

Research on Graphitic Carbon Nitride (g-C₃N₄) prepared by template-based method and its photocatalytic properties

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Abstract. The Graphitic Carbon Nitride (g-C₃N₄), a non-metallic polymer photocatalytic material, has a wide range of raw materials and a simple preparation process. Due to its unique electronic structure and excellent photocatalytic performance, g-C₃N₄ has attracted wide attention in the field of environmental purification and energy conversion in recent years. However, g-C₃N₄ faces a lot of challenges, including a wide band gap, many interlayer defects, and poor interlayer electron transport. Nevertheless, its unique semiconductor structure and chemical stability still provide the possibility to explore the effect of its piezoelectric properties on photocatalysis, which paves the way for a novel approach to environmentally friendly hydrogen production. Therefore, the paper delves into the application of different template methods in the preparation of g-C₃N₄ by reviewing the related literature, and analyzes the role of different template materials in the preparation. In addition, in this paper, the photocatalytic properties of g-C₃N₄ are explored, which are mainly reflected in the photocatalytic water separation performance and photocatalytic degradation of organic dyes. It is found that the g-C₃N₄ shows great potential in the fields of photocatalytic water decomposition for hydrogen production and degradation of organic pollutants due to its unique band gap, nontoxicity, low cost and wide range of sources. Future research should continue to explore more kinds of template materials and their preparation processes, with the aim of realizing further enhancement of the performance of g-C₃N₄ photocatalysts and promoting their practical applications in the fields of environment and energy.

Keywords: Graphitic Carbon Nitride (g-C₃N₄), Photocatalysis, Organic Matter Degradation, Water Splitting.

1. Introduction

The urgent need to address energy and environmental issues has led to a shift towards the development of clean and renewable energy sources, with hydrogen emerging as a research focus due to its high energy density. Solar photocatalytic water decomposition, which directly converts solar energy into chemical energy, represents a significant technological advancement with far-reaching scientific implications for the dual challenges of energy shortage and environmental degradation. Consequently, the development of highly efficient, stable, cost-effective, and environmentally benign visible-light photocatalysts represents a pivotal area of research. Carbon nitride (C₃N₄) is a well-known substance that exists in the form of a linear polymer, consisting of tris-s-triazine molecules linked by sec-nitrogen. In 1996, Teter and Hemley successfully predicted several isomers of C₃N₄ using the first-principles approach, such as β -C₃N₄, α -C₃N₄, graphite-C₃N₄, pseudocubic-C₃N₄, and cubic-C₃N₄.

[1], and pointed out that among these C_3N_4 isomers, the most stable ones are α - C_3N_4 and graphitic- C_3N_4 . Subsequently, researchers successfully synthesized the non-polymerized two-dimensional semiconductor g- C_3N_4 in the experimental setting [2-4]. Therefore, the paper aims to methodically investigate the use of template techniques in the g- C_3N_4 fabrication process and their effect on the photocatalytic properties of the material. In particular, the functions of different template materials in the synthesis of g- C_3N_4 are examined, and their possible impacts on the compound's photocatalytic activity are assessed. This work intends to promote and guide the optimization of g- C_3N_4 preparation and enhance its practical usefulness in energy and environmental applications by thoroughly examining the mechanisms of templating on the structure and characteristics of g- C_3N_4 .

2. Application of the Template Method to the Preparation of g- C_3N_4

The g- C_3N_4 is a doped carbon material synthesized by thermal condensation polymerization of s-triazine heterocyclic compounds, in which part of the carbon atoms are replaced by nitrogen atoms. The g- C_3N_4 has numerous advantageous properties, including a suitable band gap (about 2.7 eV), nontoxicity, low cost, ease of preparation, and abundance. In addition, its graphitic phase structure renders it highly chemically and thermally stable, and it exhibits good performance under light. And it shows great potential in the field of catalysis (photoelectric conversion, photodegradation of organic pollutants, etc.). A series of techniques have been used to modify g- C_3N_4 to enhance its photocatalytic capabilities, including defect modulation, doping, compounding with other materials, and template induction, the most straightforward and straightforward of which is the template induction approach. Features such as structural modulation and abundant sources have attracted great attention in the synthesis of g- C_3N_4 [5].

2.1. Hard Template Method

The hard template method mainly employs SiO_2 , $CaCO_3$, and other nanostructures, such as nanospheres and nanosheets, as templates, which are mixed and impregnated with precursors, such as cyanamide and melamine, relying on the morphology and structure of the template to generate hole structures. Samples prepared with the hard template exhibit a well-developed hole structure, which enhances the specific surface area of the sample and provides a greater number of reactive sites. The hard template method has been employed to prepare a variety of morphologies of g- C_3N_4 . The hollow structure allows light to be reflected and refracted multiple times, which enables the material to capture more visible light and generate more photogenerated electron-hole pairs.

2.1.1. $CaCO_3$ as the Template. Using calcium carbonate particles as a rigid template, Wang et al. created porous graphite phase carbon nitride (GPPCN), which is readily removed with diluted hydrochloric acid [6]. The cathode photocurrent of the method under visible light ($\lambda > 420$ nm) irradiation was nearly 4 times higher than that of the block GPPCN when the bias voltage was -0, once the weight ratio of the template to the GPPCN precursor and the template size were established. The created porous GPPCN had more holes and an average size that was marginally smaller than the $CaCO_3$ particle template when the w/w ratio of $CaCO_3$ particles to DCDA was 2:1, according to the data. This could be related to the volume reduction that occurs during condensation and template removal. The apparent holes decreased in number and size and were replaced by shell pieces when the w/w ratio of $CaCO_3$ particles to DCDA was raised to 4:1, suggesting that the holes had largely collapsed. The majority of GPPCN particles had irregular shapes and averaged a size of around 120 nm when the ratio of $CaCO_3$ particles to DCDA was further raised to 8:1. When the ratio of $CaCO_3$ particles to DCDA is low, the loose distribution of $CaCO_3$ particles in DCDA can account for the change in the morphology of the porous GPPCN [6]. They are therefore able to preserve the replicating $CaCO_3$ pore shape during acid etching and heat condensation. There is now more opportunity to investigate the use of g- C_3N_4 for solar energy conversion and environmental remediation thanks to the use of calcium carbonate particles, which are more affordable and

environmentally friendly than other hard templates like alumina anode films and silica nanoparticles (SiNPs).

2.1.2. Anodized Aluminum Oxide (AAO) as the Template. AAO has become one of the most widely used hard templates due to its uniform pores and high temperature resistance. Li used AAO film as a hard template to prepare carbon nitride nanorods by a three-step method. The precursor on the outside of the AAO template was cleaned using filter paper, the AAO template was submerged in a homogenous mixture of 10 g of cyanamide and 5 g of distilled water, it was incubated in a N₂ environment, and it was heated at 600 °C for four hours. After being chemically corroded for 72 hours using a 1 mol/L HCl solution, the template was repeatedly cleaned with distilled water and HCl before being dried. The increase in photocatalytic activity might be due to the increase in the specific surface area of carbon nitride (CNR) treated with AAO, as demonstrated by the results, which revealed that CNR's photocatalytic hydrogen production activity was twice that of regular porous carbon nitride. In 2021, Yang employed a hydrothermal precipitation approach to control the growth and morphology of the photocatalyst ZnO by using AAO as a template [7]. The findings demonstrated that the ZnO/AAO composite membrane degraded rhodamine B at a rate of 87.5% when the hydrothermal growth period was nine hours.

2.2. Soft Template Method

Mesoporous g-C₃N₄ preparation utilising hard templates like SiNPs and SBA-15 typically calls for extremely corrosive solutions like NH₄HF₂, HF, or NaOH aqueous solutions, which are harmful to both the environment and human health. Consequently, the effective synthesis of porous g-C₃N₄ without the need of a rigid template is crucial. Compared to hard templates, the majority of soft templates can be deleted with more care and security [8].

2.2.1. Ionic Liquids as the Template. Ionic liquids are a kind of organic molten salt in liquid state at room temperature, with good conductivity and thermal stability, so they are currently widely used in chemistry, catalysis and other fields. At present, the most extensively researched ionic liquids are imidazole ionic liquids and pyridine ionic liquids in that the donor and acceptor in the ionic liquids can produce hydrogen bonding, which endows the ionic liquids with viscosity, and electrical conductivity, further expanding the scope of application of ionic liquids. In recent years, a series of new imidazolium ionic liquids have been introduced, which are widely used in solution systems or catalyst reaction systems [9]. The application of ionic liquids in photocatalysis is mainly as a soft templating agent. Satwant et al synthesized ZnO nanostructures by hydrothermal method using different basic ionic liquids (BILs) with methanol-water as the reaction medium [5]. The results showed that, with 0.3 g/L photocatalyst, the dye solution could be fully decolorized in 2 hours, while, under comparable circumstances, commercially available ZnO could be decolorized in 2.5 hours. ZnO has better photocatalytic activity due to its smaller size, larger specific surface area, higher crystallinity, more surface oxygen vacancies, and possibly reduced electron-hole recombination effects.

2.2.2. Surfactants and Block Copolymers as the Template. Both are frequently used soft templates for creating mesoporous materials [10]. Kresge et al were the first to synthesize mesoporous materials through the process of sintering aluminum silicate sols and surfactants [11]. The maximum decomposition temperature of surfactants does not exceed 500°C, but g-C₃N₄ can be generated above this temperature, which poses a great challenge to ensure the high temperature stability of surfactants. The most commonly used surfactants and block copolymers are DCDA and P123. However, the residual carbon rate of the prepared g-C₃N₄ is excessively high, and the photocatalytic efficiency of the samples is not optimal. To address this issue, a stepwise experimental method was applied to prepare g-C₃N₄, whereby the surfactant and precursors, including melamine, are mixed in a sequential manner. Subsequently, sulfuric acid was added to generate solid salts, and the template was then removed to obtain the porous precursor. After that, this was calcined to produce g-C₃N₄. In order to accomplish

direct carbonisation from the decomposable surfactant CTAB, Zhang et al. used cetyltrimethylammonium bromide (CTAB) to alter the shell thickness of hollow mesoporous carbon spheres (HCS) [7]. This simplified the preparation procedure and eliminated the need for additional carbon precursors. This involved a change in surface roughness to smoothness and a transition from incomplete (macroporous) hollow spheres to complete hollow spheres. With its uniform spherical shape, mesoporous shells, cavities, high specific surface area, and appropriate N-doping content, the produced HCS perfectly mimicked the template's morphology and guaranteed its potential as an active electrode material in supercapacitors.

2.3. Biotemplate Method

In recent years, the biotemplate method has been shown to be effective in synthesizing materials with three-dimensional structures as a promising synthetic method that utilizes a variety of complex and fine biological structures [12]. Biotemplates refer to the use of macromolecular polysaccharide compounds, such as plant stems and petals that are rich in lignin, hemicellulose, and cellulose, which are cross-linked with each other to form regular natural micro-nano structures, and are usually utilized to prepare porous carbon materials [13]. In addition, these polysaccharide compounds contain many hydroxyl, carboxyl, and amino functional groups, which can be used as reactors for nanomaterials, provide utilization sites for the nucleation and growth of nanomaterials, and control the size of nanoparticles to obtain nanomaterials with special morphology and good dispersion [14].

3. Photocatalytic Properties of g-C₃N₄

This chapter explores the photocatalytic properties of g-C₃N₄, including its applications in rephotocatalytic hydrolysis and photocatalytic degradation of organic dyes. These aspects of the study allow for a more comprehensive understanding of its potential value.

3.1. Photocatalytic Water Splitting Performance

The basic idea behind the semiconductor photowater splitting reaction is that holes will remain in the valence band of the semiconductor after stimulated by light causes the electrons to move from the valence band to the conduction band. After then, a stepwise oxygen generation reaction (OER) will take place as the valence band holes move to an oxygen-containing species. Stepwise hydrogen production reaction (HER) will occur when the conduction band electrons migrate to a species that contains hydrogen. Whereas the electron will move to a lower energy level than its own energy level, the hole will leap to a higher energy level. The energy level of the oxygen-containing species used for OER is therefore higher than the energy level of the semiconductor valence band (VB) in terms of energy level arrangement. The energy level of the semiconductor conduction band (CB) is higher than that of the hydrogen-containing species employed for HER.

Similar to most photocatalysts, unmodified semiconductor g-C₃N₄ photocatalyzes water with very low efficiency. The quantum efficiency of pure g-C₃N₄ photodegradation of water is less than 1%² under solar radiation at 420 nm. The low quantum efficiency of g-C₃N₄ can be attributed to two main reasons. First, the electrons and holes of the 2D material g-C₃N₄ are seriously recombined, which results in the inability of electrons and holes to separate and migrate well, and thus Subsequent HER and OER. Second g-C₃N₄ can only absorb photons in the edge region of visible light, which results in its low utilization of sunlight. To solve these two problems and enhance the quantum yield of g-C₃N₄, various improvement strategies have been employed to modify g-C₃N₄, among which the common improvement strategies include the following three aspects: a) doping or defects of elements: metallic and nonmetallic elements are included, with doping mainly being mono- and co-doping, and defects being different coordination environments [15]. b) construction of heterojunction: Heterojunction may be constructed by combining two or more semiconductors together through van der Waals or covalent bonding forces. Van der Waals type and planar type heterojunctions are the two varieties that result from this. They can be classified as energy level engulfing type I, energy level cross-staggered type II and cross type II, and entirely staggered energy level III based on the various energy levels of the

valence band and conduction band of each semiconductor in the heterostructure [16]. c) Copolymerization: By grafting additional π conjugated structures on top of g-C₃N₄, the intrinsic π conjugation degree of g-C₃N₄ is increased, which serves to increase g-C₃N₄'s photocatalytic activity [17–18]. Broad-spectrum absorption (absorbing as many photons as possible in the visible region of the solar spectrum, which makes up a large portion of the solar spectrum) and complete decomposition of water absorption (the catalyst photolyzes water to produce both hydrogen and oxygen without the need for a sacrificial reagent or co-catalyst), as well as efficient and rapid carrier separation and migration (the improved catalyst greatly inhibits recombination between electrons and holes) are made possible by these improved strategies [19–20].

3.2. Photocatalytic Degradation of Organic Dyes

There are four primary phases in the g-C₃N₄ photocatalytic breakdown of organic contaminants [21]. First, the electrons in the valence band will be stimulated to undergo a leaping behaviour and migrate to the conduction band when the energy of incident light recorded by the photocatalyst exceeds its band gap value. Second, a crucial element that greatly affects the photocatalytic effectiveness is the recombination of lost electrons and holes from the charge carriers when the photogenerated electron-hole pairs migrate to the surface. Third, the reactant (organic dye pollutant) and the charge carriers that are available. The reactants, or organic dye pollutants, and the available charge carriers will undergo surface chemical reactions. Fourth, additional active chemicals will be produced to take part in the oxidative degradation reaction as a result of the surface adsorbed pollutants being oxidised or reduced by interfacial charge transfer. For instance, the active ingredients in the aforementioned processes include holes, superoxide radicals, hydroxyl radicals, and single-linear oxygen. Hydroxyl radicals are created when photogenerated holes react with water, H₂O₂, or hydroxyl groups (H₂O/OH⁻). Methyl orange (MO), for instance, is an artificially produced heterocyclic sulfonated anionic colour that dissolves well in water. Extended exposure to it can lead to a variety of illnesses. Without proper treatment, its release into rivers or soil can seriously affect biological populations and the ecological environment. Low levels of MO in water sources can also have a negative impact on the quality of the water because water colouring increases the demand for chemical and biological oxygen as well as total organic carbon and total dissolved solids. This is because water colouring reduces sunlight penetration and decreases photosynthetic activity, dissolved oxygen content, and gas solubility [22]. Therefore, a pollution-free and ecologically benign degradation method is the photocatalytic degradation of MO dye by defective g-C₃N₄.

4. Conclusion

In this paper, the application of the template method in the preparation of graphitic phase carbon nitride (g-C₃N₄) and its effect on the photocatalytic performance were systematically investigated. It is shown that g-C₃N₄'s microstructure can be drastically altered by the template approach, which also increases its specific surface area and efficiently widens its light absorption range. All of these improvements greatly improve the material's photocatalytic activity. More specifically, g-C₃N₄'s structure can be improved and its photocatalytic activity can be increased in visible light by using template materials such mesoporous silica. This work offers fresh concepts and techniques for synthesizing g-C₃N₄ photocatalytic materials, which are anticipated to have extensive application in the sectors of energy conversion and environmental purification. Therefore, the template approach offers a number of advantages for improving the photocatalytic performance of g-C₃N₄, which provides an important theoretical basis and useful direction for the design of effective photocatalytic materials. Future studies should investigate more types of template materials and further optimise the template method process in order to further improve the performance of g-C₃N₄ photocatalysis, increase its widespread use, and encourage practical applications.

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