Graphitic carbon nitride: A futuristic material with nascent applications

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Abstract:

The quest for advanced materials with a wide range of applications is never-ending. A plethora of materials have been invented in the recent past to address the emerging needs of the evolving society. Research has been focused on exploring the new possibilities of existing materials and the development of new materials altogether. Many of these materials show unequivocal improvement in their respective fields of application. Along with the multifunctionality, ease of synthesis, performance stability and shelf life are also important for the newly developed materials. Graphitic carbon nitride is an attractive 2-D material with a layered structure. The exceptional optical and electronic properties of the material along with chemical stability, ease of production with high yield and long shelf life make graphitic carbon nitride a possible futuristic material with applications ranging from photocatalysis to bioimaging and nano ion transport. Numerous investigations on the photocatalytic applications of graphitic carbon nitride have been reported in the recent literature. It can be chosen as a representative material for visible light photocatalyst analogue to TiO_2 in this regard. Strategies to overcome the bottlenecks of graphitic carbon nitride-mediated photocatalysis have gained quite a research momentum in recent years. Strikingly properties like hydrophobicity, electrical conductivity and thermal behaviour remain largely unexplored. Exploring these properties could contribute to a better understanding of the characteristics of the material so that it could be successfully utilized as a multifunctional futuristic material for emerging applications.

Introduction

Over the past few decades, the significant growth of various industries has put tremendous strain on several aspects of sustainability, mainly in environmental areas. Sustainability has become a key factor affecting both industrial and academic fields, which leads to research in different areas such as photochemistry, supercapacitors, batteries, energy harvesting, polymers, biomass conversion, etc. The semiconductors are the robust materials behind these ongoing technology applications, ranging from electronics to renewable energy. Among the semiconductor family, graphitic carbon nitride (g-C_3N_4) has become a gemstone due to its extraordinary properties [1]. The g-CN is composed of earth-rich carbon and nitrogen elements. Its high chemical and thermal stability, resistance to corrosion and photochemical degradation, attractive electronic structure, suitable energy gap (2.7 eV), low density, and nontoxic nature make it an appropriate material for versatile applications [2]. As a result of these exciting properties and two-dimensional structure, it has gained significant attention in the field of photocatalytic degradation [3], gas sensors [4], hydrogen evolution [5], microwave absorbers [6], etc. Its inherent photocatalytic activity combined with its visible light-responsive band gap, makes it a promising material for various catalytic processes. The g-CN can efficiently use solar energy to trigger chemical reactions, such as CO_2 reduction, water splitting [7], and organic pollutant degradation [8]. These are important for renewable energy production and environmental remediation. Furthermore, its robustness allows for extended use in various applications, owing to its potential use in practical applications. This chapter will present the properties, synthesis, and applications of g-CN and g-CN-based nanomaterials. Starting with a brief history of g-CN, we will move on to its physical and chemical properties. Afterwards, their numerous applications and mechanism behind photocatalytic organic pollutant degradation under visible light exposure are discussed in detail. Finally, the chapter includes an overview of g-CN applications, future challenges, and their emerging interest in several fields, which will pave the way to focus on the scope of g-CN in various areas.

A brief history of Graphitic carbon nitride

The g-CN has a remarkable history. The research on carbon nitride begins with the production of yellow polymer by the calcination of mercury thiocyanate by Berzelius [9]. Later, in 1834 Liebig named the linear polymer $(C_3N_3H)_n$ as "melon"[10], which opened a new platform for the chemical world. As a novel material, several research works have been carried out due to its structural curiosity. In 1966, Teter and Hemley predicted cubic-CN, g-CN, α-CN, β-CN, and pseudo-CN phases of carbon nitride [11]. In 1989, Liu and Cohen studied the properties of the hypothetical covalent compound β polymorph of hydrogen-free C_3N_4 using an empirical model developed in 1985 to study the bulk modulus of tetrahedral solids [12],[13]. The β-CN resembles the crystal structure β-Si_3N_4, which was reviewed in 1993 and showed diamond-like properties such as hardness, low ionicity, and metastability [14]. Among the carbon nitride family, g-CN is the most stable allotrope. It has gained attention due to its graphite-like layered structure. Instead of a C-C bond, g-CN bears strong C-N covalent bonds in each layer. g-CN also attains an attractive electronic band structure, high physical and chemical stability, and a visible light-responsive band gap. So, it is used in various applications.

Since Wang et al. introduced g-CN as a metal-free photocatalyst for H_2 generation in 2009, much work has been initiated on the compound [15]. Afterward, due to its fascinating properties, it has become one of the curious photocatalytic materials for environmental remediation. In 2012, Wang et al. confirmed that tri-s-triazine (C_6N_7) units-based g-CN are more stable than s-triazine (C_3N_3) based g-CN [16]. Then, several research works are carried out using this most stable g-CN form. A detailed discussion of several physicochemical features is provided in the next subsection.

Properties of g-CN

The applications of g-CN are mainly based on the materials inherent structural, optical, and electrical properties. Thus, an in-depth understanding of these properties will lead to the successful production and utilization of g-CN for several applications.

Structural Properties

As a novel synthetic polymer with carbon and nitrogen, g-CN has become a research hotspot due to π- conjugated graphite-like layered structure [17]. The g-CN is in the form of 2D sheets made up of s-triazine or tri-s-triazine (heptazine) tectonic unit via tertiary amines

(Figure 1). Density functional theory showed that the s-triazine phase is thermodynamically weaker than the tri-s-triazine phase [18]. These two allotropes energy stability is different based on the nitrogen electronic environment and pore size of the nitrogen atom. Analogous to graphene, the layer arrangement of g-CN is of the ABAB type. Attractively, g-CN layers are much closer together (0.319 nm) than crystalline graphite layers (0.335 nm), which suggests a tight binding, increased packing density, and more charge flow perpendicular to the layers [19].

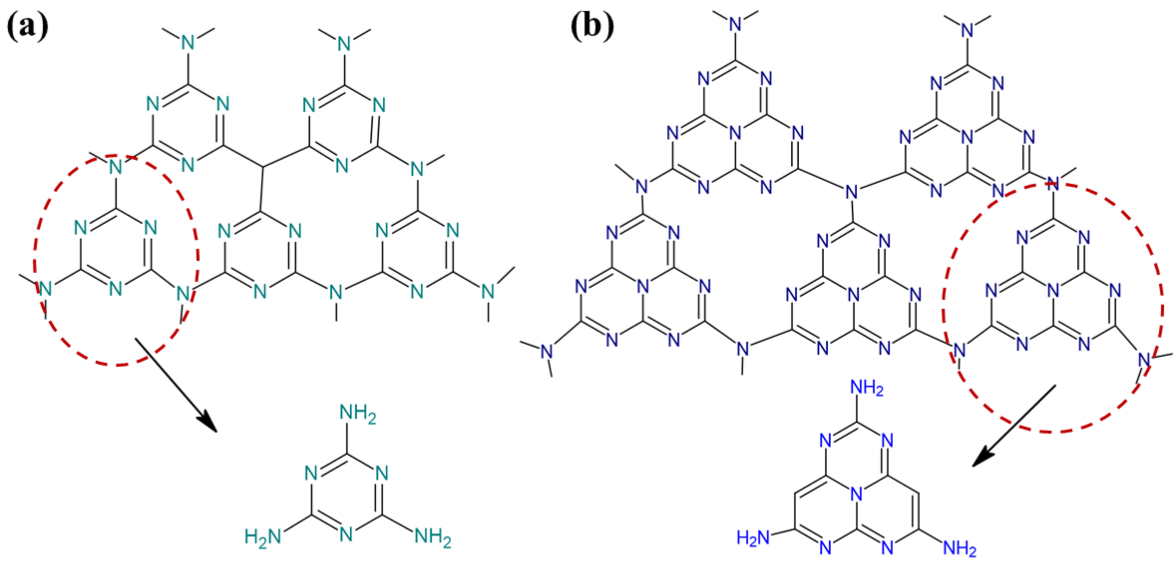

Figure 1. *Structure of (a) s-triazine and (b) tri-s-triazine (heptazine) based g-CN.*

Additionally, the strong van der Waals interactions among g-CN interlayers make it chemically stable, allowing it to withstand most organic solvents, alkali, and acid solutions [20]. Furthermore, the 2D nanosheets of g-CN provide a significant specific surface area (Theoretically, the specific surface area of g-CN monolayer up to 2500 m^2g^{-1}), which is appropriate for reactant adsorption and hence improves photocatalytic activity [21].

Optical propertie

Photoluminescence (PL) and UV/Vis diffuse reflectance spectroscopy are typically used to describe the optical characteristics of g-CN, and these studies are crucial for various applications. Generally, the optical band gap of g-CN is ~2.7 eV [22], which can be altered based on different precursors and synthesis procedures. Moreover, at room temperature, the g-CN exhibits strong blue photoluminescence at $\lambda = 460$ nm. In 2013, Zhang et al. confirmed the luminescence of g-CN depends on the calcination temperature [23]. Emissions can range widely from 430 to 550 nm, depending on the synthesis temperature. In the case of melamine precursor-based g-CN preparation, the emission band is centred at 462 nm, 458 nm, and 426 nm with respect to the calcination temperature of 600 °C, 550 °C, and 500 °C, respectively. Here, the transitions between several active energy-splitting energy levels change the emission band [24].

Additionally, the g-CN exhibits an advantageous two-photon absorbance behaviour. The g-CN could simultaneously produce intense visible light fluorescence and absorb two near-infrared photons. Zhang et al. demonstrated that the g-CN produced a strong intense green light when activated by the 780 nm red laser. However, when two-photon excitations were compared to one photon, g-CN nanopowder showed a significant redshift [25].

Electronic properties

The g-CN is a metal-free n-type semiconductor polymer. Due to the band gap (2.7 eV) in visible-light region, making it a good candidate for use as a photoelectric material. The electronic structure of g-CN is mainly responsible for the combination of positions of lonepair electrons and a unique π-bonding conjugated delocalized system [26]. In 2014, Guoping Dong et al. reviewed the photocatalytic and electronic properties of g-CN [20]. The electrical band structure of g-CN is formed by lone pair electrons from nitrogen atoms, which also create a lone pair valence band (VB). So, the lone pair electrons in the nitrogen atom have gained significant attention in the electronic band structure. According to DFT theory, the HOMO-LUMO band gap of melem is 3.6 eV, which decreases after melon (2.6 eV) formation. Afterward, which is decreases to 2.1 eV for g-CN [15]. The wave function studies show that the valance and conduction band (CB) of g-CN depend on carbon and nitrogen- Pz orbitals. After that, Wei et al. investigate optical and electronic properties using the many-body Green's function method, which gives a band gap of 4.24 eV for monolayered triazine-based g-CN. In the case of tri-s-triazine-based g-CN, 5.22 eV corresponds to the direct band gap, and 4.15 eV corresponds to the indirect band gap [27],[28]. Nowadays, to get enhanced photocatalytic and optical properties, the band gap of g-CN is usually altered using several methods including doping, heterojunction formation, etc., making them a functional material for various electronic devices.

Synthesis of g-CN

The bulk g-CN is usually synthesized via a simple thermal polymerization method using nitrogen-abundant precursors like thiourea, cyanamide, urea, melamine, dicyanamides, etc. (Figure 2). Initially, the precursor is converted to melamine. Afterwards, it transforms into melam at 317 ℃ and gets converted to melem at 390 ℃. Later, melem is changed into melon at 500 ℃ (i.e., 1D tri-s-triazine chain). Then, it is polymerized into a 2D conjugated g-CN polymer framework (at 520 °C) [Figure 3]. The g-CN is typically thermally stable in air up to 600 °C. Later, Zhang et al. synthesized nanosheets from bulk g-CN through liquid exfoliation. Then, several studies are focused on the preparation of nanosheets.

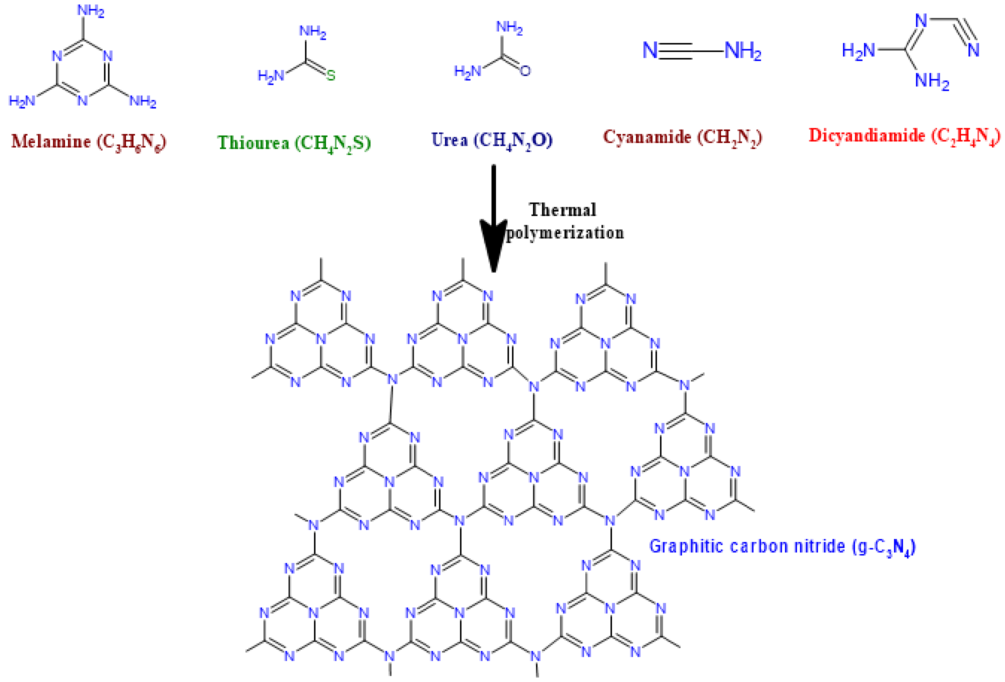

Figure 2. *Schematic representation of the synthesis of g-CN by thermal polymerization of different precursors.*

Afterwards, liquid, wet chemical, and thermal exfoliation methods and acid treatments are used to prepare 2D nanosheets. Later, utilizing template-based approaches, a regulated morphology, enhanced nanostructures, and surface area are developed for various applications [29],[30]. The g-CN QDs emit strong fluorescence and are metal-free, nontoxic, and stable. So, it attains more attention than other traditional QDs [31]. Moreover, the g-CN nanotubes also get much attention due to their one-dimensional geometry, which allows fast charge transfer and delays undesired electron-hole recombination.

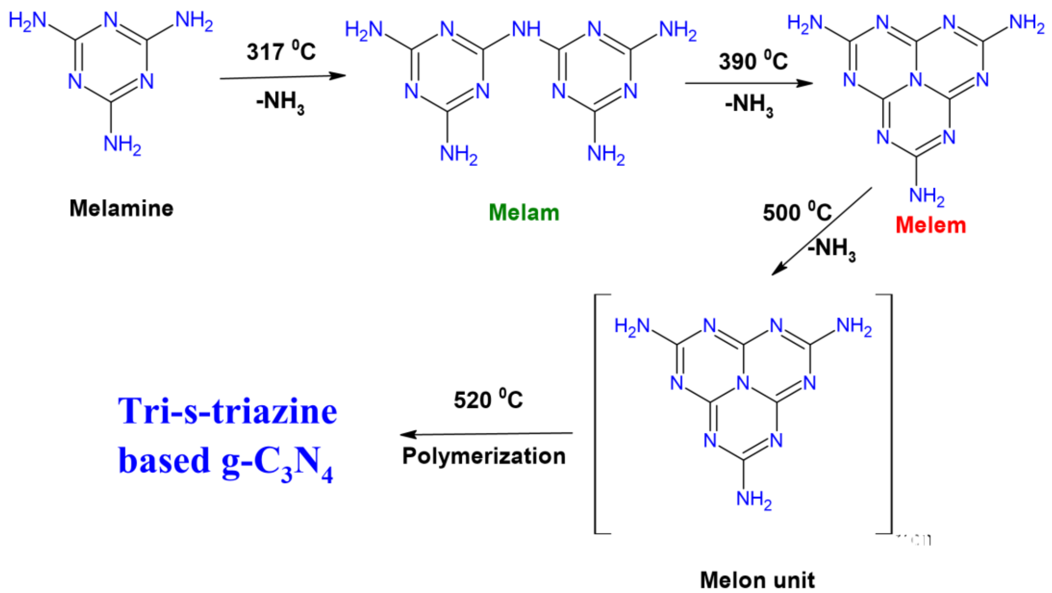

Figure 3. *The synthesis process of g-CN from melamine.*

Even though its outstanding properties include ease of synthesis in bulk scale, it is surprising that g-CN didn't get proper attention compared to other semiconductors. Therefore, here we are focusing on enhancing the properties of g-CN- based nanomaterials for different applications. So, in the next section, we have discussed the applications of g-CN in various fields.

Applications of g-CN

G-CN has found applications in a variety of fields, where conventionally metal oxide semiconductors were used. Due to its unique structure, visible light absorption capacity, chemical inertness and photostability in aqueous solutions, g-CN is widely used in various fields such as catalysis, optical devices, biomedical applications, fuel cells, sensors and nanofluidic ion transport[29],[32]–[36]. Figure 4 gives a brief impression of the applications of g-CN in various domains. It can be seen that the applications of g-CN are predominantly focused on the optoelectronic properties of the material since studies related to physical chemistry, nanotechnology, environmental engineering etc. contribute the major share. Hence, the status quo of the applications of g-CN can be broadly classified into photocatalysis-based and non-photocatalysis-based disciplines.

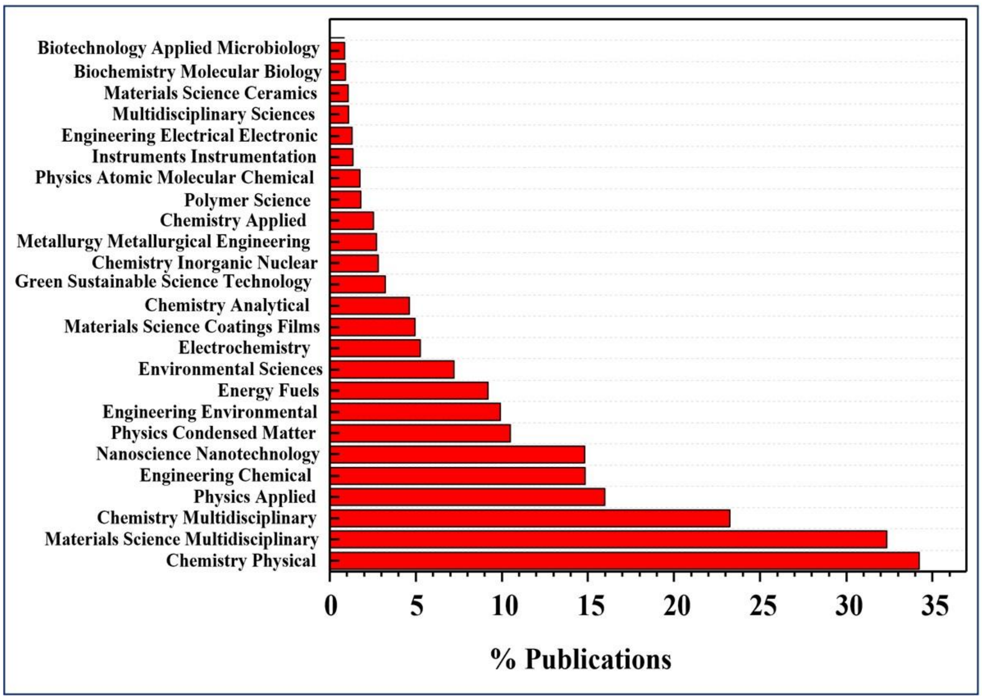

Figure 4. *Reports on the applications of g-CN by discipline**,** source: web of Science*

Ever since the discovery of the photocatalytic application of g-CN, the material has become a strong contender to conventional photocatalysts such as TiO_2, ZnO etc. The metal-free nature and visible light responsiveness and photostability of g-CN have sparked its wide acceptance [37]. According to Web of Science records, photocatalysis alone constitutes ~55 % of the total reports on the application of g-CN. Figure 5 (a) supports this claim and recent reports suggest that with appropriate modifications g-CN possesses the prospects of industrial production [32]. Electrochemistry, development of novel 2D materials, biosensors, nanoparticle synthesis and water treatment together contribute ~ 30% of the total applications of the g-CN. Emerging applications such as bioengineering, hydrogen storing, microfluidics, polymer science etc. are yet to be explored since contributions from these areas are scarce to date and cumulatively furnish only ~10 % of publications as depicted in Figure 5 (b).

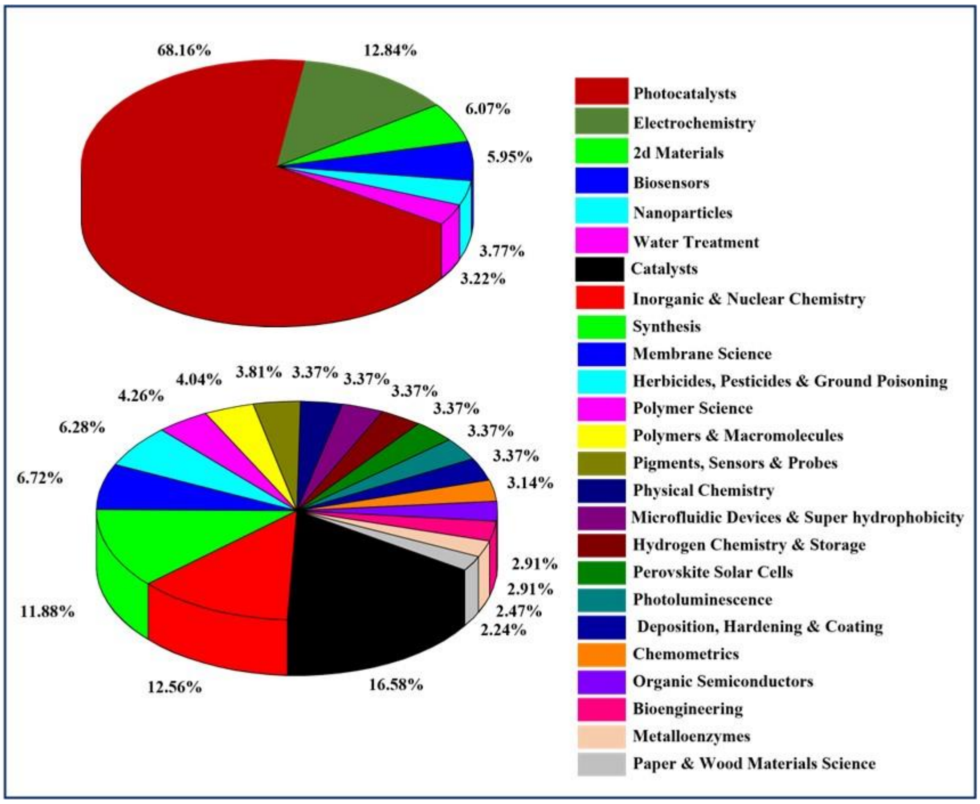

Figure 5. *Reports on the applications of g-CN in various fields, Source: Web of Science*

Photocatalysis on g-CN can be explained with the schematic diagram shown in Figure (6). The process involves light absorption by the semiconductor, charge carrier excitation, charge separation and migration, and subsequent redox reaction on the catalytic surface in case of successful photoexcitation. In other cases, the photoexcited charge carriers undergo recombination either due to deexcitation or surface charge recombination. Both processes lead to energy loss. In the first case, upon irradiation of light with sufficient energy to excite electrons from the VB to the CB of g-CN, electrons are transferred from the highest occupied molecular orbital (HOMO) of the VB to the lowest unoccupied molecular orbital (LUMO) of the CB. Then these charge carriers namely, electrons in the CB and holes in the VB react with dissolved oxygen and hydroxyl groups present in the aqueous solution to produce active oxygen species such as superoxide radical and hydroxyl radical etc. The active oxygen species further react with the pollutants and degrade them to simple molecules through oxidation and reduction reactions. The whole act of semiconductor-based photocatalysis can be summarised into the following set of equations.

$$h\upsilon + Semiconductor \rightarrow e_{CB}^{-} + h_{VB}^{+} \quad [1]$$

$$O_2 + e^-_{CB} \rightarrow O_2^{*-} \qquad [2]$$

$$H_2O + h^+_{VB} \rightarrow OH^* + H^+ \qquad [3]$$

$$Organic\ pollutant + \ O_2^{*-}\ or\ OH^* \ \rightarrow Intermediates \rightarrow \ H_2O + CO_2 \qquad [4]$$

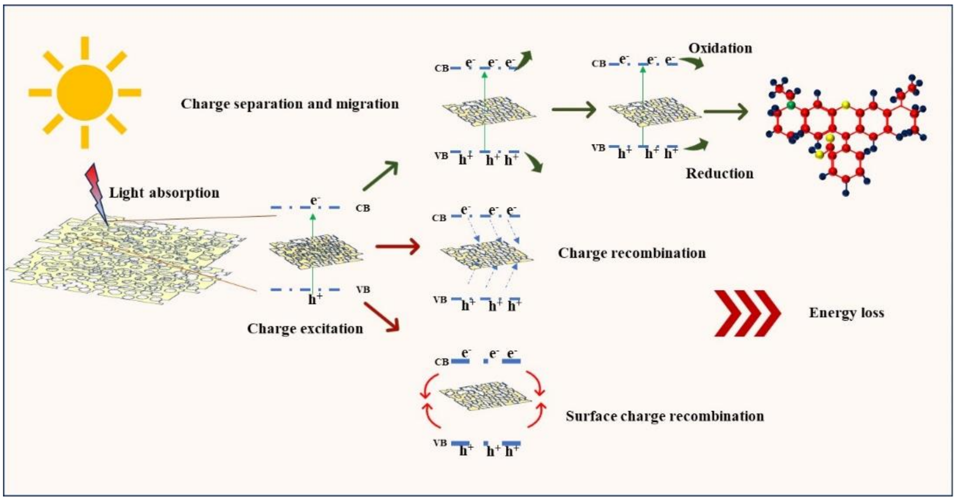

Figure 6: *Steps involved in the photocatalytic activity on g-CN*

The fundamental principles of photocatalysis have found applications across various fields which can be broadly classified into energy conversion and pollution abatement techniques. g-CN-based energy conversion methods focus on the production of cleaner energy sources such as water splitting and hydrogen peroxide production. New research areas such as nitrogen fixation and CO_2 capture are emerging as these procedures support the efforts to reduce carbon footprint and vital nutrient supply for agriculture.

Conventional applications of g-CN-based photocatalysis

Energy conversion	Pollution abatement		
	Gaseous pollutant removal	Treatment of organic pollutants	Removal of heavy metals
CO_2 capture	Nitrogen oxides(NO_x)	Antibiotics	Cr(IV)
Nitrogen fixation	Formaldehyde (HCHO)	Pesticides	Hg^0
Hydrogen peroxide generation	Sulpher containing gases	Endocrine disruptors	AS(III)
Water splitting		Textile effluents	

Energy conversion

Photocatalytic CO_2 capture by g-CN is carried out by converting the CO_2 present in the environment to useful simple molecules such as formaldehyde, formic acid, methanol etc. the process can be stoichiometrically represented in the following equations [38].

$$CO_2 + 2e^- + 2H^+ \rightarrow HCOOH$$

$$CO_2 + 4e^- + 4H^+ \rightarrow HCHO$$

$$CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O$$

Similarly, nitrogen fixation converts nitrogen to ammonia according to the following equation [39].

$$N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$$

Photocatalytic hydrogen peroxide generation over g-CN is achieved through oxygen reduction according to the equations [40]. H_2O_2, which is used in large amounts for bleaching of paper and pulp is currently produced by anthraquinone method which has serious environmental implications. Photocatalysis assisted H_2O_2 production hence offers an environmentally benign alternative.

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2$$

Water splitting is a long-researched area in the applications of semiconductor photocatalysis since the groundbreaking discovery of Electrochemical Photolysis of Water over TiO_2 electrode by Hujishima and Honda [41]. G-CN has received striking recognition in this field. The process of photocatalytic water splitting can be illustrated with the help of Figure (7).

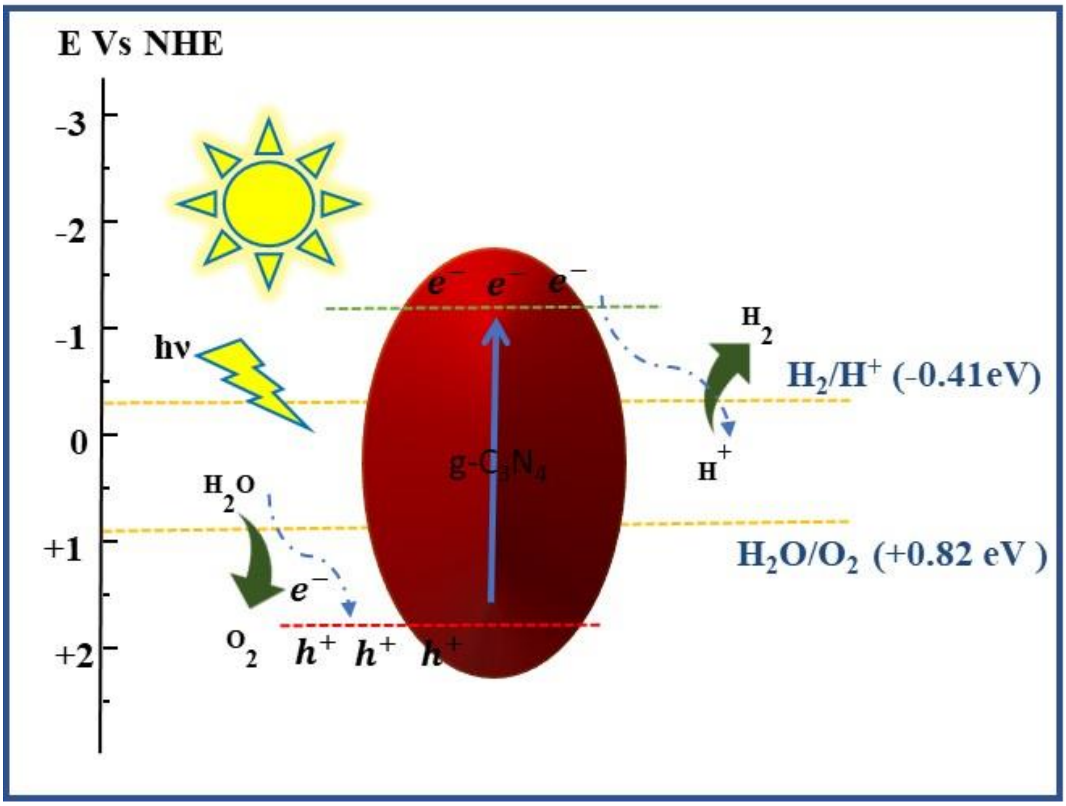

Figure 7: *schematic diagram of the generation of active oxygen species over g-CN during photocatalysis*

Photoexcited electrons from the CB of g-CN react with H^+ ions and produce H_2. Simultaneously, the holes in the VB oxidize water into O_2 and H^+ ions.

Pollution abatement with g-CN-based photocatalysis.

Ecological contamination mitigation finds the largest application of g-CN-rooted photocatalysis owing to its fundamental virtues as a representative visible light photocatalyst. Aquatic pollutants such as antibiotics, endocrine disruptors, pesticides and textile dye effluents have been successfully degraded by g-CN-assisted photocatalysis in the last decade. Similarly, the removal of heavy metals such as Cr(IV), Hg^0 and AS(III) from aqueous solutions has been reported recently. Volatile organic carbon compounds such as HCHO produced from plastic and synthetic leather manufacturing, sulfur-containing toxic gases and nitrogen oxide compounds are also degraded into simple inorganic molecules by G-CN-based photocatalytic reactions.

Strategies to improve photocatalytic properties of g-CN

Though the use of g-CN as a representative photocatalyst has increased in recent years, innate limitations such as high charge recombination, difficulty in charge separation and low surface area have restricted the applications of the material. Hitherto, the development of a suitable catalyst with appropriate light utilization, recyclability, ease of synthesis and cytotoxically benign has not been developed. The quest for such a favourable catalyst has contributed to various modifications to the g-CN photocatalysts. Methods such as photo enzyme catalysis, dual metallo catalysis, development of carbon dot-G-CN composites and G-CN-based plasmonic catalysis are some of these techniques to name illustrated in Figure 8 [42]–[48].

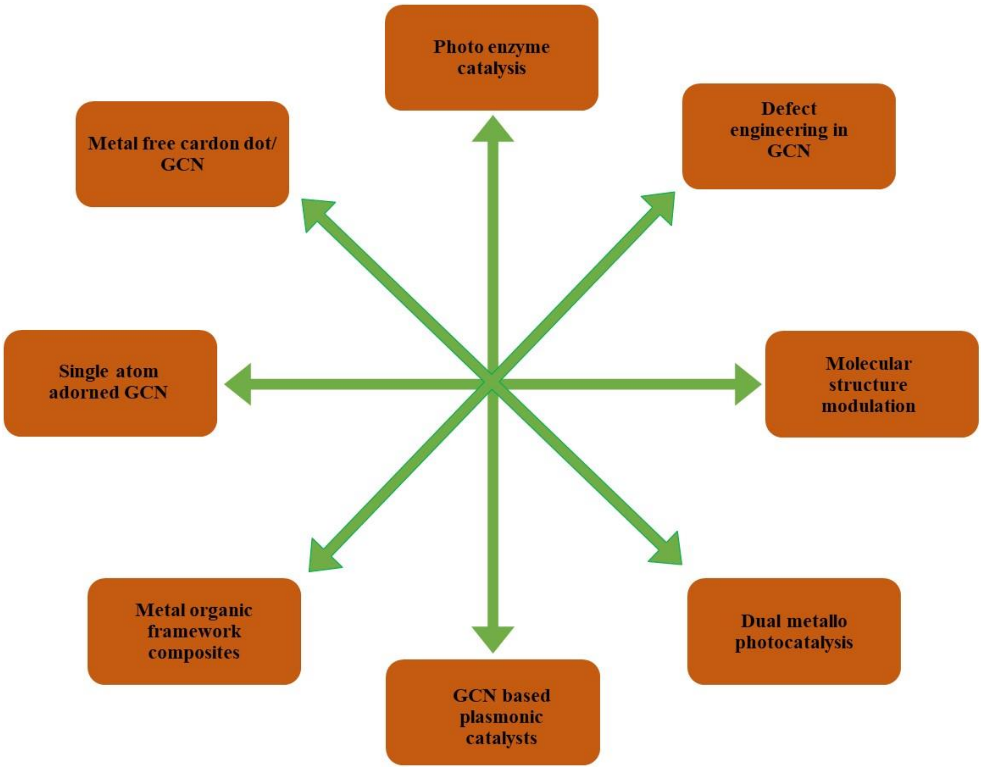

Figure 8 *Strategies to improve the photocatalytic activity of g-CN*

Nascent applications

Investigating the emerging scopes of g-CN in fields like biomedical applications, incorporation with fuel cells, chemical sensing for hazardous materials, development of optoelectronic devices and in nanofluidic ion transfer are prospering. Figure 9 depicts the nascent applications of g-CN. The biomedical applications of g-CN are an emerging field of new research interest and are widely being studied in bioimaging, biosensing and therapeutic purposes such as cancer treatment[49]. The 2D structure and innate ability to absorb oxygen molecules through the nitrogen-rich sites of g-CN make it an attractive material for oxygen reduction reactions in fuel cells. [50]. Similarly, G-CN finds emerging applications in the sensing of the variation in humidity and volatile organic compounds [51]. Hazardous materials such as phenolic compounds, pesticides, heavy metals and drugs are also detected with g-CN sensors[52]. Research on thin films based on g-CN as cutting-edge materials for the development of new optoelectronic gadgets is in bloom because of the optoelectronic characteristics of the material [53]. The stability of g-CN in aqueous solutions provides an exceptional opportunity to design and fabricate composite membranes for ion transport in applications such as osmotic energy conversion [54]. Heat transfer applications involving nanofluids utilize the ability of g-CN to enhance the thermal diffusivity of the base fluid for increasing heat flux between surfaces [55].

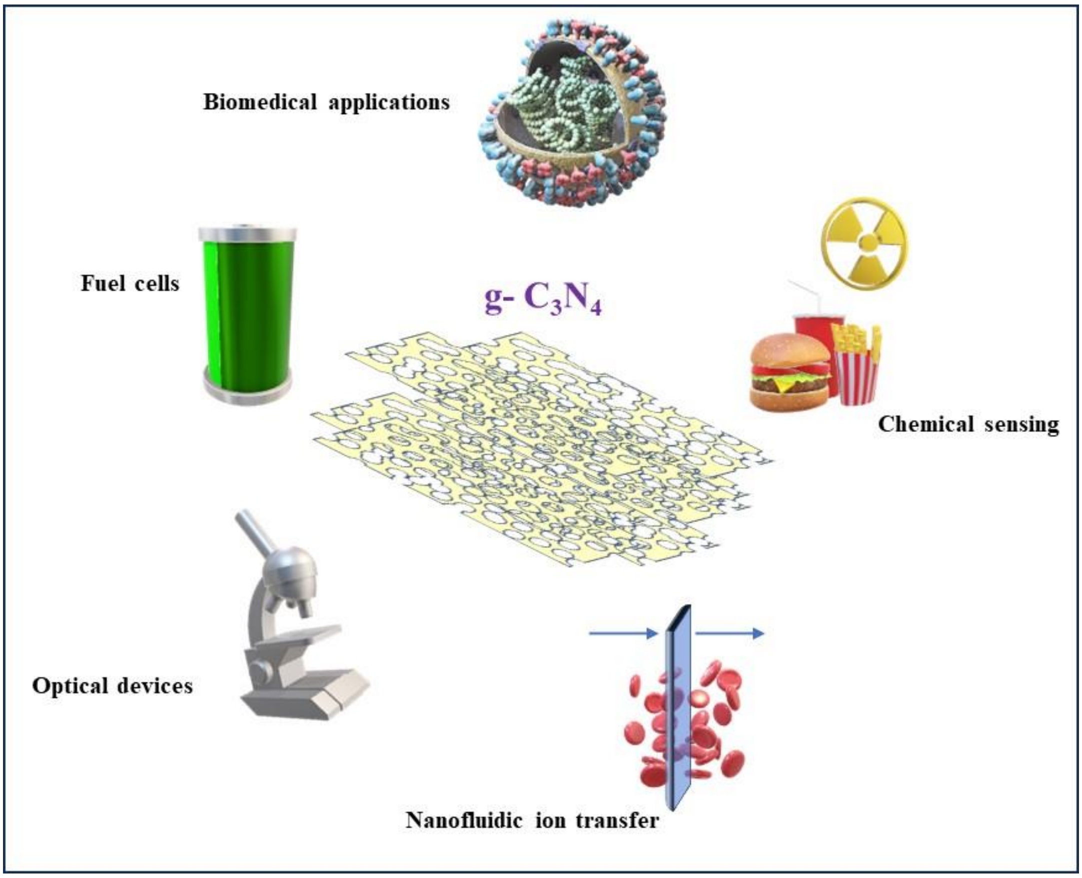

Figure 9 *Emerging application of g-CN in various fields*

Future scopes

The properties of g-CN except for the optoelectronic characteristics are largely unexplored to date. With new inventions in bandgap tuning, heterojunction creation with materials of appropriate band alignment and defect engineering offers a whole new arena in exploiting the optoelectronic properties for energy and environmental applications. New research horizons such as the design and development of g-CN-assisted osmotic membranes for desalination, nanofluidic ion transport in nanofluidic heat transfer enhancement, heavy metal uptake inhibition by engineering g-CN single atom thick sheets etc. explores the prospects of sustainable development.

Conclusions

G-CN is a 2D material with a layered structure. The optical, electronic, chemical and thermal characteristics of the material have found abundant applications in various fields from gas sensing to oil-water separation. The favourable bandgap and visible light absorption have given the material wide acceptance in visible light-responsive photocatalysis. Even though the material possesses exceptional optical activity and resistance to photo corrosion, the photocatalytic application of the material is largely limited due to low surface area and high photoinduced charge recombination. Excessive research has been carried out to overcome these restrictions and advanced techniques such as plasmonic catalyst development, defect engineering and nonmetal material incorporation are in wide practice. Except for the optical properties, features such as hydrophobicity, thermal resistance etc have been largely understudied and further research and development are required to explore the complete potential as a multifunctional material sustainable applications.

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