CATALYTIC APPLICATIONS OF CARBON-NITRIDE-BASED NANOMATERIALS

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Catalytic Applications of Carbon Nitride-Based Nanomaterials

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FOREWORD

"Catalytic Applications of Carbon Nitride-Based Nanomaterials," edited by Professors Vijai Kumar Rai, Manorama Singh, and Ankita Rai, is an admirable compilation of scientific knowledge on various aspects of synthesis, modification, functionalization, and chemical and electrochemical applications of graphitic-carbon nitride-based nanocatalytic systems. Carbon-nitride-based nanomaterials – most notably graphitic carbon nitride (g-C_3N_4) – are metal-free two-dimensional polymeric semiconductors with potential applications in electronic, catalytic, and energy sectors. Composed entirely of earth-abundant elements, these nanomaterials have attracted a great deal of attention in recent years. This is because of their exceptional thermal and chemical stability, unique electronic band structures, biocompatibility, metal-free nature, and sustainable and cost-effective synthesis. These nanomaterials are widely used for green technologies such as visible-light-driven photocatalysis, environmental remediation, and biomedical applications. However, while promising, the pristine g-C_3N_4 suffers from a low surface area and limited charge-carrier mobility. To overcome these limitations, researchers have adopted several strategies to modify g-C_3N_4 and enhance its physico-chemical properties and photocatalytic efficiency. For instance, g-C_3N_4 has been modified *via* heterojunction formation (*i.e.*, coupling g-C_3N_4 with other semiconductors to improve electron-hole pair separation), doping (*i.e.*, incorporation of non-metals or metals, to enhance catalytic activity, and nanostructuring (*i.e.*, fabricating quantum dots or porous nanosheets to increase active surface area). Enhanced awareness, education, and research on such a new class of catalytically functional nanomaterials are indeed a desideratum today. In this context, this book is of great significance. I commend the editors and the authors for their efforts in presenting this book.

The narrative of the book, comprising eleven chapters, is built on sustainable chemistry, enabling efficient photocatalytic chemical reactions for the synthesis of a wide range of organic molecules, oxidation and reduction reactions, and developing electrochemical sensors for efficient detection of environmentally hazardous molecules. All the chapters are written with great acumen and perspectives of several learned authors, with expertise and experience in the chemistry of g-C_3N_4 -based nanomaterials. This book is a pleasure to read, in part because it gives a concise yet clear description of the subject matter, together with other aspects germane to the development of photo-nanocatalysis for sustainable design and development of a wide range of molecules and electroanalytical tools.

The learned authors have compiled useful scientific information on various aspects of synthesis, structure, and physico-chemical properties of g-C_3N_4 -based nanocatalytic materials, with a focus on their photocatalytic applications in organic synthesis and electrochemical sensor design and development. The book provides an insightful analysis of present-day scenarios and future prospects. In doing so, the authors have discussed ideas and observations of many researchers. The authors have discussed the matter in reasonable detail, and various aspects of the subject are illustrated by suitable examples of reactions and synthetic transformations together with figures and mechanisms, where appropriate and necessary. At the end of each chapter, the authors have included pertinent references on the scientific matters discussed. This will facilitate easy access to several relevant references and will prove of considerable value to students, teachers, and researchers alike.

The topics discussed in the book will surely sensitize and promote new thinking among researchers with an interest in g-C_3N_4 -based systems and their photocatalytic applications.

With the kind of research advancements made in recent years, as evident from the material covered in this book, it can be safely said that the coming years are destined to witness further development of this area with much greater stride and novelty. More and more new imperatives and vistas are expected to be discovered and developed, which are pivotal to further developing this fascinating area of interest to many researchers across several disciplines of science and technology.

For this book, the editors and the authors deserve the heartfelt thanks of the community of students, teachers, and researchers in chemistry and allied disciplines for their commendable efforts in making this book available on a subject of much current interest. I congratulate the editors and the authors and convey my best wishes to them and all the readers.

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PREFACE

Designing and developing a green, sustainable, and economical reaction is one of the major challenges in chemistry. Besides the traditional need for efficient and selective catalytic reactions, recent chemical synthesis strives to design new and efficient catalytic systems with high rates of catalyst recovery. The initial papers in the field of nanocatalysis were published as early as 1941 on palladium and platinum nanoparticles as catalysts, which were prepared by reduction of the metal salts. This research of Rampino was evocative of the work of Prof. Paul Sabatier (Chemistry Nobel Prize in 1912), who discovered catalyzed hydrogenation using finely divided nickel particles prepared upon reduction of nickel oxide or hydroxide. Then, in 1987, Haruta *et al*. made another breakthrough in the field of nanocatalysis by reporting the catalytic activity of gold nanoparticles smaller than 5 nm towards the oxidation of CO.

Inspired by the above initial discoveries of nanoparticles as catalysts, nanostructured materials have attracted the scientists' community and are now recognized as efficient heterogeneous catalysts for various organic transformations and electroanalytical processes. The efficiency, selectivity, and recyclability of nanocatalysts depend on their size, shape, composition, and assembly, which further enhance the appeal of well-defined nanostructured materials as green and sustainable heterogeneous catalysts that are used in a wide variety of organic transformations as well as electroanalytical processes. The role of nanocatalysts in organic synthesis and electroanalysis helps to control the chemical reactions by varying their shape and size, chemical composition, dimensionality, etc. to improve the kinetics of the reaction. Several catalytic sites are explored due to variations in the shape, size, and composition of nanocatalysts, as a specific site can show good selectivity towards a particular reaction pathway.

This book offers an exclusive link between the domains of nanocatalysts and their exploitation in organic syntheses, as well as electrochemistry using nanotechnology-based catalysts and electrode structures, respectively. The book is aimed at preparing a quick and highly condensed knowledge base, which, in turn, is expected to promote further advances in the field of nanocatalysis. Also, the book will open up new dimensions for designing novel nanocatalysts for unexplored chemical reactions important for academia and industries. The topic chosen in the proposed book will benefit a broad range of readers, such as graduate, postgraduate, Ph. D. students, faculty members, and research & development (R & D) personnel, working in these areas as well.

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CHAPTER 1

Graphitic Carbon Nitride ($g\text{-}C_3N_4$) as a Robust Catalytic Material for Carbon-Carbon Coupling Reactions

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Abstract: Polymeric graphitic carbon nitrides ($g\text{-}C_3N_4$) have gained enormous recognition for their suitability in the sustainable industry. This polymeric material has a π-bonded planar layered structure similar to that of graphite, which helps to anchor metal nanoparticles, *N*-rich basic surface sites, a large surface area, and high thermal stability. They can be easily obtained through a one-step polymerization of raw materials like urea, melamine, thiourea, and cyanamide. These surfaces have been effectively utilized to obtain desirable conversions in carbon-carbon cross-couplings like Suzuki-Miyaura, Sonogashira, Stille, and Heck coupling reactions. The following chapter discusses the various heterogeneous modifications of graphitic carbon nitride, along with its applications in carbon-carbon bond-formation reactions developed by various research groups. It particularly focuses on the role of graphitic carbon nitride as a heterogeneous catalytic support, a photocatalyst, and a component of hybrid catalysts for C-C Cross-Coupling Reactions.

Keywords: Allotropic forms, Carbon-carbon cross-coupling reaction, Carbon materials, Graphitic carbon nitride, Heterogeneous catalyst.

INTRODUCTION

Carbon materials can exist in numerous allotropic forms such as graphite, carbon nanotube, graphene, carbon fibre, carbon black, activated carbon, fullerene, diamond, *etc*. These materials exhibit various physical and chemical properties arising from their diverse structures, which range from the layered structure of graphene, containing hexagonal rings of sp2-hybridized C-atoms, to the three-dimensional network structure of diamond, containing sp^3 C-atoms. Among them, carbon nitrides are a distinguished class of carbon and nitrogen-containing compounds. Like most carbon materials, these compounds also exhibit different

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properties based on their structural phases, which can be attained by controlling the temperature and pressure conditions of synthesis [1]. There are seven known phases of carbon nitride. These are α-C_3N_4, β-C_3N_4, g-*h*-triazine, g-*h*-heptazine, g-*o*-triazine, cubic C_3N_4 and pseudo-cubic C_3N_4 [2]. Among these phases, the two-dimensional layered structure, g-C_3N_4 is considered as the most stable at room temperature.

g-C_3N_4 is a polymer that consists mainly of C, N, and a small amount of H. The atoms are linked based on heptazine (or tri-*s*-triazine) units and poly (triazine imide) units (Fig. **1**). The history of g-C_3N_4 is traced back to 1834, when Berzelius synthesized a polymer similar to carbon nitride. Leibig termed it as 'melon' [3]. 'Melon' is a linear polymer made of tri-*s*-triazine units connected *via* secondary nitrogen, while g-C_3N_4 is a 2D sheet of tri-*s*-triazine units connected by tertiary amines.

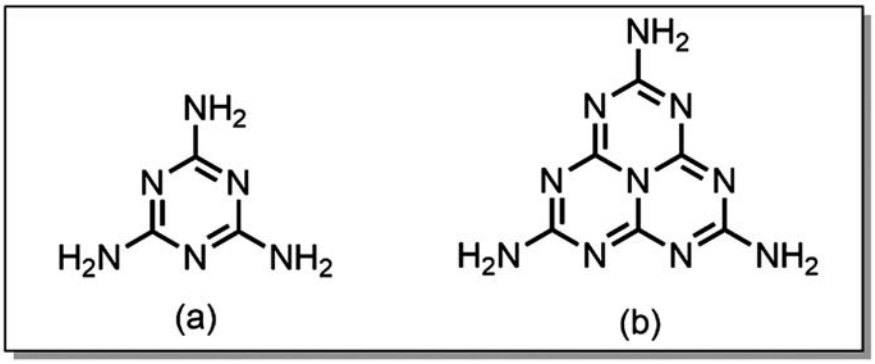
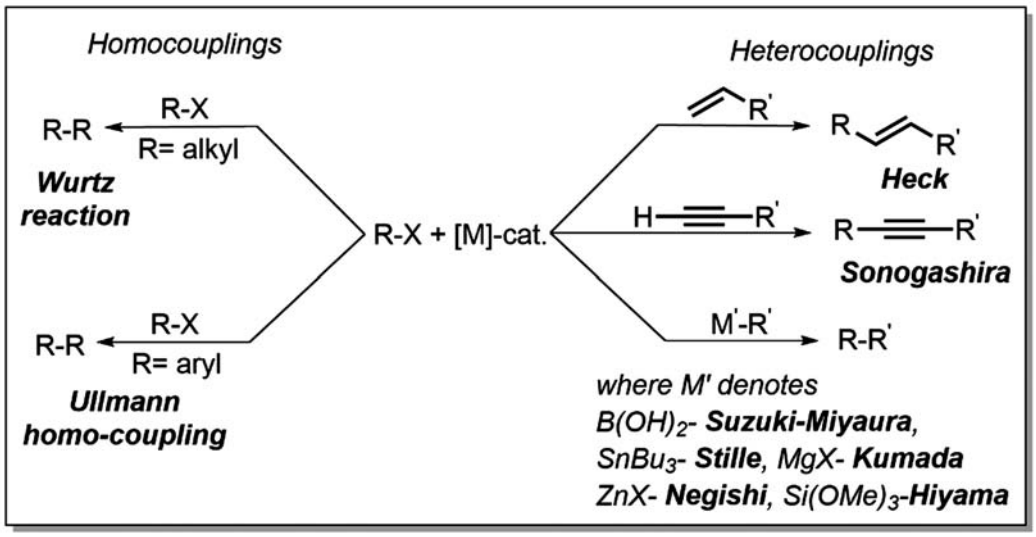


Fig. (1). (**a**) *s*-triazine and (**b**) heptazine or tri-*s*-triazine units of g-C_3N_4.

Graphitic carbon nitride (g-C_3N_4) has gained widespread attention in recent times owing to its high thermal stability, large surface area, tunable electronic structure, and a wide band gap [4]. In addition, these materials are abundant and can be readily obtained *via* one-step polymerization of raw materials such as urea, melamine, thiourea, cyanamide, and dicyandiamide [5 - 14]. Because of these remarkable characteristics, g-C_3N_4 is an eminent candidate for various organic transformations, including N_2 fixation, selective oxidation of alcohols, hydrogen evolution, Friedel-Crafts reaction, CO_2 reduction, and visible light photocatalysis [15 - 20].

C−C bond-forming/coupling reactions are considered a significant tool in modern organic synthesis. The growing demand for C−C coupling reactions is due to its widespread applications in the synthesis of agrochemicals, pharmaceuticals, and natural products [21, 22]. In Organic Chemistry, coupling reactions are reactions

in which two substrates are joined together, using a metal catalyst. Two broad classes of such reactions are the homocoupling reactions and the heterocoupling reactions. Wurtz reaction [23], Ullmann homo-coupling [24], and Glaser coupling [25] are some examples of homocoupling reactions that involve coupling between two identical partners. However, in hetero-coupling or cross-coupling reactions, a new C−C bond is formed when an organometallic compound R−M' (R= organic fragment, M'= metal centre) and an organic halide, R'−X, are made to couple with the help of a transition metal catalyst to form R−R'. Some notable examples of cross-coupling reactions are Cadiot-Chodkiewicz reaction [26], Suzuki-Miyaura cross-coupling [27], Heck coupling [28], Sonogashira cross-coupling [29], Stille coupling [30], Kumada coupling [31], Negishi coupling [32], and Hiyama coupling reactions [33] (Scheme **1**).



Scheme 1. Some common metal-catalyzed C-C coupling reactions.

Although homogeneous catalytic systems are employed for these reactions on most occasions, they suffer from numerous drawbacks like difficulty in recovery and reusability of the catalyst, high cost of ligands, and potential contamination of the products with residual heavy metals. These limit their industrial applications [34]. Moreover, significant loss of catalytic activity is observed with homogeneous catalysts due to metal nanoparticle aggregation and leaching. Hence, to overcome this problem, the development of heterogeneous catalytic systems with good stability and excellent reusability has attracted much attention across the scientific community. Due to the presence of electron-rich *N*-functionalities on the g-C_3N_4 surface, which can act as Lewis basic sites, and the π-bonded 2-D layered configuration, graphitic carbon nitride surfaces are used to

CHAPTER 2

Graphitic Carbon Nitride (g-C_3N_4): Synthesis, Structure, and Catalytic Applications towards Carbon-Heteroatom Bond Formation

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Abstract: The general formula of graphitic carbon nitride (g-C_3N_4) is $(C_3N_3H)_n$. This is one of the oldest recorded polymers in the literature. The beginnings of development may be traced back to 1834. In the 1990s, theoretical predictions such as diamond-like C_3N_4 may have exceptionally high hardness values, sparking research on this material system. At atmospheric temperatures, g-C_3N_4 is a highly stable allotrope. g-C_3N_4 is a stacked substance analogous to graphite, where the van der Waals force binds the layers (covalent C–N bonds) together, and every stacked layer comprises tri-s-triazine units joined by planar amino groups. Catalytic energy-efficient, sustainable, and economical techniques are highly demanded in today's scientific and industrial societies. In this regard, 2D graphite-like polymeric graphitic carbon nitride (g-C3N4) materials have attracted significant attention as metal-free composite catalysts in organic synthesis. g-C_3N_4 possesses excellent catalytic activity, good stability, a small band gap, non-toxicity, easy structure, easy synthesis, nitrogen-rich carbon, and particular tunable features with diverse metals, unlike typical carbon-based materials and hazardous catalysts. In recent years, graphite carbon nitride (g-C_3N_4) has been used enormously in a variety of organic transformations, like reduction, C–C bond formation, C–H activation, oxidation, and hydrogenation of alkenes and alkynes, cyclization, and epoxidation. Furthermore, g-C_3N_4 absorbed light in the visible region due to its narrow band gap. As a result, g-C_3N_4 has excellent photocatalytic capabilities and is frequently utilized as a photocatalyst in various processes. In general, g-C_3N_4 can be used as a catalyst support, a catalyst cover, or the catalytic centre itself. This chapter summarizes the very recent achievements in the design, processing, and fabrication of g-C_3N_4-based materials and their implications in catalysis in the field of carbon-heteroatom bond formations. There's also a look ahead at anticipated advances in g-C_3N_4-based research for new characteristics and uses.

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Keywords: Chemical vapour deposition, Carbon-heteroatom bond formation, Electrodeposition, Electronic structure, Graphitic carbon nitride (g-C_3N_4), Microwave irradiation, Polymerization, Solvothermal, Sol-gel synthesis.

INTRODUCTION

Graphitic carbon nitride (g-C_3N_4) is a very new carbon-based material that has attracted considerable interest since the development of its ultrathin nanosheet form in 2012. This interest comes from its strong intrinsic photoabsorption, semiconducting properties, high photoreactivity, physiological stability, and biocompatibility [1]. The pronounced Photoluminescence (PL) intensity of g-C_3N_4 nanosheets makes them potential candidates for bioimaging applications. Structurally, g-C_3N_4 consists of sp^2-hybridized carbon and nitrogen atoms, forming a framework very similar to graphite, but composed of alternate C–N bonds [2]. In contrast to graphite, g-C_3N_4 features nitrogen-surrounded vacancy defects. Depending on the number of valence nitrogen atoms, g-C_3N_4 generally exists in two main structural configurations: triazine and heptazine [3].

These structural imperfections contribute to its difficulty in synthesizing long-range ordered crystalline forms of g-C_3N_4, and as a consequence, it is obtained as an amorphous powder [4]. Moreover, g-C_3N_4 nanoparticles have proven highly valuable in the development of quick, precise, cost-effective, and reliable sensors, owing to their excellent biocompatibility and distinctive electroluminescent and photoelectrochemical properties [5]. Generally, carbon nitride materials are synthesized through thermal polycondensation of C-N-rich precursors, such as urea, thiourea, melamine, dicyandiamide, cyanamide, guanidine hydrochloride, guanidine thiocyanate, and thiourea oxide, at temperatures ranging from 400 to 600 °C [6]. The continued development of g-C_3N_4-based photocatalysts holds promise for addressing energy and environmental challenges related to the reduction of fossil fuels and the harmful effects of their combustion [7].

As a metal-free semiconductor, g-C_3N_4 exhibits a range of remarkable activities, including visible-light responsiveness due to a medium band gap of approximately 2.7 eV, favorable band alignment, earth-abundant and non-toxic composition, easy synthesis route, and ground-breaking chemical stability [8]. Compared to 0D and 1D nanostructures, 2D g-C_3N_4 materials exhibit higher charge-carrier mobility, and reduced electron-hole recombination [9]. However, despite these promising advantages, pristine 2D g-C_3N_4 faces several limitations, including inefficient separation of photogenerated electron-hole pairs, a narrow visible-light absorption range (typically below 460 nm), a lower specific surface area, and poor electrical conductivity [10]. Moreover, there are several challenges that researchers and engineers need to address for its successful application in these devices, including low conductivity, limited charge storage, structural

stability, scalability, production cost, and electrolyte compatibility, which limit its application in electrochemistry [11].

Various modifications of bare g-C_3N_4, such as nanostructure design, intercalation with Li^+ and Cl, elemental doping, copolymerization, coupling with metals or noble metals, integration with other semiconductors, hybridization with metal phosphides, and many others, have all been investigated to improve photocatalytic efficiency for practical benefits [12]. So far, several outstanding review articles have been published on g-C_3N_4-based photocatalysts, covering topics such as materials synthesis, functionalization, and hybridization, as well as a variety of applications, including photocatalytic water splitting [13, 14]. This can demonstrate this research area's importance in the scientific community [15]. There are even reports of carbon nitride synthesis using potassium hydroxide molten salt, which has significant utility in photocatalytic uranyl extraction. The material so obtained possesses triazine-s-heptazine structure and exhibits wider visible light absorption than graphitic carbon nitride (g-C_3N_4) [16]. In recent times, designing 2D/2D nanocomposites by combining 2D g-C_3N_4 photocatalyst with other 2D nanomaterials has attracted significant attention, and it is not surprising [17 - 19]. The stacked heterojunction of different 2D nanomaterials is expected to significantly affect charge transfer and separation due to the built-in electric field at the well-defined ultrathin interface [20]. Consequently, research on 2D/2D heterojunctions with close face-to-face interfaces is critical, as it will help us better understand the photocatalytic reaction process at the molecular level [21]. Recently, S. Mukhtar *et. al*. reported bio-inspired synthesis of Ag-g-C_3N_4 nanocomposites, which was successfully used for photocatalytic degradation of p-nitrophenol, a potential environmental pollutant [22]. Most interestingly, graphitic carbon nitrides have been reportedly used as a support for 'Single Atom Catalyst (SAC)', a novel catalyst known for its effective utilization towards environmental remediation. The extraordinary structure of graphitic carbon makes it extremely suitable as a carrier for anchoring SAC, and the combination attains many improved characteristics as well [23]. All these research developments prompted us to provide an overview of cutting-edge research on 2D/2D g-C_3N_4 heterojunction nonocomposites in this chapter to shed light on the future research horizon of g-C_3N_4 in carbon-heteroatom bond formation reactions [24].

PREPARATION OF GRAPHITIC CARBON NITRIDE-BASED NANOPARTICLES

The most common starting materials for g-C_3N_4 chemical synthesis are rich in nitrogen and compounds that are free of oxygen with pre-bonded CN core structures, such as triazine and heptazine derivatives, the majority of which are unstable, difficult to acquire, and/or very explosive [25]. Single-phase sp^3-

CHAPTER 3

$g\text{-}C_3N_4$ Catalyst in Carbon-Heteroatom Bond Formations

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Abstract: Graphitic carbon nitride ($g\text{-}C_3N_4$) has attracted significant attention as an interesting, efficient, and durable carbon-based nanomaterial due to its important characteristics in academia and industry. The $g\text{-}C_3N_4$ plays a noteworthy role as a catalyst in chemical synthesis due to its high activity, selectivity, and productivity. Herein, we have discussed a variety of carbon-heteroatom bond-forming organic transformations, catalysed by numerous graphitic carbon nitride-based sustainable catalysts to produce biologically active scaffolds. The carbon-based heterogeneous (recyclable and reusable) catalysts exhibited greater catalytic efficiency as compared to traditional catalysts for the fabrication of diverse heterocyclic scaffolds. This chapter demonstrated the versatility of carbon nitride in organic synthesis and the vigorous research activities in the field.

Keywords: Carbon-based nanomaterials, Carbon-heteroatom bond formation, Graphitic carbon nitride, Heterogeneous catalyst.

INTRODUCTION

With the emergence and advancement of sustainable and green science, the present-day organic synthesis seeks to avoid harmful and hazardous reagents and solvents, harsh reaction conditions, and costly and complex catalysts [1]. Over the last ten years, there has been a shift in perspective toward energy conservation, nuclear energy, and the use of green solvents and alternative legislation techniques that reduce waste by the design of new, greener processes for the fabrication of organic scaffolds [2]. In addition, the use of clean, green compounds advances the industry, in addition to being beneficial for the production of important synthetic materials. Given the difficulties of the world-

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wide economy and the need for viable synthetic processes. Catalytic reactions play an important role in developing new strategies for the growth of target particles in just a few steps and with minimal measurement of synthetic waste [3, 4]. Impetuses (catalysts) that affect the rate of reaction and increase product yield with great selectivity and security are of extraordinary innovative significance [5]. Nano-impetuses copy homogeneous (high surface area, effectively available) as well as heterogeneous (steady, simple to deal with, simple to separate) catalyst processes. Heterogeneous impetuses offer a few inherent benefits over their homogeneous partners: simplicity of product partitioning and impetus reuse; bifunctional peculiarities, including activation of the reactant between the active and support stages; and interaction benefits through reactor activity in a consistent flow versus a batch arrangement [6]. Notwithstanding, to keep up with financial feasibility, an appropriate heterogeneous system should limit the creation of waste, yet ought to likewise show activities and selectivity equivalent to or better than the current homogeneous course.

CATALYSIS

In these environmentally conscious days, manufacturing of value-added materials requires greener and safer reaction procedures, which can minimize the energy and raw material requirements and can eventually reduce pollution effects [7]. To accomplish this goal, one of the most promising ways is to bring efficient and productive catalysts into the reaction game.

Catalysis performs a crucial function in chemical reactions and lies at the core of endless synthetic protocols, from scholastic exploration at the research centre level to chemical production [8]. With the help of catalytic reagents, we can decrease the temperature of a transformation, diminish reagent-based waste, and improve the reaction's selectivity, potentially avoiding undesirable side reactions, thereby promoting green technology [9]. In other words, we can say that the advancement of sustainable and cost-effective avenues for large-scale manufacturing; current strategies are described by four limitations: catalytic efficiency of the reactions, atom-economy, selectivity, and step-selectivity. Among them, improving reactive systems with higher mobility and better selectivity plays a foremost role. Alters the organic reaction pathway by lowering the activation energy barrier without consuming itself in a catalytic process [10]. The fabrication of advanced catalytic systems with high selectivity, high activity, enhanced reaction rates, improved product yield, and stability is a pressing need in chemical technology to fulfil sustainable, eco-friendly goals [11]. Therefore, the search for suitable catalytic structures is constantly evolving to achieve sustainable, green manufacturing of chemical materials, which allow the elimination of toxic and hazardous chemical substances, a stoichiometric amount

of promoter, lower energy use, and fewer side products. This approach offers advantages such as lower energy consumption, reduced by-products, and fewer reaction steps [12]. However, the frequent use of expensive metal salts and ligands, along with tedious purification procedures and challenges in catalyst recovery, remains a significant limitation. Although both homogeneous and heterogeneous nanocatalysts have been developed, substantial effort is still required to design catalysts with improved activity and selectivity [13].

Nanocatalysis

The measurement of a catalyst's productivity rests on the desired product yield and selectivity, even under nominal reaction conditions. Hence, there is a growing need to develop effective catalytic approaches that enable green, sustainable, and economical chemical manufacturing [14]. To assist in achieving this objective, nanotechnology comes into play. Nanotechnology embraces the use of technologies and approaches that can assist in the engineering, composition, configuration, production, and application of materials and devices whose dimensions lie at the nanoscale level [15]. The nanoscale aspect of any given material exhibits vastly different electrical, chemical, physical, and mechanical properties, which enable its widespread implementation [16]. Nanomaterials display unique chemical reactivity because their nanoscale size and shape increase the surface area to volume ratio, which eventually determines surface effects and quantum effects as well as their mechanical, electric, optical, and magnetic properties [17, 18]. While approaching the idea of a sustainable future, the amalgamation of nanomaterials with green chemistry can surely give positive outcomes. To explore competent green alternatives to traditional compounds, nanoparticles have emerged as powerful heterogeneous catalysts with high surface areas and as catalyst supports [19].

Metal-Free Carbon-Based Nanomaterials

In the past few years, metal-free catalysts have emerged as green catalytic materials that are attracting more attention in synthetic organic chemistry [20]. In numerous academic and industrial catalytic processes, metal-free carbon-based nanomaterials have found widespread use in organic transformations due to their advantages, such as superb catalytic activity, selectivity, non-toxicity, environmental friendliness, excellent chemical/thermal stability, and low-cost synthesis [21]. There are different types of metal-free nanocatalysts such as Graphene Oxide (GO) [22], Reduced Graphene Oxide (rGO) [23], graphitic carbon nitride (g-C_3N_4) [24], Carbon Quantum Dots (CQDs) [25] and Carbon Nanotubes (CNTs) [26] that have been widely used in numerous organic transformations such as alkylation, carbonylation, oxidation, reduction, diverse

CHAPTER 4

g-C_3N_4-Based Composite/Doped Nanoparticles as Heterogeneous Catalyst for Oxidation Reactions

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Abstract: Due to the rapid growth of population and industrialization, energy concerns have become one of the major issues. Solar energy, the green and abundant form of energy, can prove to be highly efficient in this regard and meet the growing demand for energy consumption. Photocatalysis is a prominent strategy in which photocatalytic material converts solar energy into its usable form, satisfying the energy demand by catalyzing a range of reactions. In this regard, graphitic carbon nitride has emerged as a promising photocatalyst for various photocatalytic reactions. It is cost-effective, nontoxic, and responsive to visible light. But pure g-C_3N_4 has some pitfalls associated with it. The fast recombination rate of photogenerated electron-hole pairs, the small surface area, and the few adsorption and active sites lower the photocatalytic activity. To overcome this limitation, various modifications are made to enhance its photocatalytic behaviour. Doping and coupling g-C_3N_4 with other components to fabricate g-C3N4-based nanocomposites has been proposed as an efficient and simple strategy to adjust its structural properties, including the band gap, reduce interlayer resistance, enhance charge separation, respond to visible light, and thus accelerate photocatalytic behaviour. In this chapter, we have discussed the important roles and applications of metal-free/metal/semiconductor/metal oxide-based g-C_3N_4 nanocomposites for various oxidation reactions. Lastly, this chapter outlines recent progress in the design and synthesis of cost-effective g-C3N4-doped nanoparticles.

Keywords: Bandgap, Green, g-C_3N_4, Nanocomposite, Oxidation, Photocatalyst.

INTRODUCTION

The metal-free polymeric semiconductor graphitic carbon nitride (g-C_3N_4), composed solely of carbon and nitrogen, has recently attracted tremendous attention [1]. g-C_3N_4 offers various advantages, including good physicochemical stability and an attractive electronic structure featuring a band gap of 2.7 eV [2]. Owing to its medium band gap, g-C_3N_4 shows visible-light response, enabling

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the utilization of solar energy, which is environmentally friendly and virtually limitless. Thus, graphitic nitride quickly emerges as the standout green catalyst in photocatalysis, converting solar energy into chemical energy (Fig. **1**).

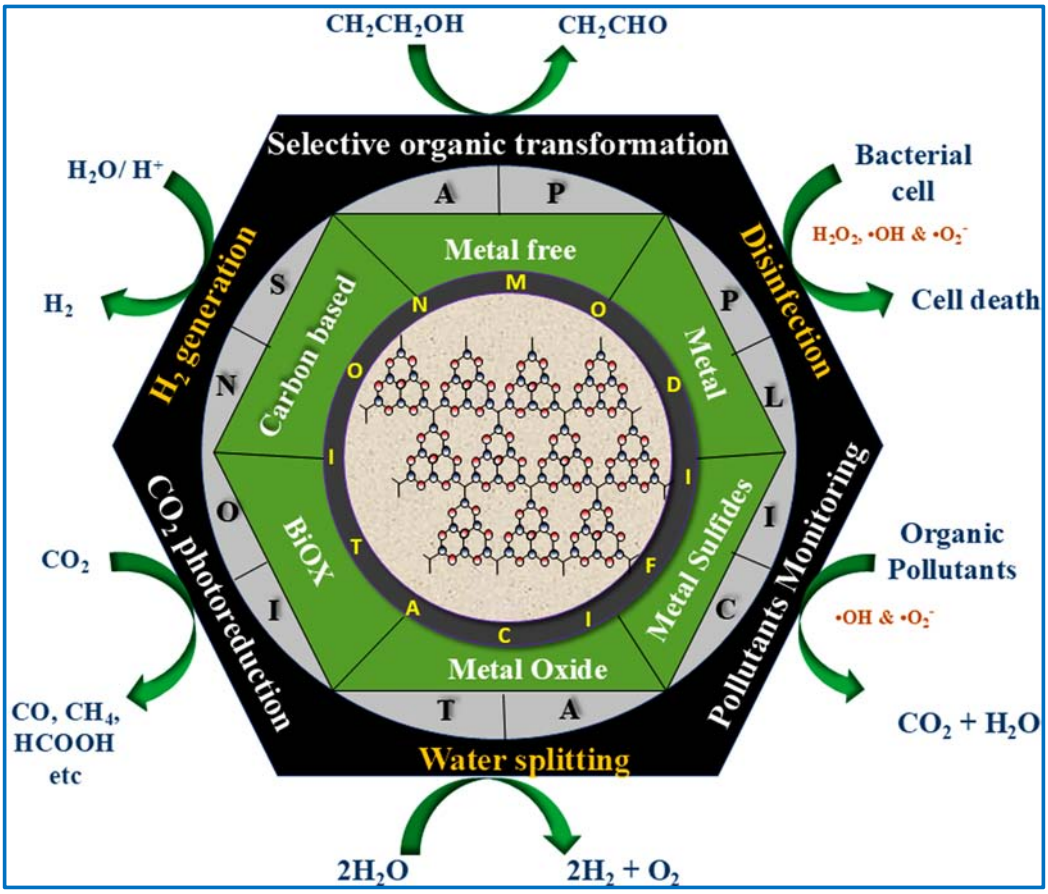

Fig. (1). A schematic representation showing various modifications of g-C_3N_4 and its application in a number of photocatalytic reactions.

Being abundant, stable, and metal-free, the polymeric solid g-C_3N_4 is suitable for a wide range of organic transformations [3]. Under mild conditions and with only visible light, g-C_3N_4 can catalyze various oxidation reactions, including the conversion of alcohols to aldehydes, benzene to phenol, alkanes to aldehydes, the oxidation of ammonia, and NO, all of which are significant in industrial applications. However, high recombination of Electron-hole Pairs (EHP), low solar energy absorption efficiency, and photo-corrosive concerns remain the "bottleneck" of g-C_3N_4, limiting its practical applications [1, 4]. To overcome these limitations, various modification strategies have been employed to tailor its

composition and properties, alter the molecular orbital shape and position, such as the HOMO, which is crucial for oxidation, and hence improve the strength and selectivity of the oxidation process [4, 5].

This chapter focuses on various modifications of g-C_3N_4 for composite formation, highlights their roles in oxidation reactions, and provides insight into the g-C3N--based heterostructures engineered to date.

MODIFICATION OF G-C_3N_4

g-C_3N_4 possesses an adjustable band gap where the Lowest Unoccupied Molecular Orbital (LUMO) and Highest Occupied Molecular Orbital (HOMO) can be tuned as required [5], which significantly impacts the photoelectronic performance of C_3N_4 as a functional photo-catalyst. In order to improve the photocatalytic activity of g-C_3N_4, a number of modification approaches have been explored, including the formation of surface coupling hybridization [6], doping of species [7], constructing a nanocomposite with conductors and semiconductors [8, 9], synthesis of mesoporous g-C_3N_4 [10], and preparation of two-dimensional (2D) nanosheets [11]. For efficient separation of the electron–hole pairs and the smooth flow of charge carriers across the heterostructure interface, thereby preventing recombination, the development of heterostructures holds great promise for enhancing the photocatalytic activity of g-C_3N_4.

g-C_3N_4-based heterostructures may be generated by combining them with a wide range of materials, ranging from narrow band gap semiconductors to semiconductors with large band gaps [12, 13], thus broadening their potential application. However, g-C_3N_4 is not capable of bonding with all materials in forming a heterostructure. The contenders for constructing an efficient visible-light-active hybrid structure with g-C_3N_4 must possess an appropriate band configuration that facilitates effective coupling [14]. Defects caused by a lattice mismatch at the interface may trap photo-generated electronic carriers, preventing electron and hole diffusion. As a result, designing g-C_3N_4-based heterostructure (nanocomposites) is a good way to improve charge separation, leading to better and improved photocatalytic activity.

CATEGORIES OF G-C_3N_4-BASED NANOCOMPOSITES AND THEIR APPLICATION IN OXIDATION REACTION

Heterogeneous photocatalysis using g-C_3N_4-based nanocomposite has emerged as a viable approach for a variety of chemical reactions utilizing solar energy in recent years. The following section discusses some of the categories of heterogeneous g-C_3N_4 nanocomposites and their applications in oxidative reactions.

CHAPTER 5

Carbon Nitride (g-C_3N_4) Based Nanomaterials as a Photocatalyst in Water Splitting Reaction

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Abstract: Hydrogen gas now attracts the world as a substitute for fossil fuel and, therefore, as a remedy for the current energy crisis and environmental pollution arising from that. The photocatalytic water-splitting reaction is a promising route for hydrogen production. The process is primarily constrained by the difficulty of designing an efficient photocatalyst, which must meet stringent requirements to drive water splitting. g-C_3N_4 is reported as a fascinating species exploited widely in photocatalysis as a metal-free catalyst. The use of g-C_3N_4 possesses the merits of nature-friendly response, ease of synthesis, suitable band structure with a band gap of 2.7 eV, and suitably located valence band/conduction band positions. Given the vast popularity, this chapter reviews developments in g-C3N4-based systems for photocatalytic HER. The advanced strategies for improving the photo reactivity of g-C_3N_4 are discussed. The challenges in g-C_3N_4-assisted catalysis are understood to support researchers in designing efficient catalysts with a clear understanding of the hurdles.

Keywords: Carbon nitride, Hydrogen evolution reaction, Photocatalyst, Nanocatalyst, Transition metal oxides, Water splitting process.

INTRODUCTION

Hydrogen gas has gained worldwide popularity as a viable alternative to fossil fuels. Being renewable, economically viable, and eco-friendly, hydrogen production is in high demand. Among the many hydrogen production methods, water splitting is the most attractive [1, 2]. There are various water-splitting techniques, including electrocatalytic water splitting, photocatalytic water splitting, photoelectrochemical water splitting, photobiological water splitting, steam reforming reaction, and thermal decomposition reaction [3 - 6]. Many methods require expensive inputs and unique temperature of about 2000 °C is

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required. Similarly, steam reforming is a process in the petrochemical industry and thus involves the production of greenhouse gases. Unlike other methods, photocatalytic water splitting is greener and less costly. The Photocatalytic water splitting technology came to light in 1972, after Fujishima *et al*. [7] pioneered photochemical water splitting by light irradiation using TiO_2.

In 1938, Goodeve and Kitchener discovered that TiO_2 could be used for dye decolorization in air and vacuum, but TiO_2 remains unaffected [8]. At that time, TiO_2 was not recognized as a photocatalyst but as a photosensitizer. Then, in 1972, Fujishima and Honda demonstrated photoelectrochemical water splitting on TiO_2 film under solar light irradiation [7]. The work demonstrated the photocatalytic mechanism and the generation of O_2 and H_2 on the TiO_2 and Pt films, respectively. The work attracted immediate attention worldwide. TiO_2 powder was again used by Inoue and co-workers for the photocatalytic reduction of CO_2. After that, many inorganic semiconductors, such as ZnO, $BiVO_4$, BiOBr, α-Fe_2O_3, CdS, CdSe, $ZnIn_2S_4$, Ag_3PO_4, Ta_2O_5, Cu_2O, CeO_2, WO_3, Al_2O_3, *etc*., have proven their efficiency to catalyze photolysis [9 - 15]. Subsequently, many research studies were conducted, and a wide variety of photocatalysts were discovered and developed to improve their catalytic properties. Today, photocatalysis technology is used in many fields, including contaminant degradation, CO_2 fixation, and bacterial disinfection [8].

In photocatalysis, light energy achieves water splitting on a semiconductor material. A semiconductor photocatalyst is composed of a vacant Conduction Band (CB) and a filled valence band (VB). These two are separated by a band gap (Eg). The first step in a photocatalytic process is the absorption of light. When the energy of the photon is greater than or equal to the band gap (Eg), photon absorption causes an electronic transition within the photocatalyst and generates electron-hole pairs. The electrons in the CB then migrate to the catalyst surface to participate in the reduction reaction to produce H_2. It is the holes in the valence band that drive the oxidation reaction. If the photocatalyst semiconductor has a large band gap, then the hydrogen production efficiency will be reduced. Hence, photocatalytic materials are explored to have a broad absorption range and low recombination of charges [1, 2, 5, 6].

Previously, heterogeneous photocatalysis was focused on inorganic semiconductors as catalysts and failed to explore metal-free, environment-friendly semiconductors. Wang and co-workers in 2009 discovered that graphitic carbon nitride (g-C_3N_4) can be used for photocatalytic water splitting under visible radiation [2]. Since then, research on g-C_3N_4 has attracted particular attention. The merits of g-C_3N_4 compared with other inorganic semiconductors are that it is a green, environmentally friendly compound, its synthesis is facile, and it has a

flexible band structure. It also has a suitable optical absorption range (ca. 460 nm) and appropriate band positions, making it a good semiconductor for photocatalytic water splitting and hydrogen production. Compared with other types of C_3N_4, g-C_3N_4 is the most distinguished and widely exploited in the field of photocatalysis, owing to the advantages of easy synthesis, good semiconducting properties, and high stability.

Today, studies on g-C_3N_4-based photocatalytic materials have increased significantly. In this chapter, we discuss the relevance and application of g-C_3N_4 as a photocatalyst in the water splitting process. The chapter comprises the basic theory of photocatalysis and the developments in g-C_3N_4-based photocatalysis. The advanced strategies for improving the photoactivity of g-C_3N_4 are well illustrated. The concluding section addressed the challenges associated with g-C_3N_4-mediated photocatalysis. The chapter could definitely benefit the students and academicians interested in the field.

FUNDAMENTALS OF PHOTOCATALYSIS

Since the dawn of time, humans have used fossil fuels for energy. It is now a pressing need to create renewable energy sources to lessen our reliance on fossil fuels. Hydrogen production *via* light-assisted water splitting is a viable alternative to traditional fossil fuels and can alleviate energy and environmental problems [16]. Photocatalytic water splitting is a promising approach for producing clean H_2 at a cost-effective, environmentally friendly scale [17].

A photocatalyst can be a semiconductor material that absorbs photons with energy equal to or greater than its band gap energy and produces exciton pairs, which are then separated and delivered to the target contaminant for the redox reaction [18]. A semiconductor has an electrical band structure, with a band gap separating the highest occupied energy band, the valence band (VB), and the lowest empty band, the conduction band (CB). The generation of photo-excited charge carriers is the basic mechanism behind semiconductor-based photocatalysis [16].

The overall mechanism of photocatalytic water splitting on a semiconductor photocatalyst is depicted in Fig. (**1**). Charge-carrier recombination challenges the process. In step 1, the photocatalyst absorbs photon energy greater than its band gap energy (E_{bg}) and generates photo-excited electron–hole pairs in the bulk. In the second step, the photo-excited carriers separate and migrate to the surface without recombination. Finally, adsorbed water molecules are reduced and oxidized by photogenerated electrons and holes to produce H_2 and O_2, respectively.

CHAPTER 6

Advances in g-C_3N_4-Catalyzed Synthesis of Heterocycles: Doping Strategies and Mechanistic Insights

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Abstract: Among the plethora of catalysts, graphitic carbon nitride (g-C_3N_4) has been a non-metal semiconductor having low cost, an easy preparation process, relatively good stability, a suitable electronic structure, and excellent photocatalytic performance. Applications of g-C_3N_4 as a heterogeneous catalyst have been found to promote various reactions, such as Friedel-Crafts reactions, redox reactions, C-H activation, cascade annulation, and cyclocondensation, in addition to other applications. The present work reports the synthesis of numerous heterocycles using doped g-C_3N_4 as a heterogeneous catalyst, achieving higher yields under optimal conditions, along with the coverage of their exceptional stability and reusability.

Keywords: Catalysis, Metal nanoparticles, Nanocatalysis, Graphitic carbon nitride (g-C_3N_4), Heterocycles.

INTRODUCTION

Graphitic carbon nitride (g-C_3N_4) has been recognized as the new 2-dimensional graphene analogue having five different carbon nitride structures, including α-C_3N_4, β-C_3N_4, g-C_3N_4, cubic-C_3N_4, and pseudocubic-C_3N_4, wherein g-C_3N_4 has been one of the most stable allotropes at ambient conditions [1, 2]. This highly active form of g-C_3N_4 allows a significantly large variation in its structure without a change in its overall composition. It is composed of carbon-nitrogen bonds and lacks active basicity due to the absence of an electron localized in the π state [2 - 4]. It is a medium bandgap semiconductor of ~2.7 eV [5] and expresses various properties, including chemical and thermal stability, super hardness, low friction

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coefficient, low density, high photocatalytic activity, good biocompatibility, surface modification methods, *etc.* [2, 6 - 8].

Beyond pristine forms, the functionalization of g-C_3N_4 in its monomeric and polymeric surface scaffold has further developed them as catalysts. Recently, sulfonated g-C_3N_4 (Sg-C_3N_4) was shown to be a highly active and heterogeneous organocatalyst in condensation reactions, including imidazoles and quinoxalines, with high yields and recyclable under mild and green conditions. Identifying alternative catalysts offers a new route for the synthesis of heterocycles, as well as structural analogues in sustainable catalytic systems [9].

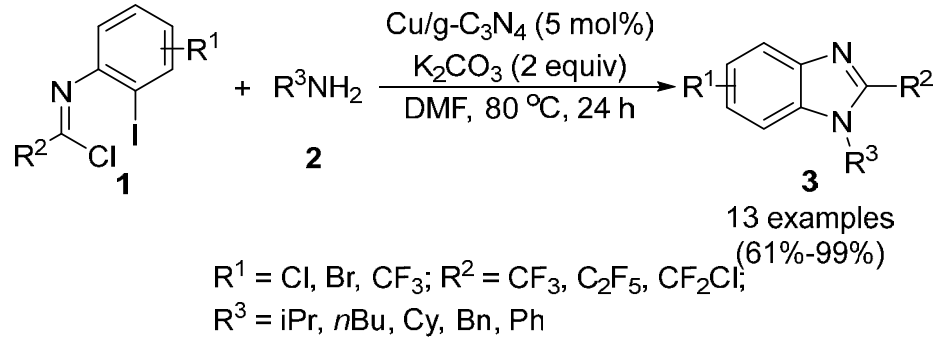
C_3N_4, such as melamine [10, 11], thiourea, urea [12], hexamethylenetetramine [13], melamine-cyanuric acid [14], and *N*-containing ionic liquids [15, 16]. Most US FDA-approved drugs also contain nitrogen- and oxygen-containing heterocycles [17]. These heterocycles have been recognized as important scaffolds that possess key pharmacophoric features relevant to biological activity against many infectious diseases [18 - 25]. The synthesis of such heterocycles has gained momentum through the effective use of greener catalysts in the field of synthetic organic transformations [26 - 28]. Recently, Vijai and his co-workers reported the use of catalysts for several organic transformations [29]. To the best of our knowledge, the present work shall be the first unleashed compilation of catalytic applications of g-C_3N_4 for the synthesis of aza- and oxa-heterocycles to offer the compelling vision to the reader of the present work.

SCOPE AND APPLICATIONS OF DOPED G-C3N4 NPS IN SYNTHESIS OF HETEROCYCLES

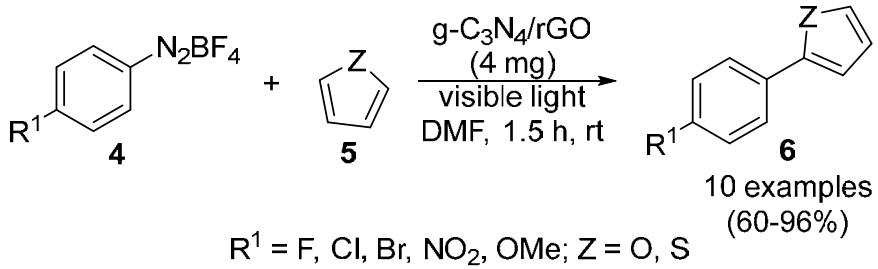
Wu *et al*. (Scheme **1**) have reported efficient synthesis of *N*-aryl trifluoroacetimidoyl chlorides (**3**) prepared from differently substituted 2-iodoanilines (**1**) reacted with *N*-aryl/alkyl/arylalkyl amines (**2**) using copper-doped g-C_3N_4 catalysts in DMF at 24 °C for 24 h in 61-98% yields [30]. The catalyst, Cu/g-C_3N_4, used could be easily recycled and catalyzed the cascade annulation reaction three times to give 69-92% yields of **3**. The heterogeneous Cu/gC_3N_4-catalysed reaction proceeded well, with the amidine intermediate obtained from 1 and 2 undergoing copper-assisted oxidative addition, followed by intramolecular nucleophilic attack by the amine to form a C-N bond and reductive elimination to yield **3**.

Cai *et al*. have reported the photocatalytic effect of C-H arylation of furan/thiophene (**5**) using aryldiazonium salts (**4**) catalyzed by g-C_3N_4/rGO nanocomposites in DMF at room temperature (Scheme **2**) [31]. Among all the aryl diazonium salts used for the direct arylation of furan, electron-acceptor (nitro) and neutral (halogen) substituted diazonium salts were found to be more efficient for

the formation of **6** as compared to electron-donor-substituted ones (methoxy). The g-C_3N_4/rGO catalysts were reused more than 5 times without a significant loss of activity, confirming their excellent stability. The single-electron transfer process of 4 formed an aryl radical, which reacted with 5 to yield a heteroaryl radical, which then transformed into a carbocation intermediate *via* radical chain transfer, ultimately yielding **6**.



Scheme 1. Cascade annulation reaction for the synthesis of 2-trifluoromethyl-benzimidazoles (**3**).



Scheme 2. Photocatalytic direct C-H arylation using g-C_3N_4/rGO-1 nanocomposites. Yields of **6** determined through GC have been provided in parentheses.

Mallick *et al*. (Scheme **3**) have reported carbon nitride-supported copper nanoparticles (Cu-*g*CN) for the *N*-arylation of various hetero aromatic systems such as indole/pyrrole/pyrazole (**7**) using different substituted aryl bromides (**8**) as the coupling partners to yield **9** in the range of 75-92% [32]. The sequential drying of urea in a Muffle furnace, followed by the addition of CuSO4 · 5H2O and reduction of the copper salt to Cu(0) using $NaBH_4$, yielded final catalysts, which were later characterized using Transmission Electron Microscopy (TEM) and X-ray Diffraction (XRD) techniques. The present protocol was also reported to be successful for the C-N cross-coupling of benzamide with aryl bromides. At the end of each cycle, the catalyst was recovered and reused for the next cycle, up to 6 reuses, with more than 80% yields of **9**. The copper-catalyzed coupling reaction proceeded *via* oxidative addition of **8** with the catalyst, transmetalation of

CHAPTER 7

Doped Graphitic Carbon Nitride-based Photocatalytic Reactions

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Abstract: Graphitic carbon nitride (g-C_3N_4), an organic semiconductor without a metal atom, is gaining popularity as a photocatalyst worldwide. The g-C_3N_4 is an intermediate band gap (2.7 eV) material with the absorption of blue light at 450 nm. This acceptable band gap, along with its chemical and thermal durability, makes it ideal for photochemistry and photocatalysis applications. This chapter discusses recent trends in developing competent, affordable doped g-C_3N_4 systems across a range of applications, including light-catalysed hydrogen evolution, carbon dioxide reduction, and photocatalytic pollutant elimination from various sources.

Keywords: Absorbance, Composite, Degradation, Doping, Heterojunction, Hydrothermal method, Metals, Nanosheet, Non-metal, Oxygen radical, Photocatalyst, Pollutant, Quantum yield, Semiconductor, Stability, Tunable emission.

INTRODUCTION

Green chemistry seeks to minimise pollution at its source by designing chemical processes with a low environmental impact. Improvements in catalyst performance are essential for optimising existing chemical processes and developing new, environmentally friendly strategies. As a result, photocatalysis has a significant impact on the advancement of modern sustainable chemistry [1 - 7]. Photocatalysis based on semiconductors has been hailed as a renewable, cost-effective, safe, and environmentally friendly technology for several uses, including splitting of water [8 - 12], reduction of CO_2 [13 - 17], organic pollutant removal [18 - 26], bacteria disinfection [27 - 29], and synthesis of particular organic compounds [30 - 33]. However, the low solar-energy utilisation efficiency, the low band-gap utilisation efficiency, and broad band gap of the

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photocatalysts remain a roadblock in meeting the demands of practical applications. Two-dimensional (2D) nanomaterials such as graphene, graphitic carbon nitride (g-C_3N_4), and boron nitride have found various applications recently, including electronic devices, optical sensors, chemical sensors, energy production, energy storage, and pollutant removal *etc.* [34, 35]. Carbon nitrides (C.N.) are semiconductors with metal-free organic polymeric chains that have recently received significant attention as light-based photocatalysts for water splitting and as heterogeneous catalysts for Friedel-Crafts-type reactions, cyclisation of functional nitriles, and so on. A new allotrope in the carbon nitride family, Graphitic carbon nitride (g-C_3N_4), has recently been shown to be a viable contender for a wide range of applications due to the availability of precursor materials, cost-effectiveness, simple fabrication, and excellent stability [36 - 40]. Several methods are available to improve the photocatalytic activity of g-C_3N_4, including doping with other elements and molecules [41, 42], mesoporous g-C_3N_4 [43], 2D nanosheet formation [44], binary composite with conductors [45, 46], nanocomposite structure construction with other semiconductors [47], and sensitisation with dyes [48].

It is well known worldwide that g-C3N4 has an adjustable band gap, with a configurable Lowest Unoccupied Molecular Orbital (LUMO) and a Highest Occupied Molecular Orbital (HOMO). The adjustable band gap of g-C_3N_4 facilitates the amendment procedure, primarily by doping or heterojunction structure creation [49]. Doping is an efficient way of tuning the band gap of g-C_3N_4, and the interstitial or substitutional doping of g-C_3N_4 with P, S, I, or B has been used to change its texture and electronic structure [50 - 54]. Alkali transitional metals such as K, Cu, Na, Fe, and W have also been added to the g-C_3N_4 to improve photocatalytic activity [55 - 59].

Nowadays, the field of element-doped g-C_3N_4 photocatalyst research and development has witnessed exciting growth with rising successes [60 - 62]. An illustration of different g-C_3N_4-based photocatalytic systems is shown in Fig. (**1**). In this chapter, we outline current developments in implementing effective, cost-effective doped g-C_3N_4 systems across diverse fields. In addition, the present obstacles and critical concerns of doped g-C_3N_4 photocatalysts that require further investigation are also briefly discussed.

Classification of Doped Graphitic Carbon Nitride

Metal Doped

In general, the insertion of a metal atom creates additional binding sites, endowing the modified system with unique light-catalytic capabilities by reducing the band gap and increasing visible-light absorption. To incorporate metals into

the carbon nitride framework, the relevant soluble salt is always added evenly with g-C_3N_4. For the thermal condensation, the metal particle will be doped into the g-C_3N_4 at the same time [55, 56, 63, 64]. Metal doping effectively increases light-harvesting efficiency, reduces the band gap, accelerates charge-carrier mobility, and extends the excited-state lifetime.

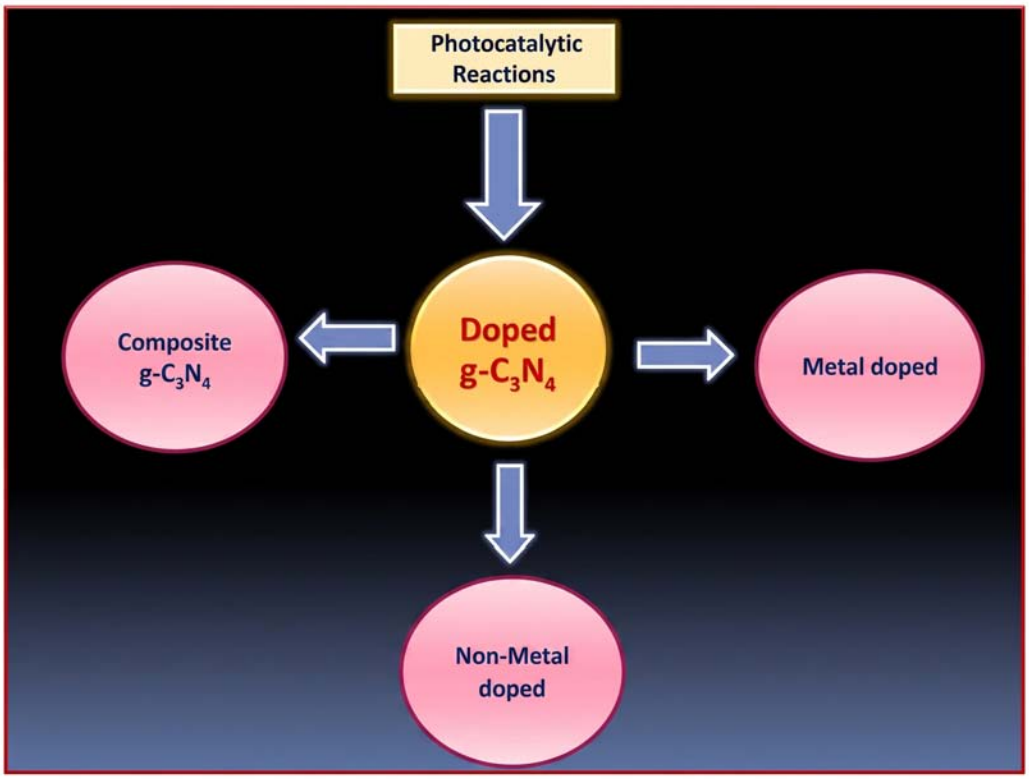

Fig. (1). The schematic representation of various g-C_3N_4-based systems.

Species such as K^+ and Na^+ were bound with the nitrogen atom of the g-C_3N_4, which considerably improves charge carrier movement and separation power to improve the properties of the photocatalyst [55, 65]. Hu and his team created the band gap altered potassium-doped g-C_3N_4 from a mixture of dicyandiamide and potassium hydrate [59]. The K ion may be attached to the carbon-nitrogen rings during the reaction. Interestingly, they discovered that by varying the K concentration, the C.B. and V.B. potentials of g-C_3N_4 could be modified, as depicted in Fig. (**2a**). Interestingly, they found that by varying the K concentration, the C.B. and V.B. potentials of g-C_3N_4 could be modified, which is depicted in Fig. (**2b**). As a result, both • O.H. and •O_2^- might be produced, resulting in a substantially greater photodegradation rate. Simultaneously, Zhang

CHAPTER 8

Photocatalysis in Organic Reactions Using Doped g-C_3N_4

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Abstract: To address emerging energy and environmental issues, polymeric graphitic carbon nitride (g-C_3N_4) photoredox catalysts have been developed as the most promising and attractive photocatalysts in photoredox reaction applications because of their excellent chemical stability, long service lifecycle, cost-effectiveness, and high surface area. Despite obvious accomplishments in the arena of photocatalysis, the most significant limitation of g-C_3N_4 is its high gap between the conduction band and valence band, fast charge recombination, and low charge carrier mobility, which makes it scarcely possible to initiate photocatalytic development. In this regard, the chapter presents g-C_3N_4 frameworks for photocatalytic reactions that are upgradeable *via* doping (*i.e.,* metal, non-metal, and molecular), facilitating applications of sustainable photocatalysts in CO_2 reduction, oxidation, bond-forming reactions, and reduction reactions. Hopefully, this chapter will motivate the advancement of practical and innovative photoredox catalysts and stimulate the essential knowledge base for additional developments in sustainable photoredox catalytic nanotechnologies.

Keywords: Chemical synthesis , Doped g-C_3N_4, Photocatalyst, Organic reactions, Visible light.

INTRODUCTION

Visible-light-driven catalysis has revolutionized within the synthetic community, with tremendous accomplishments made throughout the past several decades, such as in biological sectors [1], chemical synthesis [2], energy [3], nanotechnology [4], *etc*. Photocatalysis is the most interesting and favourable technique that targets to deliver a green and sustainable approach for addressing global energy and environmental difficulties [5]. Heterogeneous photocatalysis

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has been widely applied in various fields, including organic transformations [6], CO_2 reduction [7], oxidation reactions [8], water splitting [9], and environmental remediation [10].

Heterogeneous photocatalysts play a crucial role in functional group transformation, using light as a driving force with quantum efficiency. Since few decades, several accessible photocatalyst materials such as TiO_2 [11], ZnS [12], ZnO [13], CdS [14], $SrTiO_3$ [15], SrO_2 [16], Cu_2O [17] and their nano series structured materials have been generally engaged as photocatalysts to direct the transformation of photon energy into chemical energy through diverse photocatalytic reactions. In these photocatalysts, the large bandgap (TiO_2, 3.2 eV; SrO_2, 3.68 eV), low surface area, and optical and physicochemical properties restrict the consumption of a wide range of solar light, catalytic activities, and selectivity. A range of modification approaches [18], particularly doping methods, are being used to enhance the photocatalytic efficiency (up to 43% of the light) and surface sensitization and introduce defects. Up to now, no photocatalyst material is available that can achieve all necessities like stability, cost-effectiveness, high quantum efficiency of visible light, and safety [19]. Therefore, to deal with these challenges, it will be advantageous to explore new visible-light photocatalyst materials for organic transformations with high selectivity.

Recent years have witnessed growing attention toward the use of carbon-based materials as heterogeneous photocatalysts for a wide range of applications [20]. Alternatively, polymeric graphitic carbon nitride (g-C_3N_4), a variety of photocatalysts that contain graphite-like layered arrangement [21], have fascinated a lot of curiosity, Fig. (**1**) due to their extraordinary properties, physicochemical [22], structural [23], optical [24], and unique electric properties [25], which make g-C_3N_4 based raw substance a novel kind of multifarious nanoplatforms for photocatalytic [26] and optoelectronic significance [27]. These applications are accessible due to their cheap availability [28] (easily prepared by the condensation methods with the help of non-precious raw substances such as urea, triazine derivatives, ethylenediamine, dicyandiamide, melamine, thiourea *etc*.), controllable bandgaps (~2.7 eV), eco-compatibility nature, suitable band positions {-1.3 eV at the bottom of the CB (conduction band) and 1.4 eV at the top of the VB (valence band) with respect to SHE (Standard hydrogen electrode)}, good chemical stability, tailorable textures and without any heavy metal pollution [29]. Therefore, g-C_3N_4 nanosheets are developing as a model material for the variation of solar energy and conservational photocatalytic importance, much as organic transformations, supercapacitors, electrocatalysis, degradation of pollutants, batteries, water reduction, carbon dioxide reduction, solar cells, oxidation, bioimaging, fluorescence sensors, *etc* [30].

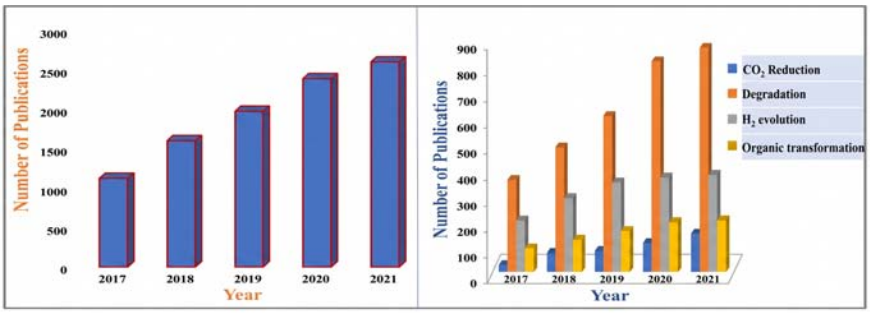

Fig. (1). (a) The yearly publications of "carbon graphitic nitride" since 2017. (b) The yearly publications for CO_2 reduction, H_2 evolution, dye degradation, and organic transformations using g-C_3N_4 catalyst (Using SciFinder Web).

Although, g-C_3N_4 exhibits high stability and durability (because of the existence of the tri-s-triazine ring and depends on variant packing and several degree condensations) [31], strong photoluminescence (visible region, 430-550 nm) [32], heterogeneous nature (due to the Waals interactions between the layers) [33], best light harvesting (strongly reliant on the surface morphology and structure) [34] and easily charge excitation (related with its unique electronic structures) [35], still numerous research scientists are shifting towards the modification of g-C_3N_4 *via* structures/properties, by the implementation of foreign substances, construction of the heterojunction, and nanostructures, hereby improving the photocatalytic activity Fig. (**2**).

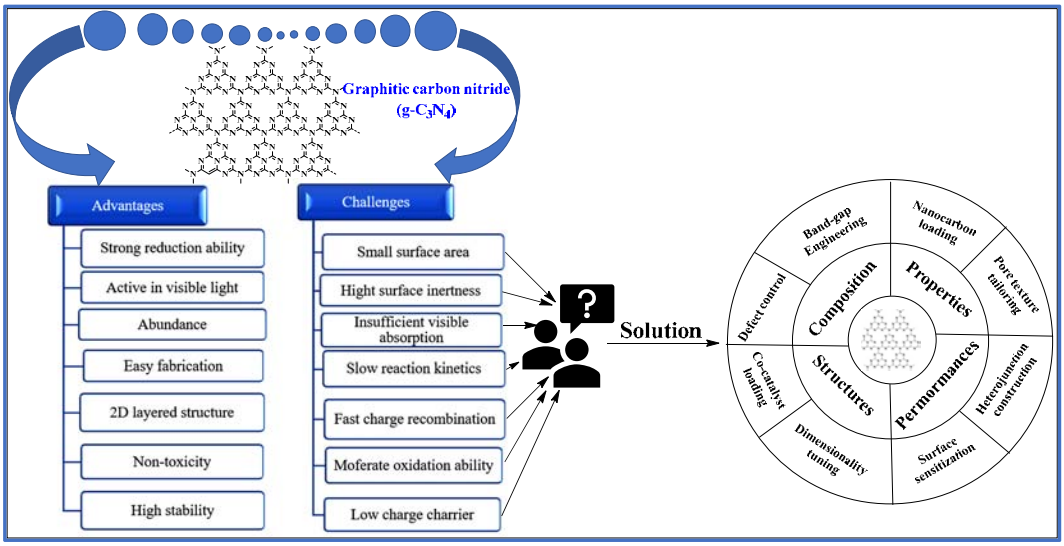

Fig. (2). Intrinsic properties of g-C_3N_4 (graphitic carbon nitride) and their photocatalytic stages.

CHAPTER 9

Metal Nanoparticles Decorated Carbon-Nitride Based Nanomaterials for Electrochemical Sensing of Environmental Pollutants

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Abstract: The graphitic carbon nitride (g-C_3N_4) nanomaterials decorated with metals have enhanced electron transfer between the material surface and the surroundings. As a result of these mobile and accessible electrons, the materials can be used as sensors for environmental pollutants. The enhanced redox reaction against a given analyte at the interface of the nanomaterial and electrolyte enhances the detection ability of the material for small concentrations of analyte. The longer linear range of analyte concentration with the electrochemical response of metal-decorated g-C_3N_4 nanomaterials provides insight into the applicability of the as-prepared sensors in different levels of analyte concentration. These sensors could be applicable to real samples containing interfering species. The high selectivity of the as-prepared sensor can confirm this. Bulk and thin films of g-C_3N_4 have been prepared from nitrogen-rich precursors by using thermal condensation and chemical vapor deposition methods, respectively. Metallic NPs decorated g-C_3N_4 have been synthesized by photo-assisted technique, photo-deposition methods, thermal polycondensation, pyrolysis methods, heat treatment, and heating methods. The morphological, optical, physical, and chemical properties of g-C_3N_4 have been tuned by metal incorporation.

Keywords: Catalytic, Decorated g-C_3N_4, Environmental pollutants, Metals, Peak currents.

INTRODUCTION

Recently, researchers and industry have been fascinated by graphitic carbon nitride (g-C_3N_4), a two-dimensional conjugated polymer with outstanding analytical properties, including low-cost synthesis, excellent durability, distinct electronic properties, catalytic activity, high quantum efficiency, low toxicity, metal-free nature, a narrow band gap, and electron-rich properties. It is the most

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stable allotrope of carbon nitrides. It has been used in a variety of fields, including energy storage [1, 2], electrocatalysis [3, 4], heavy metals detection [5], pesticide detection [6], photocatalysis [7, 8], photoelectrocatalysis [9], and sensing applications [9, 10]. Furthermore, a g-C_3N_4 nanostructure plays a vital role in the growth of g-C_3N_4-based materials in electrochemical sensor applications [11]. The modified electrode materials can easily interact with chemical and biological analytes and can control the functional moieties, resulting in highly selective and sensitive sensing with a low limit of detection due to their impressive electrocatalytic activity and conductivity [12].

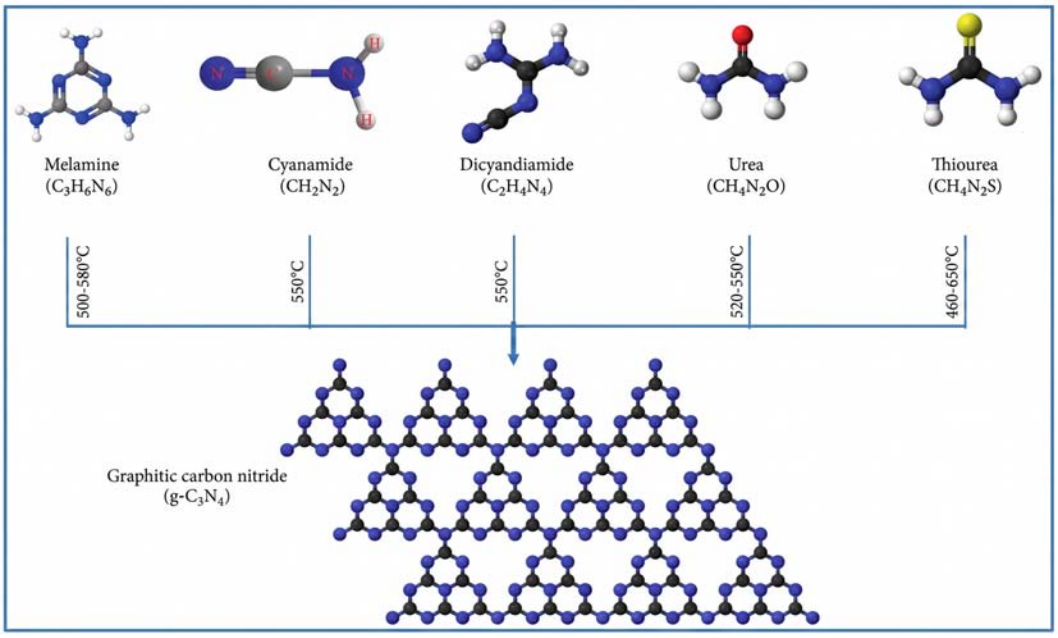
However, the quality of g-C_3N_4 nanostructures, including thickness and/or size, surface area, electronic structure, and bandgap, still needs to be significantly improved to achieve the required electrocatalytic activity. To fix this, several metallic NPs have been incorporated into a g-C_3N_4 matrix. The hybrid of a noble metal and a g-C3N4 nanostructure has been employed as an outstanding electrocatalyst because noble metal NPs can serve as effective electron mediators, exhibiting enhanced localized surface plasmon resonance [13]. Furthermore, metal NPs possess unique properties, including a high surface area, improved stability, good conductivity, and the ability to act as an electron-conducting channel in electrochemical sensors, thereby improving direct electron transfer [14]. For example, copper (Cu) NPs are well-known for their significant electrocatalytic activity, low cost, low toxicity, high stability, and reasonable conductivity, suggesting that mixing Cu with g-C3N4 could improve the sensitivity of the proposed sensors [12].

Well-defined g-C3N4 nanostructures have been generally fabricated from various nitrogen-rich precursors, such as melamine [15], urea [16], thiourea [17], dicyandiamide [18], and cyanamide [19], and applied for the electrochemical detection of different analytes with outstanding detection limits [12]. In addition, metallic NPs doped g-C_3N_4 nanomaterials could be easily developed from the above-mentioned precursors in the presence of metallic salts by employing photo-assisted technique and/or photo-deposition methods, pyrolysis process, thermal polycondensation technique, and heat treatment methods [20, 23].

The development of electrochemical sensors based on metal NPs coated g-C_3N_4 with various electroanalytical methods for environmental pollution monitoring applications is the subject of this chapter. This chapter also discusses how metal-doped g-C_3N_4 modified electrode sensors have been used to detect explosives, hazardous substances, heavy metals, inorganic anions, and phenolic compounds. In addition, the electrocatalytic activity of the above-mentioned based nanomaterial in real samples has been investigated.

SYNTHESIS OF METALLIC NPS DOPED G-C_3N_4

A g-C_3N_4 has been widely synthesized by using thermal condensation techniques and chemical vapor deposition methods. The thermal condensation technique is the most common method used to prepare a bulk g-C_3N_4 on a large scale by heating carbon and nitrogen-rich precursors such as thiourea (CH_4N_2S) [24], melamine ($C_3H_6N_6$) [25], cyanamide (CH_2N_2) and dicyandiamide ($C_2H_4N_4$) [8], and urea (CH_4N_2O) [26] (see Scheme **1**). Exfoliation of bulk g-C3N4 yields single- or multilayered nanosheets with large active surfaces [27].



Scheme 1. Thermochemical condensation of several precursors to produce g-C_3N_4 [28].

In another case, chemical vapor deposition has been widely used to make g-C_3N_4 films from carbon- and nitrogen-rich precursors are introduced into an Ar gas stream flowing through a quartz tube at low pressure. Due to the low vacuum inside the quartz tube and the passage of Ar gas, powder vapors permeate the warm region of the furnace (600 °C). The g-C_3N_4 is produced by heating the precursor to high temperatures. In an Ar atmosphere, the furnace should be allowed to cool to ambient temperature after deposition [29]. Similarly, after the dissociation of reactive gas molecules in a plasma, plasma-enhanced chemical vapor deposition enables the deposition of thin layers of g-C_3N_4 on various substrates (glass, Si, *etc*.).

CHAPTER 10

Photocatalytic Applications of Carbon Nitride-Based Nanomaterials in Oxygen Reduction Reaction

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Abstract: The future energy crisis and environmental problems can only be diminished by harvesting solar light into safe, economical, renewable, and clean technology. Carbon nitride-based nanomaterials are an alluring class of nanomaterials useful for different applications. The oxygen reduction reaction plays a crucial role in advancing clean energy conversion processes like fuel cells and metal-air batteries. Due to low cost and good durability, carbon-based nanomaterials are promising materials for Oxygen Reduction Reactions (ORR). Graphitic carbon nitride ($g\text{-}C_3N_4$) has emerged as an attractive photocatalyst, attributed to its unique electronic properties, high physicochemical stability, and metal-free framework. For an efficient photocatalytic oxygen reduction reaction, modifying $g\text{-}C_3N_4$ through doping or the preparation of composite/hybrid materials is very important. This chapter discusses the potential photocatalytic applications of various $g\text{-}C_3N_4$-based nanoparticles, along with their mechanisms for the photocatalytic oxygen reduction reaction. We also summarize the current advances and future developments of various modification strategies for $g\text{-}C_3N_4$-based nanoparticles and the effects of these modifications on oxygen reduction reactions.

Keywords: Band gap, $g\text{-}C_3N_4$, photocatalysis, H_2O_2 production, Oxygen reduction.

INTRODUCTION

Graphitic carbon nitrides ($g\text{-}C_3N_4$) possess unique graphite-like structures, and the composites of $g\text{-}C_3N_4$ are useful in a variety of applications. These are metal-free, have favourable band gaps, and show high thermal and photostability. The advantages of using this material in various catalytic processes include its non-toxic behaviour, chemical inertness, good biocompatibility, and mechanical properties. A simple method for preparing $g\text{-}C_3N_4$ involves the thermal treatment

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of suitable carbon-based precursors containing nitrogen, such as cyanamide, dicyanamide, thiourea, urea, and melamine [1]. In recent times, g-C_3N_4 has been widely used as a visible light-responsive photocatalyst. g-C_3N_4 possesses a relatively narrow band gap of about 2.7 eV, making it suitable for absorbing visible light from the solar spectrum. Due to its low surface area, the photocatalytic activity of g-C_3N_4 is not optimal when used alone. The fast recombination of photogenerated electron-hole pairs is the main drawback here. Therefore, different strategies have been developed to improve the photocatalytic performance of g-C_3N_4. Doping of metals, such as rare-earth, alkali, and noble metals, with g-C_3N_4 is a popular strategy to slow recombination, modulate the band gap as required, and enhance the catalyst's surface properties. During metal doping, metal ions are incorporated into the graphitic carbon nitride structure, where the lone-pair electrons on nitrogen atoms form strong interactions with the positively charged metal cations, facilitating their effective immobilization [2]. Another strategy for tuning the structure and increasing the efficiency of g-C_3N_4 includes nonmetal doping, wherein the non-metal replaces the carbon and nitrogen atoms of g-C_3N_4 [3]. The formation of heterojunctions and homojunctions, as well as nanostructured quantum dots, rods, tubes, wires, and sheets, is another common modification strategy to boost the photocatalytic efficiency of g-C_3N_4 [2, 3]. Separating the stacked layers of bulk g-C_3N_4 using techniques such as sonication, thermal exfoliation, and liquid ultrasonic exfoliation also increases charge separation efficiency, electron transport, and specific surface area [1, 4]. Converting bulk g-C_3N_4 into two-dimensional nanosheets increases the exposure of active sites, thereby enhancing its catalytic potential [5, 6].

g-C_3N_4 is used in a number of photocatalytic applications, including oxygen and carbon dioxide reduction, oxygen and hydrogen generation, and degradation of organic pollutants. In addition to these photocatalytic applications, g-C_3N_4 and its derivatives are efficient candidates for catalysis, electrocatalysis, templating, sensing, and bioimaging [7]. The Oxygen Reduction Reaction (ORR) is a multielectron process. There are three main pathways in this reaction, and the multielectron ORR consists of many complex steps [8]. The various possible pathways are:

- 4 e^- reduction of O_2 to H_2O in acidic condition:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad \textbf{(1)}$$

- 2 e^- reduction of O_2 to H_2O_2

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad \textbf{(2)}$$

Followed by the formation of H_2O

$$H_2O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad \textbf{(3)}$$

- Single e^- superoxide pathways for H_2O_2 formation

$$O_2 + H^+ + e^- \rightarrow HO_2^{\cdot} \quad \textbf{(4)}$$

$$HO_2^{\cdot} + H^+ + e^- \rightarrow H_2O_2 \quad \textbf{(5)}$$

Followed by equation (3).

The photocatalytic Oxygen Reduction Reaction (ORR) utilizes sunlight as the energy input and O_2 and H_2O as the main building blocks for the production of H_2O_2 [9, 10]. The oxygen reduction ability of the photocatalysts is determined by their unique structure and the position of their conduction band. The Conduction Band (CB) energy level of graphitic carbon nitride is more negative (-1.3 V) as compared to the single electron Oxygen Reduction Reaction (ORR), and hence the electrons present in this CB tend to be captured by O_2 to produce superoxide, which finally helps in the production of H_2O_2 [11]. Polymeric carbon nitride structures have been utilized for H_2O_2 synthesis in a safe, economic, and environmentally friendly manner [8, 12]. The electron-deficient aromatic diimides containing g-C_3N_4 have also served as an efficient photocatalyst for the preparation of H_2O_2 [13]. A study reveals that g-C_3N_4, grafted with cationic Polyethylenimine (PEI) molecules, served as an exceedingly effective photocatalyst for the synthesis of H_2O_2 due to increased intermolecular charge separation and high selectivity for the two-electron reduction of O_2 [14]. By loading active noble metals such as Pd and Pt onto g-C_3N_4, the photoinduced charge separation can be increased, and the O_2 binding mode on the g-C_3N_4 surface can also be modified [15, 16]. The oxygen reduction reaction is also a key process in fuel cell technology, which offers high efficiency and potential for large-scale application, making it a strong candidate to replace conventional energy sources [17].

In this chapter, the role of g-C_3N_4 and its different modifications in altering photocatalytic activity is described, along with its applications in the Oxygen Reduction Reaction (ORR) and related mechanisms. Moreover, some additional applications, such as photocatalytic CO_2 reduction and photocatalytic oxidation, are discussed at the end.

CHAPTER 11

Carbon-Nitride Polymer-Based Nanomaterials as Electrocatalysts in Sensors

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Abstract: The existence of various pollutants like antibiotics, heavy metal ions, phenolic compounds, biomolecules, pesticides, foodborne pathogens, *etc*., is a serious risk to human health and the environment. Electrochemical sensing is a powerful analytical method for detecting pollutants due to its excellent sensitivity and selectivity. Polymeric carbon nitrides (C_3N_4) are promising materials for electrochemical sensing due to their good physicochemical stability, relatively high specific surface area, and unique electroluminescent and photoelectrochemical properties. Cyclic Voltammetry (CV), Differential Pulse Voltammetry (DPV), impedance, amperometry, and Square Wave Voltammetry (SWV) are different electrochemical techniques used to monitor pollutants in real samples with excellent detection limits. This chapter provides a detailed account of polymeric carbon nitride-based electrochemical sensors for detecting various pollutants in real samples.

Keywords: Analyte, Anions, Antibiotics, Aromatic nitro compounds, Biomolecules, Carbon nitride, Electrocatalyst, Electrochemiluminescence, Electrode, Electrochemical sensor.

INTRODUCTION

Graphitic carbon nitrides (g-C_3N_4) are 2D materials with a structure similar to that of graphite. They have emerged as ideal catalysts, photoelectrochemical sensors, biosensors, and bioimaging agents, as they are inexpensive, non-metallic semiconductors with an appropriate bandgap [1, 2]. They are analogous to graphite structures with excellent properties, containing C-N bonds instead of C-C bonds [3]. Due to easy synthesis and excellent stability, it also has a wide range of applications in photo and electro-catalysis and sensing. There are various synthe-

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tic pathways, including Chemical Vapour Deposition (CVD) [4 - 6], pyrolysis of carbon molecules [7 - 9], hydrothermal method, *etc* [10 - 12], to fabricate g-C_3N_4 nanoparticles. The non-metallic elements, such as nitrogen, sulphur or oxygen atoms, can be incorporated into carbon sources by co-polymerisation from a heteroatom-containing molecule at high temperatures or by direct thermal calcination of (bio)molecules, such as amino acids and ionic liquids [13 - 15]. Among these, the most frequently reported method is nitrogen insertion into a carbonaceous matrix because it gives straightforward synthetic pathways. For fabricating g-C_3N_4, various nitrogen-containing starting materials such as thiourea [16], dicyandiamide [17], cyanamide [18], and melamine [19] are frequently used.

Many studies have reported the direct use of g-C_3N_4-based systems for electrochemical sensing applications, utilizing physicochemical properties such as surface area, porosity, absorption, bandgap, and photoluminescence of the developed system, depending upon the types of precursors and treatments used in the studies [20]. In addition to the catalytic activity and conductivity, the nature of interaction and electrocatalytic behaviour of the electrode material also have a vital role in both sensitivity and selectivity of the developed system towards several molecules with excellent linear range and Limit of Detection (LOD) values [21].

Several traditional techniques, such as calorimetric analysis and spectroscopic methods, are readily available to detect and analyse blood samples, serum samples, water samples, and food samples. However, these techniques require sophisticated instruments, well-trained lab personnel, and complex sample preparation, limiting their practical applicability. There is a chance of false-positive detection due to interference from other chemicals or biomolecules in the system [22]. As a solution to these problems, g-C_3N_4-based electrochemical sensors are developed as miniaturised devices for use in environmental and healthcare sectors [23, 24]. The detection mechanism involves the selective and sensitive conversion of the chemical/biochemical signals of the analyte to an electrical signal by the electrochemical sensor/ biosensor [25]. Cyclic Voltammetry (CV), Square Wave Voltammetry (SWV), amperometry, Differential Pulse Voltammetry (DPV), and impedimetric techniques are important electroanalytical techniques widely used for detection purposes. The modified g-C_3N_4 system can interact with the analytes using electrostatic interaction of electroactive species or covalent linkage of bio-receptor to the transducer through the large molecules containing the C 1s and N 1s atoms. Some works reported the formation of a quarantine arrangement of g-C_3N_4 sheets through a π-π^* interaction while detecting molecules with aromatic and phenolic structures [26].

The electrochemical signal produced by the g-C_3N_4 coupled electrochemical system was enhanced in the presence of an analyte due to the electrode kinetics, improved catalytic properties, and electrodes with a high electrochemically active surface area [27]. Effective interaction between the chemical or biological analytes and the g-C_3N_4 modified system allows the detection process with excellent selectivity and sensitivity [28]. The properties such as low cost, low toxicity, and metal-free polymeric material allow the direct use of g-C_3N_4-based systems in biosensing applications [29].

This book chapter primarily discusses various g-C_3N_4-based electrochemical and biosensors for detecting molecules in living systems and hazardous materials to the environment and human health. The discussion includes the identification of an analyte, such as hazardous chemicals, heavy metal ions, inorganic anions, phenolic substances, aromatic nitro compounds, biomolecules, neurotransmitters, pesticides, and foodborne pathogens. In addition, the efficiency of the developed electrochemical sensor for detecting chemical and biomolecules in real sample analysis, challenges, and future perspectives in g-C_3N_4-based systems have also been discussed. A graphical abstract for g-C_3N_4-based biosensors, electrochemical sensors, and for healthcare and environmental applications is illustrated in Fig. (**1**).

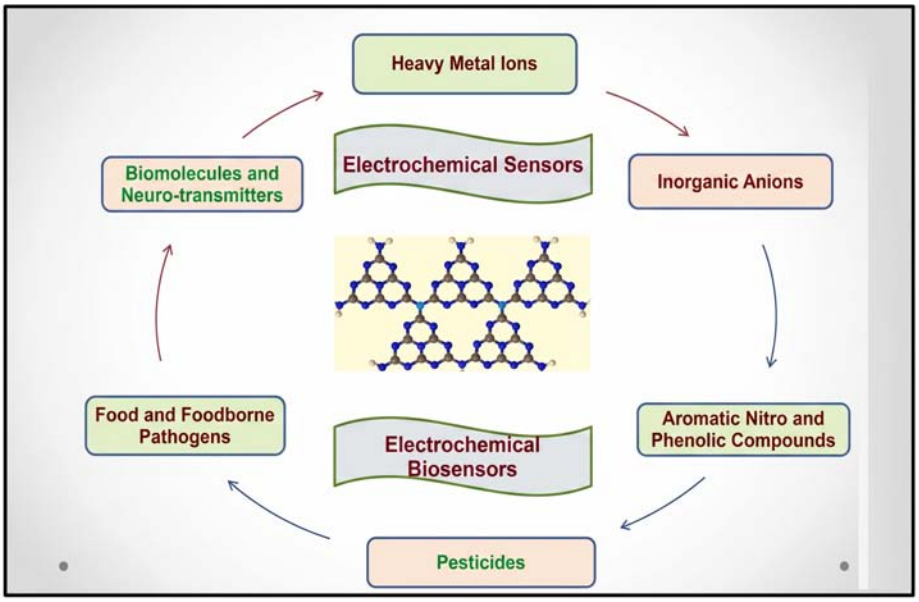

Fig. (1). A schematic representation of g-C_3N_4-based bio and electrochemical sensors for healthcare and environmental applications.

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