# **Graphitic Carbon Nitride as a Photocatalyst**

Subjects: Chemistry, Physical

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Carbon nitride, albeit known for a long time, has been tested as a photocatalyst only since 2009. Extensive searches for reliable visible-light-activated semiconductor photocatalysts revealed the next generation photocatalyst based on a polymeric semiconductor—graphitic carbon nitride.

g-C3N4 hydrogen photocatalysis platinum

# 1. Introduction

Fossil fuels are a limited and exhaustible resource for conventional energy production that induces reasonable concerns of energy and economic crises <sup>[1]</sup>. Besides, wide use of fossil fuels causes environmental and human health impacts <sup>[2]</sup>. In this context, triggering hydrogen as an alternative energy source is a promising trend, since hydrogen is an environmentally benign fuel <sup>[3][4][5]</sup>. Currently, numerous industrial processes to produce hydrogen are available, but they all are energy intensive, require high temperatures, and appear economically efficient only at large scales <sup>[6]</sup>. In this regard, the photocatalytic production of hydrogen attracts particular interest as the process proceeding at ambient conditions and simulating photosynthesis, i.e., the direct conversion of solar energy into the energy of chemical bonds <sup>[7][8][9][10][11][12][13][14][15][16]</sup>.

The process of photocatalytic splitting of water using TiO<sub>2</sub> catalysts under UV radiation was pioneered by Fujishima and Honda in 1972 <sup>[17]</sup>. Since that time, a great number of research has been performed to produce hydrogen by photocatalytic splitting of water with various semiconductor photocatalysts <sup>[18][19][20][21][22]</sup>. However, this process has an intrinsic problem of hydrogen-oxygen recombination <sup>[23]</sup>. To improve the process' quantum efficiency, photocatalytic reduction of water is carried out with the use of electron donor agents, such as various organic and inorganic compounds capable of donating electrons and thereby reducing the recombination of electron-hole pairs on the photocatalyst surface <sup>[24][25][26]</sup>.

Promising photocatalysts activated by UV and visible light include  $TiO_2$  <sup>[27][28][29][30]</sup>, ZnO <sup>[31]</sup>, Fe<sub>2</sub>O<sub>3</sub> <sup>[32]</sup>, CdS <sup>[33]</sup>, Cd<sub>1-</sub>Zn<sub>x</sub>S <sup>[34]</sup>, Bi<sub>2</sub>WO<sub>6</sub> <sup>[35]</sup>, BiVO<sub>4</sub> <sup>[36]</sup>, Ta<sub>2</sub>O<sub>5</sub> <sup>[37]</sup>, Ta<sub>3</sub>N<sub>5</sub> <sup>[38]</sup>, and TaON <sup>[39]</sup>. Nowadays, the research and development of high-performance semiconductor photocatalysts for solving the problems of energy shortages and environmental safety are particularly important. Recently, visible-light-activated photocatalysts have been developed, which allow efficient use of the solar spectrum containing a large fraction of visible light (about 43%) <sup>[17]</sup>. Traditional semiconductor photocatalysts, such as TiO<sub>2</sub>, have a large band gap and, therefore, are unable to absorb visible light, and can be activated only by UV light, which constitutes a small fraction of the solar radiation

spectrum <sup>[40][41][42]</sup>. Extensive searches for reliable visible-light-activated semiconductor photocatalysts revealed the next generation photocatalyst based on a polymeric semiconductor—graphitic carbon nitride <sup>[43][44][45][46]</sup>.

# 2. Graphitic Carbon Nitride as a Photocatalyst

Carbon nitride, albeit known for a long time, has been tested as a photocatalyst only since 2009 <sup>[47]</sup>. Every year, the interest of researchers in this material increases, as shown in **Figure 1**a. It can also be seen in **Figure 1**b that, to date, about 10–12% of all studies on the photocatalytic H<sub>2</sub> production devoted to the synthesis and study of photocatalysts based on g-C<sub>3</sub>N<sub>4</sub> and their applications.



**Figure 1.** (a) Number of annual publications using " $g-C_3N_4$  photocatalytic H<sub>2</sub> production" as a keyword since 2011. (b) Proportion between the number of publications with keywords " $g-C_3N_4$  photocatalytic H<sub>2</sub> production" and "photocatalytic H<sub>2</sub> production" based on data of Science Direct (Elsevier).

It reveals various allotropic forms, such as  $\alpha$ -C<sub>3</sub>N<sub>4</sub>,  $\beta$ -C<sub>3</sub>N<sub>4</sub>, graphitic, cubic, and pseudocubic <sup>[48]</sup>. The most stable modification is a polymeric graphitic structure in which s-triazine or tri-s-triazine (s-heptazine) units are bound to each other through tertiary amines <sup>[47]</sup>. Graphitic carbon nitride g-C<sub>3</sub>N<sub>4</sub> has the band gap of 2.7 eV and the conduction band-edge potential -1.3 V vs. NHE, which enables an efficient hydrogen production process <sup>[47]</sup>. This material is thermally and chemically stable, safe for the environment, acid and alkali resistant; its surface can be modified without infringing its composition and structure <sup>[49]</sup>. It is easily synthesized by thermal polycondensation of inexpensive nitrogen-containing precursors, such as dicyandiamide, cyanamide, melamine, urea, and thiourea <sup>[46]</sup> [<sup>50]</sup>[<sup>51]</sup>[<sup>52]</sup>. The downside of this process is that it yields materials with low specific surface areas and high electron-hole recombination rates that provokes the loss in the catalytic activity <sup>[53]</sup>. To stabilize the photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub>, the following approaches are used:

Alteration of textural characteristics by introducing templates, pore formers, or pretreatment method [54][55][56][57]
 [58][59][60][61][62][63][64][65][66].

- Doping with heteroatoms [67][68][69][70][71][72][73];
- Modification with metals [74][75][76][77][78][79][80][81][82][83][84][85][86][87][88][89][90]:
- Creation of composite photocatalysts [91][92][93][94][95][96][97][98][99][100]

The formation of graphitic carbon nitride proceeds by various routes at thermal condensation of the abovementioned precursors. At thermal pyrolysis, the cyclization of any of the above mentioned nitrogencontaining precursors yields melamine <sup>[49]</sup>. The dimerization of melamine at 350 °C yields melem and melon that transforms into polymeric  $g-C_3N_4$  at temperatures above 500 °C (**Figure 2**).



Figure 2. Thermal condensation of dicyandiamide to form  $g-C_3N_4$ .

Graphitic carbon nitride is known to have a defect-rich structure, which results from incomplete deamination during thermal polycondensation <sup>[49]</sup>. For this reason, synthesizing high-crystalline  $g-C_3N_4$  is a difficult task, albeit exact crystallinity (correct arrangement of atoms) is a critically important parameter affecting the band structure and charge recombination rate ( $e^{d_e}/h^+$ ) of a photocatalytically active material. A large number of structural defects increases the charge recombination rate, and thus impedes photocatalyst activity. Texture controlling can improve the chemical, physical, and optical properties of  $g-C_3N_4$  <sup>[101]</sup>. The relationship between the  $g-C_3N_4$  morphology and photocatalytic hydrogen evolution performance is discussed below.

### 2.1. Textural Characteristics and Methods to Control Them

#### 2.1.1. The Use of Templates

The textural and morphological characteristics, such as porosity, specific surface area, and pore size distribution, of a carbon nitride based material can be controlled by using appropriate templates, which are subdivided into hard and soft ones. Hard templates are, for example, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> <sup>[56][57]</sup>. Graphitic carbon nitrides, synthesized using these templates, possess high specific surface area and porosity, and a large number of the surface active sites. Nevertheless, soft templates, such as starch and glucose, seem much more attractive, as they are safe for the environment, require no corrosive chemicals for elimination <sup>[58][59]</sup>, and provide g-C<sub>3</sub>N<sub>4</sub> with a specific surface area of >60 m<sup>2</sup>·g<sup>-1</sup> <sup>[59]</sup>. After elimination of solvents and templates, the g-C<sub>3</sub>N<sub>4</sub> nanoporous structure turns quite delicate (fragile) and easily destroyable, which presents one of the main problems of creating polymeric hollow nanospheres. A green soft-template approach allows synthesizing various g-C<sub>3</sub>N<sub>4</sub> structures through relatively simple routes, keeping these structures durable even after template removal. Amphiphilic molecules, surfactants, ionic liquids, and gas bubbles are used as soft templates <sup>[60]</sup>. However, the template polymeric materials are inclined to early decomposition that results in some carbon residue in the material, which induces pores isolating, and thus affects negatively the g-C<sub>3</sub>N<sub>4</sub> structure and photocatalytic activity.

#### 2.1.2. The Use of Pore-Forming Agents

Pore-forming agents can significantly improve the photocatalytic characteristics of graphitic carbon nitride due to their affecting of its textural characteristics. Ammonium chloride <sup>[61]</sup> and urea <sup>[62]</sup> are among the most commonly used pore-forming agents reported in the literature. This approach ensures the synthesis of complex porous structures, such as ultrathin nanosheets <sup>[61]</sup>. Favorably compared to hard templates, the pore-forming agents require no eliminating from the target material by using harmful compounds or procedures. For example, ammonium chloride (NH<sub>4</sub>Cl) additive in the g-C<sub>3</sub>N<sub>4</sub> precursor decomposes at temperatures of 280–370 °C into NH<sub>3</sub> and HCl thus facilitating the formation of a loose ultrathin nanosheet structure (thickness 1–2.4 nm or 3–7 atomic layers) with a defective matrix <sup>[61][63]</sup>. The bottleneck of this process is the cost-efficiency and ecological issues; obviously, the cheaper and environmentally benign pore-forming agents should be developed.

#### 2.1.3. Pretreatment Method

There are many studies in which precursors are modified prior to calcination in order to obtain  $g-C_3N_4$  with improved properties <sup>[64][65][66]</sup>. One such modification method is the pretreatment of the precursor with acids (H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>), which makes it possible to obtain a much higher specific surface area of resulting  $g-C_3N_4$  [65]. The strong oxidizing power of the acids separates the  $g-C_3N_4$  layers into thinner nanosheets, weakening the van der Waals force between them <sup>[65]</sup>. The addition of strong alkalis (NaOH) also facilitates the creation of ultrathin nanosheets. However, despite the ability to improve textural characteristics, it is difficult to control the yields and reproducibility of the resulting material in these pretreatment methods <sup>[65]</sup>.

#### 2.2. Doping Heteroatoms

The polymeric structure of graphitic carbon nitride is suitable for doping by other atoms or molecules by means of appropriate chemical procedures. The introduction of various atoms affects the electronic structure of the polymer material. Doping with nonmetals or anions leads to the  $g-C_3N_4$  band gap narrowing. It is assumed that the band gap narrowing results from the formation of localized states and elevation of the valence band maximum due to the presence of doping atoms <sup>[67]</sup>. Besides doping with mono-nonmetal heteroatoms, co-doping with several heteroatoms is applied to provide more efficient band gap width variation <sup>[68][69][70]</sup>.

Particular attention is focused on the doping of graphitic carbon nitride with halogens: Br, I, CI [71][72]. For example, doping with bromine increases optical absorption, conductivity, charge carrier transfer rate, and photocatalytic activity without disturbing the g-C<sub>3</sub>N<sub>4</sub> structural stability. It is assumed that halogen doping shifts the optical absorption spectrum towards longer wavelengths in the UV-visible spectrum <sup>[72]</sup>. The hindering of the charge carrier recombination at the introduction of Br atoms is attributed to the delocalization of the Br valence electrons to  $\pi$ -conjugated g-C<sub>3</sub>N<sub>4</sub> structures. Graphitic carbon nitride doped with halogen atoms (F, Cl, Br, I) exhibited enhanced optical absorption and improved photocatalytic characteristics <sup>[72]</sup>. It was found that electronegativity of the halogen atoms affects the photocatalytic properties of g-C<sub>3</sub>N<sub>4</sub>. The higher the halogen atomic number, the lower is its electronegativity, and more electrons can transfer from the halogen atoms facilitate the electron escape from the g-C<sub>3</sub>N<sub>4</sub> surface to participate in photocatalytic reactions.

Doping is an effective approach to improve the photocatalyst light absorption capacity, oxidizability, and separation efficiency of photoinduced charge carriers <sup>[73]</sup>.

#### 2.3. Doping Metals

One of the most frequently used and guite simple methods to modify the surface of graphitic carbon nitride is the use of metal dopants. The nanoparticles of noble and non-noble metals improve photocatalyst ability to absorb visible light and resist recombination of photoinduced charges. Also, metal nanoparticles can act as catalysts for the formation of molecular hydrogen. Noble metals attract particular attention, as they have the most suitable electronic and optical characteristics [74][75]. The Schottky barrier, also known as the space charge separation region, is formed at the noble metal-semiconductor heterojunction; it impedes electron migration from one material to another, and reduces the charge recombination. The creation of the Schottky barrier allows for the accumulation of additional negative charges (electrons) and positive charges (holes) in the noble metal and semiconductor, respectively. Noble metals also have the ability to absorb visible light owing to the plasmon resonance effect. There are two main approaches for depositing noble metal particles on the catalyst surface: impregnation with a precursor followed by reduction with NaBH<sub>4</sub> [76] or another reductant [83], and photodeposition under the action of ultraviolet radiation [77][84]. There is also a possibility to attach pre-synthesized nanocrystals of desired sizes and shapes on graphitic carbon nitride nanosheets through electrostatic attraction [85]. The chlorocomplexes are common precursors for the deposition of noble metals onto a  $g-C_3N_4$  surface [86][87][88]: for example, hexachloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>) is usually used as the platinum precursor [78][84][89]. The photodeposition method does not use high-temperature treatments or hazardous materials. The downside of using noble metals as cocatalysts is that they are very expensive, especially in view of the high metal loading in the catalysts (1–5 wt.%) <sup>[79]</sup>. Currently, many studies are aimed at replace noble metals with non-noble ones, such as copper or nickel, which are much less expensive and are able to absorb visible light <sup>[80][81][90]</sup>.

Although metal doping facilitates significant acceleration of the hydrogen production reaction, an excess of cocatalyst on the surface reduces the catalyst ability to absorb light in the visible region and acts as an electron trap <sup>[82]</sup>.

### 2.4. Development of Composite Photocatalysts

In order to provide efficient light utilization and enhanced the redox ability of a material, it is common practice to shift the energy levels of the valence and conduction bands by creating a composite of two different materials. Composite materials are used to develop photocatalysts with enhanced light absorption in the visible region, efficient charge separation retarding charge recombination, and improved redox performance. There are various composite photocatalysts differing by heterojunction types: type I <sup>[91]</sup>, type II <sup>[91][92]</sup>, S-scheme <sup>[93][94]</sup>, Z-scheme <sup>[95]</sup>

The creation of effective composites between two different compounds depends on their crystal structures, electron affinities, band structures, and the strength of the interfacial interaction. The type I heterojunctions assume that the valence band (VB) of semiconductor 1 lies higher than the VB of semiconductor 2, and the conduction band (CB) lies lower; in such a system, both electrons and holes are transferred to one semiconductor, where redox reactions occur <sup>[91]</sup>. Such a transfer of photogenerated charges from one semiconductor to another does not improve the efficiency of charge separation.

In type II heterojunctions, the level of VB and CB potentials of semiconductor 1 are higher than the level of VB and CB potentials of semiconductor 2. Here, the separation of photogenerated electrons and holes occurs through double charge transfer: an electron migrates from the CB of semiconductor 1 to the CB of semiconductor 2; a hole moves from the VB of semiconductor 2 to the VB of semiconductor 1. Electrons are accumulated in the CB of semiconductor 2, while holes accumulate in the VB of semiconductor 1, which facilitates efficient charge separation and reduced recombination <sup>[91][92]</sup>. Although traditional type II heterojunctions improve charge separation, they reduce the initial redox ability of electrons and holes.

The formation of S-scheme heterojunctions facilitates efficient charge separation without affecting the intrinsic redox ability of semiconductors <sup>[93]</sup>. To achieve successful construction of the S-scheme, the position of the CB and the Fermi level of the photocatalyst on which the reduction reaction proceeds must be higher than respective characteristics of the photocatalyst which runs the oxidation process. The internal electric field caused by the band deviation due to the difference in the Fermi levels of the two semiconductors enhances the charge mobility. The synthesis of two different semiconductors for subsequent integration into an S-scheme is considered rather difficult <sup>[94]</sup>. To date, the S-scheme heterojunction approach is considered to be the best choice for the development of photocatalysts with high charge separation efficiency and redox ability. Compared to S-scheme, the Z-scheme

heterojunction photocatalysts have higher charge separation efficiency and are easier to synthesize <sup>[97]</sup>. Electrons from the CB of semiconductor 1 migrate through electron mediators (metals) to the VB of semiconductor 2 to recombine with photoinduced holes.

In the case of type I heterojunction photocatalysts <sup>[98]</sup>, the redox process occurs on one semiconductor. The type II <sup>[99]</sup> heterojunctions significantly promote the separation of photoinduced electrons and holes, but have a weak redox ability that is detrimental for the photocatalytic reaction. Currently, the S-scheme approach is the most promising with regard to efficient charge separation and redox reactions <sup>[100]</sup>. However, the creation of S-scheme heterojunction photocatalysts is a difficult task that requires the structural modification of both semiconductors.

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