

Chapter 1

Introduction

Majority scenarios for future global energy predicts that energy demand will triple over twenty-first century. Seeing complete dependence of energy on fossil fuels, it can be predicted that upcoming harmful emissions will bring threats towards the environment. In order to overcome these obstacles, scientists are developing advanced materials with functionalities that can effectively help in conversion of energy, protecting the environment from upcoming threats. Over the past decades, nanomaterials have attracted the attention in building awareness of environmental pollution and energy conversion through its unique and fascinating properties. Although a number of materials, along with various approaches have been discovered so far, semiconductor materials have gained the attention for harvesting solar energy for feasible technology. Being one of the oldest semiconductor materials, burgeoning fluorescent carbon nitride has triggered its tremendous effort on its functional and structural modifications for aiming towards better performances, fulfilling future requirements. Thanks to the broad attempts devoted in investigating and enhancing its based chemistry for which its limitations have been feasibly drawn far beyond what people could visualize initially. This chapter attempts to briefly overview the enhancement of nitrogen-rich carbon nitride with its excellent performances in newly disclosed applications for depicting the broad spectrum of this semiconductor.

1.1 History of Carbon Nitride

Till date, a number of semiconductor materials have been designed as high quality photocatalysts to compensate for energy deficiency and environmental threats by utilizing the solar spectrum [1-5]. One among them is carbon nitride which is semiconductor in nature bearing heptazine ring structure possessing

many advantageous and interesting properties [6-7]. With the growth of metal-free and non-metal-based catalysis, C_3N_4 , an old metal-free material, developed significant awareness in the research fraternity back in 1834. The material was reported by Berzelius in 1830, meanwhile, Liebig found that melamine, melem, melam, and melon are used to confirm the basic units of tri-s-triazine and triazine [8]. Later on, Liebig while polymerizing aluminum chloride and potassium thiocyanate found yellow solid powder which was reported as "melon" by him. But unfortunately, the material fails to draw the attention of researcher towards itself. Later on, Franklin [9] in 1922 analysed this material where he claimed that by polymerizing series of ammonia carbonic acids, C_3N_4 can be formed. Again in 1937, Pauling and Sturdivant [10] confirmed that tri-s-triazine was the unit of melon. As C_3N_4 cannot be dissolved with other agents, so research drive using C_3N_4 extremely slowed down. Enthusiastic research on C_3N_4 both in theory and applications was observed from 1989, only when Liu and Cohen [11] derived β - C_3N_4 , which becomes as hard as diamond after replacing Si by C in β - Si_3N_4 . Further in 1996, Teter and Hemley [12] predicted 5 types of C_3N_4 , i.e. α - C_3N_4 , β - C_3N_4 , pseudocubic- C_3N_4 , cubic- C_3N_4 , and g- C_3N_4 , among which α - C_3N_4 , β - C_3N_4 , pseudocubic- C_3N_4 , and cubic- C_3N_4 are found to be hard materials. Among all, g- C_3N_4 owns brilliant semiconducting property with excellent stability and easy preparation technique. This polymeric semiconductor material consists solely assembly of carbon and nitrogen bonds without electron localization in the π state and has excellent mechanical, thermal and physicochemical stability, making them suitable in many aspects. Graphitic like structure, built from tri-s-triazine/heptazine or triazine units are linked by planar amino groups which exhibits zigzag like structure. Further it is bonded together by hydrogen bonding where each layer is stacked together through van der Waals forces. [13] Wang and co-workers [14] in 2009 discovered usefulness of g- C_3N_4 as photocatalyst in hydrogen production in presence of visible-light irradiation. This created a great landmark in history after which significant studies were carried out and also numbers of papers were published using the system.

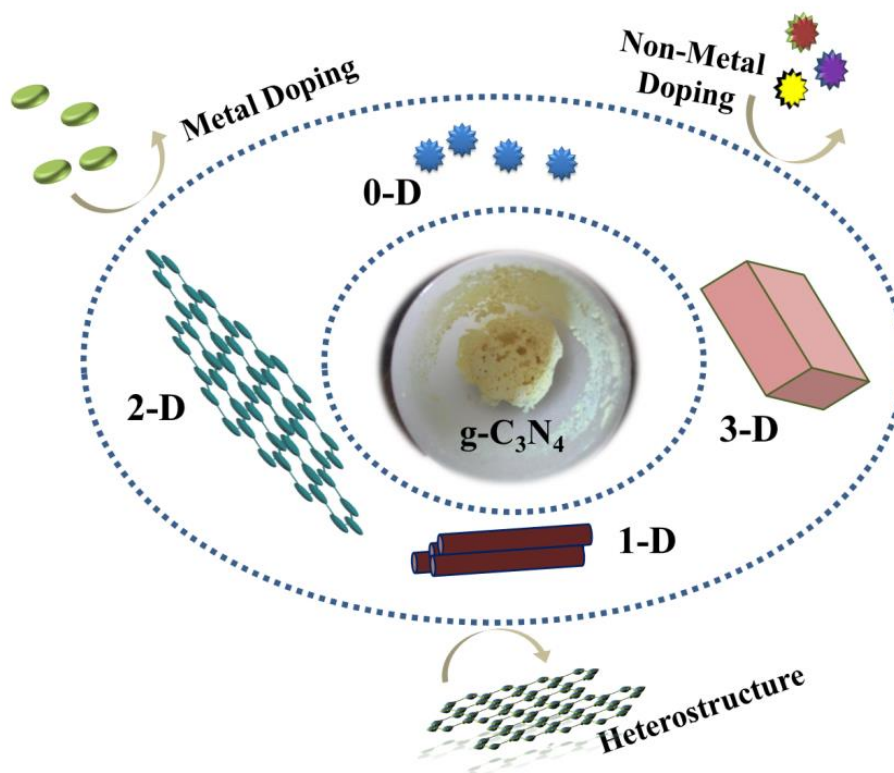


Figure 1.1: Different Strategies to improve the functionalities in Carbon Nitride based materials beyond catalyst.

1.1.1 Structure of $g\text{-C}_3\text{N}_4$

Carbon nitrides are compounds of carbon and nitrogen whereas $g\text{-C}_3\text{N}_4$ is one of most steady allotrope of carbon nitride compounds. With band gap of ~ 2.7 eV, yellow-colored carbon nitride possesses excellent optical absorption with high photo-generated rate of electrons (e^-) and holes (h^+), producing high fluorescence yield [15]. Synthesis can be easily done, simply by pyrolysing or polymerizing nitrogen containing molecules such as urea, [16] melamine, [17] thiourea [18] etc. The structure and nitrogen content of this material depends on precursors and reaction conditions used during synthesis. Hence, due to incomplete pyrolysis of nitrogen content precursors, it sometimes fails to develop the product without any defect sites. However, an amount of hydrogen may be present representing number of defects occurring on surface of $g\text{-C}_3\text{N}_4$ [19]. This can be found when the system is not perfectly or fully condensed. Moreover, impurities can be

introduced into pristine C_3N_4 matrix either by doping or copolymerization, which helps in changing the atomic and electronic configuration.

1.1.2 Functional characteristics of g- C_3N_4

Having graphite-like structure, g- C_3N_4 with exceptional features such as thermal stability, smart electronic properties, environment friendly nature have attracted significant consideration in many domains. High content of nitrogen enriches the system characteristics, whose capacitances are much higher in comparison to traditional EDLCs without losing the fast charge/discharge kinetics. In case of bulk systems, small surface area and low electronic conductivity hinder its application for electrochemical study. In many cases, a material's inadequacy can be overwhelmed by finding different physical/chemical methods to modify the morphology and textures. Excellent physical, chemical, and mechanical properties of g- C_3N_4 , attract the researchers to explore more in this system. In general, N-rich functional groups include oxidized pyridine-N (N-X), pyrrolic N (N-5), quaternary N (N-Q) and pyridinic/pyridone N (N-6). Pyrrolic N atoms and pyridinic N, which are always placed at the edge, are bonded to two carbon atoms and therefore give rise to electron donor properties. Similarly, when pyridine is adjacent to a ring carbon-hydroxyl group, it donates an electron. Electron transfer and electrical conductivity of the material are significantly elevated by the N-Q atoms, which are located both within graphene layers and at the edges, bonded with three carbon atoms. Under mild electrochemical conditions and thermal treatment above $800^{\circ}C$, alternation of pyridinic N to quaternary N occurs. At temperatures above $600^{\circ}C$, Pyrrolic N tends to get changed to pyridinic and quaternary N. Alternatively, conversion between pyridone nitrogen and N-6, or N-X and N-6 are achieved under collective electrochemical conditions. In the subsequent sections, the various routes for synthesis of g- C_3N_4 were reported.

1.2 Role of Dimensionality in the era of Nanotechnology

Collection of scientific evidences and technology seems to have grown in a slightly exponential and self-improving manner. Frequencies of technological revolutions have improved from previous centuries and will possibly boost at a superior magnitude throughout 21st century and onwards as universal properties are permitting for a better future. Presently, we are at the basis of an advanced empirical and technological rebellion called “The age of Nanotechnology” which ensures us to operate material in nano dimensions, thus opening up new frontiers for innovation. One of the main features that distinguish numerous categories of nanostructure is their dimensionality. It is one of the utmost essential material parameters which not only describes micro structure of material but also regulates properties to a significant degree [20]. In addition to rise of new technologies, a novel class of low dimensional 2D g-C₃N₄ system distinguishes development of nanoscale technology. In past decades, several strategies (shown in **Figure 1.1**) have been adopted to classify this nanomaterial for its extraordinary photocatalytic activity, increasing its prerequisite for target-specific applications. Dimensionality affects the regime of confinement of electrons. Different dimensionalities consequently show different properties, making them efficient for interesting applications. Varying the synthesis parameter and precursors, dimension of g-C₃N₄ can be controlled which ultimately influences the structural properties such as specific surface area, pore construction, optical and electronical properties, and separating rate of electron-hole pairs of the system. g-C₃N₄ exhibits 2D layered structure similar to that of graphene. Each layer is bounded by 3-s-triazine rings forming an expanded network-like planar structure, where the interlayers are further bounded with van der Waals forces. 2D g-C₃N₄ nanosheets can be easily developed from bulk g-C₃N₄ whereas, 0D and 1D g-C₃N₄ can be obtained by modifying the arrangement of structural units (shown in **Figure 1.2**). For example, treating bulk g-C₃N₄ with external force such as ultra-sonication, its morphology can be changed to 2D. Meanwhile 0D can be developed through heat treating bulk g-C₃N₄. Thus, using various techniques, g-C₃N₄ with multi dimensionality can be developed,

maximising its possibility in diverse domains. Moreover, brilliant structural manipulation has always been motivated by explicit functionality in performance, giving rise to different architectural structures. The only difference in structure of $g\text{-C}_3\text{N}_4$ to that of graphite is the arrangement of nitrogen atoms along with carbon lattice in $g\text{-C}_3\text{N}_4$. Because of presence of one nitrogen lone pair, it shows rich surface and electronic properties. According to prior literature, it was mentioned that heat treatment of various precursors influences the properties (surface area, porosity, nanostructure etc.) of the resultant carbon nitride. In order to get desired structure without losing its pristine properties, various techniques, optimizations and modifications have been imposed. Synthesis of $g\text{-C}_3\text{N}_4$ can also be executed using melamine under hydrothermal method. However, synthesizing $g\text{-C}_3\text{N}_4$ with urea precursors has emerged as most convenient method due to cheap as well as earth-abundant precursors. Wang *et al.* [21] reported the first work on developing $g\text{-C}_3\text{N}_4$ where the precursor used was cyanamide. At initial stage of temperature $\sim 203 - 234^\circ\text{C}$, cyanamide molecules were condensed to dicyanamide then later on to melamine. In next stage, ammonia was removed at temperature 335°C resulting in development of melamine-based products. On further heating up to temperature 390°C , melamine precursor gets relocated which results in development of tri-s-triazine units. Further condensation of the unit at 520°C , polymeric $g\text{-C}_3\text{N}_4$ was formed. However, overheating of sample resulted in disappearance of $g\text{-C}_3\text{N}_4$. Further, experimental results were correlated using theoretical calculations, where reaction mechanism and formation of melamine were analyzed. In case of thermal condensation method, most commonly used precursor includes compounds having pre-bonded C-N core structure, which are rich in nitrogen and free from oxygen atoms. In addition to cyanamide, dicyanamide, urea and thiourea, triazine and heptazine derivatives also had been tested as a precursor for synthesis of $g\text{-C}_3\text{N}_4$. In terms of structural design, convenient morphologies with diverse geometrical shapes have been engineered using different approaches. Effort has been put to increase the photocatalytic performances of pristine carbon nitride by different approaches via doping or by coupling it with

other materials [22]. In addition, organic or inorganic compounds have been tailored onto the surface of $g\text{-C}_3\text{N}_4$ to enhance its functionality. Also, various approaches have been identified for building heterojunction with $g\text{-C}_3\text{N}_4$, where band alignment studies were performed, showing charge separation enhancement for photocatalytic applications.

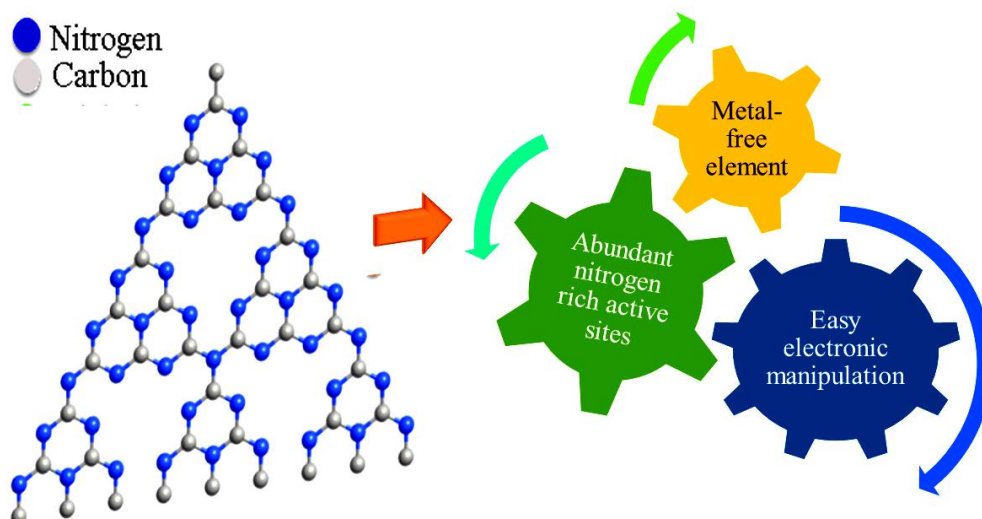


Figure 1.2: Geometrical structure of Carbon Nitride along with its fascinating properties.

1.2.1 3D Architecture of $g\text{-C}_3\text{N}_4$

Bulk $g\text{-C}_3\text{N}_4$ has a 3D assembly that owns the possibility in engineering applications due to its easy recycling ability. Engineering $g\text{-C}_3\text{N}_4$ in 0D, 1D and 2D endows versatile and excellent properties, broadening the application field compared to its 3D $g\text{-C}_3\text{N}_4$. Apart from exfoliation from bulk to 2D, 1D or to 0D, various forms of nanocomposites and heterostructure (such as 2D/1D, 2D/2D or 2D/0D) were also explored in these areas. *Chen et al.* developed 3D $g\text{-C}_3\text{N}_4@\text{G}$ electrode material through a one-step hydrothermal reduction process [23]. Hydrothermal treatment controls the formation of loosely packed 3D structure, where $g\text{-C}_3\text{N}_4$ was grafted on graphene basal planes. This method of preparation allowed good distribution of $g\text{-C}_3\text{N}_4$ on graphene basal planes resulting formation of a composite structure, which was investigated from XRD through

peak shifting. Uniform distribution of g-C₃N₄ in the composite structure was further confirmed from SEM images. Further existence of mesopores increases the surface area of the composite system. The hierarchical architecture eases charge transfer and accelerates the electrochemical performances, providing multi way electron transfer. The 3D morphology shows good performances as a symmetrical supercapacitor exhibiting enhanced specific capacitance of 264 F g⁻¹ along with good stability in cycling process. In addition, *Luo et al.* established a facile method having first acid protonation and secondly thermal oxidation to create porous 3D g-C₃N₄ resulting outstanding photocatalytic activity [24]. Combination of protonation and thermal oxidation led towards formation of pores which improved the photocatalytic activity by activating mass transfer through abundant active sites, channels and edges. While carrying out the protonation and calcination technique, there was slight decrease in the intensity peak of XRD. Such behavior signifies the formation of few layers from the bulk system. During the calcination process, thermal etching effect of oxygen further leads towards formation of corroded surface, which results in formation of pores in the structures. Compared to the pristine form, hydrogen evolution rate was 29.5 times higher in case of developed 3D system.

1.2.2 g-C₃N₄ in its OD quantum dots dimensionality

OD or quantum dots refer to nanomaterials where electrons and holes are incapable to move freely. Looking into the appealing properties including biocompatibility and bright fluorescence, O-D g-C₃N₄ has gained more attention, opening a wide range of possibilities in various prospects. *Barman et al.*, through a simple microwave method, developed blue fluorescence g-CNQDs [25]. The developed quantum dots consist of single to few layers of sheets, with size distribution of 2-15 nm, average diameter of 7nm and average height of 1.1 nm confirmed through transmission electron microscopy (TEM) and atomic force microscopy (AFM) analysis. The developed QDs were highly sensitive on pH, solvent and also on excitation wavelength. *Zhang et al.* for first time developed fluorescent g-C₃N₄ from bulk g-C₃N₄ through hydrothermal method. TEM

analysis was conducted to identify the structural morphology of the system. Hydrothermal treatment decreases bulk dimension and convert it into several micrometers in magnitude with crumpled formation on the surface. The size of quantum dots was analyzed using particle size distribution histograms, where it was identified that the dots were around 5 to 20 nm in diameter, well separated from each other. Having high quantum yield and blue emission properties, the aforementioned QDs were used for detection of Cu^{2+} and Fe^{3+} ions from water [26]. *Chen et al.* developed a hybrid design approach which is established on SnO_2 /graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) quantum dots designed for improving perovskite solar cells stability [27]. The formation of graphitic Carbon Nitride Quantum Dots (g-CNQD) was carried out in two ways, first acid etching in bulk g-CN , which lead towards formation of pores g-CN and secondly, through hydrothermal treatment on the porous g-CN for formation of the final g-CNQD system. Diameter of the developed g-CNQD were around 5-10 nm, investigated using TEM analysis. Apart from delivering high conductivity, existence of $\text{g-C}_3\text{N}_4$ helped in recasting distribution of electronic density by eliminating oxygen-vacancy-reduced trap centers around neighboring SnO_2 crystal unit. Nevertheless, in case of water purification applications also, $\text{g-C}_3\text{N}_4$ QDs with its active visible-light photocatalytic behavior have shown interesting outcomes.

1.2.3 1D tube/rod/wire arrangement of $\text{g-C}_3\text{N}_4$

1D morphology refers to nano-micro rods, nano-micro tubes where electrons restrict its movement within one direction only. $\text{g-C}_3\text{N}_4$ 1D nanowires and nanorods have shown significant activities due to their lower recombination rate, high surface area, smooth carrier transport, improved electron hole separation etc. Taking advantage of high surface area with greater number of active sites, 1D $\text{g-C}_3\text{N}_4$ nanostructure materials with its functionalities provide a basic platform towards environmental uses. *Xie et al.* reported synthesis of $\text{g-C}_3\text{N}_4$ nanowires and nanofibers using cyanuric chloride and melamine precursor dispersed in a solvothermal reaction [28]. Compared to bulk, the developed 1D nanostructures showed enhanced activities with average diameter of nanowire to be 10-20 nm

and that of nanofiber was ~15 nm. Using solvothermal method, 1D morphology of CN was developed simply by optimizing the reaction time. Through SEM analysis, it was revealed that CNWs (solvothermal reaction time of 24 h) exhibited wire-like morphology, loose and rough in nature with diameter around 20-30 nm and length from several hundreds of nanometers to several micrometers. Whereas, in case of CNFs (solvothermal reaction time of 48 h), the diameter was around 15nm, having low surface roughness with abundant number of pores, leading towards increase in surface area compared to CNWs. Further from TEM images, it was revealed that ultrathin 1D structure of nanowires are micrometer-long wrinkles, reducing the surface energy by increasing stability. However, in case of CNFs, the surface was inhomogeneous in nature with some agglomeration occurred due to uneven temperature and long reaction time. The designed 1D nanostructure opens a broad platform towards adsorption and photocatalytic degradation of pollutants. *Lin et al.* [29] developed CDots/g-C₃N₄ hybrids with different morphologies simply by changing the ratio of the precursors used (i.e. urea and glucose). Reducing the dimensionality, crystallinity decreases. In case of TCN-200 (g-C₃N₄ nanotubes) the crystallinity was decreased. This was confirmed through XRD. From Raman Analysis, the graphitizing degree of carbon material ratio (I_D/I_G) was investigated. I_D/I_G in case of TCN-200 (1.07) was increased compared to Carbon (0.696), indicating strong coupling of the system. Further SEM and TEM images confirmed tubular arrangement of the structure with diameter of 45-80 nm in range. Owing to synergistic benefits of high conductive carbon and nanotubular constructions, the developed electrode material achieved improved specific capacitance two times more compared to bulk g-C₃N₄. 1D structure with efficient charge separation and low carrier migration distance can lead towards novel findings. *Xu et al.* developed rich-nitrogen carbon nitride nanotubes (CNNTs) using an easy supermolecule self-assembly method providing a solution towards environmental pollution [30]. Melamine precursor was mixed with hydroxylamine sulfate for formation of supramolecular intermediates which was further developed into g-C₃N₄ nanotubes through thermal polycondensation

process. The supramolecular intermediates developed initially, appeared to be thin solid strips of 1D in structure having 20 μm length identified using SEM analysis. Thermal polycondensation process, results in effective modification of supramolecular intermediates to hollow thin-tubular structure. Further from TEM analysis the diameter of the nanotube was observed to be around 10 nm in size. The unique morphology showed brilliant photocatalyst performances with a degradation rate of bisphenol A (BPA) i.e., 92% along with a quantum yield of 12.55 %. Compared to bulk, the specific surface area achieved was $62.85 \text{ m}^2 \text{ g}^{-1}$, 7.3 times higher to that of bulk. Thus, more active sites were generated due to high surface area, provides contribution towards efficient photocatalytic activity.

1.2.4 2D nanosheets with lamellar structure

2D usually refers to nanosheets where electrons can move freely only in two dimensions and are predominantly confined in thickness direction. Two dimensional (2D) materials are the class of materials by means of particular quantum size effect with high degree of anisotropy. 2D materials due to its weak interlayer coupling can be vertically stacked to form van der Waals (vdW) heterostructure circumventing limitation induced by large lattice mismatch, giving rise to an entirely new paradigm. These materials are made up of sheets or planes of atoms held together by interplanar forces, which are weaker than intraplanar binding forces for which two layers can be easily exfoliated. Insertion of atomic or molecular guest species between the layers controls the distinction of physical and chemical properties. These materials have high conductivity and superior electron mobility. Such diverse properties make 2D materials suitable for a broader range of applications. 2D $\text{g-C}_3\text{N}_4$ nanosheets exfoliated from bulk simply by liquid exfoliation method. Also, many other strategies (such as wet ball-milling method, chemical exfoliation, gas exfoliation etc.) have been utilized to exfoliate the 2D sheets from bulk to achieve its favorable properties such as high surface area and quantum confinement effects. In order to enhance its application in intrinsic light absorption applications, 2D nanosheets with improved quantum efficiencies are preferable. In prior literature, *Yan et al.*

developed g-C₃N₄ nanosheets by mixing and heating ammonium chloride with melamine. The optimizing temperature was 520°C and reaction time was 4 hrs [31]. It was explained that melamine precursor was used for formation of g-C₃N₄ and NH₄Cl precursors, which helped in separating the layers from bulk through releasing ammonia gas during the reaction. Moreover, the developed system was further used to investigate rhodamine B dye degradation. Similarly, using the same precursors *Zhang et al.* [32] developed a heterojunction of a 2D/2D BiOBr/CDs/g-C₃N₄ nanocomposite as a photocatalyst. Through SEM images, the author investigated the morphology of heterostructure, consisting of two different nanosheets, one transparent nanosheet belonging to CCN (Carbon dots /g-C₃N₄) and another nanosheet which belongs to BOR (pristine BiOBr). The developed system signifies high surface area with pores resulting efficient degradation within the present active sites. Further, efficiency was compared with its pristine form, where the hybrid system shows high efficiency with photostability and reusability. Recently, *Hao et al.* [33] synthesized 2D g-C₃N₄ nanosheets simply by exfoliating it in DMF and further nitrogen atoms were incorporated into its surface for better outcome. XRD and Fourier Transform Infrared Spectroscopy (FTIR) results were convincing to prove that no structural changes were recognized due to surface nitrogen modification. Moreover, through XPS analysis, C-N bonds were revealed due to insertion of N atoms into g-C₃N₄ lattice. Three differentiated types of sp² hybridized nitrogen were investigated respectively. Among Tertiary nitrogen (N-C₃), Pyridinic nitrogen (C-N=C), and noncondensing amino group (C-N-H), the authors confirmed that highest content of pyridinic N atoms is beneficial for higher photocatalytic efficacy. Energy-Dispersive Spectroscopy (EDS) analysis corroborated the presence of nitrogen content in surface of N-g-C₃N₄. In addition, *Fu et al.* [34] developed 2D g-C₃N₄ through thermal etching with melamine precursor. Further 2D/2D WO₃/g-C₃N₄ heterostructure was prepared through electrostatic self-assembly of the same. Lastly, the photocatalyst was used to investigate its efficiency in production of hydrogen. Through TEM and AFM analysis, its interlayer spacing and thickness were investigated. The thickness of the

developed seven molecular layers of g-C₃N₄ nanosheet was about 2.5 nm with interlayer spacing of 0.36nm. Similarly, *Hatamie et al.* [35] synthesized thin nanosheets of g-C₃N₄ by liquid exfoliation technique. Initially, bulk g-C₃N₄ was prepared using melamine precursor by thermal decomposition and later on it was exfoliated using deionized water. Through TEM and AFM analysis, the dimension of the nanosheets were investigated which was to be in the range of 100 to 150 nm having thickness 6 Å.

1.3 Intelligent Surface and interface engineering of g-C₃N₄

In order to overcome shortcomings of pristine g-C₃N₄ in multiple applications, numerous strategies including surface modification, making hybrid systems, doping metal/nonmetal, creating heterostructures etc. have been attempted to effectively improve and enhance its functionality. Although various methods have been used to advance g-C₃N₄ functionality, remarkable gap still exists for efficient strategies. These methods affect morphology and surface chemistry [36] of g-C₃N₄ producing defect sites, which easily increase charge transfer between g-C₃N₄ and the electrolyte. On the other hand, there are more novel methods whose efficiency and environment friendliness still needs to be significantly improved for mass production of g-C₃N₄. Large-scale production of g-C₃N₄ depends on the development of effective synthetic methods such as (mechanical exfoliation, liquid phase exfoliation. chemical vapor deposition etc.) but somehow, they fail to provide the desired amount. For example, thermal oxidation method provide product with high specific surface area but its yield is low, not suitable for large scale production. Layer exfoliation using ultrasonication is easy to operate, but it is time consuming. Moreover, the solvent removed after its subsequent use during exfoliation can affect the environment. Similarly chemical exfoliation technique used for development of nanosheets also raises strong environmental alarms, as huge quantity of strong acid is used during the preparation procedure. Hence, it is needed to choose the appropriate technique (high yield, low energy and most importantly environment friendly) accordingly for mass production of g-C₃N₄. Besides aforementioned methods,

other emerging techniques are advantageous for further experimentation. It is expected that after proper functionalization of carbon nitride with other materials, its application possibilities will further expand (shown in **Figure 1.3**). On the other hand, the aforesaid shortcomings can be overcome through numerous ways such as selecting proper precursor for developing $g\text{-C}_3\text{N}_4$, optimizing reaction temperature and time, controlling morphology of the system, various route of synthesis. More comprehensive theoretical and experimental analysis are required in order to understand the proper mechanism occurring in the abundant active sites and well-developed morphology for understanding better mass transfer over bulk $g\text{-C}_3\text{N}_4$. An outside the box thinking is needed in order to overcome all the challenges.

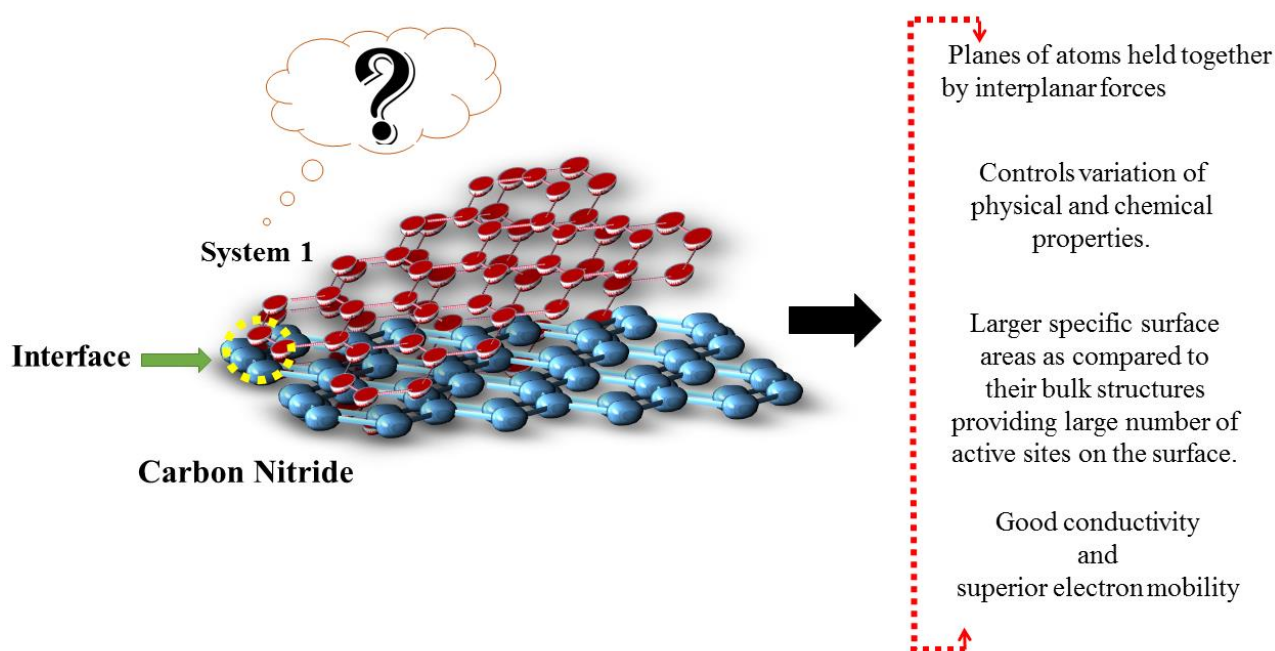


Figure 1.3: Engineering the surface and interfaces of Graphitic Carbon Nitride ($g\text{-C}_3\text{N}_4$) for its use in various applications.

1.3.1 Engineering with Non-Metal Doping

Doping or weaving impurities into a system helps in enhancement in electrical conductivity. 2D layered $g\text{-C}_3\text{N}_4$ possesses cavities within the system that allows foreign elements causing changes in bands without interfering with the visible

light absorption. Introducing heteroatoms into g-C₃N₄ surface regulates morphology and properties of system, and also reduces recombination of photogenerated electrons and holes. Incorporating non-metal elements into g-C₃N₄ helps in designing high performance and environmentally friendly photocatalyst, triggering the efficient performances multiple times for energy conversion. *Zheng et al.* constructed sulfur-doped polymeric carbon nitride microrods as photocatalysts with increased surface area for purification of water and air [37]. The formation of the system was conducted through thermal polymerization with optimizing the temperature where more surface distortion was formed with more activation of $n \rightarrow \pi^*$ transitions. Highly porous microrods were formed with enhanced photocatalytic activity when the fabricated temperature is 650°C. The XPS study indicated presence of S in nanosheets in terms of S-N bonds. Further PL study revealed the charge separation and photogenerated electron-hole pairs recombination of the system. The more effective photoinduced carrier separation was obtained by a non-radiative pathway confirming PL quenching. In another research, 24 times higher photocatalytic degradation efficiency of Cr (VI) was confirmed using sulfur-doped g-C₃N₄ under visible light than that of an un-doped sample. The improved photocatalytic activity was ascribed to considerable smooth layered structure formation and stability. *Cui et al.* developed this system using a one-pot solvothermal method [38]. Modification of bare system with sulfur doping induced the lattice distortion. It was proved that photocatalytic degradation was greatly influenced by S doping. Another group of researchers concerned development of a Lead-Ion Sensor using S doped carbon nitride. *Zou* along with his coworkers developed 12-fold magnitude larger S-g-C₃N₄ by one-step thermal polycondensation method [39]. High surface area S-g-C₃N₄ results in strong affinity towards heavy metal with the help of active sites. Presence of g-C₃N₄ accelerated the reduction in oxidation peak of lead. Successful formation of the system was confirmed by XPS through the C-S bond. Moreover, selectivity performance of the sensor was also theoretically proved using DFT calculations.

Therefore, it was concluded that highly stable S-g-C₃N₄ can be used in near future as a heavy metal ion detecting sensor.

1.3.2 Enhancing the functionalities with Metal Doping

To control the structure of g-C₃N₄, one of the common strategies is to create some defects through introduction of metal elements. Multiple numbers of applications have been investigated considering these approaches. Metal-doping opened new possibilities and built the material with advanced properties. A Schottky barrier is generated due to doping metal into semiconductor g-C₃N₄, which helps in fermi level alignment through electron transfer, preventing the recombination rate. Also due to metal doping into g-C₃N₄, it could increase the visible light utilization which opens up new possibilities in enhancing the catalytic activities. Fe-doped g-C₃N₄ nanosheets loaded with different contents of Fe, were studied for their dye degradation performance using xenon lamp illumination by *Van et al.*,[40] The results confirmed that Fe was an adequate co-catalyst for g-C₃N₄ photocatalytic activity. Optimal Fe loaded on g-C₃N₄ was found to be 7 mol%, enabling 100% RhB dye degradation within 30 minutes. The system with Fe 7 % mol achieved enhanced surface area of 132 m²/g, whereas the surface area decreases with further increase in Fe content. Further, decrease in PL intensity could be due to low electron-hole pair recombination occurred due to Fe²⁺/Fe³⁺ ions in the host g-C₃N₄. Effective doping of Fe in g-C₃N₄ was approved through XPS study, ensures presence like Fe in form of Fe³⁺ atoms and hence representing the construction of the system. This work proved that Fe dopant acts as a very promising co-catalyst to combine with g-C₃N₄ for water purification. In the same line, *Ma et al.*,[41] prepared Fe doped g- C₃N₄ photocatalyst through uniform distribution of iron on g-C₃N₄ semiconductor that demonstrated an improved photocatalytic activity for Rhodamine B (RhB) photodegradation using visible light irradiation. Apparently, developed material demonstrated higher photocatalytic performances compared to pristine g-C₃N₄. However, Fe doped g-C₃N₄ surface area was less compared to bare g-C₃N₄. Presence of Fe destroyed the layered morphology of g-C₃N₄ due to which surface area was comparatively low.

The reason behind this excellent performance lies due to doping of heteroatoms, which decreases the band gap, leading towards enhanced visible light absorption. These exciting outcomes led to emergence of idea that this simple strategy of doping metals into semiconductors could be applied for achieving noble materials with brilliant properties. To study the stability of metal doping, *Cometto et al.* [42] reported the CO₂ reduction through copper atoms embedded in g-C₃N₄. 2D g-C₃N₄ was developed from bulk through exfoliation. Due to strong Cu-N interaction, g-C₃N₄ was able to stabilize Cu atoms without aggregating Cu atoms. Further through XPS analysis, the authors confirmed the presence of Cu in the system and also correlated it with DFT calculations. The CO₂ reduction was performed using two electrolytes i.e., 0.5 M KHCO₃ and 0.1 M phosphate buffer solution. During the reaction, it was confirmed that the activity induced in promoting hydrogen evolution was mainly due to the presence of Cu atoms. Morphology of g-C₃N₄ materials alters the electrochemical activity. To understand this briefly, *Zhang et al.* [43] used a simple and easy technique through liquid-mediated pathways to develop Ni embedded g-C₃N₄. Increase in Ni concentration showed a linear photocurrent increment, claiming a good linear relationship between the concentration and photocurrent. Thus, 3% Ni doped g-C₃N₄ electrode showed better performances compared to other concentrations. However, at higher concentration of Ni, photocurrent is largely masked by high electrocatalytic current. Moreover, higher oxidation state of Ni facilitates oxygen evolution reaction.

1.3.3 Creating heterointerface for achieving brilliant performances

Engineering the interface of 2D materials can lead towards a new direction for achieving advanced material with outstanding performances. To explain the above mechanism, *Zhu et al.* [44] developed 2D heterostructure using cobalt oxide and g-C₃N₄ for investigating the CO₂ reduction. The authors concluded significant improvement in photo reduction of CO₂, owing to promising high charge separation at interface. The behavior of electron occurring at interval of the two photocatalysts was elucidated and verified by ultraviolet-visible

absorption spectrometry (DRS) and XPS-VB measurements. Further through XPS, formations of respective characteristic bonds were also demonstrated justifying the formation of the interface between the two semiconductors. Interface acts as a mediator for migration of excited electrons from Co_3O_4 to 2D $\text{g-C}_3\text{N}_4$, thus enhancing charge density of $\text{g-C}_3\text{N}_4$ on its active sites. Lastly, production of hydrocarbon was governed by the easy proceeding of CO_2 photoreduction which arose due to high CB localization of 2D $\text{g-C}_3\text{N}_4$. *Zhong et al.* [45] fabricated 2D/2D $\text{TiO}_2\text{-g-C}_3\text{N}_4$ composites by using co-calcination, solvothermal reaction and charge induced aggregation approaches. The authors claimed that $\text{TiO}_2\text{-g-C}_3\text{N}_4$ synthesis carried using solvothermal reaction showed maximum H_2 evolution rate with $587 \mu\text{mol g}^{-1} \text{h}^{-1}$. The reason behind the outstanding outcome was attributed to separation and migration of photo induced carriers which were formed due to Ti-O-N covalent bonds at the interfaces. *Jiang et al.* [46] employed two methods i.e., photo deposition and chemical-deposition for loading CdS on $\text{g-C}_3\text{N}_4$. Also, they produced two dissimilar kinds of CdS- $\text{g-C}_3\text{N}_4$ composite photocatalysts respectively. The author proposed that during photo deposition reaction, the electron flow direction occurred from $\text{g-C}_3\text{N}_4$ to CdS at the interfaces. Moreover, charge transfer routes and energy level diagrams obtained for the different kinds of CdS- $\text{g-C}_3\text{N}_4$ composite i.e., p-CSCN and c-CSCN catalysts, suggested dissimilar charge transfer mechanisms within the individuals. Although many strategies have been proposed to improve the efficiency, construction of *type II* heterojunction is one of the most effective ways to improve the activity where individual component promote the separation of photogenerated carriers and integration respectively. 2D/2D heterojunction system can not only promote the separation of photogenerated carriers, it also maintains the initial strong redox ability which is another important and highly desired for various applications including dye degradation.

1.4 Motivation behind this work

Currently there is renewed interest in remarkable properties especially in electronic and mechanical properties of 2D single layer materials. Theoretical

studies specified that two-dimensional (2D) crystal formed by one layer ensures extraordinary electronic properties, controlled by relativistic quantum effects. $g\text{-C}_3\text{N}_4$ is the only C/N ratio-based material that produces long-range ordered 2D crystalline materials, in which sp^2 bonded C and N atoms are perfectly interchanging. Presence of nitrogen in the system is a significant feature in modulating the electrical properties of $g\text{-C}_3\text{N}_4$. Depending on specific chemical composition and void morphology within layers, tunable band gap of 2D $g\text{-C}_3\text{N}_4$ can make them suitable for fulfilling the required application. $g\text{-C}_3\text{N}_4$ material, with its exceptional electronic, optical, and biocompatible properties, shows great potential in many domains.



Figure 1.4: Diverse technological applications in research field using Carbon nitride-based materials.

Though graphite is black in appearance and $g\text{-C}_3\text{N}_4$ is yellow, both share similar structures which ultimately lead these systems to be extensively explored in various aspects. Various approaches are explored to propose condensed $g\text{-}$

C_3N_4 with low defects, but there is still limitation in development of ideal condensed g- C_3N_4 . Its unique behaviour, such as abundant nitrogen, suitable electronic structure and unusual thermal stability, has driven the attention of the researchers to explore it in different domains. Its intrinsic features having appropriate band position, high stability and unique electronic structure mark it as a favorable candidate beyond photocatalysts. Although, it displays a number of attractive and intrinsic properties, low electronic conductivity, lack of absorption above 460 nm and low surface area in bulk carbon nitride hinders its pristine applications. Challenge of developing g- C_3N_4 based heterostructures for practical applications still lies ahead. Although, the researcher claims to show superior catalytic properties with the prepared material however it lacks an efficient protocol for examining the photocatalytic properties.

1.5 Objective of This Thesis

Research related to g- C_3N_4 based materials has spread out in much broader range than what we could envision in its early stage due to its non-toxicity and low-cost synthesis has reached much further away. From the prospect of its structure, well-endowed micro and nanopores feature along with 2D sheets is undoubtedly favoured for its storage and absorbent applications. However, tuning its surface area and creating abundant active sites for better mass transfer within the system is a new approach to be carried out. Also creating heterojunction or doping with foreign atoms can lead towards increase in conductivity, which overall improves the performances of the system. In order to accelerate the functionalities of pristine g- C_3N_4 nanosheets in various technological applications (shown in **Figure 1.4**), the following objectives of the thesis have been formulated.

✓ Looking into the advantageous properties such as high surface area, porosity and abundant nitrogen content within 2D materials, the prime objective of this thesis work is development of 2D g- C_3N_4 heterostructure using suitable chemical/physical techniques. Also, corroborating the experimental with theoretical results using *ab initio* density functional theory simulation for better

understanding of the atomic structure, local density of states, electronic and magnetic properties.

✓ High surface area with porosity is an important feature for enhancing performances in applications such as energy storage, water purification and oil-water separation. Presence of pores in the exposed surface area creates accessible channels, promoting high surface reaction resulting in charge separation. To overcome the global challenges like oil spillage, in the present chapter reports a two dimensional nanocomposite of nontoxic iron nickel (FeNi_3) magnetic nanoparticles with 2D $\text{g-C}_3\text{N}_4$ sheet for safe, efficient and fast removal of oils from water bodies. The study has reported magnetic hydrophobic/oleophilic graphitic nanosheets exhibiting excellent oil sorption performance and instantaneous removal of absorbed oil using magnetic field. The brilliance of surface structure and magnetic functionality combined with hydrophobicity/oleophilicity has marked this system as an ideal sorbent for oil recovery.

✓ Significant increase in energy crisis has deteriorated the environment for which high efficiency energy storage devices are urgently required. In this chapter, development of hybrid graphitic carbon nitride along with FeNi_3 nanoparticles, conjugating both EDLC and faradaic material based flexible in-plane micro supercapacitor for fabricating miniature electronic devices is carried out. The resultant flexible microsupercapacitor exhibit brilliant quantum capacitance, high power densities, areal capacitance of 19.21 mFcm^{-2} , flexibility, excellent cycling stability and high capacitive retention upto 94%.

✓ From decades, there is a practice of using plastics and most of the packaging materials are made of petroleum-based polymers, which are non-biodegradable, ultimately causing threats to environment. With time, new development of biodegradable polymer materials is studied and verified for their use as an alternative to plastics. In this chapter, reports utilization of layered 2D materials as nanofillers in a flexible composite film as a substitute to traditional non-biodegradable materials in order to improve the film efficacy and functionality. In the comparative study, $\text{g-C}_3\text{N}_4@\text{CuSe}$ system has convincingly

shown superior mechanical and barrier performances additional to antimicrobial properties. The prepared film minimizes the defects that promote permeation, resulting in outstanding barrier performance, which can be used to cover varied types of food packaging. The results of this research demonstrated the retention of activity and its antimicrobial effectiveness against foodborne pathogens. Further, the experiments carried on biodegradability and ecotoxicology supports the claim of 2D heterostructure based composite film as a promise of being environmentally benign.

✓ Bandgap is the key equipment for photocatalytic applications. Apart from high surface area, porosity and visible-light activity, $g\text{-C}_3\text{N}_4$ n-type semiconductor has a bandgap of 2.7 eV but due to high recombination rate and less active sites, its photocatalytic efficiency is low. Various strategies have been used to balance its drawbacks. One among them is by creating heterojunction (type II) with other nanomaterial to make this system more promising in rising realistic $g\text{-C}_3\text{N}_4$ -based photocatalysts. 2D graphitic carbon nitride has engrossed more consideration towards photocatalytic applications due to its appropriate conduction band (CB), valence band (VB) positions, high surface area, and suitable band gap energy. Apart from the aforementioned properties, it possesses suitable stability with N-atoms, which are unsaturated for anchoring active sites. But pristine $g\text{-C}_3\text{N}_4$ due to its fast recombination of the charge carrier leads towards poor photocatalytic efficiency, which limits its wide possibilities. One of the strategies is to couple $g\text{-C}_3\text{N}_4$ semiconductor with narrow bandgap material lying in visible regime with suitably positioned conduction band minima and valence band maxima. The present chapter reports development of a 2D/2D heterostructure where 2D CuSe nanoflakes have been coupled with 2D $g\text{-C}_3\text{N}_4$ nanosheets, for efficient photo catalytic application, having rapid charge transfer and catalytic dispersion. The study focused on 2D/2D heterostructure system as 2D nanosheets (NS) possess extraordinary properties in comparison to other dimensional materials. Due to formation of such heterointerface, it shortens the diffusion path coupled to quantum confinement effects, eventually making the system a promising photocatalysts. 2D/2D face-to-face stacking heterostructures

has the largest interfacial contact area and strongest interactions, which enable moderately improved coupling hetero-interfaces, altering the surface potential of the catalyst.

✓ Being one of the classes of burgeoning fluorescent polymeric materials, with multipurpose advantages properties such as stable fluorescence, high quantum yield, good biocompatibility and nontoxic, carbon nitride has attracted much consideration in the field of biomedical applications. Highly stable g-C₃N₄ with further modification and surface engineering are used for higher therapeutic outcomes. In this chapter, development of 2D/2D heterostructure of g-C₃N₄@FeNi₃ with inherent fluorescent property is developed, further to be used in clinical screening for the diagnosis of abnormal organ/tissue growth. The developed system with advanced properties can trace the targeted cells after in vivo injection. Comparison to existing fluorophores, the developed system exhibits broad absorption spectra, with high stability and narrow emission bands.

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