Graphitic Carbon Nitride Materials for Photocatalytic Hydrogen Production via Water Splitting: A Short Review

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Abstract: The generation of photocatalytic hydrogen via water splitting under light irradiation is attracting much attention as an alternative to solve such problems as global warming and to increase interest in clean energy. However, due to the low efficiency and selectivity of photocatalytic hydrogen production under solar energy, a major challenge persists to improve the performance of photocatalytic hydrogen production through water splitting. In recent years, graphitic carbon nitride (g-C₃N₄), a non-metal photocatalyst, has emerged as an attractive material for photocatalytic hydrogen production. However, the fast recombination of photoexcited electron–hole pairs limits the rate of hydrogen evolution and various methods such as modification, heterojunctions with semiconductors, and metal and non-metal doping have been applied to solve this problem. In this review, we cover the rational design of g-C₃N₄-based photocatalysts achieved using methods such as modification, metal and non-metal doping, and heterojunctions, and we summarize recent achievements in their application as hydrogen production photocatalysts. In addition, future research and prospects of hydrogen-producing photocatalysts are also reviewed.

Keywords: graphitic carbon nitride; photocatalysis; H₂ generation; water splitting

1. Introduction

As interest in the fossil fuel depletion and environmental pollution has increased, the development of clean energy has also recently attracted increased attention. It is important to find new alternative energy sources because of the increased use of energy, depletion of fossil fuels, and the need for sustainable energy development [1]. Among the many alternative energy sources, hydrogen-based energy systems are considered candidates for future energy because they are nonpolluting, inexhaustible, efficient, and can provide high-quality energy services in a wide range of applications [2,3]. However, most hydrogen production processes are based on natural gas [4], coal [5], crude oil [6], or the electrolysis of water [7], and unfortunately, the application of most of these processes is limited because heat and electrical energy are required. Thus, photocatalytic hydrogen production using solar energy, a clean energy resource for the foreseeable future, is considered to be an attractive way of solving the global energy issue and environmental pollution [8,9].

The overall water splitting by a photocatalyst under sunlight irradiation enables the production of environmentally friendly molecular hydrogen and does not use fossil fuel [10]. A photocatalytic system should consider the following prerequisites. First, to absorb as many photons as possible, the photocatalyst must have a narrow band-gap; to generate hydrogen from water splitting, the bottom of the conduction band (CB) must be more negative than the reduction potential of H⁺/H₂ and the top of the valence band (VB) must be more positive than the oxidation potential of H₂O/O₂ [11]. Second, efficient charge separation and fast charge transport that simultaneously avoid bulk and surface charge...
recombination are essential to transfer the photogenerated charge to the surface reaction site [12]. Third, because the charge carriers at the interface lack the capacity to boost the transportation process, the charge carriers mostly move via a random path and require a surface chemical reaction that is active between the charge carrier and the water or other molecules [13]. A variety of semiconductor materials such as TiO$_2$, ZnO, CdS, and WO$_3$ have been extensively studied for hydrogen generation via photocatalytic water splitting [14–17]. Among them, WO$_3$ absorbs visible light but has a problem in that the CB is not useful for hydrogen production because it is lower than the H reduction potential [18,19]. In addition, hydrogen evolution through photocatalytic water splitting has been extensively studied for metal oxides, quantum dots, and metal–organic frameworks, etc. However, some methods are difficult to use due to their low efficiency under visible light and the fast recombination rate of the electron–hole pairs [20–25]. Therefore, it is a major challenge to develop photocatalysts that exhibit stable water-splitting performance under visible-light irradiation for the efficient use of solar energy.

Recently, graphitic carbon nitride (g-C$_3$N$_4$) has attracted attention as a hydrogen-generating photocatalyst via water splitting. g-C$_3$N$_4$ is synthesized by the thermal condensation of nitrogen-rich precursors with a tri-s-triazine ring structure such as cyanamide, dicyandiamide, urea, or thiourea, resulting in a graphene-like structure after exfoliation (Figure 1) [26]. In addition, it has a band gap of ~2.7 eV corresponding to 460 nm in the visible range and high thermal and chemical stability [27].

Figure 1. Schematic illustration of the synthesis process from the possible precursors of g-C$_3$N$_4$. Reproduced with permission from [26]; copyright (2016), the American Chemical Society.

However, there are some drawbacks to using g-C$_3$N$_4$ as a water-splitting photocatalyst. The relatively large band-gap and low charge-carrier mobility limit the electron and hole separation and transport and thus limit the effective use of visible light [28]. Thus, increasing hydrogen production during photocatalytic water splitting under visible-light irradiation is necessary through a variety of methods such as creating heterojunctions with semiconductors and doping with other elements [29–33]. As a result, the focus of this review is on summarizing the current and prospective advances in photocatalysis research based on g-C$_3$N$_4$ that make it effective even under visible-light irradiation.

2. The Principles of H$_2$ Generation via Water Splitting

Photocatalytic reactions can be divided into three parts. The first step is to obtain photons with energies that exceed the photocatalyst’s band gap of the electron–hole pairs, the second step is the separation of the carrier in the photocatalyst by transfer, and the third step is the reaction between the carrier and H$_2$O. In addition, the electron–hole pairs are concurrently combined with each other.
The photocatalyst is involved in the production of hydrogen, but the lowest position of the CB should be lower than the reduction position of H₂O/H₂ and the position of the VB should be higher than the potential of H₂O/O₂ [34–40].

Figure 2 shows the band gap and band edge positions of various semiconductor photocatalysts [41]. A variety of these, such as ZnO, TiO₂, and WO₃, have been studied for solar hydrogen production and degradation of organic pollutants [42–45]. However, although there are exceptions for some semiconductor photocatalysts, most of the semiconductor photocatalysts have low efficiency under visible-light irradiation. Therefore, it is a major challenge to develop photocatalysts that efficiently exploit solar energy.

Recently, g-C₃N₄, which has a unique electron band structure for photo-oxidation and reduction, has been confirmed by several researchers as an efficient photocatalyst for visible-light activation for photochemical reactions [46]. This achieves the photoexcited state when creating electron–hole pairs where photogenerated electrons are involved in the reduction process while the holes are consumed in the oxidation process [47]. The excited electrons and holes act as reactive species that are highly oxidizing and reducing. The excited electrons and holes travel to the active sites on the surface, thereby splitting the water into oxygen and hydrogen (Figure 3) [48]. However, despite its excellent electron and optical properties, g-C₃N₄ has low efficiency for visible-light utilization and a high recombination speed of photoelectric carrier, resulting in the poor formation of radical species causing redox reaction during the photocatalytic reaction [49]. It has a low specific surface area, provides fewer reactive sites, and reduces light harvesting. In addition, the low bandgap (2.7 eV) of g-C₃N₄ is still quite large for efficient visible-light harvesting and has limited use, leaving much of the visible-light spectrum unexploited.
The band gap is 2.75 eV for the monolayer mesoporous g-C$_3$N$_4$ nanomesh and 2.59 eV for the bulk counterparts. The band gap is 2.75 eV for the monolayer mesoporous g-C$_3$N$_4$ nanomesh and bulk counterparts. The band gap is 2.75 eV for the monolayer mesoporous g-C$_3$N$_4$ nanomesh and bulk counterparts. The band gap is 2.75 eV for the monolayer mesoporous g-C$_3$N$_4$ nanomesh and bulk counterparts.

In 2016, Han et al. [59] reported an atomically thin mesoporous nanomesh of g-C$_3$N$_4$ for hydrogen evolution by highly efficient photocatalysts (Figure 4a) fabricated via the solvothermal exfoliation of mesoporous g-C$_3$N$_4$ prepared by the thermal polymerization of freeze-dried nanostructured precursors. The delamination of the layer material to provide the two-dimensional single-atom sheet has led to unique physical properties such as a large surface area, a very high unique carrier mobility, and a significant change in the energy band structure [60]. The mesoporous g-C$_3$N$_4$ nanomesh shows inherent structural advantages, electron transfer capability, and efficient light harvesting. Figure 4b shows the electronic band structure of the monolayer mesoporous g-C$_3$N$_4$ nanomesh and bulk counterparts. The band gap is 2.75 eV for the monolayer mesoporous g-C$_3$N$_4$ nanomesh and 2.59 eV for the bulk counterpart, as determined from optical absorption spectra. The VB of the monolayer mesoporous g-C$_3$N$_4$ nanomesh (2.41 eV) identified via X-ray photoelectron spectroscopy is also 0.35 eV higher than the bulk counterparts (2.06 eV). The CB is upshifted by 0.51 eV when considering the 0.16 eV increase in the VB and a negative shift of 0.35 eV. The monolayer mesoporous g-C$_3$N$_4$ nanomesh exhibits significantly improved the light-harvesting ability mainly due to the multiple scattering effect and the presence of defect sites associated with the mesoporous surface. A 30 h reaction was performed with intermittent evacuation every 5 h to confirm the hydrogen production ability of mesoporous g-C$_3$N$_4$.
nanomesh under visible-light irradiation (Figure 4c). As a result, the 2.6 mmol H₂ gas (59 mL) produced by the atomically thin mesoporous g-C₃N₄ nanomesh was not visibly deactivated and the H₂ gas was generated continuously. Wavelength-dependent H₂ evolution shows the optical absorption spectrum of monolayer g-C₃N₄ nanomesh, indicating that the H₂ generation is driven by photoinduced electrons in g-C₃N₄ (Figure 4d). In conclusion, the mesoporous g-C₃N₄ nanomesh produces an atomically thin mesoporous layer during the freeze-dried assembly and solvothermal exfoliation. Its good application benefits from structural advantages for light harvesting, electron transport, and accessible reaction sites [61]. This new type of mesoporous g-C₃N₄ nanomesh could be applied to photocatalytic and various engineering fields.

Figure 4. (a) Schematic illustration of atomically thin mesoporous g-C₃N₄ nanomesh photocatalyst and (b) a band gap schematic of the monolayer mesoporous g-C₃N₄ nanomesh and bulk counterparts. (c) Hydrogen production rate of the monolayer mesoporous g-C₃N₄ nanomesh, the bulk counterpart, and the traditional g-C₃N₄ bulk under visible-light irradiation. (d) H₂ evolution rate on the monolayer mesoporous g-C₃N₄ nanomesh with wavelength dependence. Reproduced with permission from [59]; copyright (2016), American Chemical Society.

In 2018, Zhao et al. [62] reported the fabrication of a mesoporous g-C₃N₄ consisting of hollow nanospheres (MCNHN) via a simple vapor-deposition method that improved hydrogen production under visible-light irradiation. Figure 5a shows the photocatalytic hydrogen evolution by MCNHN under visible-light irradiation. Both MCNHN and bulk g-C₃N₄ achieved a stable average rate of hydrogen production within 4 h, but the hydrogen evolution of MCNHN was 659.8 µmol g⁻¹ h⁻¹, which is 22.3 times greater than bulk g-C₃N₄ (29.6 µmol g⁻¹ h⁻¹). The excellent hydrogen production activity of MCNHN is due to its well-defined structure. The increased surface area provides more active sites in the photocatalytic reaction, thereby allowing more light to be harvested. Moreover, the planarized unit layer and the decreased interlayer space of g-C₃N₄ crystals facilitate the transfer and separation of photoinduced charge carriers in MCNHN. As a result, photocatalytic hydrogen generation is significantly improved due to the large surface area and decreased interlayer space of g-C₃N₄. Figure 5b shows the proposed photocatalytic mechanism of H₂ evolution for MCNHN based on the aforementioned results and the literature. The active site of MCNHN absorbs visible
light. Electrons in the VB are excited to the CB by absorption of photons, and are then transferred to the Pt nanoparticles loaded on the surface of MCNHN; the corresponding photoexcited holes remain in the VB. The electron-rich Pt nanoparticles become active sites where water can be split into hydrogen. In addition, multiple reflections of visible light in the MCNHN with Pt nanoparticles improves light absorption.

![Figure 5](image_url)  
**Figure 5.** (a) Time course of H$_2$ evolution and (b) a schematic mechanism for photocatalytic H$_2$ evolution on MCNHN. Reproduced with permission from [62]; copyright (2018), Elsevier.

### 3.2. Heterojunctions and Photocatalysis

Electron–hole charge pairs formed by the photocatalytic hydrogen evolution reaction are transferred to the surface of the photocatalyst or else recombine with each other. To better understand this point, let us illustrate it by reviewing the presentation in [63]: a comparison of the influence of gravitational force on a man jumping off the ground and electrons jumping from the VB to the CB (Figure 6a,b, respectively). If a man (electron) jumps from the ground (VB) into the sky (CB), it will return to the floor quickly (recombine with the hole) due to gravitational force. However, a stool (semiconductor B) can be provided to get the man off the ground (separate the photogenerated electron–hole pair), as illustrated in Figure 6c,d, respectively. Subsequently, the aforementioned man will land again on the stool rather than the ground (the electron–hole pair recombination will be inhibited). Preventing electron–hole recombination is an urgent issue, but it can be achieved by the proper design of materials [64–66]. Many methods have been proposed to achieve better separation of the photogenerated electron–hole pairs in semiconductor photocatalysts, such as element combining, metal and non-metal doping, and heterojunctions [67–72]. Among these strategies, heterojunctions in photocatalysts have proved to be one of the most promising methods for efficient photocatalyst preparation due to their improved separation of electron–hole pairs [73].
3.2.1. Semiconductor Heterojunction Photocatalysts

Suppressing the electron–hole recombination rate is the most important solution to increase photocatalytic efficiency. Bulk g-C\textsubscript{3}N\textsubscript{4} has low ability to collect visible light, low charge-transport properties, and small surface area, so there have been many studies to make it an efficient photocatalyst [74]. Various strategies have been proposed to achieve better electron–hole pair separation such as element combining, metal doping, and creating heterojunctions. Among these strategies, g-C\textsubscript{3}N\textsubscript{4}/semiconductor heterojunctions have shown the improved separation capability of electron–hole pairs; the charge carrier is transferred through the heterostructure interface to inhibit recombination, thereby improving the photocatalytic performance [75–77]. In addition, a g-C\textsubscript{3}N\textsubscript{4}/semiconductor heterostructure can be formed by combining a visible-light excited photocatalyst semiconductor material having a narrow band-gap and a photoexcited photocatalyst having a large band-gap in a coupling process; the connection between the two different kinds of photocatalyst having different band structures induces a new band arrangement [78,79].

In 2017, Zhang et al. [80] reported the in situ synthesis of a g-C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} heterostructure photocatalyst which greatly improved the hydrogen evolution performance under visible light. The g-C\textsubscript{3}N\textsubscript{4} nanosheets were synthesized by calcining urea at 550 °C for 4 h. Two hundred milligrams of the as-prepared g-C\textsubscript{3}N\textsubscript{4} nanosheets were dispersed in 20 mL ethanol and sonicated for 1 hour to obtain a homogeneous suspension. Under continuous stirring, 40 mL of ammonia solution (~28 wt%) and tetrabutyl titanate (TBT) (0, 100, 200, 300 and 400 μL) were added and stirred for 12 h to achieve the in situ synthesis of amorphous TiO\textsubscript{2}. The obtained products were expressed as CNTO-\(x\) (\(x = 0–4\)) according to the TBT content. As shown in Figure 7a, the shape of the CNTO-2 sample seen in a transmission electron microscopy (TEM) image shows that the TiO\textsubscript{2} nanoparticles are uniformly distributed in the g-C\textsubscript{3}N\textsubscript{4} nanosheets. As a result, there is uniform interfacial contact between the

![Figure 6. Schematics of (a) the influence of gravitational force on a man jumping; (b) recombination of photocatalyst electron–hole pair; (c) using stool to keep a man from returning to the ground; and (d) electron–hole pairs separated in a heterojunction photocatalyst. Reproduced with permission from [63]; copyright (2017), John Wiley & Sons, Inc.](image-url)
TiO$_2$ phase and the g-C$_3$N$_4$ phase. Figure 7b shows the average rate of hydrogen production within 3 h. Pure TiO$_2$ does not react with visible light and produces negligible H$_2$, while CNTO-0 exhibits a low hydrogen production rate of 15 µmol h$^{-1}$ due to the fast recombination of photogenerated charge carriers. In contrast, the CNTO-2 sample exhibits significantly improved hydrogen production performance at 40 µmol h$^{-1}$. However, as the amount of TiO$_2$ is further increased, TiO$_2$ occupies the surface of g-C$_3$N$_4$ resulting in less active sites for H$_2$ evolution. The proposed mechanism of heterostructure composites is also shown in Figure 7c. According to previous reports, the CB and VB potentials of g-C$_3$N$_4$ and TiO$_2$ are $-1.12$ and $+1.58$ V, and $-0.29$ and $+2.91$ V, respectively. Under visible light irradiation, only g-C$_3$N$_4$ can absorb light to generate electron–hole pairs. However, in pure g-C$_3$N$_4$, photogenerated electrons and holes recombine rapidly, and only a few of the electrons participate in the reaction, resulting in low reactivity. When g-C$_3$N$_4$ is modified by TiO$_2$ to form a heterojunction structure, the CB edge of g-C$_3$N$_4$ is more negative than TiO$_2$, so that electrons excited in the CB of g-C$_3$N$_4$ can be injected directly into the CB of TiO$_2$. Consequently, Pt$^{2+}$ adsorbed on the surface is reduced by electrons transferred from the CB of TiO$_2$, and newly formed Pt nanoparticles are deposited on the surface of TiO$_2$ as an efficient cocatalyst for hydrogen production. The electrons then accumulate in Pt nanoparticles and participate in hydrogen evolution. Therefore, the photocatalytic activity of the g-C$_3$N$_4$/TiO$_2$ composite with Pt nanoparticles as a cocatalyst is significantly improved.

Figure 7. (a) A TEM image of CNTO-2, (b) H$_2$ evolution rates of the CNTO-$x$ samples under visible light ($\lambda \geq 420$ nm), and (c) an illustration of the g-C$_3$N$_4$/TiO$_2$ heterojunction system. Reproduced with permission from [80]; copyright (2017), The Royal Society of Chemistry.

3.2.2. Z-Scheme Heterojunction Photocatalysts

In 2017, Lu et al. [81] reported a Z-scheme photocatalyst that improved the photocatalytic hydrogen production of g-C$_3$N$_4$ nanosheets by loading porous silicon (PSi). The Z-scheme heterostructure improved the photocatalytic H$_2$ evolution performance by loading PSi onto the g-C$_3$N$_4$ photocatalyst. g-C$_3$N$_4$/PSi composites were prepared by the facile polycondensation reaction of PSi with urea at various PSi content ratios and included pure g-C$_3$N$_4$ that was not PSi loaded for comparison. The photocatalytic performance of the g-C$_3$N$_4$/PSi composites and pure g-C$_3$N$_4$ in Figure 8a was evaluated by H$_2$ evolution from water under visible-light irradiation. For composite materials loaded with PSi on g-C$_3$N$_4$ nanosheets, the rate of H$_2$ evolution was better than that of pure g-C$_3$N$_4$ (427.28 µmol g$^{-1}$ h$^{-1}$). In particular, the g-C$_3$N$_4$/2.50 wt% composite exhibited the highest photocatalytic activity with a hydrogen evolution rate of 870.58 µmol g$^{-1}$ h$^{-1}$, which is around twice as high as that of pure g-C$_3$N$_4$. However, in the case of the Si-based photocatalyst, a passive oxide film was formed on the Si surface, and thus the stability suffered. When the PSi content was larger than 2.50 wt%, the H$_2$ generation activity was lower. Figure 8b depicts an energy band diagram of g-C$_3$N$_4$/PSi with the redox potential of the photocatalytic reaction. The Z-scheme heterostructure system is recognized as the photocatalytic mechanism for the g-C$_3$N$_4$/PSi composite, and the electrons excited from the CB of PSi in the photocatalyst system can be transferred to the VB of g-C$_3$N$_4$. In addition, the holes generated in g-C$_3$N$_4$ can move to the CB of PSi through the interface formed between g-C$_3$N$_4$ and PSi. The recombination at the interface between the electrons and the holes accumulates a large number of bonds and acts as a recombination center for the electron–hole pairs [82,83]. As a result, the efficiency
of the photogenerated electron–hole pairs is improved, thereby improving photocatalytic hydrogen production under visible-light irradiation.

![Figure 8](image-url)

**Figure 8.** (a) Photocatalytic H₂ evolution with 100 mg pure g-C₃N₄ and g-C₃N₄/PSi composite photocatalysts under visible light (400 nm) and (b) a schematic diagram of the g-C₃N₄/TiO₂ heterojunction system. Reproduced with permission from [81]; copyright (2017), Elsevier.

### 3.3. Metal- and Non-Metal-Doped g-C₃N₄

Among the strategies for making g-C₃N₄ as a photocatalyst capable of effective hydrogen production, sufficient doping with metallic and nonmetallic elements is known to enhance the photocatalytic activity of g-C₃N₄. Metal doping is an effective strategy to adjust the electronic structure of g-C₃N₄ and promotes surface kinetics to accelerate photogenerated electron transfer and provide active sites for better photocatalytic hydrogen production. In addition, the light transmittance can be maximized since the spatial distribution and the particle size of the metal can be finely controlled to provide a sufficient active size.

In 2016, Li et al. [84] reported water splitting by Cu- and Fe-doped g-C₃N₄ visible-light-activated photocatalysts. Figure 9a shows the mechanism of water splitting by light-driven catalysis with Fe- and Cu-doped g-C₃N₄. Under visible-light irradiation, water is converted to H₂ and H₂O₂, and then H₂O₂ is further converted to O₂ and H₂O via the photocatalytic imbalance path. After absorbing visible light, g-C₃N₄ forms excited electrons and holes by electron catalysis, and the electrons move from the energy potential difference between g-C₃N₄ and Fe or Cu to the metal Fe or Cu sites. The potential of these electrons is around −0.25 eV and has enough force to induce H₂O₂ disproportionation to form ·OH and OH⁻. In the hole catalytic process (HCP), OH⁻ and H₂O₂ could form the ·O₂⁻ and H₂O species reaction with the holes. Finally, O₂⁻ and OH can recombine to form O₂. Electron catalysis is an energy-consuming process whereas HCP and recombination processes can be viewed as energy-releasing processes. Figure 9b shows the oxygen and hydrogen evolution rates of FeC₃N₄ (0.37 wt%) and CuC₃N₄ (0.42 wt%) under visible-light irradiation (λ ≥ 420 nm) for 12 h. In this case, the production of hydrogen and oxygen by the CuC₃N₄ and FeC₃N₄ photocatalysts were 1.4 and 0.5 μmol, and 2.1 and 0.8 μmol, respectively. In addition, the potential of the FeC₃N₄ photocatalyst is obviously lower than those of the g-C₃N₄ and Cu/g-C₃N₄ photocatalysts, which leads to the O₂ and H₂ evolution activity over the Fe/g-C₃N₄ photocatalyst being clearly higher than that over the g-C₃N₄ and Cu/g-C₃N₄ photocatalysts. The findings of this study give new insight into the designing of efficient catalysts for overall water splitting.
Non-metal doping is a useful strategy to adjust the electronic structure of g-C$_3$N$_4$ and to increase the photocatalytic effect by promoting the reaction surface. When the non-metal elements B, N, O, P, and S are used to dope g-C$_3$N$_4$, the photocatalyst is efficiently optimized by lowering the charge recombination rate due to optical absorption and accelerated charge mobility, and thus the amount of H$_2$ produced can be increased [85,86]. Consequently, the potential of the Fe/g-C$_3$N$_4$ photocatalyst is obviously lower than those of the g-C$_3$N$_4$ and Cu/g-C$_3$N$_4$ photocatalysts. This indicates that the Fe/g-C$_3$N$_4$ photocatalyst has higher activity on photocatalytic hydrogen evolution than the g-C$_3$N$_4$ and Cu/g-C$_3$N$_4$ photocatalysts. The findings of this study give new insights into designing efficient photocatalytic hydrogen generation and catalysts through overall water splitting.

In 2018, Feng et al. [87] reported P nanostructures with P-doped g-C$_3$N$_4$ as light photocatalysts for H$_2$ evolution. P nanostructures and P-doped g-C$_3$N$_4$ (P@P-g-C$_3$N$_4$) were synthesized via a solid reaction, and P@P-g-C$_3$N$_4$ showed increased optical absorption, high-efficiency transmission, and efficient separation of photogenerated electron–hole pairs. When C atoms are replaced with P atoms (the gray and red balls in Figure 10a, respectively) in the base frame of g-C$_3$N$_4$, the extra electrons are decentralized into a π-conjugated triazine ring and generate a positive-charge P$^+$ center, thereby facilitating rapid separation of the photogenerated excited electrons. Furthermore, efficient band gap transfers between the P and P-doped g-C$_3$N$_4$ leads to a significant improvement in photoactivity (Figure 10b). P-doped g-C$_3$N$_4$ photoexcited electrons can be delivered to phosphorus via intimate contact because the CB edge of g-C$_3$N$_4$ (−1.2 V vs. normal hydrogen electrode (NHE)) is more negative than P (−0.25 V vs. NHE) which provides an interface under the buildup of the internal electric field. Thus, the extra electrons superimposed on the P surface can easily be captured by the oxygen molecules in the solution and react with ·O$_2^-$ and ·OH. Figure 10c,d shows the hydrogen evolution yield and the improvement in hydrogen production ability of the photocatalysts prepared at different weight ratios of P@g-C$_3$N$_4$. P@P-g-C$_3$N$_4$-15 showed the highest hydrogen production rate (941.80 μmol h$^{-1}$ g$^{-1}$), which is around four times that of conventional g-C$_3$N$_4$. 

Figure 9. (a) A schematic diagram of the water splitting mechanism by Fe/C$_3$N$_4$ and Cu/C$_3$N$_4$ photocatalysts under visible-light irradiation. (b) Production of H$_2$ and O$_2$ by water splitting by the Fe/C$_3$N$_4$ and Cu/C$_3$N$_4$ photocatalysts under visible-light irradiation for 12 h. Reproduced with permission from [84]; copyright (2015), American Chemical Society.
4. Summary and Perspectives

Photocatalytic action is a key factor for the future of environmental pollution and hydrogen generation due to water splitting. Over the past several years, photocatalytic reactions have emerged as a promising method to generate hydrogen, and interest in the photocatalyst g-C₃N₄ has received attention in a variety of scientific disciplines. However, a major problem that limits the rate of production of H₂ by g-C₃N₄-based photocatalysis is the fast recombination of photoexcited electron–hole pairs. This problem can be solved in a variety of ways, including modification, heterojunctions, and metal and non-metal doping. Table 1 summarizes the literature on the photocatalytic H₂ generation of g-C₃N₄-based materials. We reviewed the rational design of photocatalysts for efficient H₂ generation though a variety of methods. Furthermore, the improvement of g-C₃N₄-based photocatalysts will likely result from advances in science. Herein, we have covered the recent progress of g-C₃N₄-based materials involved in hydrogen production in improving their overall photocatalytic activity and have characterized their performance and importance. We hope that this report will support further research efforts related to photocatalytic development.
Table 1. Photocatalytic H$_2$ generation of g-C$_3$N$_4$-based materials.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Type</th>
<th>Mass Fraction of g-C$_3$N$_4$</th>
<th>Mass of Photocatalyst</th>
<th>Reactant Solution</th>
<th>Light Source</th>
<th>H$_2$ Generation Rate ($\mu$mol h$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 4</td>
<td>Monolayer mesoporous g-C$_3$N$_4$ nanomesh</td>
<td>100 wt%</td>
<td>0.01 g</td>
<td>100 mL of 10 vol% triethanolamine aqueous solution; 3 wt% Pt as a cocatalyst</td>
<td>300 W Xe lamp (&gt;420 nm)</td>
<td>85.10</td>
<td>[59]</td>
</tr>
<tr>
<td>Figure 5</td>
<td>Mesoporous g-C$_3$N$_4$ comprising hollow nanospheres</td>
<td>100 wt%</td>
<td>0.1 g</td>
<td>100 mL of 10 vol% triethanolamine aqueous solution; 3 wt% Pt as a cocatalyst</td>
<td>300 W Xe lamp (&gt;420 nm)</td>
<td>65.98</td>
<td>[62]</td>
</tr>
<tr>
<td>Figure 7</td>
<td>g-C$_3$N$_4$ nanosheets/TiO$_2$</td>
<td>50 wt%</td>
<td>0.05 g</td>
<td>100 mL of 10 vol% triethanolamine aqueous solution; 3 wt% Pt as a cocatalyst</td>
<td>300 W Xe lamp (&gt;420 nm)</td>
<td>40</td>
<td>[80]</td>
</tr>
<tr>
<td>Figure 8</td>
<td>Porous Si-loaded g-C$_3$N$_4$</td>
<td>97.50 wt%</td>
<td>0.1 g</td>
<td>100 mL of 10 vol% triethanolamine aqueous solution; 3 wt% Pt as a cocatalyst</td>
<td>300 W Xe lamp (&gt;400 nm)</td>
<td>87.05</td>
<td>[81]</td>
</tr>
<tr>
<td>Figure 9</td>
<td>Fe-doped g-C$_3$N$_4$</td>
<td>99.63 wt%</td>
<td>0.01 g</td>
<td>Pure water; without other cocatalyst</td>
<td>300 W Xe lamp (&gt;420 nm)</td>
<td>0.175</td>
<td>[84]</td>
</tr>
<tr>
<td>Figure 10</td>
<td>Cu-doped g-C$_3$N$_4$</td>
<td>99.58 wt%</td>
<td>0.01 g</td>
<td>Pure water; without other cocatalyst</td>
<td>300 W Xe lamp (&gt;420 nm)</td>
<td>0.175</td>
<td>[84]</td>
</tr>
<tr>
<td>Figure 8</td>
<td>P@P-doped g-C$_3$N$_4$</td>
<td>75 wt%</td>
<td>0.1 g</td>
<td>100 mL of 10 vol% triethanolamine aqueous solution; 1 wt% Pt as a cocatalyst</td>
<td>300 W Xe lamp (&gt;420 nm)</td>
<td>94.18</td>
<td>[87]</td>
</tr>
</tbody>
</table>
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