

Synthesis of Graphene Based Graphitic Carbon Nitride Hybrid Nanocomposite Photocatalysts for Hydrogen Generation: A Mini Review

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Abstract

The discovery of visible active photocatalysts for H₂ evolution via water splitting is the most awaited and critical goal of many researchers in recent years. Novel polymeric graphitic carbon nitride (GCN/g-CN) has emerged as a versatile material which has attracted the scientific community and industrialist because of its distinctiveness and outstanding electronic properties. g-CN is a metal free semiconductor as well as non-toxic, biodegradable polymeric material with low band gap energy which makes it a promising candidate as a photocatalyst and its efficiency as a catalyst can be modified by forming a hybrid nanocomposite with other semiconducting materials. Reduced graphene oxide, another metal free 2D material is a very good choice for this purpose. This review is an outlook for the synthesis processes and various properties of both g-CN and graphene. Further, it gives the approaches attempted towards the modifications required and done towards the development of a metal-free nano-hybrid material which is cost-effective, eco-friendly, and highly active visible light catalyst for the water-splitting process.

Keywords: Graphitic Carbon Nitride, H₂ Generation, Reduced Graphene Oxide, Visible Light Photocatalyst, Water Splitting

1.0 Introduction

A better comprehension of energy conservation and the utilization of renewable energy sources is important for the current energy problem. The exploration and production of clean and sustainable energy is critical to meeting the world's growing energy needs while also preserving fossil fuels. Harnessing of energy from

renewable sources has taken the front seat for the investigators. Solar energy¹ is the most important clean energy, which must be captured, converted and stored in semiconductor devices. Hydrogen is another front runner in the list as a clean and green fuel and considered as the most efficient fuel². The energy content of H₂ is higher than the hydrocarbon fuel and varies from 120-142 MJ/kg and no elimination of any harmful by products on

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combustion^{3,4}. Therefore, H₂ will be the major clean energy source of the future. Different techniques like electrolysis of water, photocatalytic water splitting, wind powered H₂ production, steam methane reforming etc. have been used for H₂ production^{5,6}. Photocatalytic H₂⁷⁻⁹ formation via water splitting over semiconductor photocatalysts has gained worldwide interest as an ecologically friendly, economically viable, renewable, and adaptable technology. Here we intend to emphasise on the photocatalytic water splitting (PCWS) technique which involve the use of a semiconductor photocatalyst. H₂ can be produced from H₂O via electrolysis or by employing a catalyst to divide water into H₂ and O₂. The method of splitting of water is not feasible and a proper visible-light active catalyst is required to achieve this process in an indirect way. Therefore we require advanced materials that can harness solar light and can induce photoactive reactions just like photosynthesis. Scientific community believes that if an efficient technology is developed to generate H₂, it can eventually replace petrol in the coming days. But the production of H₂ has taken a back seat due to its economic concerns and the complexity in its large scale production.

The idea of photo-induced water splitting was first published by Fujishima and Honda in 1972¹⁰, and they used nano sized TiO₂ as the semiconductor material. Since then extensive research towards the fabrication of photoactive materials were carried out by many investigators. TiO₂¹¹, ZnO¹², MoS₂¹³, WO₃¹⁴, etc. are some of the most studied semiconductor materials. Certain compounds have been discovered to be great catalysts when exposed to UV light, but have limited effectiveness when exposed to visible light. This is owing to such materials' high band gap, low visible light absorption coefficient, rapid electron-hole pair recombination, and reduced specific surface area.

As a result, researchers prioritized research into the development of Visible Light Active Photocatalysts (VLAPC) for high-efficiency water splitting. The majority of the effort has gone towards proper design and structural adjustments to the foundation material. The following parameters are critical while preparing a VLAPC: 1) To maximize the light absorption coefficient, the semiconductor should have a low band gap. 2) Efficient charge separation is essential to avoid charge carrier recombination and to boost the rate of surface catalytic

photo splitting, 3) good surface properties and large surface area is required for the catalytic splitting of water¹⁵. Great efforts has been made in developing solar light active semiconductors for water splitting for eg; GaInP¹⁶, GaAs¹⁷ etc. and their composites but these materials are very expensive nanomaterials. VLAPC aided in the discovery of graphitic carbon nitride in the quest for considerably cheaper, non-polluting, readily available materials (g-CN). Wang et al.¹⁸ reported pioneering work on GCN in this area in 2009, demonstrating the use of g-CN as a photocatalyst for water splitting for the creation of H₂. Since then the research and applications of g-CN and its composites as VLAPC has taken the prime consideration of chemists¹⁹⁻²¹. g-CN has become the hotspot and has gained multidisciplinary regards due to its non-metallic nature, excellent electronic and structural properties and due to its visible light harnessing character²²⁻²⁴. g-CN has remarkable properties and applications²³⁻²⁶ owing to the ordered structure which is in close relation with graphite. This review article is aimed to give a crisp and detailed facets on the structure, advantages, limitations, synthesis process and the modifications required to be done for the use of g-CN as an effective visible light active catalyst. We hope to gain an insight on the material's effectiveness as a good photocatalyst, paving the way for the use of g-CN to provide a clean and sustainable source of H₂ energy.

2.0 Structure

g-CN has the basic unit formula of g-C₃N₄ and contains only C and N atoms bonded by strong covalent bonds. It has a 2D graphitic like structure of tri-s-triazine,

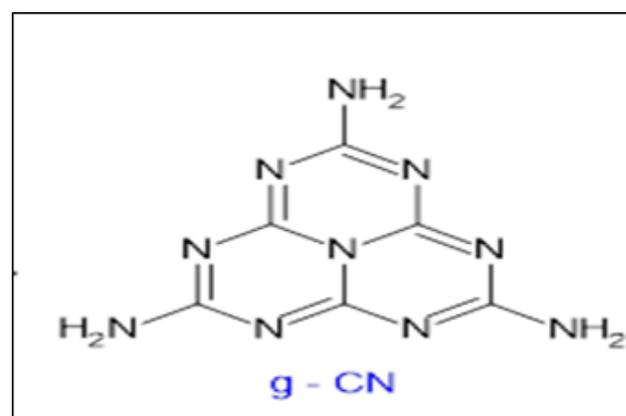


Figure 1. Structure of g-CN.

containing alternate C and N atoms exhibits a unique delocalized and highly conjugated polymeric structure²⁷ as shown in the Figure 1 which makes them highly stable both thermally and chemically and a good conductive material as shown in the Figure 1. Due to this spatial structural arrangement, g-CN possesses a variety of unique physicochemical properties as listed.

3.0 Prospects of g-CN as a Visible Light Active Photocatalyst

3.1 Advantages of g-CN

- 1) The band gap energy of g-CN is 2.7eV which is suitable to act as semiconductor.
- 2) Its optical wavelength is ~ 460nm
- 3) Thermal properties in air up to 600°C
- 4) Good chemical endurance towards acids, alkali and organic solvents
- 5) It has a good visible light responsive atomic arrangement.
- 6) g-CN has a suitable band structure for water reduction and oxidation to occur on its surface.
- 7) Ease of synthesis from cheap and easily available precursors.

Combination of these unique properties and the ease of preparation makes it an interesting candidate for various applications and especially much work towards the use as photocatalyst. It is employed as a photocatalyst for the breakdown of harmful organic molecules, for photo induced sewage treatment, for the generation of hydrocarbon from CO₂, for the reduction of CO₂, and for water splitting under visible light to generate H₂ and O₂. Nonetheless, it has some limitations which confine its use as good candidate for Visible Light Active Photocatalyst (VLAP) are listed below.

3.2 Limitations of g-CN

- 1) Pure g-CN synthesised was found to be of less efficient at visible region as it lacks absorption above 460 nm
- 2) Quick recombination of electron-hole pair takes place, which limits the application of light induced reactions.

- 3) Due to the obvious stacking of the polymeric graphitic layered structure, the specific surface area is usually less than 10 m².
- 4) g-CN has a small pore space and consequently fewer active sites on its surface.
- 5) Thickness of the g-CN prepared may be high which does not support charge transfer.

Thus, as a matter of fact a single photocatalyst cannot become a super star, but good combinations with suitable cocatalyst can make it achieve incredible and efficient photocatalyst.

3.3 Strategies to Overcome these Deficiencies

Various strategies in the modulation and designing of the g-CN structure was tried and tested to increase the efficiency as VLAP²⁹. Some are listed below and the detailed methods adopted to overcome are explained later.

- 1) Reduce the band gap energy by doping process using suitable material or a heteroatom
- 2) Lower the thickness of the layered structure to increase the specific surface area
- 3) Exfoliate g-CN to form single layered 2 dimensional nanosheets so as to increase the pore volume
- 4) Control morphology while preparing g-CN
- 5) Coupling of g-CN with other semiconductors or photosensitised dye molecules to increase the active sites
- 6) Shortening the bulk diffusion distance for retarding the charge recombination

The above said strategies need to be considered while synthesising a modified g-CN³⁰. This can be achieved by coupling g-CN with other semiconductors or other hetero atoms to create a heterojunction in the composite. The most important criterion to get an efficient VLAP is that the heteroatom should have narrow bandgap energy to absorb the visible light photons and a suitable band structure to create a coupling hybridisation^{31,32}. As a result, correct doping profiles and band alignment are critical for charge carrier mobility. The alignment of the Conduction Band (CB) and Valence Band (VB) of the component materials at the interface determines the semiconductor heterojunction in a composite material. At the interface, there are three types of semiconductor

heterojunctions: (1) straddling gap (Type I), (2) staggered gap (Type II), and (3) broken gap (Type III). Various models are available to verify the type of heterojunction formed. In type I we can see that the as the band gap of one material is smaller the charge carriers move in the same directions which results in faster recombination, which may decrease the photoinduced reactivity rate. Therefore type I heterojunction is not preferred for Photocatalysis. In staggered Type II kind of heterojunction, the charge separation is feasible as the lowest energy state for holes may be on one side whereas the lowest energy for electrons on the other side which results in the movement of electron and hole in opposite directions. Type II nanoscale heterojunctions are so chosen for photoinduced processes, particularly photocatalytic water splitting with solar energy. It is also feasible to modify the heterojunction for the same material from Type I to Type II by changing the particle size or crystal density. The VB and CB of one semiconductor are lower than those of the other in a Type III broken gap heterojunction. During photoinduced reactions, the electrons on the lower CB semiconductor recombine with the holes on the other semiconductor's higher VB. This result in the efficient charge separation in the Z scheme heterojunction is achieved which can be enhanced with the use of a charge carrier bridge³³. Thus, to develop an effective photocatalyst several requirements must be considered. The efficient visible light absorption takes place with narrow band gap energy, adequate charge separation to control the electron hole recombination and passable redox potential for the photocatalysis reaction to take place. More importantly the stability of the photocatalyst is highly desirable. These could be achieved by synthesising the nanocomposite complex based on GCN using semiconducting nanomaterials possessing high absorption efficiency. Moreover the stability of the complexes can be achieved by protecting the semiconductor by surface passivation³⁴.

4.0 g-CN Based Nanocomposites

Thus g-CN nanosheets can be made as an exceptional 2D material to prepare nanocomposite with much-admired incredible VLAPC and based on the cocatalyst we choose, the following different types of nanocomposite material can be synthesised.

- 1) g-CN -non-metal based catalyst
- 2) g-CN -noble metal based catalyst
- 3) g-CN -metal oxide based catalyst
- 4) g-CN -mixed metal oxide based catalyst
- 5) g-CN -magnetic material based catalyst

Hypsochromic shift takes place when g-CN is incorporated, which results in the shifting of CB and VB in opposite direction. This improves the photo induced activity of the charge carriers and improves the redox capability of the charge carriers and helps on extended lifetime. Hence modified g-CN exhibits outstanding solar light activity for the generation of hydrogen from water. Here we mainly intend to explain non-metal based cocatalyst especially graphene as a strategic material to create a metal free, less toxic nanocomposite. In the last decade we have seen the growing interest in the graphene and g-CN for various applications due to their unique properties. Therefore, many researchers developed the combination of graphene and g-CN, a hybrid nanocomposite as a promising material with improved catalytic properties. As there is not many reviews are available for graphene-graphitic carbon nitride nanocomposite, its appropriate to discuss further on graphene co-catalyst³⁵.

4.1 Graphene

4.1.1 Structure of Graphene

Graphene has a 2D planar honeycomb structure where the carbon atoms are stacked in layers with a separation of 0.142nm. Each layer has single atom thickness of carbon with an interplanar spacing, $d = 0.335\text{nm}$. It is the lightest but hardest substance ever discovered by scientists. Because of its high thermal conductivity, electrical conductivity, and mechanical qualities, it is an excellent choice for a variety of uses. Furthermore, because of its low cost, low toxicity, and good chemical stability, it is an excellent option for biosensing, energy storage, nanoelectronics, medicinal applications, waste water treatment, and photoreactions³⁶. Graphene can also be transformed in various ways, such as graphene oxide, chemically reduced graphene, bidirectional graphene, and so on.

4.1.2 Graphene Oxide Synthesis (GO)

Graphene was first prepared by Bordie by the oxidation of graphite using potassium chlorate in the presence of nitric acid. Later, Staudenmaier *et al.* synthesized graphene using strong acids and potassium chlorate, which is deemed safer than the prior method. Hummer *et al.* established a new process for preparing graphene oxide in 1958 utilizing KMnO_4 , NaNO_3 , and H_2SO_4 to oxidize graphite into graphite oxide in a matter of hours. This approach is more favorable and produces less hazardous gases than the other two methods, and it will be the most often utilized method in the future. These methods produce graphene oxide sheets with a high concentration of oxygen functional groups such as $\text{C}=\text{O}$, $\text{HO}-\text{C}=\text{O}$, $\text{C}-\text{O}-\text{C}$, $\text{C}-\text{OH}$, and so on. These functional groups may produce flaws in the nanosheets, such as sp^3 defect sites, and distort the conjugated system, reducing strength and conductivity. This makes graphene an insulator. Therefore, graphene has to be modified to reduce the oxygen functional groups. This is carried out by the reduction process, wherein we can tune the bandgap energy by reducing the oxygen functionalities.

4.1.3 Synthesis of Reduced Graphene Oxide (RGO)

GO is chemically reduced to RGO also called as chemically modified graphene oxide, by removing the oxygen-containing groups by chemical, thermal, electrochemical, photo-reduction or by green reduction. The commonly used reducing agent is hydrazine and its derivatives like hydrazine hydrate ($(\text{NH}_2\text{NH}_2 \cdot x\text{H}_2\text{O})$) and dimethyl hydrate. Other metal hydrides like sodium borohydride, lithium aluminium hydride and sodium hydride are also used for reduction. S. Some *et al.*, used thiophene and M.J. Fwrnandes Merino *et al.*, used pyrogallol, vitamin C along with hydrazine and compared with the other methods. He found that vitamin C has yielded the highest suspension. T.T. Dang *et al.* investigated the effect of temperature on the reduction of graphene oxide by hydrazine in N, N-dimethylformamide (DMF)/ H_2O , finding that the dispersibility of the resulting graphene in DMF increased from 25 to 80 °C³⁷.

Thermal annealing involves the heating of graphite to high temperature by heating or microwaving under inert gas atmosphere. Green synthesis approach involves the use of biomolecules, microbes, plant extract etc.,

for the reduction process. This method is affordable, environmentally friendly, and does not require the use of toxic or harsh chemicals. Vitamin C (ascorbic acid) has lately been discovered to have numerous advantages over hydrazine as a reducing agent. Ascorbic acid is nontoxic, has higher stability, is readily available, and does not cause aggregation. Considering the environment and human health, RGO has recently been synthesized through green reduction of GO using ascorbic acid, glucose, fructose, and sucrose, tea leaves, melatonin, and alcohols.

4.2 Synthesis of g-CN

Nitrogen rich precursors are generally used for the synthesis of g-CN. It is easily made by controlled thermal decomposition or condensation of urea, melamine, thiourea, cyanamide, and dicyanamide. The precursors are placed in a crucible and heated at 500°C in a muffle furnace at around 4 hours at a heating rate of 10°Cmin⁻¹. After slow cooling, the powder obtained is ground using mortar and pestle.

4.3 Synthesis of Graphene g-CN Nanocomposites

Several works were reported in this regard and these heterojunction composites are classified as follows. Graphene-g-CN complex is an outstanding candidate among metal free nanocomposite with very high specific surface area and has the highest thermal conductivity and outstanding mechanical and electrical properties, which makes it possible to use in nanoelectronics, biosensing, capacitors, catalysis etc., to name a few.

The planar honeycomb structure of graphene helps in 2D/2D layered face to face interaction with the g-CN, resulting in the charge separation, which further restricts the recombination of electron-hole pair. This enhances the catalytic efficiency for photoreactions. To prepare graphene/ g-CN hybrids, various synthesis methods such as thermal annealing, solvent-thermal treatment, and molecular contact were used. A one-pot single step calcination of the aqueous combination of graphene materials and g-CN precursors at 823K was used to create a simple synthesis of graphene materials and g-CN composite photocatalysts. This thermal annealing avoids the intermediary phases of product washing and drying that are frequent in previous investigations. Various

precursors (melamine and urea), Graphene Materials (GO and RGO), and weight ratios were used in the manufacture of g-CN composites, and their photocatalysis of BPA was tested. This method immobilized g-CN onto chemically modified graphene. According to reports, expanding the amount of graphene can minimize the band gap. Furthermore, the composite's specific surface area increases, allowing for greater absorption of visible light. Nano-casting was done to prepare the sandwich model of graphene-g-CN nanosheets, which showed better catalytic activity due to reduced agglomeration between the components.

The bulk g-CN has very small specific surface area as low as 10 m²/g and small pore size. Therefore the designing and surface modulation of bulk g-CN by combining with co catalyst to build a semiconductor heterojunction is significant. But all the materials will not combine with g-CN to form an efficient VLAP. Various synthesis approaches have been used by scientists which includes Ultrasonic solution mixing, solid state calcination, Hydrolysis, Hydrothermal, sol-gel process, microwave irradiation process. Some of these process will be explained in detail below.

4.3.1 Ultrasonication

Ultrasonication method of preparation of nanomaterial involves sonochemical method which utilizes the high intensity of ultrasounds which can induce chemical reactions. Thus this is one of the simplest route to obtain g-CN based nanocomposite, where mixing of the g-CN and co-catalyst in a suitable organic solvent or in aqueous medium is required and subjected to ultrasonic vibrations. Now this homogeneous solution is allowed to vibrate under ultra-sonication for about 3 hours under the following conditions. The noise in the liquid should be in the range of 1000-1500 m/s and wavelength required is between 10 cm to 100µm and 20KHz to 15MHz frequency range is required. The energy of ultrasonic vibration helps the dispersion of the cocatalyst on the surface of the g-CN and even form a heterostructure in which both the materials will be in close combination.

4.3.2 Hydrothermal Method

Hydrothermal process is very promising and a well-known method for the preparation of nanomaterials, which

involves the hydrolysis reaction at high temperature. Here the precursor is mixed with an organic solvent in the presence of a hydrolysing agent, usually KOH, and is autoclaved for a certain period of time. The reaction mixture is kept in an oven at round 70 - 200° for about 12 to 24 hours in a hydrothermal autoclave made up of Teflon, which can withstand high temperatures and pressures, at a temperature and pressure below the critical point for a specific solvent. The resulting precipitate is filtered, washed and dried and calcined to obtain the required nanomaterial composite. This method is adopted mainly for designing of nanomaterials, modulation of crystal size, controlling of the morphology, crystallinity of the material and it is possible by adjusting the processing time, and processing conditions. This process is done under in a slow and controlled manner at a higher temperature and pressure, the growth of the crystal is controlled, thus forming smaller size particle with increased specific surface area as compared to the other methods. Here the reaction time, temperature, pH, pressure and the precursor concentration can be controlled based on the requirements.

4.3.3 Calcination Method

This is a strong chemical method in which the pre-synthesised catalyst or commercially available catalyst is extensively premixed with the g-CN precursors in a silica crucible and calcined at a higher temperature in a muffle furnace. The technique is frequently utilized in the synthesis of nanomaterials and their composites because it is simple and inexpensive, and the desired product forms after 2-3 hours of heating and exhibits improved activity. Here since the precursors are not dissolved in any medium, the chances of crystal defects, low surface area, large particle size, uneven distribution of the catalyst over the base of GCN are possible compared to other methods.

4.3.4 Sol-gel Method

In sol-gel preparation of nanocomposites, the metal alkoxides or nitrates are used as the precursors, which are dispersed in a suitable solvent and stirred well so as to form sol. Sol is nothing but the colloidal suspension of oligomers. This sol is kept undisturbed and a period of time, when the sol undergoes hydrolysis and further the colloidal particle aggregates and undergoes

polycondensation reaction. This leads to the formation of gel which mainly consists of metal hydroxide or oxide bridges. The gel formed is dried and the resulting product is transformed into xerogel, which is annealed to form nanocomposite material. During this polycondensation process the metal hydroxide nuclei deposits on the surface of g-CN and establishes a bond with g-CN and precipitate as the nanocomposite material. This method can be used to obtain highly pure and homogeneous composites at low temperature than the other conventional methods. Sol-gel allows us to obtain nanomaterial in various forms like films, fibres, submicron particles etc.

4.3.5 Microwave Method

It is an ideal technique for faster process at high temperature is required. Microwave radiation can be used for the preparation of nanocomposite just like the solid state calcination process, wherein the cocatalyst and the precursor of g-CN is mixed and irradiated. Here the process is very quick due to the high energy irradiating into the molecular structure. But here the high thermal radiation can cause the g-CN to decompose as it's an organic molecule and the decomposition is faster when the oxygen in the cocatalyst gets activated.

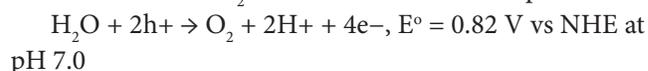
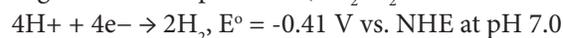
4.3.6 Hydrolysis Method

Hydrolysis way of synthesising nanocomposite involves the addition of the metal precursor and g-CN in distilled water and mixed under constant stirring at a higher temperature. The metal precursor hydrolyses on the surface of g-CN during the process, resulting in the development of a precipitate comprising nanocomposite. The nanocomposite is crystallized by drying in an oven at 80-90 °C and further calcinated at higher temperature for about 2 to 3 hours. The thus obtained nanocomposite is ground to a fine powder.

5.0 Graphene-g-CN Nanocomposite for Photocatalysis Water Splitting

The basic principle behind the hydrogen generation by water splitting is the photocatalysis reaction which involve the in-situ formation of e-hole pair, upon the incidence of visible light on the surface of a semiconductor material.

Here the photons having energy equal to or greater than the band gap of the semiconductor, on the surface of the semiconductor. These charge carriers separate and initiate the conversion of H⁺ to H₂, resulting in the Hydrogen Evolution Reaction (HER), meanwhile, the holes generated oxidises H₂O to O₂ resulting in Oxygen Evolution Reaction (OER). Water splitting can be achieved by a semiconductor only if it meets specific requirements. The highest height of VB must be greater than the water oxidation potential (EO₂/H₂O, 1.23 V vs. NHE), and the minimum position of the CB must be greater than the hydrogen reduction potential (EH₂/H₂O, 0 V vs. NHE).



As a result, the total reaction produces H₂ and O₂. To achieve the minimum dynamic requirement, the semiconductor should have a bandgap greater than 1.23 eV. This can be achieved by the combination of suitable materials. Graphene quantum dots have a band gap < 2.1eV, which makes them visible light active catalyst. Even though a lot of research is happening towards water splitting, only a very few single materials could achieve HER and OER. g-CN is one such material but the water splitting efficiency is unsatisfactory. Graphene, a two-dimensional macromolecular sheet of carbon atoms with a very high specific surface area and thermal conductivity, also demonstrated excellent photocatalytic efficacy for hydrogen or oxygen synthesis. The composite of Graphene and GCN with proper modifications in the structure could be a proper candidate for water splitting reactions. Through theoretical analysis and experiments, for the first time, Qiao *et al.*, showed the use of g-C₃N₄ linked nitrogen doped graphene (g-C₃N₄@NG) hybrid catalysts for electrocatalytic HER. Following the insertion of graphene sheets, g-C₃N₄ is immobilized to create layered composites, which significantly enhanced the BET surface area and hence demonstrated good catalytic activity. In this device, graphene sheets serve as conductive channels, efficiently segregating photogenerated charge carriers and improving H₂ production's visible-light capabilities. The ideal graphene content was found to be 1.0 wt%, and the associated H₂ generation rate was 451 mol h⁻¹ g⁻¹, which was more than 3.07 times that of pure g-C₃N₄. The utilization of a g-C₃N₄@NG catalyst in HER has been described

in acidic circumstances. The Volmer-Heyrovsky and Volmer-Tafel routes are the two most widely established HER response pathways. The free-energy difference of the second-step Tafel reaction for the Volmer-Tafel reaction under equilibrium potential is 0.33 eV, which is greater than the free-energy difference of the Heyrovsky reaction, according to DFT calculations (0.19 eV). The researchers then mixed porous g-C₃N₄ nanolayers with NG sheets to generate a film with unparalleled HER activity. The flaws and corners of g-C₃N₄ were considered to constitute the HER's catalytic centres.

A 3D design of 1D g-C₃N₄ nanoribbons with 2D graphene sheets (g-C₃N₄ nanoribbon-G) with high HER activity, a low-onset overpotential of 80 mV, and a Tafel slope of 54 mV was recently produced. The g-C₃N₄ nanoribbon-G catalyst displayed decent constancy at various scan rates, with a low overpotential of 207 mV to generate a 10 mA cm² HER current density, which was lower than that of g-C₃N₄@NG hybrids. At the same time, the resulting nanohybrid displayed outstanding long excellent reliability, which is critical for long-term hydrogen evolution. However, the g-C₃N₄ nanoribbon-G catalyst shown outstanding action of HER, Its production takes time and requires a huge number of organic solvents (e.g., concentrated H₂SO₄, NaNO₃, KMnO₄). Thus, employing a simple template-free technique, a dual-mesh of 2D g-C₃N₄ meshes in situ were generated over 2D graphene meshes (g-C₃N₄@G MMs). This material demonstrated an increase in specific surface area, resulting in greater hydrogen adsorption sites. This resulted in excellent HER activity.

6.0 Conclusion

The outstanding properties possessed by graphene modified g-CN makes them a potential, yet not much explored candidate for photocatalytic hydrogen generation applications. The attractive architecture that can be formed on the formation of hybrid nanostructures of curved nanosheet like morphology is an additional advantage of graphene based g-CN photocatalysts. The physicochemical properties such as porosity also enhances the ability to adsorb and hence to improve the overall hydrogen evolution capability. The role of graphitic carbon nitride in the composite can also be envisioned as a substrate wettability enhancer owing to the probability

of forming hydrogen bonds between water molecules and the nitrogen atoms in the graphitic carbon nitride. This mini review concentrated mainly on the synthesis techniques that can be resorted to construct the nano heterostructure between two 2D nanomaterials that are already reported which can be successfully used for the generation of hydrogen via photocatalytic water splitting reactions.

7.0 References

1. Gray HB. Powering the planet with solar fuel. *Nature chemistry*. 2009; 1(1):7-7.
2. Li X, Low J, Yu J. Photocatalytic hydrogen generation. *Photocatalysis. Applied*. 2016; 255-302.
3. Ateş F, Pütün AE, Pütün E. Fixed bed pyrolysis of *Euphorbia rigida* with different catalysts. *Energy Conversion and Management*. 2005; 46(3):421-432.
4. Audus H. Decarbonization of fossil fuels: hydrogen as an energy carrier. In *Fuel and Energy Abstracts*. 1997.
5. Martino M, Ruocco C, Meloni E, Pullumbi P, Palma V. Main hydrogen production processes: An overview. *Catalysts*. 2021; 11(5):547.
6. Marnellos GE, Klassen T. Welcome to Hydrogen. *A New International and Interdisciplinary Open Access Journal of Growing Interest in Our Society. Hydrogen*. 2020; 1(1):90-92.
7. Batzill, M. Fundamental aspects of surface engineering of transition metal oxide photocatalysts. *Energy & Environmental Science*. 2011; 4(9):3275-3286.
8. Huang H, He Y, Lin Z, Kang L, Zhang Y. Two novel Bi-based borate photocatalysts: crystal structure, electronic structure, photoelectrochemical properties, and photocatalytic activity under simulated solar light irradiation. *The Journal of Physical Chemistry C*. 2013; 117(44):22986-22994.
9. He DC, Fu QM, Ma ZB, Zhao HY, Tu YF, Tian Y, Lu HB. Facile synthesis and photocatalytic activity of ZnO/zinc titanate core-shell nanorod arrays. *Materials Research Express*. 2018; 5(2):025006.
10. Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. *Nature*. 1972; 238(5358):37-38.
11. Nguyen VH, Vo DVN, Nanda S. *Nanostructured Photocatalysts: From Fundamental to Practical Applications*. Elsevier. 2021.
12. Dhiman P, Rana G, Kumar A, Sharma G, Vo DVN, Naushad M. ZnO-based heterostructures as photocata-

- lysts for hydrogen generation and depollution: a review. *Environmental Chemistry Letters*. 2022; 1-35.
13. Li Y, Zhai X, Liu Y, Wei H, Ma J, Chen MS. WO₃-based materials as electrocatalysts for hydrogen evolution reaction. *Frontiers in Materials*. 2020; 7:105.
 14. Wang S, Lu A, Zhong CJ. Hydrogen production from water electrolysis: Role of catalysts. *Nano Convergence*. 2021; 8(1):1-23.
 15. Zhang X, Zhang J, Yu J, Zhang Y, Yu F, Jia L, Hou B. Enhancement in the photocatalytic antifouling efficiency over cherimoya-like InVO₄/BiVO₄ with a new vanadium source. *Journal of Colloid and Interface Science*. 2019; 533:358-368.
 16. Hu J, Sun Q, Ye ZS, Ling X. Sequential degradation-based burn-in test with multiple periodic inspections. *Frontiers of Engineering Management*. 2021; 8(4):519-530.
 17. Wang W, Jimmy CY, Shen Z, Chan DK, Gu T. g-C₃N₄ quantum dots: direct synthesis, upconversion properties and photocatalytic application. *Chemical Communications*. 2014; 50(70):10148-10150.
 18. Wang H, Yuan X, Wang H, Chen X, Wu Z, Jiang L, Zeng G. Facile synthesis of Sb₂S₃/ultrathin g-C₃N₄ sheets heterostructures embedded with g-C₃N₄ quantum dots with enhanced NIR-light photocatalytic performance. *Applied Catalysis B: Environmental*. 2016; 193:36-46.
 19. Zhou L, Tian Y, Lei J, Wang L, Liu Y, Zhang J. Self-modification of g-C₃N₄ with its quantum dots for enhanced photocatalytic activity. *Catalysis Science & Technology*. 2018; 8(10):2617-2623.
 20. Yang R, Zhang Y, Fan Y, Wang R, Zhu R, Tang Y, Zeng Z. In VO₄-based photocatalysts for energy and environmental applications. *Chemical Engineering Journal*. 2022; 428: 131145.
 21. Goettmann F, Fischer A, Antonietti M, Thomas A. Metal-free catalysis of sustainable Friedel-Crafts reactions: direct activation of benzene by carbon nitrides to avoid the use of metal chlorides and halogenated compounds. *Chemical Communications*. 2006; (43):4530-4532.
 22. Gago R, Jiménez I, Caceres D, Agulló-Rueda F, Sajavaara T, Albella JM, Rauhala E. Hardening mechanisms in graphitic carbon nitride films grown with N₂/Ar ion assistance. *Chemistry of Materials*. 2002; 13(1):129-135.
 23. Ma Z, Sa R, Li Q, Wu K. Interfacial electronic structure and charge transfer of hybrid graphene quantum dot and graphitic carbon nitride nanocomposites: insights into high efficiency for photocatalytic solar water splitting. *Physical Chemistry Chemical Physics*. 2016; 18(2):1050-1058.
 24. Ding F, Yang D, Tong Z, Nan Y, Wang Y, Zou X, Jiang Z. Graphitic carbon nitride-based nanocomposites as visible-light driven photocatalysts for environmental purification. *Environmental Science: Nano*. 2017; 4(7):1455-1469.
 25. Li G, Nie X, Chen J, Jiang Q, An T, Wong PK, Yamashita H. Enhanced visible-light-driven photocatalytic inactivation of *Escherichia coli* using g-C₃N₄/TiO₂ hybrid photocatalyst synthesized using a hydrothermal-calcination approach. *Water research*. 2015; 86:17-24.
 26. Kroke E, Schwarz M, Horath-Bordon E, Kroll P, Noll B, Norman AD. Tri-s-triazine derivatives. Part I. From trichloro-tri-s-triazine to graphitic C₃N₄ structures. *New Journal of Chemistry*. 2002; 26(5):508-512.
 27. Tonda S, Kumar S, Kandula S, Shanker V. Fe-doped and-mediated graphitic carbon nitride nanosheets for enhanced photocatalytic performance under natural sunlight. *Journal of Materials Chemistry A*. 2014; 2(19):6772-6780.
 28. Gao H, Jia J, Guo F, Li B, Dai D, Deng X, Liu G. The electronic structure and photoactivity of TiO₂ modified by hybridization with monolayer g-C₃N₄. *Journal of Photochemistry and Photobiology A: Chemistry*. 2018; 364:328-335.
 29. Yan Y, Chen J, Li N, Tian J, Li K, Jiang J, Chen P. Systematic bandgap engineering of graphene quantum dots and applications for photocatalytic water splitting and CO₂ reduction. *ACS Nano*. 2018; 12(4):3523-3532.
 30. Zhang J, Sun J, Maeda K, Domen K, Liu P, Antonietti M, Wang X. Sulfur-mediated synthesis of carbon nitride: band-gap engineering and improved functions for photocatalysis. *Energy & Environmental Science*. 2011; 4(3):675-678.
 31. Asadzadeh-Khaneghah S, Habibi-Yangjeh A, Vadivel S. Fabrication of novel g-C₃N₄ nanosheet/carbon dots/Ag₆Si₂O₇ nanocomposites with high stability and enhanced visible-light photocatalytic activity. *Journal of the Taiwan Institute of Chemical Engineers*. 2019; 103:94-109.
 32. Acharya R, Parida K. A review on TiO₂/g-C₃N₄ visible-light-responsive photocatalysts for sustainable energy generation and environmental remediation. *Journal of Environmental Chemical Engineering*. 2020; 8(4):103896.
 33. Park S, An J, Jung I, Piner RD, An SJ, Li X, Ruoff RS. Colloidal suspensions of highly reduced graphene oxide

- in a wide variety of organic solvents. *Nano letters*. 2009; 9(4):1593-1597.
34. Gilje S, Han S, Wang M, Wang KL, Kaner RB. A chemical route to graphene for device applications. *Nano letters*. 2007; 7(11):3394-3398.
35. Huang C, Li C, Shi G. Graphene based catalysts. *Energy & Environmental Science*. 2012; 5(10):8848-8868.
36. Poh HL, Šaněk F, Ambrosi A, Zhao G, Sofer Z, Pumera M. Graphenes prepared by Staudenmaier, Hofmann and Hummers methods with consequent thermal exfoliation exhibit very different electrochemical properties. *Nanoscale*. 2012; 4(11):3515-3522
37. Bachina AK, Popkov VI, Seroglazova AS, Enikeeva MO, Kurenkova AY, Kozlova EA, Rempel AA. Synthesis, Characterization and Photocatalytic Activity of Spherulite-like r-TiO₂ in Hydrogen Evolution Reaction and Methyl Violet Photodegradation. *Catalysts*. 2022; 12(12):1546.