Polymeric Carbon Nitrides: Semiconducting Properties and Emerging Applications in Photocatalysis and Photoelectrochemical Energy Conversion

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ABSTRACT
As an analogue of graphite, graphitic carbon nitride polymers also possess a stacked two-dimensional structure, which could be regarded as N-substituted graphite in a regular manner. The history of carbon nitride polymers could trace back to 1834 when Liebig firstly prepared “melon,” a carbon nitride derivative, but their potential applications have only emerged in the very recent years. As an organic semiconductor, carbon nitrides have several interesting features as follows. Firstly, both of carbon and nitrogen are among the most abundant elements in our planet, and it is facile for mass-preparation with a very competitive prices of order of several $/Kg, which is always preferred. Secondly, because of intrinsic organic nature, it is easy to chemical functionalize/doping, thus manipulating their electronic band-gap structures. Thirdly, distinct to many other organic semiconductors, carbon nitrides have a high stability against oxidation up to 500 °C in air, making handling them in air possible. Here we briefly review the proof-of-concept applications of polymeric carbon nitrides for photovoltaic and photocatalytic fields in the past several years, and the performance optimization by morphology and electronic band gap engineering.

KEYWORDS: Polymeric Carbon Nitride, g-C₃N₄, Organic Semiconductor, Photovoltaics, Photocatalysis, Doping, Mesoporous Materials.

1. INTRODUCTION
Due to the rapid depletion of limited fossil energy sources and the increasingly worsening environmental pollution, the development of alternative energy supply has attracted worldwide attentions. It is expected to be clean, safe, economic and renewable. As the largest source of energy, solar light is readily available and renewable, thus has been regarded as an idea alternative.¹ Among them, the devices, which use the photovoltaic effect to harness solar radiation, such as solar cells and solar fuels, have drawn many attentions. For example, silicon-based solar cells are now commercially available with satisfied efficiency. But they still suffer from high costs, thus a new generation of photovoltaic conversion devices based on organic (polymers) and metallic nanocrystalline semiconducting materials might offer a solution to make such devices cheaper.²⁻⁹ At the same time, considerable effort has been devoted to the development of active, stable photocatalysts for H₂ evolution from water, CO₂ reduction, or photodegradation of organic pollutions that can work under the abundant visible light in the solar spectrum.¹⁰⁻²¹

Regarded as “doped” carbon-materials in which some carbon atoms in graphite are replaced by nitrogen atoms in a regular manner, carbon nitrides stand for a large family of related compounds (CₓNᵧ) in general.²²⁻²⁷ More interestingly, β-C₃N₄, another allotrope of carbon nitride solid, was theoretically predicted to possess a similar
hardness and low compressibility as diamond.\textsuperscript{28} Therefore, larger efforts have been devoted to prepare such covalently bonded carbon nitride materials in the past twenty years.\textsuperscript{25,29-39} However, instead of diamond-like $\beta$-C$_3$N$_4$, in most cases, graphitic carbon nitride, which has layered structure, was synthesized and found to be the most stable allotrope at ambient conditions. For example, a typical way to prepare bulk graphitic carbon nitride by thermal condensation of dicyandiamide (DCDA) and the proposed full-condensed structure ($\gamma$-C$_3$N$_4$) is shown in Figures 1(a–c).\textsuperscript{40} It should be noted that the obtained carbon nitride solids by this method were not perfect fully condensed $\gamma$-C$_3$N$_4$, e.g., C/N molar ratio is ca. 0.72, and a small amount of H (1.5 wt.%) is detectable from elemental analysis. Ideally, carbon nitrides only consist of carbon and nitride atoms, and no other atoms. Up to now, perfect $\gamma$-C$_3$N$_4$ with structure shown in Figure 1(a) has not been prepared in experiment. Nevertheless, the unique conjugated structure had already make as-prepared graphitic carbon nitride polymer stable up to 500 °C in air just like graphite (Fig. 1(d)). For simplicity, in this review paper, we use $\gamma$-C$_3$N$_4$ as the whole family of graphitic carbon nitride compounds with C/N ratio close to 0.75. Actually, the history of polymeric carbon nitride solids could trace back to 1834 when Liebig firstly prepared “melon” (C$_6$N$_9$H$_3$), a carbon nitride derivative, thus they could be regarded as one of the oldest synthetic polymers.\textsuperscript{41-42} Several excellent reviews by Kroke and Schwarz,\textsuperscript{33} and Thomas et al.\textsuperscript{51} were given recently about the history, basic structures, preparations, properties, and the applications of carbon nitride polymers such as metal-free catalysts for various organic reactions as well.

Interestingly, polymeric carbon nitrides was found to be a typical semiconductor with band gap ranging up to 5 eV upon structural variations or adatoms by theoretic calculations.\textsuperscript{44} Therefore, it is promising to consider carbon nitrides as an alternative candidate for the sunlight harness and conversion. In this case, carbon nitrides have several unique features, which are listed as follows. Firstly, it is facile for mass-preparation with a very competitive prices of order of several $/Kg, which is always preferred. Secondly, because of intrinsic organic natures, it is

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REVIEW

Fig. 1. Proposed motif of full-condensed g-C3N4 (a, C-atoms are black, N-atoms are blue), one possible reaction pathway by thermal condensation of dicyandiamide (DCDA) (c) and photograph of bulk g-C3N4 powder (c, yellow). TGA curve for bulk g-C3N4 showing high stability in air, heating rate: 10 °C/min (d). Reproduced with permission from [43], Y. J. Zhang and M. Antonietti, Chem.-Asian J. 5, 1307 (2010). © 2010, Wiley-VCH Verlag GmbH.

easy to chemical functionalize/doping. Thirdly, contrary to many other organic semiconductors, carbon nitrides have a high thermal and chemical stability against oxidation (Fig. 1(d), stable in air up to 500 °C), making handling them in air possible. Lastly, but not less important, both of carbon and nitrogen are among the most abundant elements on our planet, which is in accordance of the sustainable energy. Therefore, in this article, the new exploration of carbon nitrides, especially g-C3N4, as new organic semiconductors in photocatalytic H2 evolution from water splitting and degradation of organic pollutants, and photoelectric conversion in the past several years will be reviewed.

2. H2 EVOLUTION FROM PHOTOCATALYTIC WATER SPLITTING

In the recent years, photocatalysis, by present of which a photoreaction is accelerated, has been well developed. As a pioneered work, Fujishima and Honda showed the H2 evolution by splitting water photoelectrochemically based on n-type TiO2. In general, semiconductors, such as TiO2, WO3, and Zn2GeO4, are utilized to generate electron–hole pairs upon irradiation, which if separated, are able to undergo secondary reactions, which is the key point for the photocatalytical reactions. As an organic semiconductor, graphitic carbon nitride was also found to be a possible for H2 evolution by photocatalytical water splitting in the present of a sacrificial donor upon visible light irradiation by Wang et al. Figure 2(a) shows the steady H2 production using g-C3N4 powder as photocatalyst from water containing triethanolamine as a sacrificial electron donor on light illumination. This result indicated that g-C3N4 functioned as a stable metal-free photocatalyst for visible light driven H2 production. The H2 production rate increased with increasing Pt content to a plateau at around 2–4%, beyond which it decreased again. Although the estimated quantum efficiency of the Pt-modified g-C3N4 catalyst was still very low (approximately 0.1% with irradiation of 420–460 nm), the result proved it was possible to utilize common available oxidation-stable polymeric carbon nitride as organic semiconductor in water splitting. Moreover, a stable visible-light-driven O2 evolution was observed by modification of g-C3N4 with RuO2 (Fig. 2(b)). Interestingly, by using magnesium phthalocyanine as the sensitizer, the absorption
region of g-C₃N₄-based photocatalyst could be further extend at wavelengths longer than 600 nm.51

We found that the carbon nitride polymer could also be utilized as the sensitizer for N-doped tantalic acid in photocatalytic water splitting.52 The incorporation of carbon nitride on the surface of N-doped tantalic acid made the absorption of N-doped tantalic acid red-shifted remarkably to the visible light region. As a result, carbon nitride sensitized N-doped tantalic acid showed a high photocatalytic activity and good stability for hydrogen evolution from an aqueous methanol solution under visible light irradiation, and up to 4.8% of the apparent quantum yield was achieved at 420 nm. It was explained that the strong acid-base interactions between the tantalic acid and carbon nitride made the separation of photogenerated charge carriers easier (Fig. 3).

3. PHOTOCATALYTIC DEGRADATION OF ORGANIC POLLUTIONS

Similarly, photogenerated electrons and holes could produce free radicals such hydroxyl radicals (•OH) and oxygen radicals (O₂), which are both strong oxidation species for degrading organic pollutions. Li and Zou et al. investigated the photocatalytic activity of as-prepared g-C₃N₄ from melamine by using the methyl orange dye (MO) as the model photodegrading molecules (Fig. 4).53 They found the photocatalytic activity of g-C₃N₄ could be
largely improved by using Ag as the co-catalyst. In addition, the strong acid radical ion can promote the degradation rate. Control experiments showed the MO degradation over the g-C₃N₄ was mainly attributed to the photoreduction process induced by the photogenerated electrons. Therefore, it clearly indicated the potentials of metal-free g-C₃N₄ in photodegradation of organic pollutants.

4. PHOTOELECTRIC CONVERSION

In comparison with solar fuels technology, such as H₂ evolution via photocatalytic water splitting, which needs further development of high efficient fuel cells to solve the energy problems, photoelectric conversion devices, such as solar cells, would provide a more direct way to convert solar energy into electricity. Facts as a low price (of the order of some $/kg), facility for mass-preparation and chemical modification, and especially, contrary to many other traditional organic semiconductors used in photoelectric conversion devices, a high thermal and chemical stability against oxidation (Fig. 1(d), stable in air up to 500 °C), make carbon nitride solids a very promising candidate for solar cells. In a standard photoelectrochemical cell, we firstly investigated experimentally the electronic band gap structures and the ability to generate photocurrents of some carbon nitrides, including bulk g-C₃N₄, regerated g-C₃N₄ by protonation and deprotonation (rpg-C₃N₄), mesoporous g-C₃N₄ (mpg-C₃N₄) and an Fe-doped g-C₃N₄ (Fe-g-C₃N₄). The “proof-of-principle” experiments (Fig. 5) showed that the photocurrent generation could be up to 150 μA/cm² (IPCE ~ 3% at 420 nm) under visible light irradiation (λ > 420 nm, 150 W Xe lamp) in aqueous solution. It was worthy of noting that in these initial tests, the device layout was far from being optimized. For instance, a granular texture with micron-sized features, made grain boundary effects a limiting issue. Thus, the efficiency of carbon nitride solids are low for competitive solar cells, but can be well compared with some classic light-harvesting systems, e.g., single walled carbon nanotube-porphyrin assemblies. Therefore, the preliminary results could be regarded as a possible starting point for the future applications of carbon nitride solids in photovoltaic applications, which also relied on sophisticated engineering.

5. PERFORMANCE OPTIMIZATION BY MORPHOLOGY ENGINEERING

In most cases, graphitic carbon nitride solids are prepared by thermal polycondensation of various monomers, for instance, DCDA at 550 °C, which results in bulk materials with low surface area (~10 m²/g). In fact, together with boundary effect, such low surface has become one disadvantage which hinders the wide potential application of this new emerging material. It is well-know in material science that morphology engineering has been in principle generally used to investigate the correlations with performance. It is because surface area plays important...
roles not only in enhancing mass transfer during the reaction but also offering more active sites, thereto improving the performance of materials. Moreover, especially in photovoltaic applications, the diffusion path of free carriers from the bulk to the surface of higher surface area materials is shorter and as such their recombination during the transfer is greatly suppressed. This concept has already successfully applied in the dye-sensitized solar cells and other photocatalysts. Vinu reported mesoporous C$_x$N$_y$ (x/y ~3–5, Figs. 6(a, b)) with pore diameters from 4.2 to 6.4 nm from SBA-15 materials with different pore diameters as hard templates via polymerization between precursors such as ethylenediamine (EDA) and carbon tetrachloride (CTC). Groenewolt et al. prepared g-C$_3$N$_4$ nanoparticles using mesoporous silica as the hard exotemplate. Due to the rich variety of mesoporous silica template, the particle size of carbon nitride could be easily replicate ranging from 5 to 70 nm. Interestingly, the quantum confine effect was further identified by observing the blue shift of the maximum emission peak in photoluminescence investigations. Similarly, when silica nanoparticles were used as the hard endotemplate, mesoporous g-C$_3$N$_4$ could be prepared, and the specific surface area could be as high as 400 m$^2$/g (Figs. 6(c, d)). As a result, the photocatalytic H$_2$ evolution from water splitting efficiency could be enhanced by nearly 10 times. However, it is worthy of noting that the decrease of crystalline was also observed for high surface area g-C$_3$N$_4$, which was against effective excited charger separation. Therefore, how to increase the crystalline of g-C$_3$N$_4$ polymer and at the same time keeping a high surface area is still a challenge.

Nevertheless, the removal of the silica host matrices involves aqueous ammonium bifluoride (NH$_4$HF$_2$) or hydrogen fluoride (HF), which is hazardous and not environmentally friendly. Actually, there has been a growing interest over the past few years in the use of surfactants and block polymers as “soft templates” for the production of nanoporous materials, including carbons. But owing to thermodynamic and physicochemical reasons, preparing soft porous materials by non-hard templates is still very difficult, and only very few specific exceptions have been reported to be successful so far. In the case of g-C$_3$N$_4$, the practical problem is that the condensation towards larger extended CN-structures takes place around or above the decomposition temperature of the common used soft template. We partially solved this problem by delicately introducing holding sequences at intermediate temperatures around the template decomposition or each important condensation step to suppress volatilization, followed by the final condensation step at 550 °C, at which temperature the soft template had already decomposed. As a result, nanoporous graphitic carbon nitride was synthesized by using different soft templates such as Triton-X 100 through the self-polymerization reaction of DCDA. But

unfortunately the porosity was not highly ordered and uniform, i.e., it gave a broad pore size distribution. Therefore, developing a reliable and facile environmentally friendly strategy to synthesize highly ordered mesoporous graphitic carbon nitride is still an urgent topic in order to enable larger-scale access to these materials.

6. TAILORING THE ELECTRONIC STRUCTURE BY CHEMICAL DOPING

Although the proof-of-principle applications of g-C₃N₄ in photovoltaic and photocatalytic fields have been examined recently, the efficiency is rather low, which greatly hampers its promising potentials, thus demanding to be urgently improved. The low efficiencies are partially due to not only poor adaption of the materials interfaces in the photoelectrochemical cell but also the universal grain boundary effects. Moreover, the optical band gap of as-prepared C₃N₄ is ca. 2.7 eV, absorbing only blue light up to 450 nm contributing to another primary drawback. All these facts are unfavorable for potential applications, especially as organic semiconductors for photovoltaic and photocatalytic applications. Generally, chemical doping is an effective strategy to modify the electronic structures of semiconductors as well as their surface properties, thus improving their performances. According to the bonding type of the dopants, three types of chemical doping have been developed so far, i.e., ionic, covalent, and non-covalent functionalization.

Wang et al. prepared metal-containing carbon nitride via mixing transition metal salts such as Fe (III) with the precursor of g-C₃N₄ and co-thermal condensation (Fig. 7(a)). They found the electronic and optical functions of g-C₃N₄ can be easily modified after the inclusion of metal-ion species in its structure. The metal species lowered the band gap and expanded the light absorption of the material further into the visible region of the electromagnetic spectrum, thus providing the material with additional new functionalities, such as mimicking metalloenzymes in H₂O₂ activation. By using a post co-annealing method, we implanted Zn species into the matrix of g-C₃N₄ (Fig. 7(a)), and found that the absorption edges of Zn/g-C₃N₄ red-shift remarkably. Moreover, the obtained Zn/g-C₃N₄, a new type of organic-metal hybrid materials, showed 10 times

![Fig. 7. Typical molecular structures of ion-doped polymeric carbon nitrides and their properties. Fe(III)/Zn(II) was stabilized in the electron-rich g-C₃N₄ structure mainly through Fe/Zn–N bonds, with/without minor charge balance by Cl⁻ (not shown) (a). Photocatalytic H₂ evolution on Pt (0.5%)-loaded pure and Zn/g-C₃N₄ photocatalysts under visible light irradiation (λ ≥ 420 nm) (b). Reproduced with permission from [61], B. Yue et al., Sci. Tech. Adv. Mater. 12, 034401 (2011) © 2011. Under Creative Commons Attribution-Non-Commercial-ShareAlike 2.5 license. Protonated g-C₃N₄ with counteranions (X⁻) exchangeable for extended functionalities (c), and controllable light absorption and emission (d). Reproduced with permission from [62], Y. J. Zhang et al., Am. Chem. Soc. 131, 50 (2009). © 2009, American Chemical Society.](image)
higher photocatalytic activities in comparison with pristine g-C3N4 for hydrogen evolution from an aqueous methanol solution under visible light irradiation (Fig. 7b), and good stability as well.61 In addition, it was noted that the framework of g-C3N4 is rich of base functionalities, thus, direct protonation of as-prepared g-C3N4 would be another convenient ionic modification route (Fig. 7(c)).62 In previous works, the protonation has been utilized to disperse carbon nanotubes,63 control the conductivity of various conductive polymers,64 and even enhance proton conductivity and photoluminescence properties of polyamidoamine dendrimers.65 Indeed, post-functionalization of g-C3N4 has the extra advantage of introduction of functional groups into g-C3N4 after the lattice is formed at elevated temperatures, since not all dopants are tolerant to high temperatures. We firstly explored such post-functionalization of pristine g-C3N4, and found that facile protonation not only provided better dispersion and exposed a high surface area for g-C3N4 but also enabled an adjustment of electronic band gaps (Fig. 7(d)) and higher ionic conductivity.66 Furthermore, deprotonation toward the original g-C3N4 could be obtained by simple heating in inert atmosphere, which not only improved sintering for g-C3N4 photoelectrodes but also enabled a potential preservation of the higher surface area of the protonated material. Besides, by aid of protonation, other promising g-C3N4 based hybrid composites could also be facilely obtained by counteranion exchange, such as of artificial enzyme center and electrocatalytic oxygen-reduction center.

Several light elements have been covalently doped into g-C3N4. For example, we prepared phosphorus-doped polymeric g-C3N4 (see structure in Fig. 8(a)) by a co-condensation between DCDA and a phosphorus containing ionic liquid.66 Because the P-concentration was low, it was found that P replaced some corner- or bay-carbon places in the framework of g-C3N4, while the doping well retained most of the structural features of g-C3N4. But electronic features had been seriously altered. This provided not only a much better electric (dark) conductivity up to 4 orders of magnitude but also an improvement in photocurrent generation by a factor of up to 5. Wang et al. reported that boron- and fluorine-enriched g-C3N4 (see structure in Fig. 8(b), for clarity, fluorine atoms not shown) could be synthesized by using DCDA and 1-butyl-3-methylimidazolium tetrafluoroborate, which not only acted as a soft template to introduce mesoporous textural features but also enters the materials condensation scheme.67 They found the B atoms entered C sites in g-C3N4 with F saturating residual bonds. The resulting materials showed good photoactivity under visible light. In addition, if using NH4F as the dopant precursor, only F was doped into the framework of g-C3N4 by forming C-F bond (see structure in Fig. 8(c)).68 Zou et al. prepared boron-doped g-C3N4 (see structure in Fig. 8(d)) by heating melamine and the mixture of melamine and boron oxide, and found boron-doped g-C3N4 can promote photodegradation of Rh B because the boron doping improved the dye adsorption and light absorption of catalyst.69 Moreover, Chen et al. reported sulfur-doped g-C3N4 (see structure in Fig. 8(e)) by post treatment of pristine g-C3N4 at 450 °C in gaseous H2S atmosphere.70 In contrast to conventional anion doping of photocatalysts for wider light absorption at the cost of reduced redox potentials and/or charge-carrier mobility, their sulfur-doped g-C3N4 illustrated an increased valence bandwidth, an elevated conduction band minimum, and a slightly reduced absorbance as well. As a result, photoactivity of H2 evolution was 8.0 times higher than g-C3N4 under the visible light. In addition, the complete oxidation process of phenol under visible light was observed for sulfur-doped C3N4, which was impossible for pristine g-C3N4. Copolymerization provides another kind of covalent pathway to modify the electronic structure of g-C3N4. Zhang et al. reported the optical absorption of carbon nitride polymer could be
extendable into the visible region up to about 750 nm by simple copolymerization of DCDA with barbituric acid, and since some ring nitrogen was replaced by carbon (see structure in Fig. 8(f)), the identical C/N ratio is ca. 1:1.73 Consequently, after doping, the rate of H2 evolution in the visible light increase nearly 4 times. Using a post-functionalization strategy, Zou et al. coupled anhydride group into g-C3N4 framework through a amidation reaction (see structure in Fig. 8(g)), which offered a higher photocatalytic activity via an enhanced separation of the photoinduced electrons and holes.72 Therefore, in comparison with inorganic semiconductors, the diversity of organic chemistry would provide more possibility for a rational design of doped carbon nitride polymers with controlled functions for light-harvesting semiconductors.

Indeed, the pristine bulk g-C3N4 exhibited an ambipolar behavior, i.e., its flat-band did not sit in the vicinity of conduction-band (CB) like n-type semiconductors, or of valance-band (VB) like p-type semiconductors. In contrast to the aforementioned strong covalent or ionic interaction, by which the electronic structure of g-C3N4, e.g., edges of CB and VB significantly changed, we found that the weaker non-covalent interaction could be utilized to manipulate the flat-band potential up to 0.24 V by intercalating graphene (≤1 wt.%) into g-C3N4 sheets via a π–π stacking interaction.73 Consequently, in a photoelectrochemical cell configuration, a significant increase of either anodic or cathodic photocurrent from doped g-C3N4, was obtained in a controlled manner, respectively. For instance, when bias potential was 0.4 V (vs. Ag/AgCl), the anodic photocurrent could be 300% higher after doping. Complementary to ionic and covalent doping, such non-covalent doping, i.e., the third strategy would establish a more comprehensive understanding of the correlations between chemical doping and semiconducting performance of g-C3N4.

7. SUMMARY AND PERSPECTIVES

As a metal-free organic semiconductor, old polymeric carbon nitride solids have attracted many attentions again in the very recent years via revealing their potential applications in photovoltaic and photocatalytic fields. In comparison with their counterpart, the merits of carbon nitride family include but not limit to cheap price, facility in task-specific structure-engineering, and “noble” property (against oxidation in air at high temperature). However, in the initial attempts, the overall efficiencies of photoelectric conversion or photocatalytic water splitting are still rather low. The grain boundary effects and low crystallinity may be one of the most limited issues. Moreover, due to poor dissolvability in common solvents, finer details of local structure and composition of as-synthesized g-C3N4 are still lacking in many cases, which result also in limitations and uncertainties in potential applications. For example, it is not inevitably convincible to date which is the primary building block, tri-s-triazine or triazine of the carbon nitrides frameworks.22,39,44,74–77 In addition, the chemistry of the as-synthesized carbon nitride was hardly touched,62,70,72 which is reminiscent of the similar challenge of carbon nanotubes, suggesting some of the handicaps of g-C3N4 might be circumvented by post-functionalization. Besides, new synthesis method78 and new potential applications, such as oxygen-reduction reaction catalyst for fuel cells,79–80 and chemical sensor81 are also highly worthy of investigation for more comprehensive understanding and utilization of such unique carbonaceous materials. Nevertheless, all these challenges should be well addressed before polymeric carbon nitride solids become more widely used, which needs contributions from all chemists, physicists, and material scientists.

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References and Notes