Chapter 5

Graphitic Carbon Nitride based Photocatalytic Systems for High Performance Hydrogen Production: A Review

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Abstract

The hydrogen (H₂) production using solar-power is a novel way of harvesting and meeting the ever-increasing energy demands. It also helps in alleviating the global warming issues by decreasing the carbon footprints. The photocatalyst required for H₂ production should possess some specific properties such as high charge separation, appreciable H₂ production activity, chemical and thermal stability, abundant availability, and cost effectiveness, etc. The metal free graphitic- carbon nitride (g-C₃N₄)-based photocatalysts have grabbed considerably large interest in the area of visible-light photocatalytic H₂ production. It has extraordinary chemical stability, earth-abundant, attractive band structure, and easy fabrication. Herein, various approaches such as band gap engineering, nanostructure design, and heterojunction construction using various examples presented in literature are described. We have also discussed various nano heterojunctions of g-C₃N₄ which have been used effectively for the hydrogen production.

Keywords

g-C₃N₄, Visible Light, Hydrogen Generation, Heterojunction, Photocatalytic

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1. Introduction

The rapid enhancement in the consumption of fossil fuels as an energy source has led to their fast depletion since they are limited and have high exhaustibility. Presently, 85% of the H₂ production is achieved by the combustion of fossil fuels, that leads to the annual production of ~500 metric tonnes of carbon dioxide (CO₂) as a by-product [1]. Solar energy on the other hand is an inexhaustible, pure and sustainable source. So, we require highly efficient materials that can convert the solar energy into some other form that could be utilized by the human race [2, 3]. In recent years, conversion of solar energy to chemical energy via water splitting has fascinated many researchers because about 72% of the earth's surface is covered with water [4, 5]. Until now, multiple techniques have been formulated for the production of H₂ and that includes coal gasification, renewable liquid, pyrolysis of biomass, and bio-oil processing, water splitting using energy resources, water splitting by electrochemical and biological materials [6].

The water splitting using TiO₂ catalyst under the influence of UV radiations was performed firstly by Fujishima and Honda in 1972 [7]. Following that, various studies were performed using variety of semiconductors. Process of water splitting for H₂ generation occurs in three steps; (i) production of electrons and holes upon light illumination; (ii) separation of

generated charges and their proper movement over the catalyst surface and (iii) reduction of H^+ to H_2 by the electrons and oxidation of H_2O to O_2 by the holes [8]. During water splitting, there occurs two processes, namely, oxygen evolution reaction (OER) by holes and hydrogen evolution reactions (HER) by electrons. The material or catalyst performance during water splitting is determined by solar to hydrogen conversion efficiency (STH) and apparent quantum efficiency (AQE). Their characteristic equations are [9]:

$$STH = \frac{\text{Output energy as } H_2}{\text{Energy of incident solar light}} \quad (i)$$

$$AQE = \frac{n * H_2 \text{ generation}}{\text{Incident photon}} \quad (ii)$$

Where n represents the number of electrons required for the process (2 in case of H_2 production)

2. Metal free photocatalyst: Graphitic carbon nitride

As mentioned in the above section, the semiconductor materials can be used for water splitting. It should meet some of the characteristic features such as (a) the valence and conduction band or both should match with the reduction and oxidation potential of water; (b) the photocatalyst should be active in the visible range and (c) it should have high separation and easy transportation of charges [10, 11]. Metal-free photocatalysts have high utilization in the past few decades as a substitute to metal-based photocatalysts [12]. Some of the metal free photocatalysts illustrates even similar and enhanced activity as compared to the metal-based photocatalysts. In the recent decades, the utilization of carbon-based metal-free photocatalysts for water splitting have experienced much significance due to their low cost, easy availability and ecofriendly nature. Among these, g- C_3N_4 is the most popular photocatalyst [13, 14].

2.1 Chemical structure of g- C_3N_4

The molecular formula of this family is near to C_3N_4 , however, it does contain some amount of hydrogen too. These structures are based on s- heptazine and s-triazine units which exhibits different properties under different reaction conditions [15]. The final structure formed using these two different units are shown in Figure 1. The s-triazine based C_3N_4 units exhibits some special electronic properties due to the presence of delocalized electrons and lone pair of electrons on nitrogen. In addition, its thermal and chemical permanence marks it a favourable candidate for several applications. Because of its

distinctive semiconductor properties, it can display high catalytic activity for multiple reactions [16].

Various methodologies have been reported in literature for the synthesis of $g\text{-C}_3\text{N}_4$ such as solvothermal, chemical vapour deposition (CVD), thermal nitration, and solid state reaction [10, 17, 18]. However, recently employed method, thermal condensation is quite a facile technique as compared to the above mentioned. In this method, the nitrogen-rich species such as melamine, urea, cyanamide, and dicyandiamide are used that experience self-condensation with deammoniation process via thermal reaction. Figure 2 shows the different fabrication methods with the probable precursors for the synthesis of $g\text{-C}_3\text{N}_4$.

In spite of the above advancements, the complete crystal structure of $g\text{-C}_3\text{N}_4$ has not been fully determined. To the best of our knowledge the most recent work on the 3D structure of $g\text{-C}_3\text{N}_4$ is carried out by Tyborski [19]. They used XRD to solve the structure of $g\text{-C}_3\text{N}_4$. However, due to the lack of long range order in the material which prevents the proper structure refinement, conventional XRD alone is not sufficient. On the other hand, total scattering data, which associates information from the diffuse scattering regarding short range order, can provide additional information useful for its structure determination [19].

Figure 1: Chemical structure of triazine.

Figure 2. Different fabrication methods with the probable precursors for the synthesis of $g\text{-C}_3\text{N}_4$.

2.2 Electronic properties of $g\text{-C}_3\text{N}_4$

At ambient environment, $g\text{-C}_3\text{N}_4$ is considered to be the most stable allotrope [20, 21]. They are polymeric organic materials that have five different allotropes such as α , β , cubic, pseudocubic, and graphitic [22]. The $g\text{-C}_3\text{N}_4$ is a unique semiconductor photocatalyst that has visible-light response up to 455 nm, equivalent to the narrow band gap of 2.7 eV [23, 24]. Its valence band is formed by the N2p orbitals and the conduction band displays the hybridized C2p and N2p orbitals [25, 26].

The $g\text{-C}_3\text{N}_4$ is a poly conjugated semiconductors made of carbon and nitrogen atoms and it is characterized by a layered graphitic-like structure [27]. The fully polymerized form of $g\text{-C}_3\text{N}_4$, characterized by a C: N of 0.75, cannot be practically attained. It can be easily prepared via solid state synthesis from cheap materials such as melamine. It is insoluble in most solvents and shows great stability in superlative conditions (pH=0 and pH=14). Due

to these properties, it has currently attracted great attention for various catalytic applications, in specific photo catalysis for hydrogen evolution from water [27].

2.3 Strategies for improving the properties of g-C₃N₄

The g-C₃N₄ with a layered structure has shown brilliant applications, like as in the field of hydrogen evolution reaction and oxygen reduction [28]. However, there is still limited electron transfer ability of perfect g-C₃N₄ due to its chemical stability. Proof of concept studies has been focused on promoting electron transfer and enhancing the concentration of active site [15, 29], among which several strategies has been reported such as (a) hetero atoms doping is a successful strategy to modify the materials with various morphologies and electronic structures [30, 31]. Zhu *et al.*, 2015 synthesized the doped g-C₃N₄ by a condensation method, as a result, doping not only significantly changed its morphology and its surface property of g-C₃N₄ but also changed its electronic structure and increased its ionic conductivity [32]. (b) The structural modification has also been reported for increasing the activity of pristine g-C₃N₄. By modifying the structure to 0-D, 1-D, 2-D and 3-D structures, the optical, physiochemical, diffusion distance of charge carriers and number of redox active sites can be properly optimized [33]. (c) In addition, copolymerization of pristine g-C₃N₄ helps in narrowing the band gap that aids in utilizing the entire visible range. (d) Formation of heterojunction with other semiconductors enhances the separation of charge carriers and transfer to different sites [34, 35].

2.3.1 Structural modification

By monitoring the nanostructure, the physical, chemical, and optical properties of g-C₃N₄ based photocatalysts can be easily controlled or modified. Various factors can be easily tuned by just controlling the nanostructure such as number of redox sites, and diffusion distance of e⁻ and h⁺ to reach these sites. Different dimensional structures of g-C₃N₄ have been reported in literature such as 1-D (nanorods), 2-D (sheets) and 3-D (various porous structures). The transformation of structures into 1-D nanorods or tubes, decreases the charge diffusion length and helps in improving the light harvesting by increasing the light interactions. In case of 2-D nanosheets, the charge transport along the sheet got enhanced and the recombination rate decreases drastically. It also increases the availability of abundant reactive sites for various activities. Single layered g-C₃N₄ nanosheets can be easily prepared by exfoliation process using H₂SO₄ which led to its intercalation between the g-C₃N₄ nanosheets [36]. However, the 3-D nanostructures acquired by accumulating 1-D nanostructural units possess high specific surface area, less mass transport resistance, high light absorption ability, and large number of active sites. However, the construction of 3-D nanostructures by using the 2-D nanosheets is tough because of the randomness in their sizes and orientations [37].

2.3.2 Doping

Doping is quite an effective way for enhancing the properties of g-C₃N₄ based photocatalysts by narrowing the band gap. Addition of dopant increases the localized states and also lifts the valence band maximum that helps in the narrowing of band gap. Doping of non-metals increase the delocalization of conjugated electrons, which helps in enhancing the conductance, mobility and separation of photo-generated charges [38]. Instead of a single atom doping, co-doping and more than one heteroatom doping is also preferable since it tune the band gap to a much greater extent. Among the halogens, bromine (Br), fluorine (F) and iodine (I) have been used as dopants for g-C₃N₄. Instead of non- metals, if the doping of g-C₃N₄ is done with organic molecules, then it may result in delocalization of π -conjugated electrons and red shift. However, the doping of aromatic molecules enhances the charge separation on the g-C₃N₄ surface [39].

2.3.3 Heterojunction formation

Designing of a heterojunction of g- C₃N₄ with other semiconductors helps in enhancing the optical properties, thus improving the charge separation [40, 41]. The coupling of g-C₃N₄ with other semiconductors with diverse properties prompts the band bending of the heterojunction at interface with the aid of inner electric field. This helps in improving the transfer and separation of photo-generated charges. In general, heterojunction systems can be categorized into; Type II, Z- scheme and S- scheme [42, 43].

The type II heterojunction is typically composed of two semiconductors, SI and SII in which one semiconductor possesses higher valence and conduction band potential. When the heterojunction is irradiated with sufficient energy, this generates electron-hole pairs. The electrons then move from the higher conduction band position of one semiconductor to the lower conduction band position of the other. The holes in the other hand follow the reverse path. The photoinduced electrons and holes get accumulated on the different semiconductors and thus helps in promoting the separation of charges and suppressing their recombination. This significantly enhances the energy conversion ability of synthesized heterojunction.

On the other hand, the Z- scheme mimics the natural photosynthesis process. This system is similar to type II heterojunction but the difference occurs in its charge-carrier migration mechanism. The charge-carrier migration pathway of this system looks like the letter “Z” [44]. This system comprises of a unique charge transfer mechanism in which the oxidation photocatalyst with strong oxidation ability exhibits low VB position and the reduction photocatalyst with robust reduction capability own high CB value [45]. The presence of charge carrier mediator and the type which is used, distinguishes the Z-scheme photocatalysts into three types: (i) traditional Z-scheme photocatalyst, (ii) all-solid state Z-

scheme photocatalyst, and (iii) direct Z-scheme photocatalyst [46]. The traditional Z-scheme photocatalyst consists of two different photocatalysts, in which an appropriate shuttle redox ion mediator is used to couple these two photocatalysts. $\text{Fe}^{3+}/\text{Fe}^{2+}$ and IO_3^-/I^- are the most common used shuttle redox ion pairs. When these photocatalysts are irradiated with light, the electron acceptor species consumes the photogenerated electrons of CB of photocatalyst having lower potential value while the electron donor species consumes the photogenerated holes of VB of other photocatalyst. The other remained photogenerated holes and electrons take part in separate oxidation and reduction reactions that have the required potential for carrying out effective reactions [47]. The all-solid state Z-scheme photocatalysts contains an electronic solid conductor which is used as charge carrier transfer-bridge. In the first reported all-solid state Z-scheme photocatalysts, Au as electronic conductor was used to create a bridge between CdS and TiO_2 photocatalysts [48]. In this system, the selection of suitable electron conductor is most important because it is not only limited to efficient transfer of photogenerated charge carriers but also helps in improving the stability of the photocatalyst. Various nanoparticles such as Au, Ag, and Cu have been reported as excellent electron mediators to construct all-solid state Z-scheme photocatalysts [49]. Apart from these two, the direct Z-scheme photocatalyst consists of two semiconductors which are in close contact with one another without any charge carrier mediator. These photocatalyst systems are resistant to corrosion. In contrast to traditional heterojunction, the back reactions in direct Z- scheme are considerably suppressed due to the absence of redox mediators [50].

S- scheme or “Step- scheme” is a recently formulated explanation for the mechanism of charge transfer in heterojunction. In this scheme, the two photocatalysts are arranged in similar way as in case of type-II heterojunction but follow a different charge transfer route. with staggered band structures. Here, an electric field is generated between the two photocatalysts that results in band bending. As a result of band bending, the electrons from the low potential conduction band moves to the higher potential valence band. Thus, the higher oxidation and reduction potential bands remain conserved for the generation of reactive radicals [43].

Figure 2. Different types of heterojunctions possible with their possible charge transfer mechanism.

3. C_3N_4 based heterojunctions for H_2 production

H_2 is the most abundant element in the universe available in water and organic compounds. It is the lightest element which contains only one electron and one proton. It is a colorless, odorless, and a flammable gas. It is non- toxic and spread rapidly when released. It is transportable, storable, and utilizable and has the ability to act as alternate energy storage system. By using solar energy, water splitting for the production of H_2 is considered as one of the most proficient approaches to deal with the current global energy issues [44, 51-53].

Considering the above discussion, numerous work has been done on the utilization of g- C_3N_4 based photocatalyst for solving the issue of energy crisis. In the same context, $Bi_2MoO_6/g-C_3N_4$ based heterojunction was designed by in-situ solvothermal method using 2-D g- C_3N_4 nanosheets. The H_2 production ability of $Bi_2MoO_6/g-C_3N_4$ from water splitting was performed. They also studied the bacterial disinfection under visible light. The

complete mechanism of H_2 production and bacterial disinfection is presented in Figure 3. They exfoliated the bulk $g-C_3N_4$ to $g-C_3N_4$ nanosheets that considerably increased the surface area and reduced the diffusion distance for photogenerated charges. This helped in promoting not only the photocatalytic activity [54]. The photocatalytic H_2 production by $Bi_2MoO_6/g-C_3N_4$ was approximately 3.84 time higher than bulk $g-C_3N_4$ and 32.19 times higher than Bi_2MoO_6 .

Figure 3: (a) Photocatalytic mechanism for H_2 production by $Bi_2MoO_6/g-C_3N_4$ heterojunction [54].

In another study, novel C_{60} /graphene/ $g-C_3N_4$ composite was utilized as a photocatalytic material for H_2 production by water splitting. The superior electron conduction ability of graphene and strong electron-attracting tendency of C_{60} made the composite quite effective for the H_2 production. The synergistic effect between graphene and C_{60} helped in expanding the movement and utilization proficiency of photo-generated electrons and enhanced the separation of photo-generated charges. The H_2 production amount and rate of C_{60} /graphene/ $g-C_3N_4$ (10 mg/L C_{60} and graphene) was found to be about 539.6 times greater than that of pure $g-C_3N_4$ under the same experimental conditions. Also, the rate obtained was 50.8 and 4.24 times higher than that of graphene/ $g-C_3N_4$ and $C_{60}/g-C_3N_4$, respectively. The quantum yield of the synthesized composite in 97 h was about 7.2% [55].

Due to higher redox capability, ample oxygen defects and cost effectiveness, the CeO_2 and its various derivatives have high potential as photocatalysts. Based on this, $\text{CeO}_2/\text{g-C}_3\text{N}_4$ was designed with tuneable CeO_2 crystal planes [56, 57]. Characterization techniques such as photoelectrochemical, Raman, XPS, and ESR results proposed that the charge separation efficacy, oxygen defects and $\text{Ce}^{3+}/\text{Ce}^{4+}$ reversibility pairs were dependent on the CeO_2 and $\text{g-C}_3\text{N}_4$ contact. The photocatalytic activity of H_2 production under visible light was of the order: $\text{CeO}_2(110)/\text{g-C}_3\text{N}_4 > \text{CeO}_2(100)/\text{g-C}_3\text{N}_4 > \text{CeO}_2(111)/\text{g-C}_3\text{N}_4 > \text{g-C}_3\text{N}_4$ [58].

Aiming for the synthesis of highly efficient photocatalyst, Chen and his co-workers, synthesized 2D/2D $\text{MnIn}_2\text{S}_4/\text{g-C}_3\text{N}_4$ photocatalyst by hydrothermal method. They carried out the in-situ loading of MnIn_2S_4 nanoflakes on the nanosheets of $\text{g-C}_3\text{N}_4$. The synthesized photocatalyst formed a direct Z-scheme heterojunction that showed higher activity than that of the individual components under the visible light irradiation. Complete transfer mechanism of the photogenerated charges for the H_2 production and degradation of pharmaceutical wastewater is shown in Figure 4. The formation of direct Z-scheme between the two components significantly increased the photocatalytic activity due to the efficient charge separation and high charge transfer. They even reported the excellent stability of the synthesized photocatalyst [59].

In one another very interesting study, $\text{g-C}_3\text{N}_4/\text{KNbO}_3$ heterojunction and Pt-loaded $\text{g-C}_3\text{N}_4/\text{KNbO}_3$ heterojunctions were synthesized for studying its H_2 production ability under simulated sunlight using water splitting. In the Pt-loaded $\text{g-C}_3\text{N}_4/\text{KNbO}_3$ heterojunction, the Pt acted as the co-catalyst that helped in enhancing the light absorption ability and in reducing the charge recombination. The H_2 production efficiency of the heterojunction was even compared with the individual components and the results proved its high ability. The schematic presentation of $\text{g-C}_3\text{N}_4/\text{KNbO}_3$ and Pt- $\text{g-C}_3\text{N}_4/\text{KNbO}_3$ for H_2 production is shown in Figure 5 [60].

Figure 4: Charge transfer mechanism in direct Z-scheme heterojunction formed between MnIn₂S₄ and g-C₃N₄ [59].

Figure 5: Schematic presentation of g-C₃N₄/KNbO₃ and Pt-g-C₃N₄/KNbO₃ for H₂ production [60].

Pure g-C₃N₄ shows negligible activity for H₂ production due to its high recombination rate. So, as a modification, a heterojunction of g-C₃N₄ and NiS₂ was synthesized and studied for H₂ generation. The production was found to be dependent upon the amount of NiS₂. The H₂ production rate varied significantly with variation in the content of NiS₂. For 3%, 5%, 7%, and 10% NiS₂ content, the corresponding H₂ production rates were 365.72, 550.81, 715.83, and 540.1 $\mu\text{mol/h/g}$ respectively. They studied the effect of co-catalyst loading with 2% Pt. They found that the H₂ production rate was 2.75 times as much as that of 2% Pt as a co-catalyst. They suggested that the enhanced activity was due to a wide range of photoresponse and efficient separation of photogenerated charges [61].

The g-C₃N₄, rGO and TiO₂ are some of the most capable substance for photocatalytic hydrogen production activity. However, the H₂ evolution rate reported for bare g-C₃N₄, P25 (degussa), TiO₂, g-C₃N₄/TiO₂, and TiO₂/rGO [62, 63] nanocomposites in the literature are comparatively low. In 2017, Hafeez with his co-workers fabricated rGO supported g-C₃N₄-TiO₂ using simple ultrasound assisted wet impregnation. Various concentrations of photocatalyst were synthesized by varying the concentration of TiO₂ and g-C₃N₄ and they found that 70:30 (g-C₃N₄: TiO₂) exhibited the highest activity of 23,143 $\mu\text{mol/g/h}$ for H₂ production. High light absorption and efficient charge transfer resulted in the excellent activity of the synthesized photocatalyst [64]. A probable mechanism for H₂ production using g-C₃N₄-TiO₂/rGO was also proposed and is presented in Figure 6.

In 2016, Liu and his co-workers reported the designing of complete metal- free photocatalyst in which they synthesized isotype triazine/heptazine- g-C₃N₄ based heterojunction by microwave-assisted molten-salt process. They used eutectic mixture of KCl/LiCl as the molten salt and melamine as the nitrogen- rich precursor and treated them in the microwave. A complete synthesis procedure is presented in Figure 7 (a). A huge improvement in HER proficiency was attained that was linked to the isotype triazine/heptazine based g-C₃N₄ heterojunctions. It had an appropriate arrangement of the electronic band structures that provided the proficient transport path and high separation of photo-generated charges. Furthermore, the synergistic effect of microwave reaction and molten-salt liquid polycondensation condition afford an improved way for the fabrication of g-C₃N₄ based photocatalysts [65]. A probable charge transfer mechanism involved in the synthesized photocatalyst for HER is shown in Figure 7 (c).

Figure 6: A possible mechanism of H_2 production using $\text{g-C}_3\text{N}_4\text{-TiO}_2/\text{rGO}$ under UV-light [64].

Figure 7: (a) Microwave-assisted molten-salt route for designing of isotype triazine/heptazine based $\text{g-C}_3\text{N}_4$ heterojunctions; (b) Structure of the isotype $\text{g-C}_3\text{N}_4$ heterojunction; and (c) Probable charge transfer paths in the isotype $\text{g-C}_3\text{N}_4$ heterojunction [65].

H₂ evolution by water splitting using a semiconductor photocatalyst is deliberated as quite an interesting and a supreme procedure for obtaining a clean and sustainable energy [66-68]. The photocatalytic performance and stability of any photocatalyst can be proficiently amended by coupling with other semiconductors and doping as explained in Section 2.3 [69]. Liu and his co-workers [70] revealed that the coupling of g-C₃N₄ with ZnIn₂S₄ formed a highly proficient photocatalyst that showed advanced H₂ production and degradation ability than that of the individual components [71].

The sunlight-driven water splitting at semiconductor's boundaries has fascinated extensive attention due to its cost and energy saving nature [72, 73]. In the same context, Cheng and Jiang fabricated the g-C₃N₄/nanocarbon/ZnIn₂S₄ nanocomposite. The resulting nanocomposite showed artificial Z-scheme that was active under visible light for the photocatalytic H₂ evolution and maximum rate obtained was 50.32 $\mu\text{mol}\cdot\text{h}^{-1}$ [74].

Using in-situ photo-deposition method, a novel Co-Pi/g-C₃N₄ was synthesized. The photocatalytic activity of Co-Pi/g-C₃N₄ for oxygen and hydrogen production via water splitting was analyzed under visible light irradiation. The Co-Pi modified g-C₃N₄ exhibited considerably improved photocatalytic activity, and the g-C₃N₄ with deposition time of 20 min (CP-20) displayed the maximum activity. The H₂ production performance reported was about 9.6 times than that of bulk g-C₃N₄. The photo-deposition of Co-Pi onto g-C₃N₄ significantly improved the separation of photogenerated carriers and improved the H₂ and O₂ production rate [75]. A possible mechanism of charge transfer in the Co-Pi/g-C₃N₄ is shown in Figure 8.

Figure 8: The hydrogen generation by Co-Pi/g-C₃N₄ composite photocatalysts [75].

A novel CuS-ZnS_{1-x}O_x/g-C₃N₄ heterostructure based photocatalyst was synthesized by combination of thermal decomposition and hydrothermal method. The introduction of CuS into the nanocomposite significantly improved the absorption of the resulting photocatalyst. The decoration of CuS highly improved the H₂ production rate from 9200 to 10,900 $\mu\text{mol/h/g}$ and g-C₃N₄ provided the efficient separation of photogenerated charges. The CuS-ZnS_{1-x}O_x/g-C₃N₄ nanocomposite displayed superior photocatalytic activity for H₂ production. The composite photocatalyst CuS-ZnS_{1-x}O_x with 5 wt% g-C₃N₄ showed the maximal H₂ production rate of 12,200 $\mu\text{mol/g/h}$ [76].

Semiconductor hybridization is a proficient substitute practice for enhancing the utilisation of g-C₃N₄ for H₂ production under visible light. This approach is established on the alignment of bands between g-C₃N₄ and other semiconductors, forcing the photogenerated charges to migrate in the opposite directions. It ultimately results in the spatial separation of the charges on the heterojunction and to decrease the charge recombination to advance the photocatalytic proficiency. In the same context, CdS/g-C₃N₄ heterojunction was synthesized. In this, the CdS quantum dots were grown on the surface of g-C₃N₄ [77]. In another study, the CdS/g-C₃N₄ core/shell nanowires were prepared [69]. The formation of a heterojunction between CdS and g-C₃N₄ resulted in efficient charge separation and the transfer of corrosive holes from CdS to g-C₃N₄ (as shown in Figure 9). As a result, highlighting the permanence of CdS and attained a much higher H₂ production rate under visible light irradiation as compared to that for pure CdS and pure g-C₃N₄ [77].

Similarly, in another study, the in-situ growth of In₂O₃ nanocrystals on the g-C₃N₄ nanosheets was carried out. The synthesized In₂O₃-g-C₃N₄ photocatalyst showed substantial advancement in the photocatalytic activity for H₂ production. The improved rate was due to the efficient transfer of photogenerated charges between the two constituting components [78].

At the same time, g-C₃N₄ can also be excited by absorbing photons with energy exceeding its band gap and subsequently transfer the photo induced electrons directly to the Pt co-catalyst to generate H₂. As a result, the sensitized photocatalyst shows a high H₂ evolution rate. Activity under irradiation of visible light longer than the absorption edge of g-C₃N₄ and achieves an apparent quantum efficiency of 19.4% even at 550 nm. Wang and his co-workers also attained a high deceptive quantum efficiency of 33.4% at 460 nm by alerting the g-C₃N₄ layer with low-cost Erythrosin B dye, which is greater than that of CdS-cluster-decorated graphene nanosheets [79] and comparable to that of CdS quantum dots/graphene/ZnIn₂S₄ heterostructures [80].

Figure 9: The hydrogen generation by CdS/g-C₃N₄ photocatalysts [69].

Delamination of layered materials into 2-D single sheets prompt some extraordinary properties in it, such as, high surface area, extreme charge carrier mobility, and distinct variations in the band energy system. With the exclusive structural benefits of aligned energy levels, charge transfer, increased light absorption range, and reaction site availability, the as-prepared mesoporous g-C₃N₄ displayed an AQE of 5.1% at 420 nm and photocatalytic H₂ evolution rate of 8510 $\mu\text{mol/h/g}$, maximum among all the metal-free photocatalyst [81].

InVO₄ was a capable photocatalyst for H₂ production under visible light irradiation. The conduction band of InVO₄ was appropriate for H₂ production [82]. Additionally, many data reported that the preferred morphology and size of photocatalysts could regular the position of energy band for achieving higher redox ability [67, 83]. Yan et al reported that the nano-sized InVO₄ nanoparticles with the size of 20 nm showed higher photocatalytic activity of H₂ production than InVO₄ microspheres [84, 85]. In another study, the g-C₃N₄/nano-InVO₄ nanocomposites were designed by hydrothermal technique. The g-C₃N₄ sheets performed a very important role in the establishment of g-C₃N₄/InVO₄ nanocomposites, which revealed that g-C₃N₄ was an auspicious support for in-situ growth of other nano-sized components. The construction of interfaces enhanced the charge transfer and introverted the recombination of charges, which considerably enriched the photocatalytic H₂ evolution [86].

Table 1: g-C₃N₄ based photocatalysts for H₂ production with their synthesis method.

Sr. No.	g-C ₃ N ₄ based photocatalyst	Synthesis method	Amount of H ₂ produced in $\mu\text{mol/g/h}$	References
1.	g-C ₃ N ₄ /MoS ₂	Photodeposition	660	[87]
2	g-C ₃ N ₄ nanodots	Templateless infrared heating	57.8	[88]
3	g-C ₃ N ₄ /TiO ₂	Vapour deposition method	513	[89]
4	3-D g-C ₃ N ₄ nanobelts	Hydrothermal	27.2	[37]
5.	ZnO/ZnS/g-C ₃ N ₄	Chemical conversion	1205	[90]
6	Br-doped g-C ₃ N ₄	Heating urea with NH ₄ Br	48.00	[91]
7	O self- doped g-C ₃ N ₄	Hydrothermal treatment	158.7	[92]
8	N self- doped g-C ₃ N ₄	Thermal treatment	44.28	[93]
9	Graphene/g-C ₃ N ₄	Impregnation-chemical method	36.08	[94]
10	N-GQDs/g-C ₃ N ₄	Chemical	43.6	[95]
11	C-ZIF/g-C ₃ N ₄	Calcination	32.6	[96]
12	Tapered C-PAN/g-C ₃ N ₄ nanotubes	Thermal treatment	177.5	[97]
13	g-C ₃ N ₄ /SrTiO ₃	Calcination	440	[98]
14	Pt-Pd/g-C ₃ N ₄	Chemical deposition precipitation	1600.8	[99]
15	Oxygen-doped g-C ₃ N ₄	Heating treatment	189.3	[100]
16	g-C ₃ N ₄ /SiC	In- situ precipitation	182	[101]
17	CoP/g-C ₃ N ₄	Thermal decomposition + Electroless plating	936	[102]
18	Zn _x Cd _{1-x} In ₂ S ₄ /g-C ₃ N ₄	Hydrothermal	170.3	[103]
19	Carbon fibre/g-C ₃ N ₄	Electrospinning + Calcination	1080	[104]
20	Cu ₂ O/g-C ₃ N ₄	In-situ technique	33.2	[105]

21	CdSe Quantum Dots/g-C ₃ N ₄	Thermal polymerization + chemical method	615	[106]
22	Organic-Organic Hybrid g-C ₃ N ₄ /ethanediamine	Solvothermal reaction	3055	[107]
23	g-C ₃ N ₄ /CoO	Calcination + Chemical reaction	651.3	[108]
24	g-C ₃ N ₄ /WS ₂	Gas- solid reaction	101	[109]
25	0D-ZnO/g-C ₃ N ₄	Solution conversion and calcination	322	[110]
26	SnS ₂ /g-C ₃ N ₄	In-situ growth method	928	[111]
27	N-ZnO/g-C ₃ N ₄	Hydrothermal and calcination	152.7	[112]
28	SnFe ₂ O ₄ /g-C ₃ N ₄	In-situ precipitation	132.5	[113]
29	2D WO ₃ /g-C ₃ N ₄	Hydrothermal	1853	[114]
30	Ta ₂ O ₅ /g-C ₃ N ₄	One- step heating	36.4	[115]
31	Sulfur-doped holey g-C ₃ N ₄ nanosheets	Self- templating approach	6225.4	[116]
32	Benzene ring modified g-C ₃ N ₄	Thermal approach	8.9	[117]
33	Black phosphorus/MXene/Ultrathin-g-C ₃ N ₄ composite	Chemical method	18.42	[118]
34	Nb ₂ O ₅ /2D g-C ₃ N ₄	Subtractive manufacturing method	22,600	[119]
35	S,N-co-doped carbon dots (S,N-CDs)/g-C ₃ N ₄ nanosheet	Hydrothermal	832	[120]
36	Hollow tubular g-C ₃ N ₄	Hydrothermal calcination	235.68	[121]

Conclusions

In conclusion, the advancements in the utilization of g-C₃N₄ based photocatalysts have perceived an epitome of novel research work in the utilization of abundantly available solar light for H₂ production. From this perspective, the H₂ generation via water splitting have well- exploited the exclusive features of g-C₃N₄, which comprises the abundant availability

of its constituting elements; carbon and nitrogen, visible-light absorbance, required band-energy gap, metal-free 2-D structure, and high chemical stability. A tremendous work has been done in this field since its first utilization in 2009. Various methodologies have been discussed for enhancing the H₂ production ability of g-C₃N₄ based photocatalysts such as band gap engineering, introduction of various dopants, and nanostructure designing, etc. Finally, it is supposed that this chapter will be helpful in understanding the utilization of g-C₃N₄ based photocatalysts for H₂ production and their modification with nanoscale features for substantial advances in accomplishing an effective, eco-friendly and economical energy production system.

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