Recent development in electronic structure tuning of graphitic carbon nitride for highly efficient photocatalysis

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Abstract: The utilization of solar energy to drive energy conversion and simultaneously realize pollutant degradation via photocatalysis is one of most promising strategies to resolve the global energy and environment issues. During the past decade, graphite carbon nitride (g-C$_3$N$_4$) has attracted dramatically growing attention for solar energy conversion due to its excellent physicochemical properties as a photocatalyst. However, its practical application is still impeded by several limitations and shortcomings, such as high recombination rate of charge carriers, low visible-light absorption, etc. As an effective solution, the electronic structure tuning of g-C$_3$N$_4$ has been widely adopted. In this context, firstly, the paper critically focuses on the different strategies of electronic structure tuning of g-C$_3$N$_4$ like vacancy modification, doping, crystallinity modulation and synthesis of a new molecular structure. And the recent progress is reviewed. Finally, the challenges and future trends are summarized.

Key words: g-C$_3$N$_4$; photocatalyst; electronic structure

1. Introduction

With the rapid development of the world economy and the increase of the population, the energy crisis and environmental pollution have gradually become the key challenges for the sustainable development of mankind. As a powerful and sustainable strategy, photocatalysis has been regarded as one of the most promising energy conversion processes to utilize green and inexhaustible solar energy for exploiting ideal fuels and simultaneously promoting environmental remediation[1–3]. As a critical part of the photocatalytic process, plenty of semiconductor photocatalysts, such as TiO$_2$, ZnO, Ag$_3$PO$_4$, SrTiO$_3$, BiVO$_4$ and CdS, etc., have been synthesized for different photocatalytic reactions during the past few decades[4–8]. However, most metal–oxide semiconductors can only respond to a small part of the solar spectrum due to their wide band gaps. Although metal sulfides, metal phosphides, and metal nitrides photocatalysts possess a narrow bandgap, the deleterious and volatile properties due to the photocorrosion and self-oxidation, severely limit their wide application in the field of photocatalysis[9]. Moreover, most photocatalysts are inorganic semiconductors whose optical and electronic properties can only be regulated in a small range. Thus far, the development of highly efficient semiconductor

photocatalysts has received extensive attention and gradually become a research hotspot.

In the development of robust visible-light-responsive photocatalysts for utilizing solar energy, graphitic carbon nitride (g-C$_3$N$_4$), a metal-free polymeric semiconductor with triazine or heptazine as a basic structural unit (Fig. 1)[10], has gradually opened up a new vision in the photocatalytic field since it was first used in solar water splitting by Wang and coworkers[11]. Lately, g-C$_3$N$_4$ has attracted extensive attention in the scientists working in the field of photocatalysis owing to its advantageous characteristics, such as good physicochemical stability, non-toxicity, appropriate electronic band structure with visible light response, composition of earth-abundant elements and easy functionalization. g-C$_3$N$_4$-based materials are believed to be the most promising candidates for environmental and energy-concerned photocatalytic applications[9, 10]. However, several obstacles and shortcomings that impede its industrial applications have been discovered, such as high recombination rate of charge carriers, poor visible light responsiveness, low electrical conductivity, relatively small solvent-accessible surface area, and low intrinsic quantum efficiency. Therefore, to optimize the photocatalytic properties and performances of g-C$_3$N$_4$, much research has been dedicated to developing highly crystalline, porous, doped, heterostructured or composite g-C$_3$N$_4$ based materials to achieve target-specific applications[3, 12–14]. In most cases, it is an effective strategy to enlarge light harvesting, reduce the charge recombination rate and improve photocatalytic performance of g-C$_3$N$_4$ by modulating its electronic structure, which can tune the band

Chao Li and Jie Li contributed equally to this work.

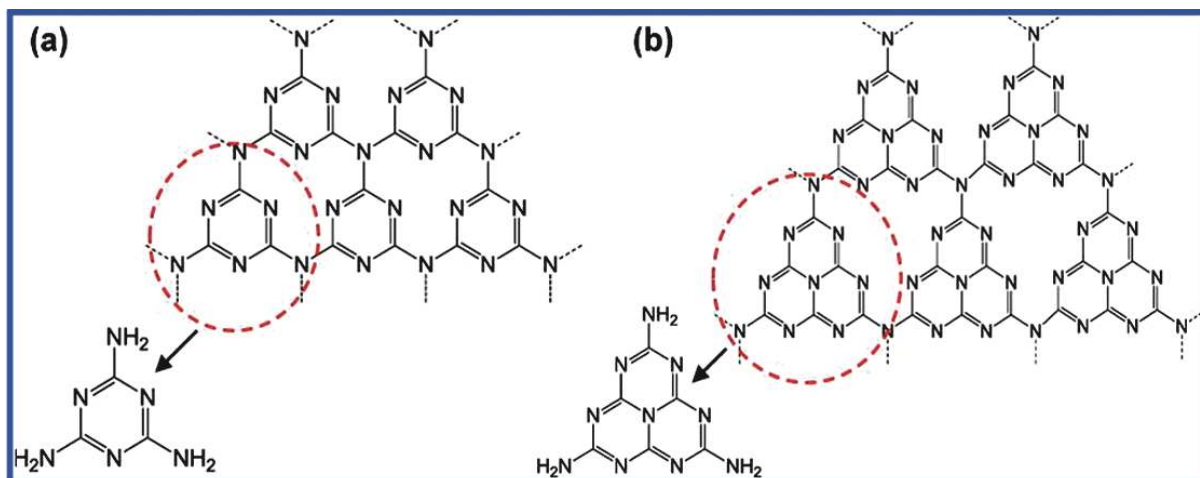Correspondence to: Y B Huang, huangyb@hebeu.edu.cn; J Liu, liujun1993@semi.ac.cn; Z J Wang, wangzj@semi.ac.cn

Fig. 1. (Color online) The schematic structure of triazine (a) and tri-s-triazine (heptazine) (b) in g-C_3N_4. Reprinted from Ref. [10].
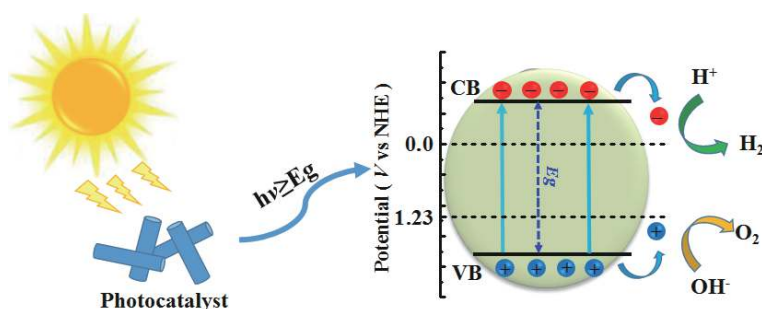

Fig. 2. (Color online) The process of overall solar water splitting over a semiconductor photocatalyst.

positions, narrow the band gap, broaden the visible-light absorption range and improve the separation and migration rate of charge carriers.

Up to now, although many interesting reviews on the strategies to improve the photocatalytic property of g-C_3N_4 have been reported, a crucial review focusing on the electronic structure tuning of g-C_3N_4 is lacking to provide the researchers with a panorama of the latest advances in this field. Herein, we present a comprehensive and updated review on the most recent progress in the electronic structure tuning of g-C_3N_4 for highly efficient photocatalysis. The diverse design and regulation strategies for optimizing the electronic structure of g-C_3N_4 are elaborated on and the effect of the electronic structure tuning on the properties and photocatalytic activities of g-C_3N_4 are also summarized. Moreover, this review will present some novel insights on the crucial challenges, opportunities, and inspiring perspectives for the design of highly efficient g-C_3N_4-based photocatalysts, which should be a guide for future research in this hot area.

2. Role of electronic structure modulation in optimizing the photocatalytic activity of g-C_3N_4

It is a well-known fact that modulating the electronic structure of g-C_3N_4 serves as a key strategy to optimize not only light absorption ability but also the redox reaction kinetics. Precisely, according to semiconductor theory, a semiconductor material can only absorb the photons whose energy is equal to or greater than its bandgap energy. As shown in Fig. 2, when it was used as a photocatalyst and exposed to sunlight, the electrons can be excited to the higher conduction band

(CB) and participate in reduction reactions, resulting in the formation of holes in the valence band (VB) where they can take part in oxidation reactions. Usually, if a semiconductor has a large bandgap energy (>2.8 eV), it can only absorb solar light in the ultraviolet (UV) region (λ < 420 nm), which is only about 5% of the total solar spectrum. While if a semiconductor material has a small bandgap energy (0 < E_g < 2.8 eV), its absorbable spectrum can reach the visible region (420 < λ < 780 nm) or near-infra-red (NIR) region (780 < λ < 2500 nm), which accounts for about 43% and 52% of the total solar spectrum, respectively[15, 16]. Moreover, midgap defective states induced by defects or doping can also affect the light absorption efficiency of semiconductor materials[17, 18]. Therefore, the light absorption ability of semiconductor material depends strictly on its electronic structure. And as a semiconductor, the light absorption ability can be effectively optimized by regulating the electronic structure of g-C_3N_4. Furthermore, the redox abilities of the system are critically related to potential edges of the semiconductor photocatalysts. A photocatalyst with more positive VB or negative CB can foster the charge carriers' kinetics and cause greater force to drive photocatalytic reactions. Also, the appropriate potential edges can endow the photocatalyst with optimal redox abilities[17]. Therefore, through modulating the electronic structure of g-C_3N_4, the redox ability and light absorption property can be effectively optimized, and in turn increase the surface photoreaction kinetics.

3. Strategies of electronic structure tuning

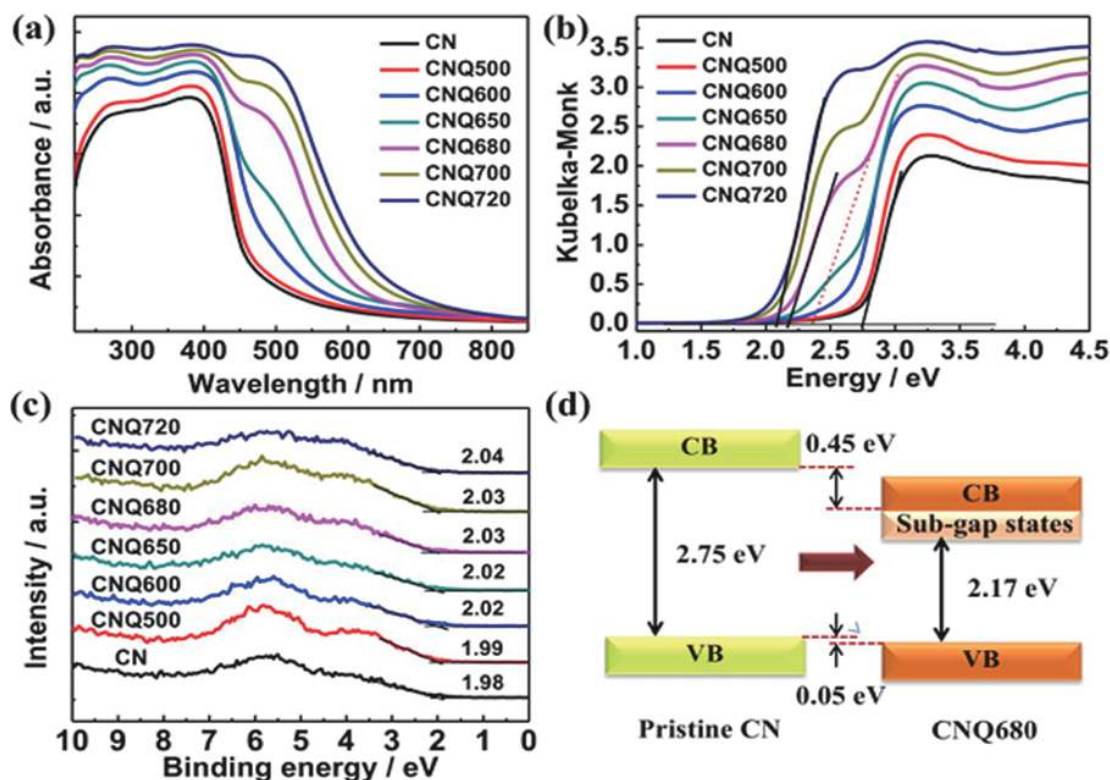The photocatalytic properties of materials are directly re-

Fig. 3. (Color online) (a) The UV–vis absorption spectra, (b) converted Kubelka–Munk vs. light energy plots and (c) XPS valence band spectra of CN and CNQs. (d) The schematic band structures of CN and CNQ 680. Reprinted from Ref. [22].

lated to their electronic structures, which determine the spectral response properties and chemical kinetics of photocatalysts. In recent years, with the development of materials science and engineering, electronic structure tuning has received a lot of attention, especially in the field of photocatalysis. Ever since it has been used as a photocatalyst, tremendous effort has been devoted to designing and optimizing the photocatalytic performances of g-C_3N_4. The approaches, including vacancy modification, doping, crystallinity modulation and synthesis of new molecular structure, are the main strategies to tune the electronic structure of g-C_3N_4.

3.1. Vacancy modification

Recent studies found that defect engineering by the introduction of carbon and/or nitrogen vacancy defects into the motif of g-C_3N_4 has a pronounced effect on its electronic structure and photocatalytic performance, which is mainly due to that the VB and CB of g-C_3N_4 are composed of nitrogen P_Z orbitals and carbon P_Z orbitals, respectively[11]. The calculation based on DFT had found that a mid-gap energy level has appeared above the VB when the N vacancy was introduced into the framework of g-C_3N_4[17, 19]. Moreover, the C or N defects can serve as trapping and active sites to improve the separation of photo-generated carriers, and enhance the adsorption ability of g-C_3N_4 to the reactant. For example, Li and coworkers recently designed a N-vacancy-rich g-C_3N_4, and found that N vacancies acted as active sites, which could obviously promote the adsorption of CO_2 during the CO_2 reduction[20]. Therefore, the appropriate introduction of vacancies into the framework of g-C_3N_4 can regulate its band structure effectively, and improve the light-responding range and photocatalytic performance, simultaneously.

In order to investigate the effect of band structure chan-

ging, induced by vacancy defects on light absorption of g-C_3N_4, Yang and coworkers synthesized a N-vacancy-rich g-C_3N_4 through a hard template method with a high pressure and high temperature (HPHT) technique. The measurements showed that the bandgap energy of the resulted sample was significantly narrowed and reduced from 2.97 to 1.88 eV due to the up-shifted VB and down-shifted CB edge potential. As a result, the light-responding range of N-vacancy-mediated g-C_3N_4 was greatly extended and showed a maximum absorption of 660 nm[21]. At the same time, Zhai and coworkers reported distinctive defect engineering to introduce a large amount of N defects into g-C_3N_4. As shown in Fig. 3, when the N vacancies were introduced into the framework, the light absorption edge was extended to above 500 nm and the absorbance was enhanced with the increase of the concentration of nitrogen vacancy. The DFT calculations suggested the newly occurred light absorption edges were mainly attributed to the defect energy level in the bandgap originated from the introduced nitrogen vacancies[22].

Generally, the C or N defects can be successfully introduced into the framework when the bulk g-C_3N_4 is thermally treated under H_2, Ar, NH_3 or N_2 atmosphere[23]. For example, Zhou and coworkers presented a novel route to prepare N- vacancy-rich g-C_3N_4 by heating the bulk g-C_3N_4 to different temperatures under N_2 conditions. This rich N vacancy in g-C_3N_4 produce an obvious electron-deficient effect, which not only contribute to stabilizing the Pt single atom, but also endow the Pt single atom with an optimized geometric and electronic structures for capturing electrons and producing hydrogen[24]. However, the post treatment strategy by gas etching is time-consuming and difficult to control the defects. Moreover, the inappropriate defect location and defect

Fig. 4. (Color online) Schematic illustration of synthesis methods of DTLP-CN via thermal polymerization of melamine, urea, and KOH. Reprinted from Ref. [25].

concentration may not only destroy the lattice structure of g-C_3N_4 but also impede the separation and transportation of photo-generated carriers, which finally deteriorate the photocatalytic performance of g-C_3N_4. Therefore, it is very necessary to develop new, facile and controllable strategies for the synthesis of g-C_3N_4 with appropriate defects and significantly improved photocatalytic activity.

To meet this challenge, many new defect engineering strategies that can control the concentration of the defect have been developed. As shown in Fig. 4, our group has designed a novel and facile urea and KOH-assisted thermal polymerization (UKATP) strategy for the preparation of defect-modified thin-layered and porous g-C_3N_4 (DTLP-CN), wherein the thickness of g-C_3N_4 was dramatically decreased, and nitrogen vacancies, cyano groups and mesopores were simultaneously introduced. Especially, the roles of N defects and structures of g-C_3N_4 can be targeted, regulated and optimized by changing the mass ratio of precursors. Consequently, the band structure and charge carrier transportation of g-C_3N_4 were well-optimized, and the photocatalytic hydrogen evolution performance of the DTLP-CN was significantly improved more than 48.5 times with the average apparent quantum yield (AQY) of as high as 0.82% at 500 nm[25]. Similarly, the facile ammonium salt (($NH_4)_2S_2O_3$, ($NH_4)_2SO_4$ or ($NH_4)Cl$) or alkali (KOH or NaOH)-assisted thermal polymerizing of nitrogen-rich precursors to C/N vacancy g-C_3N_4 are designed, and the concentration of vacancy can be adjusted by changing the composition and proportion of the precursor[17, 26–28]. As a result, the prepared deficient g-C_3N_4 displayed vacancy amount-dependent electronic structure and photocatalytic performance. In addition, Wang and coworkers recently prepared a carbon-deficient g-C_3N_4 (V_C-OCN), and the C vacancy concentration could be well-controlled by changing the formaldehyde dosage. The experimental results and theoretic calculations revealed that the bandgap of V_C-OCN was decreased with increasing the amount of C vacancies, which was mainly due to the mid-gap state induced by C vacancies[29].

3.2. Doping

Owing to regulating the physical-chemical property of semiconductors effectively, doping is widely used to optimize the photocatalysts for efficient solar energy conversion. Recently, doping has been proven as a valid method to regulate the electronic structure of g-C_3N_4, which can be facilely realized by incorporating foreign elements or a structure-matching organic group into the framework of g-C_3N_4[9, 30]. Generally, according to the impurity types, the strategies of g-C_3N_4 doping can be mainly divided into two types: heteroatom doping and molecular doping[31]. Specifically, elemental doping that can be realized by replacing the C or N atoms with non-metal elements or by implanting metal ions into the motifs of g-C_3N_4, which plays an essential role in tuning the electronic structure and the positions of the VB and CB of g-C_3N_4 on account of the hybridization between the dopant orbitals and the molecular orbitals of g-C_3N_4.

Many non-metal elements, such as O, B, P, S, F, Br and I, have been incorporated into the motif of g-C_3N_4[32–35]. As shown in Fig. 5(a), our group prepared O-doped g-C_3N_4-based photocatalysts by a one-step calcination method of combing oxalic acid and urea as a precursor. The X-ray photoelectron spectroscopy (XPS) study showed that N atoms could be replaced by O or C for O-g-C_3N_4. Moreover, as shown in Fig. 5(b), the bandgap of g-C_3N_4 was narrowed efficiently by doping oxygen, which can enhance the utilization of visible light significantly. Further characterization showed that the composite photocatalyst showed a synergistic effect for improving the photocatalytic degradation of a representative antibiotic, lincomycin, both in the degradation rate and the degree of decomposition[36]. In addition, Qiao and co-workers found that P atom doping could induce empty mid-gap states, and the doped PCN exhibited much better electronic structure and light absorption[37]. Recently, boron-doped and nitrogen-deficient g-C_3N_4 were successfully synthesized by simply calcining the mixture of g-C_3N_4 (or melamine) and $NaBH_4$ (or KHB_4) in a nitrogen atmosphere. The DFT calculation results showed that the bandgap was decreased after introduction of defects. And further narrowing could be observed when the B atom was doped in the framework of g-C_3N_4. These mainly attribute to the downward shift of CB caused by the defect and B doping. It is demonstrated that the electronic structure of the obtained samples can be effectively modulated by the doped element and N defects. As a res-
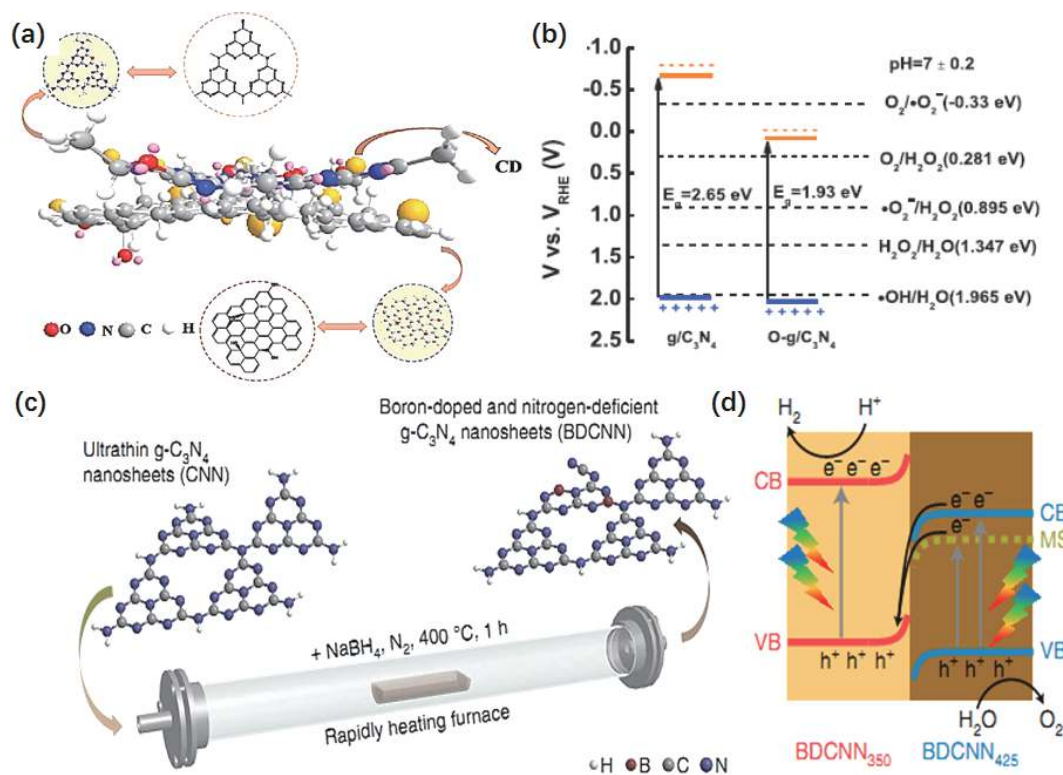
Fig. 5. (Color online) (a) Schematic structure of the O-doped g-C₃N₄-based photocatalyst. (b) Band structure diagrams of g-C₃N₄ and O-doped g-C₃N₄. (c) Schematic of the fabrication of BDCNN originated from CNN and (d) the charge-transfer process in BDCNN-based heterojunction upon light irradiation. Reprinted from Refs. [36, 40].

ult, the optimized g-C_3N_4 exhibited noticeable enhancement in photocatalytic activity for O_2 (or H_2O_2) evolution[38, 39]. More recently, using a similar method (Figs. 5(c) and 5(d)), Zhao and coworkers designed and fabricated ultrathin g-C_3N_4 and B-doped g-C_3N_4 with well-optimized and properly aligned band structures for H_2 and O_2 evolving photocatalysts, and constructed a Z-scheme water splitting system via an electrostatic self-assembly strategy. As shown in Fig. 3(b), this g-C_3N_4 self-based heterostructure showed enough driving force for the water redox reactions and achieved a solar-to-hydrogen efficiency of 1.16%[40].

Similar to the non-metal doping, the introduction of metal atoms such as Na, K, Fe, Co, Cu, Mn, Zn, Ni, and Ag into the framework of g-C_3N_4 is also a successful strategy to modulate the band structure, extend the light absorption and improve the photocatalytic performance of g-C_3N_4[3, 41−44]. To understand the synergy of metal doping and electronic structure, Yan and coworkers successfully prepared metal-atom-doped g-C_3N_4 via a simple polymerization reaction of metals (Na, K, Ca, Mg) with urea during the calcination process. As shown in Fig. 6, the results demonstrated that the implantation of O and metal atoms into the structure of g-C_3N_4 could regulate the band position, narrow the band gap, and extend the visible-light response range effectively[45]. Moreover, Ding and coworkers also found that incorporation of transition-metal ions such as Fe^{3+}, Mn^{3+}, Cu^{2+}, Co^{3+} and Ni^{3+} into the framework of g-C_3N_4 can obviously tune the band structure and broaden the visible-light absorption range[46]. Furthermore, due to the different role between metal and no-metal elements, recent strategies of dual doping have been developed to improve the photocatalytic performance of g-C_3N_4. Yu and coworkers synthesized a P and Na co-doped g-C_3N_4, which showed a remarkably improved photocatalytic performance resulting from the improved charge carriers transfer and separation. Further experimental and theoretical results revealed that such improvement was mainly attributed to the doping elements and the optimized electronic structure[47]. Although the moderate introduction of metallic impurities can tune the electronic structure and modify the photocatalytic performance of g-C_3N_4, many experiment and calculation results reveal that excessive metal doping may create a new energy band which might work as a recombination center and reduce the thermal stability of the ion[3].

From the above studies, we can conclude that the electronic structure and photocatalytic properties of g-C_3N_4 can be modulated by doping of non-metal or metal elements, however, there are still many problems to be solved, such as the presence of surface trapping center, doping site, lower oxidizing and reducing ability. Additionally, many defects may originate from the excessive doping of metals and non-metals, which may reduce the separation performance of charge carriers because of doping asymmetry[3, 48, 49]. Therefore, further attention should be paid for developing new doping methods, which can optimize the properties of g-C_3N_4 better and achieve higher solar energy conversion efficiency.

3.3. Crystallinity modulation

The performances of g-C_3N_4, such as band structure, charge carrier migration, absorptivity and photoelectronic characteristics, can be effectively optimized by regulating its crystallinity, thus, the degree of crystallinity is closely related to the photoelectrochemical property of semiconductor[13, 50]. Usually, the high crystalline degree of g-C_3N_4 can be realized by temperature control or the molten-salt method, which
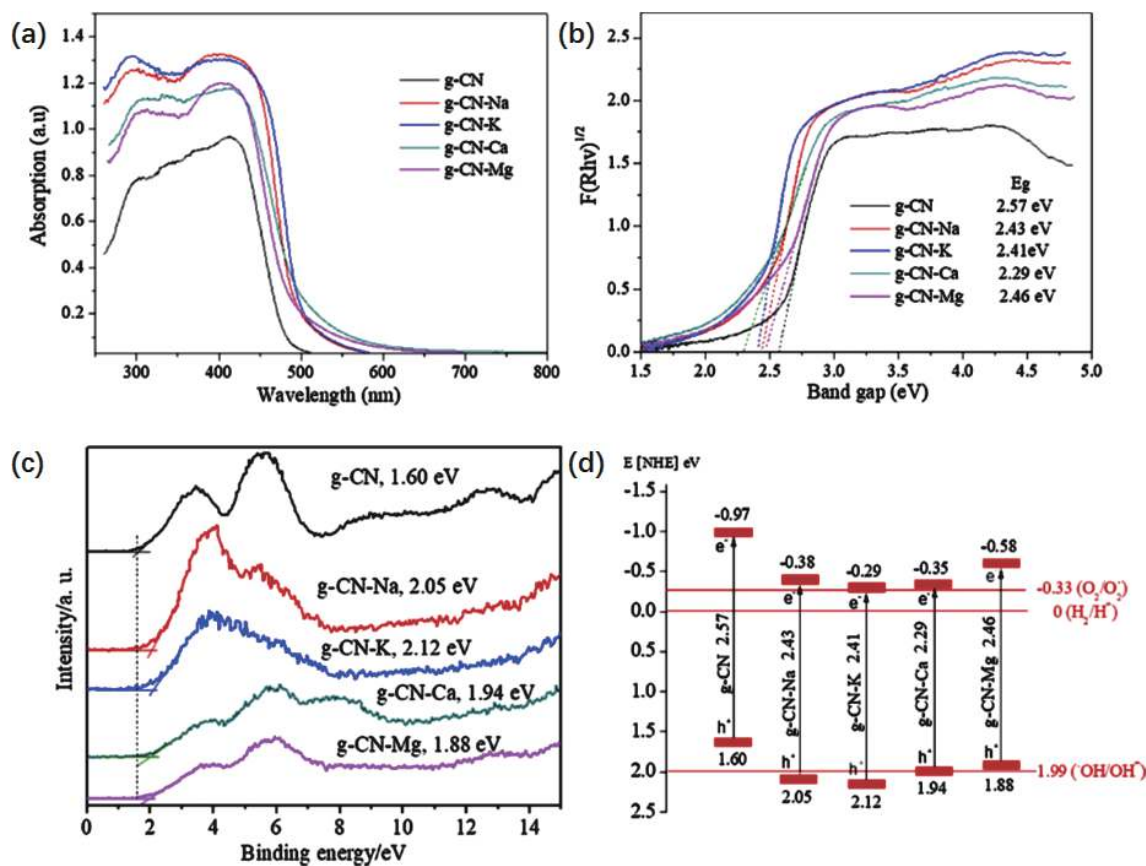
Fig. 6. (Color online) (a) UV–vis diffuse reflectance spectra, (b) the band gap from $(ahv)^{1/2}$ vs. photon energy, (c) valance band XPS spectra, and (d) schematic illustration of the band gap structure of pristine and doped g-C_3N_4 samples. Reprinted from Ref. [45].

may lead to a decrease of the π–π stacking distance and narrowing of the band gap, resulting in higher charge separation efficiency and improved solar energy utilization. Therefore, enhancing the crystallinity is also a strategy to tune the electronic structure of g-C_3N_4.

In order to understand the effect of crystallinity on the electronic structure and photocatalytic performance of g-C_3N_4, Zhang and coworkers proposed a facile ion thermal strategy to enhance the crystallinity of g-C_3N_4 where most of the photons can be used to drive photocatalytic reactions. The measurements demonstrated that this thermal condensation in the molten salt method can result in highly crystalline g-C_3N_4 with a maximum π–π layer stacking distance of 0.292 nm. Moreover, the band gap can be regulated from 2.74 to 2.56 eV by the addition of oxamide. As a result, the visible-light response range of CN-OA-m is extended to 700 nm and its H_2 evolution activity is dramatically improved[51]. In another example, Zhang and coworkers reported a simple post calcination method that utilized NaCl/KCl as eutectic salts to modulate the polymerization process and optimize the crystallinity of g-C_3N_4. After post-modification (Figs. 7(a) and 7(b)), the measurements showed that the band-gap of CN-NaK was decreased to 2.58 eV, which is 0.17 eV less than that of pristine g-C_3N_4. This study provides a simple and rational manner to modulate the electronic structure and activity of g-C_3N_4[52]. Moreover, Xu and coworkers reported a solid-salt-assisted growth strategy to synthesize highly crystalline polymer carbon nitride (CPCN). The results show that the high crystallinity endows CPCN with a wide and sharp light absorption, which is mainly attributed to the shift of valence-band, indicat-

ing that the electronic structure can be changed by this method[53]. Additionally, Yuan and coworkers presented a one-step ion-thermal strategy to fabricate crystalline carbon nitride with cyan-amide. As shown in Figs. 7(c) and 7(d), the measurements indicate that the texture and electronic band structure of g-C_3N_4 could be facilely tuned by changing the dosage of KCl[54]. Recently, in order to investigate the effect of the pre-heated temperature of a precursor on crystalline g-C_3N_4, Lin and coworkers prepared crystalline g-C_3N_4 under different temperatures. The measurements showed that the crystallinity of the samples was improved with the increased pre-heated temperature up to 550 °C, and the light absorption and the photocatalytic performance of the samples showed the similar trend[55]. Therefore, rationally engineering the crystalline degree of g-C_3N_4 offers excellent opportunities for optimizing its band structure and photocatalytic activity.

3.4. Development of new molecular structure

Carbon nitride is usually composed of triazine building units, which forms melon or crystallinity-modulated poly triazine imide (PTI) and poly heptazine imide (PHI)[56]. The ideal structure of triazine-based carbon nitride is C_3N_4, which has a N/C ratio of 1.33 due to the covalently crosslinked sp2 hybridized C and N atoms[11]. However, the recent investigations show that the C : N stoichiometry can be varied according to experimental conditions, which plays an important role to regulate the properties of the finally evolved carbon nitrides in C_xN_y (x, y: number of C and N)[57]. Specifically, the nitrogen content had been considered critical to regulate the electronic band structure of carbon nitride. Therefore, as
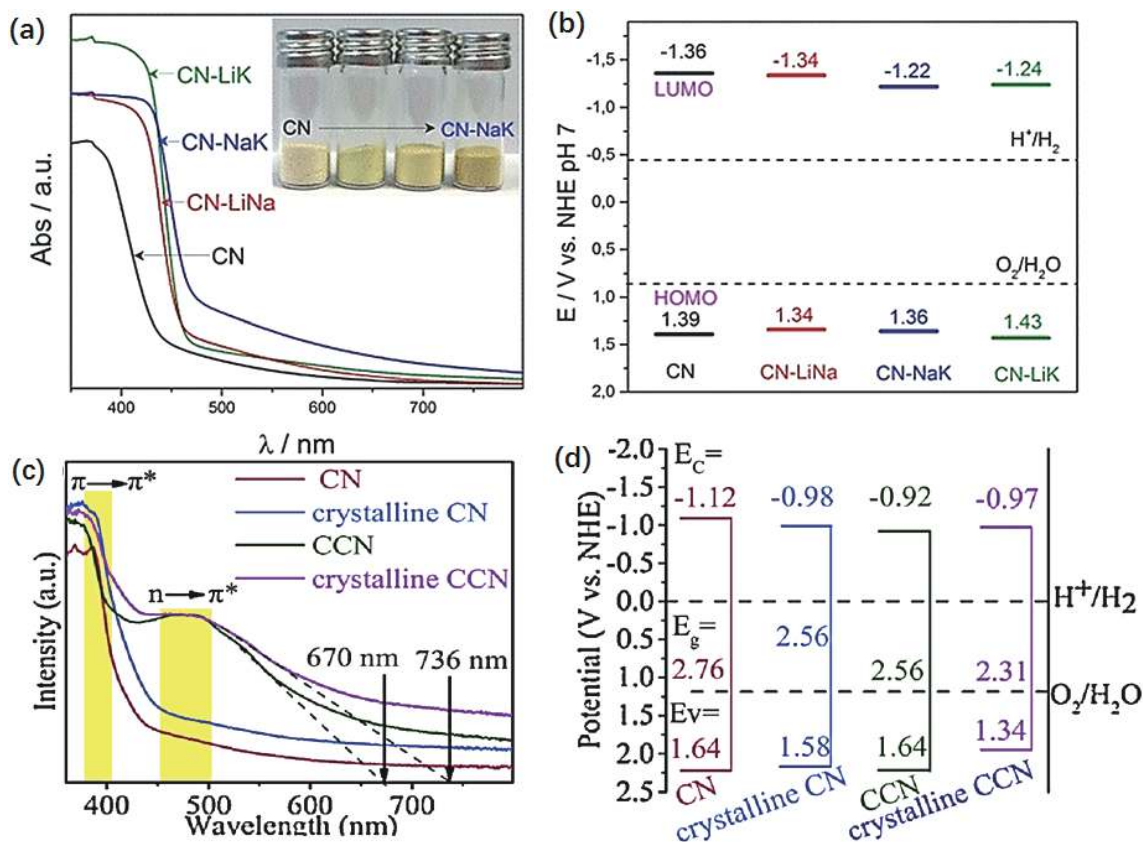
Fig. 7. (Color online) (a) UV–visible diffuse reflectance spectrum (DRS) and (b) HOMO and LUMO positions of CN, CN-LiNa, CN-NaK, and CN-LiK. (c) UV–vis DRS and (b) bandgap structures for CN, crystalline CN, CCN and crystalline CCN. Reprinted from Refs. [52, 54].
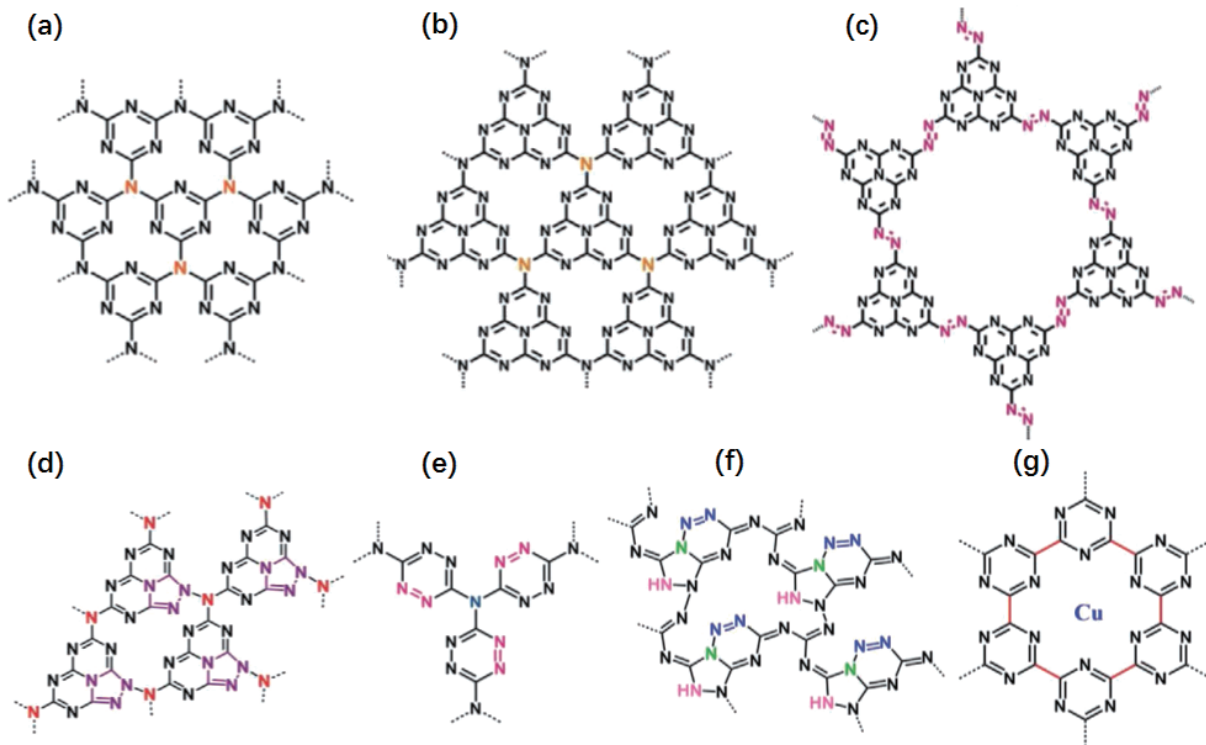

Fig. 8. (Color online) Schematic illustrations of basic structural units of polymeric carbon nitride with different C and N stoichiometric ratios: (a) triazine-based graphitic carbon nitride, (b) heptazine-based graphitic carbon nitride, (c, d) polymeric C_3N_5, (e) C_3N_6, (f) C_3N_7, and (g) C_3N_3. Reprinted from Ref. [56].

shown in Fig. 8, in order to develop robust visible-light-active carbon nitride with a tunable band gap, many efforts have been put into development of new molecular structure of carbon nitride with different C and N stoichiometric ratios, such as C_2N, C_3N, C_4N, C_3N_5, C_3N_6 and C_3N_7 etc. for solar energy conversion[56, 58–62].

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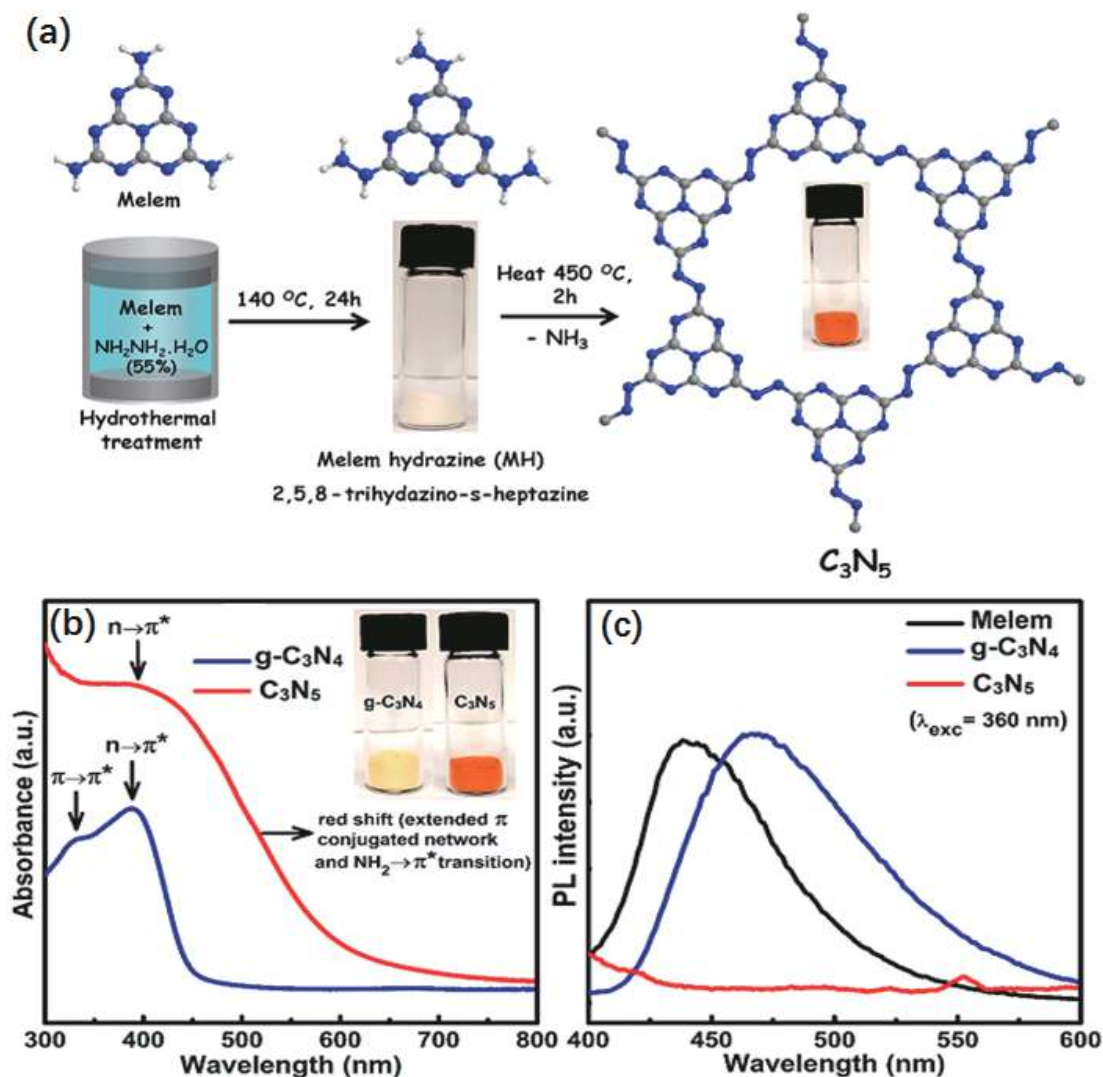
Fig. 9. (Color online) (a) Synthesis scheme of C_3N_5. (b) UV–Vis DRS for C_3N_5 compared with bulk g-C_3N_4. (c) Steady-state PL spectra of melem, g-C_3N_4 and C_3N_5. Reprinted from Ref. [61].

Recently, C_4N has attracted significant attention as a new class of low-band-gap polymeric carbon nitride owning to its excellent physiochemical properties for efficient solar energy conversions. Li and coworkers firstly fabricated the exfoliated C_4N nanosheets for highly efficient oxygen reduction via a top-down method. The obtained C_4N demonstrated a small band gap of 1.41 eV and an extended absorption band at around 500 nm due to n→π* transition[63]. Those are markedly different from that for g-C_3N_4. Moreover, Fang and coworkers reported a facile synthesis of narrow-band-gap C_4N particles, which were used as bifunctional oxygen catalysts for a visible-light-sensitive, rechargeable Zn-air battery and polymer-air battery. Compared to g-C_3N_4, C_4N exhibits a smaller band gap of 1.99 eV with a broadened absorption spectrum and strong UV-vis absorption, and an appropriate band structure, which endows C_4N the efficient photocoupling for enhancing the oxygen reaction[60]. As shown in Fig. 9, Kumar and coworkers reported a modified carbon nitride framework with C : N stoichiometric ratio of 3 : 5 via a novel thermal deammoniation of 2,5,8-trihydrazino-s-heptazine. Characterization investigations demonstrated that the obtained C_3N_5 framework was constructed by heptazine moieties bridged with azo linkage (−N=N−), which led to the over-

lap between the p orbitals of N atoms in the azo bond and π system of heptazine motif, and resulted in the significant decrease of its band gap to 1.76 eV. As a result, the C_3N_5 exhibited a superior visible-light catalytic activity for solar water splitting and sensing of acid molecules[61]. Besides, C_3N_5 was also synthesized and used as an activator for peroxymonosulfate. Due to the excellent chemical and electronic structure, the C_3N_5 showed an excellent peroxymonosulfate activation capacity for emerging micropollutants degradation, even better than common g-C_3N_4[64]. In addition, metal-free half-metallic carbon nitride including C_2N and C_3N with a proper band structure has also been fabricated and used for solar energy conversion[58, 59, 65].

4. Conclusions and perspectives

In this review, the strategies and recent progresses in the electronic structure tuning of g-C_3N_4 for highly efficient photocatalysis are summarized, which is critical for highly efficient solar energy conversion, such as water splitting, organism degradation, and CO_2 reduction, etc. Specifically, the regulation strategies based on vacancy modification, doping, crystallinity modulation and molecular structure construction are elaborated in detail. Thus, with the rational designing and

modifying of the electronic band structure of g-C$_3$N$_4$, the light harvesting, charge separation and photocatalytic properties of g-C$_3$N$_4$ would be dramatically enhanced. This review provides a multi-angle cognition to cater to actual production demand in the field of solar energy conversion.

Despite plenty of progress on electronic structure having been made, there are some trends or challenges of pivotal issues, which are elaborated on in the following:

(1) As summarized above, various strategies have been demonstrated to tune the electronic band structure of g-C$_3$N$_4$ so as to improve light harvesting and accelerate photo-generated carriers transfer kinetics for enhanced photocatalysis. Nevertheless, the approaches that synergistically use different regulatory strategies to precisely regulate the different features of g-C$_3$N$_4$ need to be researched further.

(2) With the development of g-C$_3$N$_4$ research, the strategies that combine the regulation of electronic structure with the construction of g-C$_3$N$_4$-based heterostructure have attracted great attention. However, the synergetic effect and interaction mechanism of the different components have not been clearly elucidated. Therefore, much attention on new experimental methods and theoretical calculations should be paid to clarify these problems.

(3) Although it is believed that g-C$_3$N$_4$ has strong chemical and thermal stability, the existing photocatalytic decays are often ignored when the electronic structure is modulated. Therefore, the stability of modified g-C$_3$N$_4$ should be of concern for future research.

Acknowledgements

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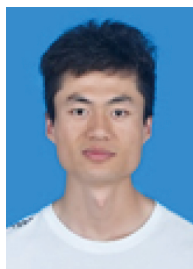
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