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Chapter

Graphite Carbon Nitride

Yamuna Ezhumalai, Prabakaran Kumaresan and Tirupathy Jayapalan

Abstract

Graphitic carbon nitride $(g-C_3N_4)$, is a synthetic polymer made up of carbon, nitrogen, and some impurity hydrogen that is linked together using tris-triazine-based patterns. Because of the inclusion of N and H atoms, it has electron-rich characteristics, basic surface functions, and H-bonding motifs, compared to the bulk of carbon materials. Consequently, it's seen as a possible replacement for carbon in material applications. A brief introduction to $g-C_3N_4$ is included in this chapter, as are the methods for synthesizing this material with various textural structures and surface morphologies, as well as its physicochemical properties. Furthermore, four parts of $g-C_3N_4$ applications are discussed. We anticipate that this work will motivate readers to look for new applications for this material in catalysis and other domains.

Keywords: metal-free catalyst, functional material, graphitic carbon nitride, synthesis, applications

1. Introduction

Carbon nitrides are a type of a polymeric substance that is mostly made up of carbon and nitrogen [1, 2]. They may be prepared from carbon materials by replacing carbon atoms with nitrogen atoms, making them intriguing possibilities for a range of uses. Due to the chemical inertness of carbon nitride, solubility problem in acidic, neutral, and basic solvents. Hence, the structure of the material was not completely appreciated until recent decades [3]. Because of the presence of basic surface sites, graphitic carbon nitride ($g-C_3N_4$) is not only the most stable allotrope of carbon nitrides in the ambient atmosphere, but it also exhibits rich surface characteristics that are appealing for various applications, including catalysis [4]. In the state (this material is a -conjugated polymer), the ideal $g-C_3N_4$ consists only of an assembly of CN bonds with no electron localization [5, 6].

As shown in **Figure 1**, real materials, such as those made by polycondensation of cyanamide, contain a minor amount of hydrogen, which is present as primary and/or secondary amine groups on the terminal edges. The presence of hydrogen indicates that the real $g-C_3N_4$ is incompletely condensed and that a number of surface defects exist, which can be useful in catalysis and are thought to promote electron relocalization on the surface, inducing Lewis-base character toward metal-free coordination chemistry and catalysis.

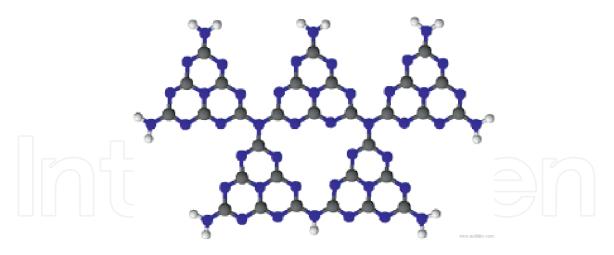


Figure 1. Multiple surface functionalities reproduced from [7] with permission from the Royal Society of Chemistry.

The energy positions of the conduction band (CB) and valence band (VB) versus the normal hydrogen electrode (NHE) are -1.1 and 1.6 eV, respectively, in g-C₃N₄ (2.7 eV bandgap). Furthermore, g-C₃N₄ is extremely resistant to heat, strong acids, and strong alkaline solutions. The only elements in g-C₃N₄ are carbon and nitrogen, and it can be made by pyrolyzing nitrogen-rich precursors such as melamine, urea, thiourea, and cyanamide. It has been observed that the choice of precursor and pyrolysis temperatures have a significant impact on the electrical structure and bandgap of g-C₃N₄, which will have implications for its prospective uses in a variety of disciplines.

Recently, tremendous progress has been made in the field of $g-C_3N_4$ research. As a result, a paper summarizing the synthesis of $g-C_3N_4$ -based materials and their prospective energy storage applications is required. The characteristics, production, and possible applications of $g-C_3N_4$ and $g-C_3N_4$ -based nanocomposites in energy storage and conversion, such as photocatalytic hydrogen evolution, oxygen reduction reaction (ORR), and Li-based battery, are discussed in this book chapter.

2. Synthesis of g-C3N4 materials

It is a stable polymer semiconductor with only C and N components. Many nitrogen-rich organic precursors are now utilized to make $g-C_3N_4$, including urea, melamine, dicyandiamide, thiourea, and cyanamide. Carbon nitride materials made from direct condensation of these precursors, on the other hand, have bulk structures with low specific surface areas. It's required to introduce well-controlled porous structures in bulk $g-C_3N_4$ for practical usage as catalysts. Several strategies for obtaining porous $g-C_3N_4$ have been devised by scientists.

2.1 Synthesis of g-C3N4 materials

2.1.1 Template method

Under the structural inversion, "templating" entails the copying of one structure into another. In its broadest sense, a template is a structure-directing agent. Because the size and shape of the resulting pore structures may be easily controlled by the

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proper template, the template method is a versatile methodology for the fabrication of nanostructured or porous materials. In $g-C_3N_4$, hard templates [7] are employed to build porous materials and create hierarchical pore topologies. To regulate nanostructures, silica templates are commonly utilized as a structure directing agent. Groenewolt et al. used multiple pore size mesoporous silica matrices to synthesize unique g-C3N4 nanoparticles of different sizes. Many studies on mesoporous g-C₃N₄ materials made with silica-based hard templates have been published since then. Using aminoguanidine hydrochloride as a precursor and SBA-15 as rigid templates, highly ordered mesoporous g-C₃N₄ with variable pore sizes was produced. To make ordered porous $g-C_3N_4$, Fukasawa et al. employed uniform-sized silica nanospheres as templates. Using guanidinium chloride as a precursor used a nanocasting process to make mesoporous $g-C_3N_4$. Two types of pores and high specific surface areas were found in the as-prepared g-C₃N₄ samples. Park et al. used the incipient wetness method to create 2-dimensional (2D) and 3-dimensional (3D) mesostructured g-C₃N₄ using mesoporous silica as a hard template. Open pores and a large specific surface area characterize these materials. The hard-template technique, in particular, necessitates the removal of the template in order to get the requisite g-C₃N₄ structure. This procedure typically uses aqueous NH4HF2 or HF, which can harm the environment (Figure 2).

2.1.2 Template-free method

A simple thermal treatment of dicyandiamide is used to make porous g-C₃N₄. The synthesized porous g-C₃N₄ has a large pore volume and a high BET surface area $(0.50-0.52 \text{ m3 g}^{-1})$. A simple template-free technique to make g-C₃N₄ nanofibers (GCNNFs). Melamine was first reacted with ethanol, then annealed at 450°C for 2 hours to produce GCNNFs, which had a 1D structure and a large specific surface area. Thermal calcinations were also used to make graphene-modified porous g-C₃N₄ (porous g-C₃N₄/graphene). The polymerization process was carried out at various temperatures in this approach, with high calcination temperatures yielding porous g-C₃N₄.

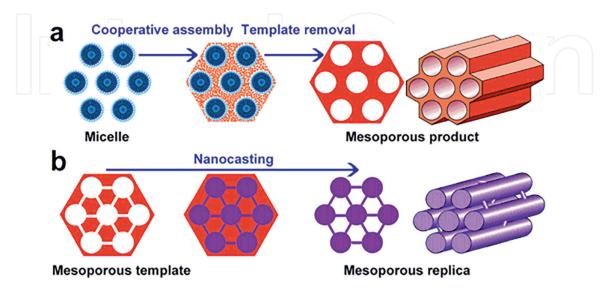


Figure 2.

Scheme of two representative synthesis routes for ordered mesoporous materials: (a) soft templating method and (b) hard templating (nanocasting) method. Reproduced from [8] with permission from the Royal Society of Chemistry.

2.1.3 Fractional thermal polymerization method

Using melamine, guanidine carbonate, and dicyandiamide as starting ingredients, a fractional thermal polymerization process was used to create $g-C_3N_4$ particles with a large surface area. Melamine, guanidine carbonate, and dicyandiamide were polymerized to create g-C3N4 at 515, 550, and 515 degrees Celsius, respectively. At the temperatures given, no residual component of precursors could be established. Around 200–240°C, all of the products for these three precursor materials had the structure of $C_3H_6N_6$, which converted to tri-s-trizines at 350–500°C. The dense packing between the conjugated aromatic system of $g-C_3N_4$ became stable using this fractional thermal polymerization approach. After 120 minutes of irradiation, the MO of $g-C_3N_4$ -M (600°C) could reach 54.67 %, whereas that of $g-C_3N_4$ -G (550°C) and $g-C_3N_4$ -D (590°C) could reach 23.46 % and 22.16 %, respectively.

2.1.4 Simple pyrolysis method

Simple pyrolysis of affordable, environmentally friendly, active oxygen-evolving urea in a covered crucible yielded porous $g-C_3N_4$ with a band gap of 2.87 eV. The photocatalytic hydrogen evolution activity of $g-C_3N_4$ produced from urea as a precursor was higher than that of thiourea or melamine in the presence of methanol as a sacrificial reagent and Pt as a co-catalyst. This is due to the structure's porous nature and large surface area. The $g-C_3N_4$ from urea has a somewhat lower degree of polymerization, resulting in more structural flaws acting as active photocatalytic sites for the Pt nanoparticle co-catalyst photodeposition as well as hydrogen production, according to XRD, TGA, XPS, and NMR data.

2.1.5 Ionothermal method

The synthesis of highly crystalline graphitic carbon nitride by dicyandiamide self-condensation in a salt melt of lithium chloride and potassium chloride has been demonstrated, and the resulting $g-C_3N_4$ has been compared to LiebigLs melon made using the typical bulk condensation technique. The product's FTIR and elemental analysis point to a structure with few flaws and unreacted end groups, indicating a highly condensed framework. Powder XRD analysis and high-resolution TEM reveal pronounced in-plane ordering with a repeat distance of d = 7.30 K, which corresponds to the separation of co-planar, covalently linked heptazine units, and a planar graphitic interlayer distance of d = 3.36 K, which corresponds to the separation of co-planar, covalently linked heptazine units.

3. Applications of g-C3N4 materials

3.1 Friedal: crafts reaction

Friedel–Crafts reactions are a type of aromatic C–H activation reaction that is known to be one of the least environmentally friendly industrial processes, creating roughly 88 percent waste. AlCl₃ boosted the standard version. According to Goettmann et al. [9] that meso-g- C_3N_4 is an important Lewis base catalyst allowed for some quite strange aromatic substitution reactions to take place. A Friedel–Crafts type that has been generalized. This metal-free catalyst is not just good for the environment. Only environmentally friendly alkylation agents, such as alcohols or acids, but they also showed unexpected reactivity in the direction of urea and quaternary ammonium compounds.

3.2 Selective oxidation reaction

The selective oxidation of hydrocarbons using pure oxidants is an important step in the synthesis of a wide range of products, from commodity chemicals to specialty medications. Chen et al. [10] proved that the Fe/g-C₃N₄ catalyst was capable of converting benzene to phenol without the use of hydrogen peroxide. The yield of phenol synthesis might be significantly increased by utilizing the photocatalytic capabilities of g-C₃N₄. Su et al. [11] demonstrated that under visible light irradiation, meso-g-C₃N₄ can operate as a photocatalyst to activate O₂ for the selective oxidation of benzyl alcohols.

3.3 Oxygen reduction reaction in fuel cells

Fuel cells have sparked a lot of interest since they provide cleaner, more sustainable energy. The high cost of Pt catalyst and the slow kinetics of ORR now limit the practical applications of fuel cells. Carbon compounds containing nitrogen, such as $g-C_3N_4$, are worth exploring because they give enough active sites for ORR. However, the low electron transport of $g-C_3N_4$ limits its electrocatalytic effectiveness. One option for addressing this issue is to use conductive carbon materials as a support to boost electron accumulation and consequently electrocatalytic performance. Lyth et al. employed $g-C_3N_4$ as an oxygen reduction catalyst and discovered that, while the electrocatalytic activity of $g-C_3N_4$ was higher than pure carbon, the current densities were low, presumably due to its low surface area. It was discovered that combining C_3N_4 with carbon black boosted current densities. Yang et al. used nanocasting to make graphene-based C_3N_4 (G-CN) nanosheets. The G-CN nanosheets had a high nitrogen content and a large specific surface area, and their electrical conductivities were improved.

4. Advantages of g-C3N4 materials in photocatalyst

The advantages of photocatalysts with varied morphologies are obvious. Twodimensional photocatalysts made in a specific way, for example, have a bigger specific surface area and more reactive sites. Other decorative components introduced throughout the construction process can also be used. However, there are still certain issues, such as a tight reaction temperature requirement and uneven particle distribution.

4.1 Doping of elements

The use of element doping to change the band structure of photocatalysts and enlarge the light absorption zone is an effective method [9]. Non-metallic (B, O, S, I) doped $g-C_3N_4$ has been widely utilized to alter the optical absorption of internal bandgap structure and to adjust the photocatalytic performance of $g-C_3N_4$ to promote the redox potential in visible light [10–14]. The light absorption range of nanosheets, on the other hand, reduces due to the quantum confinement effect, which increases the band gap [15, 16]. As a result, we can apply elemental doping to change the band structure of g-C₃N₄, which improves both light absorption and charge separation [17]. Oxygen doping, boron doping, phosphorus doping, and halogen doping will all be investigated.

4.2 Oxygen doping

By doping oxygen into $g-C_3N_4$, Wei *et al.* [18] significantly increased photocatalytic performance. **Figure 3** shows the process of making oxygen-doped $g-C_3N_4$ nanospheres. The copolymerization of the precursor can be used to adjust the degree of oxygen doping. As a result, oxygen-doped $g-C_3N_4$ demonstrated exceptional photocatalytic performance, with a Rhodamine B visible light degradation rate of 0.249 min⁻¹ which was greater than traditional $g-C_3N_4$, respectively. Zhang et al. [19] also doped varied oxygen element concentrations in typical carbon nitride materials by introducing different quantities of oxalic acid. Photocatalysis efficiency has been significantly enhanced. The addition of oxygen to the energy band structure can change the energy band structure and boost visible light absorption.

4.3 Boron doping

Thaweesak et al. [20] used one-pot thermal condensation to create a novel form of boron-doped graphitic carbon nitride nanoscale material. The best time catalytic hydrogen evolution activity is reported to be 1880 mol $g^{-1} h^{-1}$ (> 400 nm), which is more than 12 times greater than bulk g-C₃N₄. The combination of band structure development and morphological control is credited with the strong photocatalytic performance. He et al. [21] successfully doped boron into a line-shaped carbon nitride photocatalytic material using sodium borohydride corrosion. The photocatalytic performance was successfully improved. Boron doping not only narrows the band gap and absorbs more visible light, but it also has a larger surface area than bulk g-C₃N₄, improving photocatalytic activity significantly. These works show two different preparation tactics that work together.

4.4 Phosphorous doping

Kumar et al. [22] used solid thermal condensation of urea, citric acid, and 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF₆) in a reactor at 200°C to make phosphorus-doped carbon nitride quantum dots (CNPQDs). **Figure 4a** depicts the fabrication of carbon nitride-doped quantum dots (CNPQDs). By condensation polymerization, urea and citric acid produce a basic carbonitride skeleton, and

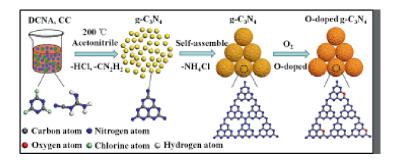


Figure 3.

The preparation of oxygen-doped g-C3N4 nanospheres. Reproduced with permission [18]. Copyright 2018, Royal Society of Chemistry.

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BMIM-PF₆ serves as a phosphorus doping source in this synthesis. **Figure 4b** depicts the steady-state photoluminescence (PL) spectra of phosphorus-doped carbon nitride quantum dots (CNPQDs) and carbon nitride quantum dots (CNQDs) in water. 15 N and 31P are two of the most common elements found in nature. **Figure 4c** shows the CPMAS NMR spectra of CNPQDs. **Figures 4d** and **e** depict the process of (CNPQDs) alteration in a titanium dioxide array.

4.5 Iodine doping

Iqbal et al. [23] used a straightforward one-step technique to make a nano-mesoporous g-C₃N₄ doped with iodine and N vacancy at the same time. Synergistic iodinedoped mesoporous g-C₃N₄ epidermoid shedding and the introduction of N vacancy due to the release of nitrogen-rich gas has been observed when glucose and NH₄I are heated simultaneously. Under simulated solar light, the produced iodine-doped mesoporous g-C₃N₄ has an exceptional photocatalytic hydrogen generation performance of 7819.2 mol g⁻¹ h⁻¹, approximately 6.5 times greater than bulk g-C₃N₄ and other types of iodine doped g-C₃N₄ photo-catalysts. This paper demonstrates a straightforward and practical method for synthesizing high-performance metal-free g-C₃N₄ photo-catalysts by altering the electronic transition via a well-designed band structure (**Figure 5**).

4.6 Bromine doping

A bromide doped graphite phase carbon nitride technique was proposed by Lan et al. [24]. While preserving the core structure of Triazine as the main component of the material, bromine alteration can increase the optical, conductance, and photocatalytic capabilities of $g-C_3N_4$. **Figure 6** depicts the photocatalytic mechanism of the CN-Br photocatalyst. The process can be used to modify a variety of $g-C_3N_4$ precursors, including urea, dicyandiamide, ammonium thiocyanate, and thiourea. This work also demonstrates a viable method for rationally designing and synthesizing $g-C_3N_4$ -based photocatalysts.

Element doping can significantly improve catalytic performance, particularly for visible light. However, there are some drawbacks that cannot be overlooked, such as the lengthy preparation procedure, increased production costs, and decreased industrial production.

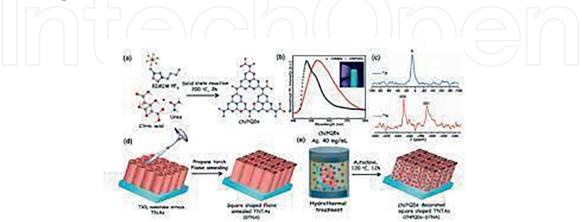


Figure 4.

(a) Schematic diagram illustrating the synthesis of phosphorus-doped carbon nitride quantum dots (CNPQDs).
(b) Steady-state PL spectrum of CNPQDs and carbon nitride quantum dots (CNQDs) in water. Inset showing fluorescence of CNPQDs sample under UV light irradiation. (c) N and P CPMAS NMR spectra of CNPQDs.
(d-e) the preparation of CNPQDs decorated square-shaped TNTAs. Reproduced with permission [21]. Copyright 2019, Wiley-VCH.

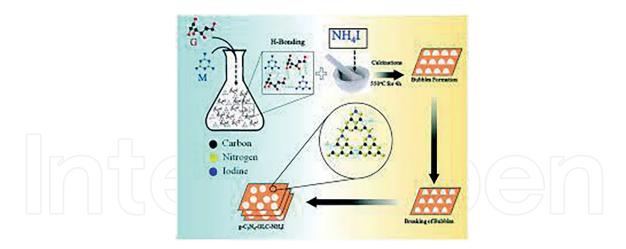


Figure 5.

Schematic of synthesizing N-vacant iodine doped mesoporous g-C3N4 nanosheets. Reproduced with permission [23]. Copyright 2019, Royal Society of Chemistry.

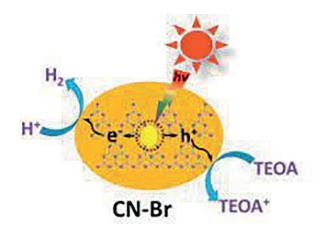


Figure 6.

Photocatalytic mechanism of CN-Br photocatalyst. Reproduced with permission from [24]. Copyright 2016, Elsevier.

5. Conclusions

In summary, this chapter focuses on the synthesis methods and applications of $g-C_3N_4$ and $g-C_3N_4$ -based materials in energy storage. Because of its unique characteristics and wide range of applications, $g-C_3N_4$ is a good candidate for effective energy storage. As a result, research into $g-C_3N_4$ -based composites for energy storage and conversion is expected to pick up speed in the near future. Despite significant progress over the years, there are still numerous hurdles in the use of this material in catalysis.

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