**Ben-Gurion University of the Negev**

**Faculty of Natural Sciences**

**Department of Chemistry**

**Rational Design of Carbon Nitride Materials by Supramolecular Preorganization**

Thesis submitted in partial fulfillment of the requirements for the degree

**"DOCTOR OF PHILOSOPHY"**

**By: Jesús Barrio Hermida**

**Submitted to the Senate of Ben-Gurion University of the Negev**

**January 2020**

**BEER-SHEVA, ISRAEL**

**Rational Design of Carbon Nitride Materials by Supramolecular Preorganization**

Thesis submitted in partial fulfillment

of the requirements for the degree of

“DOCTOR OF PHILOSOPHY”

**By**

**Jesús Barrio Hermida**

**Submitted to the Senate of Ben-Gurion University**

**of the Negev**

## Approved by the advisor:

**Approved by the Dean of the Kreitman School:**

**January 2020**

**BEER-SHEVA**

**This work was carried out under the supervision of**

**Professor Menny Shalom**

**In the Department of Chemistry**

**Faculty of Natural Sciences**

**Ben-Gurion University of the Negev**

**Research-Student's Affidavit when Submitting the Doctoral Thesis for Judgment**

I Jesús Barrio Hermida, whose signature appears below, hereby declare that

(Please mark the appropriate statements):

\_**X**\_\_ I have written this Thesis by myself, except for the help and guidance offered by my Thesis Advisors.

\_**X**\_ The scientific materials included in this Thesis are products of my own research, culled from the period during which I was a research student.

\_**X**\_ This Thesis incorporates research materials produced in cooperation with others, excluding the technical help commonly received during experimental work. Therefore, I am attaching another affidavit stating the contributions made by myself and the other participants in this research, which has been approved by them and submitted with their approval.

Date: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ Student's name: Jesús Barrio Hermida Signature:\_\_\_\_\_\_\_\_\_\_\_\_\_\_

**Acknowledgements**

I would like to thank my supervisor, Prof. Menny Shalom, for believing in me since my first internship, and for providing me with the privilege of being the first of his students in his research group in Israel. I would like to thank him for his charisma, his patience, for teaching me, and showing me how to become a better scientist, how to deal with success, and also with frustration. His teachings, pep talks and scientific chitchat have had an immeasurable impact on me as a scientist and as a person that I will always remember. I want to thank also to the amazing group I had the pleasure to share lab and office with, thanks so much Yoni, Dr. Guiming Peng, Dr. Jingwen Sun, Metial, Dr. Neeta Karjule, Adi, Dr. Jiawei Xia, Liel, Ayelet, Dr. Michael Volokh, Dr. Jiani Qin, Dr. Ying Wang, and Junyi. Working with each one of you has taught me something different, you have also made my working experience in Israel truly valuable, and enjoyable. Thanks as well to the research groups of Dr. Idan Hod, Prof. Gabriel Lemcoff, and Prof. Maya Bar Sadan.

Thanks to all the scientific collaborators and friends that I had the pleasure to meet during this journey, from the Max Planck Insitute for Colloids and Interfaces in Potsdam, Germany, thanks to its director Prof. Dr. Markus Antonietti, and to the great scientist I got to share institute with, Dr. Jingsan Xu, Dr. Thomas Jordan, Dr. Valerio Molinari, Katharina, Dr. Baris Kumru, Dr. Remi Cazelles, Dr. Ryan Guterman, Dr. Alexandr Savateev, and Dr. Bernhard V. K.J Schmidt. From the Instituto Universitario Mixto de Tecnología Química in Valencia, Spain, thanks Dr. Diego Mateo, Dr. Josep Albero, Amparo, Esther, and Prof. Hermenegildo García. Thanks also to the members of the nanomaterials group at Universidad Autónoma de Madrid, Spain, thanks, Dr. Carlos Gibaja, Dr. Pilar Amo Ochoa and Dr. Félix Zamora.

I want to thank as well to Raya Ifraemov and her family, for making me feel like home, for all the love and experiences together during this time, and to my best sources of support and encouragement in the distance, thanks Daniel, Pablo, Dr. Noah Al Nakeeb, and Dr. Alessandro Dani, for your friendship.

Finally, I would like to thank my parents, Almudena and Sebastián, my role models. They have raised me in the culture of respect and hard work, have supported me in all my decisions and inspired me in a way no one could. Thanks to Ignacio, Rocio and Leyre, for their immeasurable support during the last 4 years, for their love and their kindness, I could not be more proud of you, and to the rest of my family, because you have all been there for me.

**Table of contents**

**Abstract**

1. **Scientific background**
   1. **Semiconductor-based hydrogen generation**
   2. **Graphitic carbon nitride materials**
   3. **Synthetic approaches** 
      1. **Copolymerization**
      2. **Templating**
      3. **Ionothermal synthesis**
      4. **Supramolecular preorganization**
   4. **Post-synthetic methods**
      1. **Exfoliation**
      2. **Covalent functionalization**
      3. **Hybrid materials**
   5. **Prospects and challenges**
2. **Research description and objectives**
3. **Published papers**
4. **Conclusions**
5. **References**

**List of abbreviations**

|  |  |
| --- | --- |
| NHE | Normal hydrogen electrode |
| CB | Conduction band |
| VB | Valence band |
| OER | Oxygen evolution reaction |
| HER | Hydrogen evolution reaction |
| UV | Ultraviolet |
| g-CN | Graphitic carbon nitride |
| 2D | Two dimensional |
| eV | Electron volts |
| DCDA | Dicyanamide |
| BA | Barbituric acid |
| Eg | Band gap |
| AAO | Anodic aluminum oxide |
| SBA-15 | Mesostructured silica nanoparticles |
| PTI | Poly(triazine imide) |
| AQY | Average quantum yield |
| CM | Cyanuric acid-melamine |
| EG | Ethylene glycol |
| mg | Milligram |
| mL | Milliliter |
| DOS | Density of states |
| CNTs | Carbon nanotubes |
| NPs | Nanoparticles |
| rGO | Reduced graphene oxide |
| BCN | Boron carbonitride |
| BN | Boron nitride |

**Abstract**

The search for sustainable energy resources, and environmental remediation has become during the last decades one of the major challenges of materials science, and the direct conversion of solar energy to fuels has been addressed as a feasible way to face energy and environmental crisis. The development of an efficient system that mimics biology where sunlight is used in order to drive an uphill reaction, such like water splitting or CO2 reduction to produce fuels remains as a standing challenge. A photo-driven conversion of natural feedstock to potential fuels such like hydrogen represents a green energy alternative against fossil fuels; and this photocatalytic production requires low-cost, robust, and highly efficient semiconductors, which are capable to harvest a big portion of the visible light, display good charge separation properties, and have a suitable energy band position for the desired reaction. One of the semiconductors that has provided a step forward in the search for a low-cost material capable to yield efficient solar-to-fuel conversions is graphitic carbon nitride (g-CN). Over the past few years, graphitic g-CN has attracted widespread attention due to its outstanding electronic properties, which have been exploited in applications including in photo- and electro-catalysis, CO2 reduction, water splitting, LEDs, solar cells and more. g-CN comprises only carbon and nitrogen, and its synthesis entails the polymerization of C and N rich monomers, such like dicyanamide or melamine. However, the traditional solid-state reaction usually yields unordered materials with grain boundaries and low photo-catalytic activity. Despite the recent progress achieved in the field by employing approaches such like doping, the use of hard and soft templates, or the fabrication of hybrid composites, it still remains as a challenge the fine control of g-CN chemical and electronic properties, as well as morphology from the synthetic point of view. Our group has showed that the supramolecular preorganization of g-CN monomers by using non-covalent interactions prior their calcination at high temperatures results in highly active materials for photocatalytic applications. The clever selection of the parameters that take part in the in the synthesis of self-assembled hydrogen bonded frameworks, including monomer sequence, solvent, intermolecular interactions, etc., will determine the aggregation shape and size of the precursors. Upon calcination, the morphology and monomer sequence will be projected in the prepared g-CN, allowing its rational design for a given application.

In my doctoral Thesis I show that the rational design of supramolecular assemblies, that serve as reactants for the synthesis of g-CN, allows the control of chemical, photophysical and catalytic properties of g-CN toward its utilization as photocatalyst for various reactions. The manipulation of supramolecular interactions between different starting monomers employing halogen acids and interfaces between two non-miscible solvents and its effects in the later g-CN material are thoroughly explored and discussed. Furthermore, I have developed a method for the successful projection of morphologies and chemical composition in g-CN materials by utilization of highly ordered supramolecular single crystals as reactants which has opened new opportunities in the rational design of C/N-based macrostructures for semiconductor devices.

1. **Scientific background**
   1. **Semiconductor-based photocatalytic materials for hydrogen generation**

The search for sustainable energy resources, and environmental remediation has become during the last decades one of the mayor challenges of material science, and the direct conversion of solar energy to fuels has been addressed as a feasible way to face energy and environmental crisis.1 The development of an efficient system that mimics biology where sunlight is used in order to drive an uphill reaction such as water and CO2 reduction to produce fuel, that can replace the currently utilized worldwide fossil fuels remains as an actual standing challenge.2 A photo-driven conversion of water to gaseous hydrogen represents a green energy alternative against fossil fuels, due to the capability of hydrogen being used as a potential energy carrier and the lack of harmful CO2 emission to the environment.3,4 The processes in a photocatalytic generation of hydrogen include: light absorption by a semiconductor catalyst, generation of photo-excited charges (electrons and holes or excitons), charge separation and migration to the surface of the catalyst and transfer of excited charges to water molecules (Figure 1).5 Such a photocatalytic production of hydrogen requires low-cost, robust, and highly efficient semiconductors, which should have good charge separation properties and that can transfer charge rapidly at the semiconductor/liquid interface, display long-term stability, possess good light-harvesting properties, and have a suitable energy band position for the desired reaction.6 The band gap of a semiconductor is one of the key parameters that determines its photocatalytic performance under light irradiation; in order to produce hydrogen in a photocatalytic manner, it should be more than 1.23 eV versus the normal hydrogen electrode (NHE) which is the energy required to split water into hydrogen and oxygen. Therefore, the conduction band (CB) energy level shall be more negative than the water reduction potential (EH2-H+) and the valence band (VB) energy level more positive than the water oxidation potential (EO2- H2O).7,8



**Figure 1**. Processes in photocatalytic water splitting.

TiO2 semiconductors are one of the most widely exploited materials in photocatalytic scenarios since the discovery by Fujushima et al of the water splitting using a Pt-attached n-TiO2 photoelectrochemical cell.9 In this work, they showed the oxygen evolution reaction (OER) in a TiO2 photoelectrode and hydrogen evolution reaction (HER) in the platinum counter electrode upon illumination with UV light. 10 Since then, a broad range of semiconductor materials exhibiting high photocatalytic activities have been reported, being the most utilized transition metal oxides,11 dichacogenides12 or vanadates13,14 amongst others.15,16 However, despite the great progress in this field, most of the oxide based photo-catalysts display wide band gap which hinders their light harvesting ability, making them able to perform photocatalytic reactions just under UV-light illumination, and other semiconductors as sulfides, nitrides and selenides suffer from low stability to oxidation and expensive cost which makes unfeasible its utilization in an industrial scale (Figure 2).



**Figure 2**. Band gaps of typically utilized semiconductors. Reprinted with permission of reference 15 copyright 2015 The Royal Society of Chemistry

Therefore, it is essential to develop photocatalysts which are potentially capable to produce high amount of hydrogen, with stability to corrosion and narrow band gaps. In addition to the water splitting to produce H2 and O2, photo-catalysis with an appropriate semiconductor could drive other kind of reactions; for example, the degradation of organic pollutants in water. In this case their degradation typically occurs through attack of superoxide (O2-**.**) and hydroxyl (**.**OH) species to the pollutant, which are formed when atmospheric oxygen reacts with a photogenerated electron from the CB of a semiconductor or when water or -OH ions are oxidized in the presence of a photogenerated hole, respectively.17 Additionally, photogenerated excitons can directly reduce or oxidize organic pollutants in water environments, depending on their oxidation and reduction potential and the energy band gap of the semiconductor.18 The photoassisted CO2 reduction to fuels by semiconductors has also attracted widespread attention due to the potential capability of reducing atmospheric CO2 emissions.19 In this case high-value products can be obtained such like carbon monoxide, formic acid or methane, depending on the energy band positions of the utilized semiconductor and the underlying photocatalytic mechanism.20,21 Despite significant progress in this field, the design of stable and cheap semiconductors with good electronic and catalytic properties that can harvest a large portion of the visible light and convert it into fuels is still considered a major challenge, and novel approaches for the production of such semiconductors are much sought after.

* 1. **Graphitic carbon nitride materials**

One of the semiconductors that fulfills the requirements to become an efficient, robust photocatalyst for the scalable production of solar fuels is graphitic carbon nitride (C3N4, g-CN). Despite the wide variety of C3N4 allotropes,22–24 graphitic carbon nitride, a carbon-nitrogen based analogue of graphene, which is composed by aromatic stacked sheets of tri-s-triazine (or heptazine) units that interact by Van der Waals forces is the most widespread studied in the last 15 years owing to its remarkable chemical and electronic properties (Figure 3).25



**Figure 3**. In plane (a) and stacking sheets (b) structure of g-CN with the corresponding *d* spacing for the (100) and (002) crystal planes. Fourier transformed infrared (FTIR) (c) and absorption (d) spectrum of g-CN, and its X-ray diffraction (XRD) crystal patterns (e).

Particularly, g-CN is a visible-light responsive semiconductor with a 2.7 eV band gap, which has allowed its exploitation in a wide variety of different energy-related scenarios. Since the report in 2009 where Wang et al. described its utilization as a metal-free visible-light photocatalyst for water splitting,26 g-CN has been extensively applied in fields such like photo-electrochemical water splitting,27 CO2 reduction,28 nitrogen fixation,29 solar cells,30 sensing,31 and more.32 The synthesis of g-CN entails the thermal annealing of C-N based monomers, such like dicyanamide, melamine, or urea amongst others,33,34 at high temperatures; upon condensation in the solid-state, ammonia is released forming reaction intermediates like melem, built by in-plane aromatic tri-s-triazine units that interact by Van der Waals forces, upon further thermal treatment (400-600 °C) the formation of a C3N4 polymeric adduct whit terminal amine groups due to a non-ideal condensation is achieved (Figure 4).35 Nevertheless, the solid-state reaction that initial C-N-based reactants undergo during the preparation of g-CN results often in materials displaying a high amount of grain boundaries, and along with the poor solubility of the resulting product impedes the fine control over its chemical and electronic properties, as well as its functionalization or implementation in devices. Consequently, in order to fabricate a high-performance g-CN based material or device with future perspectives of industrial application, new synthetic approaches that can overcome the difficulties of the solid-state reaction shall be explored and optimized.

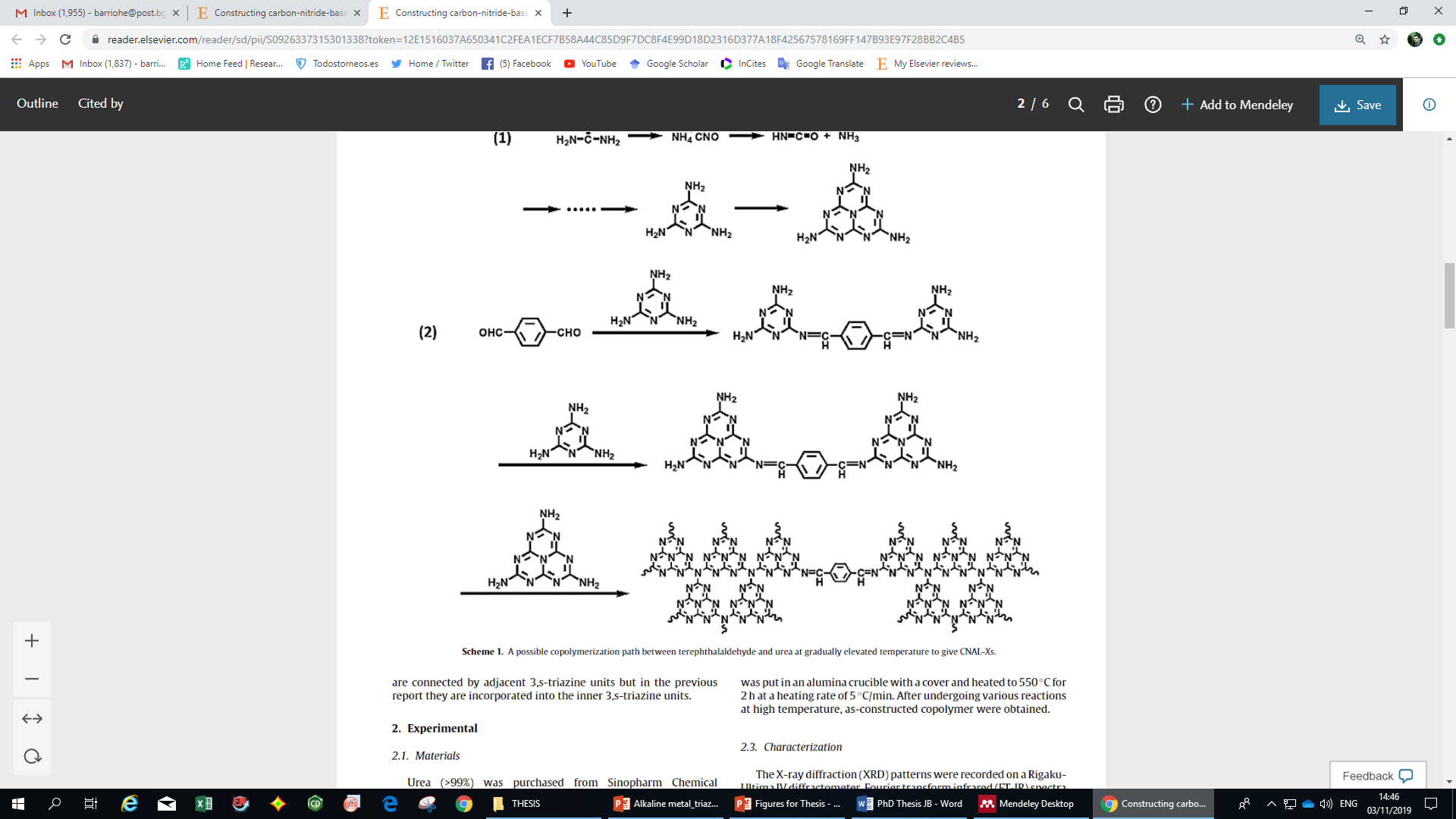


**Figure 4**. Scheme of the synthesis of g-CN from the thermal treatment of melamine.

During the last decade, several synthetic approaches have emerged for modifying g-CN chemical and electronic properties and achieving a high activity in photo-catalytic scenarios. Tailoring the optical absorption by manipulating the energy band positions, enhanced the porosity for creating more catalytically active sites or prolonging the life of the photogenerated electron-hole pairs are the main goals of the synthetic pathways utilized up to now. The fine tuning and control is very challenging due to the solid-state reaction, and despite the recent progress designing efficient g-CN-based photocatalysts, remains as a current standing challenge.

* 1. **Synthetic approaches**
     1. **Copolymerization**

Copolymerization is one of the most widely used synthetic protocols for preparing g-CN derivatives with enhanced light harvesting properties. Here, a combination of two or more small organic molecules obtained typically by physical means (like grinding or ball-milling) is thermally treated at high temperatures and the organic moieties react in the solid state, typically by Schiff-base reactions or nucleophilic attacks (Figure 5).36



**Figure 5**. Synthesis of conjugated g-CN frameworks by Schiff-base reaction copolymerization. Reprinted with permission of reference 36 copyright 2015 Elsevier.

One early report of a g-CN material prepared by copolymerization was described by Zhang et al. who utilized dicyanamide (DCDA) along with different amounts of barbituric acid (BA) as precursor for the high temperature reaction. Here the C/N ratio rose up to 0.96 due to the partial replacement of nitrogen atoms by carbon, narrowing the band gap (Eg) to 1.58 eV which resulted in the enhancement of the photocatalytic performance in the HER.37 Since this pioneering work, a wide variety of novel molecules have been utilized for modifying g-CN properties through copolymerization. In this way, the introduction of conjugated aromatic rings using benzene derivatives was achieved, which results generally in the improvement of the charge transfer and separation properties and contributes to a higher photocatalytic activity.38 The choice of the monomers utilized as precursors determines the microstructure, electronic properties and the overall (photo)catalytic performance. Additionally, utilizing building blocks containing heteroatoms (metal, halogen, chalcogen, pnictogen, etc) can induce certain doping in the final g-CN, which has been predicted to have beneficial effects on the charge transfer and separation efficiency of photogenerated excitons.39

* + 1. **Templating**

The number of catalytically active sites in a material is one of the main parameters for achieving a high performance in catalysis. Modifying the porosity and nanostructure of g-CN is therefore one of the most important bottlenecks for enhancing its photoactivity. The utilization of hard and soft templates for the synthesis of g-CN has provided significant progress in the controlled preparation of nanostructures with defined porosity, morphology, and particle size. This synthetic pathway entails the filling or coating of a rigid template with a defined morphology, typically made of porous inorganic materials, with a C-N precursor, followed by its thermal treatment at high temperatures for achieving g-CN. Finally, the template is removed by etching the template in an acid/base (Figure 5).40 Therefore, hard templates such like anodic aluminum oxide (AAO) or mesostructured silica (SBA-15) have been widely utilized for the synthesis of g-CN nanoparticles, nanorods or nanotubes with enhanced surface areas (up to 800 m2g-1) and photocatalytic activity in a wide variety of scenarios.41–43

 **Figure 6**. Schematic representation of the synthesis of nanostructured g-CN utilizing a hard template.

Soft templating has several main differences versus the synthesis with hard inorganic porous structures. Here, molecular building blocks such like ionic liquids, block copolymers or surfactants are utilized for directing the thermal polymerization process of g-CN. During the thermal condensation, these molecules self-assemble with C-N monomers and influence the growth of the graphitic phases and modifying parameters such like pore size and distribution, or specific surface area. Given the high temperatures required for the synthesis of g-CN (>500 °C), the templating molecules are often decomposed and typically, the prepared g-CN shows certain enrichment with residual carbon .44

* + 1. **Ionothermal synthesis**

The crystallinity of g-CN is a key factor in the achievement of an efficient charge separation efficiency and therefore a high photocatalytic performance. Merschiann et al. showed that the electronic transport in g-CN occurs perpendicular to the graphitic sheets, in the opposite that for graphene-based materials.45 Consequently, achieving a more ordered packing of the g-CN sheets can substantially promote the electron-hole pair mobility, one of the main bottlenecks in photo-catalysis. Unlike the copolymerization of a C-N monomer with an alkaline salt, which results often in the doping of g-CN with the alkali metal or the anionic counterpart,46 the utilization of an eutectic salt mixture for the synthesis of g-CN has emerged as an effective approach for the preparation of highly crystalline condensed materials with good photocatalytic performances.47 An eutectic mixture is composed by two or more species that when thermally treated together, melt simultaneously at a given temperature (which varies from 100 to 1000 °C) depending on the mixture, and therefore it provides a liquid environment in the synthesis of g-CN materials which allows an optimal condensation of the C-N monomers and a tight packing of the graphitic sheets.48 When an eutectic salt mixture is utilized for the synthesis of g-CN, such like LiCl/KCl, the final product does not display the typical tri-s-triazine (or heptazine) structure, but a poly(triazine imide) (PTI) framework with the given metal and anionic counterparts intercalated (Figure 6).49 Since the pristine reports showing semiconducting behavior and altered crystal structures compared to the well-known tri-s-triazine moieties, plenty of reports have been shown utilizing different eutectic mixtures and C-N starting monomers and photocatalytic activities in the HER reaching up to 10% external quantum yield (AQY) were described.50



**Figure 6**. Scheme of the synthesis of PTI materials by a eutectic mixture approach.

* + 1. **Supramolecular preorganization**

During the last 6 years, utilizing supramolecular assemblies as reactants for the synthesis of g-CN has exploited as an effective approach to rationally design the final material properties due to the possibility of obtaining ordered morphologies and electronic structures. This synthetic pathway relies on supramolecular interactions between C-N monomers (hydrogen or halogen bonding, π-π stacking, etc.) in different solvents before their thermal treatment at high temperatures (Figure 7).51



**Figure 7.** Scheme of the synthesis of self-assembled supramolecular structures and their thermal calcination for the synthesis of g-CN. Reprinted with permission of reference 51, copyright Wiley.

The utilization of self-assembled hydrogen bonded frameworks based on C-N monomers for the synthesis of nanostructured g-CN was shown by our group and others, where the supramolecular complex based in cyanuric acid and melamine (CM complex) was prepared in different solvents and utilized as reactant for the high temperature reaction (Figure 8a).52,53 This complex is one of the most utilized platforms for the preparation of complex supramolecular structures, and it is typically built through 3 hydrogen bonds that can adopt several forms depending on the solvent added in the synthesis. The versatility of the CM framework and the possibility to tune its basic features by using different solvents or suitable C-N monomers has allowed its exploitation as a reactant for the synthesis of nanostructured g-CN (Figure 8b). Despite the widespread utilization of the CM lattice, the broad bonding possibility of common monomers such like melamine, allow the creation of versatile supramolecular structures that can modify the properties of g-CN and result in a high photocatalytic performance.54 For example, the protonation of common organic monomers with halogen acids permits the growth of supramolecular assemblies with different dimensions. Organic microsheets built by hydrogen bonds, π-π, and electrostatic interactions can be obtained by protonating melamine with different acids, resulting in ordered morphologies and altered electronic structures after thermal condensation (Figure 8c).55,56 Additionally the solvent that is used for the synthesis of the supramolecular assemblies has a big impact on the aggregation shape and size of the framework. In the case of a hydrogen bonded complex, a polar solvent can perturb the molecular forces and coordinate within the C-N monomers inducing a complete rearrangement, meanwhile a non-polar solvent cannot perturb the bonds and will just modify the surface of the complex (Figure 8d).57–60 Furthermore, the solubility of the organic molecules can direct the aggregation process. Typically, just a slight solubility in a given solvent is necessary for the establishment of non-covalent interactions between neighboring monomers, nevertheless a better solubility of the organic molecules taking part in the supramolecular assembly can lead to a higher number of stablished hydrogen bonds and therefore a higher thermodynamic stability of the formed aggregate.



**Figure 8.** Scheme of the preparation f g-CN utilizing the CM supramolecular complex (a). Possible modifications of the CM lattice by insertion of suitable C-N monomers (b), reprinted with permission of reference 51, copyright Wiley. (c) supramolecular assembly based on protonated melamine with HCl and HBr, and CM structure with coordinated ethylene glycol (EG) molecules (d) reprinted from reference 60, copyright Wiley.

This technique therefore offers the possibility of fine tuning chemical composition, structural features and photophysical properties of g-CN by the clever selection of parameters such like monomer sequence, intermolecular forces or reaction conditions in the synthesis of the supramolecular structures. The wide library of available C-N monomers, bonding modes and suitable building blocks (such like halogen acids or coordinating solvents) allow the insertion of new arrangements or chemical bonds that can result in suitable electronic structures for photocatalytic scenarios, such like heterojunctions or defects.61 Consequently using this approach we can target specific properties in the resulting material from the molecular level. The broad range of choices and its simplicity makes it a very attractive technique for the design of g-CN-based metal-free photocatalyst.

* 1. **Post-synthetic methods**

Despite the relatively straight-forward manipulation and alteration of g-CN structural and electronic features from the synthetic point of view, modifying the C-N based polymeric framework in a post-synthetic manner is more challenging given the stability and low dispersibility in most common solvents of g-CN. The polarity of the –C=N- bond within the conjugated sheets, or the terminal –NH2 groups are one of the few possibilities to alter g-CN electronic properties and structure once the polymer is formed. Nevertheless, given the complicated of modifying the graphitic layers by covalent functionalization, mechanical means such like exfoliation are necessary for the successful separation and isolation of individual sheets. Additionally, more straightforward approaches have been widely utilized for creating defects in the g-CN structure or induce certain doping as well as enhancing the conductivity, such like consecutive thermal treatments, hydrothermal and solvothermal means or the protonation with strong acids.62,63

* + 1. **Exfoliation**

The exfoliation of layered materials (the successful separation of the 2D counterparts that comprise a given material by mechanical means) is a widespread, useful approach for the isolation of 2D layers or flakes of different low dimensional materials for a wide range of applications such like electronics. The exfoliation of a bulk material into nanosheets enhances the amount of active sites and consequently its reactivity in a catalytic scenario, additionally, the choice of the exfoliation technique such like mechanical, thermal or liquid-phase can have a big impact in the yield and resulting morphology of the nanosized material and therefore in its performance for a given application.64 The exfoliation of g-CN materials has a great interest due to the possibility of obtaining single layers suitable for optoelectronic devices. The g-CN nanosheets interact by weak Van der Waals forces that can be easily perturbed by mechanical means, and their exfoliation typically through liquid-based methods has attracted widespread attention because of the generation of a high number of catalytically active sites and altered electronic structures due to quantum confinement effect.65 The first studies carrying out the liquid-phase exfoliation of g-CN materials show that polar solvents benefit the exfoliation in ultrathin sheets, reaching concentrations of 0.15 mg mL-1, comprised by nanosheets of 2.5 nm thickness and diameter ranging 70-160 nm. DFT calculations have proven that single layered g-CN displays an enhancement in the density of states (DOS) at the conduction band edge compared to the bulk, which stands for a higher number of charge carriers leading to improved photoresponse.66

During the last decade, this approach has allowed to establish relationships between the nanoscale features of the g-CN exfoliated sheets and the utilization of different solvents, surfactants, strong acids, etc. The intercalation of foreign agents can promote the successful exfoliation, which typically perturbs the crystal structure by shifting the (002) crystal planes towards lower angles, indicating the expansion of the inter layer distance. The selection of the exfoliation technique and external agent can lead to the preparation of stable g-CN based colloids in a wide variety of solvents, which in turn can be suitable for many applications.

* + 1. **Covalent functionalization**

The creation of covalent bonds between foreign molecules and g-CN frameworks can strongly affect parameters such like colloidal stability, or surface chemistry of this kind of materials and as well allows the formation of nanostructures that are not achievable by other conventional means due to the possibility of covalently linking foreign macromolecules or nanomaterials such like porphyrins,67 fullerenes,68 carbon nanotubes,69 and others.70 Despite the low solubility of g-CN frameworks in most common solvents, the lone electron pair in the –NH2 terminal groups and the polar –C=N- bond within the framework have been exploited for the creation of new covalent bonds. These chemical species allow the hybridization of g-CN with conjugated molecules of different dimensionality and as well has opened the gate for the application of g-CN in polymer chemistry due to the capability of the –C=N- bond of acting as a radical acceptor in intermolecular alkyl radical additions.71 The first report on the covalent functionalization of g-CN frameworks described the amidation of 1,2,4,5-benzene tetracarboxylic dianhydride and the –NH2 groups in the graphitic framework, which extended the polymer conjugation toward improved visible-light harvesting properties.72 Following this report, several groups reported the modification of the electronic properties and photocatalytic performance of g-CN by covalently bonding conjugated molecules, such like thiophene derivatives or phthalocyanines. The hybridization of –C=N- bonds allowed in 2014 the 1,2-dipolar cycloaddition of azomethine ylides (Prato's reaction) and therefore a wide library of organic groups such like ionic liquids or aryls were successfully introduced and a general enhancement of the light harvesting properties was observed.73

* + 1. **Hybrid materials**

The exciton lifetime is a key factor for improving the photocatalytic activity of g-CN materials because it increases the probability of the photoexcited charges to react with a given molecule. The creation of an electronic heterojunction has been proven to successfully increase exciton life-time owing to the enhanced charge separation, resulting in high photocatalytic activity.74

A heterojunction is constructed when two semiconductors with different electronic band structure are placed in an intimate contact resulting in the band alignment, and those can be grouped in several different kinds. Type-I heterojunctions are those where the CB and VB of a given semiconductor are in a more negative and more positive energy level (respectively) than the second semiconductor (Figure 9a). In this scenario, upon photoexcitation the electron-hole pairs migrate from the semiconductor with a wider band gap to the one with narrower band gap where they carry the reduction and oxidation reactions, respectively. In type-II heterojunctions, the CB and VB of a semiconductor display a more negative energy level than the corresponding bands of the second material taking part in the junction (Figure 9b). In this case, the electrons flow from the CB of the first semiconductor to the second one, and the holes migrate from the most positive VB to the less positive, achieving the spatial separation of charge carriers. These heterojunctions are the most effective for enhancing the lifetime of photogenerated charges and therefore the most applied with g-CN materials; their combination with typically utilized semiconductor photocatalysts such like metal oxides, phosphates, sulfides and others results in 2D-2D sandwiched Van der Waals heterostructures with improved photocatalytic activities.74,75 Nevertheless, type-III heterojunctions do not promote the charge separation and migration like in the other two cases, as both the CB and VB values of a given semiconductor don’t overlap with the counterpart, making them non-suitable for improving the photocatalytic activity (Figure 9c).76



**Figure 9.** Scheme of the different kind of heterojunction photocatalysts.

However, despite the efficiency of type-II heterojunctions for promoting the charge separation of the electron-hole pairs, after the migration the electrons are located in the less negative CB and the holes in the less positive VB and therefore the reduction and oxidation potentials of the resulting hybrid are slightly more positive and negative, respectively. In order to maintain optimal reduction and oxidation potentials while at the same time achieving the spatial charge separation of the photogenerated excitons, obtaining a Z-Scheme charge transfer pathway between two semiconductors has emerged as an efficient strategy. Here, the more positive position of the CB of one semiconductor can directly transfer photoexcited electrons to the less positive VB of the second semiconductor, where they recombine with its photogenerated holes. As a result, the electrons in the more negative CB and holes in the more positive VB are sufficiently separated and display optimal reduction and oxidation potentials (Figure 9d).77

Besides the semiconductor-semiconductor junctions, the combination of 2D g-CN materials with metal nanoparticles (NPs), also known as Mott-Schottky junctions, results in very efficient catalysts due to the charge transfer between the semiconductor to the NPs which act as very reactive binding sites for performing reduction and oxidation processes. Upon intimate contact of a 2D g-CN layer with metal NPs, due to the difference in the work function of both counterparts, an external electric field is built which promotes the migration of excitons to the NPs. Nevertheless, the energy density in the NPs surface strongly depends on the nature of the photoexcited semiconductor. In the case of an n-type, where the DOS is located close to the CB edge, upon illumination and generation of excitons the electrons are transferred from the CB to the NPs, rising their Fermi level, meanwhile for a p-type (where the DOS is located close to the VB edge) the current will consist of holes.78

Additionally, metal-free carbon-carbon nitride junctions have gathered much attention due to the remarkable physicochemical properties of carbon allotropes such like high conductivity, surface area, chemical stability and low prize.79 Graphene, carbon nanotubes or fullerenes can act as electron acceptors promoting the charge separation upon photoexcitation, and also successfully transfer the electrons to reactant molecules. An intimate contact between both counterparts can result in specific chemical bonds, such like covalent C-O-C moieties in the case of reduced graphene oxide (rGO) and g-CN, which results in the narrowing of the band gap and the improvement in the light harvesting properties.80

1. **Research description and objectives**

Despite the outstanding catalytic activity, applicability and unique optical and chemical properties of g-CN, it is still a standard problem to control the material properties and structure in a one-pot synthetic manner due to the solid-state chemistry conditions. Therefore, it is important to develop new approaches to achieve ordered and more efficient g-CN structures for the desired applications. With this aim, the overall goal of the Thesis has been to design and develop new g-CN based materials with controlled properties by using highly ordered supramolecular aggregates and crystals as the reaction reactants. The ordered supramolecular aggregates were achieved by pre-organization of C/N monomers (in different conditions and with additional suitable building blocks). In addition, the g-CN materials were utilized as photocatalysts and their electrical and photocatalytic properties were studied in depth. The novel monomer sequences prepared in this research will be directly projected onto the electronic and photocatalytic properties of the final g-CN product, that means that the g-CN product will inherit the sequence of the monomers in the starting supramolecular assembly, determined by the interaction between the different building blocks. This will create beneficial electronic structures such as heterojunctions, thus allowing a rational design of the photo-physical and photocatalytic properties of g-CN by appropriately selecting the starting monomers. Also creating unique electronic and photo-physical properties that result beneficial for photocatalysis.

One of the main C/N monomers present in g-CN synthesis and H-bonded networks is melamine (2, 4, 6-triamino-s-triazine), a six-membered heterocyclic aromatic organic compound with a high nitrogen content which can be assembled in a wide variety of supramolecular interactions, that will determine the final structure, ranging from 1D to 3D. When treated with a halogen, melamine can form a 3D structure through multiple hydrogen bonding as well as pi-pi stacking. The creation of new supramolecular complexes based on halogen-hydrogen interactions, brings a wide diversity of new chemical and photo-physical properties in the final g-CN materials. Therefore, we aim to further study the role of halogen acids in complex supramolecular structures and its projection in the final g-CN material.

Cyanuric acid-melamine based complexes (CM), have been proven to yield well-ordered g-CN architectures with different morphologies and photo-physical and catalytic properties. By manipulation of these hydrogen-bonded frameworks through the clever selection of the monomer sequence, we can introduce new spatial arrangements or chemical bonds that are expected to project novel electronic properties beneficial for photo-catalysis in the g-CN materials. Furthermore, the formation of an atomic gradient structure is really attractive, as if it is projected on the final g-CN material, we could achieve the creation of a material with richer and poorer C regions that lead to a variation of the energy bands positions, resulting in a beneficial electronic structure for photo-catalysis. We envision that the insertion of HCl in a supramolecular complex comprising of cyanuric acid, melamine, and barbituric acid can perturb the hydrogen bonded framework by partial removal of barbituric acid units through selective bonding of HCl to melamine units, which suppresses its well-known sublimation.81,82 This novel approach results in the creation of a carbon gradient in the supramolecular assembly which is transferred to the g-CN product, creating nanojunctions between C-rich and C-poor region which significantly improve the separation of the photoexcited charges and therefore the photocatalytic activity in different scenarios (Figure 10).83



**Figure 10.** Scheme of the creation of a supramolecular assembly with an atomic gradient structure.

Following our pristine work, we elucidated that the utilization of hydrochloric acid promoted the limited solubility of C/N monomers in aqueous solutions by generating the hydrochloride complex. However, complex hydrogen bonded supramolecular structures (like the ones derived from CM assemblies) are just partially soluble in water, which impedes the preparation of single crystals and therefore the elucidation of their molecular structure. Given this situation, most of the utilized hydrogen-bonded frameworks utilized in the synthesis of g-CN are just partially crystalline. In our follow-up work we utilized HCl for promoting the dissolution of melamine by generating the melaminium chloride hemihydrate supramolecular complex, which upon slow evaporation of the aqueous solution resulted in single crystals with a defined shape and molecular structure (Figure 11). Furthermore, we wanted to utilize the prepared single crystals as reactants for the high-temperature reaction, which successfully promotes the preservation of physical features such like size and shape of the initial crystals (even up to 650 °C), and chemical composition. We strongly believe that the utilization of highly ordered supramolecular single crystals for the synthesis of C-based materials can open the gate towards the precise control of its physical parameters and electronic composition towards their implementation in a wide variety of semiconductor, and energy-related devices.84



**Figure 11.** Scheme of the synthesis of a single crystal based in melamine and hydrochloric acid.85

After deeply exploring the role of Cl- ions in the synthesis of highly ordered hydrogen bonded framework we wanted to elucidate the interaction between different halogen acids and C/N monomers, its impact in the size and shape of supramolecular structures and the projected features in the g-CN material after thermal condensation. For that, will use melamine along with different halogen acids (hydrochloric or hydrobromic) in different concentrations and reaction time ranges. Furthermore, we will perform sequential halogen treatments, meaning that following the reaction of an organic monomer with a halogen acid, there will be a second treatment with a different one, which implies different halogen-monomer interactions within the structure. This kind of treatments will play a key role for the determination of the aggregation shape and size, alongside the strength and types of supramolecular interactions due to thermodynamic and kinetic factors, which will be studied in depth. The calcination at high temperature of the finely tuned supramolecular assembly will determine the morphology, electronic structure and photoactivity of the g-CN material.86

Following the study of the self-assembly of hydrogen bonded frameworks mediated by halogen acids, we wanted to focus in the effect of the solvent in supramolecular frameworks that serve as reactant for the synthesis of g-CN. Solvents, play a key role for the determination of aggregations shape and size, as well as bond strengths, due to thermodynamic and kinetic factors.87 The solubility of the starting monomers, the supramolecular interactions of the solvent with the monomers and the thermodynamic stability of the formed aggregates will govern the aggregation process. Hence, the morphology of supramolecular aggregates as well as the photo-physical and catalytic properties of the final g-CN materials are strongly dependent on the solvent from which the pristine assembly was arranged. Therefore, we will study the formation of hydrogen bonded frameworks based in cyanuric acid, melamine and barbituric acid (CMB), in both aqueous and organic solvents. g-CN derived from CMB supramolecular assemblies is one of the most photoactive catalyst developed by our group; in aqueous solution the supramolecular assembly shows a rod morphology which after thermal calcination at high temperature results in hollow rolls. The utilization of organic solvent for the synthesis of this kind of framework will strongly affect the surface energy and therefore the morphology of the assembly, which will also perturb the electronic structure and morphology of the final material.88

Additionally, the influence of a second solvent on a supramolecular assembly can lead to a full rearrangement of a supramolecular structure or just to a surface modification while preserving the bulk morphology, depending on the solvent polarity, as shown previously by our group.89 Following these previous results, the last work of my PhD thesis consist on the utilization of solvents mixtures (miscible, and non-miscible) for the synthesis of new supramolecular structures. We will perform a series of reactions between a solution of an organic monomer in one solvent (melamine in water) and another solution of a different monomer in a different solvent (cyanuric acid in chloroform), kinetic and thermodynamic factors will govern the aggregation process towards the interface between the two solvents. The study will be focused in the use of different monomers (barbituric acid, benzene derivatives etc) and different solvents mixtures (water-dichloromethane, water-tholuene, water-acetone...), as well as concentrations and reaction times.90

1. **Published papers**
2. **Conclusions**

In conclusion, my doctoral work highlights the advantages of using ordered supramolecular assemblies and crystals as reactants for the synthesis of g-CN. Herein I showed the ability to rationally design electronic structure, morphology, and chemical composition by a clever selection of parameters such like solvent selection, interaction type, or crystallinity in a supramolecular assembly for the synthesis of photoactive g-CN materials with controlled properties. In particular chlorine ions have been proven to perturb the chemical composition of hydrogen bonded frameworks, as shown in the cyanuric acid-melamine-barbituric acid (CMB) complex; the selective removal of barbituric acid imprints an atomic gradient, which after thermal condensation results in nanojunctions between C-rich and C-poor regions which improves the charge separation and hydrogen evolution performance of the g-CN. This fact confirms that *in situ* heterojunctions can be created from the molecular level. The enhanced solubility of triazine-based molecules in HCl solutions by formation of hydrochloride complexes allowed the large-scale synthesis of supramolecular single crystals. Their thermal condensation projected a unique morphology and chemical composition in g-CN which opened the gate to their application in semiconductor optoelectronic devices. The halogen effect in supramolecular assemblies was further studied by synthetizing melamine-based hydrogen bonded frameworks comprising HCl and HBr. Molecular dynamic simulations confirmed the more feasible binding of melamine amine groups and triazine nitrogens to HBr. Additionally, the solvent effect in C/N based supramolecular structures has been carefully studied. Parameters such like morphology or chemical composition can be completely tailored by utilization of solvents with different polarity, as well as interfaces between non-miscible solvents. Leading to g-CN materials with optimal porosity, electronic properties, and photocatalytic activity. These establishment of structure-activity relationships between a supramolecular assembly and a C/N based material will potentially allow the manufacture of semiconductor devices with tailored properties for a given application. Furthermore, this approach can potentially be extended to other metal-free materials such like boron carbonitrides (BCN), boron nitrides (BN), N-doped carbons or porous carbons by appropriately selecting the molecular building blocks in the monomer sequence, namely heteroatom-containing monomers, and organic molecules with different C/N ratios. The scalability, simplicity and the good control of the chemical composition provided by this approach will allow to obtain controlled directionality and tunable electronic properties towards the implementation of novel nanostructured materials in the next generation of photo-electronic devices.

1. **References**

(1) Dau, H.; Fujita, E.; Sun, L. Artificial Photosynthesis: Beyond Mimicking Nature. *ChemSusChem* **2017**, *10* (22), 4228–4235. https://doi.org/10.1002/cssc.201702106.

(2) J. Bard, A.; Anne Fox, M. Artificial Photosynthesis: Solar Splitting of Water to Hydrogen and Oxygen. *Acc. Chem. Res.* **2002**, *28* (3), 141–145. https://doi.org/10.1021/ar00051a007.

(3) Hu, B.; Wang, K.; Wu, L.; Yu, S.-H.; Antonietti, M.; Titirici, M.-M. Engineering Carbon Materials from the Hydrothermal Carbonization Process of Biomass. *Adv. Mater.* **2010**, *22* (7), 813–828. https://doi.org/10.1002/adma.200902812.

(4) Maeda, K.; Domen, K. Photocatalytic Water Splitting: Recent Progress and Future Challenges. *J. Phys. Chem. Lett.* **2010**, *1* (18), 2655–2661. https://doi.org/10.1021/jz1007966.

(5) Chen, X.; Shen, S.; Guo, L.; Mao, S. S. Semiconductor-Based Photocatalytic Hydrogen Generation. *Chem. Rev.* **2010**, *110* (11), 6503–6570. https://doi.org/10.1021/cr1001645.

(6) Liao, C.-H.; Huang, C.-W.; Wu, J. C. S. Hydrogen Production from Semiconductor-Based Photocatalysis via Water Splitting. *Catalysts* . 2012. https://doi.org/10.3390/catal2040490.

(7) Opoku, F.; Govender, K. K.; van Sittert, C. G. C. E.; Govender, P. P. Recent Progress in the Development of Semiconductor-Based Photocatalyst Materials for Applications in Photocatalytic Water Splitting and Degradation of Pollutants. *Adv. Sustain. Syst.* **2017**, *1* (7), 1700006. https://doi.org/10.1002/adsu.201700006.

(8) Hisatomi, T.; Kubota, J.; Domen, K. Recent Advances in Semiconductors for Photocatalytic and Photoelectrochemical Water Splitting. *Chem. Soc. Rev.* **2014**, *43* (22), 7520–7535. https://doi.org/10.1039/C3CS60378D.

(9) FUJISHIMA, A.; HONDA, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* **1972**, *238* (5358), 37–38. https://doi.org/10.1038/238037a0.

(10) Nakata, K.; Fujishima, A. TiO2 Photocatalysis: Design and Applications. *J. Photochem. Photobiol. C Photochem. Rev.* **2012**, *13* (3), 169–189. https://doi.org/10.1016/J.JPHOTOCHEMREV.2012.06.001.

(11) Navalón, S.; Dhakshinamoorthy, A.; Álvaro, M.; Garcia, H. Photocatalytic CO2 Reduction Using Non-Titanium Metal Oxides and Sulfides. *ChemSusChem* **2013**, *6* (4), 562–577. https://doi.org/10.1002/cssc.201200670.

(12) Lu, Q.; Yu, Y.; Ma, Q.; Chen, B.; Zhang, H. 2D Transition-Metal-Dichalcogenide-Nanosheet-Based Composites for Photocatalytic and Electrocatalytic Hydrogen Evolution Reactions. *Adv. Mater.* **2016**, *28* (10), 1917–1933. https://doi.org/10.1002/adma.201503270.

(13) Konta, R.; Kato, H.; Kobayashi, H.; Kudo, A. Photophysical Properties and Photocatalytic Activities under Visible Light Irradiation of Silver Vanadates. *Phys. Chem. Chem. Phys.* **2003**, *5* (14), 3061–3065. https://doi.org/10.1039/B300179B.

(14) Xi, G.; Ye, J. Synthesis of Bismuth Vanadate Nanoplates with Exposed {001} Facets and Enhanced Visible-Light Photocatalytic Properties. *Chem. Commun.* **2010**, *46* (11), 1893–1895. https://doi.org/10.1039/B923435G.

(15) Li, J.; Wu, N. Semiconductor-Based Photocatalysts and Photoelectrochemical Cells for Solar Fuel Generation: A Review. *Catal. Sci. Technol.* **2015**, *5* (3), 1360–1384. https://doi.org/10.1039/C4CY00974F.

(16) Martin, D. J.; Liu, G.; Moniz, S. J. A.; Bi, Y.; Beale, A. M.; Ye, J.; Tang, J. Efficient Visible Driven Photocatalyst, Silver Phosphate: Performance, Understanding and Perspective. *Chem. Soc. Rev.* **2015**, *44* (21), 7808–7828. https://doi.org/10.1039/C5CS00380F.

(17) Gaya, U. I.; Abdullah, A. H. Heterogeneous Photocatalytic Degradation of Organic Contaminants over Titanium Dioxide: A Review of Fundamentals, Progress and Problems. *J. Photochem. Photobiol. C Photochem. Rev.* **2008**, *9* (1), 1–12. https://doi.org/10.1016/J.JPHOTOCHEMREV.2007.12.003.

(18) Shiraishi, Y.; Hirai, T. Selective Organic Transformations on Titanium Oxide-Based Photocatalysts. *J. Photochem. Photobiol. C Photochem. Rev.* **2008**, *9* (4), 157–170. https://doi.org/10.1016/J.JPHOTOCHEMREV.2008.05.001.

(19) Remiro-Buenamañana, S.; García, H. Photoassisted CO2 Conversion to Fuels. *ChemCatChem* **2019**, *11* (1), 342–356. https://doi.org/10.1002/cctc.201801409.

(20) Mao, J.; Li, K.; Peng, T. Recent Advances in the Photocatalytic CO2 Reduction over Semiconductors. *Catal. Sci. Technol.* **2013**, *3* (10), 2481–2498. https://doi.org/10.1039/C3CY00345K.

(21) INOUE, T.; FUJISHIMA, A.; KONISHI, S.; HONDA, K. Photoelectrocatalytic Reduction of Carbon Dioxide in Aqueous Suspensions of Semiconductor Powders. *Nature* **1979**, *277* (5698), 637–638. https://doi.org/10.1038/277637a0.

(22) LIU, A. M. Y. Y.; COHEN, M. L. Prediction of New Low Compressibility Solids. *Science (80-. ).* **1989**, *245* (4920), 841 LP – 842. https://doi.org/10.1126/science.245.4920.841.

(23) Gmelin, L. Ueber Einige Verbindungen Des Melon’s. *Ann. der Pharm.* **1835**, *15* (3), 252–258. https://doi.org/10.1002/jlac.18350150306.

(24) Kroke, E.; Schwarz, M. Novel Group 14 Nitrides. *Coord. Chem. Rev.* **2004**, *248* (5–6), 493–532. https://doi.org/10.1016/J.CCR.2004.02.001.

(25) Thomas, A.; Fischer, A.; Goettmann, F.; Antonietti, M.; Müller, J.-O.; Schlögl, R.; Carlsson, J. M. Graphitic Carbon Nitride Materials: Variation of Structure and Morphology and Their Use as Metal-Free Catalysts. *J. Mater. Chem.* **2008**, *18* (41), 4893. https://doi.org/10.1039/b800274f.

(26) Wang, X.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J. M.; Domen, K.; Antonietti, M. A Metal-Free Polymeric Photocatalyst for Hydrogen Production from Water under Visible Light. *Nat. Mater.* **2009**, *8* (1), 76–80. https://doi.org/10.1038/nmat2317.

(27) Volokh, M.; Peng, G.; Barrio, J.; Shalom, M. Carbon Nitride Materials for Water Splitting Photoelectrochemical Cells. *Angew. Chem. Int. Ed.* **2019**, *58* (19), 6138–6151. https://doi.org/10.1002/anie.201806514.

(28) Fang, Y.; Wang, X. Photocatalytic CO 2 Conversion by Polymeric Carbon Nitrides. *Chem. Commun.* **2018**, *54* (45), 5674–5687. https://doi.org/10.1039/C8CC02046A.

(29) Wang, Z.; Hu, X.; Liu, Z.; Zou, G.; Wang, G.; Zhang, K. Recent Developments in Polymeric Carbon Nitride-Derived Photocatalysts and Electrocatalysts for Nitrogen Fixation. *ACS Catal.* **2019**, *9* (11), 10260–10278. https://doi.org/10.1021/acscatal.9b03015.

(30) Safaei, J.; Mohamed, N. A.; Mohamad Noh, M. F.; Soh, M. F.; Ludin, N. A.; Ibrahim, M. A.; Roslam Wan Isahak, W. N.; Mat Teridi, M. A. Graphitic Carbon Nitride (g-C 3 N 4 ) Electrodes for Energy Conversion and Storage: A Review on Photoelectrochemical Water Splitting, Solar Cells and Supercapacitors. *J. Mater. Chem. A* **2018**, *6* (45), 22346–22380. https://doi.org/10.1039/C8TA08001A.

(31) Chen, L.; Song, J. Tailored Graphitic Carbon Nitride Nanostructures: Synthesis, Modification, and Sensing Applications. *Adv. Funct. Mater.* **2017**, *27* (39), 1702695. https://doi.org/10.1002/adfm.201702695.

(32) Liu, J.; Wang, H.; Antonietti, M. Graphitic Carbon Nitride “Reloaded”: Emerging Applications beyond (Photo)Catalysis. *Chem. Soc. Rev.* **2016**, *45*, 2308–2326. https://doi.org/10.1039/C5CS00767D.

(33) Yan, S. C.; Li, Z. S.; Zou, Z. G. Photodegradation of Rhodamine B and Methyl Orange over Boron-Doped g-C 3 N 4 under Visible Light Irradiation. *Langmuir* **2010**, *26* (6), 3894–3901. https://doi.org/10.1021/la904023j.

(34) Liu, J.; Zhang, T.; Wang, Z.; Dawson, G.; Chen, W. Simple Pyrolysis of Urea into Graphitic Carbon Nitride with Recyclable Adsorption and Photocatalytic Activity. *J. Mater. Chem.* **2011**, *21* (38), 14398–14401. https://doi.org/10.1039/c1jm12620b.

(35) Jürgens, B.; Irran, E.; Senker, J.; Kroll, P.; Müller, H.; Schnick, W. Melem (2,5,8-Triamino-Tri-s-Triazine), an Important Intermediate during Condensation of Melamine Rings to Graphitic Carbon Nitride:  Synthesis, Structure Determination by X-Ray Powder Diffractometry, Solid-State NMR, and Theoretical Studies. *J. Am. Chem. Soc.* **2003**, *125* (34), 10288–10300. https://doi.org/10.1021/ja0357689.

(36) Fan, X.; Zhang, L.; Wang, M.; Huang, W.; Zhou, Y.; Li, M.; Cheng, R.; Shi, J. Constructing Carbon-Nitride-Based Copolymers via Schiff Base Chemistry for Visible-Light Photocatalytic Hydrogen Evolution. *Appl. Catal. B Environ.* **2016**, *182*, 68–73. https://doi.org/10.1016/J.APCATB.2015.09.006.

(37) Zhang, J.; Chen, X.; Takanabe, K.; Maeda, K.; Domen, K.; Epping, J. D.; Fu, X.; Antonietti, M.; Wang, X. Synthesis of a Carbon Nitride Structure for Visible-Light Catalysis by Copolymerization. *Angew. Chem. Int. Ed.* **2010**, *49* (2), 441–444. https://doi.org/10.1002/anie.200903886.

(38) Jinshui, Z.; Guigang, Z.; Xiufang, C.; Sen, L.; Lennart, M.; Grzegorz, D.; Grzegorz, L.; Markus, A.; Siegfried, B.; Xinchen, W. Co‐Monomer Control of Carbon Nitride Semiconductors to Optimize Hydrogen Evolution with Visible Light. *Angew. Chemie* **2012**, *124* (13), 3237–3241. https://doi.org/10.1002/ange.201106656.

(39) Jiang, L.; Yuan, X.; Pan, Y.; Liang, J.; Zeng, G.; Wu, Z.; Wang, H. Doping of Graphitic Carbon Nitride for Photocatalysis: A Reveiw. *Appl. Catal. B Environ.* **2017**, *217*, 388–406. https://doi.org/10.1016/j.apcatb.2017.06.003.

(40) Thomas, A.; Goettmann, F.; Antonietti, M. Hard Templates for Soft Materials: Creating Nanostructured Organic Materials †. *Chem. Mater.* **2008**, *20* (3), 738–755. https://doi.org/10.1021/cm702126j.

(41) Vinu, A. Two-Dimensional Hexagonally-Ordered Mesoporous Carbon Nitrides with Tunable Pore Diameter, Surface Area and Nitrogen Content. *Adv. Funct. Mater.* **2008**, *18* (5), 816–827. https://doi.org/10.1002/adfm.200700783.

(42) Bian, S.-W.; Ma, Z.; Song, W.-G. Preparation and Characterization of Carbon Nitride Nanotubes and Their Applications as Catalyst Supporter. *J. Phys. Chem. C* **2009**, *113* (20), 8668–8672. https://doi.org/10.1021/jp810630k.

(43) Sun, J.; Zhang, J.; Zhang, M.; Antonietti, M.; Fu, X.; Wang, X. Bioinspired Hollow Semiconductor Nanospheres as Photosynthetic Nanoparticles. *Nat. Commun.* **2012**, *3* (1), 1139. https://doi.org/10.1038/ncomms2152.

(44) Yang, Z.; Zhang, Y.; Schnepp, Z. Soft and Hard Templating of Graphitic Carbon Nitride. *J. Mater. Chem. A* **2015**, *3* (27), 14081–14092. https://doi.org/10.1039/C5TA02156A.

(45) Merschjann, C.; Tschierlei, S.; Tyborski, T.; Kailasam, K.; Orthmann, S.; Hollmann, D.; Schedel-Niedrig, T.; Thomas, A.; Lochbrunner, S. Complementing Graphenes: 1D Interplanar Charge Transport in Polymeric Graphitic Carbon Nitrides. *Adv. Mater.* **2015**, *27* (48), 7993–7999. https://doi.org/10.1002/adma.201503448.

(46) Wu, M.; Yan, J.-M.; Tang, X.; Zhao, M.; Jiang, Q. Synthesis of Potassium-Modified Graphitic Carbon Nitride with High Photocatalytic Activity for Hydrogen Evolution. *ChemSusChem* **2014**, *7* (9), 2654–2658. https://doi.org/10.1002/cssc.201402180.

(47) Lin, L.; Yu, Z.; Wang, X. Crystalline Carbon Nitride Semiconductors for Photocatalytic Water Splitting. *Angew. Chem. Int. Ed.* **2019**, *58* (19), 6164–6175. https://doi.org/10.1002/anie.201809897.

(48) Liu, X.; Fechler, N.; Antonietti, M. Salt Melt Synthesis of Ceramics, Semiconductors and Carbon Nanostructures. *Chem. Soc. Rev.* **2013**, *42* (21), 8237–8265. https://doi.org/10.1039/C3CS60159E.

(49) Wirnhier, E.; Döblinger, M.; Gunzelmann, D.; Senker, J.; Lotsch, B. V; Schnick, W. Poly(Triazine Imide) with Intercalation of Lithium and Chloride Ions [(C3N3)2(NHxLi1−x)3⋅LiCl]: A Crystalline 2D Carbon Nitride Network. *Chem. – A Eur. J.* **2011**, *17* (11), 3213–3221. https://doi.org/10.1002/chem.201002462.

(50) Zhang, G.; Li, G.; Lan, Z.-A.; Lin, L.; Savateev, A.; Heil, T.; Zafeiratos, S.; Wang, X.; Antonietti, M. Optimizing Optical Absorption, Exciton Dissociation, and Charge Transfer of a Polymeric Carbon Nitride with Ultrahigh Solar Hydrogen Production Activity. *Angew. Chem. Int. Ed.* **2017**, *56* (43), 13445–13449. https://doi.org/10.1002/anie.201706870.

(51) Barrio, J.; Shalom, M. Rational Design of Carbon Nitride Materials by Supramolecular Preorganization of Monomers. *ChemCatChem* **2018**, *10* (24), 5573–5586. https://doi.org/10.1002/cctc.201801410.

(52) Shalom, M.; Inal, S.; Fettkenhauer, C.; Neher, D.; Antonietti, M. Improving Carbon Nitride Photocatalysis by Supramolecular Preorganization of Monomers. *J. Am. Chem. Soc.* **2013**, *135*, 7118–7121. https://doi.org/10.1021/ja402521s.

(53) Jun, Y.-S.; Lee, E. Z.; Wang, X.; Hong, W. H.; Stucky, G. D.; Thomas, A. From Melamine-Cyanuric Acid Supramolecular Aggregates to Carbon Nitride Hollow Spheres. *Adv. Funct. Mater.* **2013**, *23* (29), 3661–3667. https://doi.org/10.1002/adfm.201203732.

(54) Roy, B.; Bairi, P.; Nandi, A. K. Supramolecular Assembly of Melamine and Its Derivatives: Nanostructures to Functional Materials. *RSC Adv.* **2014**, *4*, 1708. https://doi.org/10.1039/c3ra44524k.

(55) Xu, J.; Wu, G.; Wang, Z.; Zhang, X. Generation of 2D Organic Microsheets from Protonated Melamine Derivatives: Suppression of the Self Assembly of a Particular Dimension by Introduction of Alkyl Chains. *Chem. Sci.* **2012**, *3*, 3227. https://doi.org/10.1039/c2sc20871g.

(56) Tahir, M.; Cao, C.; Butt, F. K.; Butt, S.; Idrees, F.; Ali, Z.; Aslam, I.; Tanveer, M.; Mahmood, A.; Mahmood, N.; et al. Large Scale Production of Novel G-C3N4 Micro Strings with High Surface Area and Versatile Photodegradation Ability. *CrystEngComm* **2014**, *16* (9), 1825. https://doi.org/10.1039/c3ce42135j.

(57) Sun, J.; Xu, J.; Grafmueller, A.; Huang, X.; Liedel, C.; Algara-Siller, G.; Willinger, M.; Yang, C.; Fu, Y.; Wang, X.; et al. Self-Assembled Carbon Nitride for Photocatalytic Hydrogen Evolution and Degradation of p-Nitrophenol. *Appl. Catal. B Environ.* **2017**, *205*, 1–10. https://doi.org/10.1016/j.apcatb.2016.12.030.

(58) Li, P.; Arman, H. D.; Wang, H.; Weng, L.; Alfooty, K.; Angawi, R. F.; Chen, B. Solvent Dependent Structures of Melamine: Porous or Nonporous? *Cryst. Growth Des.* **2015**, *15* (4), 1871–1875. https://doi.org/10.1021/acs.cgd.5b00039.

(59) Robertson, C. C.; Wright, J. S.; Carrington, E. J.; Perutz, R. N.; Hunter, C. A.; Brammer, L. Hydrogen Bonding vs. Halogen Bonding: The Solvent Decides. *Chem. Sci.* **2017**, *8* (8), 5392–5398. https://doi.org/10.1039/C7SC01801K.

(60) Peng, G.; Xing, L.; Barrio, J.; Volokh, M.; Shalom, M. A General Synthesis of Porous Carbon Nitride Films with Tunable Surface Area and Photophysical Properties. *Angew. Chem. Int. Ed.* **2018**, *57*, 1186–1192. https://doi.org/10.1002/anie.201711669.

(61) Shalom, M.; Guttentag, M.; Fettkenhauer, C.; Inal, S.; Neher, D.; Llobet, A.; Antonietti, M. In Situ Formation of Heterojunctions in Modi Fi Ed Graphitic Carbon Nitride: Synthesis and Noble Metal Free Photocatalysis. *Chem. Mater.* **2014**, *26*, 5812–5818.

(62) Zhou, L.; Zhang, H.; Sun, H.; Liu, S.; Tade, M. O.; Wang, S.; Jin, W. Recent Advances in Non-Metal Modification of Graphitic Carbon Nitride for Photocatalysis: A Historic Review. *Catal. Sci. Technol.* **2016**, *6* (19), 7002–7023. https://doi.org/10.1039/C6CY01195K.

(63) Ong, W. J.; Tan, L. L.; Ng, Y. H.; Yong, S. T.; Chai, S. P. Graphitic Carbon Nitride (g-C3N4)-Based Photocatalysts for Artificial Photosynthesis and Environmental Remediation: Are We a Step Closer to Achieving Sustainability? *Chem. Rev.* **2016**, *116* (12), 7159–7329. https://doi.org/10.1021/acs.chemrev.6b00075.

(64) Coleman, J. N.; Lotya, M.; O’Neill, A.; Bergin, S. D.; King, P. J.; Khan, U.; Young, K.; Gaucher, A.; De, S.; Smith, R. J.; et al. Two-Dimensional Nanosheets Produced by Liquid Exfoliation of Layered Materials. *Science (80-. ).* **2011**, *331* (6017), 568 LP – 571. https://doi.org/10.1126/science.1194975.

(65) Zhang, J.; Chen, Y.; Wang, X. Two-Dimensional Covalent Carbon Nitride Nanosheets: Synthesis, Functionalization, and Applications. *Energy Environ. Sci.* **2015**, *8* (11), 3092–3108. https://doi.org/10.1039/C5EE01895A.

(66) Zhang, X.; Xie, X.; Wang, H.; Zhang, J.; Pan, B.; Xie, Y. Enhanced Photoresponsive Ultrathin Graphitic-Phase C3N4 Nanosheets for Bioimaging. *J. Am. Chem. Soc.* **2012**, *135* (1), 18–21. https://doi.org/10.1021/ja308249k.

(67) Zhao, G.; Pang, H.; Liu, G.; Li, P.; Liu, H.; Zhang, H.; Shi, L.; Ye, J. Co-Porphyrin/Carbon Nitride Hybrids for Improved Photocatalytic CO2 Reduction under Visible Light. *Appl. Catal. B Environ.* **2017**, *200*, 141–149. https://doi.org/10.1016/J.APCATB.2016.06.074.

(68) Chen, X.; Chen, H.; Guan, J.; Zhen, J.; Sun, Z.; Du, P.; Lu, Y.; Yang, S. A Facile Mechanochemical Route to a Covalently Bonded Graphitic Carbon Nitride (g-C3N4) and Fullerene Hybrid toward Enhanced Visible Light Photocatalytic Hydrogen Production. *Nanoscale* **2017**, *9* (17), 5615–5623. https://doi.org/10.1039/C7NR01237C.

(69) Zhao, S.; Guo, T.; Li, X.; Xu, T.; Yang, B.; Zhao, X. Carbon Nanotubes Covalent Combined with Graphitic Carbon Nitride for Photocatalytic Hydrogen Peroxide Production under Visible Light. *Appl. Catal. B Environ.* **2018**, *224*, 725–732. https://doi.org/10.1016/J.APCATB.2017.11.005.

(70) Pan, J.; Guo, L.; Zhang, S.; Wang, N.; Jin, S.; Tan, B. Embedding Carbon Nitride into a Covalent Organic Framework with Enhanced Photocatalysis Performance. *Chem. – An Asian J.* **2018**, *13* (13), 1674–1677. https://doi.org/10.1002/asia.201800506.

(71) Chauhan, D. K.; Jain, S.; Battula, V. R.; Kailasam, K. Organic Motif’s Functionalization via Covalent Linkage in Carbon Nitride: An Exemplification in Photocatalysis. *Carbon N. Y.* **2019**, *152*, 40–58. https://doi.org/https://doi.org/10.1016/j.carbon.2019.05.079.

(72) Guo, Y.; Chu, S.; Yan, S.; Wang, Y.; Zou, Z. Developing a Polymeric Semiconductor Photocatalyst with Visible Light Response. *Chem. Commun.* **2010**, *46* (39), 7325–7327. https://doi.org/10.1039/C0CC02355H.

(73) Zhang, P.; Li, H.; Wang, Y. Post-Functionalization of Graphitic Carbon Nitrides by Grafting Organic Molecules: Toward C–H Bond Oxidation Using Atmospheric Oxygen. *Chem. Commun.* **2014**, *50* (48), 6312–6315. https://doi.org/10.1039/C4CC02676D.

(74) Ong, W.-J. 2D/2D Graphitic Carbon Nitride (g-C3N4) Heterojunction Nanocomposites for Photocatalysis: Why Does Face-to-Face Interface Matter? *Front. Mater.* **2017**, *4* (April), 1–10. https://doi.org/10.3389/fmats.2017.00011.

(75) Barrio, J.; Gibaja, C.; Tzadikov, J.; Shalom, M.; Zamora, F. 2D/2D Graphitic Carbon Nitride/Antimonene Heterostructure: Structural Characterization and Application in Photocatalysis. *Adv. Sustain. Syst.* **2019**, *3* (2), 1800138. https://doi.org/10.1002/adsu.201800138.

(76) Low, J.; Yu, J.; Jaroniec, M.; Wageh, S.; Al-Ghamdi, A. A. Heterojunction Photocatalysts. *Adv. Mater.* **2017**, *29* (20), 1601694. https://doi.org/10.1002/adma.201601694.

(77) Fu, J.; Yu, J.; Jiang, C.; Cheng, B. G-C3N4-Based Heterostructured Photocatalysts. *Adv. Energy Mater.* **2018**, *8* (3), 1–31. https://doi.org/10.1002/aenm.201701503.

(78) Li, X. H.; Antonietti, M. Metal Nanoparticles at Mesoporous N-Doped Carbons and Carbon Nitrides: Functional Mott–Schottky Heterojunctions for Catalysis. *Chem. Soc. Rev.* **2013**, *42* (16), 6593–6604. https://doi.org/10.1039/c3cs60067j.

(79) Han, Q.; Chen, N.; Zhang, J.; Qu, L. Graphene/Graphitic Carbon Nitride Hybrids for Catalysis. *Mater. Horizons* **2017**, *4* (5), 832–850. https://doi.org/10.1039/C7MH00379J.

(80) Li, Y.; Zhang, H.; Liu, P.; Wang, D.; Li, Y.; Zhao, H. Cross-Linked g-C3N4/RGO Nanocomposites with Tunable Band Structure and Enhanced Visible Light Photocatalytic Activity. *Small* **2013**, *9* (19), 3336–3344. https://doi.org/10.1002/smll.201203135.

(81) König, A.; Fehrenbacher, U.; Kroke, E.; Hirth, T. Thermal Decomposition Behavior of the Flame Retardant Melamine in Slabstock Flexible Polyurethane Foams. *J. Fire Sci.* **2009**, *27* (3), 187–211. https://doi.org/10.1177/0734904108099329.

(82) Lotsch, B. V; Schnick, W. New Light on an Old Story : Formation of Melam during Thermal Condensation of Melamine. *Chem. - A Eur. J.* **2007**, 4956–4968. https://doi.org/10.1002/chem.200601291.

(83) Barrio, J.; Lin, L.; Wang, X.; Shalom, M. Design of a Unique Energy-Band Structure and Morphology in a Carbon Nitride Photocatalyst for Improved Charge Separation and Hydrogen Production. *ACS Sustain. Chem. Eng.* *6* (1), 519–530. https://doi.org/10.1021/acssuschemeng.7b02807.

(84) Barrio, J.; Lin, L.; Amo-ochoa, P.; Tzadikov, J.; Peng, G.; Sun, J.; Zamora, F.; Wang, X.; Shalom, M. Unprecedented Centimeter-Long Carbon Nitride Needles : Synthesis , Characterization and Applications. *Small* **2018**, *14*, 1800633. https://doi.org/10.1002/smll.201800633.

(85) Janczak, J.; Perpe, G. J. Melaminium Chloride Hemihydrate. *Acta Crystallogr.* **2001**, *C57*, 1120–1122. https://doi.org/10.1107/S0108270101011283.

(86) Barrio, J.; Grafmüller, A.; Tzadikov, J.; Shalom, M. Halogen-Hydrogen Bonds: A General Synthetic Approach for Highly Photoactive Carbon Nitride with Tunable Properties. *Appl. Catal. B Environ.* **2018**, *237* (June), 681–688. https://doi.org/10.1016/j.apcatb.2018.06.043.

(87) Cook, J. L.; Hunter, C. A.; Low, C. M. R.; Perez-Velasco, A.; Vinter, J. G. Solvent Effects on Hydrogen Bonding. *Angew. Chem. Int. Ed.* **2007**, *46* (20), 3706–3709. https://doi.org/10.1002/anie.200604966.

(88) Barrio, J.; Shalom, M. Ultralong Nanostructured Carbon Nitride Wires and Self-Standing C-Rich Filters from Supramolecular Microspheres. *ACS Appl. Mater. Interfaces* **2018**, *10* (46), 39688–39694. https://doi.org/10.1021/acsami.8b13873.

(89) Sun, J.; Xu, J.; Grafmueller, A.; Huang, X.; Liedel, C.; Algara-Siller, G.; Willinger, M.; Yang, C.; Fu, Y.; Wang, X.; et al. Self-Assembled Carbon Nitride for Photocatalytic Hydrogen Evolution and Degradation of p-Nitrophenol. *Appl. Catal. B Environ.* **2017**, *205*, 1–10. https://doi.org/10.1016/j.apcatb.2016.12.030.

(90) Dolai, S.; Barrio, J.; Peng, G.; Grafmueller, A.; Shalom, M. Tailoring Carbon Nitride Properties and Photoactivity by Interfacial Engineering of Hydrogen-Bonded Frameworks. *Nanoscale* **2019**, *11*, 5564–5570. https://doi.org/10.1039/C9NR00711C.