction/oxidation ability (**Figure 8b**). Compared with the type II heterojunctions, the g-C₃N₄-based Z-scheme heterojunctions can not only improve the exciton separation but also maintain the reduction/oxidation ability of the system, because the photogenerated electrons and holes are still kept in the more negative CB and the more positive VB in this heterojunction, respectively (**Figure 8d**) [124-127].

In order to fabricate the g-C₃N₄-based composite films with the Z-scheme heterojunctions, the mixture powders of NiTiO₃ and g-C₃N₄ was calcined at 400 °C for 2 h to form the powdery composites of NiTiO₃/g-C₃N₄ heterojunctions (**Figure 12a**). Next, the NiTiO₃/g-C₃N₄ composite films were obtained from the slurry of NiTiO₃/g-C₃N₄ by the spinning-coating process [128]. Importantly, the NiTiO₃/g-C₃N₄ composite films exhibit an ability of photocatalytic degradation for rhodamine B (**Figure 12b and c**), indicating that the mechanism of exciton separation and transfer in this films is the Z-scheme (**Figure 12d**).

Figure 12 (2-column). (a) TEM image of NTCN-50. (b) Photodegradation rate and (c) mineralization efficiency of rhodamine B by using pure g-C₃N₄, NiTiO₃ and NTCN-30, NTCN-50 and NTCN-70 as photocatalyst. (d) Schematic diagram of mechanism of the NiTiO₃/g-C₃N₄ Z-scheme heterojunction under visible-light LED irradiation. (e) LSV and (f) calculated photoconversion efficiencies results for the pure g-C₃N₄, NiTiO₃ and NTCN-30, NTCN-50 and NTCN-70 film photoanodes. Here, NTCN-30, NTCN-50, and NTCN-70 refer to the NiTiO₃/g-C₃N₄ with various NiTiO₃ mass ratios of 30, 50, and 70 w.t.%, respectively. Reprinted from ref. [128] with permission.

Due to the accumulated separation of photogenerated electrons and holes by NiTiO₃/g-C₃N₄

Z-scheme heterojunctions, NiTiO₃/g-C₃N₄ composite films showed an enhanced PEC water splitting performance. Especially, the composite films with 50 wt.% NiTiO₃ owned the best PEC property, and its photocurrent density and photoconversion efficiency were 400 mA cm⁻² and 0.066% at about 0.8 V vs. Ag/AgCl, respectively (**Figure 12e and f**).

4.4. g-C₃N₄-based Composite Films for Photocathodes

The above mentioned PEC water splitting processes are based on the photoanodes with *n*-type semiconductors as the working electrode. Besides, the PEC water splitting cells can also utilize the *p*-type semiconductor as the photocathode to carry out the water splitting reaction under solar light radiation [129-131]. In a water splitting process based on the photocathode, when the incident light irradiates the photocathode, electrons in the VB are excited, and then transfers to the CB, leaving the holes in VB (**step 1 in Figure 13**). Next, the photogenerated electrons in CB are migrated from interior to surface of photocathode (**step 2 in Figure 13**), and then reduce the dissociated protons in electrolyte and generate hydrogen gas (HER) (**step 3 in Figure 13**). The holes in VB are transported to the anode through the outer circuit (**step 4 in Figure 13**), and then oxidize the water to produce oxygen gas (OER) (**step 5 in Figure 13**). Apart from the ones that drive the water splitting reaction, the rest of the photogenerated electrons and holes, which fail to reach the photoelectrode surface in their migration process, will be recombined and neutralized (**step 6 in Figure 13**).

Figure 13 (1-column). Schematic illustration of basic procedure and main reaction for photocathode-based PEC water splitting process.

Similar to the composite films of $g\text{-C}_3\text{N}_4$ and n -type semiconductors for photoanodes, the $g\text{-C}_3\text{N}_4/p$ -type semiconductor composite films for photocathode can also suppress the recombination of photogenerated electrons/holes, leading to enhancing PEC efficiency. In this regard, $g\text{-C}_3\text{N}_4$ has been combined with a number of p -type semiconductors to construct photocathodes, such as Cu_2O [132, 133], NiO [134], BiOBr [135], CuGaSe_2 [136], and so on.

As a typical p -type semiconductor, Cu_2O is an attractive photocathode material for PEC water splitting process because of its direct band gap of ~ 2.0 eV as well as the suitable VB band and CB potentials for water splitting [9, 132, 133]. A theoretical research manifests that a photocurrent density of 14.7 mA cm^{-2} and the solar-to-hydrogen conversion efficiency of 18% could be obtained on a Cu_2O photocathode [137, 138]. However, the Cu_2O photocathode still has two main drawbacks for practical application: 1) the high recombination rate of photogenerated electrons and holes, and 2) the serious photo-corrosion in electrolyte solution [132, 139]. Due to the compatibility between VB and CB of $g\text{-C}_3\text{N}_4$ and Cu_2O , $g\text{-C}_3\text{N}_4$ can be coupled with Cu_2O to form the type II heterojunctions [140], which not only accelerates the separation of photogenerated electron and

hole pairs, but also acts as a protection layer to avoid the photo-corrosion of Cu_2O .

Recently, a Cu_2O foam film was modified by $\text{g-C}_3\text{N}_4$ nanosheets to form the $\text{g-C}_3\text{N}_4/\text{Cu}_2\text{O}$ heterojunctions through a simple dip-coating method (**Figure 14a-c**) [132]. The n -type $\text{g-C}_3\text{N}_4$ did not change the p -type characteristic of Cu_2O for this Cu_2O foam/ $\text{g-C}_3\text{N}_4$ composite film, and the composite film produced a cathode current under AM 1.5 illumination (**Figure 14d**). Therefore, the Cu_2O foam/ $\text{g-C}_3\text{N}_4$ composite film was suitable to be a photocathode for PEC water splitting. Particularly, this Cu_2O foam/ $\text{g-C}_3\text{N}_4$ composite film also showed a higher photocurrent density (-3 mA cm^{-2}) than Cu_2O foam photocathode (-2.5 mA cm^{-2}) at -0.1 V vs. RHE under AM 1.5 illumination, which was resulted from the increased separation efficiency of photogenerated electron/hole pairs.

Figure 14 (1.5-column). Surface SEM image of (a) Cu_2O foam and (b) Cu_2O foam/ $\text{g-C}_3\text{N}_4$ composites. Inset in (a) is low-resolution SEM image of Cu_2O foam surface. Inset in b is the corresponding EDS mapping of Cu_2O foam/ $\text{g-C}_3\text{N}_4$ composites. (c) TEM image of $\text{Cu}_2\text{O}/\text{g-C}_3\text{N}_4$ heterojunctions. (d) LSV curves of $\text{g-C}_3\text{N}_4$, Cu_2O film, Cu_2O foam and Cu_2O foam/ $\text{g-C}_3\text{N}_4$ films under AM 1.5 illumination. Reprinted from ref. [132] with permission.

Apart from Cu_2O , another important p -type semiconductor is NiO , which has also been widely

used as photocathode materials for PEC water splitting. Similar to Cu_2O , the recombination of photogenerated electron/hole pairs also reduces its PEC efficiency. Besides, the large band gap of NiO (~ 3.4 eV) further limits its visible light absorption [141-143]. To solve these issues, $\text{g-C}_3\text{N}_4$ has been incorporated with NiO , to suppress the recombination of the photogenerated electrons/holes and to expand the light adsorption range at the same time, which functions on the basis of the type II heterojunction mechanism.

To achieve this, the $\text{NiO/g-C}_3\text{N}_4$ composite films have been fabricated by a facile thermal polycondensation technology [134]. This $\text{NiO/g-C}_3\text{N}_4$ composite film is suit to an effective photocathode (**Figure 15a**). Importantly, $\text{NiO/g-C}_3\text{N}_4$ composite films not only expand the light absorption range (**Figure 15b**), but also accelerate the separation of photogenerated electrons and holes due to the formation of $\text{NiO/g-C}_3\text{N}_4$ type II heterojunctions (**Figure 14c-e**). Consequently, the photocurrent density of $\text{NiO/g-C}_3\text{N}_4$ composite film was greatly increased to ~ 0.02 mA cm^{-2} at 0 V vs. RHE, which was almost 20 and 10 times higher than that of $\text{g-C}_3\text{N}_4$ and NiO films, respectively (**Figure 15f**).

Figure 15 (2-column). (a) LSV curves of NiO/g-C₃N₄ composite film photocathode under a 300 W Xe arc lamp irradiation or dark condition. (b) UV-vis absorption spectra, (c) PL spectra and (d) Nyquist plots of g-C₃N₄, NiO, and NiO/g-C₃N₄ composite films. (e) Mechanism illustration of PEC H₂ generation using NiO/g-C₃N₄ composite film photocathode. (f) Photocurrent density vs. times curves of g-C₃N₄, NiO, and NiO/g-C₃N₄ film photocathodes at 0 V vs. RHE under a 300 W Xe arc lamp irradiation. Reprinted from ref. from ref. [134] with permission.

Apart from the *p*-type semiconductors, graphdiyne (GDY) can also be compounded with g-C₃N₄ as the efficient photocathodes for PEC water splitting. Recently, a GDY/g-C₃N₄ composite nanosheet array with 2D/2D heterojunctions has been fabricated by a simple solvothermal reaction between GDY nanosheets array and g-C₃N₄ nanosheets (**Figure 16a-c**). Importantly, the excellent hole-transfer property owned by GDY can speed the separation rate of photogenerated electrons/holes. Moreover, the ultrathin structure of 2D/2D heterojunctions between GDY and g-C₃N₄ shorten the transfer distance of holes from g-C₃N₄ to GDY. Under the synergistic effect of above reasons, an increment of approximate 700% in electron life time (610 μ s for GDY/g-C₃N₄ photocathode) and enhancement of about 300% on photocurrent density ($-98 \mu\text{A cm}^{-2}$ for GDY/g-C₃N₄ photocathode) were achieved compared to those of pure g-C₃N₄ photocathode (electron life time of 88 μ s and photocurrent density of $-32 \mu\text{A cm}^{-2}$), respectively (**Figure 16d and e**) [144].

Figure 16 (2-column). (a) Schematic illustration for the construction of GDY/g-C₃N₄ composite nanosheet array with 2D/2D heterojunctions. (b) SEM image of GDY/g-C₃N₄ composite nanosheet array. (c) TEM image of ultrathin 2D/2D heterojunctions between GDY and g-C₃N₄. The inset is the HR-TEM image for GDY/g-C₃N₄. (d) Bode phase plots of g-C₃N₄ and g-C₃N₄/GDY photocathodes. (e) LSV curves of g-C₃N₄ and g-C₃N₄/GDY photocathodes measured under dark and light. Reprinted from ref. [144] with permission.

For g-C₃N₄-based composite films, not only the recombination of photogenerated electrons/holes can be suppressed, but also the visible light absorption scope can be expanded due to the effect of heterojunctions (Type II and Z-scheme). Therefore, the design of the g-C₃N₄-based composite films with the desired heterojunctions can become a promising strategy for reaching the efficient g-C₃N₄-based photoelectrodes for PEC water splitting.

5. Summary, Challenge and Outlook

As a type of metal-free semiconducting materials, g-C₃N₄ has exhibited a versatile ability in photo(electro)- and especially PEC catalysis materials [145-148]. In this review, we have summarized the latest process in the g-C₃N₄-based films as the photoelectrodes (photoanodes and photocathodes) materials for PEC water splitting. As mentioned, although g-C₃N₄ shows a number of advantages for PEC water splitting application, there are still many challenges remaining to be

addressed, such as the difficulty in preparation of high-quality films, limited visible-light absorption up to 450 nm, high recombination rate of photogenerated electron/hole pairs, and low electrical conductivity. All of these greatly hinder the further improvement of g-C₃N₄-based films in PEC water splitting for hydrogen generation.

High-quality g-C₃N₄-based films are critical components in the photoelectrodes in the PEC water splitting process. Specifically, the g-C₃N₄ films should be uniform, continuous, and a good contact with the substrates. However, the poor dispersibility/solubility of g-C₃N₄ closes the door for us to obtain the high-quality g-C₃N₄-based films by the fairly mature top-down approaches. As a result, the novel bottom-up approaches, including TVC, microcontact-printing-assisted access, solvothermal route, and direct growth, have been developed to fabricate g-C₃N₄ films with a high quality. The bottom-up methods ingeniously avoid the poor dispersibility/solubility issue of g-C₃N₄ that usually exists in the top-down approaches for g-C₃N₄ preparation. Consequently, they commonly provide higher-quality g-C₃N₄ films and better PEC water splitting performance than the top-down approaches (**Figure 17**).

Apart from the new preparation technologies, the modification of g-C₃N₄ films, such as functional groups grafting, heteroatoms doping, and g-C₃N₄-based composite films designing, are also effective to extend the visible-light absorption, reduce the recombination of photogenerated electrons and holes, and increase the electrical conductivity, thus enhancing their PEC performance. Compared with pristine g-C₃N₄ films, the modified g-C₃N₄-based films usually show a better PEC water splitting performance (**Figure 17**).

Figure 17 (1.5-column). Key factors in $g\text{-C}_3\text{N}_4$ films for advanced PEC water splitting.

Although these breakthroughs have been proven effective in promoting the PEC water splitting performance of the $g\text{-C}_3\text{N}_4$ -based materials, the current solar-to-hydrogen conversion efficiency is not enough to develop a commercial PEC water splitting device, the efficiency needs to be further improved to greater than 10% to reach a feasible commercialization level [149-151]. Thus, efforts should still be made on some key points, which are essential to achieve the further improvement of the materials, as following:

1) The bottom-up methods should be further modified, in terms of the starting materials design, reactor parameters optimization, and substrates pre-treatment for achieving the $g\text{-C}_3\text{N}_4$ film photoelectrodes with satisfactory PEC efficiency.

2) More types of functional groups and heteroatoms should be explored and introduced into the $g\text{-C}_3\text{N}_4$ frameworks to more efficiently enhance the PEC water splitting performance. Plenty of theoretical and experimental research has indicated that the introduction of functional groups or heteroatoms into $g\text{-C}_3\text{N}_4$ frame can adjust its intrinsic π conjugated structure, leading to significant changes of electronic state, band structure, and optical/electrical properties [152-156]. Additionally,

synergistic effects of functional groups and heteroatoms should be fully utilized by simultaneous introducing them into g-C₃N₄ films.

3) The defects play a non-negligible role on g-C₃N₄-based PEC water splitting process. Specifically, the defects in g-C₃N₄ films bring both the positive and negative effects on PEC performance of g-C₃N₄-based photoelectrodes simultaneously. On the one hand, the artificial introduction of defects into g-C₃N₄ films markedly enhances the optical and electrical properties [80, 88]. On the other hand, excessive defects may become the recombination sites of photogenerated electrons and holes, which significantly reduce the PEC efficiency [37]. Therefore, the defects in g-C₃N₄ films should be precisely controlled in order to achieve the maximizing improvement on PEC performance of g-C₃N₄-based photoelectrodes.

4) Although many types of g-C₃N₄-based composite films have been utilized as photoelectrodes for PEC water splitting, their morphologies were still not well controllable. For example, the photoelectrodes on certain nanostructures, such as nanotubes, nanorods, nanowires array, can be more effectively separated due to the geometrical effects. Besides, other well-designed g-C₃N₄-based heterostructures, for example, multifarious function layers, g-C₃N₄ nanosheets wrapped morphology, 2D/2D nanostructures, and introduction of co-catalyst also could exhibit the excellent PEC properties due to their novel nanostructures [157-163]. Therefore, design and fabrication of g-C₃N₄-based composite films with these nanostructures could provide a higher PEC water splitting performance than the uniform films.

5) Single-atom catalysis (SAC) and MXene materials have become two major research hotspots in energy conversion fields in recent years due to their outstanding photo(electro)catalytic and PEC performances [164-167]. Therefore, the SAC and MXene should be introduced into g-C₃N₄-based photoelectrodes in order to achieve a high-performance water splitting process.

6) The stability of g-C₃N₄-based photoelectrodes is very important for the large-scale and long-term application. To achieve a stable run, the modified technologies should be further researched, including obtaining strong adhesion of g-C₃N₄ films on substrates and protecting g-C₃N₄ from photo- or chemical-corrosion by protective layers in the practical PEC water splitting process.

To summarize, although there are a mass of urgent issues, the prospect of g-C₃N₄-based PEC water splitting for hydrogen generation is still hopeful due to the excellent and unique physicochemical properties owned by g-C₃N₄ material. With further development of related researches, these obstacles that hinder the application of g-C₃N₄ films in PEC water splitting will be thoroughly overcome. At last, we believe that the g-C₃N₄ films can pave an avenue for us to achieve an efficient and stable PEC water splitting process.

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