Fabrication of Graphitic Carbon Nitride (g-C₃N₄) Photocatalyst and Its Metal-free Efficient Nanocomposites

1Arslan Bashir, 2Muhammadali Raza, 3Maria Khalid, 4Urooj Shahzadi

Abstract: Graphitic carbon nitride (g-C₃N₄) is a group of carbon nitride compounds with a general formula close to C₃N₄ (though commonly with non-zero quantity of hydrogen) and two important substructures dependent on heptazine and poly (Triazine imide) units which liable upon reaction conditions, display reactivities, properties and degree of condensation. Graphitic carbon nitride has high thermal stability, stable chemical structure, non-dangerous nature and medium band gap, as an interesting unique light dynamic semiconductor photocatalyst. This review exhibits the most recent advancement in formation of graphitic carbon nitride C₃N₄. Fused nanocomposites were used to investigate the photocatalytic ability for purification of water. The graphitic carbon nitride based nanocomposites were sorted as non-metal doped g-C₃N₄, noble metals/g-C₃N₄ heterojunction, transition and post transition metal based g-C₃N₄ nanocomposite and g-C₃N₄ without metal nanocomposite. Recently, Graphite carbon nitride (g-C₃N₄) has gained worldwide attention due to great redox ability, metal free nature, suitable energy gap and visible response, Graphite carbon nitride (g-C₃N₄) is more energy efficient than TiO₂ and has better photocatalytic ability through solar irradiation because it can absorb visible light directly. Small surface area, insufficient light absorption and fast recombination of hole pairs and photogenerated electron are some drawbacks of pure g-C₃N₄.

Keywords: Graphitic carbon nitride (g-C₃N₄), Nanocomposites, advance oxidation process, Waste water treatment, Photocatalysis.

1. INTRODUCTION

In a time of fast development of material science and science Limin song began his work in Polytechnic University. They started investigation on Graphitic C₃N₄ photocatalyst for Esterification of benzaldehyde and alcohol under visible light radiation. Aimed their examination they found that the reaction of alcohols and carboxylic acids catalyzed by acids is the customary strategy used to get ready esters in the chemical industry[1].

In this investigation, they report the synthesis of active graphitic carbon nitride (g-C₃N₄) that might be utilized in the one-step reaction between benzaldehyde and alcohol to advance the specific development of esters under visible light illumination. Other than Junying Liu also begun work on graphitic carbon nitride (g-C₃N₄)[2]. He began his work in Jiao Tong University on Efficient photocatalytic hydrogen evolution on N-deficient g-C₃N₄ achieved by a molten salt post-treatment approach. He saw that the carbon nitride (g-C₃N₄) is a fascinating metal-free photocatalyst for active solar hydrogen production. This disclosure may open a novel avenue to manufactured exceedingly proficient g-C₃N₄ catalysts[3].

Carbon nitride is made out of C and N with some pollution of H, which all is abundant crude materials. Semi-conducting properties of g-C₃N₄ likewise definitely recognize it from graphene[4]. The thermal and chemical stability of g-C₃N₄ in an aqueous suspension stage and under photocatalytic reaction condition makes it an remarkable material[4-5]. This g-C₃N₄ is viewed as the most seasoned engineered polymer previously announced by Berzelius and Liebig in the year 1834 and named as ‘melon’[6]. A flow sheet outline is given in (Fig. 1) showing a summary of historic improvement in understanding g-C₃N₄ and its application in photocatalysis. In 1922, Franklin found the exact synthesis of ‘melon’ to be
C₃N₄. Next, Pauling and Sturdivant determined tri-s-triazine type structure of C₃N₄ in the year 1937[7]. By 1940 it was realized that this material ‘melon’ has a graphite structure as detailed by Redemann and Lucas. Photocatalysis got huge consideration received after Fujishima and Honda announced photocatalysis of water on TiO₂ in 1972[1].

![Fig.1. Historic development on understanding g-C₃N₄ and photocatalysis over it][8]

In excess of 5500 research article investigating photocatalytic activity of graphitic carbon nitride were distributed till March 2018 with high significance and huge research premium (Fig. 2).

![Fig.2. Annual publication details of g-C₃N₄ applications from 1994 to 2018][9]

Wide assortments of materials, for the most part inorganic semiconductors were assed for photocatalytic application. Graphitic carbon nitride (g-C₃N₄) is a group of carbon nitride compounds with a general formula close to C₃N₄ (through normally with non-zero amount of hydrogen) and two major substructures dependent on heptazine and poly (Triazine imide) units which, contingent on reaction conditions, display various degrees of condensation, properties and reactivities[9]. Novel nonmetal catalysts, such as graphitic carbon nitride (g-C₃N₄), have pulled in the consideration of many researchers because of extraordinary their semiconductor properties (band gap of 2.7 eV), visible light absorption, high strength, nontoxicity, and simplicity of planning in aqueous solution. Specifically, the utilization of g-C₃N₄ in photocatalysis has been widely considered. As a photocatalyst, the primary utilization of g-C₃N₄ includes photocatalysis of water to obtain hydrogen, light degradation of organic dyes, and photocatalytic organic reactions. Numerous investigation on the use of photocatalytic oxidation to synthesize organic matter have been performed by Wang and Antonietti, including examines on oxidation of benzene to phenol, oxidation of aliphatic C-H bonds, oxidative coupling of amines, and particular oxidation of alcohols[6].

In recent times, g-C₃N₄ has arisen as the oldest polymer with general formula of (C₃N₃H)ₙ. In year 1990s, Liu and Cohen forecast research of ultra-hard carbon nitride material with diamond like potential. Wang and coworkers investigated photocatalytic action of g-C₃N₄ as metal-free and conjugated stable material for water splitting in 2009. The exclusive properties of g-C₃N₄ like engaging electronic structure, n-type semiconductor, non-poisonous, earth plentiful and adjusted band gap make it reasonable contender for visible light helped photocatalytic water sanitization (Fig. 3)
Graphitic carbon nitride based photocatalyst comprise one dimensional (1D)[10], two dimensional (2D) nanosheets and three dimensional (3D) categorized structures, widely investigated amid past years with sunlight based vitality use, capable charge transporter partition, improved surface area and uncovered reactive sites[11]. Its chemical resistance is high due to Van der Waals forces among its layer stacking[12]. It is insoluble in toluene, diethyl ether, water, ethanol and THF. Single and few layered g-C₃N₄ is gotten by breakdown of these weak forces. The past reports affirmed flake structured g-C₃N₄ practically identical with graphite[13].

At the start, both hepta-triazine and tri-s-triazine ring were reflected as its tectonic units of g-C₃N₄. On the other hand, later on tri-s-triazine appeared in type of more noteworthy stable structural units associated with planar amino groups[14]. The layered 2D structure of g-C₃N₄ is developed by tri-s-triazine unit. N-type nature and tunable band gap of graphitic carbon nitride with least unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) administer its photoelectronic activity[15]. The g-C₃N₄ contains earth-rich components C and N with some substance of H[16]. Semiconductor nature of g-C₃N₄ recognizes it from graphene and different analogues. Along these lines for photocatalytic organic toxin annihilation from water, g-C₃N₄ integrated nanocomposites are viewed as a potential photocatalyst. The g-C₃N₄ pertain yellow shading because of optical absorption at 460nm[16-17]. Various review articles can be followed that centered on synthesis, alteration and catalytic uses of g-C₃N₄ in the field of water decontamination (Fig. 4)[18].

Fig. 3. Pie chart highlighting diverse photoactive applications of g-C₃N₄

Fig. 4. Mechanistic view of metal free g-C₃N₄ photocatalyst for the degradation of organic pollutants present in water
2. ELECTRONIC STRUCTURE OF g-C₃N₄

These days, g-C₃N₄ is viewed as another age photocatalyst to improve the photocatalytic activity of conventional photocatalyst like TiO₂, ZnO, WO₃ and so on. g-C₃N₄ should have graphitic like structure[19]. On the other hand, ground state structure of g-C₃N₄ is as yet not clear and elucidation of accurate ground state structure remains a test for scientists. In the main, thermal polycondensation technique is utilized to get g-C₃N₄ and X-ray diffraction technique is connected to explore the crystal structure of g-C₃N₄[21]. Anyway two temperature dependent X-ray diffraction (XRD) peaks at 2θ=13.04° and 27.25° just given insufficient data due to low crystallinity of g-C₃N₄[17]. Scientists trust that these two peaks relate to an in-plane collation with a repeated distance of 3.273Å, individually. Though, exact stacking positions of C and N atoms regarding the neighboring layers are as yet not due experimental confines, and further examination is expected to clear up the stacking order and geometry of g-C₃N₄[20]. The demand of phase strength was essential, secondary and tertiary. As opposed to other layered structures, mutilated stages in heptazine-based g-C₃N₄ were the most stable[21]. The stage 1 had direct band gap of 2.87eV and while 2 and 3 phase had indirect band gap of 3.14 and 2.27eV, separately (Fig. 5)[22].

Other research assemblies additionally investigated of g-C₃N₄, hypothetically. In g-C₃N₄, lone pair electrons of nitrogen are primarily responsible for ban structure and development of valence band. Abd EI-Kader et al[23]. Moreover, gave related view about concerning result of nitrogen content on optical properties of g-C₃N₄ to certain degree[24]. Fundamentally, C₃N₄ is available in seven stages for example a-C₃N₄, b-C₃N₄, cubic C₃N₄, pseudocubic C₃N₄, g-h-triazine, g-o-triazine and g-h-heptazine with band gaps of 5.49, 4.85, 4.30, 4.13, 2.97, 0.93 and 2.88eV, respectively[25].

![Fig.5. Predicted images of heptazine-based g-C₃N₄. (a) predicted most stable configuration, phase 1, (b) second stable distorted configuration, phase 2, (c) most stable planar configuration, phase 3. The atoms in the middle layer of the lattices are labeled with yellow crosses. (With permission from ACS-Applied materials and interface) (For interpretation of the references to color in this figure legend](image-url)

The different allotropes of g-C₃N₄ were shaped by triazine (C₃N₃) and tri-s-triazine/heptazine (C₃N₇) rings unit. Tri-s-triazine based g-C₃N₄ is viewed as most stable period of g-C₃N₄. Pseudocubic and g-h-triazine phases of g-C₃N₄ have direct band gaps and all various phases have indirect band gaps[26]. The reduction and oxidation potentials are associated with positioning of valence and conduction band as for standard reduction potential scale of hydrogen. Kroke et al. used functional theory (DFT) calculations to investigate electronic structure of g-C₃N₄[27]. The optical band gap of melon was 2.6eV that reduced from 3.5eV of melem and lastly accomplished the value of 2.1eV with complete formation of condensed g-C₃N₄[28]. The wave function examination investigated that valence and conduction band are fundamentally directed by nitrogen (N) P₂ orbitals and carbon (C) P₂ orbitals, respectively[26, 29]. The EHP partition proposes free oxidation and reduction sites for water splitting in nitrogen and carbon atom. Wei and colleagues utilized many body Green’s function technique for examination of electronic and optical properties of g-C₃N₄[30]. The got outcomes guaranteed that electronic band gap of g-C₃N₄ was 4.24eV[31]. While, tri-s-triazine based catalyst had 5.22eV (direct) and 4.15eV (indirect) band gaps. In addition, it was affirmed that in electronic structure of g-C₃N₄ valence and conduction are shaped by overlap of 2p orbital of nitrogen and 2p orbital carbon atom together[32]. Decisively, two-dimensional (2D) structure of
g-C₃N₄ can be considered as a nitrogen atom-substituted graphene system having conjugated graphitic planes with sp² hybridization of carbon and nitrogen atoms in an atomic ring[30, 33]. The lone pair electron of nitrogen is supposed to form lone pair valence band which is balanced out by stabilized by π electronic state. The mid-way band gap (2.7eV) allows it to absorb light over wide range of wavelengths in visible region[34]. While, suitable situating of reduction level of conduction band (-1.3eV) and oxidation level of valence (+1.4eV) band initiates the catalytic reactions[29].

3. PREPARATION OF GRAPHITIC CARBON NITRIDE BASED NANOCOMPOSITE

In recent times, advancement has been seen in improved techniques for preparation of g-C₃N₄ based photocatalysts including relationship between structural/morphological features and there photocatalytic activity[35]. Essentially, top down and bottom up approaches have been approved for production of g-C₃N₄ based photocatalysts[56]. Top down approach includes the systematic and stepwise breaking down of larger blocks of g-C₃N₄ into smaller units, namely, g-C₃N₄ nanosheets and few-layered g-C₃N₄, while “bottom up” method contains the combination of smaller molecules to form bigger complex molecules[37]. All through synthesis of g-C₃N₄ and its composite photocatalyst, previous method has been mostly utilized in liquid and thermal exfoliation approaches[38]. While last methodology mainly involves soft and hard template method, solvothermal method and supramolecular aggregation. Mostly, techniques for preparation of g-C₃N₄ can be categorized[37, 39] as:

3.1 Thermal polymerization method

Graphitic carbon nitride (g-C₃N₄) can be prepared by thermal polymerization of oxygen-free and nitrogen-rich compounds precursors having bonded core structures (triazine and heptazine derivatives)[28] e.g. urea, melamine, dicyandiamide, cyanamide, thiourea, guanidine thiocyanate, guanidine hydrochloride etc. The C and N precursors have basic and effective condensation pathways to form polymeric g-C₃N₄ network[40]. Precursor type and synthesis process can strongly affect physical and chemical properties of g-C₃N₄ and C/N ratio in nanostructures[35]. Polyaddition and polycondensation forms are utilized to shape melamine and to expel ammonia, respectively[41]. Melamine based products are obtain above 350°C, whereas rearrangements of melamine lead to the formation of tri-s-triazine unit products at approximately 390°C. Further polycondensation of this unit forms final polymeric g-C₃N₄ product at roughly 520°C (Fig. 6).

Above 600°C g-C₃N₄ turn into slightly unstable and heating up to 700°C causes the development of nitrogen and cyanido fragments. For instance, at 550°C temperature, nitrogen rich forerunner i.e. urea can be changed to g-C₃N₄. The last result of g-C₃N₄ is generally yellow colored powders. Solid g-C₃N₄ got after thermal condensation/polymerization of monomers did not have crystalline structure with C/N molar ratio of 0.72:1 and small amount of H. 3D bulk, 2D nanosheets, 2D films, 1D nanorods, 1D nanotubes, 1D nanowires and 0D quantum dot of g-C₃N₄ were attained by introduction of many surface modifications and functionalities. The conduction and valence bands positioning were considered by density function theory (DFT) calculations with an estimate that g-C₃N₄ was mostly composed of nitrogen Pz orbitals and carbon Pz orbitals.

![Fig.6. Fabrication of g-C₃N₄ using different precursors.](image-url)
3.2 Template-assisted methods

In this technique, organic/inorganic molecules are utilized as templates to synthesize porous g-C₃N₄ based photocatalysts. The mesoporous silica and block polymers can be utilized as a layout for the planning of mesoporous carbon including g-C₃N₄. Silica nanoparticles (12nm) utilized as hard template to prepare mesoporous graphitic carbon nitride utilizing thermal condensation cyanamide[23b, 42]. The mesoporous g-C₃N₄ displayed fluctuated surface area from 8 to 373 m²/g. The mesoporous g-C₃N₄ had a band gap of 2.7eV.

The portrayal results describe the controlled surface area of 445-585 m²/g with a controlled surface area of mesoporous g-C₃N₄. Zheng et al.[43] Reported helical graphitic carbon nitride with twisted hexagonal rod-like morphology using chiral silicon dioxides as template[44]. This helical g-C₃N₄ exhibited C₃N₄ optical and photocatalytic activities for the fabrication of optical devices and asymmetric photocatalysis[45]. He used 1-butyl-3-methylimidazolium tetrafluoroborate (BmimBF₄) as soft template for the preparation of B and F doped mesoporous graphitic carbon nitride. The mesoporous g-C₃N₄ showed high surface area of 444 m²/g with active sites for catalytic reactions[46].

3.3 Chemical functionalization of g-C₃N₄

Because of 2D nanosheets structure and π conjugated frameworks, graphitic carbon nitride can be utilized to ideal host stage for the manufacture of metal/non-metal nanocomposites utilizing chemical functionalization process[47]. The band gap arrangement between g-C₃N₄ and other semiconductor photocatalysts arisen as a potential procedure to limit the electron-hole pair recombination during photocatalytic processes[48]. Ag₂CO₃ and g-C₃N₄ based photocatalytic were set up by utilizing in situ precipitation strategy. The Ag⁺ ions were in situ precipitated to Ag₂CO₃ by the addition of NaHCO₃ and shaped a tight junction between Ag₂CO₃ and NaHCO₃. Ag₂CO₃ nanoparticles (5-10nm) were evenly dispersed over g-C₃N₄[49]. The photoluminescence results demonstrated the decrease in recombination rate of photo generated electron hole-pair in Ag₂CO₃/g-C₃N₄ nanocomposite[50].

The decreased recombination rate was because of migration of hole from VB of Ag₂CO₃ to VB of g-C₃N₄ while electrons were removed from CB of g-C₃N₄ to CB of Ag₂CO₃. So as to additionally improve the activity of photocatalytic system, binary photocatalyst have been hybridized with g-C₃N₄ to get ready ternary photocatalyst. To the mixture of Zn(NO₃)₂·6H₂O and In(NO₃)₃·4H₂O/Zn/In molar ratio 3.0) were broken up in distilled. 50ml of each NaOH (0.24M) and Na₂CO₃ (0.1M) were added dropwise to get ZnIn-LDH. The ZnIn-LDH was mixed with melamine via grinding process to obtain ZnIn-LDH/g-C₃N₄[51]. The photocatalytic activity of ZnIn-LDH/g-C₃N₄ was assessed the removal of Rhodamine-B dye. The improved surface area and effective charge separation of photogenerated electron hole pair were in charge of improved photocatalytic activity[52]. Huang et al. arranged amine-functionalized g-C₃N₄ by heating urea at 500°C, with asubsequent functionalization treatment using monoethanolamine solution and effectively exhibited that surface amine functionalization represented itself as an effective approach to enhance CO₂ adsorption capacity of g-C₃N₄. The amine-functionalized g-C₃N₄ demonstrated enhanced photocatalytic performance on CO₂ photoreduction[53].

3.4 Ultrasound Assisted Exfoliation Method

Encouraged by exfoliation of graphene, ultrasonication assisted liquid exfoliation routes have been broadly utilized for fabrication of g-C₃N₄ and its nanocomposites. Zhang et al. detailed that multilayered g-C₃N₄ can be adequately isolated into few layered 2D sheets utilizing continuous ultrasonication[41]. The exfoliation procedure is greatly influenced by the surface energies of the utilized solvent molecules[54]. The enthalpy of mixing was decreased because of surface energy of g-C₃N₄ flakes when formamide and tetrahydrofuran were utilized as solvent. Ma et al. arranged protonated ultrathin 2D g-C₃N₄ nanosheets from dicynandiamide forerunner utilizing 10M HCl solvent and sonication treatment[55]. So as to keep the agglomeration g-C₃N₄ sheets before heating by heating dicynandiamide at 550°C. The acquired sheets had 6-12 monolayers of g-C₃N₄ with high dispersion in water. The facile penetration of Li⁺ ions into layers of bulk g-C₃N₄ nanosheets advanced the synthesis of better superiority of few layered g-C₃N₄ sheets[56].

3.5 Sol-gel method

Because of high purity and homogeneity of sol-gel strategies are much of time used to manufacture g-C₃N₄ and its nanocomposites[57]. It is considered as one of the reasonable technique because of low cost, ambient processing temperature and easy synthesis route. Fabricated g-C₃N₄-TiO₂ nanocomposite via facile sol-gel method using tetra-n-butyl titanate as precursor, which undergone hydrolysis and polycondensation reaction to form a colloid solution. The characterization results confirmed the intimate contact between g-C₃N₄ to form hetrojunction structures[58]. The sol-gel...
conserved as most suitable technique for the formation of g-C₃N₄ and metal oxide semiconductor photocatalyst due to formation of metal –OH network. TiO₂/C₃N₄ nanocomposite exhibited surface area of 140.13m²g⁻¹[39].

4. GRAPHITIC CARBON NITRIDE BASED METAL-FREE NANOCOMPOSITES

4.1 C₆₀/g-C₃N₄ nanocomposites

Metal-free semiconductors have been given important consideration to solve environmental and energy issues to great potential. Broad research was directed to couple g-C₃N₄ with non-metal/carbonaceous compounds and a portion of these are multi-walled carbon nanotubes (MWCNTs)/g-C₃N₄, polypyrrole/C₃N₄, P/C₃N₄, CN/CNS and C₆₀/g-C₃N₄. Fullerenes, CNT, graphene and carbon nanodots with π-conjugated structures were viewed as effective supports for photocatalytic nanomaterials to reduce EHP owing to structural, optical properties and electronic features[60]. Numerous research groups have fabricated heterojunctions of g-C₃N₄ with carbonaceous nanomaterials to make increasingly efficient and recyclable photocatalyst for water purification. C₆₀/g-C₃N₄ nanocomposite possessed high visible light absorption due to gray color of C₆₀/g-C₃N₄[61]. Fig. 7 demonstrated mechanism for EHP separation and transportation of electrons at C₆₀/g-C₃N₄ interface. Upon experience to visible light, electrons (e⁻) were excited from VB (occupied by N2p orbitals) to CB (formed by C2p orbitals of g-C₃N₄) leaving behind holes (h⁺) in VB[62].

![Fig.7. Mechanism of charge separation as well as photocatalytic process of g-C₃N₄ and C₆₀/g-C₃N₄ photocatalyst under visible light irradiation for pollutants degradation.](image)

The photogenerated electrons on CB of g-C₃N₄ were exchanged to C₆₀ particles in C₆₀/g-C₃N₄ nanocomposites and advanced EHP separation. Fullerenes (C₆₀) have 30 molecular orbitals with 60 π-electrons with closed-shell configuration leading to effective shuttling and transportation of photogenerated electrons. In view of huge excitation diffusion length and high exciton mobility of C₆₀ photogenerated electrons from g-C₃N₄ were instantly transferred on C₆₀ to enhance separation of EHP[60]. The separation of EHP caused effective ring benzene opening aimed degradation process and eventually mineralized organic pollutants into inorganic ions.

4.2 CNT/g-C₃N₄ nanocomposite

Carbon nanotube (CNT) is an significant carbon allotrope with excellent conductivity and large specific surface area favoring improved photocatalytic degradation of aqueous phase pollutants[64]. A number of reports guarantee the advantages of coupling of g-C₃N₄ with CNT to fabricate nanocomposite for different photocatalytic energy and environmental applications. Ge and Han coupled MWCNTs with g-C₃N₄ to report CNT/g-C₃N₄ photocatalyst. The improved activity was because of remarkable electron storage ability of CNTs that prohibited past EHP recombination. The coupled CNT/g-C₃N₄ nanomaterial with negative polarity is not easy to prepare due to electrostatic repulsion between CNT and g-C₃N₄. CNT/white g-C₃N₄ nanocomposites were manufactured by treating g-C₃N₄ with HCl accompanied by hydrothermal process based addition of CNT. White g-C₃N₄ acquired polarity of +3.3mV after g-C₃N₄ protonation, favoring coupling with negatively charged CNT. The decrease in zeta potential (+1.6mV) of CNT/g-C₃N₄ compared to white g-C₃N₄ (+3.3mV) was due to interface contact between CNT and g-C₃N₄. The transfer of photogenerated electrons
to CNT and hetero-structure formation between CNT and white g-C\textsubscript{3}N\textsubscript{4} played an important role for efficient charge carrier (EHP) separation\cite{65}.

### 4.3 Graphene/g-C\textsubscript{3}N\textsubscript{4} nanocomposite

In recent times, two dimensional graphene has involved much consideration due to its outstanding properties e.g. thermal, mechanical, electrical properties, high specific surface area (\textasciitilde 2600m\textsuperscript{2}g\textsuperscript{-1}), marvelous thermal conductivity (\textasciitilde 5000Wm\textsuperscript{-1K\textsuperscript{-1}}) and mobility of charge carriers (200000cmV\textsuperscript{-1s\textsuperscript{-1}})\cite{66}. Subsequently, graphene is regarded as a potential candidate to construct layered graphene and g-C\textsubscript{3}N\textsubscript{4} based metal free nanocomposites. Graphene/g-C\textsubscript{3}N\textsubscript{4} nanocomposite was organized by means of numerous approaches for photocatalytic degradation of MO under visible-light irradiation\cite{67}.

The g-C\textsubscript{3}N\textsubscript{4} was embedded between graphene sheets via polymerization of pre-adsorbed melamine molecules on graphene oxide sheets. The compact structure of graphene/g-C\textsubscript{3}N\textsubscript{4} led to high photocatalytic activity when electrons (e\textsuperscript{−} CB) of g-C\textsubscript{3}N\textsubscript{4} excited from valence band (VB) to conduction band (CB), fabricating hole (h\textsuperscript{+} VB) in VB under solar light. The transferred electrons get composed on Pt nanoparticles overloaded on graphene sheets via percolation process\cite{16,68}. Amid immobilization of g-C\textsubscript{3}N\textsubscript{4} on graphene sheets surface, photogenerated electrons on conduction band of g-C\textsubscript{3}N\textsubscript{4} had inclination to got exchange on graphene sheets inferable from astounding electronic conductivity of graphene and prevent electron-hole pair recombination to form layered composites. The photocatalytic mechanism including graphene/g-C\textsubscript{3}N\textsubscript{4} nanocomposites under visible light is described by Eqs.

\[
g\text{graphene} / g\text{C}_3\text{N}_4 \rightarrow \text{hv} \rightarrow \text{graphene}(e^−) / g\text{C}_3\text{N}_4(h^+) \\
g\text{graphene}(e^−) + \text{Pt} \rightarrow \text{graphene} + \text{Pt}(e^+) \\
\text{Pt} (e^−) + 2\text{H}^+ \rightarrow \text{Pt} + \text{H}_2 \\
g\text{C}_3\text{N}_4(h^+) + \text{CH}_3\text{OH} + 6\text{OH}^- \rightarrow g\text{C}_3\text{N}_4 + \text{CO}_2 + 5\text{H}_2\text{O}
\]

Ternary g-C\textsubscript{3}N\textsubscript{4}/graphene / S heterojunction were accounted by immobilizing reduced graphene oxide and g-C\textsubscript{3}N\textsubscript{4} sheets on cyclooctasulfur crystal. g-C\textsubscript{3}N\textsubscript{4}/graphene / S ternary composite showed important photocatalytic activity for bacterial evacuation under visible light\cite{69}.

### 4.4 Carbon quantum dot / g-C\textsubscript{3}N\textsubscript{4} hybrid nanocomposite

Carbon quantum dots (CQDs) show great properties, for example, outstanding conductivity, being chemical composition and photo-chemical stability. CQDs characterize their different appropriateness in chemical modification and surface passivation with different organic, polymeric, inorganic or biological materials. The forerunners utilized for preparation of both nanomaterials were combined together and heated at 650°C to get hybrid heterojunction. Carbon nano-particles with 60nm sizes were in situ prepared from a zeolitic imidazolate framework involving thermal polymerization of melamine into g-C\textsubscript{3}N\textsubscript{4}. The entire composite was treated with HCl solution to remove residual Zn\textsuperscript{2+} before performing photocatalytic activity test\cite{70}. CQD modified g-C\textsubscript{3}N\textsubscript{4} hybrid was combined using C-dots and dicyandiamide as precursor molecules. CQD resulted in distortion of g-C\textsubscript{3}N\textsubscript{4} lattice. CQD/g-C\textsubscript{3}N\textsubscript{4} showed improved photocatalytic activity for the degradation Rhodamine dye under UV light. The absorption edge displayed a blue shift compared to bulk g-C\textsubscript{3}N\textsubscript{4} and emission peak was shifted towards lower wavelength with decrease in optical band gap. Graphitic carbon nitride nanosheets were altered through heating of bulk graphitic carbon nitride in presence of NH\textsubscript{3}. The modified g-C\textsubscript{3}N\textsubscript{4} nanosheets had wide band gap of 2.95eV and self-developed carbon vacancies\cite{71}. The permeable nanosheets showed great improvement in photocatalytic proficiency in comparison to bulk g-C\textsubscript{3}N\textsubscript{4}. The modified g-C\textsubscript{3}N\textsubscript{4} nanosheets were very steady under test conditions and photocatalytic activity was 20 times higher as compared to bulk material under visible light.

### 4.5 g-C\textsubscript{3}N\textsubscript{4}/g-C\textsubscript{3}N\textsubscript{4} isotype nanocomposite

g-C\textsubscript{3}N\textsubscript{4}/sulphur doped C\textsubscript{3}N\textsubscript{4} (CNS) nanocomposite was manufactured by utilizing a facile surface-assisted polymerization i.e. CNS-CN (CN acting as the host) and CN-CNS (CNS acting as the host)\cite{72}. Layered g-C\textsubscript{3}N\textsubscript{4} / g-C\textsubscript{3}N\textsubscript{4} metal free nanocomposite was produced by using urea and thiourea as precursors to obtain different band structures\cite{73}. TEM images showed effective development of layer between CN-T and CN-U nanosheets. Under visible light, photo-excited electrons were moved from CN-T to CN-U driven by conduction band offset of 0.10eV, while the photo-excited holes drifted from g-C\textsubscript{3}N\textsubscript{4} (urea) to g-C\textsubscript{3}N\textsubscript{4} (thiourea) due to valence band offset of 0.40eV (Fig. 8).
The addition of electrons on one side of heterojunction (CN-U) as well as holes on other side (CN-T) reduced EHP recombination and prolonged the life time of charge carriers, ensuing high photocatalytic efficacy of the synthesized materials.\(^\text{[74]}\).

5. PRACTICAL APPLICATIONS OF g-C\textsubscript{3}N\textsubscript{4} PHOTODEGRADATION

When the different g-C\textsubscript{3}N\textsubscript{4} nanocomposites are used in the useful applications of photocatalysis for waste water treatment, additional consideration should be given to few important working parameters.

5.1 Reusability of g-C\textsubscript{3}N\textsubscript{4} Photocatalysts

All through wastewater treatment at commercial scale, the retrieval and reprocess of the catalyst are important in order to make the procedure competitive. The catalyst of Ag\textsuperscript{+}AgCl-g-C\textsubscript{3}N\textsubscript{4} permeable nanosheet is an illustrative example due to relatively high degradation efficacy and the reusability was assessed by reprocessing the photocatalyst for RhB elimination under visible light. Afterward each cycle of photodegradation, the catalyst, Ag\textsuperscript{+}AgCl-g-C\textsubscript{3}N\textsubscript{4} permeable nanosheet was centrifuged, washed three times with distilled water, and dried out at 150°C for 4 h.\(^\text{[73]}\). The consequences (Fig. 9A) display only an insignificant reduction in the degradation rate being detected after eight sequential photocatalysis cycles. As a result this material has not only high photo catalytic capability but also outstanding strength, both of which empower the catalyst to be encouraging visible-light driven catalyst for pollutant elimination. In another study, manufactured a metal-doped catalyst (Na-g-C\textsubscript{3}N\textsubscript{4}) which was repetitive for the photodegradation process four times, with no observable reduction in the deprivation rate being observed(Fig.9B) and demonstrating good reusability.\(^\text{[73]}\).

**Fig. 8.** Photocatalytic mechanism illustrating comparison between CN-T (T-Thiourea) and CN-U (Urea)

**Fig. 9.** Recycle tests of (A) Ag\textsuperscript{+}AgCl-g-C\textsubscript{3}N\textsubscript{4} porous nanosheets and (B) Na-g-C\textsubscript{3}N\textsubscript{4} under visible light irradiation for RhB removal.
Also, some different components engaged with the pragmatic applications, for example, impetus stacking and the stream rate of wastewater may cause potential effect on the reusability of the impetus. In exploring the photocatalysis by TiO2, Li (2010) announced that 6.0 g L⁻¹ of impetus would prompt the most elevated photodegradation rate of COD evacuation while high stream rate negatively affected the corruption adequacy of COD expulsion. Be that as it may, there is an information hole on variables affecting impetus execution among TiO2 and g-C3N4. In this manner, further research is expected to decide the affecting elements for the activity and reusability of combined g-C3N4 in reasonable applications.

5.2 Photocatalytic Reactor for g-C3N4 Nanocomposites

Photocatalytic reactor is intended for the photodegradation of the toxins from water and wastewater. Many reactors have been intended for TiO2 immobilization while few are useful for g-C3N4. Contrasted with the difference of the reactors, g-C3N4 catalyst just need visible light as opposed to UV light which is necessary for TiO2 due to the different absorption ability of light source between the two catalysts. Moreover, unadulterated g-C3N4 catalysts own the non-metal property so the leakage and recycle of the metal should not be a problem for consideration in the reactor. Regularly the photocatalytic tests directed in the research facility utilize a suspension photocatalytic reactor as shown in Fig. 10A, which has the benefits of basic structure, convenient task, frequent compound transmission, and high rate of reaction. However, it additionally has few drawbacks: firstly, the particle size has strong influence on the suspended state of the catalyst, namely, too small size would result in particle deposition. Moreover, the particle size as well affects the light transmission as large size or high concentration would lead to a turbid solution so that the light transmission will be disturbed and light absorption reduced. All the more significantly, the catalysts suspended in the solution are difficult to be isolated and re-used.

In this manner, the loaded photocatalytic reactor is desirable to be utilized for g-C3N4 nanocomposite application. As shown in Fig. 10B, g-C3N4 on structured Al2O3 ceramic foam synthesized by Dong et al. (2014a) could be fixed at one side of the reaction pool and the unclean water flows from intake to outlet passing however the loaded g-C3N4 materials. On the other hand, such a reactor structure would definitely produce two problems: one is the restricted reaction area which is just the cross-sectional zone of g-C3N4 on the Al2O3 foam; the other one is comparatively short residence time of contacting the catalyst, which will prompt to the incomplete photodegradation. Therefore, tubes, fibers, and floated glass balls have been planned for the substitution of the single tiled catalyst. Particularly, among them, fibers have the advantages of large reaction area, low catalyst loss aimed the transmission, and high efficacy of optical transmission. For example, the doped TiO2 was utilized to coated quartz fiber membranes in a photocatalytic reactor as shown in Fig. 10C, which driven out to have durable degradation ability with high efficiency. It is sensible to forecast that when g-C3N4 nanocomposite replaces TiO2, they should accomplish similarly stable and high degradation performance for the contaminant evacuation. Though, the fiber reactor as well has its disadvantages such as being easily broken, expensive, and difficult to load the catalysts on the fiber. As a result, distinctive sorts of photocatalytic reactors ought to be completely assessed when treating real wastewater of commercial scale utilizing g-C3N4.
5.3 Influence of environmental conditions on photocatalysis

Amid the photodegradation procedure, numerous ecological conditions, for example, pH of solution, reaction temperature, and broke down organic matters (DOM) assume noteworthy job for the photocatalytic execution which are not yet explored in the examination of g-C3N4 photocatalysis [76]. The solution pH impacts the ionization level of the chemical speciation. The oppositely charged contaminants and catalysts will advance the combination among them and along these increases the photodegradation adequacy. Moreover, the response temperature would seriously affect the photodegradation progress, as high temperature can quicken the redox response albeit too high temperature would change the nanostructure of the catalyst prompting potential catalyst deactivation [77].

Furthermore, DO assume an imperative job in debasing the contaminants. Moreover, DOM ordinarily exists in natural water and waste water and may pronouncedly effect on photochemical procedure due to the age of DOM-derived oxidative intermediates or their physicochemical extinguishing impacts. On one hand, DOM may cover the outside of the catalyst through adsorption, which prompts the less adsorption capacity of the catalyst and poor degradation effectiveness. Then again, DOM, for example, humid acid in the reaction blend can assimilate photons and produce active groups and consequently would decidedly influence the photo-oxidation rate [76]. These ecological conditions have been accounted to effects the catalytic capacity of TiO2. In this way, when another sort of g-C3N4 composites is integrated, pH, reaction temperature, DO, and DOM ought to be examined to determine the best conditions for the photocatalytic execution [7, 46].

6. DISADVANTAGES OF g-C3N4 AS A PHOTOCATALYST

Besides its good catalytic activity, g-C3N4 is also inherited with a number of shortcomings that restricted its application as an efficient photocatalyst in water purification. The main drawbacks of g-C3N4 are (1) photoexcited EHP recombination (2) poor visible light absorption (3) low surface area and, (4) low quantum yield. Moreover, as discussed before, separation of g-C3N4 photocatalyst from reaction solution is very difficult, time consuming and involves wastage of
photocatalyst by centrifugation or filtration process. Various strategies to enhance photocatalytic activity such as (1) doping with metallic/non-metal elements, (2) coupling with other semiconductors, (3) manufacturing of the mesoporous structures, (4) co-polymerization and (5) magnetization by coupling with magnetic materials have been used.\(^{[77]}\)

To increase performance of g-C\(_3\)N\(_4\) based nanocomposites, a few crucial necessities must be viewed as, for example, semiconductor light harvesting photocatalyst having narrow band gap for greatest absorption of solar energy favoring photogenerated EHP partition and encouraging transference of EHP.\(^{[78]}\) Semiconductor photocatalyst must have appropriate redox potential for favored photochemical responses with an explanatory mechanism for strength of catalysts. In any case, satisfaction of every one of these prerequisites for a specific photocatalyst is difficult.\(^{[80]}\) Nanocomposite photocatalyst have a few favorable circumstances, for example, (1) more absorption of light: semiconductors with limited band gap have more visible light absorbability to use and functionalize semiconductor photocatalyst with substantial band gapes; (2) viable photogenerated EHP partition and transference utilizing p-n junction or schottky junction development between metal/semiconductor heterojunction, (3) co-catalyst impact: assimilation with an appropriate co-catalysts can diminish redox potential at individual active sites; (4) stability achieved by shielding of active sites and functional groups on semiconductor surface through surface passivation.\(^{[19]}\)

Heterojunction development includes connection of mesoporous g-C\(_3\)N\(_4\) (mpg-C\(_3\)N\(_4\)) having expanded internal surface area with characteristic properties of those activities as suitable host for semiconductor.\(^{[82]}\) In this review, we are shortening different synthesize strategies for class of graphitic carbon nitride photocatalyst with its potential uses in waste water treatment.\(^{[83]}\) Electronic structure and manufacture of g-C\(_3\)N\(_4\) by various precursors have been talked about. The structuring and manufacture of various kinds of g-C\(_3\)N\(_4\) based photocatalytic frameworks with different changes have been talked about with their job in waste water treatment.\(^{[73]}\) The alterations incorporate nanocomposite with without metal, noble metals, non-metals and transportation, enhancing activity of catalyst and propagating charge transporter lifetime.

7. CONCLUSION

Fundamentally, this research was centered around the imperative difficulties stay in the development of g-C\(_3\)N\(_4\) based complex nanocomposites with very much structured design. Detailed examination is expected to research the variations in electronic and lattice structure of g-C\(_3\)N\(_4\) when coupled or doped with different semiconductors. The specialists working in ecological photocatalysis must concentrate on use of g-C\(_3\)N\(_4\) based photocatalysts for oxidation or evacuation of unstable organic compounds and both indoor and open air decontamination. By heterojunction development with different non-metallic and metallic semiconductors, the reuse productivity and photocatalytic activity could be improved. Due to the appropriate band gap energy and great redox capacity of the photogenerated transporters, Graphitic carbon nitride has higher photocatalytic capacity than TiO\(_2\) for the organic contaminants being examined. Component and intensifying doping is generally looked into, of which K doping is viable in advancing degrading efficacy with the k estimation of 0.0110min\(^{-1}\).

What’s more, semiconductor doping likewise exhibits the capability of nearly high exploitation viability under irradiation of visible light, notably Z-scheme composite doping for example, Z-plots Ag\(_3\)PO\(_4\)-g-C\(_3\)N\(_4\) which has indicated remarkable adequacy by degrading 100% MO inside 5 min with k value of 0.236 min\(^{-1}\). In all the different photoactive applications, noble nanoscale photocatalyst without metal frameworks dependent on g-C\(_3\)N\(_4\) exhibited positive outcomes for its adaptable applications. Particularly, the great accomplishments in H\(_2\) evaluation response outperforming that of with the Pt co-catalysts are exceptionally encouraging towards a maintainable generation of green and sustainable power source. Moreover, more endeavors ought to be dedicated to synthesize better functionalized yet minimal cost g-C\(_3\)N\(_4\) composites to break down the obstinate natural contaminants with high and stable viability, to advance the business scale utilizations of photocatalysis.

ACKNOWLEDGEMENT

I am very thankful to my ALLAH (SWT) and my family. I dedicate this humble effort to my family and my teacher S.F. Zhang, who gave me good instructions. My fellow Muhammad Ali Raza gave me strength and helps me to complete this task.


[34] Z.-X. Li, F.-B. Shi, T. Zhang, H.-S. Wu, L.-D. Sun, C.-H. Yan, Chemical Communications 2011, 47, 8109-8111.


