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**Structural and Environmental Modulation on
Graphitic Carbon Nitride Materials for Efficient
Photocatalytic Hydrogen Evolution**

（構造及び反応場を制御したカーボンナイトライド
光触媒による水素生成に関する研究）

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Abstract

Photocatalytic H₂ evolution represents a promising technology for solar energy conversion and storage and therefore attracts enormous interest. Among various photocatalysts, graphitic carbon nitride (g-C₃N₄) has recently emerged as an attractive photocatalyst for H₂ production because of its unique properties, including suitable energy band structure for water reduction, high chemical and thermal stability, and cost effective metal-free composition. However, due to insufficient light absorption, fast electron-hole recombination and kinetic limitation in proton reduction, the photocatalytic performance of g-C₃N₄ for H₂ evolution still remains moderate. In this work, the object is to design and develop g-C₃N₄-based materials via structure engineering and reaction environment modulation towards superior photocatalytic activity for H₂ evolution and thus to further the understanding of g-C₃N₄-based materials as well as the corresponding mechanism of photocatalysis.

In chapter 1, an overview of photocatalysis, including photocatalytic water splitting, photocatalytic pollutant degradation and CO₂ photoreduction, was introduced firstly. As followed, a review of strategies to modify photocatalysts for more efficient photocatalysis was also given. At the end, the photocatalysis of g-C₃N₄-based materials was summarized.

In chapter 2, to extend the light absorption and to improve the carrier separation and transfer, the defect-modified g-C₃N₄ (DCN) was prepared by a NaBH₄ treatment at low temperatures (< 350 °C) in an Ar atmosphere. It was found that the resultant DCN not

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only showed much red-shifted absorption edges, but also exhibited both n- and p-type conductivities due to the implantation of cyano terminal $\text{C}\equiv\text{N}$ electron-acceptor groups, resulting in the generation of p-n homojunctions. Such homojunction structured DCN photocatalysts were demonstrated to highly efficient in the transfer and separation of photoexcited carriers and consequently presented much enhanced photocatalytic H_2 evolution activity under visible-light. The findings provide an insight into the defect-related issues of g- C_3N_4 materials and might represent a promising route for the rational design of photocatalysts with unique architectures for more efficient solar energy conversion.

In chapter 3, considering the atomic order degree in solid-state materials is crucial for the efficient separation and transfer of photogenerated charge carriers, g- C_3N_4 with improved in-plane ordering was prepared via a spatially confined poly-condensation process using self-assembled heptazine hydrate as the precursor. It was shown that the improved in-plane ordering rendered the as-prepared g- C_3N_4 much increased electron delocalization within the π -conjugated aromatic rings and meanwhile highly improved carrier separation and transfer. As a result, such material exhibited a high hydrogen evolution rate of 420 $\mu\text{mol/h}$ with an apparent quantum efficiency of 8.9% at 420 nm, which was about 14 times higher than that of reference g- C_3N_4 (prepared without structure modulation). These findings emphasized the significance of the molecular ranging regularity of g- C_3N_4 for the efficient photocatalysis.

In chapter 4, a natural photosystem inspired phosphate environmental (precisely, HPO_4^{2-} ions) modulation was further explored to improve the photocatalytic H_2 production over g- C_3N_4 nanosheets under visible light irradiation. With the optimal

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addition of HPO_4^{2-} , a H_2 evolution rate as high as $947 \mu\text{mol h}^{-1}$ was achieved for g- C_3N_4 nanosheets (with the apparent quantum yield of 26.1% at $420 \pm 14.5 \text{ nm}$) which was about 16 times higher over that of bulk g- C_3N_4 . Evidenced by photoelectrocatalytic analysis and theoretical calculations, such significant improvement in H_2 production relied on the synergy of enhanced proton reduction and improved hole oxidation. More importantly, the phosphate was confirmed to indeed play roles resembling those in natural photosynthesis: as a proton pump to facilitate the proton transfer in reaction solutions, and as a mediator that participates directly in proton reduction, thus leading to a Calvin-cycle-like H_2 -evolution pathway.

In chapter 5, an overall summary of this dissertation work was provided. This thesis revealed that, the structure engineering and reaction environment modulation on g- C_3N_4 are of significance to improve its activity for photocatalytic H_2 evolution, which not only effectively affect the intrinsic properties of g- C_3N_4 (such as band structure, electronic configuration), but also cast profound impacts on the photocatalytic H_2 evolution pathway. Furthermore, the findings in the study deepen the understanding of g- C_3N_4 -based materials, aid to shed light on the mechanism of photocatalysis and importantly, highlight some universal design principles to efficient photocatalysis

Chapter 1 Introduction

1.1 Photocatalysis

Economic and environmental concerns raised by the extensive use of fossil fuels have made alternative energy sources more attractive. Among the wide variety of ways explored for renewable energy production, artificial photocatalysis represents a promising technology for the conversion and storage of solar energy. During the past decades of year, artificial photocatalysis has been achieved substantial progress and found wide applications in various fields, such as water/air purification,^{1, 2} photocatalytic water splitting to produce hydrogen and/or oxygen,³⁻⁵ photo-conversion of CO₂ into hydrocarbons,⁶⁻¹⁰ organic photosynthesis,¹¹ and photoelectric conversion,^{12, 13} etc.

Although photocatalysis involves in various chemical reactions as presented above, the intrinsic mechanism accounted is universal.¹⁴ Ignoring the conservation of crystal momentum, electrons located in the valence band (VB) of a semiconductor are excited by photons which have energy greater than the band gap of the semiconductor ($E_{\gamma} \geq E_{BG}$); the energy difference between the top of the filled valence band and the bottom of the empty conduction band (CB). As illustrated in Figure 1.1, the photoexcited electrons are promoted from the top of the VB to the bottom of the CB, simultaneously leaving positively charged holes in the VB. This movement of charge naturally generates a photovoltage, approximately equal to the band gap of the semiconductor. After such generated carriers migrating to the surface of semiconductor, VB holes then act as strong

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oxidisers (electron donor $D \rightarrow D^+$), and CB electrons as strong reductants, for redox reactions with water, or contaminants (electron acceptor $A \rightarrow A^-$). Often however, electrons and holes recombine rapidly before reacting with water/contaminants at the surface, releasing the input energy (light) in the form of heat or fluorescence. Here, it should be noted that, not all the photocatalytic reaction are the light energy stored. From the view of thermodynamics, both spontaneous ($\Delta G < 0$) and non-spontaneous reactions ($\Delta G > 0$) could be driven by photocatalysis. In the former case, the input photon energy is used to overcome the activation barrier of the reaction *via* the excitation of electrons in photocatalysts so as to facilitate the reaction at an increase rate. As for the latter case, apart from the activation process of the reaction involved, the light energy could be converted into chemical energy and stored in the final reaction productions, like photocatalytically splitting water into hydrogen and oxygen. Considering solar light is a free, abundant and clean energy source, any photocatalysis-induced reactions should be energy-saved. What is more, in one year, around 3,850,000 EJ of solar radiation would be absorbed by earth, which is several orders of magnitude higher than our current energy consumption (around 474 EJ per year). Utilizing this power efficiently *via* artificial photocatalysis to provide us with enough clean, renewable energy, would be important for the development of human society.

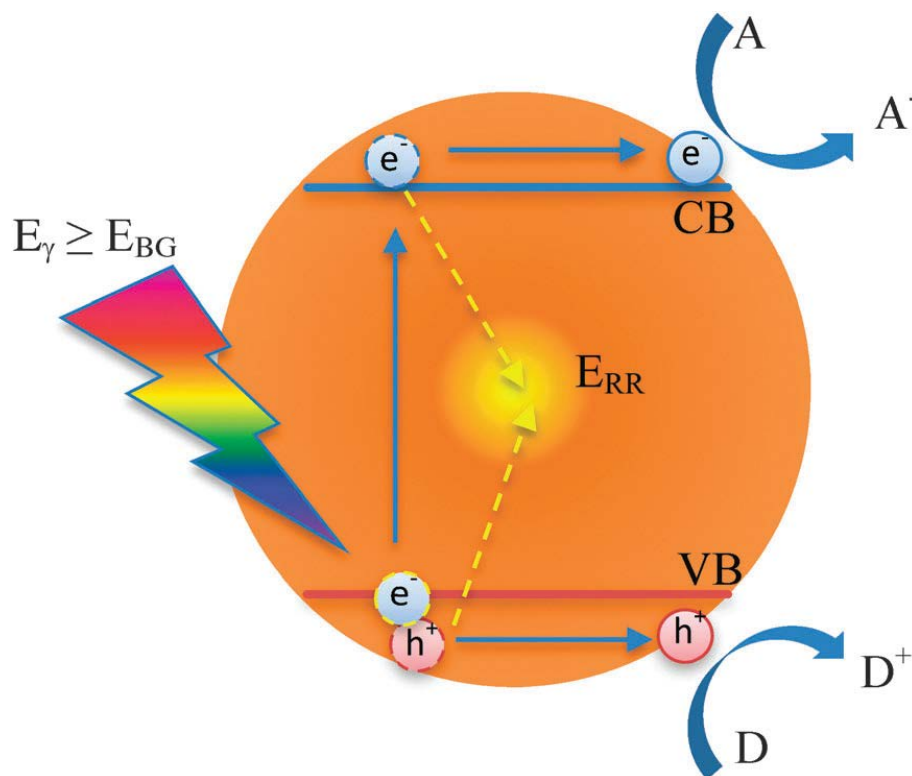


Figure 1.1 Schematic illustration of electron–hole separation in a semiconductor, and subsequent main reactions (blue arrows) and recombination reactions (RR, yellow dotted arrows).

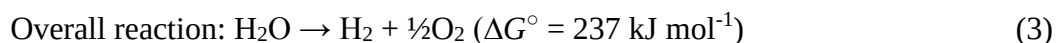
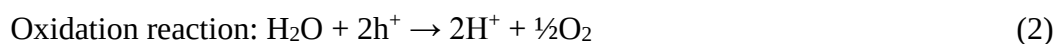
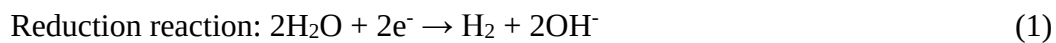
1.1.1 Photocatalytic water splitting

The main propose of photocatalytic water splitting is to produce hydrogen (H_2), which has always been considered as an ideal energy carrier because of its high specific energy density (around 140 kJ g^{-1} ; about four times higher than that of methane) and clean combustion product (only water). Traditional methods accessing to H_2 production include hydrocarbon reformation and electrolysis. For example, to date, about 95% of commercial hydrogen in U.S. was produced from hydrocarbon reformation, especially steam methane reforming ((1) $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ $\Delta H_{295} = +206 \text{ kJ mol}^{-1}$; (2) $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ $\Delta H_{298} = -41 \text{ kJ/mol.}$).¹⁵ However, a rather high temperature (700 to 1100°C) is needed to drive this reaction proceeding, therefore, leading to heavily energy-

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exhausting. Additionally, the H₂ production can be also achieved through electrolysis. Although the energy efficiency of electrolysis can reach as high as 70%, an enormous amount of electricity is required in this process, making the H₂ production cost affording about \$20.0 per GJ.¹⁶ Furthermore, most of electricity comes from the combustion of fossil fuel (like coal), therefore, the overall real energy conversion efficiency should be much lower than 70% and the undesired emission of CO₂ is also needed to be considered. Hence, exploring the approaches to sustainable and economic production of hydrogen from renewable resources, such as biomass and water, has become increasingly important and indispensable.

Photocatalytic water splitting might offer a promising way for H₂ production, in which solar light is used as the input energy and a photocatalyst triggers the reaction *via* electron excitation under mild conditions. The first example of photocatalytic water splitting can be tracked back to the report by Fujishima and Honda in 1972, which confirmed the photoelectrocatalytic hydrogen production from water over TiO₂ semiconductor electrode in the presence of an external bias.¹² After that, increasing attention has been paid to developing efficient photocatalysts for water splitting. During the process, the photocatalysts actually function like the light reaction center in the natural photosynthetic reaction, but H₂ is the production rather than ADP and NADPH, coinciding the generation of O₂, as presented by the following equation:



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Since $\Delta G^\circ > 0$, this reaction is uphill. From the view of electrochemistry, the standard Gibbs free energy change ΔG can be also calculated as:

$$\Delta G^\circ = -nFE^0 \quad (4)$$

Where n is number of electron involved for per mole product formation, F is the Faraday constant (units: $C\ mol^{-1}$) and E^0 is the minimum potential required for the reaction. Thus,

$$E^\circ = -\Delta G^\circ/nF = -(237\ kJ\ mol^{-1})/(-2e \times (9.64 \times 10^4\ C\ mol^{-1})) = 1.23\ V \quad (5)$$

Though this theoretical potential required for water splitting is rather low, the minimum practical energy for driving photocatalytically water splitting should be much higher due to the thermodynamic and kinetic limitations, which intrinsically determines the basic selection criteria of photocatalysts for water splitting: Firstly, the width of the band gap should be larger than 1.23 eV (corresponding to the light with $\lambda < 1100\ nm$); Secondly, the conduction band minimum of the photocatalysts has to be more negative than the redox potential of H^+/H_2 (0 V vs. NHE; pH = 0), and the valence band maximum be more positive than the redox potential of O_2/H_2O (1.23 V vs. NHE; pH = 0). Furthermore, according to the calculation by Murphy et al., the minimum band gap energy for water splitting should be 2.03 eV, corresponding to the limiting band gap wavelength of 610 nm.¹⁷ Figure 1.2 shows the band structures of some common semiconductor photocatalysts.⁴ TiO_2 , $SrTiO_3$, ZrO_2 , and $KTaO_3$ present suitable band positions for photocatalytical water splitting and indeed, they are active for splitting water when modified with appropriate cocatalysts. Some semiconductor photocatalysts, like ZnO and CdS , seem to have suitable band levels for water splitting, but they are not

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capable of splitting water due to the self-photooxidation.⁴ The suitable band structures of semiconductor photocatalysts is just a thermodynamic requirement rather than a sufficient condition. Other factors, such as surface/interface features, crystallinity, carrier mobility and so on, also play critical roles in such photocatalysis reaction.

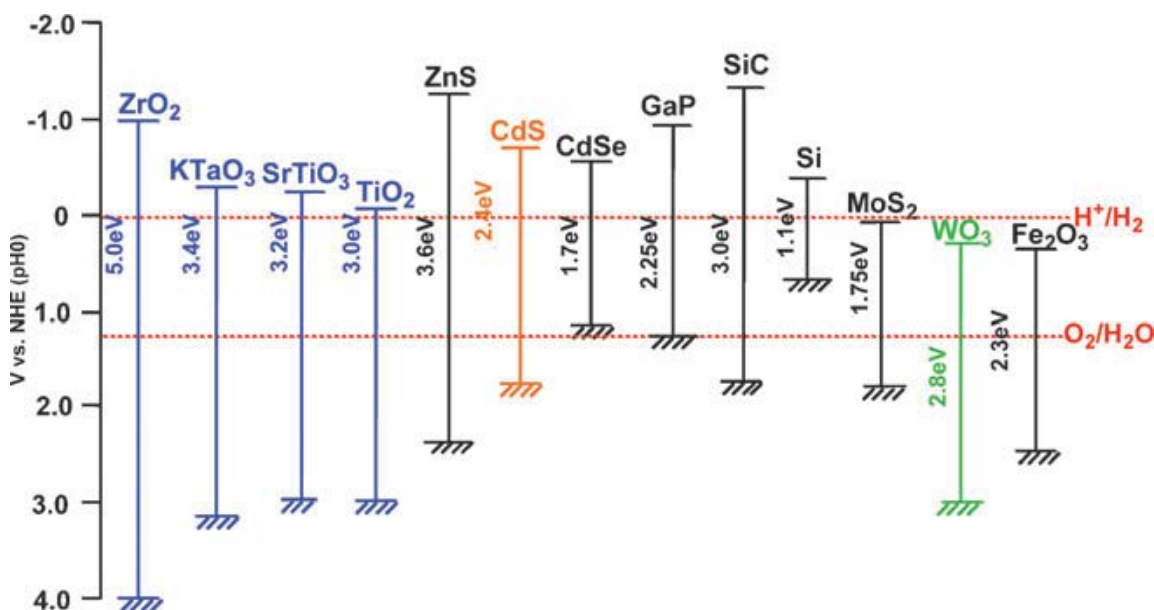


Figure 1.2 Band positions of some common semiconductor photocatalysts.⁴

Overall water splitting

Since the report by Fujishima and Honda in 1971, TiO₂ has extensively been studied for the photodecomposition of water into H₂ and O₂.¹² The first example on this over powdered TiO₂ photocatalysts should be established by Sato et al in 1980, who reported that Pt-loaded TiO₂ (Pt-TiO₂) was active for water splitting though the activity was low.¹⁸ After that, they also found that the water splitting could be effectively increased *via* the coating of NaOH over Pt-TiO₂, which was demonstrated to be effective for the suppression of back reaction on Pt co-catalysts ($\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$).¹⁹

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In the same year (1980), Domen *et al.* also reported the successful photocatalytic water splitting on a NiO-loaded SrTiO₃ (NiO-SrTiO₃) powered catalysts.²⁰ They emphasized the critical role of NiO as the co-catalyst in photodecomposing water: it possessed a Ni/NiO core/shell structure, which was beneficial for the electron migration and meanwhile did not lead to back reaction between H₂ and O₂. Furthermore, Domen *et al.* also found that the alkaline environment could remarkably enhance the reaction rate.²¹ After that, various titanate photocatalysts have been explored.⁴ Particularly, the highest activity was achieved by Ba-doped La₂Ti₂O₇ with NiO co-catalysts in an alkaline hydroxide-contained reaction system, showing the quantum yields close to 50%.²²

Tantalates and niobates are also well reported for pure water splitting. These materials usually present layered perovskite structure as shown in SrTiO₃. Such ABO₃ structure allows a wide range of options to be explored, as many different metals can fit into the A and/or B sites. Due to the high conduction band positions (composed of Ta 5d and Nb 4d orbitals) and the deep valence band positions (consist of O 2p orbitals), these materials possess large band gaps and can split water only under the illumination with high energy UV light. It was reported that NiO/NaTaO₃ is highly active for both hydrogen and oxygen production among tantalates.^{23, 24} Moreover, the performance could be further enhanced by doping NaTaO₃ with lanthanide ions. Under the optimal conditions, the photocatalyst (NiO (0.2 wt%)/NaTaO₃:La (2%)) showed an extreme high water splitting activity with an apparent quantum yield of 56%, which is the current record for UV driven water splitting.²⁵ It was shown that lanthanum doping not only reduced the particle size but also created ordered surface nano-steps on the particles. The former factor could significantly decrease the migration distance of photogenerated electrons and holes in

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order to reach reaction sites on the surface, thus decreasing carrier recombination probability and increasing the activity. The latter factor would be helpful for the separation of reduction and oxidation sites (in the present case, the H₂ and O₂ evolution sites are the edges and grooves of the nano-steps, respectively), consequently suppressing the back reaction.

The photocatalysts discussed above are capable of splitting water efficiently, but they are responsive to UV light, which occupies only about 4% in the solar energy. In an effort to utilize solar energy more efficiently, the development of efficient visible-light sensitive photocatalyst materials for water splitting is highly anticipated. The first accomplishment was reported by Zou and Ye in 2001.²⁶ They showed that nickel doped indium-tantalum-oxide could directly split water into stoichiometric amounts of oxygen and hydrogen under visible light irradiation, achieving a quantum yield of about 0.66%. After that, Domen *et al.* reported a solid solution material ((Ga_{1-x}Zn_x)(N_{1-x}O_x)) of GaN and ZnO for visible-light driven water splitting.²⁷⁻²⁹ In contrast to the relatively wide band gaps for GaN (3.4 eV) and ZnO (3.2 eV), (Ga_{1-x}Zn_x)(N_{1-x}O_x) exhibited much decreased band gap of 2.58 eV with an absorption edge at about 510 nm. It was shown that after loading with co-catalysts (RuO₂ or Rh_{2-x}Cr_xO₃, but the latter was confirmed to be better), the solid solution material is able to realize the pure water splitting under visible light irradiation. At 420 nm, the quantum efficiency of overall water splitting reached 5.9%. More recently, the same group designed a complex perovskite-type oxynitride, LaMg_xTa_{1-x}O_{1+3x}N_{2-3x} ($x \geq 1/3$), which showed to be active for overall water splitting at wavelengths of up to 600 nm, much widening the utilization of solar light.³⁰ To improve the stability of the catalyst and prevent the reverse reaction between H₂ and O₂, a facile surface modification method

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based on the coating of the catalysts with a layer of amorphous oxyhydroxides was explored.³¹ Although the much extended light absorption, this material still suffers from the low quantum efficiency (ca. 0.03% at 440 ± 30 nm).

Z-Scheme System Overall Water Splitting

Z-scheme system is a combination of two semiconductor excitation systems: one for H₂ evolution and another for O₂ evolution.³² Such architecture is analogous to the natural photosynthesis system, in which the two half reactions are spatially separated and take place in PSII and PSI.³³ Particularly, in a Z-scheme system, an appropriate shuttle electron mediator is required to help the electron transfer between the two photocatalysts, serving as the similar role of the electron transfer chain in natural photosynthesis system. Since the candidate photocatalysts are required to be active only for half reactions of water splitting, the kinetical and thermodynamical limitations for the section of suitable photocatalyst to construct a Z-scheme system are much lower relative to those for single photocatalyst driven water splitting system, making the Z-scheme more flexible and optional.

The common used H₂-evolution photocatalysts in Z-scheme systems include TiO₂, TaON and Rh doped SrTiO₃.^{4, 5, 33-37} To improve the H₂ evolution from such catalysts, Pt co-catalysts are usually introduced. Due to the high stability and good photocatalytic oxygen evolution performance, WO₃ and BiVO₄ are two mostly used O₂-evolution photocatalysts. Though a Z-scheme system is consist of two semiconductors, the utilization of light is limited by that with larger band gap. For example, as for all TiO₂-contained Z-scheme system, they are only active for UV light. Reversible redox mediators, like Fe^{3+/2+}, and IO₃⁻/I⁻, are well explored as electron transfer mediators in Z-

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scheme.⁴ However, because of the thermodynamic favor, undesirable backward reactions easily occur for such reversible redox mediators, which are competitive with water splitting reactions, significantly decreasing the efficiency. To address such issue, some solid state electron mediators were also developed for Z-scheme water splitting, including reduced graphene oxide, Au and Ag *etc.*^{36, 38-40}

The example presented here is a latest advance for Z-scheme water splitting. Domen et al reported a Z-scheme pure water splitting based on particulate photocatalyst sheets (Figure 1.3).³⁶ Here, Au was used as the electron transfer mediator. The $\text{SrTiO}_3\text{:La,Rh}/\text{Au}/\text{BiVO}_4\text{:Mo}$ photocatalyst sheet was prepared by the particle transfer method. In this research, they found that the electric contact between Au and the semiconductor photocatalysts is important for the electron transfer and consequent water splitting efficiency. Under the optimal conditions, the material exhibited an apparent quantum efficiency of 33% at 419nm and an STH of 1.1% for overall water splitting.

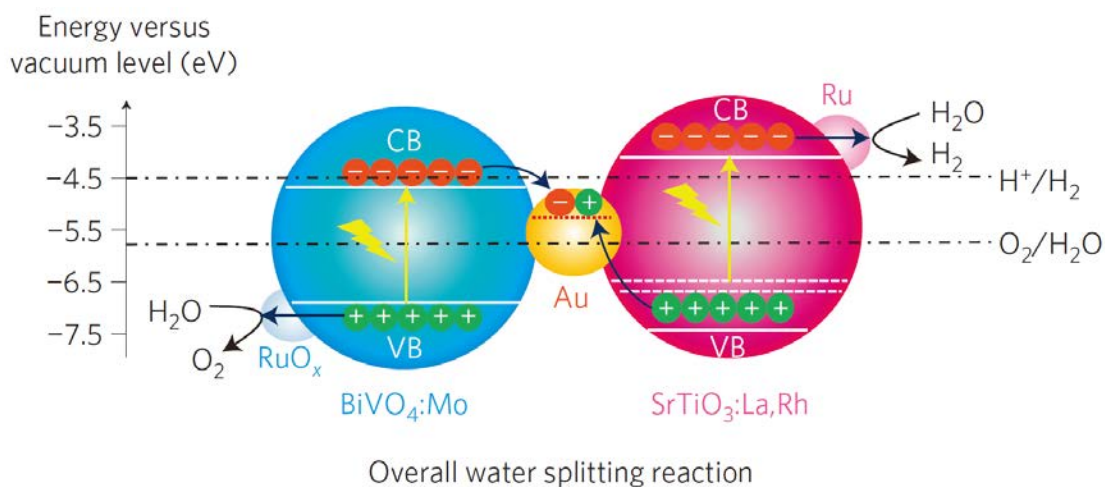


Figure 1.3 Schematic of Z-scheme overall water splitting on the Ru-modified $\text{SrTiO}_3\text{:La,Rh}/\text{Au}/\text{BiVO}_4\text{:Mo}$ sheet.

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H₂ evolution with sacrificial reagents

Although direct photocatalytic pure water splitting to produce H₂ is very attractive for solar energy storage and conversion, the efficiency of the water splitting systems explored so far is still rather low, far from meeting industrial requirements. Using sacrificial reagents as electron donors or hole scavengers would remarkably promote the photocatalytic H₂ evolution. This is because: 1) holes are irreversibly trapped by these sacrificial reagents, thus the carrier recombination would be greatly reduced; 2) no O₂ is produced and the back reaction to form water can be prevented. This reaction is meaningful and important for the exploration of efficient photocatalysts for H₂ production from biomass and abundant compounds in nature and industries, and also offers a good way to screen suitable H₂-evolution photocatalysts for Z-scheme water splitting, and importantly, helps us deepen the understanding of photocatalysts and related photocatalysis mechanism.^{4, 41, 42}

Though the addition of sacrificial agents favors the photocatalytic H₂ evolution process, the modification of photocatalysts with appropriate co-catalysts is still needed to obtain further improved activity. Due to the largest work function and the lowest activation energy for H₂ evolution, Pt is generally the preferential choice.⁴³ Considering the high cost of Pt, some transition metal disulfides (like MoS₂, WS₂) have been explored recently as alternative co-catalysts to Pt.⁴³ Also some biomimetic hydrogenases (such as [(μ-SPh-4-NH₂)₂Fe₂(CO)₆], and Co(III)(dmgH)₂pyCl)) have also been applied to molecular photocatalytic systems for proton reduction to H₂.^{44, 45}

Various organic compounds such as alcohols (methanol over Pt-TiO₂,⁴⁶ ethanol over Pt-Ru/Y₂Ta₂O₅N₂,⁴⁷ isopropanol over Ni/NiO/KNbO₃/CdS,⁴⁸ and ethylene glycol over

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Cu(OH)₂-TiO₂⁴⁹), and hydrocarbons have been and are being employed as electron donors (i.e., as hole scavengers) for photocatalytic H₂ generation.⁵⁰ Particularly, methanol is mostly used. Moreover, the overall methanol-involved photocatalytic H₂ evolution reaction have a positive Gibbs free energy, thus, such process could realize the harvesting of solar energy, though the energy stored is much lower than that of direct water splitting ($\Delta G^\circ = 237 \text{ kJ mol}^{-1}$). It should be noted that, as the sacrificial reagents are consumed in the reaction, the continuous H₂ production is not guaranteed unless the sacrificial reagents are supplied consistently (here, giving that the photocatalyst is stable enough to keep a reaction proceeding steadily). An appropriate sacrificial reagent is important for the enhancement of H₂ evolution over a certain photocatalyst. For example, as for Pt-TiO₂, the rankings in terms of the degree of H₂ production enhancement capability were found to be: EDTA > methanol > ethanol > lactic acid.⁵¹

Inspired by the mineralization of organic sacrificial reagents during the photocatalytic H₂ evolution process, researchers designed a dual-function photocatalytic system, in which the organic compounds are used as electron donors and thus the degradation of organic compounds into CO₂ and the H₂ evolution can be simultaneously achieved. For instance, Choi et al. reported enhanced photocatalytic hydrogen production over F-TiO₂/Pt (surface fluorinated and platinized) photocatalysts with 4-chlorophenol as the electron donor.⁵² They found that the decomposition of 4-chlorophenol was consistent with H₂ production. In such ingenious designment, not only the clean hydrogen energy could be obtained, but also the target organic pollutants were photodegraded, showing the promise of the integration of environmental-protection and renewable energy production.

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Apart from the organic compounds mentioned above, the inorganic, such as S^{2-} and SO_3^{2-} , are also widely used as sacrificial reagents for enhanced photocatalytic H_2 evolution.⁵⁰ Furthermore, it has been argued that S^{2-} and/or SO_3^{2-} are advantageous over organic alcohols as electron donors because they are more easily oxidizable than the alcohols.⁵⁰ For example, in the presence of S^{2-}/SO_3^{2-} , Pt-PdS/CdS exhibited an extremely high quantum yield of about 93% at 420 nm for H_2 evolution.⁵³ However, when methanol was used as electron donors, little amount of H_2 was detected. More importantly, regarding to the metal sulfide photocatalysts, the use of S^{2-} can significantly prevent the photo-corrosion of catalysts and improve the stability: the presence of sulfide in the surrounding solution can help the regeneration of metal sulfide photocatalysts.⁴

1.1.2 Photocatalytic organic pollutant degradation

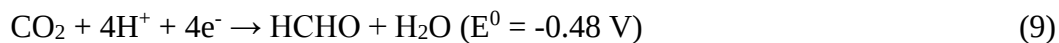
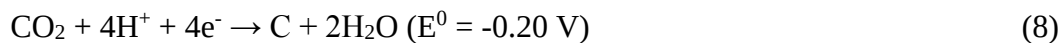
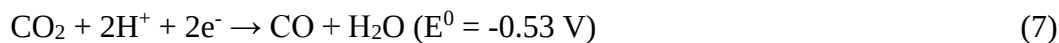
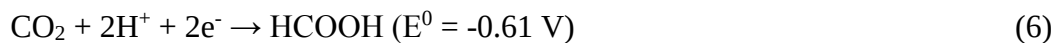
Intrinsically, the oxidative degradation of organic pollutants with O_2 is a spontaneous thermodynamic process, but it is kinetically slow at room temperature because of the high energy barrier originating from the spin-reverse pairing of electrons and the relatively low one-electron reduction potential of O_2 (-0.35 V vs. NHE, pH = 0).² Distinguished from traditional strategy employing catalysts to lower the energy barrier for facilitating the reaction, the emerging photocatalytic strategy is aiming to overcome the energy barrier directly by aid of photon energies via the excitation of electrons. In general, the photocatalytic degradation of organic pollutants involves three key processes: firstly, the semiconductor absorbs photons with energy larger than its band gap and produces reductive conduction band electrons and oxidative valence band holes; secondly, the reductive electrons react with O_2 to yield superoxide radical anions $\bullet O_2^-$ species (oxygen reduction reaction, ORR); thirdly, the oxidative holes contribute to oxidizing surface

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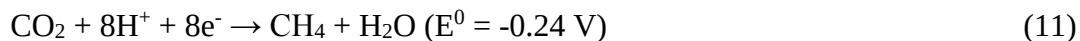
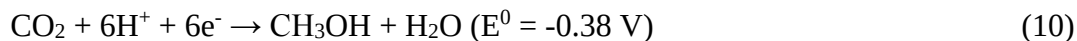
absorbed H_2O to form $\bullet\text{OH}$ radicals which attack organic contaminants or directly oxidize organic molecules. Because of the strong oxidation capability of hole ($E^0 = +2.7$ V vs. NHE for anatase TiO_2 , pH = 0) and $\bullet\text{OH}$ radicals ($E^0 = +1.9$ V vs. NHE, pH = 0), such oxidation can lead to the complete mineralization of organic pollutants.

1.1.3 Photocatalytic CO_2 reduction

With industrialization and the consumption of fossil fuel growth, CO_2 emission is increasing year by year and becomes the major origin of global warming. Photocatalytic CO_2 reduction to produce hydrocarbon fuels not only realizes the solar energy storage and conversion, but also offers a promising solution to CO_2 over-emission induced environmental crises, and therefore intensively attracts the attention from global researchers.⁷ However, the developing of this technology still remains challenges. On one hand, CO_2 molecules present linear symmetric structures and they are so thermodynamically stable that the molecules' activation is rather difficult to achieve. On the other hand, the reduction of CO_2 into hydrocarbon compounds is typical proton-coupled electron transfer (PCET) process and therefore also suffers from the kinetic limitation due to the involving of multiple e^-/H^+ transfer. Below shows the potentials (vs. NHE, pH = 7) for CO_2 reduction into various hydrocarbon compounds.⁵⁴



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From the above reaction, though the eight-electron reduction of CO_2 to CH_4 or CH_3OH requires a much lower potential than that for the two-electron reduction to CO or HCOOH , it does not mean that the former reaction is more easily achieved relative to the latter. This is because: firstly, the intermediate reactions might require a higher potential; secondly, the intermediate processes might have to conquer a high energy barrier; thirdly, the former reaction suffers from a higher kinetic limitation due to the more complex PCET process.

Organometallic complex compounds generally possess multiple and accessible redox states, and therefore exhibit multi-electron transfer reactivity. Furthermore, through the modification of the organic ligands, the multiple redox potentials could be controlled. These features make organometallic complexes promising candidates for CO_2 reduction. In addition, considering the rather negative potential for CO_2 reduction and also the rather positive potential for water oxidation, a photocatalyst which might realize the concurrent CO_2 reduction and water oxidation must possess a very large band gap as well as suitable band positions. Kudo et al. reported that $\text{ALa}_4\text{Ti}_4\text{O}_{15}$ ($\text{A} = \text{Ca}, \text{Sr}, \text{and Ba}$) photocatalysts with 3.79 - 3.85 eV of band gaps and layered perovskite structures could photoreduce CO_2 to form CO and HCOOH and simultaneously oxidize water to produce O_2 under UV light irradiation.⁵⁵ Ag was used as the co-catalyst in the case. Additionally, other semiconductor photocatalysts like Zn_2GeO_4 , TiO_2 and ZnS were also applied for CO_2 photoreduction, but they are all UV active.⁷ The development of visible-light sensitive photocatalysts for this application is highly desired.

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1.2 Modification of photocatalysts towards enhanced photocatalysis

Over the past decades, numerous progresses have been made in the designment and exploration of new photocatalysts. However, the applications of these photocatalysts are still greatly hindered due to their low photocatalysis efficiency or/and moderate light absorption. Exploring strategies of the modification of these developed photocatalysts to enhance the photocatalytic efficiency to meet engineering requirements is highly necessary and might offer opportunities for potential applications.

Band structure engineering

As mentioned in Section 1.1, UV light occupies only about 4% in the solar energy and visible light occupies about 43%. From the view of realizing more efficient utilization of solar light, the development of efficient visible-light sensitive photocatalyst materials is highly anticipated. To extend the responsive region of a photocatalyst from UV to visible, its band gap has to be narrowed below to 2.95 eV (corresponding to 420 nm), which could be achieved by lowering the conduction band level, lifting the valence band level, or both. This strategy is called “band structure engineering”.

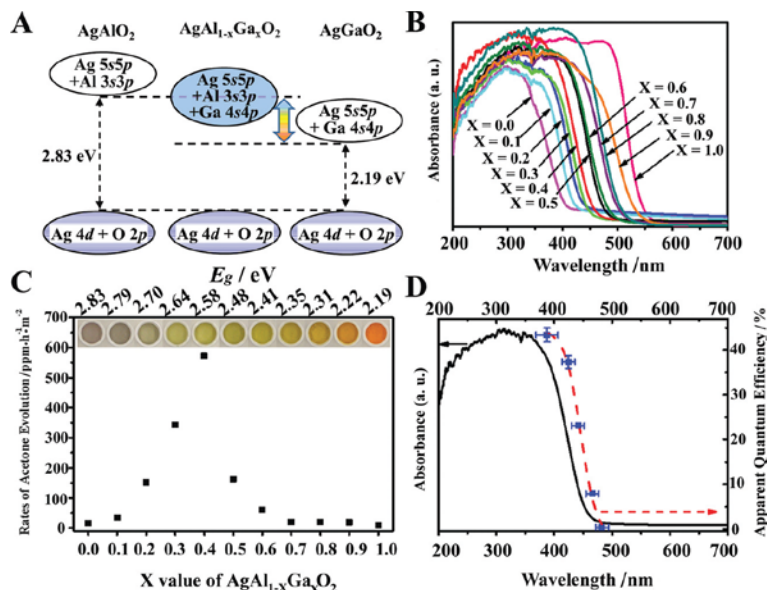


Figure 1.4 (A) Schematic electronic structures of AgAlO_2 , AgGaO_2 , and $\text{AgAl}_{1-x}\text{Ga}_x\text{O}_2$ solid solutions. (B) UV-visible absorption spectra of $\beta\text{-AgAl}_{1-x}\text{Ga}_x\text{O}_2$ solid solutions. (C) Rate of acetone evolution of $\beta\text{-AgAl}_{1-x}\text{Ga}_x\text{O}_2$ as a function of x. (D) Wavelength dependent apparent quantum efficiency of IPA photodegradation over $\beta\text{-AgAl}_{0.6}\text{Ga}_{0.4}\text{O}_2$.⁵⁶

A general way to manipulate the CB minimum is based on the substitution between p-block cations with a d^{10} electronic configuration. For example, as for a family of AgMO_2 ($M = \text{Al}, \text{Ga}, \text{and In}$) materials, their conduction bands are mainly composed of Ag 5s5p and M sp orbitals, while their valence band maximum are mainly constructed from O 2p and Ag 4d states.⁵⁷ This means that these materials possess a similar valence band level, but their conduction band could be tuned by changing the M. Since both Ga 4s4p and In 5s5p orbitals have lower potential energies than Al 3s3p orbitals, the substitution of Al by Ga and In might reduce the CBM of the materials and lead to the narrowing of band gaps. A successful example based on this discussion was established by Ouyang et al., who fabricated beta-phase $\text{AgAl}_{1-x}\text{Ga}_x\text{O}_2$ solid solution materials.⁵⁶ It was shown that, with the substitution of Al by Ga, the conduction bands of $\text{AgAl}_{1-x}\text{Ga}_x\text{O}_2$ were gradually

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negatively shifted and the band gaps were decreased from 2.8 to 2.2 eV (Figure 1.4). Benefit from the continuous adjustment on band structure, an optimal balance between light absorption and redox capability of photogenerated carriers could be achieved. Consequently, when the band gap was 2.6 eV with $x = 0.4$, the material exhibited the highest photocatalytic activity towards IPA degradation.

By lifting up the valence band, the band gap of a semiconductor could be also narrowed, thus allowing for visible-light sensitivity. In general, three approaches have been explored so far to achieve this goal, including doping with 3d-transition elements, cations with d^{10} or $d^{10}s^2$ configurations, and non-metal elements.¹⁴ Theoretical calculation have revealed that the localized 3d levels could shift to lower energy with increasing atomic number of the dopants, thus making the split 3d states capable to mix with the valence band or form a interband in the original bandgap. A typical example is Rh^{3+} doped SrTiO_3 , in which the introduction of Rh^{3+} could induce a new band of Rh^{3+} above the original valence band, much narrowing the band gap of SrTiO_3 to 2.38 eV. In this case, La or Sb were usually co-doped into SrTiO_3 with Rh to balance the valence state.⁵⁸ In another way, the doping of cations with d^{10} or $d^{10}s^2$ configurations could introduce occupied d or s –states into the valence band, which could hybridize with the original O $2p$ states and consequently up-shift the original valence band level. The corresponding examples could be found for Ag^+ -based and Pb^{2+} -based oxides such as AgNbO_3 , AgAlO_2 , $\text{Pb}_3\text{MgNb}_2\text{O}_9$, $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ and so on.¹⁴ The doping with non-metal elements is a widely used method to raise up valence band of the semiconductor. For example, after doping with N, C, and S element, TiO_2 could exhibit a red-shifted absorption into visible region and perform visible-light driven photocatalysis.⁵⁹ Recently, Ye's group reported the

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synthesis of N-doped HNb_3O_8 using urea as the N source, which shown much decreased band gap from 3.5 to 2.7 eV.⁶⁰ Importantly, under visible light irradiation, N-doped HNb_3O_8 exhibited superior catalytic activity to N-doped TiO_2 and P25 TiO_2 for RhB degradation (Figure 1.5).

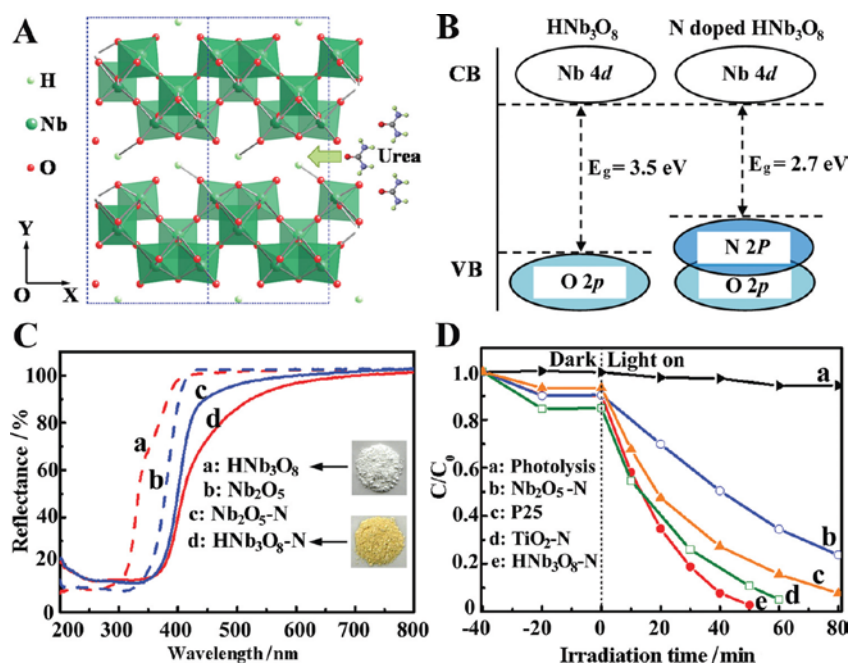


Figure 1.5 (A) Schematic of N-doping in the lamellar solid acid (HNb_3O_8) using urea as the N-source. (B) Schematic band structures of HNb_3O_8 and N-doped HNb_3O_8 . (C) UV-visible diffuse reflectance spectra (D) Photocatalytic degradation of Rhodamine B (RhB) under visible light irradiation ($\lambda > 400 \text{ nm}$).⁶⁰

Continuous adjustment of both valence band and conduction band is also an effective strategy to optimize the band structure towards efficient photocatalysis. For instance, Ye et al. reported the $\text{Ca}_{1-x}\text{Bi}_x\text{V}_x\text{Mo}_{1-x}\text{O}_4$ solid solution materials, in which the conduction band could be continuously adjusted by controlling the ratio of V 3d states to Mo 4d states, and the valence band were tuned by modulating the ratio of Bi 6s states to O 2p

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states.⁶¹ With the optimal band structure, the material achieved the much enhanced O₂ evolution activity from AgNO₃ aqueous solution under visible light irradiation.

Nanostructure engineering

1) Increasing the surface area

It is well known that all photocatalytic reactions occur at the surface. An increase in surface area is often beneficial for the enhancement of photocatalytic activity. As reducing the particle size can lead to quadratic growth of the specific surface area and hence reactive sites, the exploration of nanostructured photocatalysts has attracted considerable attention in recent decades. Furthermore, in comparison with larger particles, charge carriers travel shorter distances to the surface in nanostructured photocatalysts and thus bulk electron-hole recombination can be suppressed, resulting in an improved photocatalytic activity. For example, Do et al. prepared uniform Ag₃PO₄ nanocrystals with a high degree of particle size control, ranging from 8 to 16 nm.⁶² Such Ag₃PO₄ nanocrystals exhibited twofold photocatalytic activity under visible light compared to micron-sized Ag₃PO₄ particles for MB decomposition. Also, Zhang et al. found that the mesoporous Zn₂GeO₄ with a large surface area of about 163 m² g⁻¹ possessed a 2.5-fold enhanced photoactivity for CO₂ reduction in comparison with the bulk Zn₂GeO₄ photocatalysts (surface area of about 0.6 m² g⁻¹) prepared by solid state reaction.⁶³

It should be noted that, increasing the surface area by reducing particle size also has some adverse effects on charge separation and transport. Firstly, if the feature size, particularly of a spherical particle, is comparable with the electron mean free path, a strong quantum confinement effect occurs, increasing the recombination probability of

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photogenerated electron-hole pairs. Secondly, synthetic methods for producing nanoparticulate powders often use considerably low temperatures ($< 200\text{ }^{\circ}\text{C}$), producing polycrystalline particles with a large percentage of grain boundaries, defect sites and surface states. These act as carrier recombination centers and reduce the photocatalytic ability of the sample. Therefore, it is imperative to optimize both morphology and surface area of nanostructured photocatalysts to achieve an overall net positive effect.

2) Exposed facets engineering

All of the photocatalytic reactions take place on the surface of the photocatalysts, therefore, the exposed crystal facets play important roles in determining the corresponding photoactivity. Fundamental studies have demonstrated that high-index facets, having a high density of atomic steps, ledges, kinks, and dangling bonds, usually exhibit much higher chemical activities. Facet engineering has been proven to be a promising and efficient approach for the improvement of the photocatalytic performance of a photocatalyst. For example, the $\{001\}$ facets of anatase TiO_2 were shown to be highly reactive for the decomposition of azo dyes.⁶⁴ Similarly, Ye's group reported that, Under visible-light irradiation, the rhombic dodecahedron Ag_3PO_4 single crystals exhibited much higher catalytic activities than cubes for the degradation of methyl orange (MO) and RhB dyes.⁶⁵ These results suggest the $\{110\}$ facet is more reactive than $\{001\}$ facet, consistent with the higher surface energy values for $\{110\}$ facet and $\{001\}$ facet (Figure 1.6). Therefore, it was speculated that highly reactive $\{110\}$ facets provided a more catalytically active site and enhanced the adsorption of organic molecules during photocatalysis, thus resulting in a higher photocatalytic activity.

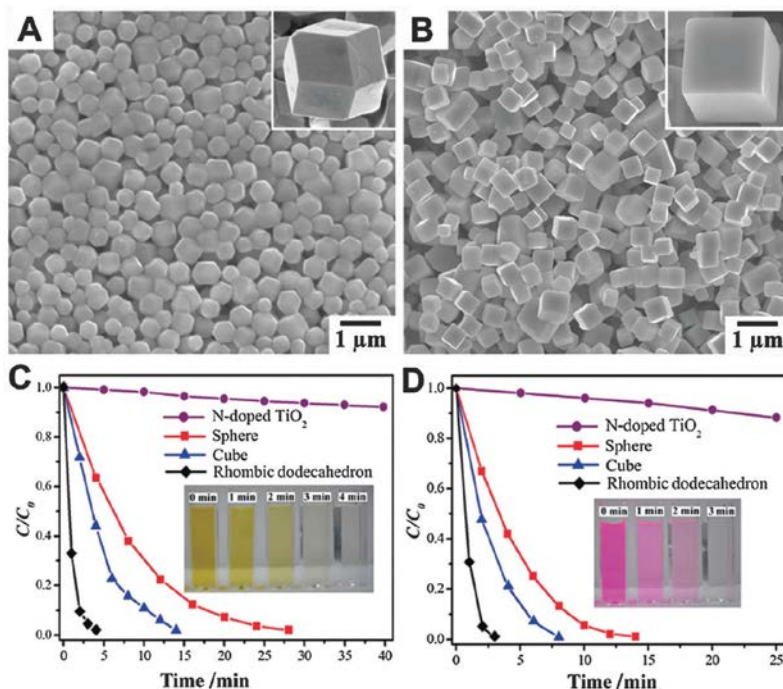


Figure 1.6 SEM images of Ag_3PO_4 sub-microcrystals with different morphologies: (A) rhombic dodecahedrons and (B) cubes. The photocatalytic activities of Ag_3PO_4 rhombic dodecahedrons, cubes, spheres, and N-doped TiO_2 are shown for the degradation of (C) MO and (D) RhB under visible light irradiation.⁶⁵

On the other hand, different crystal facets with different atomic arrangement always present distinct electronic structure and adsorption capability. If a single semiconductor crystal is enclosed by two or more different facets, a selective transfer of photogenerated carriers from one facet to another facet or a selective adsorption for different molecules onto different facets can occur.⁶⁶ For example, the electron transfer from $\{001\}$ to $\{101\}$ facets in TiO_2 crystals has been observed and the corresponding origin has been established;⁶⁷ the difference in energy of the valence and conduction bands between $\{001\}$ and $\{101\}$ facets by theoretical calculation, resulting in an electron cascade. On the basis of this phenomenon, a “surface heterojunction” concept was purposed by Yu and

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Jaroniec. Furthermore, they found that at a 45:55 ratio of exposed {101} and {001} facets the photocatalytic activity was at a maxima. This result importantly reveals the optimal ratio of exposed facets in semiconductor crystals and their effect on the enhancement of the overall photocatalytic performance.

3) Heterojunction photocatalyst designment

Generally speaking, the photocatalysis efficiency is intrinsically determined by the separation and transfer of the photogenerated electron/hole pairs. To enhance the separation and transfer of the photogenerated carriers and improve the photocatalysis efficiency, heterostructural photocatalysts composed of two distinct semiconductors are usually designed. In such heterojunction structure, the alignment of the Fermi levels of the two semiconductors will occur and will be equilibrated again under irradiation. Since these two semiconductors possess different band structure, the band matching will be finally built in the heterostructure. Thus, the photoexcited electrons trend to be transferred from the high CB of one semiconductor to the relatively low CB of another semiconductor, meanwhile holes are transferred from low VB to relatively high VB. Through selecting appropriate band matching, the transfer directions of electrons and holes can be tuned. An ideal band matching can realize the vectorial transfers in the opposite directions for electrons and holes, respectively, which is believed to be capable of improving the separation and transfer of the photogenerated carriers significantly.⁶⁸ Such enhanced transfer of carriers can be experimentally demonstrated by photofluorescence analysis, in which a decreased steady photofluorescence spectrum and a prolong photofluorescence lifetime are typically exhibited.

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Apart from improving the separation and transfer of photogenerated carriers, constructing heterostructural photocatalysts can also endow the compositions other advantages, such as enhanced surface/interface catalysis, extended light absorption, and improved stability.⁶⁹ Therefore, this strategy has been widely applied to the design of efficient photocatalysts.

Plasmon sensitization

It was discovered that the incorporation of plasmonic Au or Ag nanoparticles onto semiconductors (e.g. TiO₂) has been shown to greatly increase their photocatalytic activity with a concomitant reaction rate enhancement in the visible light region by using the surface plasmon resonance (SPR) of such metal nanoparticles.⁷⁰ SPR can be described as the resonant photon-induced collective oscillation of valence electrons, established when the frequency of photons matches the natural frequency of surface electrons oscillating against the restoring force of positive nuclei.⁷¹ When the plasmonic-metal nanoparticles are in contact with a semiconductor, the hot electrons produced through the non-radiative excitation of SPR can be directly injected into the conduction band of the semiconductor over the Schottky barrier, which offers the intrinsic driving force for the visible-light photocatalysis in these heterostructures.⁷² The SPR absorption of plasmonic metals is not only highly dependent on the metal compositions (for example, the maximum SPR absorption for ordinary Cu, Ag and Au spherical nanoparticles are located at 580, 400 and 530 nm, respectively), but also strongly related to the size and shape of the nanoparticles.⁷¹ This feature makes plasmonic photocatalysts highly flexible for the light response. For example, Liu et al. reported that the Au nanocage-loaded TiO₂

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plasmonic photocatalysts exhibited excellent photoactivity over a wide visible range from 480 to 910 nm.⁷³

Actually, even in the plasmonic photocatalysts where the semiconductor and plasmonic metals are separated from each other by thin, non-conductive spacers preventing any direct charge exchange between the two building blocks, SPR-induced enhancement in the photoactivity of the semiconductor is still observed.^{74, 75} This can be explained by the near-field electromagnetic and resonant photon-scattering mechanisms.⁷¹ It has been confirmed that under photo-excitation, a spatially non-homogenous and strong electric fields with the intensity orders of magnitude higher than the field of incident photons will be formed and localized nearby at the plasmonic metallic nanostructure. When a semiconductor is brought into the electric fields of the plasmonic nanostructure, the rate of electron-hole formation in the semiconductor will be increased significantly. As for large plasmonic nanostructures (larger than ~50 nm in diameter) sensitized semiconductor photocatalysts, the SPR-induced scattering enhancement mechanism usually accounts for the improved photocatalysis.⁷¹ Here, the plasmonic nanostructure essentially acts as a nanomirror to scatter photons and thus greatly increase the average photon path length in the photocatalysts, ultimately causing an increased rate of electron-hole pair formation in the semiconductor and improving the photoactivity.

Reaction environment modulation

As is well known, the modulation of reaction environment is important for the photocatalysis, which is not only strongly affect the surface property of the photocatalysts, but also determines the mass transport efficiency during reaction. In this section, several

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examples will be discussed to emphasize the influence of environmental modulation on photocatalysis.

A typical example is surface acidification of TiO_2 . It was reported that Brønsted acids treated TiO_2 could dramatically accelerate the photocatalytic aerobic oxidation of alcohols. Normally, during the TiO_2 -mediated photocatalytic aerobic oxidation of alcohols, the Ti species, having a side-on peroxide, are formed, which can passivate the surface of TiO_2 and thus reduce the activity. After modified with Brønsted acids, the decomposition of such Ti species would be significantly promoted because the protonation could weaken the O-O bonds in the peroxide, thereby regenerating the active Ti sites on the surface of the catalyst and improving the activity.⁷⁶ Furthermore, the same group also reported that the introduction of pendant proton relays (polyprotic acids) into the reaction medium could switch the reduction pathway of O_2 on a TiO_2 surface from a sequential single-electron process to a concerted $4\text{e}^-/4\text{H}^+$ reduction to H_2O .⁷⁷ In contrast, it was shown that monocarboxylic acids without pendant proton relays can only enhance the oxygen reduction rate but barely change the reaction pathway. This result suggests that the photocatalysis pathway is closely related to the surface environment of the photocatalysts.

Surface alkalization is another environmental modulation strategy to improve the photocatalysis efficiency. Early in 1980, Wagner and Somorjai have already reported that, in a concentrated NaOH solution, the photocatalytic H_2 evolution could be much enhanced over the Pt-free SrTiO_3 photocatalysts.⁷⁸ They proposed that the hydroxide ions adsorbed on the surface of SrTiO_3 could serve as hole acceptors and suppressed the recombination of electron-hole, thus beneficial for the photocatalysis. After that, Sato and

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Domen demonstrated that the introduction of NaOH could also enhance the overall water splitting activity over Pt-TiO₂ and NiO-SrTiO₃, respectively.^{19, 21} They believed that NaOH could suppress the H₂-O₂ back reaction on the co-catalysts. Recently, Simon reported that the photocatalytic H₂ evolution over Ni/CdS photocatalysts was greatly improved in a NaOH-contained ethanol solution.⁷⁹ In the presence of NaOH, the pH value of the reaction medium was significantly increased, which made both the valence band potential of CdS and redox potential of OH⁻/•OH shift to more negative level. Since the former shift possess a smaller slope (-33 mV/pH) than the latter (-59 mV/pH), at an appropriate pH, the valence band of CdS would be positive enough to oxidize OH⁻ to •OH. Under this conditions, the ethanol oxidation pathway would be changed from the direct hole oxidation to the indirect hole-induced •OH oxidation and the latter is much more favorable, thus remarkably promoting the H₂ evolution.

The loading of some metal oxides onto the photocatalysts to improve the photocatalysis also belongs to reaction environmental modulation. A typical metal oxide used is MgO. Li et al. reported that the coating of MgO nanolayer could regulate the surface of Ta₃N₅ from hydrophobic to hydrophilic, which was beneficial for an even deposition of hydrophilic CoO_x cocatalysts.⁸⁰ As a result, the modified photocatalysts possessed a better interfacial charge transfer and an enhanced water oxidation efficiency. Also, Xie and co-workers observed the increased photoreduction of CO₂ over MgO loaded Pt/TiO₂.⁸¹ They proposed that, due to the alkalinity of MgO, the modification of MgO could enhance the chemical adsorption of CO₂ on the photocatalysts. This facilitated the subsequent photoreduction of CO₂ into CH₄ by the accumulated electrons on Pt co-catalysts.

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Based on the above discussion, it is shown that, when the photocatalysts are optimized, the reaction environmental modulation would provide a facile and efficient way to further improve the photocatalysis.

1.3 Graphitic carbon nitride photocatalysts

Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), first discovered by Liebig and termed “melon” ($\text{C}_6\text{N}_9\text{H}_3$), with a graphitic π -conjugated stacking structure consisting of tri-s-triazine repeating units (Figure 1.7), has recently emerged as an attractive metal-free photocatalyst for water reduction or oxidation in the presence of a proper sacrificial electron donor or acceptor.⁸²⁻⁸⁵ $\text{g-C}_3\text{N}_4$ possesses a band gap of 2.7 eV, with the conduction and valence band locating at around -1.30 and +1.40 V vs. NHE (pH = 7) (Figure 1.8), respectively, which makes the photogenerated electrons reductive sufficiently to reduce water for H_2 evolution, and the photogenerated hole oxidative enough for water oxidation to produce O_2 , and also guarantees the material of visible light response. Density functional theory (DFT) calculations revealed that the valence and conduction bands of $\text{g-C}_3\text{N}_4$ are mainly constructed by the nitrogen p_z orbitals and carbon p_z orbitals, respectively (Figure 1.8).⁸² This result suggests that the electron-driven reduction and hole-driven oxidation occur independently in the carbon atoms and nitrogen atoms during $\text{g-C}_3\text{N}_4$ involved photocatalysis. Unlike other conductive polymers, $\text{g-C}_3\text{N}_4$ is rather chemically and thermally stable and is normally not subject to photocorrosion during photocatalysis. This is important for its potential applications. Up to now, $\text{g-C}_3\text{N}_4$ has been explored for various photocatalytic applications, including photocatalytic H_2 and O_2 evolution from water, photoreduction of CO_2 , photoelectric conversion, organic pollutant degradation, and photocatalytic organic synthesis.⁸³

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Moreover, to improve the photoactivity of g-C₃N₄, numerous modifications strategies have already emerged, including nanostructure design, molecule incorporation, element doping, and reaction environmental modulation.^{83, 85}

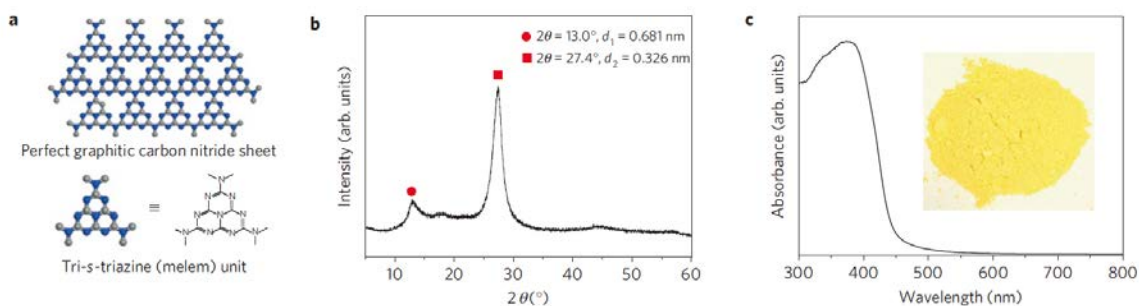


Figure 1.7 (a) Schematic diagram of a perfect graphitic carbon nitride sheet constructed from melem units. (b) Typical XRD pattern and (c) UV-vis absorption spectrum of g-C₃N₄. Inset in (c) is the photograph of g-C₃N₄ powder.

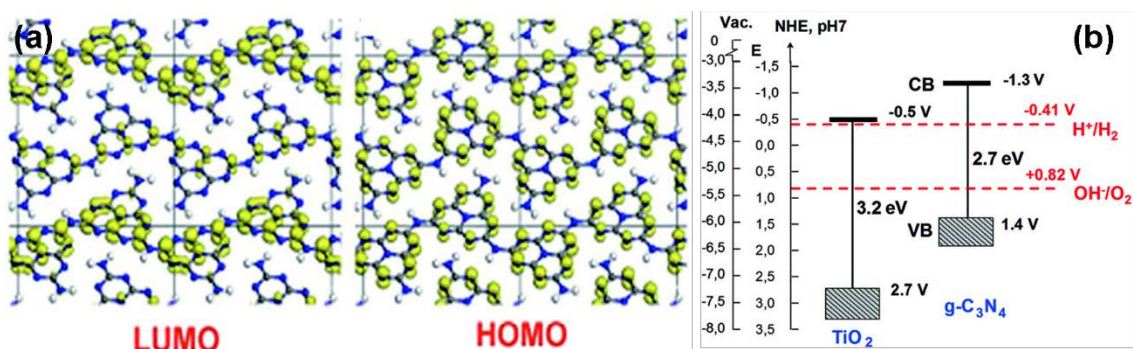


Figure 1.8 (a) Electronic structure of g-C₃N₄.⁸² (b) Electronic band structure of g-C₃N₄ and TiO₂.⁸⁶

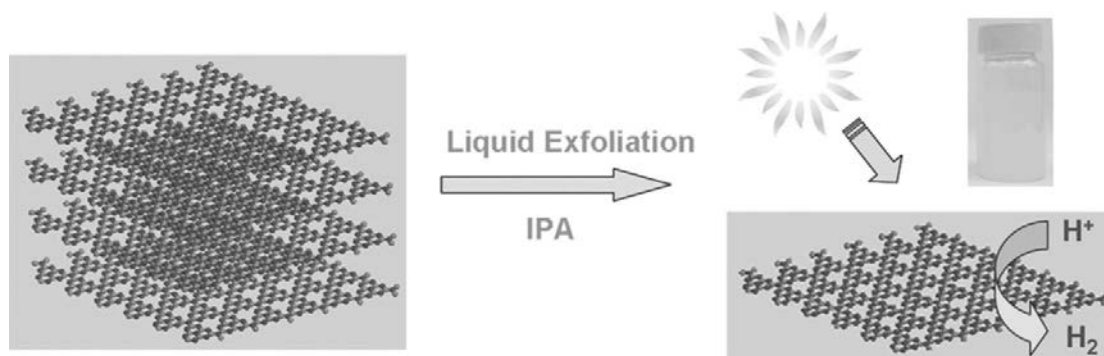


Figure 1.9 Preparation of g-C₃N₄ nanosheets by a liquid-exfoliation method for photocatalytic H₂ evolution under visible light irradiation.⁸⁷

g-C₃N₄ possesses a graphite-like layered structure which presents strong C-N covalent bonds in the in-plane direction and weak van der Waals forces between the C-N layers. Based on this, as motivated by the intriguing chemistry of graphene, the fabrication of 2D g-C₃N₄ nanosheets has attracted considerable attention and it has been demonstrated to be one of most effective strategies to improve the photoactivity of g-C₃N₄. This is because: 1) exfoliating the bulk g-C₃N₄ in nanosheets would endow the materials with the much increased surface area, effectively increasing the surface photoactive sites exposing and the surface accessibility to reactant substrates; 2) the anisotropic structure of g-C₃N₄ nanosheets could help to guide charge transfer along the in-plane direction, thus facilitating the separation of electron-hole pairs; 3) g-C₃N₄ nanosheets possess an enlarged band gap due to the quantum size effect and would offer more favorable band structures for water splitting.⁸⁸ The first preparation of g-C₃N₄ nanosheets was reported by Yang et al. and it was achieved through an ultrasonication-assisted liquid-exfoliation method (Figure 1.9).⁸⁷ They found that IPA was most effective for the g-C₃N₄ exfoliation process due to the appropriate surface energies. In comparison with bulk g-C₃N₄, the as-prepared g-C₃N₄ nanosheets with a thickness of around 2 nm indeed showed larger aspect

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ratios, higher surface area, and improved carrier separation and transfer efficiency, consequently exhibiting a more than nine-fold enhanced photocatalytic H_2 evolution activity. Apart from such liquid-exfoliation, other methods, like post-thermal oxidation etching,⁸⁹ and template-assisted synthesis,⁹⁰ were also developed in recent year to prepare g- C_3N_4 nanosheets.

Though 2D geometric morphology renders g- C_3N_4 with the many merits distinct from bulk g- C_3N_4 , the design and exploration of other different morphologies (such as porous structures, hollow structures and 1D nanostructures) are also of interest and benefit for the improvement of photoactivity of g- C_3N_4 .⁸³ For example, it was reported that mesoporous g- C_3N_4 prepared used hard (silica⁹¹) or soft (Pluronic P123⁹²) templates not only could provide a large surface area and numerous channels to enhance mass transport, but also could decrease the carrier migration distance to facilitate charge separation. Similarly, hollow structured g- C_3N_4 was also developed because such structure is helpful for the light harvesting through enhancing the successive reflections within the interior voids and the subsequent carrier generation (Figure 1.10).⁹³ Additionally, in respect to the designment of 1D nanostructures of g- C_3N_4 , through adjusting the length, diameter, and aspect ratio, the optimization of the specific-surface area and the charge carrier mobility would be achieved, consequently maximizing the photoactivity.

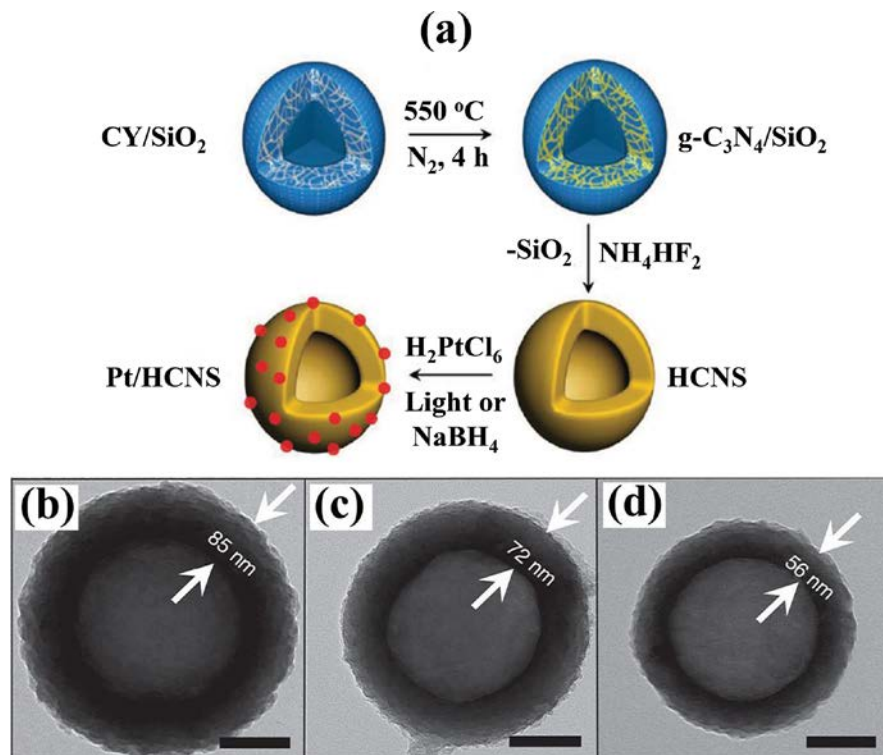


Figure 1.10 (a) An illustration of the preparation of g-C₃N₄ hollow nanospheres (CY indicates cyanamide). (b-d) TEM images of g-C₃N₄ hollow nanospheres with different shell thickness. Scale bars in (b-d) are 0.5 μm .⁹³

As discussed in section 1.2, the element doping provides a promising strategy to modify the electronic structure and the subsequent photocatalysis of photocatalysts. Therefore, the exploration of g-C₃N₄ photocatalysts through element doping was also widely investigated. Due to the metal-free feature, the doping of g-C₃N₄ are also mainly focused on non-metallic elements, such as S, P, B, F, Cl, Br, I and so on.^{83, 94-96} Such element doping generally leads to the narrowing of the band gap of g-C₃N₄ (i.e. the extended light absorption) and the increased π -electron delocalization (improved carrier separation and transfer), thus enhancing the photocatalytic activity. Besides element doping, molecule incorporation (or doping) is also shown to be a flexible and good way

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for modulating the band structure of g-C₃N₄ as well as the corresponding light absorption capability.^{97, 98} For example, Wang et al. reported that, by the in-situ copolymerization of dicyandiamide with different amounts of barbituric acid (BA), the resulting g-C₃N₄ displayed tunable bandgaps in the range of 2.67 to 1.58 eV, thus resulting in the light-absorption edge red-shifted to ca. 750 nm (Figure 1.11).⁹⁷ Compared with original g-C₃N₄, such BA-modified g-C₃N₄ exhibited a nearly two times enhanced activity for photocatalytic H₂ evolution.

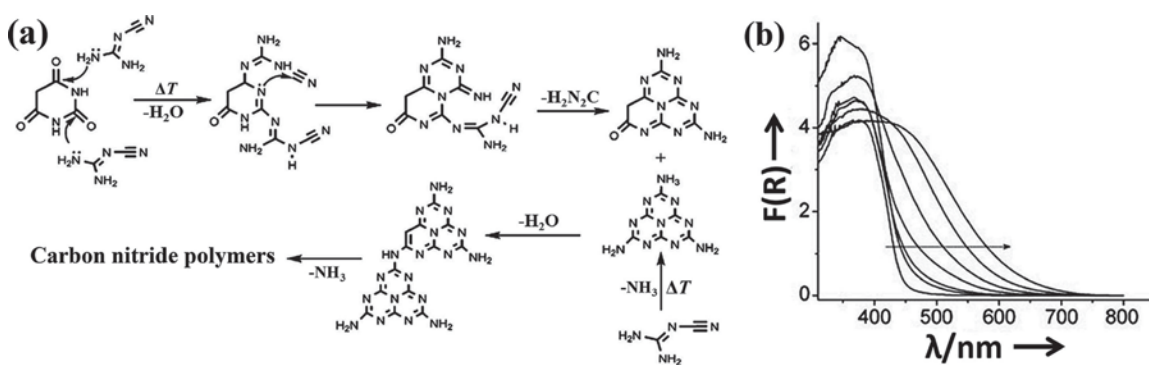


Figure 1.11 (a) Scheme of the proposed copolymerization process of dicyandiamide with barbituric acid (BA). (b) UV-vis diffuse-reflectance spectra of g-C₃N₄ and BA-modified g-C₃N₄ samples.⁹⁷

As also discussed in section 1.2, the construction of heterojunction structure is an effective way to enhance the photocatalytic performance of semiconductor photocatalysts by promoting the separation and transfer of photogenerated electrons and holes. Therefore, such strategy was also well explored to develop g-C₃N₄-based heterojunction photocatalysts. A typical research was conducted by Zhang et al., which reported on the construction of an isotype heterojunction of traditional g-C₃N₄ (CN; obtained from dicyandiamide) and sulfur-mediated g-C₃N₄ (CNS; obtained from trithiocyanuric acid) via a copolymerization process.⁹⁹ Due to the occurrence of the band alignment between

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CN and CNS, the photogenerated electrons would be migrated from CN to CNS, while photoinduced holes were transferred from CNS to CN, thus greatly increasing the carrier separation and transfer efficiency and giving rise to a much improved photoactivity (Figure 1.12). Furthermore, in contrast to the conventional g-C₃N₄/oxides or sulfides heterojunctions, such isotype heterojunction built from two different types of g-C₃N₄ would possess a more close interfacial contact due to the composition compatibility, which would be beneficial for the efficient spatial charge redistribution across the interface and promoting charge separation as well as enhancing the photocatalytic performance.⁸³

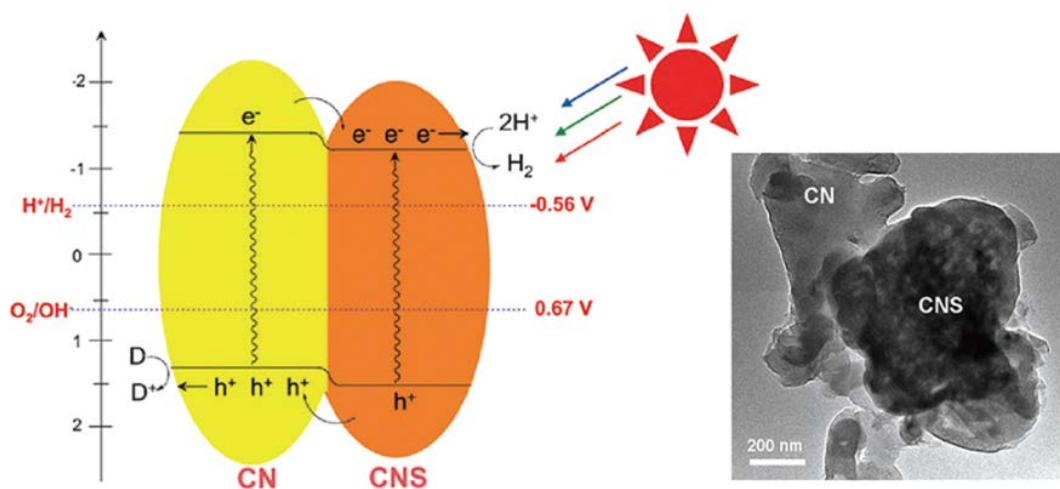


Figure 1.12 (left) Schematic illustration of heterojunction formed between carbon nitride (CN) and sulfur-mediated carbon nitride (CNS), and (right) typical TEM images of CN/CNS.⁹⁹

Reaction environmental modulation for improved photocatalysis has been a topic of intense investigation (as mentioned in section 1.2). Photocatalysis is actually a surface/interface reaction. Through the environmental modulation, the surface/interface properties of photocatalysts could be rationally adjusted, thus casting profound effects on the corresponding photocatalysis reaction. As a newly emerged photocatalyst, the related

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researches on g-C₃N₄ are relatively rarely reported. A typical one was established by Guo et al.¹⁰⁰ They demonstrated that a highly alkaline reaction environment could significantly boost the photocatalytic H₂ evolution activity of g-C₃N₄ because the hole-induced oxidation of sacrificial agents could be accelerated at high pH values. These results suggest that reaction environmental modulation might be a good way to manipulate the kinetics of electron reduction and hole oxidation, and the consequent photocatalysis reaction.

Although numerous efforts have been devoted to the exploration and development of g-C₃N₄-based photocatalysts and many pioneering successes have been achieved, the activity of g-C₃N₄ for photocatalytic H₂ generation still remains moderate. Hence, further studies are still highly urgent and required to advance this field and to provide a more deep insight into the mechanism of photocatalysis.

1.4 Thesis motivations and organization

Hydrogen (H₂) production using a photocatalyst and solar energy is an ideal solution to global energy and environmental issues and therefore attracts enormous interest. Unfortunately, the rational design and developing of a low-cost, sustainable, and efficient visible-light photocatalyst continues to be a serious challenge in this field. As mentioned in Section 1.3, graphitic carbon nitride (g-C₃N₄), also termed “melon” (C₆N₉H₃), with a graphitic π -conjugated stacking structure consisting of tri-s-triazine repeating units has recently emerged as an attractive metal-free photocatalyst for photocatalytic H₂ evolution. g-C₃N₄ possesses a suitable band positions for both water reduction and oxidation. Furthermore, it is composed of extremely abundant elements (namely C and N) and is non-toxic with proven stability, both thermally and in solutions of pH 1 to 14. These

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features make g-C₃N₄ a promising candidate photocatalyst for industrial H₂ production applications. However, the photocatalytic performance of g-C₃N₄ still remains moderate probably due to the insufficient light absorption, the fast electron-hole recombination and also the kinetic limitation in proton reduction. In this dissertation, we focused on improving the performance of g-C₃N₄ on photocatalytic H₂ evolution through both the structure and reaction environment modulations of the photocatalysts. Through structure modulations, we planned to precisely engineer the band configuration of g-C₃N₄ and control the molecular ranging regularity, thus extending the light absorption and improving carrier separation and transfer. By reaction environment modulations, we thought to modify the photocatalytic reaction pathway and lower the kinetic limitations for water reduction and hole oxidation. The final objective is to realize enhanced photoactivity. The dissertation contains five chapters and below shows the summaries of the remaining four chapters.

Chapter 2 Defect-modified graphitic carbon nitride with p-n homojunction structure towards enhanced photocatalytic hydrogen evolution activity

In this chapter, in order to extend the light absorption and to improve the separation and transfer of photogenerated carrier in g-C₃N₄, an in-situ bond modulation strategy was explored to modify g-C₃N₄ through the heating treatment with NaBH₄. Such treatment enabled the successful introduction of defects (preferential loss of N atoms) into the structure of g-C₃N₄ and thus gave rise to the obvious red-shift of the absorption edge from 450 to 620 nm. More importantly, accompanied with the formation of defects, cyano terminal C≡N groups, acting as electron acceptors, were also implanted into the g-C₃N₄ sheet edge, which endowed the DCN exhibiting both n- and p-type conductivities,

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consequently leading to the generation of p-n homojunctions. Such homojunction structured g-C₃N₄ photocatalysts have been demonstrated to highly efficient in the transfer and separation of photoexcited carriers and shows much enhanced photocatalytic H₂ evolution activity under visible-light irradiation.

Chapter 3 Fabricating in-plane highly ordered graphitic carbon nitride via heptazine self-assembling for improved photocatalytic H₂ production

In-plane ordering of g-C₃N₄ molecules is crucial for the efficient separation of photogenerated charge carriers. In this chapter, aiming at the improvement of carrier separation and transfer in g-C₃N₄ for enhanced photoactivity, a spatially confined polycondensation process was developed to fabricate the in-plane highly ordered g-C₃N₄ through using self-assembled heptazine hydrate as precursors. As confirmed by the electron spin resonance (ESR) results, photoelectrochemical data and time-resolved photoluminescence analysis, the improved in-plane ordering of g-C₃N₄ was positively related to the delocalization of unpaired electrons within the π -conjugated aromatic rings, as well as the separation and transfer of photogenerated carrier within the graphitic plane. This should be accounted for the much enhanced photoactivity as observed. These findings would present a facial approach for the designing of efficient organic semiconductors for photocatalysis.

Chapter 4 Nature-inspired environmental “phosphorylation” modulation for highly improved photocatalytic H₂ production over g-C₃N₄ nanosheets under Visible-Light Irradiation

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As confirmed in chapter 2 and 3, the structure engineering offers many benefits for the separation and transfer of carriers in g-C₃N₄ and subsequent the photoactivity. In this chapter, an environmental “phosphorylation” strategy (precisely, in the presence of HPO₄²⁻ ions) was explored to facilitate kinetics of proton reduction and hole oxidation and consequently to enhance the photocatalytic H₂ evolution reaction. This strategy was inspired by the awareness of the important roles of phosphates in natural photosynthesis: 1) phosphates, as primary components of thylakoid membranes, play vital roles in both transferring electrons in electron-transport chains and pumping protons to drive adenosine triphosphate synthesis during the light-dependent reactions; 2) some phosphates function directly as mediators to participate in carbon fixation during the “dark” reaction. With the addition of HPO₄²⁻ ions into the reaction medium, it was confirmed that the hydrogen-bonded chains of HPO₄²⁻ would form and function like the proton pump in natural photosynthesis to facilitate proton transport in the solution, and meanwhile that HPO₄²⁻ ions could provide H⁺ to produce H₂ instead of H₂O and then be regenerated by capturing H⁺ from H₂O, consequently achieving a Calvin-cycle-like H₂-evolution pathway. On the other hand, the enhancement in the hole-induced oxidation of sacrificial agents by the addition of HPO₄²⁻ ions was also demonstrated. Because of these, in the presence of HPO₄²⁻ ions, a significant improvement in photocatalytic H₂ production was achieved over g-C₃N₄ nanosheets under visible light irradiation. Additionally, this strategy of environmental “phosphorylation” is potentially applied to other semiconductor systems (such as TiO₂ and CdS) and thus provide a facile approach to efficient photocatalysis, such as H₂ production, CO₂ photoreduction, and photoelectric conversion.

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Chapter 6 Conclusion and prospective

This chapter presents an overall conclusion of this dissertation. And the future prospects based on the research are also given in the chapter.

Reference

1. J. Tang, Z. Zou and J. Ye, *Angew. Chem. Int. Ed.*, 2004, **43**, 4463-4466.
2. C. Chen, W. Ma and J. Zhao, *Chem. Soc. Rev.*, 2010, **39**, 4206-4219.
3. M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori and N. S. Lewis, *Chem. Rev.*, 2010, **110**, 6446-6473.
4. A. Kudo and Y. Miseki, *Chem. Soc. Rev.*, 2009, **38**, 253-278.
5. K. Iwashina, A. Iwase, Y. H. Ng, R. Amal and A. Kudo, *J. Am. Chem. Soc.*, 2015, **137**, 604-607.
6. S. C. Roy, O. K. Varghese, M. Paulose and C. A. Grimes, *ACS Nano*, 2010, **4**, 1259-1278.
7. W. Tu, Y. Zhou and Z. Zou, *Adv. Mater.*, 2014, **26**, 4607-4626.
8. D. D. Zhu, J. L. Liu and S. Z. Qiao, *Adv. Mater.*, 2016, **28**, 3423-3452.
9. S. N. Habisreutinger, L. Schmidt-Mende and J. K. Stolarczyk, *Angew. Chem. Int. Ed.*, 2013, **52**, 7372-7408.
10. J. L. White, M. F. Baruch, J. E. Pander Iii, Y. Hu, I. C. Fortmeyer, J. E. Park, T. Zhang, K. Liao, J. Gu, Y. Yan, T. W. Shaw, E. Abelev and A. B. Bocarsly, *Chem. Rev.*, 2015, **115**, 12888-12935.
11. F. Wang, C. Li, H. Chen, R. Jiang, L.-D. Sun, Q. Li, J. Wang, J. C. Yu and C.-H. Yan, *J. Am. Chem. Soc.*, 2013, **135**, 5588-5601.
12. A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37-38.

Chapter 1

13. T. Hisatomi, J. Kubota and K. Domen, *Chem. Soc. Rev.*, 2014, **43**, 7520-7535.
14. H. Tong, S. Ouyang, Y. Bi, N. Umezawa, M. Oshikiri and J. Ye, *Adv. Mater.*, 2012, **24**, 229-251.
15. L. Fulcheri and Y. Schwob, *Int. J. Hydrogen Energy*, 1995, **20**, 197-202.
16. X. Lu, S. Xie, H. Yang, Y. Tong and H. Ji, *Chem. Soc. Rev.*, 2014, **43**, 7581-7593.
17. A. B. Murphy, P. R. F. Barnes, L. K. Randeniya, I. C. Plumb, I. E. Grey, M. D. Horne and J. A. Glasscock, *Int. J. Hydrogen Energy*, 2006, **31**, 1999-2017.
18. S. Sato and J. M. White, *Chem. Phys. Lett.*, 1980, **72**, 83-86.
19. K. Yamaguti and S. Sato, *J. Chem. Soc., Faraday Trans. 1 F*, 1985, **81**, 1237-1246.
20. K. Domen, S. Naito, M. Soma, T. Onishi and K. Tamaru, *J. Chem. Soc., Chem. Commun.*, 1980, 543-544.
21. K. Domen, S. Naito, T. Onishi and K. Tamaru, *Chem. Phys. Lett.*, 1982, **92**, 433-434.
22. J. Kim, D. W. Hwang, H. G. Kim, S. W. Bae, J. S. Lee, W. Li and S. H. Oh, *Top. Catal.*, 2005, **35**, 295-303.
23. H. Kato and A. Kudo, *Catal. Today*, 2003, **78**, 561-569.
24. H. Kato and A. Kudo, *J. Phys. Chem. B*, 2001, **105**, 4285-4292.
25. H. Kato, K. Asakura and A. Kudo, *J. Am. Chem. Soc.*, 2003, **125**, 3082-3089.
26. Z. Zou, J. Ye, K. Sayama and H. Arakawa, *Nature*, 2001, **414**, 625-627.
27. K. Maeda, K. Teramura, D. Lu, T. Takata, N. Saito, Y. Inoue and K. Domen, *Nature*, 2006, **440**, 295-295.

Chapter 1

28. K. Maeda, T. Takata, M. Hara, N. Saito, Y. Inoue, H. Kobayashi and K. Domen, *J. Am. Chem. Soc.*, 2005, **127**, 8286-8287.
29. K. Maeda, K. Teramura and K. Domen, *J. Catal.*, 2008, **254**, 198-204.
30. C. Pan, T. Takata, M. Nakabayashi, T. Matsumoto, N. Shibata, Y. Ikuhara and K. Domen, *Angew. Chem. Int. Ed.*, 2015, **54**, 2955-2959.
31. T. Takata, C. Pan, M. Nakabayashi, N. Shibata and K. Domen, *J. Am. Chem. Soc.*, 2015, **137**, 9627-9634.
32. P. Zhou, J. Yu and M. Jaroniec, *Adv. Mater.*, 2014, **26**, 4920-4935.
33. H. Kato, M. Hori, R. Konta, Y. Shimodaira and A. Kudo, *Chem. Lett.*, 2004, **33**, 1348-1349.
34. S. Chen, Y. Qi, T. Hisatomi, Q. Ding, T. Asai, Z. Li, S. S. K. Ma, F. Zhang, K. Domen and C. Li, *Angew. Chem. Int. Ed.*, 2015, **54**, 8498-8501.
35. Q. Wang, T. Hisatomi, S. S. K. Ma, Y. Li and K. Domen, *Chem. Mater.*, 2014, **26**, 4144-4150.
36. H. Tada, T. Mitsui, T. Kiyonaga, T. Akita and K. Tanaka, *Nat. Mater.*, 2006, **5**, 782-786.
37. R. Niishiro, S. Tanaka and A. Kudo, *Appl. Catal., B*, 2014, **150–151**, 187-196.
38. Q. Wang, T. Hisatomi, Q. Jia, H. Tokudome, M. Zhong, C. Wang, Z. Pan, T. Takata, M. Nakabayashi, N. Shibata, Y. Li, I. D. Sharp, A. Kudo, T. Yamada and K. Domen, *Nat. Mater.*, 2016, **15**, 611–615.
39. H. Li, W. Tu, Y. Zhou and Z. Zou, *Advanced Science*, 2016, DOI: 10.1002/advs.201500389.

Chapter 1

40. H. J. Yun, H. Lee, N. D. Kim, D. M. Lee, S. Yu and J. Yi, *ACS Nano*, 2011, **5**, 4084-4090.
41. T. Kawai and T. Sakata, *J. Chem. Soc., Chem. Commun.*, 1980, 694-695.
42. T. Kawai and T. Sakata, *Nature*, 1979, **282**, 283-284.
43. J. Yang, D. Wang, H. Han and C. Li, *Acc. Chem. Res.*, 2013, **46**, 1900-1909.
44. F. Wen, J. Yang, X. Zong, B. Ma, D. Wang and C. Li, *J. Catal.*, 2011, **281**, 318-324.
45. F. Wen , X. Wang , L. Huang , G. Ma , J. Yang and C. Li *ChemSusChem*, 2012, **5**, 849-853.
46. H. Yi, T. Peng, D. Ke, D. Ke, L. Zan and C. Yan, *Int. J. Hydrogen Energy*, 2008, **33**, 672-678.
47. M. Liu, W. You, Z. Lei, G. Zhou, J. Yang, G. Wu, G. Ma, G. Luan, T. Takata, M. Hara, K. Domen and C. Li, *Chem. Commun.*, 2004, 2192-2193.
48. S. Y. Ryu, J. Choi, W. Balcerski, T. K. Lee and M. R. Hoffmann, *Ind. Eng. Chem. Res.*, 2007, **46**, 7476-7488.
49. J. Yu and J. Ran, *Energy Environ. Sci.*, 2011, **4**, 1364-1371.
50. J. Schneider and D. W. Bahnemann, *J. Phys. Chem. Lett.*, 2013, **4**, 3479-3483.
51. M. Ni, M. K. H. Leung, D. Y. C. Leung and K. Sumathy, *Renewable Sustainable Energy Rev.*, 2007, **11**, 401-425.
52. J. Kim, D. Monllor-Satoca and W. Choi, *Energy Environ. Sci.*, 2012, **5**, 7647-7656.
53. H. Yan, J. Yang, G. Ma, G. Wu, X. Zong, Z. Lei, J. Shi and C. Li, *J. Catal.*, 2009, **266**, 165-168.

Chapter 1

54. E. Fujita, *Coord. Chem. Rev.*, 1999, **185–186**, 373-384.
55. K. Iizuka, T. Wato, Y. Miseki, K. Saito and A. Kudo, *J. Am. Chem. Soc.*, 2011, **133**, 20863-20868.
56. S. Ouyang and J. Ye, *J. Am. Chem. Soc.*, 2011, **133**, 7757-7763.
57. S. Ouyang, N. Kikugawa, D. Chen, Z. Zou and J. Ye, *J. Phys. Chem. C*, 2009, **113**, 1560-1566.
58. R. Asai, H. Nemoto, Q. Jia, K. Saito, A. Iwase and A. Kudo, *Chem Commun (Camb)*, 2014, **50**, 2543-2546.
59. S. U. M. Khan, M. Al-Shahry and W. B. Ingler, *Science*, 2002, **297**, 2243-2245.
60. X. Li, N. Kikugawa and J. Ye, *Adv. Mater.*, 2008, **20**, 3816-3819.
61. W. Yao and J. Ye, *J. Phys. Chem. B*, 2006, **110**, 11188-11195.
62. D. Cao-Thang, N. Thanh-Dinh, F. Kleitz and D. Trong-On, *Chem. Commun.*, 2011, **47**, 7797-7799.
63. N. Zhang, S. Ouyang, P. Li, Y. Zhang, G. Xi, T. Kako and J. Ye, *Chem. Commun.*, 2011, **47**, 2041-2043.
64. S. Liu, J. Yu and M. Jaroniec, *J. Am. Chem. Soc.*, 2010, **132**, 11914-11916.
65. Y. Bi, S. Ouyang, N. Umezawa, J. Cao and J. Ye, *J. Am. Chem. Soc.*, 2011, **133**, 6490-6492.
66. R. Li, F. Zhang, D. Wang, J. Yang, M. Li, J. Zhu, X. Zhou, H. Han and C. Li, *Nat Commun*, 2013, **4**, 1432.
67. J. Yu, J. Low, W. Xiao, P. Zhou and M. Jaroniec, *J. Am. Chem. Soc.*, 2014, **136**, 8839-8842.

Chapter 1

68. H. Wang, L. Zhang, Z. Chen, J. Hu, S. Li, Z. Wang, J. Liu and X. Wang, *Chem. Soc. Rev.*, 2014, **43**, 5234-5244.
69. Y. Qu and X. Duan, *Chem. Soc. Rev.*, 2013, **42**, 2568-2580.
70. K. Qian, B. C. Sweeny, A. C. Johnston-Peck, W. Niu, J. O. Graham, J. S. DuChene, J. Qiu, Y.-C. Wang, M. H. Engelhard, D. Su, E. A. Stach and W. D. Wei, *J. Am. Chem. Soc.*, 2014, **136**, 9842-9845.
71. S. Linic, P. Christopher and D. B. Ingram, *Nat. Mater.*, 2011, **10**, 911-921.
72. C. Clavero, *Nat. Photon.*, 2014, **8**, 95-103.
73. L. Liu, T. D. Dao, R. Kodiyath, Q. Kang, H. Abe, T. Nagao and J. Ye, *Adv. Funct. Mater.*, 2014, **24**, 7754-7762.
74. D. B. Ingram and S. Linic, *J. Am. Chem. Soc.*, 2011, **133**, 5202-5205.
75. M. Lee, J. U. Kim, J. S. Lee, B. I. Lee, J. Shin and C. B. Park, *Adv. Mater.*, 2014, **26**, 4463-4468.
76. Q. Wang, M. Zhang, C. Chen, W. Ma and J. Zhao, *Angew. Chem. Int. Ed.*, 2010, **49**, 7976-7979.
77. H. Sheng, H. Ji, W. Ma, C. Chen and J. Zhao, *Angew. Chem. Int. Ed. Engl.*, 2013, **52**, 9686-9690.
78. F. T. Wagner and G. A. Somorjai, *Nature*, 1980, **285**, 559-560.
79. T. Simon, N. Bouchonville, M. J. Berr, A. Vaneski, A. Adrović, D. Volbers, R. Wyrwich, M. Döblinger, A. S. Sussha, A. L. Rogach, F. Jäckel, J. K. Stolarczyk and J. Feldmann, *Nat. Mater.*, 2014, **13**, 1013-1018.
80. S. Chen, S. Shen, G. Liu, Y. Qi, F. Zhang and C. Li, *Angew. Chem. Int. Ed.*, 2015, **54**, 3047-3051.

Chapter 1

81. S. Xie, Y. Wang, Q. Zhang, W. Fan, W. Deng and Y. Wang, *Chem. Commun.*, 2013, **49**, 2451-2453.
82. X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti, *Nat. Mater.*, 2009, **8**, 76-80.
83. S. Cao, J. Low, J. Yu and M. Jaroniec, *Adv. Mater.*, 2015, **27**, 2150-2176.
84. Y. Wang, X. Wang and M. Antonietti, *Angew. Chem. Int. Ed.*, 2012, **51**, 68-89.
85. Y. Zheng, L. Lin, B. Wang and X. Wang, *Angew. Chem. Int. Ed.*, 2015, **54**, 12868-12884.
86. Y. Cui, Z. Ding, P. Liu, M. Antonietti, X. Fu and X. Wang, *Phys. Chem. Chem. Phys.*, 2012, **14**, 1455-1462.
87. S. Yang, Y. Gong, J. Zhang, L. Zhan, L. Ma, Z. Fang, R. Vajtai, X. Wang and P. M. Ajayan, *Adv. Mater.*, 2013, **25**, 2452-2456.
88. J. Zhang, Y. Chen and X. Wang, *Energy Environ. Sci.*, 2015, **8**, 3092-3108.
89. P. Niu, L. Zhang, G. Liu and H.-M. Cheng, *Adv. Funct. Mater.*, 2012, **22**, 4763-4770.
90. X. Lu, K. Xu, P. Chen, K. Jia, S. Liu and C. Wu, *J. Mater. Chem. A*, 2014, **2**, 18924-18928.
91. X. Wang, K. Maeda, X. Chen, K. Takanabe, K. Domen, Y. Hou, X. Fu and M. Antonietti, *J. Am. Chem. Soc.*, 2009, **131**, 1680-1681.
92. H. Yan, *Chem. Commun.*, 2012, **48**, 3430-3432.
93. J. Sun, J. Zhang, M. Zhang, M. Antonietti, X. Fu and X. Wang, *Nat Commun*, 2012, DOI: 10.1038/ncomms2152, 1139.

Chapter 1

94. G. Zhang, M. Zhang, X. Ye, X. Qiu, S. Lin and X. Wang, *Adv. Mater.*, 2014, **26**, 805-809.
95. Y. Zhang, T. Mori, J. Ye and M. Antonietti, *J. Am. Chem. Soc.*, 2010, **132**, 6294-6295.
96. G. Liu, P. Niu, C. Sun, S. C. Smith, Z. Chen, G. Q. Lu and H.-M. Cheng, *J. Am. Chem. Soc.*, 2010, **132**, 11642-11648.
97. J. Zhang, X. Chen, K. Takanabe, K. Maeda, K. Domen, J. D. Epping, X. Fu, M. Antonietti and X. Wang *Angew. Chem. Int. Ed.*, 2010, **49**, 441-444.
98. J. Zhang, G. Zhang, X. Chen, S. Lin, L. Möhlmann, G. Dołęga, G. Lipner, M. Antonietti, S. Blechert and X. Wang, *Angew. Chem. Int. Ed.*, 2012, **51**, 3183-3187.
99. J. Zhang, M. Zhang, R.-Q. Sun and X. Wang, *Angew. Chem. Int. Ed.*, 2012, **51**, 10145-10149.
100. P. Wu, J. Wang, J. Zhao, L. Guo and F. E. Osterloh, *Chem. Commun.*, 2014, **50**, 15521-15524.

Chapter 2 Defect-modified graphitic carbon nitride with p-n homojunction structure towards enhanced photocatalytic hydrogen evolution activity

2.1 Introduction

Photocatalytic H₂ evolution is promising technologies for solar energy conversion and storage.^[1-6] Since the first report in 2009, graphitic carbon nitride (g-C₃N₄) has emerged as an attractive photocatalyst for photocatalytic H₂ production due to its unique properties, such as suitable energy band structure for both water reduction, high chemical and thermal stability, and cost effective metal-free composition.^[7-17] However, g-C₃N₄ obtained by the commonly-used direct thermal polymerization method generally suffers from moderate photocatalytic activities because of the fast electron-hole recombination and insufficient solar-light absorption, which significantly hinders its applications. Aiming at improving the performance of g-C₃N₄, various strategies have been explored, including nanostructure design,^[10-12, 14-19] molecule incorporation,^[20] element doping,^[21, 22] and reaction environment modulation.^[23] In particular, the in-situ defect modification of g-C₃N₄ was developed recently as an effective way to increase the photocatalytic activity.^[24-26] It was demonstrated that, the defects in the tri-s-triazine repeating units of g-C₃N₄ not only function to modify the band structure by introducing additional energy levels in the bandgap, but also act as reactive sites for photocatalysis reaction. A work on this topic was

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firstly established by Liu et al.,^[26] who reported that the implantation of nitrogen defect into g-C₃N₄ could enable a significant decrease in band gap of 0.75 eV, extending the light absorption edge from 500 to 850 nm and consequently achieving a much superior photocatalytic activity for Rhodamine B degradation. Also, Yang et al. found that the g-C₃N₄ with carbon defect modification could give the enhanced light absorption and the suppressed recombination rate of photoexcited charge carriers, therefore showing the improved photocatalytic activity.^[27] Despite these advances, the researches on defect chemistry of g-C₃N₄ based materials are still rare and the function of defect involved in the photocatalysis is also under debated. What is more, to realize the incorporation of defect into g-C₃N₄ structure, a relatively high operation temperature (> 490 °C) and a reducing atmosphere (like H₂ and NH₃) are both indispensable. Therefore, more facile and effective approaches towards the preparation of defect-modified g-C₃N₄ are also urgently required.

As mentioned above, the fast charge recombination caused intrinsically by the π - π conjugated electronic system is believed to be the main reason for the poor photocatalytic efficiency of g-C₃N₄ materials.^[7, 27, 28] To promote the charge separation, an effective option is to assembly host g-C₃N₄ with guest semiconductors and to construct heterojunction photocatalysts, which could induce a built-in interfacial electric field via the energy band offset and enable opposite migration of photogenerated electrons and holes.^[7, 29, 30] However, because of such heterojunctions built from two distinct semiconductors, achieving an efficient heterojunctions is not only governed by their energy band configurations but also affected significantly by their crystal structures, surface/interface properties and other features, which makes it difficult to manipulate in practical applications. In sharp contrast, the homojunction photocatalysts, composed of the same

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semiconductor materials, show to be much advantageous in these respects.^[30] Furthermore, the composition identity on both sides of the interface in such homojunctions could give rise to a continuous band bending, thus much favorable for charge transfer across the interface and facilitating the carrier separation.^[31, 32] Though designing homojunctions for improved photocatalysis have been a topic of intense investigation, it only limit to inorganic semiconductors (such as anatase/rutile TiO₂,^[33, 34] α/β -Ga₂O₃,^[32] and p/n-Si^[35]), and g-C₃N₄-based organic homojunction photocatalysts are still rarely reported so far. Simultaneously, as is well known, g-C₃N₄ is a typical n-doped material probably because it contains many -NH/NH₂ groups as electron donors in the structure.^[36] This inspires us to realize that replacing -NH/NH₂ electron-donor groups on the g-C₃N₄ sheet edge with electron-acceptor groups might transform g-C₃N₄ into p-type semiconductor, thus making it possible to construct p-n homostuctural g-C₃N₄ photocatalysts.

In this work, we present a facile and effective preparation of defect-modified g-C₃N₄ (denoted as DCN) through a low-temperature heating (< 350 °C) of g-C₃N₄ with NaBH₄ under inert atmosphere. It is shown that DCN not only exhibits a much extended light absorption capability, but also presents both n- and p-type conductivities due to the implantation of -C $\equiv$ N functional groups as electron acceptors into the structure of g-C₃N₄, consequently leading to the construction of p-n homojunctions. To the best of our knowledge, this should be the first successful preparation of p-n homojunctions for g-C₃N₄-based materials. As expected, such homojunction structure is found to be highly efficient in charge transfer and separation and results in a five-fold enhanced photocatalytic H₂ evolution activity under visible light. It is believed that the findings deepen the understanding on the defect-related issues of g-C₃N₄-based materials and meanwhile

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provide a promising route for the rational design of photocatalysts with unique architectures for more efficient solar energy conversion.

2.2 Experimental section

2.2.1 Material preparation

The pristine g-C₃N₄ was prepared by the commonly-used direct thermal polymerization of dicyandiamide at 550 °C for 4 h with a ramping rate of 3 °C/min in air. After cooled naturally, the yellow product was grounded in an agate mortar to obtain a powder sample. To prepare the defect-modified homojunction g-C₃N₄, the pristine g-C₃N₄ was fully mixed with NaBH₄ with a weight ratio of 5:1, followed by the heating at an appropriate temperature (ranging from 150 to 350 °C) for 30 min. Then the resultant powders were washed with water, HCl, NaOH and once again with water (washed several times until neutral) to remove all unreacted and potentially detrimental surface species. The products were denoted as DCN-x (x indicates the heating temperature).

2.2.2 Material characterization

The morphology of samples was observed by using a JEOL 6701F Field-emission scanning electron microscopy (SEM). The C/N atomic ratio in CN and DCN samples were determined using an Elemental Vario EL III Analyzer. X-ray diffraction (XRD) patterns were recorded on an X'Pert PRO diffractometer with Cu-K α radiation (PANalytical). IRPrestige-21 Fourier transform infrared (FTIR) spectrometer was used to investigate the chemical structures for samples. In-situ FTIR measurements were conducted on a JASCO FTIR-6300 spectrometer. The diffuse reflectance spectra of the samples were measured on a UV-visible spectrophotometer (UV-2600; Shimadzu Corp., Japan). Then the absorption

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spectra were calculated from the reflectance spectra by means of Kubelka-Munk transformations. A FP-6500 spectrofluorometer (Jasco, Japan) was used to record the photoluminescence (PL) spectra of CN and DCN. The wavelength of the excitation light is 360 nm. N₂ adsorption-desorption experiments were conducted at 77 K to examine the Brunauer-Emmett-Teller surface area (BELsorp II mini, BEL Japan Inc.). Before measuring, the samples were degassed in a vacuum at 100 °C for 12 h. Surface chemical analysis was performed by X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM, ULVAC-PHI Inc., Japan). Electron spin resonance (ESR) spectra were recorded on a JES-FA200 Electron Spin Resonance Spectrometer operating at about 9.0 GHz at room temperature. The gaseous products formed during the heating treatment of CN with NaBH₄ were measured by a gas chromatograph (GC-2014, Shimadzu Corp., Japan) and a gas chromatography-mass spectrometry system (GC-MS; JMS-K9, JEOL). NMR experiments were performed under ambient condition on a JEOL ECS-400 NMR spectrometer.

2.2.3 Photo-electrochemical measurements

Preparation of photoelectrodes

The photoelectrodes were prepared according to previously reported method.^[37] The indium doped tin oxide (ITO) substrates were cleaned by ultrasonication in distilled water, absolute ethanol, and isopropanol for 15 min sequentially, and then dried in vacuum. 5 mg of photocatalysts and 10 µl of Nafion solution (5 wt%) were dispersed in 1 ml water/isopropanol mixed solvent (3:1 v/v) by at least 30 min sonication to form a homogeneous catalyst colloid. Then, 150 µl of the catalyst colloid was deposited onto areas

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of ca. 1 cm² of the ITO conductive glass and then was dried in air to form the working electrode.

Photoelectrochemical measurements in a three-electrode system

The photoelectrochemical properties were investigated in a conventional three-electrode cell by using an electrochemical analyzer (Model-650A). The catalyst coated ITO glass, a Pt foil, and an Ag/AgCl electrode and 0.5 M Na₂SO₄ aqueous solution were used as the working electrode, the counter-electrode, the reference electrode and the electrolyte, respectively. A 500 W Xe arc lamp equipped with a 420 nm cutoff filter was utilized as a light source. Electrochemical impedance spectra (EIS) were recorded at an applied potential of 1.0 V vs. Ag/AgCl over the frequency range of 1 MHz to 0.01 Hz. The photocurrent with ON/OFF cycles was measured at an applied potential of 1.0 V vs. Ag/AgCl. Mott-Schottky plots were obtained under direct current potential polarization at different frequencies (1000, 1500, and 2000 Hz). The potential ranged from -0.4 to 1.6 V (vs. Ag/AgCl).

2.2.4 Photocatalytic activity measurements

The photocatalytic H₂ production was carried out in a Pyrex glass reaction cell containing 270 ml 10 vol% of triethanolamine (TEOA) aqueous solution. 25 mg of photocatalysts were used in the reaction. 3 wt.% Pt as the cocatalyst was in-situ photodeposited on the surface of photocatalysts. Before the irradiation, the reaction cell was connected to a gas-closed system with a gas-circulated pump and evacuated several times to remove the air completely. A 300 W Xenon lamp equipped with L40 cut-off filter was used as the visible-light source. The H₂ evolution was analyzed by an online gas

chromatograph (GC-8A; Shimadzu Corp., Japan) equipped with a thermal conductivity detector.

2.3 Results and discussion

2.3.1 Characterization of the p-n homojunction g-C₃N₄

The pristine g-C₃N₄ was prepared using dicyandiamide as a precursor through the commonly-used thermal polymerization strategy (that is, directly heating dicyandiamide to 550 °C for 4 h).^[38] The easy operability of this method is of significance for the practical use. X-ray diffraction (XRD) analysis was used to confirm the formation of g-C₃N₄, in which two characteristic peaks located at 13.2° and 27.3°, respectively were observed (Figure 2.1a).^[7] Then, the defect-modified g-C₃N₄ (DCN) was synthesized by simply heating the raw g-C₃N₄ with NaBH₄ to 150 ~ 350 °C for appropriate time under an argon atmosphere. Elemental analysis shows that, with the increasing of heating temperature, the C/N atomic ratio in DCN shows an obvious increase from 0.692 to 0.766 (Figure 2.1b). This result not only indicates the successful introduction of defects into g-C₃N₄ via direct heating with NaBH₄, but also suggests the preferential loss of N atoms during the defect formation.^[26] Figure 2.1c shows the optical properties of CN and all DCN samples, as measured by UV-vis Diffuse Reflection Spectra. It is clear that the implantation of defects into CN by heating with NaBH₄ much extends its light absorption. Particularly, when the heating temperature increases to 350 °C, as shown by the difference absorption spectra of DCN-350 vs. CN, the enhanced absorption nearly covers the whole visible region and exhibits the maximum at 500 nm, which endows the narrowing of band gap from 2.75 to 2.00 eV (Figure 2.2). Consistent with these absorption results, the color of the powders

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suffers a matching variation from yellow to brown as the treatment temperature increasing (Figure 2.3). On the other hand, as evidenced by XRD patterns (Figure 2.1a), scanning electron microscopy (SEM) observation (Figure 2.4) and N₂ adsorption results (Figure 2.5), the introduction of defects here presents little effect on the morphology and crystal structure of g-C₃N₄, that is, the basic (layered) structure is maintained.^[39, 40]

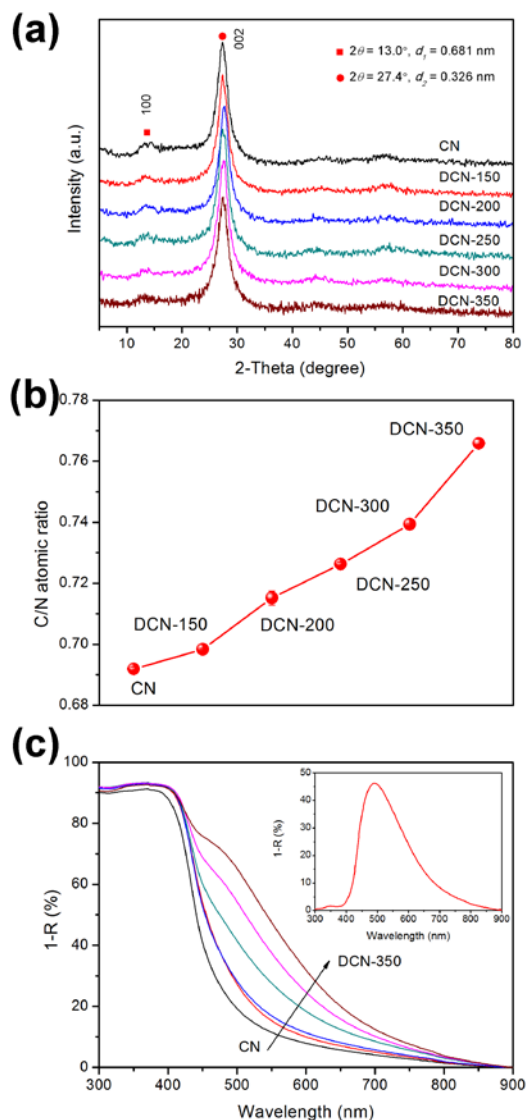


Figure 2.1 (a) XRD patterns, (b) C/N atomic ratio, and (c) UV-vis reflectance spectra of CN and DCN. Inset in (c) shows the difference UV-vis spectra vs bare CN for DCN-350.

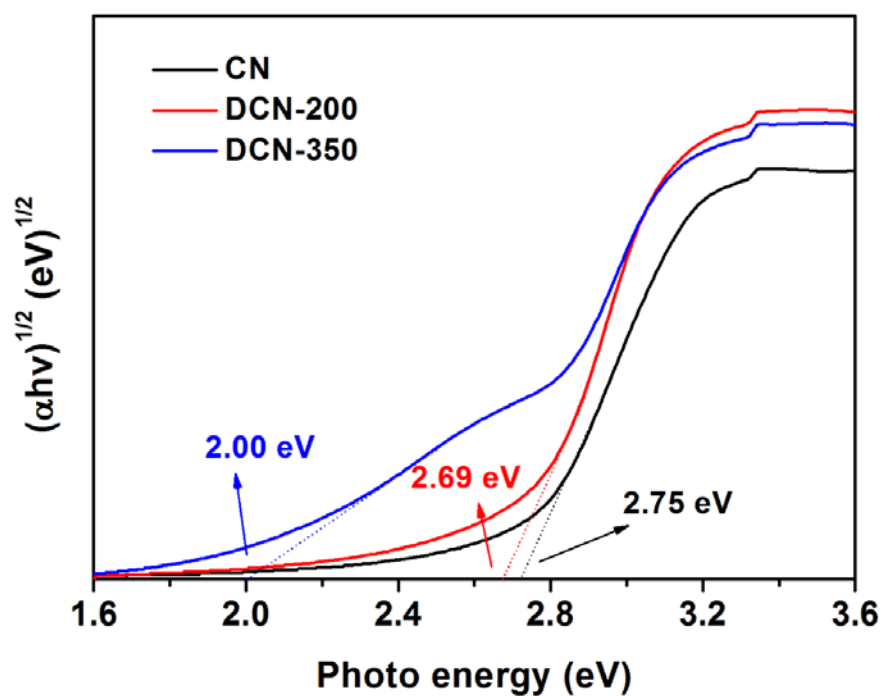


Figure 2.2 $(\alpha h\nu)^{1/2}$ versus $h\nu$ plots of CN, DCN-200 and DCN-350, showing that the corresponding band gaps are 2.75, 2.69 and 2.00 eV, respectively.



Figure 2.3 The colors of the power samples. From left to right: CN, DCN-150, DCN-200, DCN-250, DCN-300 and DCN-350.

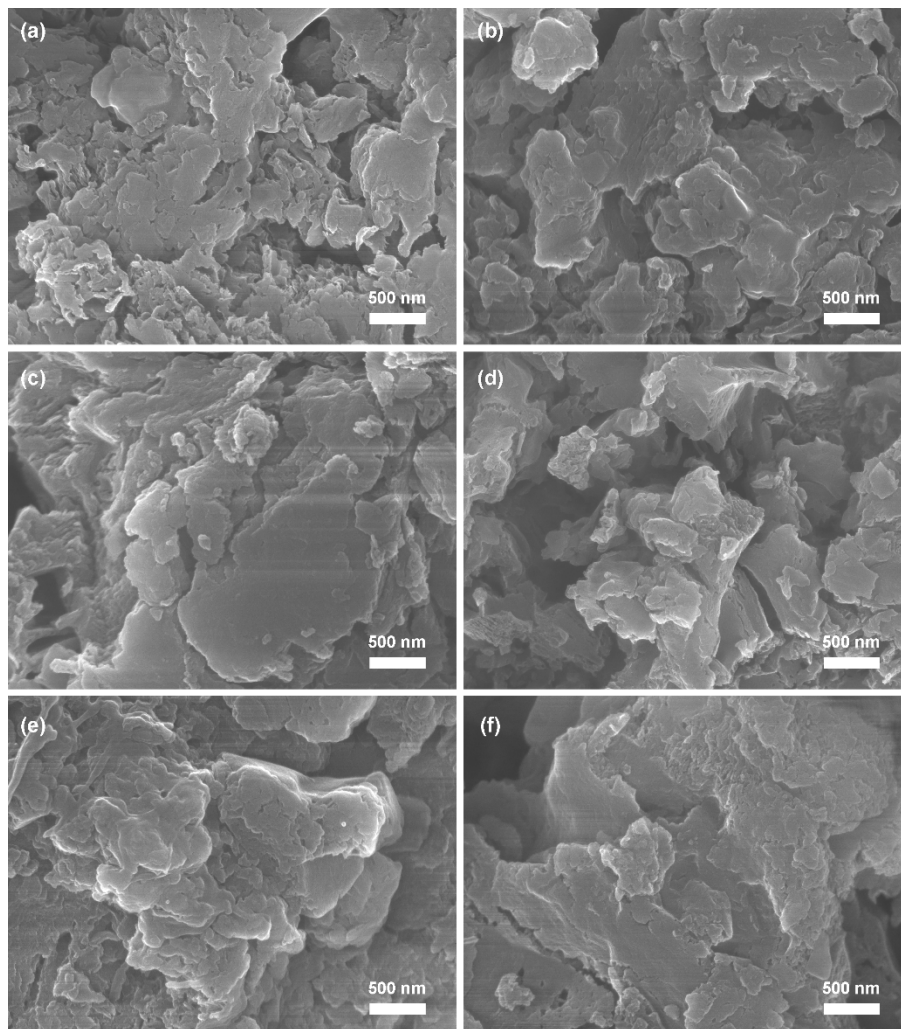


Figure 2.4 SEM images of CN and DCN: (a) CN, (b) DCN-150, (c) DCN-200, (b) DCN-250, (b) DCN-300, and (d) DCN-350.

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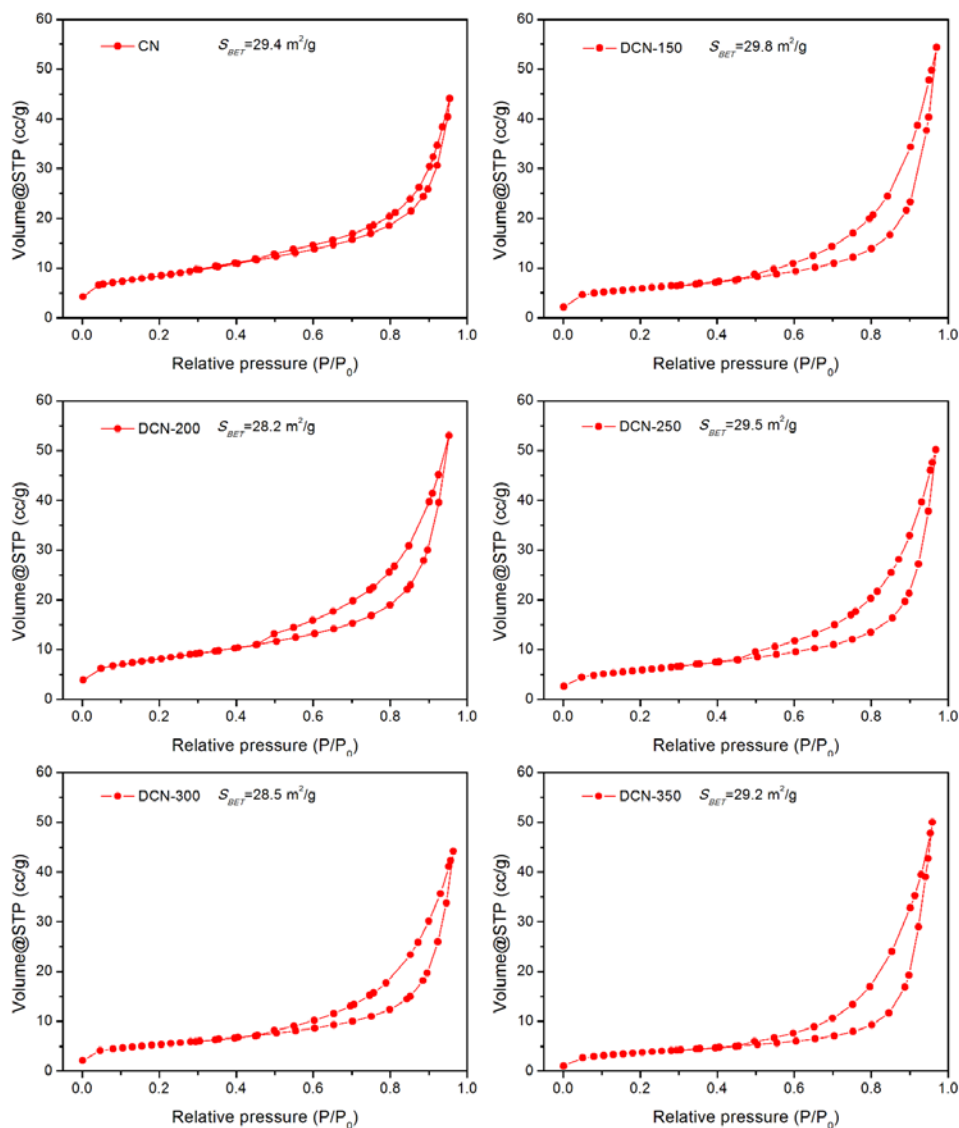


Figure 2.5 N₂ adsorption-desorption isotherms of CN and all DCN samples. In this figure, little difference in BET surface areas between CN and all DCN samples is shown.

During the preparation process of DCN, NaBH₄ could *in situ* thermally decompose and produce the active hydrogen. We therefore speculate that the interaction between the as-formed active hydrogen and g-C₃N₄ might be one cause of defects in g-C₃N₄ as presented above.^[41] In supporting of this idea, the study by Liu *et al.* has shown that H₂ could indeed reduce lattice N in g-C₃N₄ into NH₃, consequently leading to the formation of N defects.^[26]

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However, unlike this case involving the heating treatment at an elevated temperature ($> 520\text{ }^{\circ}\text{C}$), the approach explored in this study achieves the successful implantation of defects into g-C₃N₄ at a rather low heating temperature ($< 350\text{ }^{\circ}\text{C}$). This could be attributed to the relatively higher reactivity of the in-situ-produced hydrogen than H₂.^[41] Here, the emission of NH₃ during the heating treatment is experimentally proved by the gas chromatography-mass spectrometry analysis (Figure 2.6). Additionally, since NaBH₄ is intrinsically a strong and reactive reducing agent, the direct reaction with g-C₃N₄ also probably occurs, which should be another reason for the favorable formation of defects in g-C₃N₄. To gain more insight into such defect formation process, X-ray photoelectron spectroscopy (XPS) measurements were conducted. As shown in Figure 2.7a and b, with the treatment temperature increasing, the peak-area ratio of N_{2C} (two-coordinated N) to N_{3C} (three-coordinated N) shows a dramatic decrease (2.6, 2.1 and 3.8 corresponding to the original, 200- and 350 $^{\circ}\text{C}$ -treated g-C₃N₄, respectively), suggesting that the two-coordinated N atoms were preferentially lost in the reaction.^[26] Simultaneously, the formations of both the N=CH-N and C-NH-C bonding structures are also confirmed (Figure 2.7). This provides a clear evidence supporting that the s-triazine heterocycles in g-C₃N₄ could be opened by NaBH₄ treatment, thus offering more active atoms for the functionalization of g-C₃N₄.

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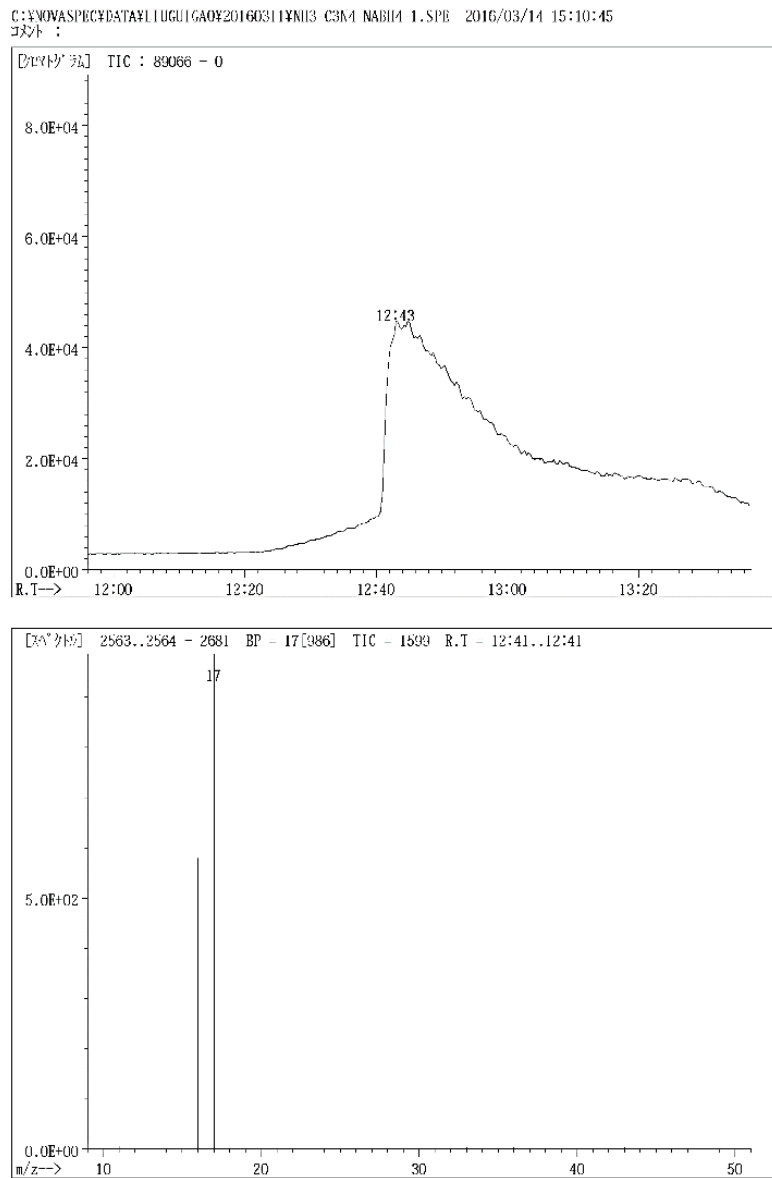


Figure 2.6 GC/MS spectra of the gas obtained during the heating of CN with NaBH₄.

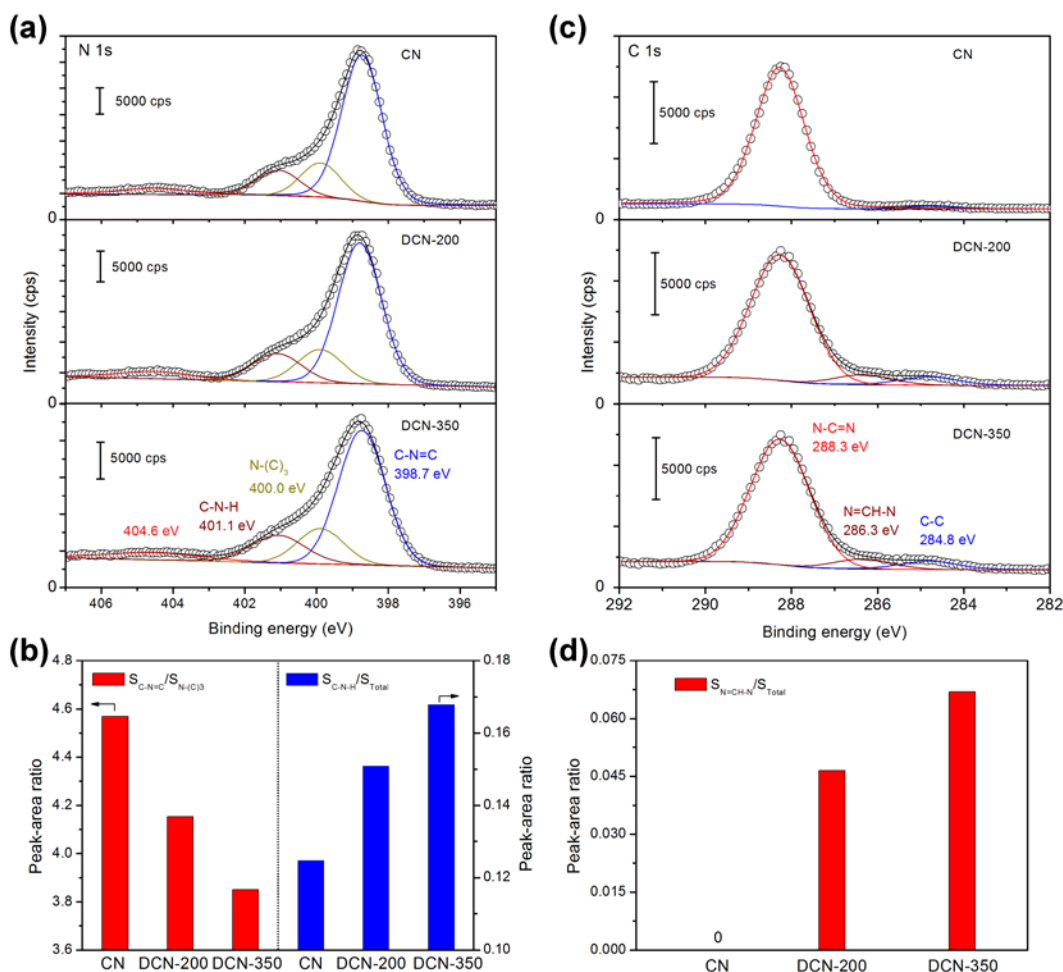


Figure 2.7 High resolution XPS spectra of (a) N 1s and (c) C 1s recorded from CN, DCN-200, and DCN-350. (b) The changes of the peak-area ratio of N_{2C} to N_{3C} and N-H to total N bonds. (d) The changes of the peak-area ratio of C-H to total C bonds.

Unlike previous reports merely focusing on the creation of N or C defects on g-C₃N₄ sheets, here, we found that the NaBH₄ treatment for g-C₃N₄ not only leads to the preferential loss of lattice N and the simultaneous opening of s-triazine heterocycles in g-C₃N₄, but also importantly, results in the formation of new functional C≡N triple bonds. This could be well proved by the Fourier transform infrared (FTIR) spectra. In Figure 2.8, the original g-C₃N₄ shows a spectrum with typical characteristic peaks: the peaks located

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at 3000-3500, 1000-1700, and 810 cm^{-1} are ascribed to the vibrational absorptions of N-H bonds, aromatic C-N heterocycles and s-triazine subunits, respectively.^[7, 10, 11] However, after NaBH_4 treatment, a new vibration band at 2180 cm^{-1} , belonging to $\text{C}\equiv\text{N}$ triple bonds,^[10] arises in the spectra of all DCN samples and the peak intensity increases gradually with the heating temperature increasing. This result clearly indicates the formation of cyano-terminal $\text{C}\equiv\text{N}$ functional groups in DCN. More evidences for supporting this conclusion could be also found in the in-situ FTIR spectra and ^{13}C NMR spectra shown in Figure 2.9 and Figure 2.10, respectively. Since N atoms are more electronegative than C atoms, the $\text{C}\equiv\text{N}$ groups possess typical electron-accepting character.^[42] As thus, introducing $\text{C}\equiv\text{N}$ groups into the structure of $\text{g-C}_3\text{N}_4$ might endow the material with p-type conductive domains.^[36] In combination with the intrinsic n-type conductivities of $\text{g-C}_3\text{N}_4$ materials, the DCN might exhibit both n- and p-type conductivities, consequently leading to the generation of p-n type photochemical homojunctions.

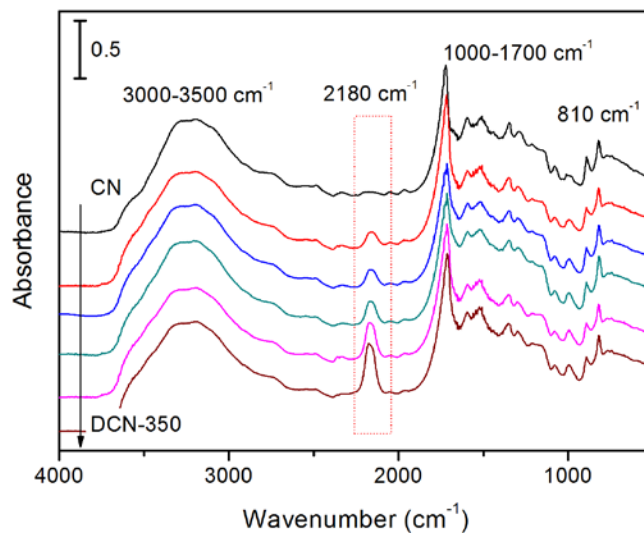


Figure 2.8 FTIR spectra of CN and DCN.

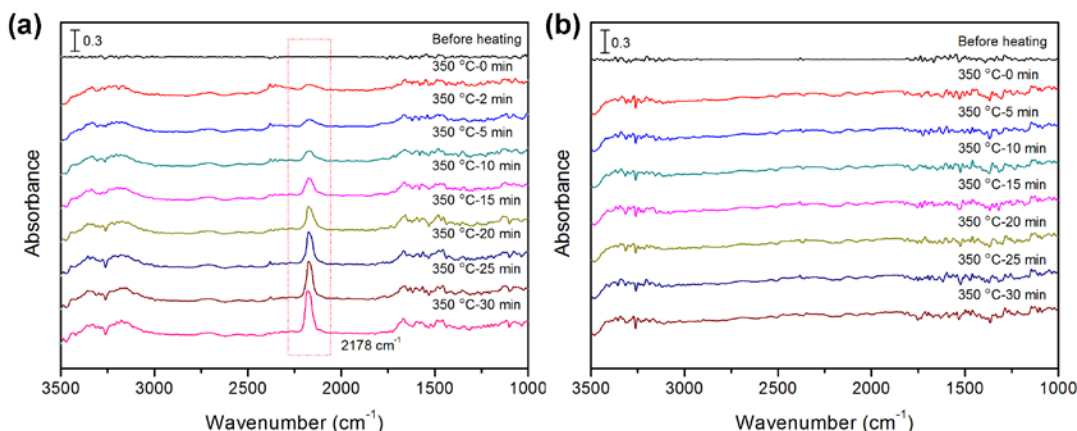


Figure 2.9 (a) In-situ FTIR spectra measured during the heating treatment of CN with NaBH₄. (b) In-situ FTIR spectra measured during the heating treatment of pure CN. As shown in Figure 2.9a, with the heating time (at 350 °C) prolonging, an absorption band located at 2178 cm⁻¹, belonging to C≡N triple bonds,^[10] appears in the in-situ FTIR spectra of the mixture of CN and NaBH₄, and the peak intensity is increased gradually. This result clearly indicates the formation of C≡N triple bonds in CN during the heating with NaBH₄. In sharp contrast, when the measurements were performed on pure CN, no signal indicative of the formation of C≡N triple bonds was observed (Figure 2.9b).

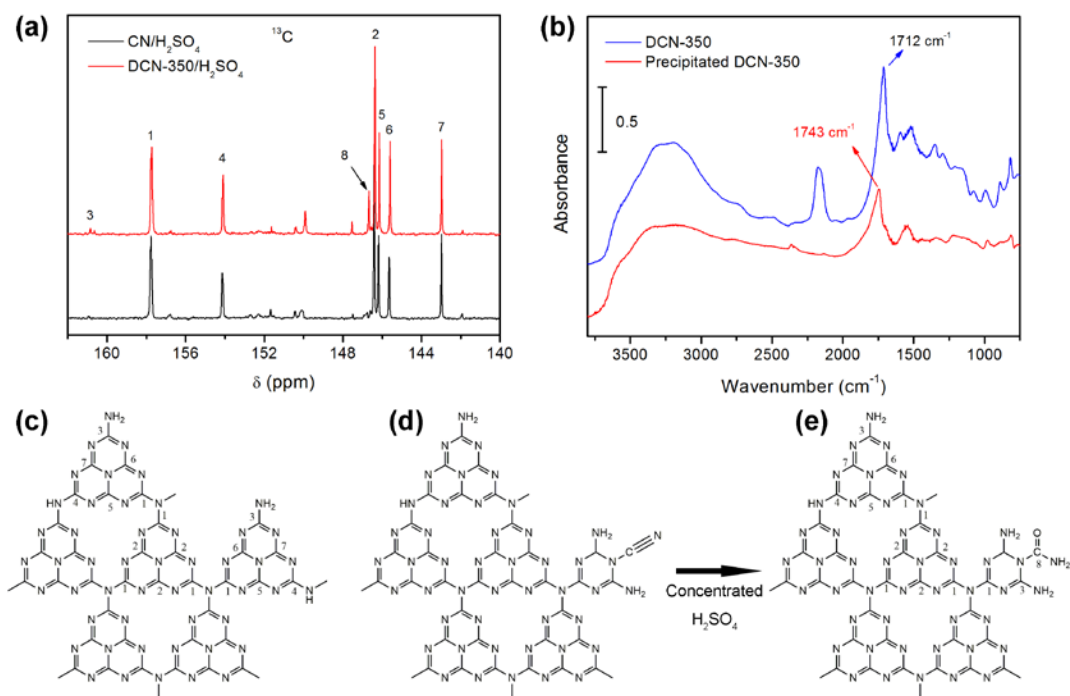


Figure 2.10 (a) ^{13}C liquid-state NMR spectra of CN/ H_2SO_4 and DCN-350/ H_2SO_4 solutions. (b) FTIR spectra of DCN-350 and the precipitated DCN-350 from the DCN-350/ H_2SO_4 solution by adding methanol. (c) The proposed structure for CN. (d and e) The proposed structure for (d) the original DCN-350 and (e) the DCN-350 after dissolved by the concentrated H_2SO_4 . In order to measure ^{13}C liquid-state NMR spectra for CN and DCN, the samples were dissolved in the concentrated H_2SO_4 (95.0-98.0%; Wako) to form clear solutions as the procedure reported by Zhang *et al.*^[43] and then the data were collected, which are shown in Figure 2.10a. In this figure, the signals in the NMR spectrum of CN/ H_2SO_4 are well matched with the data reported by Zhang *et al.*^[43] According to their report, the peak assignment in the NMR spectrum of CN/ H_2SO_4 and the structure of CN are therefore proposed in Figure 2.10c. As for DCN-350, all the peaks shown in the NMR spectrum of CN/ H_2SO_4 are also detected in that of DCN-350/ H_2SO_4 . This result indicates that the main structure of CN is maintained in DCN-350. This is in good agreement with the XRD and FTIR analysis (Figure 2.1a and Figure 2.8). However, more importantly, compared with CN/ H_2SO_4 , a new peak with the resonance at 146.7 (8) ppm arises in the NMR spectrum of

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DCN-350/H₂SO₄. This signal could be attributed to amide groups (as shown in Figure 2.10e),^[44] which is resulted from the hydrolysis of C≡N groups in the concentrated H₂SO₄.^[45] Such hydrolysis process could be confirmed by FTIR results. Figure 2.10b shows the FTIR spectra of DCN-350 and the precipitated DCN-350 from the DCN-350/H₂SO₄ solution by adding methanol. Obviously, the absorption band of C≡N groups at 2180 cm⁻¹ is not observed in the spectrum of the precipitated DCN-350 (marked by yellow color in the figure) and meanwhile a new peak located at 1743 cm⁻¹ appears, which could be attributed to the formation of C=O.^[46] This clearly demonstrates the transformation of C≡N groups into amide groups in DCN-350 when dissolved in the concentrated H₂SO₄. Together, all these results indicate the presence of new functional C≡N triple bonds in the DCN and the proposed corresponding structure is shown in Figure 2.10d.

To identify the type of conductivity of DCN samples, Mott-Schottky analysis was conducted. Based on the Mott-Schottky relationship, the carrier density could be calculated according to the below equation:^[47, 48]

$$N_d = \left(\frac{2}{e_0 \varepsilon_0 \varepsilon} \right) \left[d \left(\frac{1}{C^2} \right) / dV \right]^{-1} \quad (1)$$

where N_d is the donor density (electron donor concentration for an n-type semiconductor or hole acceptor concentration for a p-type semiconductor), e_0 is the electron charge, ε_0 is the permittivity of vacuum, ε is the dielectric constant of the material, C is the capacitance of the space charge region and V is the applied bias at the electrode. From this equation, we can see that $\left[d \left(\frac{1}{C^2} \right) / dV \right]$ indicates the slope of the MS plot. Thus, if the MS plots of a semiconductor have positive slopes, electrons should be the majority carriers in the material (n-type), while they have negative slopes, holes should be the majority carriers (p-type). As shown in Figure 2.11b, the straight lines with positive and negative slopes located

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in different potential regimes are observed. This is indicative of the co-existence of both n- and p-type conductivities in DCN,^[36, 49, 50] well supporting the above speculation. By contrast, the Mott-Schottky plots of the original g-C₃N₄ only exhibit the positive slope (Figure 2.11a), suggesting its intrinsic n-type characteristic. The co-existence of n- and p-type domains in DCN would lead to the formation of p-n type photochemical homojunctions, in which the Fermi-level (E_F) alignment of the p- and n-type domains occurs, thereby creating a built-in field at the interface (Figure 2.11c). This would enable the photogenerated electrons and holes migrating in opposite directions and effectively improve the separation of electron-hole pairs, ultimately facilitating the photocatalysis.^[30, 36] To the best of our knowledge, this should be the first report on the successful preparation of p-n homojunction g-C₃N₄ photocatalysts.

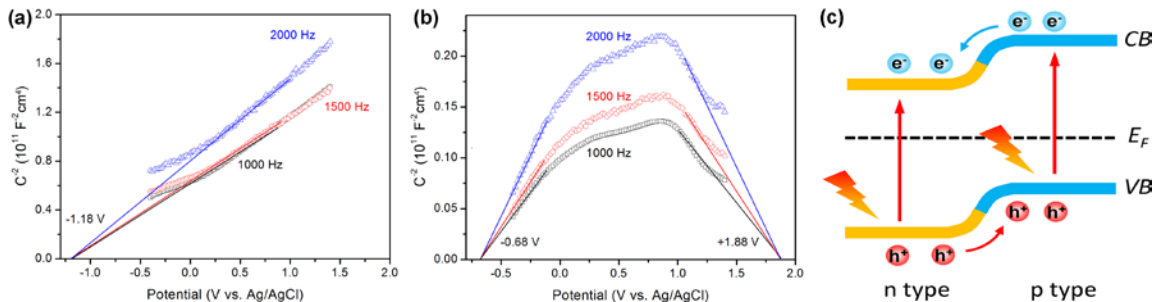


Figure 2.11 Mott-Schottky plots for (a) CN and (b) DCN-200. (c) Illustration of charge transfer in the p-n homojunction of DCN.

To monitor the evolution of the electronic band structure for DCN with a p-n homojunction structure, the room-temperature electron paramagnetic resonance (EPR) spectra were recorded. In Figure 2.12a, both DCN-200 and DCN-350 exhibit a paramagnetic absorption signal with the g value of 2.0034, which can be attributed to unpaired electrons on sp²-carbon atoms within the π -conjugated aromatic rings.^[39, 51]

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Compared with the original g-C₃N₄, this EPR signal in DCN-200 and DCN-350 is much enhanced. This is probably due to the redistribution of π electrons caused by the p-n band offset in DCN. In addition, the appearance of the shoulder peak at $g = 2.0028$ for the EPR spectra of DCN-200 and DCN-350 suggests that the introduction of cyano terminal C $\equiv$ N groups extends the π -conjugated system of the material,^[52] which could efficiently improve the photoinduced production of radical pairs,^[53, 54] as evidenced by the observation of enhanced EPR signal when irradiated with visible-light (Figure 2.12a). Furthermore, using 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPOL) ($g = 2.0060$) with a certain spin number of 3.33×10^{17} as the standard sample, the spin densities of CN and DCN materials were calculated by comparing their integrated ERP signal areas with that of TEMPOL and were summarized in Table 2.1.^[55]

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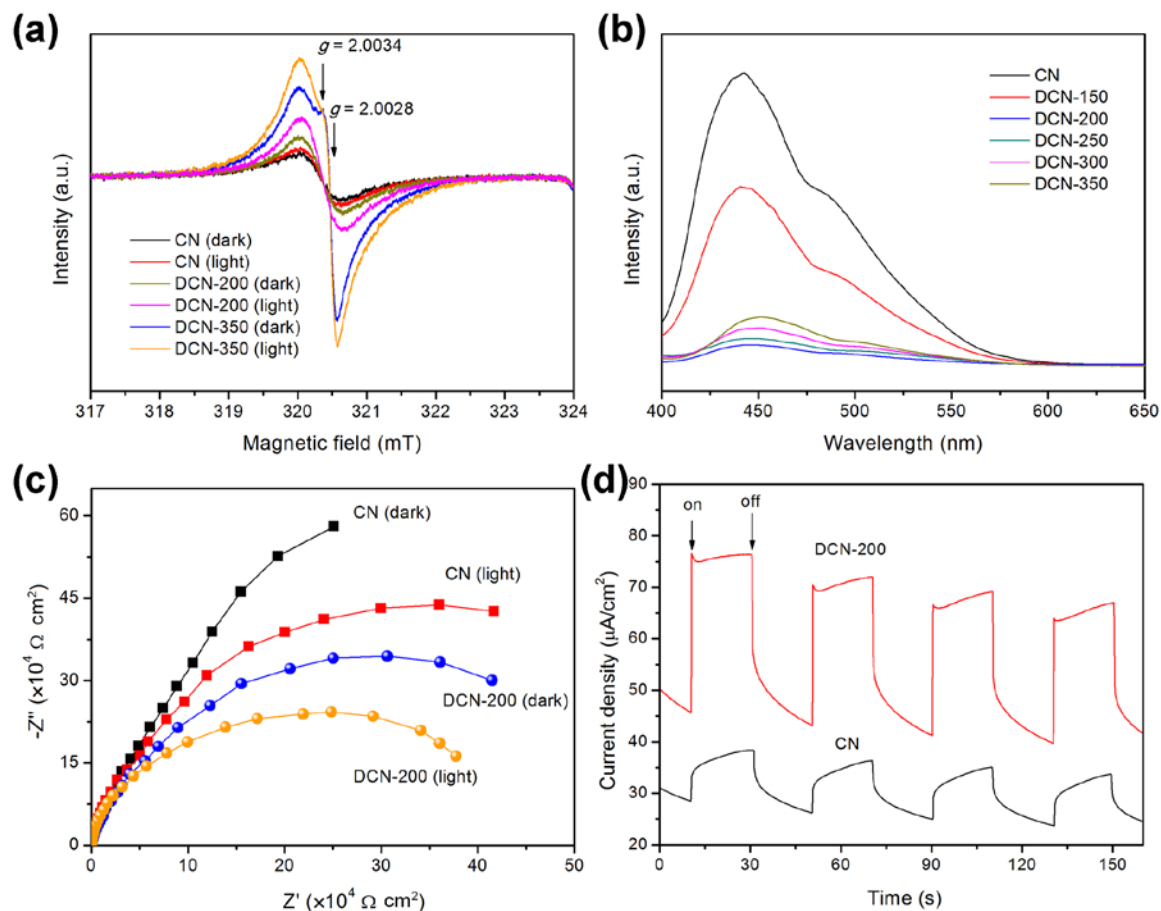


Figure 2.12 (a) Room temperature EPR spectra for CN, DCN-200 and DCN-350 measured with and without the light irradiation. (b) Photoluminescence spectra excited at 360 nm for CN and DCN samples. (c) Electrochemical impedance spectroscopy and (d) transient photocurrents ($\lambda > 420$ nm) for CN and DCN-200.

Table 2.1 The calculated spin densities of CN and DCN materials in the dark and under light irradiation.

Samples	EPR signal area	Spin density (spins g^{-1})
CN (dark)	12.2	$2.4\text{e}+19$
CN (light)	14.5	$2.9\text{e}+19$
DCN-200 (dark)	16.8	$3.3\text{e}+19$
DCN-200 (light)	24.6	$4.9\text{e}+19$
DCN-350 (dark)	39.6	$7.9\text{e}+19$
DCN-350 (light)	52.0	$1.0\text{e}+20$

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Photoluminescence (PL) emission spectrum is a powerful tool to characterize the radiative recombination process of photoexcited carriers in a photocatalyst. As shown in Figure 2.12b, in contrast to a strong fluorescence emission peak at 440 nm exhibited by the g-C₃N₄, all the DCN samples present much quenched PL signals. This result in principle indicates a more efficient separation of charge carries in DCN materials as benefited from their p-n homojunction constructions.^[53, 54] Particularly, among the treated g-C₃N₄ samples, the DCN-200 presents the highest PL quench efficiency and further increasing the heating temperature leads to a slightly increased carrier recombination. This is probably related to the over-formation of defects which could serve as recombination centers for electrons and holes, thus casting adverse effect on charge carrier separation. In addition, with the heating temperature increasing, the PL peaks show a gradual red-shift. This result is consistent with previous reports and it can be attributed to the narrowing of band gaps for DCN materials (Figure 2.1c and Figure 2.2).^[26, 40] Next, the charge transfer properties of the original g-C₃N₄ and DCN samples were evaluated by a set of photo-electrochemical experiments. And the electrochemical impedance spectroscopy (EIS) was conducted firstly. In Figure 2.12c, DCN-200 presents a representative EIS Nyquist plot with a much smaller arc radius than that of the pristine g-C₃N₄. This means that the charge transfer resistance of g-C₃N₄ is remarkably decreased by the continuous p-n band offset in DCN.^[56, 57] The consistent conclusion is also supported by photo-chronoamperometry measurements (Figure 2.12d), which shows a nearly three-fold enhanced photocurrent of DCN-200 over the original g-C₃N₄. Obviously, the construction of p-n homojunction is highly efficient in promoting the charge transfer and separation in the DCN materials, and thus a better photocatalytic performance can be highly anticipated.

2.3.2 Photocatalytic hydrogen evolution activity of the p-n homojunction g-C₃N₄

The photocatalytic activity of DCN was evaluated by H₂ production from water under visible-light using Pt as cocatalyst and triethanolamine as hole scavenger. As shown in Figure 2.13a, treating g-C₃N₄ with NaBH₄ indeed much enhances the activity. When the heat temperature is 200 °C, a peak H₂ evolution rate of 4020 $\mu\text{mol h}^{-1} \text{g}^{-1}$ is achieved, which is nearly 5 times higher than that of original g-C₃N₄. This should be a result of the synergy of the enhanced light absorption (Figure 2.1c) and the improved carrier transfer and separation (Figure 2.12) originated from the formation of p-n homojunction in DCN-200. Further increasing the temperature to 250 or 300 °C gives rise to slightly depressed activities but they are still superior to the untreated g-C₃N₄. This could be attributed to the slightly increased electron-hole recombination due to the over-introduction of defects (Figure 2.12b).^[58] It is worthy to note that, to the best of our knowledge, the H₂ evolution rate exhibited by the optimal DCN-200 sample represents an advanced photocatalytic activity for g-C₃N₄-based materials and importantly, it should be the highest among those of the defect-modified g-C₃N₄ photocatalysts reported so far. Additionally, in order to rule out the effect from Pt loading on the photocatalytic activities, the H₂ evolution over CN and DCN samples were further conducted in the absence of Pt co-catalysts (Figure 2.14), and the consistent results are also obtained: all the DCN samples possess higher activities than the original g-C₃N₄ and especially, DCN-200 achieves the highest H₂ evolution rate. Together, these results clearly suggest that the construction of p-n homojunction should represent an effective approach to improve the photocatalytic activity for g-C₃N₄-related photocatalysts.

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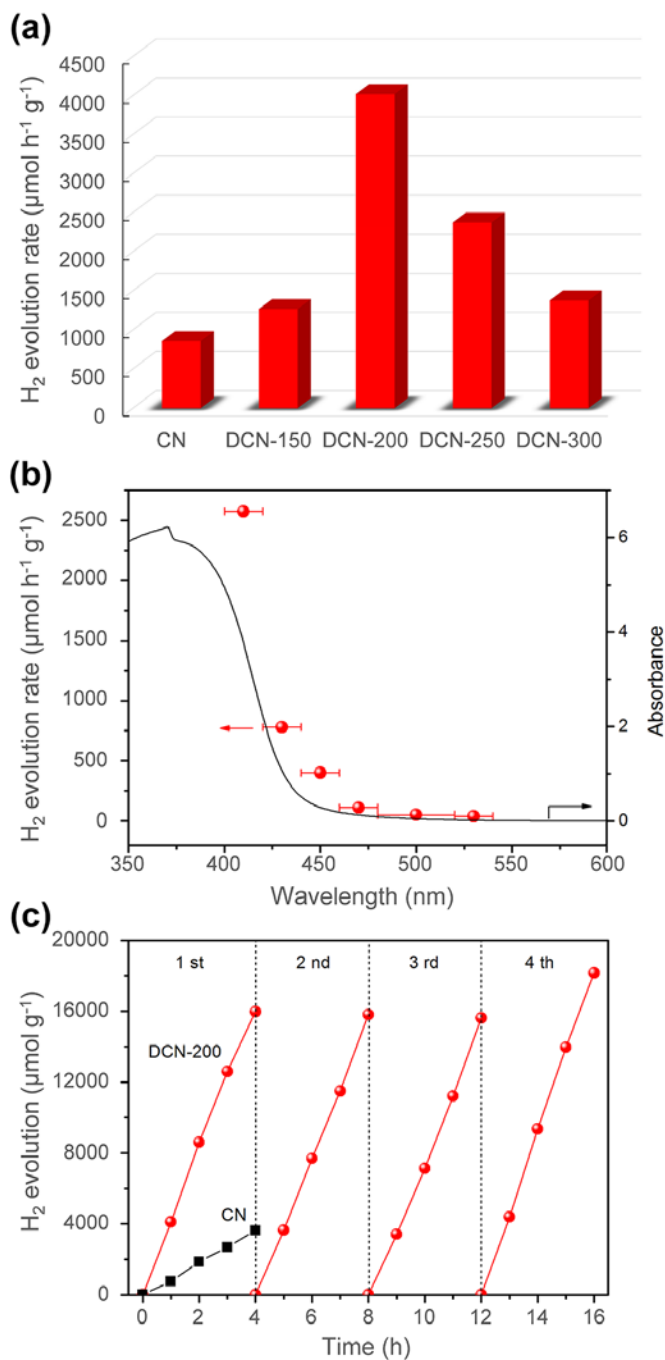


Figure 2.13 (a) Photocatalytic H_2 evolution rate for CN and all DCN samples under visible light irradiation. (b) Wavelength dependence of H_2 evolution rate for DCN-200. (c) Time courses of H_2 evolution for DCN-200 photocatalysts under visible-light irradiation, together with pristine CN as the reference.

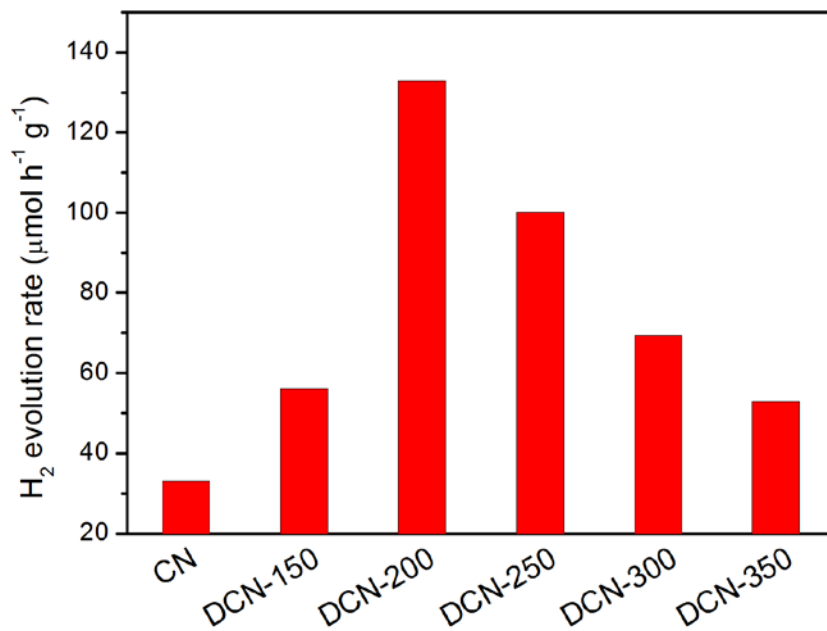


Figure 2.14 H₂ evolution rates over CN and DCN samples, which were measured in the absence of Pt co-catalysts. Without Pt co-catalysts, the H₂ evolution rates over CN and DCN samples are significantly decreased. However, DCN-200 still exhibits the peak activity among all the samples, which is more than four times higher than that of CN. Moreover, when the heating temperature is beyond 200 °C, the activities for DCN samples decrease gradually, but they are still higher than that of CN. These results are consistent with those obtained in the measurements with Pt as co-catalysts (Figure 2.13) and further suggest that the construction of p-n homojunction in CN might represent an effective strategy to improve its photocatalytic activity for more efficient solar energy conversion.

Figure 2.13b shows the wavelength-dependent H₂ evolution over the optimized DCN-200 sample. It is apparently that the photocatalytic activities of DCN-200 qualitatively tracks its characteristic absorption, primarily indicating that the H₂ production is driven by the photo-excitation.^[11, 39] The catalytic stability of this sample was also evaluated in a

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cycling experiment. As presented in Figure 2.13c, no noticeable deactivation in H₂ evolution rate was detected after 4 cycles' reactions, clearly suggesting the good stability of this DCN-200 catalyst. XRD and UV-vis absorption spectra were further employed to characterize the recovered catalyst after the reactions (Figure 2.15). As expected, we still do not observe any obvious changes in structure and optical absorption, again supporting the robust nature of DCN-200. In addition, during the reactions, about 1.6 mmol of H₂ was produced in total, much exceeding the amount of catalysts (0.14 mmol). And the turnover number (TON) respecting to Pt atoms was calculated to be 416. This result offers an additional evidence on that the reaction proceeds catalytically.^[58] Noted that, the photocatalytic performance of g-C₃N₄ based materials is highly dependent on their morphology.^[7, 59] For example, due to the higher surface area and more active site exposing, the two-dimensional g-C₃N₄ nanosheets are generally much more active than the bulk g-C₃N₄.^[10, 60] In the present study, as inherited from the original bulk g-C₃N₄ precursor, the DCN materials are also of bulk morphology with low surface area (Figure 2.4 and Figure 2.5). Therefore, we expect further significant improvement in the HER by optimizing the selection of the elementary g-C₃N₄ precursors (for instance, using g-C₃N₄ nanosheets, or nanospheres as precursors instead of the bulk g-C₃N₄).^[7, 59]

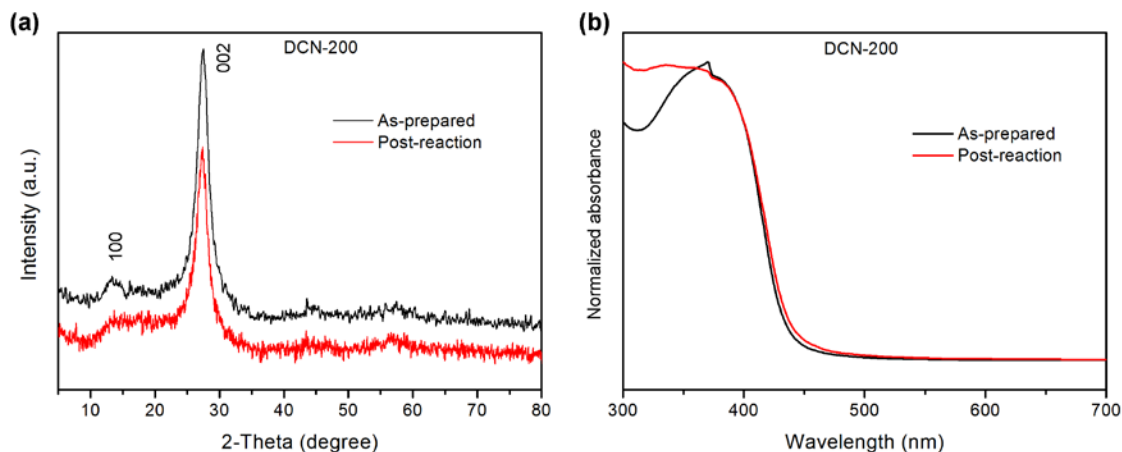


Figure 2.15 (a) XRD pattern and (b) UV-vis absorption spectra of DCN-200 before and after photocatalytic H₂ evolution tests.

2.4 Conclusions

In conclusion, a facile and effective strategy was explored here to prepare defect-modified g-C₃N₄ (DCN) photocatalysts by a NaBH₄ treatment at low temperatures (< 350 °C). DCN maintains the intrinsic 2D π -conjugated layered structure of g-C₃N₄ but shows much extended light absorption capability. Accompanied with the defect formation (preferential loss of N atoms) during the NaBH₄ treatment, cyano terminal C $\equiv$ N groups, acting as electron acceptors, were also introduced in the g-C₃N₄ sheet edge, which endowed the DCN exhibiting both n- and p-type conductivities, consequently giving rise to the generation of p-n homojunctions. Such homojunction structured DCN photocatalysts have been demonstrated to highly efficient in the transfer and separation of photoexcited carriers and shows much enhanced photocatalytic H₂ evolution activity under visible-light. The ability to build such a homojunction by the defect-induced self-functionalization without introducing foreign materials or elements as required by traditional heterojunctions presents a promising strategy for precise band engineering of g-C₃N₄ and related polymer

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semiconductors, and provides new insight into the fabrication of novel structures of these materials for more efficient solar energy conversion applications.

References

1. A. Kudo and Y. Miseki, *Chem Soc Rev*, 2009, **38**, 253-278.
2. N. S. Lewis and D. G. Nocera, *Proc. Natl. Acad. Sci. USA*, 2006, **103**, 15729-15735.
3. J. A. Turner, *Science*, 2004, **305**, 972-974.
4. F. E. Osterloh, *Chem. Soc. Rev.*, 2013, **42**, 2294-2320.
5. U. Eberle, M. Felderhoff and F. Schüth, *Angew. Chem. Int. Ed.*, 2009, **48**, 6608-6630.
6. X. Lu, S. Xie, H. Yang, Y. Tong and H. Ji, *Chem. Soc. Rev.*, 2014, **43**, 7581-7593.
7. S. Cao, J. Low, J. Yu and M. Jaroniec, *Adv. Mater.*, 2015, **27**, 2150-2176.
8. X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti, *Nat Mater*, 2009, **8**, 76-80.
9. V. W.-h. Lau, M. B. Mesch, V. Duppel, V. Blum, J. Senker and B. V. Lotsch, *J. Am. Chem. Soc.*, 2014, **137**, 1064–1072.
10. S. Yang, Y. Gong, J. Zhang, L. Zhan, L. Ma, Z. Fang, R. Vajtai, X. Wang and P. M. Ajayan, *Adv. Mater.*, 2013, **25**, 2452-2456.
11. J. Zhang, M. Zhang, C. Yang and X. Wang, *Adv. Mater.*, 2014, **26**, 4121-4126.
12. M. K. Bhunia, K. Yamauchi and K. Takanabe, *Angew. Chem. Int. Ed.*, 2014, **53**, 11001-11005.
13. C. A. Caputo, M. A. Gross, V. W. Lau, C. Cavazza, B. V. Lotsch and E. Reisner, *Angew. Chem. Int. Ed.*, 2014, **53**, 11538-11542.

Chapter 2

14. Y. Zheng, L. Lin, X. Ye, F. Guo and X. Wang, *Angew. Chem. Int. Ed.*, 2014, **53**, 11926-11930.
15. Y.-S. Jun, J. Park, S. U. Lee, A. Thomas, W. H. Hong and G. D. Stucky, *Angew. Chem. Int. Ed.*, 2013, **52**, 11083-11087.
16. D. J. Martin, K. Qiu, S. A. Shevlin, A. D. Handoko, X. Chen, Z. Guo and J. Tang, *Angew. Chem. Int. Ed.*, 2014, **53**, 9240-9245.
17. K. Schwinghammer, M. B. Mesch, V. Duppel, C. Ziegler, J. Senker and B. V. Lotsch, *J. Am. Chem. Soc.*, 2014, **136**, 1730-1733.
18. P. Niu, L. Zhang, G. Liu and H.-M. Cheng, *Adv. Funct. Mater.*, 2012, **22**, 4763-4770.
19. Y. Zhang, A. Thomas, M. Antonietti and X. Wang, *J. Am. Chem. Soc.*, 2009, **131**, 50-51.
20. M. Zhang and X. Wang, *Energy Environ. Sci.*, 2014, **7**, 1902-1906.
21. Y. Zhang, T. Mori, J. Ye and M. Antonietti, *J. Am. Chem. Soc.*, 2010, **132**, 6294-6295.
22. X. Chen, J. Zhang, X. Fu, M. Antonietti and X. Wang, *J. Am. Chem. Soc.*, 2009, **131**, 11658-11659.
23. P. Wu, J. Wang, J. Zhao, L. Guo and F. E. Osterloh, *Chem. Commun.*, 2014, **50**, 15521-15524.
24. E. Tunkara, C. Albayrak, E. O. Polat, C. Kocabas and Ö. Dag, *ACS Nano*, 2014, **8**, 11007-11012.
25. Y. Kang, Y. Yang, L.-C. Yin, X. Kang, G. Liu and H.-M. Cheng, *Adv. Mater.*, 2015, **27**, 4572-4577.

Chapter 2

26. P. Niu, L.-C. Yin, Y.-Q. Yang, G. Liu and H.-M. Cheng, *Adv. Mater.*, 2014, **26**, 8046–8052.
27. Q. Liang, Z. Li, Z.-H. Huang, F. Kang and Q.-H. Yang, *Adv. Funct. Mater.*, 2015, **25**, 6885–6892.
28. Y. Wang, X. Wang and M. Antonietti, *Angew. Chem. Int. Ed.*, 2012, **51**, 68-89.
29. Y. Qu and X. Duan, *Chem. Soc. Rev.*, 2013, **42**, 2568-2580.
30. H. Li, Y. Zhou, W. Tu, J. Ye and Z. Zou, *Adv. Funct. Mater.*, 2015, **25**, 998-1013.
31. P. Li, Y. Zhou, Z. Zhao, Q. Xu, X. Wang, M. Xiao and Z. Zou, *J. Am. Chem. Soc.*, 2015, **137**, 9547-9550.
32. X. Wang, Q. Xu, M. Li, S. Shen, X. Wang, Y. Wang, Z. Feng, J. Shi, H. Han and C. Li, *Angew. Chem. Int. Ed.*, 2012, **51**, 13089-13092.
33. T. Kawahara, Y. Konishi, H. Tada, N. Tohge, J. Nishii and S. Ito, *Angew. Chem. Int. Ed.*, 2002, **41**, 2811-2813.
34. J. Zhang, Q. Xu, Z. Feng, M. Li and C. Li, *Angew. Chem. Int. Ed.*, 2008, **47**, 1766-1769.
35. S. W. Boettcher, E. L. Warren, M. C. Putnam, E. A. Santori, D. Turner-Evans, M. D. Kelzenberg, M. G. Walter, J. R. McKone, B. S. Brunschwig, H. A. Atwater and N. S. Lewis, *J. Am. Chem. Soc.*, 2011, **133**, 1216-1219.
36. T.-F. Yeh, C.-Y. Teng, S.-J. Chen and H. Teng, *Adv. Mater.*, 2014, **26**, 3297-3303.
37. X. Yu, A. Shavel, X. An, Z. Luo, M. Ibáñez and A. Cabot, *J. Am. Chem. Soc.*, 2014, **136**, 9236-9239.

Chapter 2

38. Y. Zheng, L. Lin, B. Wang and X. Wang, *Angew. Chem. Int. Ed.*, 2015, **54**, 12868-12884.
39. G. Zhang, M. Zhang, X. Ye, X. Qiu, S. Lin and X. Wang, *Adv. Mater.*, 2014, **26**, 805-809.
40. Y. Kang, Y. Yang, L.-C. Yin, X. Kang, L. Wang, G. Liu and H.-M. Cheng, *Adv. Mater.*, 2016, **28**, 6471–6477.
41. H. Tan, Z. Zhao, M. Niu, C. Mao, D. Cao, D. Cheng, P. Feng and Z. Sun, *Nanoscale*, 2014, **6**, 10216-10223.
42. J. McMurry, *Organic chemistry 6th Edition*, Thomson Learning Brooks/Cole, 2004, pp. 539 –543.
43. Z. Zhou, J. Wang, J. Yu, Y. Shen, Y. Li, A. Liu, S. Liu and Y. Zhang, *J. Am. Chem. Soc.*, 2015, **137**, 2179-2182.
44. B. Dulla, K. T. Kirla, V. Rathore, G. S. Deora, S. Kavela, S. Maddika, K. Chatti, O. Reiser, J. Iqbal and M. Pal, *Org. Biomol. Chem.*, 2013, **11**, 3103-3107.
45. V. Y. Kukushkin and A. J. L. Pombeiro, *Inorg. Chim. Acta*, 2005, **358**, 1-21.
46. S. Ifuku, M. Tsuji, M. Morimoto, H. Saimoto and H. Yano, *Biomacromolecules*, 2009, **10**, 2714-2717.
47. A. W. Bott, *Current Separations*, 1998, **17**, 87-92.
48. J. Yan, T. Wang, G. Wu, W. Dai, N. Guan, L. Li and J. Gong, *Adv. Mater.*, 2015, **27**, 1580–1586.
49. J.-N. Nian, C.-C. Tsai, P.-C. Lin and H. Teng, *J. Electrochem. Soc.*, 2009, **156**, H567-H573.

Chapter 2

50. Y.-C. Wang, C.-Y. Chang, T.-F. Yeh, Y.-L. Lee and H. Teng, *J. Mater. Chem. A*, 2014, **2**, 20570-20577.
51. M. Tabbal, T. Christidis, S. Isber, P. Mérel, M. A. El Khakani, M. Chaker, A. Amassian and L. Martinu, *J. Appl. Phys.*, 2005, **98**, 044310.
52. J. Zhang, M. Zhang, S. Lin, X. Fu and X. Wang, *J. Catal.*, 2014, **310**, 24-30.
53. J. Zhang, M. Zhang, R.-Q. Sun and X. Wang, *Angew. Chem. Int. Ed.*, 2012, **51**, 10145-10149.
54. J. Zhang, G. Zhang, X. Chen, S. Lin, L. Möhlmann, G. Dołęga, G. Lipner, M. Antonietti, S. Blechert and X. Wang, *Angew. Chem. Int. Ed.*, 2012, **51**, 3183-3187.
55. R. C. Barklie, *Diamond Relat. Mater.*, 2001, **10**, 174-181.
56. J. Hou, C. Yang, H. Cheng, S. Jiao, O. Takeda and H. Zhu, *Energy Environ. Sci.*, 2014, **7**, 3758-3768.
57. S. Mubeen, G. Hernandez-Sosa, D. Moses, J. Lee and M. Moskovits, *Nano Lett.*, 2011, **11**, 5548-5552.
58. A. Kudo and Y. Miseki, *Chem. Soc. Rev.*, 2009, **38**, 253-278.
59. J. Zhang, Y. Chen and X. Wang, *Energy Environ. Sci.*, 2015, **8**, 3092-3108.
60. X. Lu, K. Xu, P. Chen, K. Jia, S. Liu and C. Wu, *J. Mater. Chem. A*, 2014, **2**, 18924-18928.

Chapter 3 Fabricating in-plane highly ordered graphitic carbon nitride via heptazine self-assembling for improved photocatalytic H₂ production

3.1 Introduction

The artificial photocatalytic production of hydrogen fuel by water splitting has been an active research topic in the past decades. Different kinds of semiconductors, such as metal-based oxide, nitrides, phosphides, and sulfides were developed for efficient hydrogen evolution,¹⁻³ among which, the graphite carbon nitride (g-C₃N₄; denoted as CN) has attracted intensive research interest since the pioneering work by Wang et al. in 2009.^{4, 5} Although this metal-free, visible light-responded two-dimensional conjugated semiconductor is chemically stable and easy for preparation, it still has some disadvantages, such as low absorbance in visible light, low specific surface area and low charge carriers separation. To overcome these drawbacks, many researches have been focused on the heteroatom doping,⁶⁻¹² morphology and nanostructure control of CN.¹³⁻²² However, many of these modified CN still showed poor activities,^{10, 23-27} and the intrinsic drawbacks, i.e., the poor charge carrier transport and separation, are not fully addressed.^{10, 13, 27}

Theoretically, the atomic order degree in solid-state materials is crucial for the efficient separation of photogenerated charge carriers. For the polymeric π -conjugated framework, the charge transport along the in-plane direct is considered important to the migration of photogenerated charge carriers.^{13, 28} However, up to now, it still remains a challenge to fabricate CN with well-ordered in-plane structure, which attributes to two reasons: 1) the precursors used to prepare CN, such as melamine, dicyandiamide, undergo melting before

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polycondensation reaction, which results in the disordered condensation and the tangled melon chains; 2) it is too difficult to ensure that the uniform unit is heptazine in the prepared CN, usually triazine remaining in the scaffold during the thermal polymerization, which makes the in-planar less unified. Schwinghammer et al. synthesized crystalline PTI (polytriazine imide)/Li⁺Cl⁻ in a two-step ionothermal synthesis.²⁹ Exfoliation of bulk crystalline PTI resulted in carbon nitride nanosheet with significantly enhanced hydrogen evolution.¹⁶ However, the ionothermal synthesis is hard to operate and difficult for wide application. Herein, we report a simple preparation of a low-dimensional CN with enhanced in-plane ordering by calcining the self-assembled heptazine precursors (SAHEP). The highly ordered heptazine can be transformed into poly(tri-s-triazine) with improved in-plane ordering, which showed a high hydrogen evolution rate of 420 $\mu\text{mol/h}$ and a remarkable apparent quantum efficiency of 8.9% at 420 nm.

3.2 Experimental section

3.2.1 Material preparation

Raw heptazine was obtained by heating melamine in a porcelain crucible covered by a tin foil paper in a muffle furnace at 420 °C for 4 hours. The resulted white heptazine was then placed in a dried flask, to which different solvents with various volume ratios of water (i.e., pure water, 5% water in IPA, 10% water in IPA, 20% water in IPA, pure IPA) was added before refluxing at 80 °C for 10 hours. The resulted heptazine was collected and dried at room temperature. Melons were synthesized by calcinating the different precursors under argon with different temperature-rising rates to 550 °C and kept at 550 °C for 4 hours.

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3.2.2 Material characterization

Powder XRD was carried out on an X-ray diffractometer (Rint 2000, Altima III, Rigaku Co. Japan) with a Cu K α source. The morphologies were investigated by scanning electron microscopy (Field Emission Scanning Electron Microscope, JSM-6701F). The UV-Vis absorption was measured with a UV-visible spectrophotometer (Shimadzu, UV-2600) using BaSO₄ as the reflectance standard reference. PL spectra were recorded by a JASCO FP-6500 spectrofluorometer. BET N₂-adsorption measurement was processed with Autosorb-iQ2 Quantachrome Instrument at 77 K after the samples were degassed at 100 °C overnight. FT-IR spectra were recorded by Nicolet 4700 spectrometer. Thermogravimetric measurements were conducted on a Seiko Instrument thermogravimetry/differential thermal analyzer (TG-DTA 6200).

3.2.3 Photo-electrochemical measurements

The photo-electrochemical measurements were carried out in a conventional three-electrode cell by using an electrochemical analyzer (Model-650A). A Pt foil and Ag/AgCl electrode were used as the counter-electrode and the reference electrode. Electrochemistry impedance spectroscopy (EIS) measurements were carried out in a 0.2 M Na₂SO₄ solution at 0.2 V over a frequency range from 0.01 to 1000 Hz. For Mott-Schottky experiments, the perturbation signal was 10 mV with the AC frequency at 1 kHz. For the photocurrent measurements, the irradiation was performed using an AM 1.5 light source with a manual shading using a tin foil to realize the cycling light on and off.

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3.2.4 Photocatalytic activity measurements

Photocatalytic activities were evaluated by the hydrogen evolution from water under visible light irradiation with triethanolamine (TEOA) as electron donor. Typically, 100 mg catalyst was suspended in a Pyrex glass reaction cell containing 260 mL 10 vol% of TEOA aqueous solution. 3 wt% Pt was added for the in-situ photodeposition and used as co-catalyst. Before the irradiation, the reaction cell was evacuated to remove the air completely. The produced H₂ was analyzed by an online gas chromatograph (GC-8A, Shimadzu Corp., Japan). The apparent quantum efficiency (AQE) was measured at various monochromatic lights which were obtained by using a series of band-pass filters (Optical Coating Japan). A water filter was used to avoid the overwhelmed heating. The light intensity was measured at 9 different points to obtain an average intensity with a spectroradiometer (Ushio, USR-40, Japan). The AQE at each monochromatic wavelength was calculated by the following equation: $AQE = (2 \times \text{amount of H}_2 \text{ molecules evolved in unit time} / \text{number of incident photons in unit time}) \times 100\%$.

3.3 Results and discussion

3.3.1 Self-assembly of heptazine

The SAHEP was obtained by refluxing heptazine in hot water-containing solutions. In Sophia et al.'s work, it is reported that the self-assembly of heptazine in hot aqueous solution resulted in the formation of hydrogen-bonded, hexagonal rosettes of heptazine units surrounding infinite channels with a diameter of 8.9 Å.³⁰ In our case, when heptazine was refluxed in pure water at 80 °C for 10 h, micrometer-scaled rod of melem hydrate can be formed, as shown in Figure 3.1a. It is further found that by adding different amounts of isopropyl alcohol (IPA), the size of these assembled heptazine can be tuned into sub-micro

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scale (Figure 3.1c-d). 10% of water in IPA resulted in the assembled heptazine rods with diameters about 300-600 nm and a length about 10 μm , while 20% of water in IPA induced the assembly of heptazine into rods with a larger diameter (about 0.5-1 μm).

However, no assembled rods can be found with 5% of water in IPA (Figure 3.1b), which may be due to the kinetic resistance in the presence of such a low content of water. XRD patterns (Figure 3.2) of the assembled heptazine in pure water or 10% water/IPA coincide well with that of melem hydrate formed in Sophia et al.'s work, reflecting its $R\bar{3}c$ space group, while melamine and the as prepared heptazine showed unindexed patterns.³⁰ It is also shown that the resulted heptazine refluxed in pure IPA or 5% water/IPA exhibits quite different XRD patterns, indicating heptazine assembly can be only formed with the existence of enough water molecules.

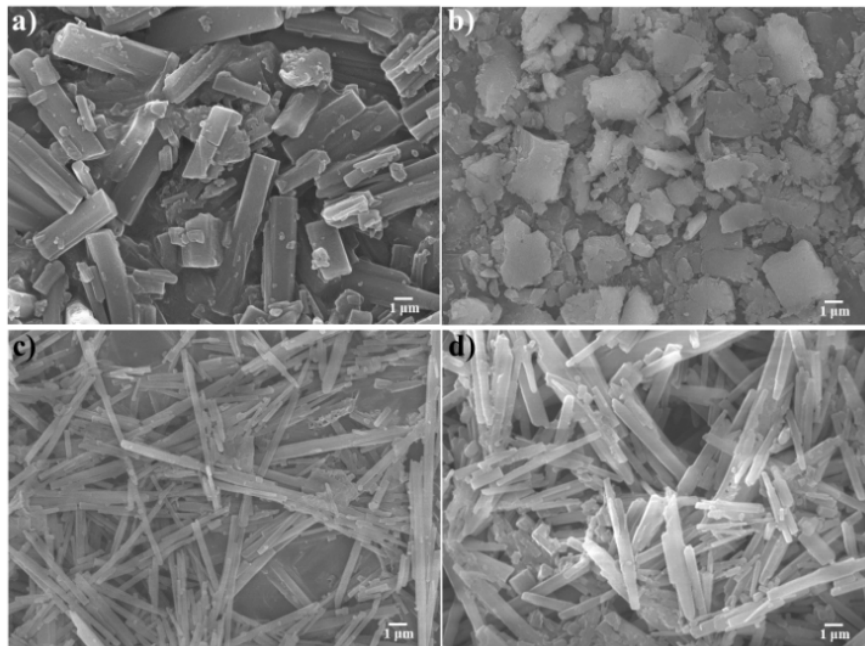


Figure 3.1 SEM images of resulted heptazine after refluxing in (a) pure water, (b) 5% of water in IPA, (c) 10% of water in IPA and (d) 20% of water in IPA.

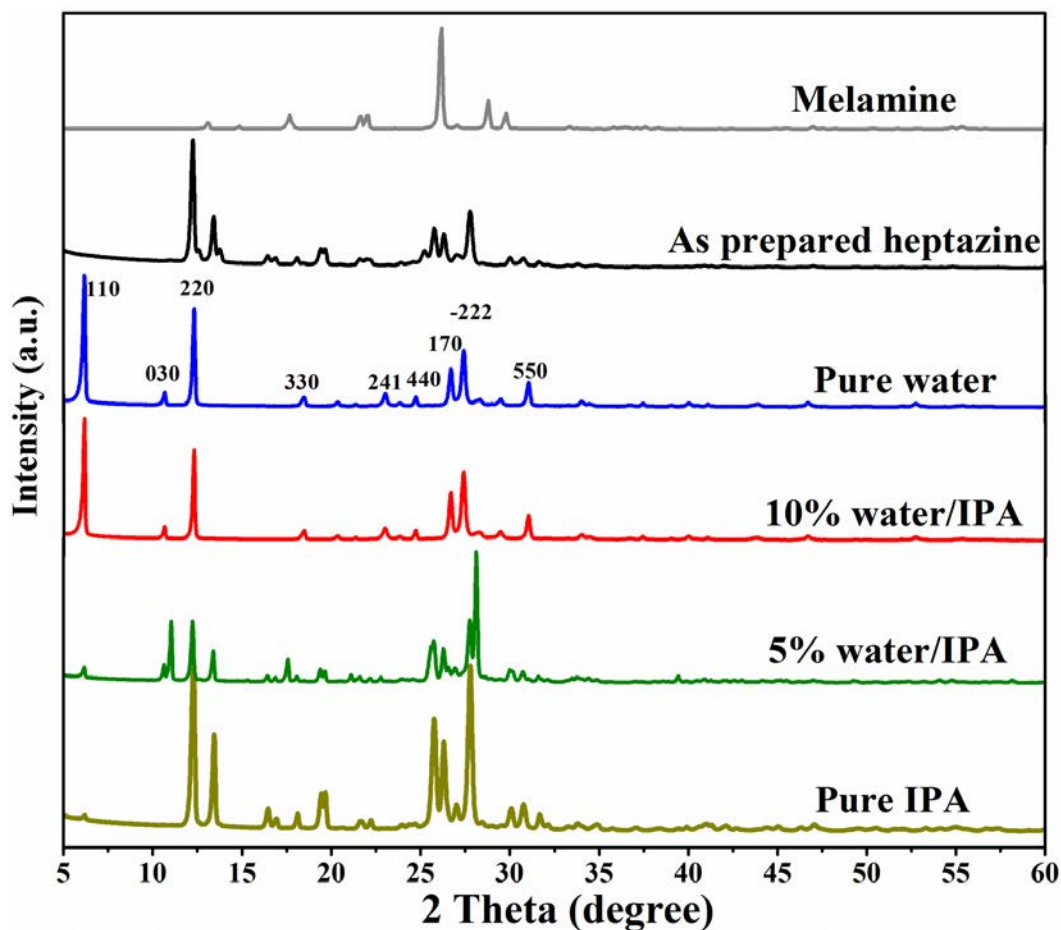


Figure 3.2 XRD patterns of melamine (grey), as prepared heptazine (black), heptazine refluxed in pure water (blue), 10% water/IPA (red), 5% water/IPA (olive) and pure IPA (dark yellow).

3.3.2 General characterization of in-plane highly ordered graphitic carbon nitride

SAHEP refluxed in 10% water/IPA was calcinated under Ar at 550 °C for 4h at different temperature-rise rates, leading to series of CNs noted as SAHEP-CNs-x, where x represents the temperature-rise rate in the calcination process. The sub-micro rod-like morphology of the precursor was well maintained during the poly-condensation without volumetric shrinkage in spite of different temperature-rise rates in the calcination process (Figure 3.3).

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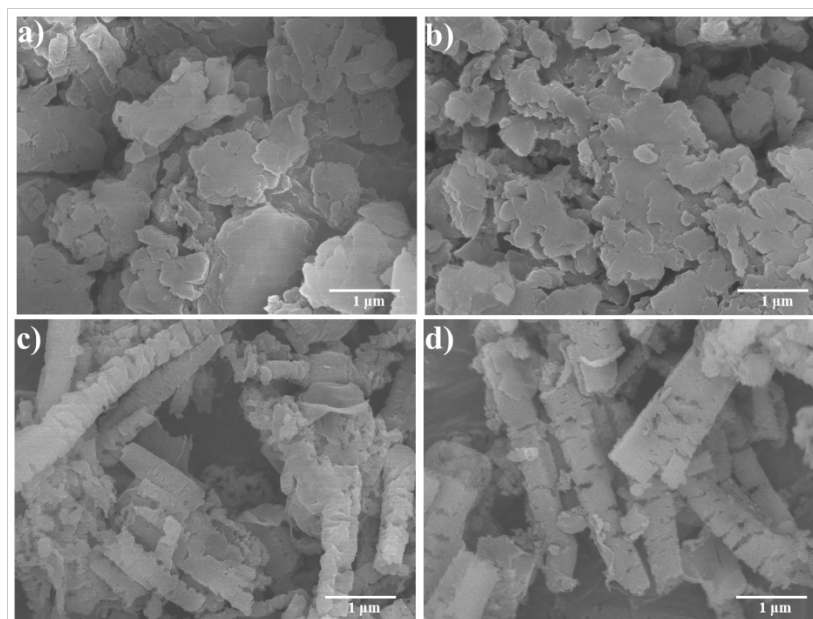


Figure 3.3 SEM images of CNs derived from different precursors. (a) MP-CNs, (b) NAHEP-CNs, (c) SAHEP-CNs-15, and (d) SAHEP-CNs-4.

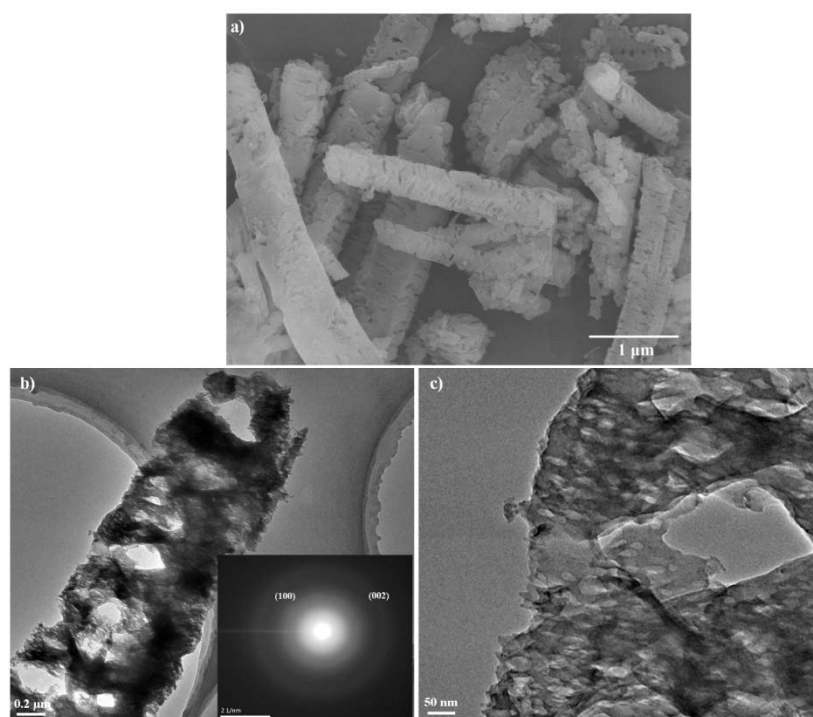


Figure 3.4 (a) SEM image, (b) TEM image and (c) HRTEM image of SAHEP-CNs-1. Inset in b is the selected area electron diffraction (SAED) pattern.

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Figure 3.4a and 3.4b show the SEM and TEM images of SAHEP-CNs-1. The layered sheet-like structure was clearly observed in TEM images (Figure 3.4b and c). Due to the in-plane shrinkage in the poly-condensation, micropore-mesopore structure was formed within the CNs sheet. Compared with CNs prepared by calcinating melamine directly in Ar (short as MP-CNs), the resulted SAHEP-CNs exhibit a different XRD pattern as shown in Figure 3.5a and b. The diffraction peak at $2\theta = 13.2^\circ$ is much sharper and more symmetric, and at the same time, the peak at $2\theta = 27.2^\circ$ is broadened, especially for SAHEP-CNs calcinated by low temperature-rise rate. The fresh heptazine prepared by calcinating melamine at 420°C was used as another controlled precursor, i.e., the non-assembled heptazine (NAHEP). In the XRD of CNs (NAHEP-CNs) resulted from the calcination of NAHEP, the feature of peaks at $2\theta = 13.2^\circ$ and $2\theta = 27.2^\circ$ is similar to that of MP-CNs. For clear comparison, the full width at half maximum (FWHM) and the relative intensity ratio of peak (100) and peak (002) for the different CNs were listed in Table 3.1. It is obviously noted that through assembly of heptazine precursor, the resulted CNs showed a much narrowed FWHM of peak (100), broadened FWHM of peak (002) and increased relative intensity ratio of peak (100) and peak (002), suggesting an enhanced in-plane ordering and decreased stack along the c-axis, especially when the assembled precursors were calcinated with a low temperature-rise rate.^{31,32} The selected area electron diffraction (SAED) pattern in Figure 3.4b showing two diffuse diffraction rings also confirmed the enhanced in-plane ordering. It is also implied that in the calcination process, temperature-rising rate plays an important role to the microstructure of the resulted SAHEP-CNs, which is also reported by Li et al.³³.

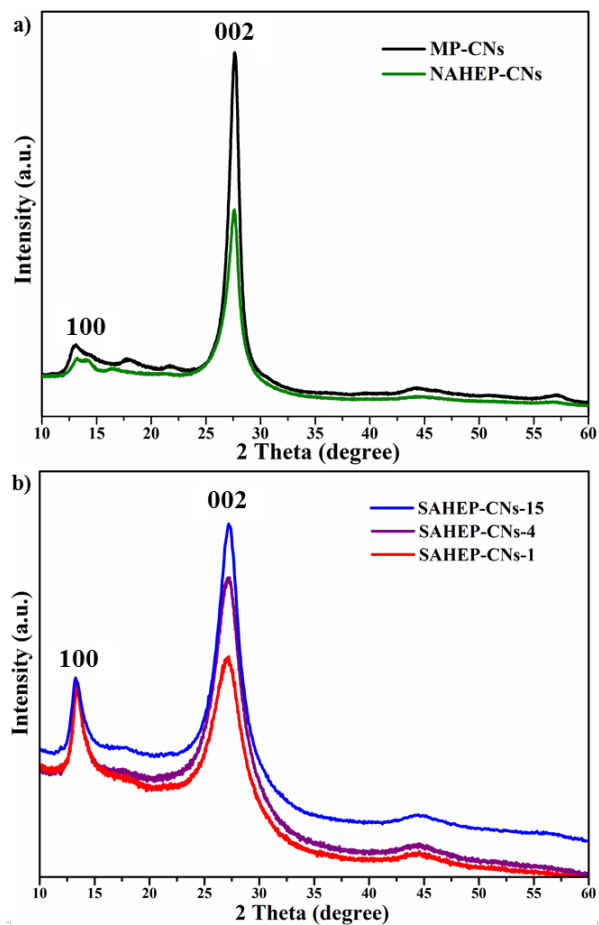


Figure 3.5 XRD patterns of the different CNs, i.e., MP-CNs (black line), NAHEP-CNs (olive line), SAHEP-CNs-15 (blue line), SAHEP-CNs-4 (purple line) and SAHEP-CNs-1 (red line).

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Table 3.1 The full width at half maximum (FWHM) and the relative intensity ratio of peak (100) and peak (002) for the different CNs and the corresponding atomic ratio of N/C.

	MP- CNs	NAHEP- CNs	SAHEP- CNs-15	SAHEP- CNs-4	SAHEP- CNs-1
FWHM of peak (100) / °	2.45	1.75	1.37	1.08	1.03
FWHM of peak (002) / °	0.99	1.37	2.28	2.54	2.56
Intensity ratio of peak (100) to (002)	0.08	0.10	0.29	0.42	0.57
Atomic ratio of N/C	1.34	1.36	1.51	1.50	1.50

According to the report by Sophia et al., the assembled melem hydrate can be presented by an average formula of $C_6N_7(NH_2)_3 \cdot 2.3H_2O$ (water mass ratio: 16.2%). Even dehydrated under vacuum at 150 °C overnight, the resulted product is formulated as $C_6N_7(NH_2)_3 \cdot 0.3H_2O$ by element analysis,³⁰ implying that strong interaction maintains between heptazine and H_2O even at high temperature. In our case, it is also indicated by the TG curves (Figure 3.6) that the structural water in SAHEP only lost partially (about 12 mass%) before 450 °C, even less weight loss with lower temperature-rising rate (Figure 3.6a). Since the detailed mechanism inside the calcination of the assembled heptazine is not clear and we can only speculate the possibility from the chemistry and material viewpoint based on the conclusion from Sophia's work. It is speculated that since the heptazine units are confined by the water molecules through hydrogen bonding, the dehydration during calcination would induce an alternative metastable structure to form some interaction between the incomplete dehydrated water and heptazine or there may be partial hydrolysis to form $(C_6N_7(NH_2)_{2.7}(OH)_{0.3})$ as inferred by Sophia et al.,^[9] in both of which case, the disordered and intense condensation of heptazine will be definitely hindered, especially when calcinated with lower temperature-rising rate.

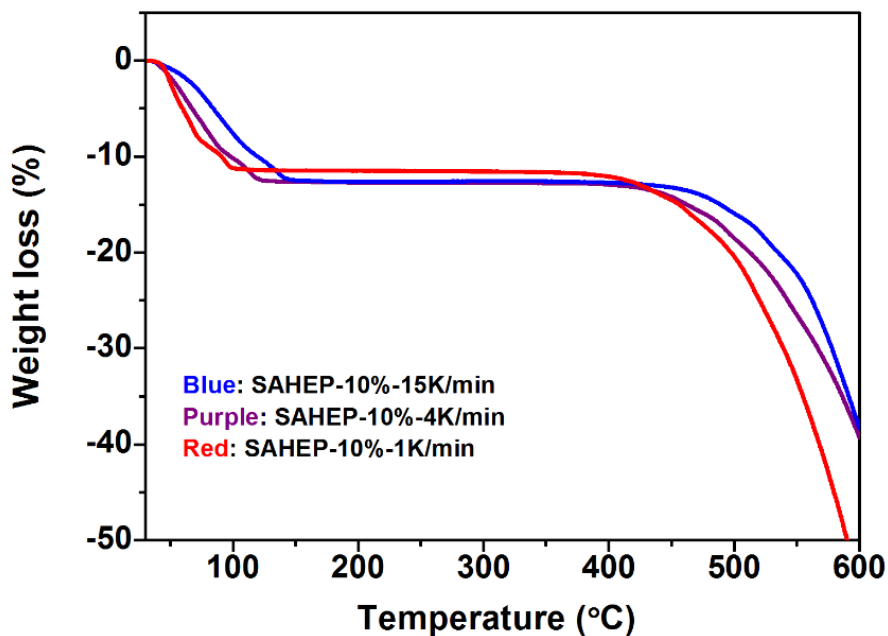


Figure 3.6 TG-DTA curves of SAHEP under Ar atmosphere at different temperature-rising rates, i.e., 15 K/min, 4 K/min and 1 K/min.

It is important to note that the symmetric electron spin resonance (ESR) spectrum (Figure 3.7a) with g value of 2.003 of SAHEP-CNs-1 was stronger than that of MP-CNs and NAHEP-CNs, which may be related with the increased delocalization of single electrons in the CN_x framework.²¹ This speculation is also confirmed by the slight red-shift photoluminescence (PL) resulted from the higher conjugated carbon-nitrogen structure (Figure 3.7b). It is suspected that the enhanced long-range ordering and conjugation would contribute to an improved charge carrier transport and electron-hole separation when this semiconductor is irradiated.

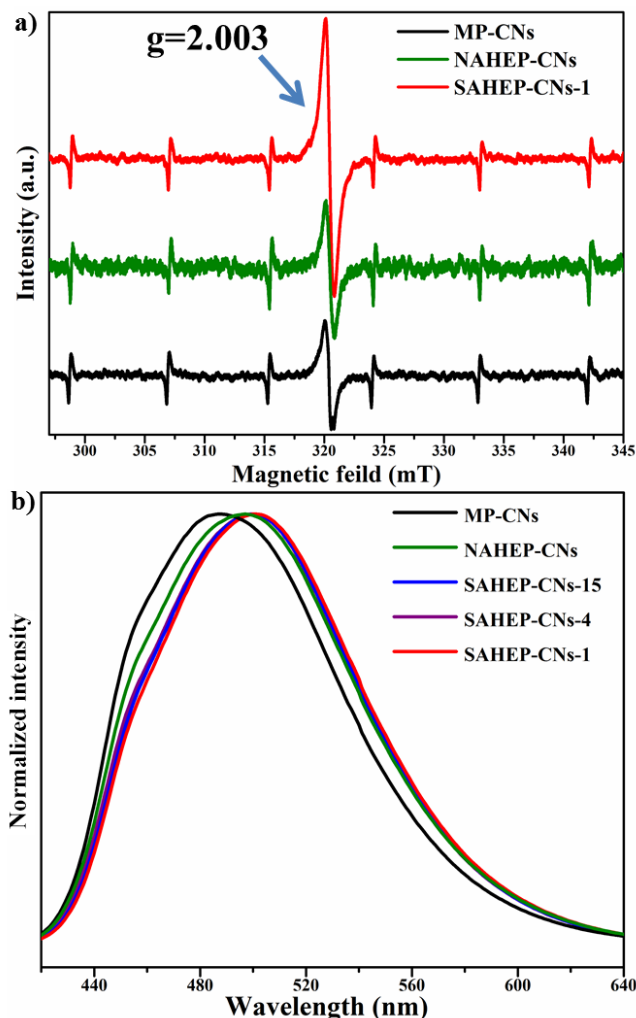


Figure 3.7 (a) ESR spectra and (b) photoluminescence spectra of the CNs prepared from different precursors.

In brief for above analysis and the crystal structure of SAHEP, water molecules were functioned as a spatial template for the self-assembly of heptazine units into SAHEP, in which (110) facet was extended in micrometer scale while (001) facet extended in hundreds of nanometers as shown in Figure 3.8a and b. The micrometer-scaled confined heptazine would undergo poly-condensation into carbon nitride with enhanced in-plane ordering, while extension of hundreds of nanometers in c-axis of SAHEP induces less stacking along

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c-axis in the resulted SAHEP-CN_s. Since low temperature-rising rate is benefit for the metastable state before condensation, the spatial confinement is more evident when calcination with a lower temperature-rising rate. Although the resulted carbon nitride is actually not crystalline in long range due to the uncontrollable thermal motion of heptazine, the in-plane ordering can be largely improved as compared with the non-assembled precursors.

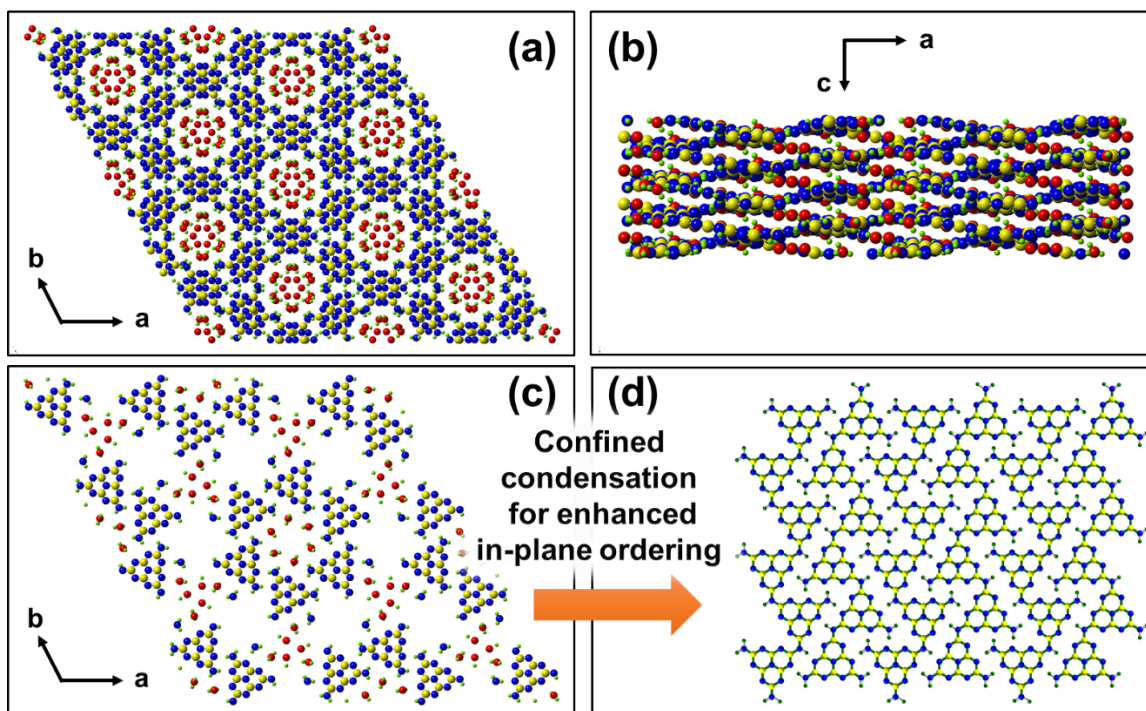


Figure 3.8 (a and b) Crystal structure ($2 \times 2 \times 2$ cells) of SAHEP in different view directions, where C,H,O,N were represented by yellow, green, red and blue balls, respectively; (c) All atoms in SAHEP aligned within 0.36 nm in c-axis; (d) The resulted carbon nitrides with enhanced in-plane ordering.

In the UV-Vis optical absorption spectra (Figure 3.9a), SAHEP-CN_s showed a similar absorption compared with MP-CN_s or NAHEP-CN_s. By the transformed Kubelka-Munk function calculation, the corresponding bandgap energy of SAHEP-CN_s turn out to be

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close to that of MP-CNs or NAHEP-CNs.³⁴ The conduction band (CB) edges of the as-prepared CNs were investigated by means of Mott-Schottky measurements (Figure 3.9b). Combined with the bandgap value obtained from Kubelka-Munk function calculation, the corresponding valence band (VB) edges of the different CNs were calculated. It is shown in Figure 3.9c that both CB and VB edges of SAHEP-CNs were very similar to those of MP-CNs or NAHEP-CNs. It is noted in Figure 3.10 that SAHEP shows a similar UV-Vis absorption feature to the as prepared raw heptazine and the onset of optical absorption is far from that of CNs mentioned above. Therefore, we can conclude that the no carbon nitride was formed after the heptazine refluxed.

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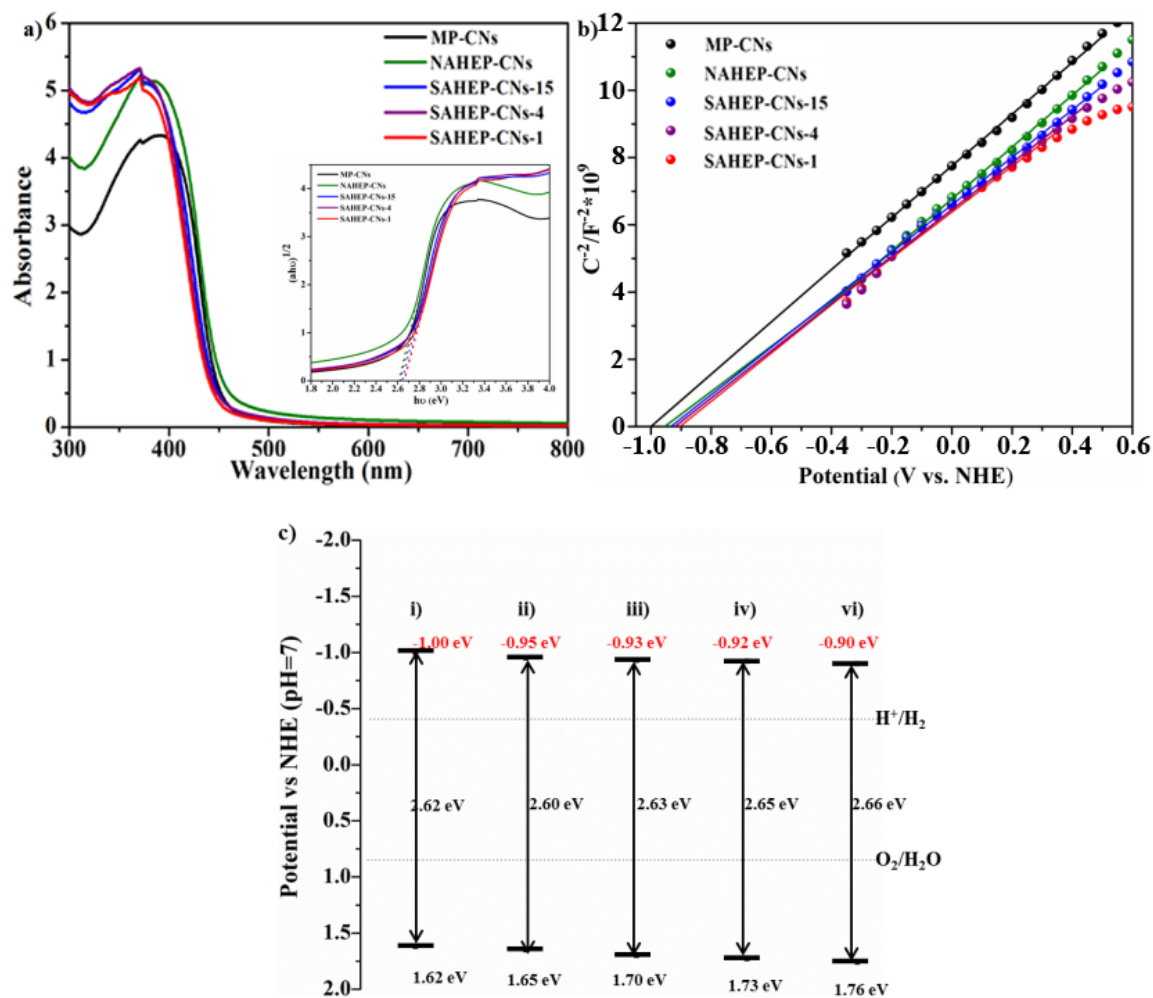


Figure 3.9 (a) UV-Vis absorption spectra, (b) Mott-Schottky plots, and (c) possible band positions of the different CNs, i.e., (i) MP-CNs, (ii) NAHEP-CNs, (iii) SAHEP-CNs-15, (iv) SAHEP-CNs-4, and (v) SAHEP-CNs-1. Inset in (a) are $(\alpha h\nu)^{1/2}$ versus $h\nu$ plots of the different CNs, showing that the corresponding band gaps.

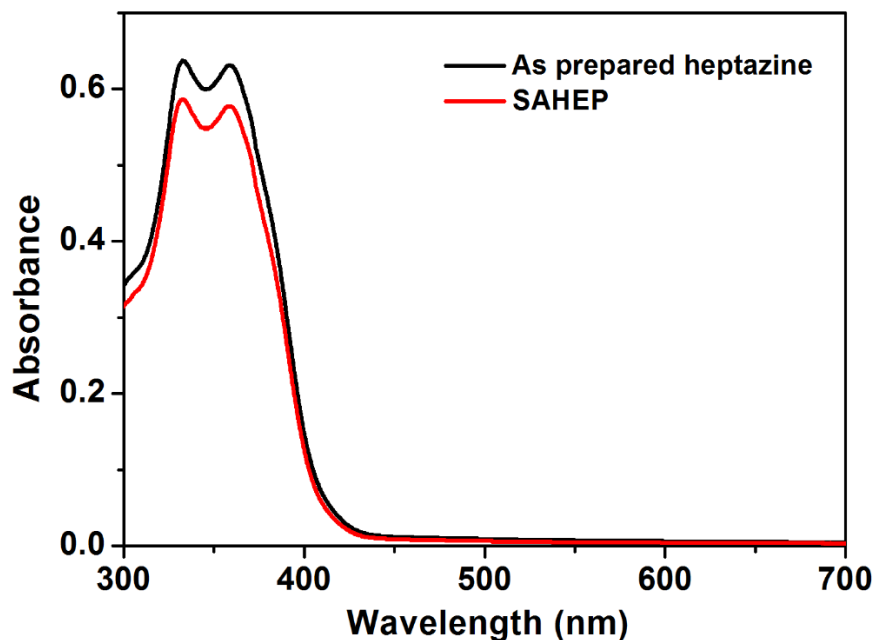


Figure 3.10 UV-Vis absorption spectra of as prepared raw heptazine and SAHEP.

N₂-adsorption measurement at 77 K indicated that all these different CNs are featured as mesoporous network (See the adsorption isotherm in Figure 3.11). The BET specific surface areas (SSA) of MP-CNs, SAHEP-CN-15, SAHEP-CN-4, and SAHEP-CN-1 are around 11.8, 22.3, 14.1 and 12.4 m²/g, respectively. This indicates that the higher heating rate is advantageous for the increase of surface area, propably due to the lower condensation of the materials resulted from the fast heating.

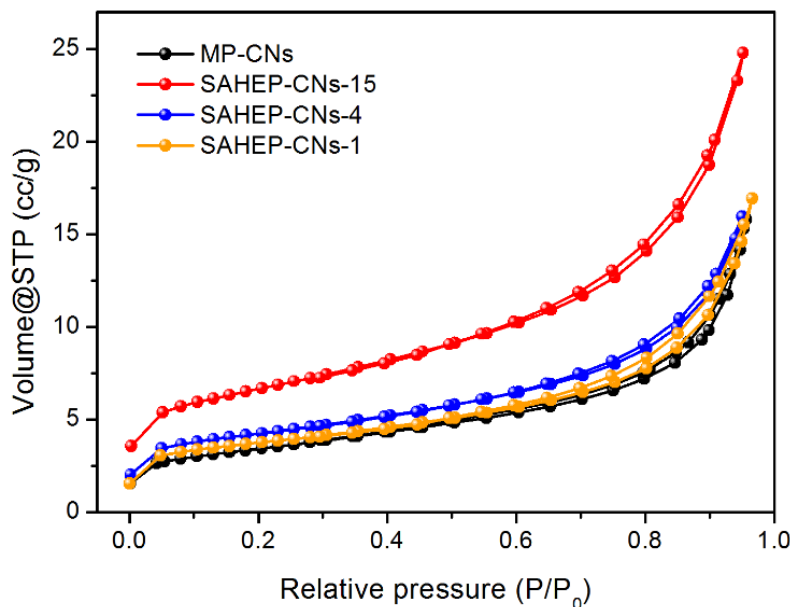


Figure 3.11 The N₂ adsorption-desorption isotherm of MP-CNs and SAHEP-CNs.

3.3.3 Photocatalytic hydrogen evolution activity of in-plane ordered graphitic carbon nitride

The photocatalytic activity of the different CNs was evaluated under visible light ($\lambda > 420$ nm) irradiation with photodeposited Pt particles as co-catalysts and triethanolamine (TEOA) as a sacrificial reagent. As shown in Figure 3.12a, MP-CNs and NAHEP-CNs showed a hydrogen evolution rate (HER) of 80 and 115 $\mu\text{mol/h}$, respectively, which were higher than that of CNs prepared by heating melamine in air as shown in Figure 3.13 (HER of 29 $\mu\text{mol/h}$). Obviously, SAHEP-CNs exhibit much improved activity especially for those calcinated at lower temperature-rising rate. Specifically, SAHEP-CNs-4 and SAHEP-CNs-15 show high HER of 360 $\mu\text{mol/h}$ and 290 $\mu\text{mol/h}$, respectively. SAHEP-CNs-1 has the highest HER of 420 $\mu\text{mol/h}$ without noticeable deactivation after 12 hr-irradiation (Figure 3.12b), which is nearly 14.6 times as high as that of CNs prepared by calcinating melamine in air.

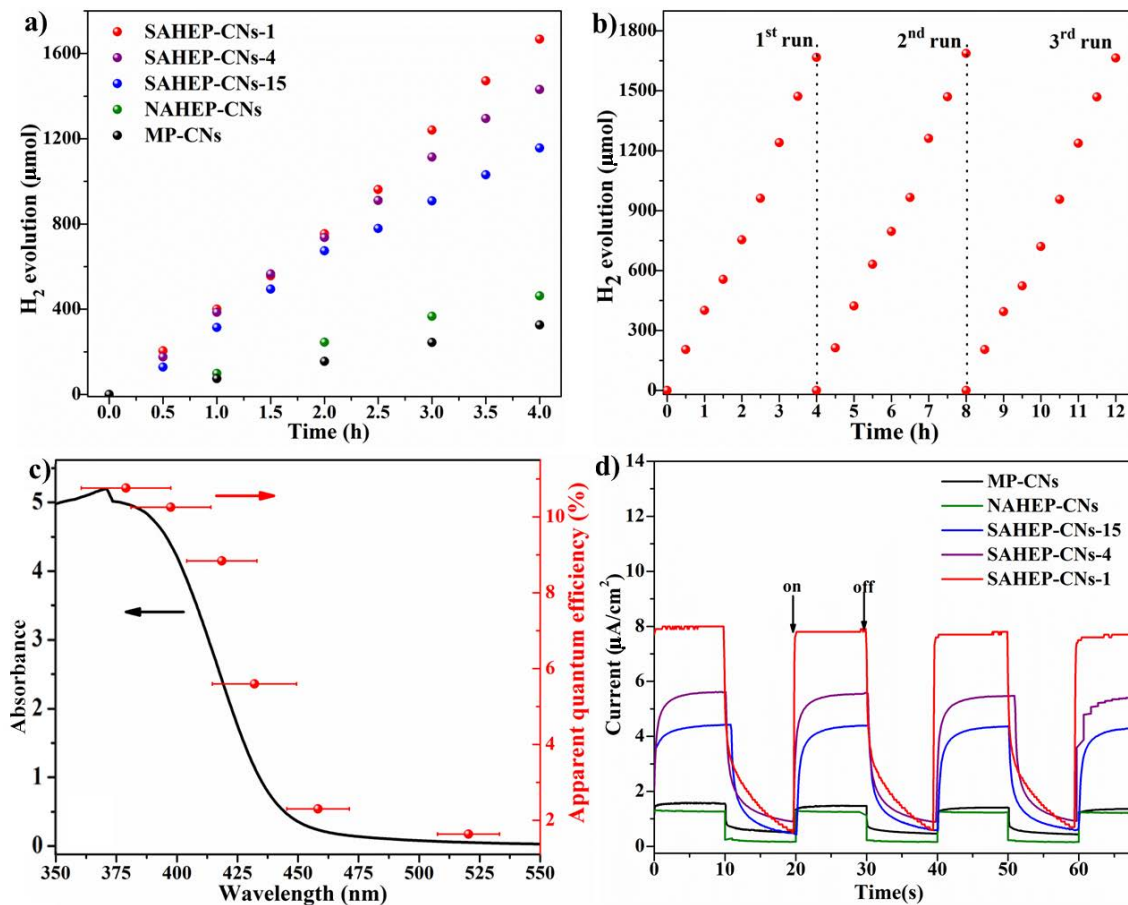


Figure 3.12 (a) Time course of H_2 evolution for different CNs under visible light ($\lambda > 420$ nm), (b) Cycling test for SAHEP-CN-1 under visible light ($\lambda > 420$ nm), (c) Wavelength-dependent apparent quantum efficiency (AQE) of H_2 evolution over SAHEP-CN-1, and (d) the photoelectrochemical responses of different CNs.

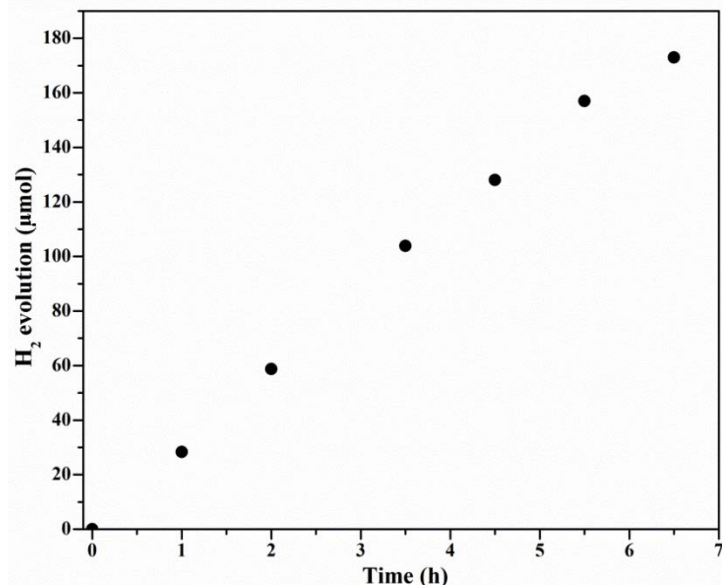


Figure 3.13 H₂ evolution performance of CN prepared by heating melamine in air.

The apparent quantum efficiency (AQE) for H₂ evolution of SAHEP-CN_s-1 was measured with various monochromatic light irradiations. As expected, the SAHEP-CN_s-1 gave high AQE in wavelength range of 370 – 520 nm and the AQE at 420 nm is as high as 8.9% (Figure 3.12c). The wavelength dependent HER activity matched well with the UV-Vis spectra, suggesting that the hydrogen evolution was resulted from the photogenerated electrons in the excited CNs. The rod-like morphology (in Figure 3.14) is rather stable even after 12 h irradiation. The Pt co-catalysts are photodeposited on the surface homogeneously, as shown in the EDS-Mapping in Figure 3.14.

To further confirm the uniformly enhanced performance of these CNs derived from assembled heptazine precursors, assembled heptazine from 20% water/IPA solvent was used as precursors to prepare CNs (SAHEP-20%-CN_s-1) by calcination at 550 °C under argon with a mild temperature-rising rate of 1 K/min. The SEM image in Figure 3.15b showed that the rod-like morphology of CNs has been inherited from the assembled

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precursors as shown in Figure 3.1d. SAHEP-20%-CNs-1 exhibits similar XRD pattern with SAHEP-CNs (Figure 3.15a) and high H_2 evolution rate of about $300 \mu\text{mol/h}$ (Figure 3.15c).

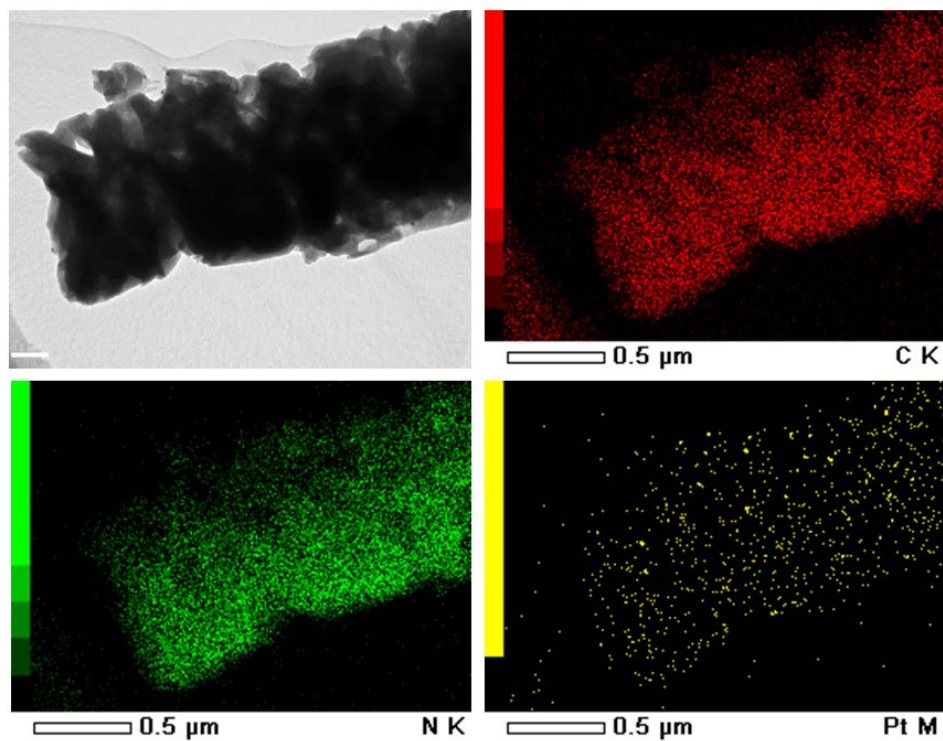


Figure 3.14 TEM images and element mapping images of SAHEP-CNs-1 after photocatalytic reaction (photodeposited with 3 wt% Pt).

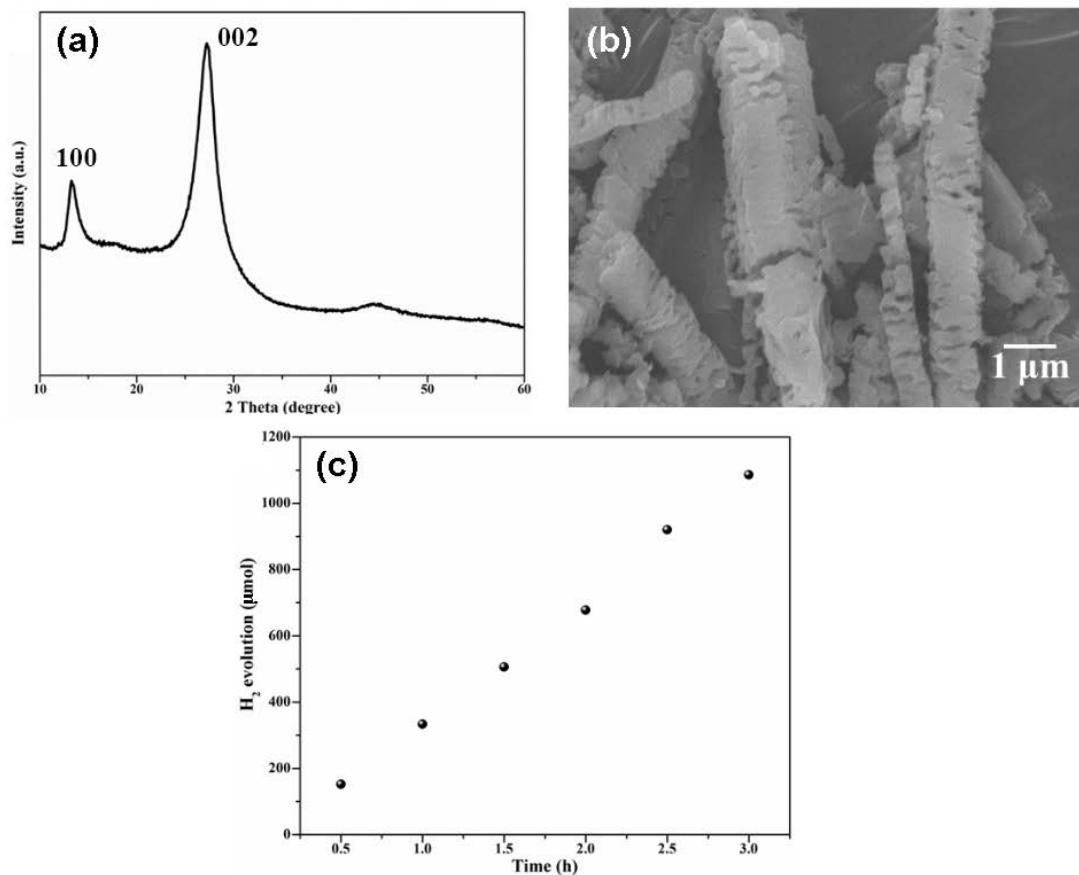


Figure 3.15 (a) XRD pattern, (b) SEM image, and (c) H₂ evolution performance of SAHEP-20%-CNs-1.

As compared in Table 3.2, the resulted hydrogen generation rate and AQE value is among the highest reported values for C₃N₄-based photocatalysts. Based on the similar UV-Vis light absorption characteristic, specific surface area (SSA) is an important factor to the photocatalytic performance. As reported, low-dimensioned carbon nitrides, such as nanosheets,^{15, 35} nanosphere,¹³ usually possess more surface-active sites for photocatalysis due to the large surface area. However, in our case, the SAHEP-CNs exhibit neither nanostructured architecture nor high surface area, but the photocatalytic performance is still very satisfied for bulk carbon nitride without doping and hetero-structure. It is reasonable to suspect that the enhanced activity may be related with the improved charge

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carrier transport inside the carbon nitride polymer. Merschjann et al. ever suggested the possible interplanar transport, intrachain and intraplanar transitions although there is not well-founded transport model.²⁸ The enhanced photocurrent (Figure 3.12d) and the decreased arc radius in the electrochemical impedance spectrum (EIS) (Figure 3.16) of SAHEP-CNs compared with MP-CNs or NAHEP-CNs further confirmed the improved charge transport and electronic conductivity within the inner planar of CNs.

The time-resolved PL spectra are further investigated and PL lifetimes are calculated by fitting the decay curve with a tri-exponential function as shown in Figure 3.17 and Table 3.3. In an obvious contrast, SAHEP-CNs-1 exhibits the longest average lifetime (23.378 ns), which is 3 times and more than twice as long as those of MP-CNs (7.707 ns) and NAHEP-CNs (10.061 ns), respectively. The ordered planar structure of polymeric CN framework with enhanced conjugation is definitely considered beneficial to the intraplanar diffusion of charge carriers, resulting the prolonged average lifetime and the tremendously improved photoactivity.

Table 3.2 Comparison of hydrogen evolution over reported carbon nitride photocatalysts

Catalysts	Surface area (m ² /g)	Reaction conditions	H ₂ evolution rate (μmol/h)	Apparent quantum efficiency	Ref.
Hollow C₃N₄ nanospheres	35	3 wt % Pt, in 10 vol % TEOA/water	224	7.5% (420nm)	36
Helical g-C₃N₄ rods	56	3 wt % Pt, in 10 vol % TEOA/water	74	N/A	21
Nanospherical g-C₃N₄	160	3 wt % Pt, in 10 vol % TEOA/water	574	9.6% (420nm)	13
PTI-0.06	119	3 wt % Pt, in 10 vol % TEOA/water	185	N/A	37

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Table 3.2 (Continued)

Catalysts	Surface area (m ² /g)	Reaction conditions	H ₂ evolution rate (μmol/h)	Apparent quantum efficiency	Ref.
PTI-0.13	93	3 wt % Pt, in 10 vol % TEOA/water	204	7% (420nm)	37
Mpg- C₃N₄	67-373	Appropriate amount of Pt, in 10 vol % TEOA/water	69-149	N/A	23
C₃N₄ nanosheets	384	3 wt% Pt, in 10 vol % TEOA/water	93	3.75% (420nm)	15
Seaweed architected carbon nitride	130	3 wt% Pt, in 10 vol % TEOA/water	99	7.8% (420nm)	34
SAHEP-CN_s-1	12.4	3 wt% Pt, in 10 vol % TEOA/water	420	8.9% (420nm)	This work

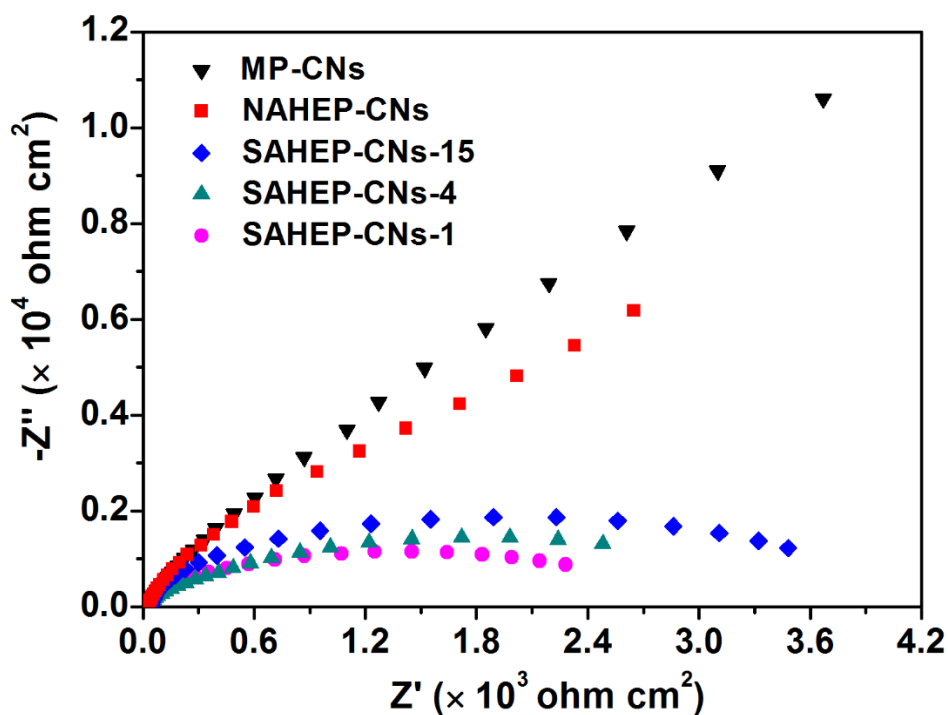


Figure 3.16 Electrochemical impedance spectroscopy Nyquist plots of the CNs from different precursors.

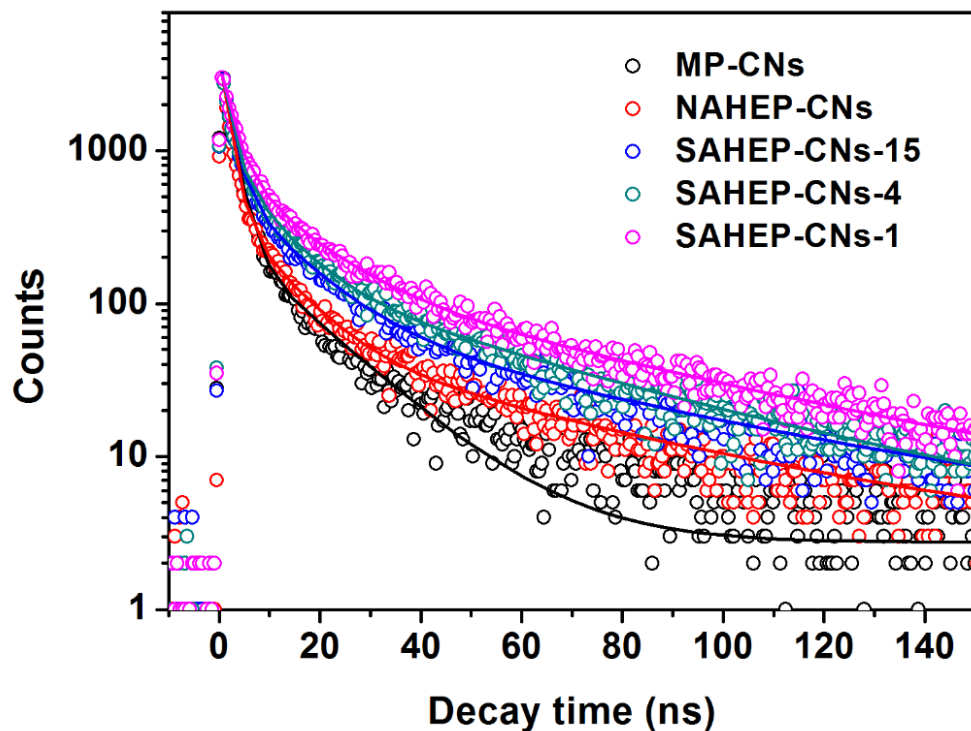


Figure 3.17 Time-resolved fluorescence decay spectra of different CNs monitored at 515, 520, 525, 525 and 525nm, respectively, by time-correlated single-photo counting. The samples were excited by the incident light of 405 nm.

Table 3.3 The fitting results of the fluorescence decay curves through a tri-exponential function.

Samples	τ_1 [ns]-Rel%	τ_2 [ns]-Rel%	τ_3 [ns]-Rel%	τ_{average} [ns]
MP-CNs	0.8-75.7%	4.0-22.8%	26.7-1.5%	7.7
NAHEP-CNs	1.6-89.5%	8.4-9.8%	52.0-0.7%	10.1
SAHEP-CNs-15	1.2-79.8%	7.5-17.3%	39.1-2.9%	16.2
SAHEP-CNs-4	1.1-77%	7.3-19.6%	41.8-3.4%	19.2
SAHEP-CNs-1	1.5-75.9%	9.6-20%	49.0-4.1%	23.4

3.4 Conclusions

In conclusion, through the preformed assembly of heptazine precursors, the resulted micro-nanostructured carbon nitrides showed enhanced ordering within the graphitic planar and decreased interlayer stacking due to the refinement of water molecules, especially in the mild calcination process with low temperature-rising rate. Attributed to the excellent charge separation by the intraplanar transport, a tremendously improved H₂ evolution rate of 420 $\mu\text{mol/h}$ under visible light ($\lambda > 420 \text{ nm}$) with an apparent quantum efficiency of 8.9% at 420 nm was obtained, which is among the highest value for C₃N₄-related photocatalyst in the literature. This work disclosed that enhanced in-plane ordering is one critical factor for the improved photocatalytic H₂ evolution of carbon nitride, attributed to the prolonged the lifetime of charge carriers by accelerating the charge transport and separation within the graphitic planar. Considering the relative facile fabrication without use of template and harsh condition, our finding can be envisaged to be more promising for efficient applications in the fields of pollutant degradation, CO₂ reduction and overall water splitting.

References

1. X. Chen, S. Shen, L. Guo and S. S. Mao, *Chem. Rev.*, 2010, **110**, 6503-6570.
2. K. Maeda, T. Takata, M. Hara, N. Saito, Y. Inoue, H. Kobayashi and K. Domen, *J. Am. Chem. Soc.*, 2005, **127**, 8286-8287.
3. H. Tong, S. Ouyang, Y. Bi, N. Umezawa, M. Oshikiri and J. Ye, *Adv. Mater.*, 2012, **24**, 229-251.
4. X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti, *Nat. Mater.*, 2009, **8**, 76-80.

Chapter 3

5. Z. Zhao, Y. Dai, J. Lin and G. Wang, *Chem. Mater.*, 2014, **26**, 3151-3161.
6. Y. Zhang, T. Mori, J. Ye and M. Antonietti, *J. Am. Chem. Soc.*, 2010, **132**, 6294-6295.
7. Y. Wang, J. Zhang, X. Wang, M. Antonietti and H. Li, *Angew. Chem. Int. Ed.*, 2010, **49**, 3356-3359.
8. J. Li, B. Shen, Z. Hong, B. Lin, B. Gao and Y. Chen, *Chem. Commun.*, 2012, **48**, 12017-12019.
9. Z. Lin and X. Wang, *Angew. Chem. Int. Ed.*, 2013, **52**, 1735-1738.
10. J. Zhang, J. Sun, K. Maeda, K. Domen, P. Liu, M. Antonietti, X. Fu and X. Wang, *Energy Environ. Sci.*, 2011, **4**, 675-678.
11. G. Liu, P. Niu, C. Sun, S. C. Smith, Z. Chen, G. Q. Lu and H.-M. Cheng, *J. Am. Chem. Soc.*, 2010, **132**, 11642-11648.
12. X. Chen, J. Zhang, X. Fu, M. Antonietti and X. Wang, *J. Am. Chem. Soc.*, 2009, **131**, 11658-11659.
13. J. Zhang, M. Zhang, C. Yang and X. Wang, *Adv. Mater.*, 2014, **26**, 4121-4126.
14. P. Niu, L. Zhang, G. Liu and H.-M. Cheng, *Adv. Funct. Mater.*, 2012, **22**, 4763-4770.
15. S. Yang, Y. Gong, J. Zhang, L. Zhan, L. Ma, Z. Fang, R. Vajtai, X. Wang and P. M. Ajayan, *Adv. Mater.*, 2013, **25**, 2452-2456.
16. K. Schwinghammer, M. B. Mesch, V. Duppel, C. Ziegler, J. Senker and B. V. Lotsch, *J. Am. Chem. Soc.*, 2014, **136**, 1730-1733.
17. X. Zhang, X. Xie, H. Wang, J. Zhang, B. Pan and Y. Xie, *J. Am. Chem. Soc.*, 2013, **135**, 18-21.

Chapter 3

18. J. Zhang, F. Guo and X. Wang, *Adv. Funct. Mater.*, 2013, **23**, 3008-3014.
19. Y.-S. Jun, E. Z. Lee, X. Wang, W. H. Hong, G. D. Stucky and A. Thomas, *Adv. Funct. Mater.*, 2013, **23**, 3661-3667.
20. A. Fischer, M. Antonietti and A. Thomas, *Adv. Mater.*, 2007, **19**, 264-267.
21. Y. Zheng, L. Lin, X. Ye, F. Guo and X. Wang, *Angew. Chem. Int. Ed.*, 2014, **53**, 11926-11930.
22. X.-H. Li, X. Wang and M. Antonietti, *Chem. Sci.*, 2012, **3**, 2170-2174.
23. X. Wang, K. Maeda, X. Chen, K. Takanabe, K. Domen, Y. Hou, X. Fu and M. Antonietti, *J. Am. Chem. Soc.*, 2009, **131**, 1680-1681.
24. K. Kailasam, J. D. Epping, A. Thomas, S. Losse and H. Junge, *Energy Environ. Sci.*, 2011, **4**, 4668-4674.
25. X. Chen, Y.-S. Jun, K. Takanabe, K. Maeda, K. Domen, X. Fu, M. Antonietti and X. Wang, *Chem. Mater.*, 2009, **21**, 4093-4095.
26. E. Z. Lee, Y.-S. Jun, W. H. Hong, A. Thomas and M. M. Jin, *Angew. Chem. Int. Ed.*, 2010, **49**, 9706-9710.
27. X.-H. Li, J. Zhang, X. Chen, A. Fischer, A. Thomas, M. Antonietti and X. Wang, *Chem. Mater.*, 2011, **23**, 4344-4348.
28. C. Merschjann, S. Tschierlei, T. Tyborski, K. Kailasam, S. Orthmann, D. Hollmann, T. Schedel-Niedrig, A. Thomas and S. Lochbrunner, *Adv. Mater.*, 2015, **27**, 7993-7999.
29. K. Schwinghammer, B. Tuffy, M. B. Mesch, E. Wirnhier, C. Martineau, F. Taulelle, W. Schnick, J. Senker and B. V. Lotsch, *Angew. Chem. Int. Ed.*, 2013, **52**, 2435-2439.

Chapter 3

30. S. J. Makowski, P. Köstler and W. Schnick, *Chem. Eur. J.*, 2012, **18**, 3248-3257.
31. I. Kang, H.-J. Yun, D. S. Chung, S.-K. Kwon and Y.-H. Kim, *J. Am. Chem. Soc.*, 2013, **135**, 14896-14899.
32. T. Tyborski, C. Merschjann, S. Orthmann, F. Yang, M. C. Lux-Steiner and S.-N. Th, *J. Phys. Condens. Matter*, 2013, **25**, 395402.
33. H.-J. Li, D.-J. Qian and M. Chen, *ACS Appl. Mater. Interfaces*, 2015, **7**, 25162-25170.
34. Q. Han, B. Wang, Y. Zhao, C. Hu and L. Qu, *Angew. Chem. Int. Ed.*, 2015, **54**, 11433-11437.
35. H. Shi, G. Chen, C. Zhang and Z. Zou, *ACS Catal.*, 2014, **4**, 3637-3643.
36. J. Sun, J. Zhang, M. Zhang, M. Antonietti, X. Fu and X. Wang, *Nat. Commun.*, 2012, DOI: 10.1038/ncomms2152, 1139.
37. M. K. Bhunia, K. Yamauchi and K. Takanabe, *Angew. Chem. Int. Ed.*, 2014, **53**, 11001-11005.

Chapter 4 Nature-inspired environmental “phosphorylation” modulation for highly improved photocatalytic H₂ production over g-C₃N₄ nanosheets under Visible-Light Irradiation

4.1 Introduction

As discussed in chapter 2 and 3, graphitic carbon nitride (g-C₃N₄) has been explored as a promising photocatalyst for photocatalytic H₂ evolution due to the suitable band structure and cost-effective feature. However, it still suffers from relatively low activity. Thus, numerous modifications on g-C₃N₄ have already emerged for activity improvement, including nanostructure design,^[1-9] molecule incorporation,^[10] and element doping.^[11, 12] Particularly, motivated by intriguing graphene chemistry, the preparation of g-C₃N₄ nanosheets has attracted considerable attention, because they are predicted to fully exploit the unique properties of such two-dimensional (2D) polymeric semiconductor for maximizing photocatalytical activities.^[1, 2, 13-15] It has been demonstrated that g-C₃N₄ nanosheets with anisotropic structure can assist to guide charge transfer along in-plane direction to facilitate the separation of electron-hole pairs and subsequent photocatalysis.^[2, 3] Moreover, they were reported possessing more favorable band structures for water splitting relative to bulk g-C₃N₄.^[2, 13] Despite these pioneer successes, the activities of g-C₃N₄ for photocatalytic H₂ generation are still moderate.

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Here, natural photosynthesis give us much inspiration to address this issue. In plant, the light dependent reactions of photosynthesis occur in thylakoid membranes. As the primary components of thylakoid membranes, phosphates (phospholipids) are well established to play vital roles in both transferring electrons on electron transport chains and pumping protons to drive adenosine triphosphate synthesis during the light dependent reactions.^[16-20] Meanwhile, in the stage of “dark” reactions of photosynthesis, some phosphates can directly work as mediators to realize the carbon fixation and finally to convert solar energy into chemical energy in the form of sugar.^[16] This process is known as the Calvin cycle. Hence, we are inspired to explore an environmental “phosphorylation” strategy for mimicking such phosphate-involved natural photosynthesis to improve the photocatalytic H₂ production of g-C₃N₄ nanosheets. Remarkably, the optimum addition of phosphates (K₂HPO₄) into the reaction system remarkably boosted the H₂ generation rate to 947 $\mu\text{mol h}^{-1}$ under visible-light. And an extremely high apparent quantum yield (AQY) of 26.1% was achieved at the wavelength of 420 ± 14.5 nm. Evidenced by (photo)electrocatalytic analysis and theoretical calculations, such significant improvement in H₂ production relied on the synergy of enhanced proton reduction and improved hole oxidation. More importantly, the phosphate was confirmed to indeed play roles resembling those in natural photosynthesis: as a proton pump to facilitate the proton transfer in reaction solutions, and as a mediator that participates directly in proton reduction, thus leading to a Calvin-cycle-like H₂-evolution pathway.

4.2 Experimental section

4.2.1 Preparation of g-C₃N₄ nanosheets

g-C₃N₄ nanosheets were prepared through a modified “bottom-up” dicyandiamide-blowing strategy.^[21] Typically, 1 g of dicyandiamide was fully mixed with 10 g of NH₄Cl. Then this mixture was heated to 550 °C within 3 h and held for 4 h. After being cooled down naturally, the g-C₃N₄ nanosheets was obtained. As a reference, bulk g-C₃N₄ was also synthesized by direct self-polymerization of dicyandiamide in the absence of NH₃Cl at 550 °C for 4 h.^[22]

4.2.2 Material characterization

The morphology of g-C₃N₄ was observed by using a JEOL 6701F Field-emission scanning electron microscopy (FESEM), Tecnai G2 F30 high-resolution transmission electron microscopy (HR-TEM) and dynamic force microscope (DFM, Nanocute SII, Seiko, Japan). The elemental composition was determined with an energy dispersive X-ray spectroscopy (EDX, EMAX-5770, HORIBA) attached to a Hitachi S-4800 microscope. X-ray diffraction (XRD) was conducted on an X'Pert PRO diffractometer with Cu-K α radiation (PANalytical). Chemical structures for samples were studied with an IRPrestige-21 Fourier transform infrared (FTIR) spectrometer. The diffuse reflectance spectra of the samples were recorded on a UV-visible spectrophotometer (UV-2600; Shimadzu Corp., Japan). Then the absorption spectra were calculated from the reflectance spectra by means of Kubelka-Munk transformations. A FP-6500 spectrofluorometer (Jasco, Japan) was used to measure the photoluminescence (PL) spectra of g-C₃N₄ nanosheets and bulk g-C₃N₄. N₂ adsorption-desorption experiments were carried out at

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77 K to examine the Brunauer-Emmett-Teller surface area (BELsorp II mini, BEL Japan Inc.). Before measuring, the samples were degassed in a vacuum at 100 °C for 12 h. The thermal analysis was carried out with the DTG-60H thermal analyzer (Shimadzu, Japan) up to 600 °C at a heating rate of around 3 °C/min in static air. Surface chemical analysis was performed by X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM, ULVAC-PHI Inc., Japan).

4.2.3 Photoelectrochemical measurements

The photoelectrochemical measurements were investigated in a conventional three-electrode cell by using an electrochemical analyzer (Model-650A). In these experiments, a Pt foil and an Ag/AgCl electrode were used as the counter-electrode and the reference electrode. The electrolyte was same as photocatalytic reaction solutions (270 ml of H₂O containing 10 vol% of TEOA, and different amounts of K₂HPO₄ (0, 0.02, 0.05, 0.10 and 0.20 mol), with or without pH adjustment by NaOH and HCl). For the electrocatalytic H₂ evolution test, Pt foil was also used as the working electrode. As for the TEOA oxidation measurements, Pt foil and the g-C₃N₄ films were respectively used as the working electrodes for the electrocatalytic and the photoelectrocatalytic reaction. The g-C₃N₄ electrode was prepared through spin-coating catalyst suspensions (5 mg of g-C₃N₄ nanosheets in 15 ml isopropanol) onto the ITO conductive glass with an area of 1 cm². This process was repeated for 150 times (30 µl suspensions per time). After air dried, the films were further dried at 393 K for 2 h to improve the adhesion. A 500 W Xenon lamp equipped with L40 cut-off filter was used as the visible-light source.

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4.2.4 Photocatalytic activity measurements

The photocatalytic H₂ production was carried out in a Pyrex glass reaction cell containing 270 ml 10 vol% of triethanolamine (TEOA) aqueous solution with different addition amounts of K₂HPO₄ (0, 0.02, 0.05, 0.10 and 0.20 mol). 50 mg of photocatalysts were used in the reaction. 3 wt.% Pt as the cocatalyst was in-situ photodeposited on the surface of photocatalysts. Before the irradiation, the reaction cell was connected to a gas-closed system with a gas-circulated pump and evacuated several times to remove the air completely. A 300 W Xenon lamp equipped with L40 cut-off filter was used as the visible-light source. The H₂ evolution was analyzed by an online gas chromatograph (GC-8A; Shimadzu Corp., Japan) equipped with a thermal conductivity detector. The apparent quantum yield (AQY) were measured at various monochromatic lights which were obtained by using a series of band-pass filters (Optical Coatings Japan). The water filter was also equipped to avoid the heat effects. The light intensity was measured at 9 different points to obtain an average intensity, using a spectroradiometer (Ushio, USR-40, Japan). The AQY at each monochromatic wavelength light was calculated by the equation: $AQY = (2 \times \text{amount of H}_2 \text{ molecules evolved in unit time} / \text{number of incident photons in unit time}) \times 100\%$. The turn over number (TON) respecting to Pt atoms in 2 h irradiation was calculated as follows:^[3, 6]

4.2.5 Theoretical calculation

All the free energy calculations were carried out at the B3PW91/6-31+G(d, p) theoretical level with water solvent model by Gaussian 09. Geometric optimizations were performed before single point calculations with the same method.

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Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

4.3 Results and discussion

4.3.1 General characterization of g-C₃N₄ nanosheets

In this study, g-C₃N₄ nanosheets (simply denoted as CN-NS) were prepared by a modified “bottom-up” dicyandiamide-blowing strategy.^[21] Bulk g-C₃N₄ (CN) as a reference was also obtained by direct polymerization of dicyandiamide.^[13, 22] Scanning electron microscopy (SEM) images of CN-NS are shown in Figure 4.1a and b. In sharp contrast from the dense, stack lamellar texture of bulk CN (Figure 4.2), a loose architecture integrated by g-C₃N₄ nanosheets with many wrinkles and irregular holes is observed in CN-NS. Transmission electron microscopy (TEM) images (Figure 4.1c) further reveal CN-NS consisting of silk-like nanosheets. Figure 4.1d and e are

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respectively the typical dynamic force microscopy (DFM) image of a giant g-C₃N₄ nanosheet and the corresponding height profile, which indicate that the nanosheet possesses a uniform thickness of 1.0 nm, containing about 3 atomic carbon nitride layers.^[23] From X-ray diffraction (XRD) patterns (Figure 4.1f), it is demonstrated that CN-NS show the same crystal and chemical structures with bulk CN. UV-vis spectra in Figure 4.3a shows CN-NS have visible light absorption with a band gap of 2.77 eV.

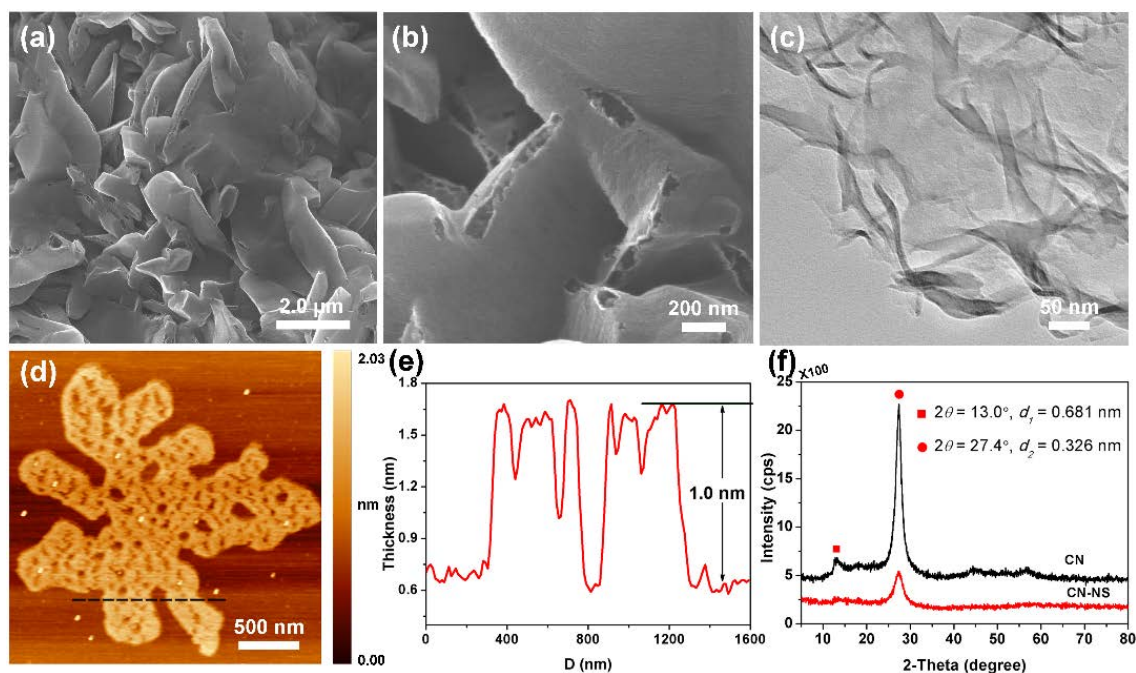


Figure 4.1 (a, b) SEM and (c) TEM images of CN-NS. (d) Representative DFM image and (e) the corresponding height profile determined along the dash line in (d), revealing a uniform thickness of about 1.0 nm for g-C₃N₄ nanosheets. (f) XRD patterns of CN-NS and bulk CN

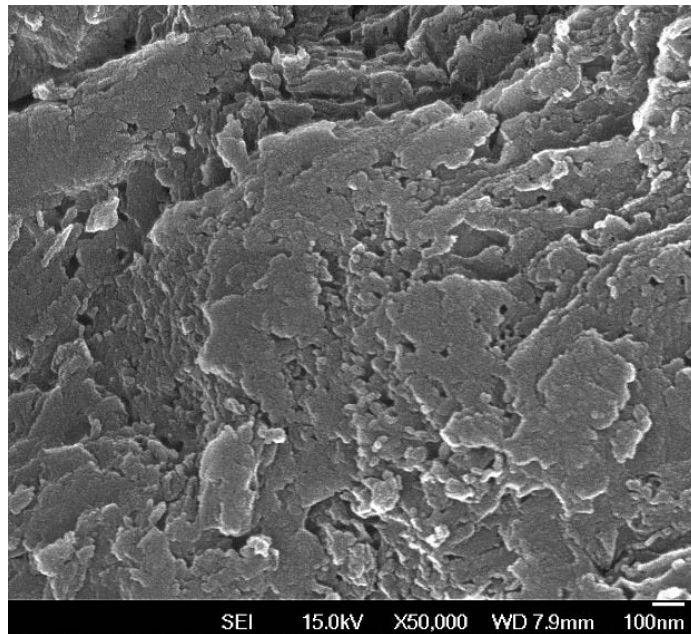


Figure 4.2 SEM images of bulk CN.

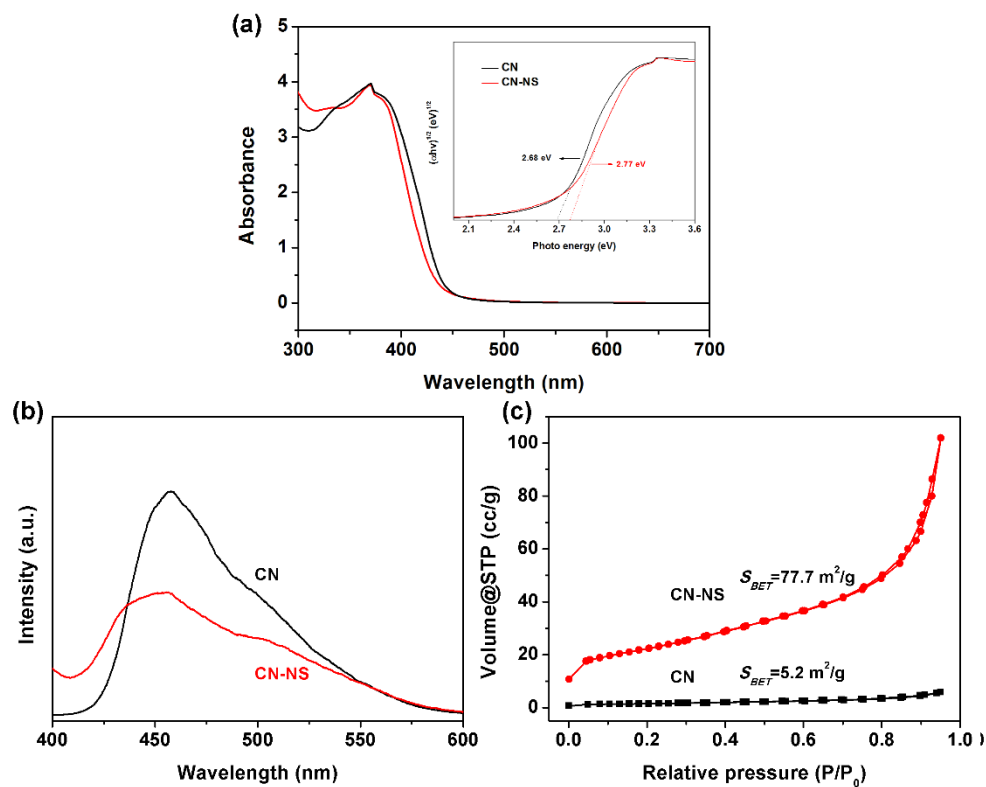


Figure 4.3 (a) UV-vis absorption spectra, (b) photoluminescence (PL) spectra, and (c) BET nitrogen adsorption/desorption isotherms of bulk CN and CN-NS. Inset in b shows the band

energies of bulk CN and CN-NS, and they are determined to 2.68 and 2.77 eV, respectively. In b, CN-NS show much lower PL intensity than bulk CN do, indicating that the former possess a relatively lower electron-hole recombination.

4.3.2 Environmental “phosphorylation” for highly improved photocatalytic H₂ production

In a procedure similar to the previously reported method, the H₂ production over CN-NS was conducted under visible light irradiation using Pt as co-catalysts and triethanolamine (TEOA) as hole scavengers.^[22] As expected, CN-NS exhibit a superior H₂ evolution activity in comparison with the bulk CN (Figure 4.4a), which might be attributed to the higher surface area and the lower electron-hole recombination rate in CN-NS (Figure 4.3b and c).^[10, 21] However, the most striking result is that, when 0.20 mol of K₂HPO₄ was added into the CN-NS photocatalysis system, the H₂ evolution was strongly accelerated. In 2 h irradiation, about 1.9 mmol H₂ gas was evolved, much exceeding the amount of catalysts (0.28 mmol). And the turnover number (TON) respecting to Pt atoms was calculated to be 247 (for details, please see Supporting Information). These results clearly indicate that the reaction proceeds catalytically.^[24] The influence of the addition amounts of K₂HPO₄ on H₂ production was further investigated. As presented in Figure 4.4b, the optimal amount of K₂HPO₄ is demonstrated to be 0.20 mol in the present photocatalysis system and the highest H₂ production rate of 947 $\mu\text{mol h}^{-1}$ (*ca.* 19000 $\mu\text{mol h}^{-1} \text{ g}^{-1}$; 50 mg of CN-NS) is achieved. Further increasing the addition would lead to a slight decrease in activity, which may be caused by the changes in pH value of the solution or surface states of CN-NS. Detailed reasons are still under investigation.

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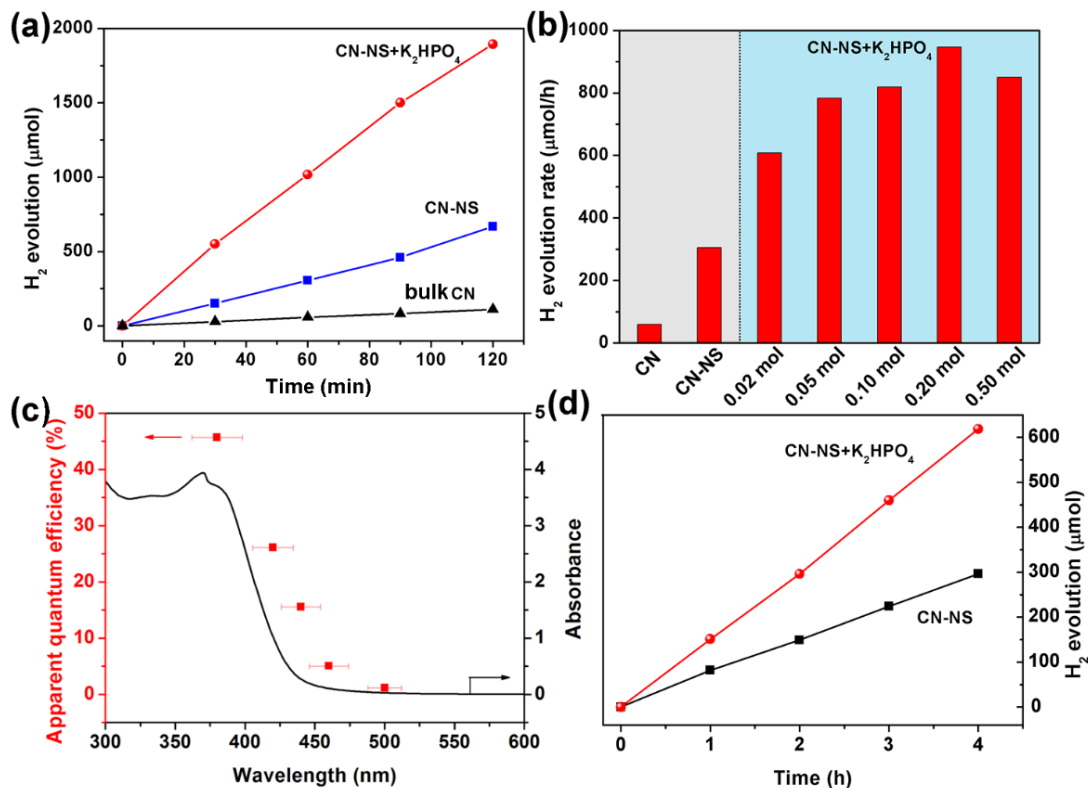


Figure 4.4 (a) H₂ production over CN-NS in TEOA aqueous solutions. (b) Rates of H₂ production from TEOA solutions with different amounts of K₂HPO₄. (c) Wavelength-dependent apparent quantum yield (AQY) of H₂ evolution over CN-NS in a TEOA solution containing 0.20 mol of K₂HPO₄. (d) H₂ evolution performance in methanol aqueous solutions. “CN-NS+K₂HPO₄” in (a, d) indicates the H₂ production was performed in the presence of K₂HPO₄ (0.20 mol). (Light source: 300 W Xenon lamp with L40 cutoff filter).

Under the optimal conditions, the wavelength-dependent apparent quantum yield (AQY) of H₂ evolution over CN-NS was measured to distinguish if the activity is driven by the light-excitation electrons in CN-NS or not. As shown in Figure 4.4c, the AQY decreases with the increasing of monochromatic light wavelength and it qualitatively tracks the characteristic absorption of CN-NS. This suggests that the H₂ production is primarily induced by the photocatalysis of CN-NS.^[3] It is worthy of note that, at 380 ± 18

nm, CN-NS achieve a peak AQY of 44.7%. Moreover, even under visible-light irradiation at 420 ± 14.5 nm, the AQY still reaches as high as 26.1%. The comparisons of light absorption, crystal structure and elemental compositions between the as-prepared and the post-reaction CN-NS are given in Figure 4.5 and 4.6, and reveal no obvious difference appearing during the photocatalytic reaction, suggesting the good stability of CN-NS. Using methanol or Na_2S as the sacrificial agent or changing CN-NS with bulk C_3N_4 or other semiconductors (like TiO_2 , CdS) as catalysts, much improved H_2 yields were also obtained after the addition of HPO_4^{2-} (Figure 4.4d and Figure 4.7), confirming the universality of this strategy.

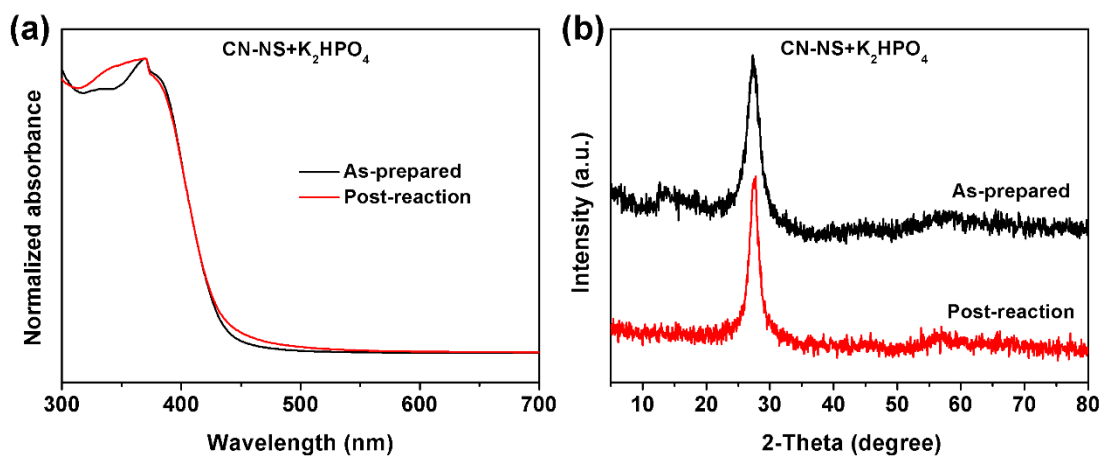


Figure 4.5 (a) UV-vis absorption spectra and (b) XRD patterns of as-prepared and post-reaction CN-NS photocatalysts. There is no obvious difference detected in their absorption properties and crystal structures, indicating the good stability.

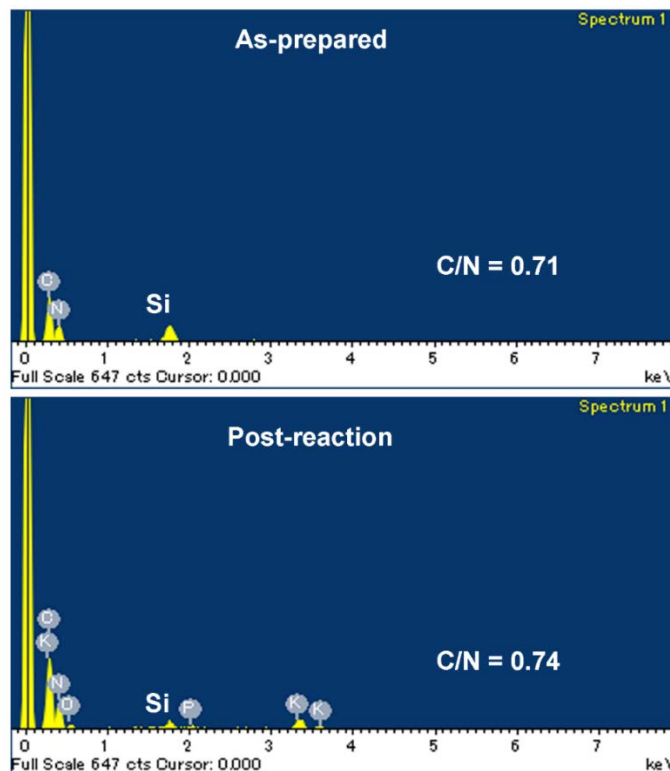


Figure 4.6 EDX analysis of as-prepared and post-reaction CN-NS photocatalysts and their C/N molar ratios are determined to 0.71 and 0.74, respectively. The slight increase can be attributed to the adsorption of TEOA by CN-NS during the photocatalysis reaction. Though the CN-NS were thoroughly washed with water, K and P signals from the residual K_2HPO_4 were still detected in the EDX spectra of the post reaction CN-NS. Si signal is coming from the Si substrate which was used for supporting samples during the measurements.

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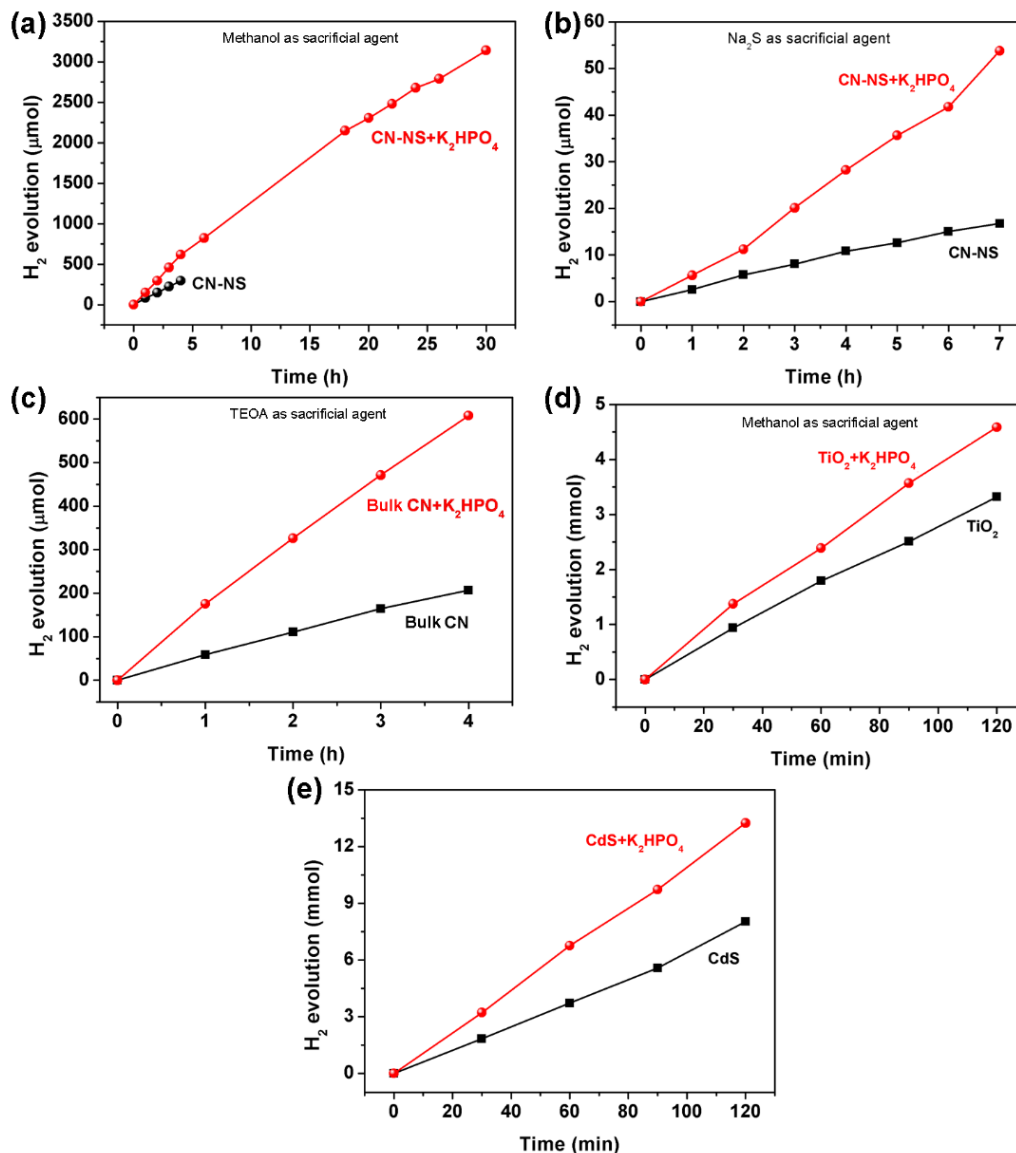


Figure 4.7 H₂ evolution over various photocatalysts with and without the addition of K₂HPO₄ from different sacrificial agent solutions: (a) 1.0 wt% Pt loaded CN-NS, methanol as the sacrificial agent; (b) 3.0 wt% Pt loaded CN-NS, Na₂S as the sacrificial agent; (c) 3.0 wt% Pt loaded bulk CN, TEOA as the sacrificial agent; (d) 0.5 wt% Pt loaded TiO₂ (commercial ST01), methanol as the sacrificial agent; (e) 0.5 wt% Pt loaded commercial CdS (Wako, 98%), 0.35 mol L⁻¹ of Na₂S-Na₂SO₃ solution. Visible light for (a), (b), (c), and (e); UV-visible light for (d). In (a), after reaction for 30 h, the H₂ evolution performance does not show obvious decrease, indicating the good photocatalytic stability of CN-NS in the K₂HPO₄ contained methanol solution.

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4.3.3 Reaction mechanism

The addition of K_2HPO_4 (0.20 mol) into the normal reaction solution (10 vol% TEOA aqueous solution) not only increases the ion concentrations (K^+ and HPO_4^{2-}) in the solution but also leads to the pH decreasing from 10.86 to 10.14 as a result of neutralization between K_2HPO_4 (a typical amphoteric salt; acting as acid here) and TEOA (a typical organic base), both of which have been demonstrated to be critical for the photocatalysis.^[25-27] However, which factors play the dominate roles in enhancing the H_2 production under present conditions still remains a question. The H_2 production in a pH-adjusted TEOA solution (pH = 10.14) was firstly conducted. In Figure 4.8, though the low pH value is beneficial for the proton reduction, it exhibits a slightly decreased activity in comparison with the case without K_2HPO_4 . This implies that the markedly enhanced H_2 production cannot be attributed to the decrease in pH value. Secondly, we also performed H_2 production with the addition of 0.4 and 0.6 mol of KCl, respectively. From Figure 4.9, they both showed very limited enhancements in activities, clearly suggesting the neglectable effect of both K^+ ions and the ion strength on H_2 evolution over CN-NS. When further adjusting the pH value of these KCl-contained solutions to 10.14 with HCl, we are surprised to observe decreased H_2 evolution rates. Combining the results above, it seems that low pH value might be adverse to H_2 production in the present system, which is probable that the hole induced oxidative half-reaction of sacrificial agents on valence band is suppressed in low pH solutions.^[27, 28] Excluding the effects from pH, K^+ ions and ion strength, we therefore speculate that it is HPO_4^{2-} ions that boost the H_2 evolution over CN-NS. A direct evidence to support this conclusion is

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also obtained from Figure 4.10, which shows that the concentration variation of HPO_4^{2-} is well consistent with trend of the photocatalytic activity.

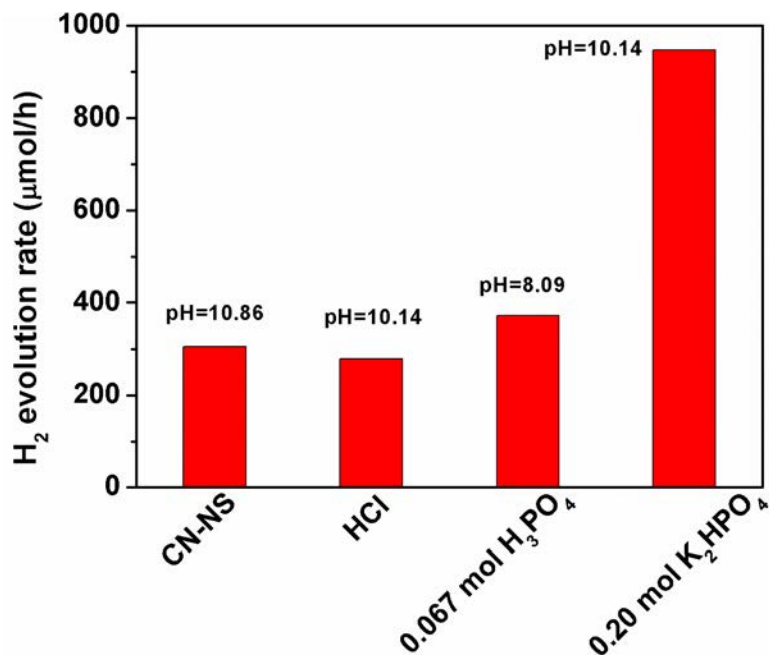


Figure 4.8 Rates of H_2 production over CN-NS under different conditions (pH values of the reaction solution in each case are given). “CN-NS” indicates the experimental was performed in the absence of phosphates. “HCl” indicates that HCl was added into the reaction solution to adjust the pH value to 10.14.

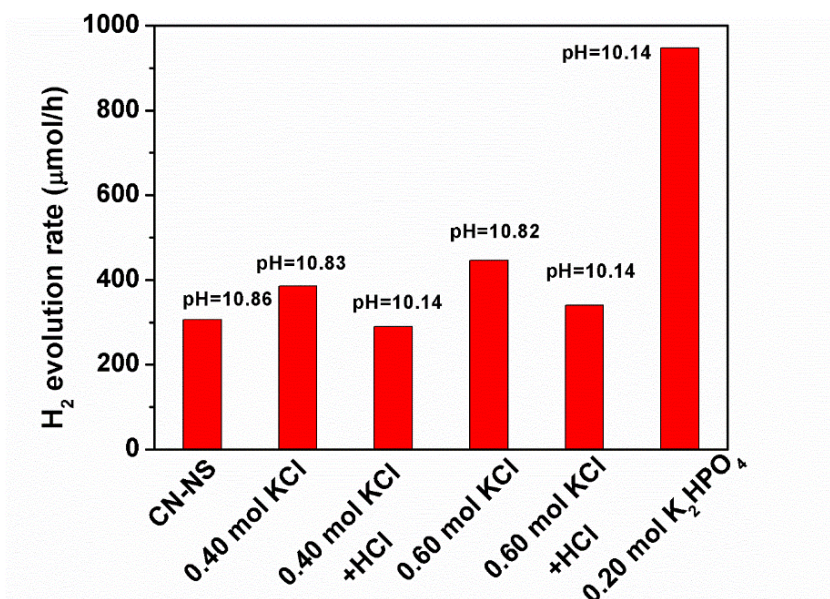


Figure 4.9 Rates of H₂ production over CN-NS under different conditions: 0.4 mol of KCl was used to keep the K⁺ concentration constant; 0.6 mol of KCl was used to keep the ion strength of the reaction solution constant. Obviously, both cases showed very limited enhancement in H₂ production, indicating the neglectable effect of both K⁺ ions and the ion strength on H₂ evolution over CN-NS.

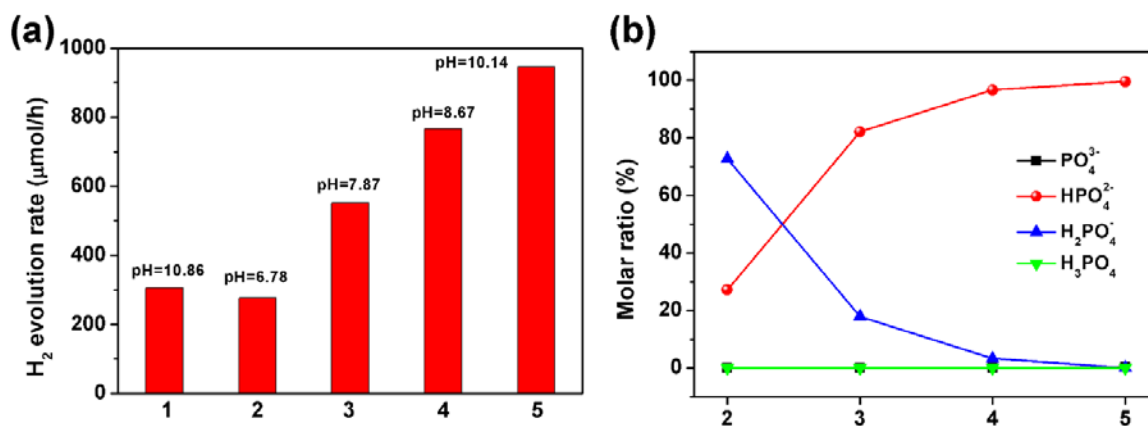


Figure 4.10 (a) Rates of H₂ production over CN-NS under different conditions. (b) Molar ratios of PO₄³⁻, HPO₄²⁻, H₂PO₄⁻, and H₃PO₄ under different conditions. (1: CN-NS; 2: 0.2 mol H₃PO₄; 3: 0.2 mol KH₂PO₄; 4: 0.1 mol KH₂PO₄ + 0.1 mol K₂HPO₄; 5: 0.2 mol K₂HPO₄). For the cases of 2, 3, 4, and 5, the same amounts of PO₄³⁻ were added into the reaction solutions, but different pH

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values were obtained. Though pH value has been proved to be not directly related to the H_2 evolution enhancement, it is of great significance to control the ionization equilibrium of HPO_4^{2-} ions in the phosphate solution. As shown in this figure, when the pH is 10.14, about 99.6% of phosphate ions are in the form of HPO_4^{2-} . With the pH decreasing to 6.78, the molar ratio of HPO_4^{2-} is gradually decreased and more H_2PO_4^- are formed (basically no H_3PO_4 and PO_4^{3-} exist in such pH range). Importantly, such variation of HPO_4^{2-} with the change of pH is well consistent with trend of the photocatalytic activity. These results offer a direct evidence for the critical role of HPO_4^{2-} in promoting H_2 production, but also show the importance of pH because of the involving of H^+ in the ionization equilibrium of HPO_4^{2-} .

To verify generated H_2 essentially originating from H_2O rather than HPO_4^{2-} , isotope tracer analyses involving D_2O were conducted on a gas chromatograph/mass spectrometer system. Considering the fast H-D exchange of TEOA with D_2O , methanol and Na_2S instead of TEOA were respectively used as sacrificial agents in the tests. As shown in Figure 4.11, both cases confirmed the formation of D_2 . Meanwhile, due to the H-D exchange between D_2O and HPO_4^{2-} , a small quantity of HD was also observed.^[29] Obviously, these results indicate that water is the hydrogen source for H_2 evolution during above photocatalytic reactions. Because PO_4^{3-} does not contain H^+ but it can be converted into HPO_4^{2-} through the ionization equilibrium with H_2O , the H_2 production with adding K_3PO_4 instead of K_2HPO_4 was further performed (Figure 4.12). As expected, an enhanced activity was also achieved, which offers an additional support to above conclusion.

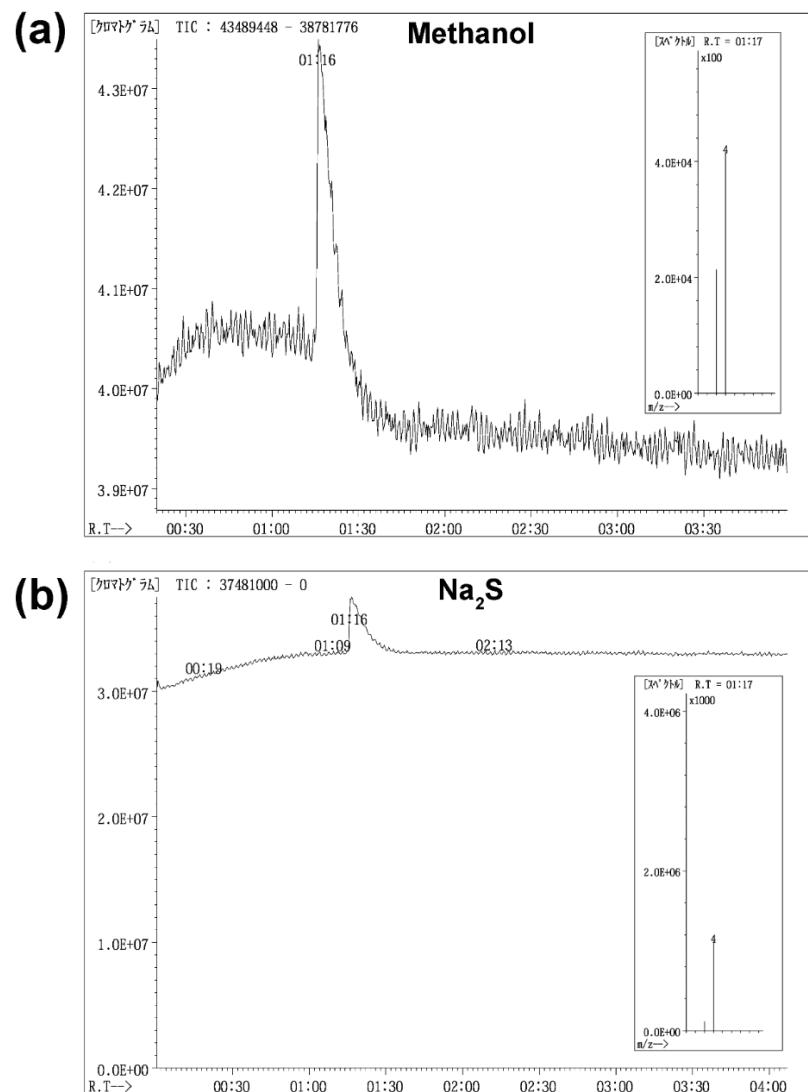


Figure 4.11 GC/MS spectra of the obtained gas when D₂O and 0.2 mol of K₂HPO₄ were used in the photocatalytic H₂ evolution test: (a) Methanol as the sacrificial agent; (b) Na₂S as the sacrificial agent.

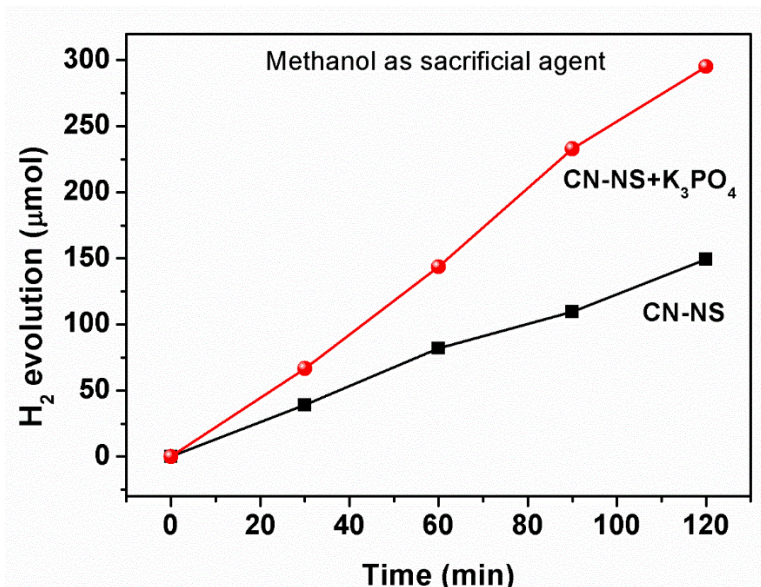


Figure 4.12 H₂ evolution over 1.0 wt% Pt loaded CN-NS from an aqueous methanol solution with and without the addition of K₃PO₄ (0.20 mol) under visible light. K₃PO₄ was used here to rule out the effect from the H⁺ in HPO₄²⁻.

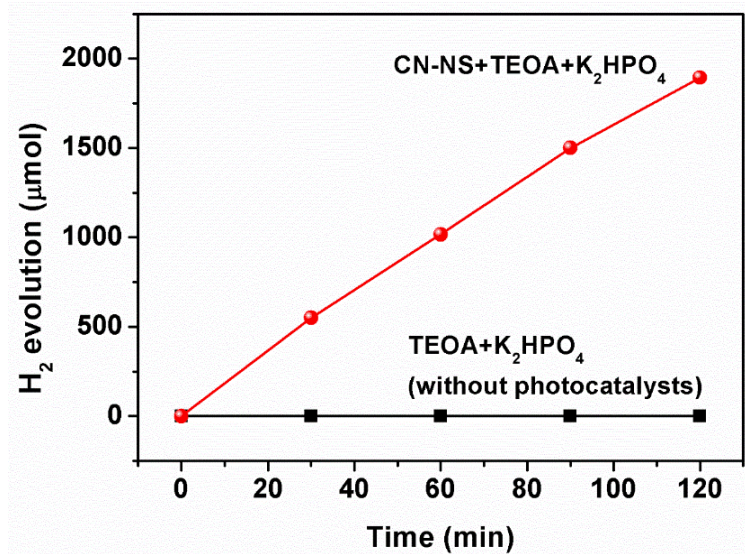


Figure 4.13 H₂ evolution in the presence and absence of CN-NS from an aqueous TEOA and K₂HPO₄ solution under visible light. Without the CN-NS, no H₂ was detected in the system, indicating that K₂HPO₄ cannot be photo-decomposed into H₂.

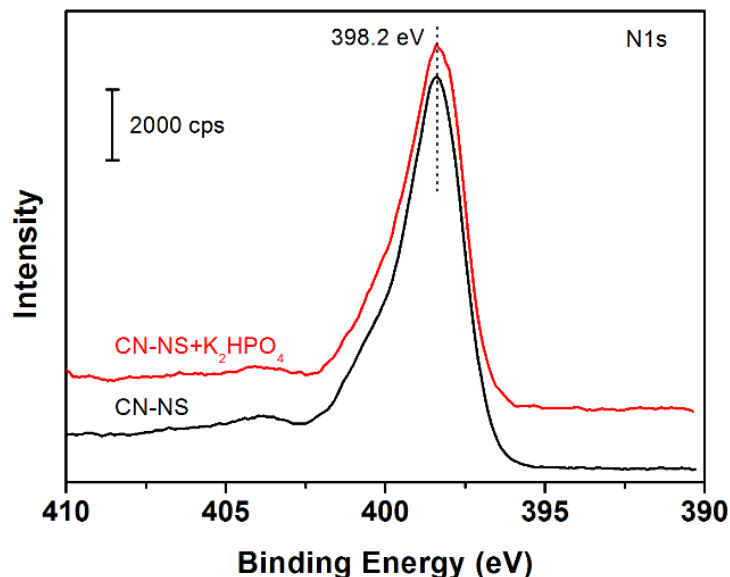


Figure 4.14 High-resolution XPS spectra of N1s for CN-NS and K₂HPO₄-loaded CN-NS. Clearly, no obvious difference is observed in these two spectra. This result suggests negligible interface interaction between g-C₃N₄ and K₂HPO₄.

Since only slight changes in pH of the reaction solution were shown after adding K₂HPO₄, the well-discussed non-Nernstian band-edge shift mechanism for explaining the enhanced H₂ production over semiconductor photocatalysts seems not to be applicable to the present case.^[25-27] Meanwhile, excluding the possibility of photo-decomposing HPO₄²⁻ into H₂ (Figure 4.13) and the influence from the interface interaction between CN-NS and K₂HPO₄ (Figure 4.14), we therefore speculate that the HPO₄²⁻ environment may exert direct influence on the surface redox reaction. Considering the identical physical nature to photocatalytic process, (photo)electrocatalytic analysis was employed to investigate the origin of the markedly enhanced H₂ evolution performance by HPO₄²⁻.^[26] Generally, semiconductor photocatalytic H₂ evolution is considered to be achieved on the surface of loaded co-catalysts (Pt here) by proton reduction.^[30] Therefore, using Pt as the working electrode, linear sweep voltammetry (LSV) of the electrocatalytic H₂

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evolution was firstly examined to simulate proton reduction pathway on Pt-loaded CN-NS during the photocatalysis. As shown in Figure 4.15a, a reduction current with onset at nearly 0 V (vs. RHE) is observed, indicating the H₂ evolution reaction occurring on Pt surface.^[31] Furthermore, with increasing the addition of K₂HPO₄ from 0 to 0.20 mol, the current density increased more than 10 times at 0.3 V, suggesting the addition of K₂HPO₄ is capable of effectively promoting the H₂ evolution on Pt surface. To rule out the effect from pH, the experiments were further performed at the same pH value of 10.14 with different additions of K₂HPO₄ and the consistent conclusion is also obtained (Figure 4.16). According to the report by Kreuer *et al.*, such promotion in H₂ evolution might be partly attributed to the increased proton conductivity: the addition of HPO₄²⁻ can lead to the formation of hydrogen-bond chains between HPO₄²⁻, which can function like the proton pumper in natural photosynthesis to facilitate the proton transport in the reaction solution.^[32]

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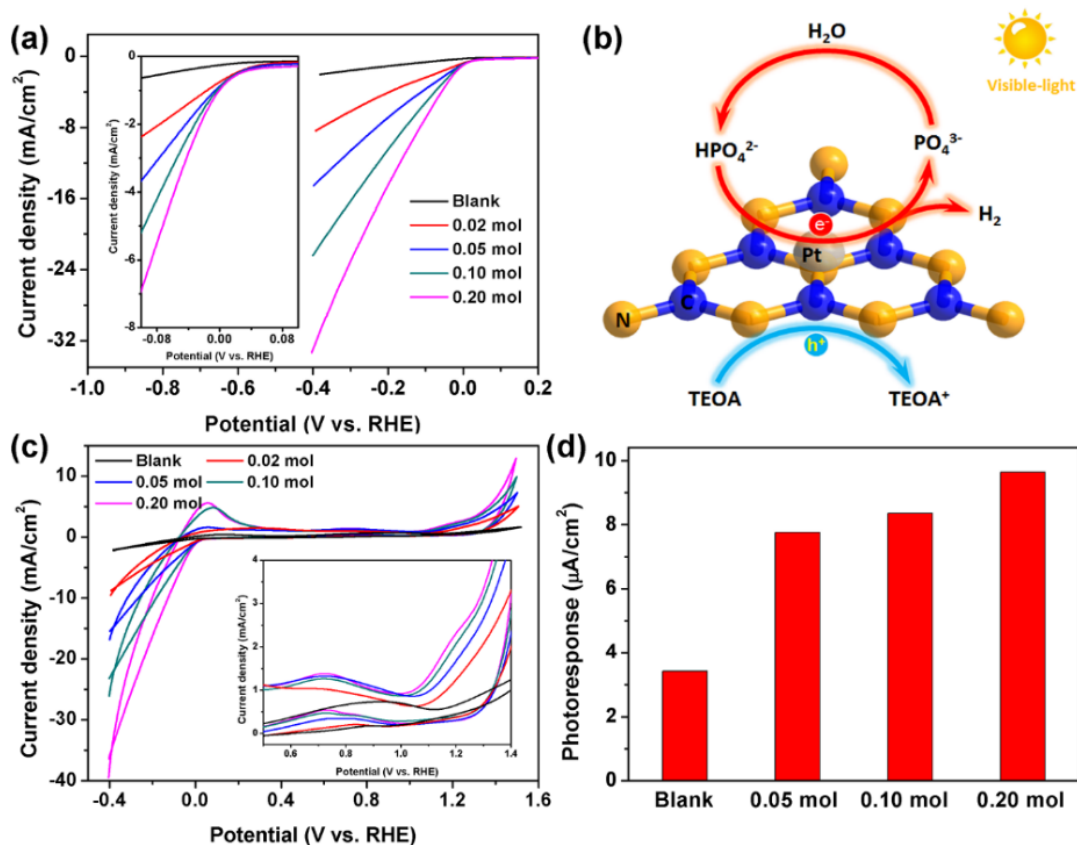


Figure 4.15 Electrochemical H₂ evolution on Pt electrodes in electrolytes containing different amounts of K₂HPO₄. Inset shows the enlarged LSV curves in the potential range of -0.1 to 0.1 V. (b) Schematic of the photocatalytic H₂ evolution under the proposed HPO₄²⁻ involved proton reduction mechanism. (c) Voltammograms obtained at Pt electrodes for TEOA solutions with and without adding K₂HPO₄. Inset shows the TEOA oxidation peaks. (d) Net oxidation photocurrent density of TEOA on CN-NS electrodes with different additions of K₂HPO₄. (The net photoresponse here was obtained by subtracting the dark current from the total photocurrent. Visible-light source: 500 W Xenon lamp equipped with a L40 cutoff filter).

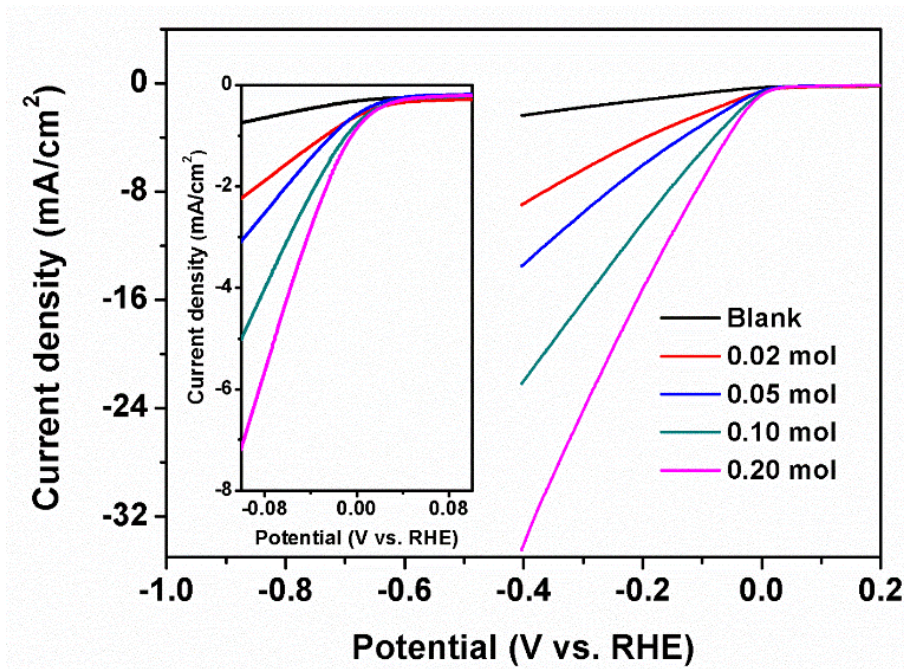


Figure 4.16 Electrochemical H_2 evolution on Pt electrodes in electrolytes containing different amounts of K_2HPO_4 with the pH values adjusted to 10.14 by NaOH and HCl. Inset shows the enlarged LSV curves in the potential range of -0.1 to 0.1 V

Free energy diagrams for H_2 evolution from H_2O and HPO_4^{2-} were further calculated, respectively, and shown in Figure 4.17. It is clearly seen that HPO_4^{2-} is much more advantageous over H_2O for combining electrons to create H_2 , evidenced by the larger decrease in free energy for the former case. Meanwhile, the LSV also shows that the addition of HPO_4^{2-} leads to a more positive onset potential for H_2 evolution (Figure 4.18). These results imply that, apart from serving as the carrier of protons to facilitate the H_2 evolution, HPO_4^{2-} is also likely to be a mediator to directly participate in the photocatalytic reaction, giving rise to a new proton reduction pathway (Figure 4.15b): HPO_4^{2-} instead of H_2O provides the H^+ to react with photogenerated electrons and subsequently to produce H_2 and PO_4^{3-} on the surface of Pt co-catalysts.^[13] As demonstrated by the energy calculations and LSV results, this process is more effective than the direct H_2 evolution

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from H_2O , thus possibly making an additional contribution to the enhancement of the photocatalytic efficiency. Because the solution pH values were found to be slightly decreased after the photocatalytic reaction (Figure 4.19), it could be speculated that, after the H_2 evolution from HPO_4^{2-} , the formed PO_4^{3-} immediately combined with H^+ from H_2O to regenerate HPO_4^{2-} and finally accomplished the proton reduction cycle (Figure 4.15b). Obviously, this process show many similarities to the Calvin cycle in natural photosynthesis for carbon fixation.

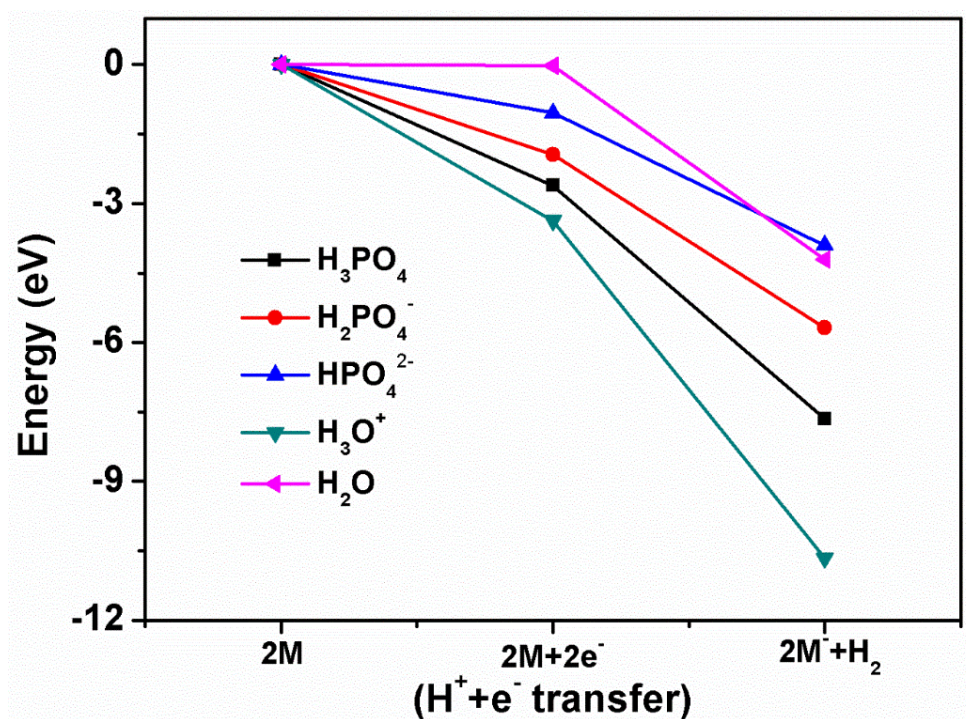


Figure 4.17 Free energy diagrams for H_2 evolution from different precursor. In the photocatalytic system with 0.20 mol of K_2HPO_4 , the pH of the reaction solution is 10.14 and around 99.6% of phosphate ions are in the form of HPO_4^{2-} . Therefore, only H_2O and HPO_4^{2-} are proposed to be the possible hydrogen source. It is shown that, in comparison with H_2O , a relatively larger decrease in free energy was observed for HPO_4^{2-} combining electrons to create H_2 . This means that HPO_4^{2-} might directly participate in the photocatalytic reaction for H_2 evolution (Figure 4.17).

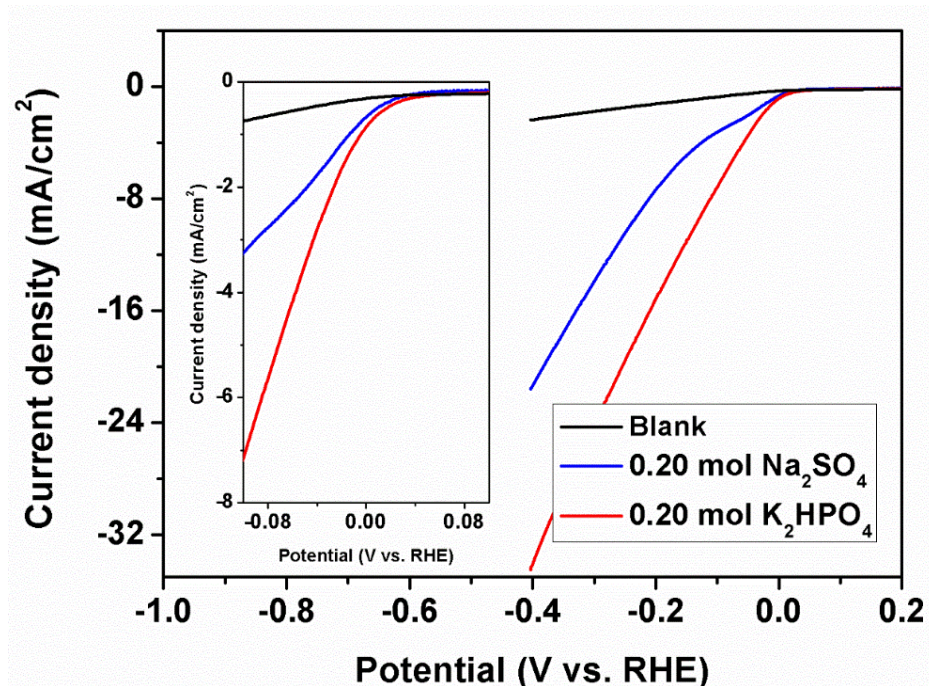


Figure 4.18 Electrochemical H₂ evolution on Pt electrodes at pH = 10.14 in electrolytes containing different salts. Na₂SO₄ was used in the tests to rule out the influence of ion strength on H₂ evolution. Obviously, a more positive onset potential for H₂ evolution was showed in the K₂HPO₄ case, indicating that HPO₄²⁻ is much more advantageous over H₂O for combining electrons to create H₂.

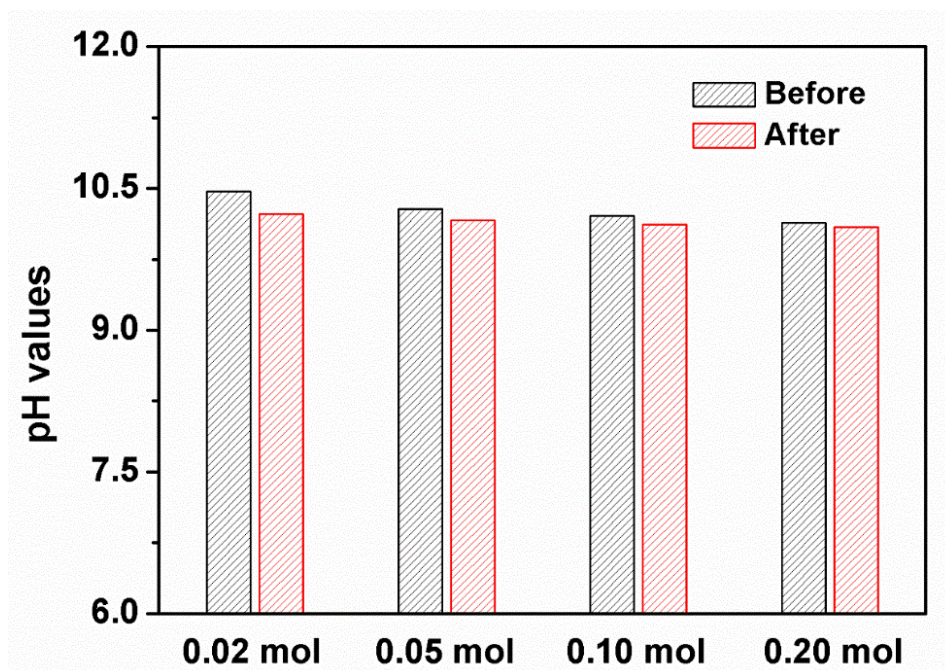


Figure 4.19 Comparisons of pH values of the reaction solutions (containing different amounts of K₂HPO₄) before and after the photocatalytic H₂ production (4 h).

The influence of adding K₂HPO₄ on TEOA oxidation was investigated by voltammograms. As shown in Figure 4.20a, an irreversible oxidation peak is observed to arise at 0.97 V (vs. RHE), which could be associated with the oxidation of TEOA.^[33, 34] Importantly, with increased K₂HPO₄ addition amounts, the oxidation current density is increased, and the peak is gradually shifted to a more negative potential (0.72 V), which is also accompanied by a second oxidation peak appearing at 1.2 V (Figure 4.15c and Figure 4.21).^[34] These results suggest that the oxidation of TEOA can be much promoted by K₂HPO₄. To gain a better simulation of the oxidation reaction occurring in the photocatalytic system, CN-NS thin films were prepared and further used as working electrodes in these photoelectrocatalytic TEOA oxidation tests (Figure 4.22). The net oxidation photocurrent density of TEOA with different additions of K₂HPO₄ is shown in

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Figure 4.15d. It is apparent that an increasing photocurrent density is exhibited with increasing K_2HPO_4 , proving that, in the presence of K_2HPO_4 , the enhanced oxidation of TEOA can be also achieved by photoexcitation of CN-NS. This feature would be beneficial for the fast consumption of holes in excited CN-NS and suppressing the e^-/h^+ recombination, consequently improving the photocatalytic efficiency.

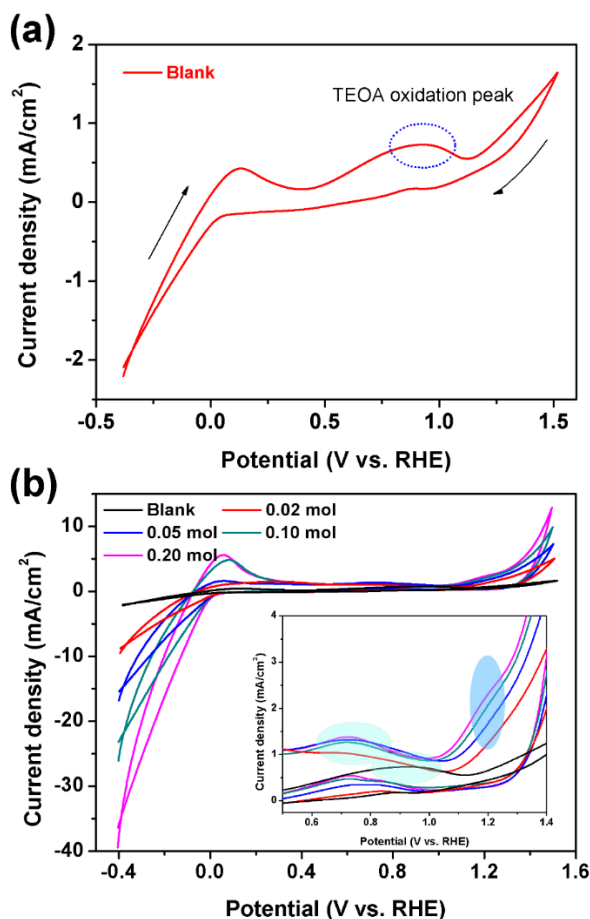


Figure 4.20 Voltammograms obtained at the Pt electrode for TEOA solutions with and without adding K_2HPO_4 . As shown in (a), the peak observed at 0.97 V can be attributed to the electrooxidation of TEOA. In (b), with increased K_2HPO_4 addition amounts, the oxidation current density of TEOA is increased, and the peak is gradually shifted to a more negative potential (0.72

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V) (marked by bright green color), which is also accompanied by a second oxidation peak appearing at 1.2 V (marked by bright blue color).

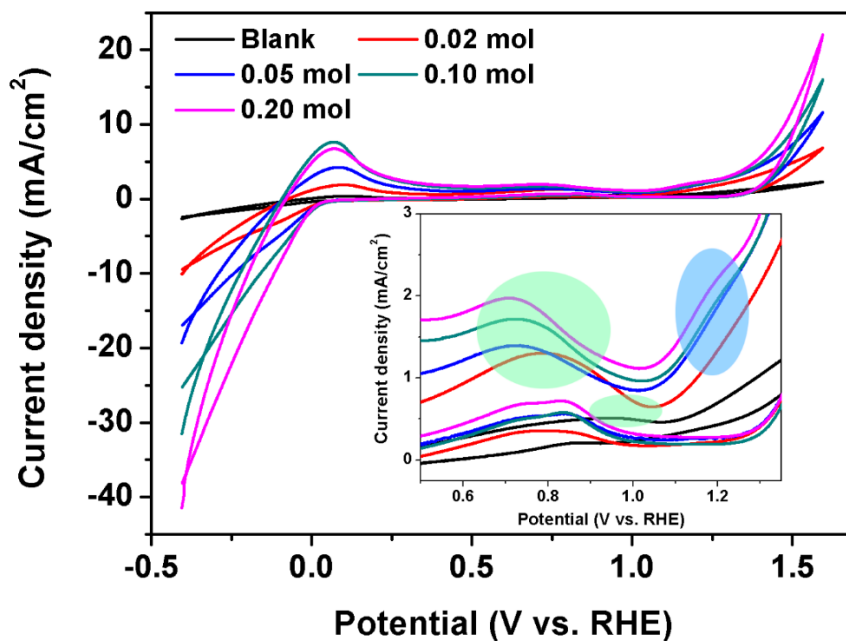


Figure 4.21 Voltammograms obtained at the Pt electrode for TEOA solutions at pH = 10.14 containing different amounts of K_2HPO_4 . The TEOA oxidation peaks are shown to be increased and negatively shifted with the increasing of K_2HPO_4 . And a new oxidation peak appears when 0.05 mol and more K_2HPO_4 added.

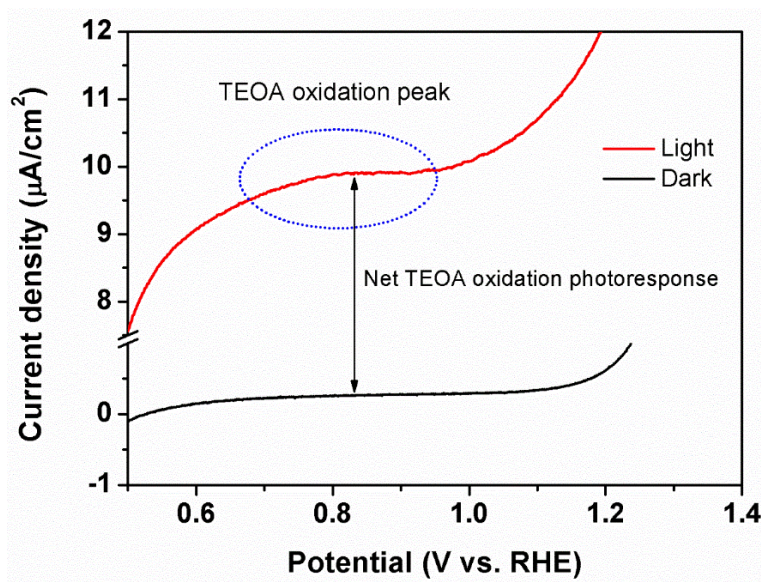


Figure 4.22 TEOA oxidation on g-C₃N₄ electrodes in dark and under visible-light irradiation. The electrolyte contains 0.20 mol of K₂HPO₄.

The enhancement in the TEOA oxidation could be attributed to the more favorable formation of mobile $\bullet\text{OH}$ free radicals in the presence of HPO_4^{2-} . As shown in Figure 4.23a, in the absence of HPO_4^{2-} , the surface of g-C₃N₄ would be hydrogen-bonded by OH groups or chemisorbed by sacrificial agent molecules (for example, TEOA) which are typical hole-trapping sites. Under light irradiation, when the holes are trapped on these surface sites in the form of surface-bound OH radicals or TEOA^+ , they would be likely to recombine with electrons trapped in Pt.^[35] Thus the photocatalysis efficiency is hindered. With the addition of HPO_4^{2-} , HPO_4^{2-} would be hydrogen-bonded on the surface of g-C₃N₄ by displacing the surface OH groups or TEOA molecules. As shown in Figure 4.23b, under this conditions, the holes would directly react with alternative hole scavengers (e.g., OH^- or TEOA in reaction medium) instead, which leads to the more favorable generation of mobile $\bullet\text{OH}$ radicals or oxidized TEOA. Therefore, the TEOA oxidation could be enhanced in the presence of HPO_4^{2-} .

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In order to further confirm the above speculation, the photocatalytic generation of $\bullet\text{OH}$ radicals was measured in the absence and presence of HPO_4^{2-} through a fluorescence method using coumarin as an $\bullet\text{OH}$ trapper (Figure 4.24). During the photocatalytic reaction, coumarin can react with $\bullet\text{OH}$ to form 7-hydroxycoumarin which is a product with high fluorescence properties (exhibiting a fluorescence peak at around 460 nm; see Figure 4.25a).^[36] Thus, the fluorescence intensity of the solution is a good index to confirm the formation of $\bullet\text{OH}$.^[36] In Figure 4.25a and b, with the irradiation time being increased from 0 to 60 min, the fluorescence measured without adding HPO_4^{2-} show a continuous increase, indicating the gradual formation of $\bullet\text{OH}$ in the solution. In sharp contrast, after the addition of HPO_4^{2-} , we can see that the formation of $\bullet\text{OH}$ is greatly enhanced, as reflected by the higher increase rate of the fluorescence intensity (Figure 4.25b). This result evidently demonstrates that the formation of $\bullet\text{OH}$ radicals could be improved by the introduction of HPO_4^{2-} , thus facilitating the TEOA oxidation.

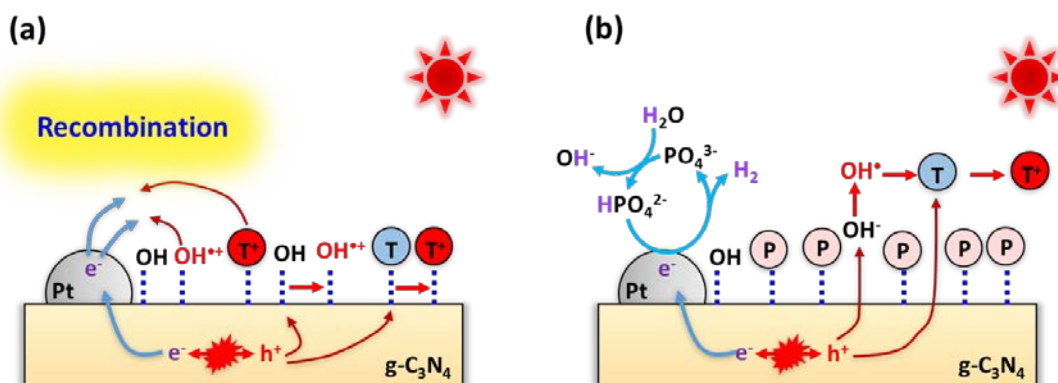


Figure 4.23 Schematic illustration of the interfacial charge transfer and recombination occurring on Pt/g- C_3N_4 in the (a) absence and (b) presence of K_2HPO_4 . P represents the surface adsorbed phosphates and T indicates the sacrificial agent molecule (Here, it is triethanolamine (TEOA)).

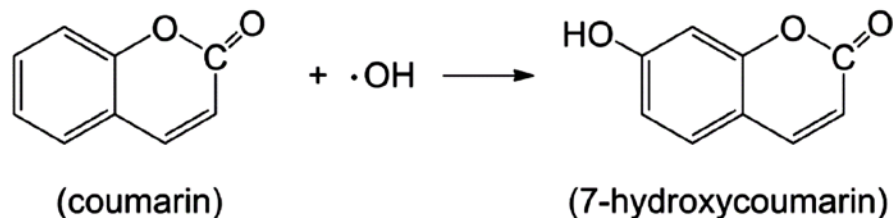


Figure 4.24 The reaction between $\cdot\text{OH}$ and coumarin to form 7-hydroxycoumarin.

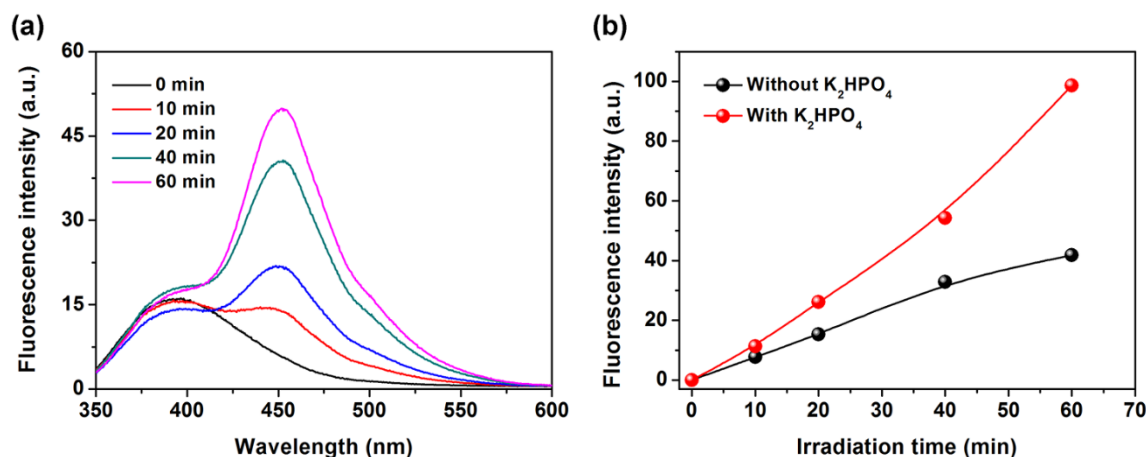


Figure 4.25 (a) Fluorescence spectral changes observed during illumination ($400 < \lambda < 800$ nm) of g- C_3N_4 nanosheets (30 mg) in a 1 mM aqueous solution of coumarin (without the addition of K_2HPO_4). (b) The evolution of fluorescence intensity (460 nm) against the irradiation time over g- C_3N_4 nanosheets measured with and without the addition of K_2HPO_4 .

4.4 Conclusions

In summary, we have demonstrated that a natural photosystem inspired phosphate environmental (precisely, HPO_4^{2-} ions) modulation can lead to a significant enhancement in photocatalytic H_2 production over CN-NS under visible light. For instance, with the optimal addition of HPO_4^{2-} , a H_2 evolution rate as high as $947 \mu\text{mol h}^{-1}$ was achieved, reaching apparent quantum yield of approximately 26.1% at 420 ± 14.5 nm, which is the highest value among reported carbon nitride photocatalysts. Such improvement relies on

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the synergy of enhanced proton reduction and improved TEOA photooxidation, evidenced by (photo)electrocatalytic analysis and theoretical calculation. As a mimic to natural photosynthesis, this strategy of environmental “phosphorylation” is potentially applied to other semiconductor systems (Figure 4.7) and thus provide a facile approach to efficient photocatalysis, such as H₂ production, CO₂ photoreduction, and photoelectric conversion.

References

1. P. Niu, L. Zhang, G. Liu and H.-M. Cheng, *Adv. Funct. Mater.*, 2012, **22**, 4763-4770.
2. S. Yang, Y. Gong, J. Zhang, L. Zhan, L. Ma, Z. Fang, R. Vajtai, X. Wang and P. M. Ajayan, *Adv. Mater.*, 2013, **25**, 2452-2456.
3. J. Zhang, M. Zhang, C. Yang and X. Wang, *Adv. Mater.*, 2014, **26**, 4121-4126.
4. M. K. Bhunia, K. Yamauchi and K. Takanabe, *Angew. Chem. Int. Ed.*, 2014, **53**, 11001-11005.
5. Y.-S. Jun, J. Park, S. U. Lee, A. Thomas, W. H. Hong and G. D. Stucky, *Angew. Chem. Int. Ed.*, 2013, **52**, 11083-11087.
6. D. J. Martin, K. Qiu, S. A. Shevlin, A. D. Handoko, X. Chen, Z. Guo and J. Tang, *Angew. Chem. Int. Ed.*, 2014, **53**, 9240-9245.
7. Y. Zheng, L. Lin, X. Ye, F. Guo and X. Wang, *Angew. Chem. Int. Ed.*, 2014, **53**, 11926-11930.
8. K. Schwinghammer, M. B. Mesch, V. Duppel, C. Ziegler, J. Senker and B. V. Lotsch, *J. Am. Chem. Soc.*, 2014, **136**, 1730-1733.

Chapter 4

9. Y. Zhang, A. Thomas, M. Antonietti and X. Wang, *J. Am. Chem. Soc.*, 2009, **131**, 50-51.
10. M. Zhang and X. Wang, *Energy Environ. Sci.*, 2014, **7**, 1902-1906.
11. Y. Zhang, T. Mori, J. Ye and M. Antonietti, *J. Am. Chem. Soc.*, 2010, **132**, 6294-6295.
12. X. Chen, J. Zhang, X. Fu, M. Antonietti and X. Wang, *J. Am. Chem. Soc.*, 2009, **131**, 11658-11659.
13. S. Cao, J. Low, J. Yu and M. Jaroniec, *Adv. Mater.*, 2015, **27**, 2150-2176.
14. T. Sano, S. Tsutsui, K. Koike, T. Hirakawa, Y. Teramoto, N. Negishi and K. Takeuchi, *J. Mater. Chem. A*, 2013, **1**, 6489-6496.
15. X. Zhang, X. Xie, H. Wang, J. Zhang, B. Pan and Y. Xie, *J. Am. Chem. Soc.*, 2013, **135**, 18-21.
16. N. A. Campbell, J. B. Reece, L. A. Urry, M. L. Cain, S. A. Wasserman, P. V. Minorsky and R. B. Jackson, *Biology 8th Edition*, Pearson Benjamin Cummings, 2008.
17. N. Sato, *J Plant Res*, 2004, **117**, 495-505.
18. P. Mitchell and J. Moyle, *Nature*, 1967, **213**, 137-139.
19. F. H. Westheimer, *Science*, 1987, **235**, 1173-1178.
20. J. Heberle, J. Riesle, G. Thiedemann, D. Oesterhelt and N. A. Dencher, *Nature*, 1994, **370**, 379-382.
21. X. Lu, K. Xu, P. Chen, K. Jia, S. Liu and C. Wu, *J. Mater. Chem. A*, 2014, **2**, 18924-18928.

Chapter 4

22. X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti, *Nat Mater*, 2009, **8**, 76-80.
23. H. Xu, J. Yan, X. She, L. Xu, J. Xia, Y. Xu, Y. Song, L. Huang and H. Li, *Nanoscale*, 2014, **6**, 1406-1415.
24. A. Kudo and Y. Miseki, *Chem Soc Rev*, 2009, **38**, 253-278.
25. P. Wu, J. Wang, J. Zhao, L. Guo and F. E. Osterloh, *Chem. Commun.*, 2014, **50**, 15521-15524.
26. S. Ouyang, H. Tong, N. Umezawa, J. Cao, P. Li, Y. Bi, Y. Zhang and J. Ye, *J. Am. Chem. Soc.*, 2012, **134**, 1974-1977.
27. T. Simon, N. Bouchonville, M. J. Berr, A. Vaneski, A. Adrović, D. Volbers, R. Wyrwich, M. Döblinger, A. S. Susha, A. L. Rogach, F. Jäckel, J. K. Stolarczyk and J. Feldmann, *Nat Mater*, 2014, **13**, 1013-1018.
28. Y. Kwon, S. C. S. Lai, P. Rodriguez and M. T. M. Koper, *J. Am. Chem. Soc.*, 2011, **133**, 6914-6917.
29. F. Wang, Y. Jiang, A. Gautam, Y. Li and R. Amal, *ACS Catal.*, 2014, **4**, 1451-1457.
30. J. Yang, D. Wang, H. Han and C. Li, *Acc. Chem. Res.*, 2013, **46**, 1900-1909.
31. J. Luo, J.-H. Im, M. T. Mayer, M. Schreier, M. K. Nazeeruddin, N.-G. Park, S. D. Tilley, H. J. Fan and M. Grätzel, *Science*, 2014, **345**, 1593-1596.
32. L. Vilčiauskas, M. E. Tuckerman, G. Bester, S. J. Paddison and K.-D. Kreuer, *Nat Chem*, 2012, **4**, 461-466.
33. L. Zheng, Y. Chi, Y. Dong, L. Zhang and G. Chen, *J. Phys. Chem. C*, 2008, **112**, 15570-15575.

Chapter 4

34. S. Karastogianni and S. Girousi, *Sensing in Electroanalysis*, 2014, **8**, 241-252.
35. J. Kim, D. Monllor-Satoca and W. Choi, *Energy Environ. Sci.*, 2012, **5**, 7647-7656.
36. K.-i. Ishibashi, A. Fujishima, T. Watanabe and K. Hashimoto, *Electrochem. Commun.*, 2000, **2**, 207-210.

Chapter 5 Conclusions and prospective

5.1 General conclusions

Photocatalytic H_2 evolution is promising technologies for solar energy conversion and storage. Recently, graphitic carbon nitride ($g-C_3N_4$) has emerged as an attractive photocatalyst for photocatalytic H_2 production due to its unique properties, such as suitable energy band structure for water reduction, high chemical and thermal stability, and cost effective metal-free composition. However, $g-C_3N_4$ still suffers from moderate photocatalytic activities because of the insufficient light absorption, the fast electron-hole recombination and also the kinetic limitation in proton reduction. In this thesis, the main objective is to investigate the effect from structure and reaction environment modulations of $g-C_3N_4$ on photocatalysis and to improve the light absorption, carrier separation and transfer as well as to facilitate the proton reduction kinetic towards high photocatalytic H_2 production activity. The detailed results could be concluded in the following parts:

1. Defect modification of $g-C_3N_4$ to construct p-n homojunction for improved photocatalytic H_2 evolution

In this part, defect-modified $g-C_3N_4$ (DCN) with extend visible-light absorption has been prepared by heating with $NaBH_4$. The introduction of cyano terminal $C\equiv N$ groups, acting as electron acceptors, into the $g-C_3N_4$ sheet edge endowed the DCN exhibiting both n- and p-type conductivities, consequently giving rise to the generation of p-n

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homojunctions, which were demonstrated to highly efficient in the transfer and separation of photoexcited carriers. Under the optimal conditions, DCN present a more than 5-fold enhanced photocatalytic H₂ evolution activity than the pristine samples. The findings deepen the understanding on the defect-related issues of g-C₃N₄-based materials. And the ability to build homojunction structures by the defect-induced self-functionalization presents a promising strategy to realize precise band engineering of g-C₃N₄ and related polymer semiconductors for more efficient solar energy conversion applications.

2. In-plane highly ordered graphitic carbon nitride towards improved photocatalytic H₂ production

In this part, using self-assembled heptazine hydrate as the precursor, g-C₃N₄ with improved in-plane ordering was prepared via a spatially confined poly-condensation process. The improved in-plane ordering rendered the as-prepared g-C₃N₄ much increased electron delocalization within the π -conjugated aromatic rings and also accelerated the separation and transfer of photogenerated carrier. As expected, such material possessed a high hydrogen evolution rate of 420 $\mu\text{mol/h}$ with a remarkable apparent quantum efficiency of 8.9% at 420 nm, which was about 14 times higher than that of reference g-C₃N₄ (prepared without modulation of molecular ranging regularity). These findings emphasized the significance of the molecular ranging regularity of g-C₃N₄ for the efficient carrier separation and transfer and subsequent photocatalysis, and also suggested that the modulation of molecular ranging in g-C₃N₄-related organic semiconductors might open new avenues towards improved photocatalysis.

3. The influence of environmental “phosphorylation” on photocatalytic H₂ evolution over g-C₃N₄ nanosheets

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In this part, we demonstrated that the environmental “phosphorylation” (precisely, HPO_4^{2-} ions) modulation could lead to a significant enhancement in photocatalytic H_2 production over g- C_3N_4 nanosheets under visible light irradiation. With the optimal addition of HPO_4^{2-} , a H_2 evolution rate as high as $947 \mu\text{mol h}^{-1}$ was achieved for g- C_3N_4 nanosheets which was about 16 times higher over that of bulk g- C_3N_4 . Furthermore, this strategy was potentially applied to other semiconductor systems, such as TiO_2 and CdS . It was confirmed that such improvement in activity relied on the synergy of enhanced proton reduction and improved hole oxidation. More importantly, the phosphates were confirmed to indeed function like roles in natural photosynthesis: 1) as proton pumps to facilitate the proton transfer in reaction solutions; 2) as mediators directly participating in the proton reduction, achieving a Calvin-cycle-like H_2 evolution pathway. As a mimic to natural photosynthesis, this strategy of environmental “phosphorylation” provide a facile approach to efficient photocatalysis, such as H_2 production, CO_2 photoreduction, and photoelectric conversion.

5.2 Prospective

In this work, based on structure modulation and reaction environment modification of photocatalysts, we demonstrated several strategies to improve the photocatalysis efficiency for H_2 production over g- C_3N_4 . Although some progresses have been achieved, the activities are still far away from the industrial requirements. Therefore, more efforts should be devoted to advance this field.

Aiming to further improve the activity of g- C_3N_4 for photocatalytic H_2 evolution, other strategies, such as molecule incorporation, element doping, nanostructure design, and heterostructure construction, should be explored in the future study. For example, Wang

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et al reported that nanospherical g-C₃N₄ frameworks with sharp edges afforded fast charge collection and separation on the surface due to the “lightning rod effect” and therefore exhibited much enhanced activity for H₂ evolution.¹ Also, by hybridizing g-C₃N₄ with other appropriate semiconductor materials, the resulted heterostructural photocatalysts not only might exhibit enhanced light absorption but also could achieve improved charge separation and transfer because of the band matching, consequently increasing the photocatalysis efficiency.² Additionally, as inspired by the results in this work, the combination of structure engineering and reaction environment modulation on one photocatalyst might lead to the synergic impact on the photocatalysis, which will be also explored in our following study. Furthermore, as a promising photocatalyst for photocatalytic H₂ evolution, the integration of g-C₃N₄ with an oxygen-evolution-active photocatalyst (like WO₃, and BiVO₄³) to construct Z-scheme water splitting systems is also pursued.

g-C₃N₄ has been demonstrated to possess very negative conduction band level (-1.3 vs. NHE, pH = 7).^{4, 5} This feature makes g-C₃N₄ a good candidate for other photoreduction reactions with high redox potentials, like photoreduction CO₂. In this regard, more potential applications of g-C₃N₄ should be explored in the future.

On the other hand, due to the sluggish kinetic, oxygen evolution reaction (OER) is the critical step not only in photocatalytic water splitting for H₂ evolution, and also in photoreduction of CO₂ for CO or hydrocarbon production. Therefore, beyond the scope of this dissertation, exploring efficient OER photocatalysts through structure engineering or reaction environment modulation is also on the time table, though g-C₃N₄ is also capable of photocatalytic O₂ evolution. Recently, Ag₃PO₄ has emerged as an attractive

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photocatalyst for O₂ evolution with rather high reaction rate under visible light irradiation.⁶ However, stability remains as a major problem for Ag₃PO₄ due to the self-photoreduction and chemical-corrosion. It might be possible to surface coating of Ag₃PO₄ with a stable semiconductor protection layer (like TiO₂) to prevent chemical-corrosion and meanwhile as electron acceptor *via* band matching to suppress self-photoreduction. Another strategy would be to remove electrons on Ag₃PO₄ using an electrical bias, for an example using a PEC-solar cell device, which can spatially separate electrons from holes, resulting in a stable Ag₃PO₄ photoanode.

References

1. J. Zhang, M. Zhang, C. Yang and X. Wang, *Adv. Mater.*, 2014, **26**, 4121-4126.
2. Y. Hou, F. Zuo, A. P. Dagg, J. Liu and P. Feng, *Adv. Mater.*, 2014, **26**, 5043–5049.
3. D. J. Martin, P. J. T. Reardon, S. J. A. Moniz and J. Tang, *J. Am. Chem. Soc.*, 2014, **136**, 12568-12571.
4. X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti, *Nat Mater*, 2009, **8**, 76-80.
5. Y. Cui, Z. Ding, P. Liu, M. Antonietti, X. Fu and X. Wang, *Phys. Chem. Chem. Phys.*, 2012, **14**, 1455-1462.
6. Z. Yi, J. Ye, N. Kikugawa, T. Kako, S. Ouyang, H. Stuart-Williams, H. Yang, J. Cao, W. Luo, Z. Li, Y. Liu and R. L. Withers, *Nat Mater*, 2010, **9**, 559-564.

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Publications & conferences

Publications

1. Guigao Liu, Peng Li, Guixia Zhao, Xin Wang, Jintao Kong, Huimin Liu, Huabin Zhang, Kun Chang, Xianguang Meng, Tetsuya Kako, and Jinhua Ye, Promoting Active Species Generation by Plasmon-Induced Hot-Electron Excitation for Efficient Electrocatalytic Oxygen Evolution. *J. Am. Chem. Soc.* **2016**, *138* (29), 9128–9136.
2. Guigao Liu, Tao Wang, Huabin Zhang, Xianguang Meng, Dong Hao, Kun Chang, Peng Li, Tetsuya Kako, and Jinhua Ye, Nature-Inspired Environmental “Phosphorylation” Boosts Photocatalytic H₂ Production over Carbon Nitride Nanosheets under Visible-Light Irradiation. *Angew. Chem. Int. Ed.* **2015**, *54* (46), 13561-13565.
3. Guigao Liu, Guixia Zhao, Wei Zhou, Yanyu Liu, Hong Pang, Huabin Zhang, Dong Hao, Xianguang Meng, Peng Li, Tetsuya Kako, and Jinhua Ye, In Situ Bond Modulation of Graphitic Carbon Nitride to Construct p-n Homojunctions for Enhanced Photocatalytic Hydrogen Production. *Adv. Funct. Mater.* **2016**, *26* (37), 6822-6829.
4. Guixia Zhao, Guigao Liu, Hong Pang, Huimin Liu, Huabin Zhang, Kun Chang, Xianguang Meng, Xiaojun Wang and Jinhua Ye, Improved Photocatalytic H₂ Evolution over g-Carbon Nitride with Enhanced In-Plane Ordering. *Small*. **2016**, DOI: 10.1002/sml.201602136.

Publications & conferences

5. David James Martin†, Guigao Liu†, Savio J. A. Moniz, Yingpu Bi, Andrew M. Beale, Jinhua Ye, and Junwang Tang, Efficient Visible Driven Photocatalyst, Silver Phosphate: Performance, Understanding and Perspective. *Chem. Soc. Rev.* **2015**, 44 (21), 7808-7828.

(† Co-first authors with equal contribution)

6. Guigao Liu, Tao Wang, Shuxin Ouyang, Lequan Liu, Haiying Jiang, Qing Yu, Tetsuya Kako, and Jinhua Ye, Band-Structure-Controlled $\text{BiO}(\text{ClBr})_{(1-x)/2}\text{I}_x$ Solid Solutions for Visible-Light Photocatalysis. *J. Mater. Chem. A* **2015**, 3 (15), 8123-8132.

7. Guigao Liu, Tao Wang, Wei Zhou, Xianguang Meng, Huabin Zhang, Huimin Liu, Tetsuya Kako, and Jinhua Ye, Crystal-Facet-Dependent Hot-Electron Transfer in Plasmonic-Au/Semiconductor Heterostructures for Efficient Solar Photocatalysis. *J. Mater. Chem. C* **2015**, 3 (29), 7538-7542.

Other publications

1. Huabin Zhang, Guigao Liu, Li Shi, Huimin Liu, Tao Wang, and Jinhua Ye, Engineering Coordination Polymers for Photocatalysis. *Nano Energy* **2016**, 22, 149-168.

2. Hai-Ying Jiang, Guigao Liu, Mu Li, Jingjing Liu, Wenbin Sun, Jinhua Ye, and Jun Lin, Efficient Organic Degradation under Visible Light by $\alpha\text{-Bi}_2\text{O}_3$ with a CuO_x -assistant Electron Transfer Process. *Appl. Catal., B* **2015**, 163 (0), 267-276.

3. Hai-Ying Jiang, Guigao Liu, Peng Li, Dong Hao, Xianguang Meng, Tao Wang, Jun Lin, and Jinhua Ye, Nanorod-like $\alpha\text{-Bi}_2\text{O}_3$: a Highly Active Photocatalyst Synthesized Using $\text{g-C}_3\text{N}_4$ as a Template. *RSC Adv.* **2014**, 4 (98), 55062-55066.

Publications & conferences

4. Hai-Ying Jiang, Guigao Liu, Tao Wang, Peng Li, Jun Lin, and Jinhua Ye, In Situ Construction of α -Bi₂O₃/g-C₃N₄/β-Bi₂O₃ Composites and Their Highly Efficient Photocatalytic Performances. *RSC Adv.* **2015**, 5 (113), 92963-92969.
5. Huabin Zhang, Zuju Ma, Guigao Liu, Li Shi, Jing Tang, Hong Pang, Kechen Wu, Toshiaki Takei, Jian Zhang, Yusuke Yamauchi, and Jinhua Ye, Highly Active Nonprecious Metal Hydrogen Evolution Electrocatalyst: Ultrafine Molybdenum Carbide Nanoparticles Embedded into a 3D Nitrogen-Implanted Carbon Matrix. *NPG Asia Materials* **2016**, 8, e293.
6. Guixia Zhao, Hong Pang, Guigao Liu, Peng Li, Huimin Liu, Huabin Zhang, Li Shi, and Jinhua Ye, Co-Porphyrin/Carbon Nitride Hybrids for Improved Photocatalytic CO₂ Reduction under Visible Light. *Appl. Catal., B* **2017**, 200, 141–149.
7. Hai-Ying Jiang, Peng Li, Guigao Liu, Jinhua Ye, and Jun Lin, Synthesis and Photocatalytic Properties of Metastable β-Bi₂O₃ Stabilized by Surface-Coordination Effects. *J. Mater. Chem. A* **2015**, 3 (9), 5119-5125.
8. Tao Wang, Xianguang Meng, Guigao Liu, Kun Chang, Peng Li, Qing Kang, Lequan Liu, Mu Li, Shuxin Ouyang, and Jinhua Ye, In Situ Synthesis of Ordered Mesoporous Co-Doped TiO₂ and Its Enhanced Photocatalytic Activity and Selectivity for the Reduction of CO₂. *J. Mater. Chem. A* **2015**, 3 (18), 9491-9501.
9. Qing Yu, Xianguang Meng, Li Shi, Guigao Liu, Peng Li, and Jinhua Ye, Hematite Homojunctions Without Foreign Element Doping for Efficient and Stable Overall Water Splitting. *RSC Adv.* **2016**, 6 (67), 62263-62269.

Publications & conferences

10. Huimin Liu, Tao Wang, Huabin Zhang, Guigao Liu, Peng Li, Lequan Liu, Dong Hao, Jian Ren, Kun Chang, Xianguang Meng, Hongmei Wang, and Jinhua Ye, Room-Temperature Driven and Visible Light Enhanced Dehydrogenation Reactions Catalyzed by Basic Au/SrTiO₃. *J. Mater. Chem. A* **2016**, 4 (5), 1941-1946.
11. Huabin Zhang, Zuju Ma, Jingjing Duan, Huimin Liu, Guigao Liu, Tao Wang, Kun Chang, Mu Li, Li Shi, Xianguang Meng, Kechen Wu, and Jinhua Ye, Active Sites Implanted Carbon Cages in Core–Shell Architecture: Highly Active and Durable Electrocatalyst for Hydrogen Evolution Reaction. *ACS Nano* **2015**, 10 (1), 684–694.
12. Xianguang Meng, Qing Yu, Tao Wang, Guigao Liu, Kun Chang, Peng Li, Lequan Liu, and Jinhua Ye, Exceptional Enhancement of H₂ Production in Alkaline Environment over Plasmonic Au/TiO₂ Photocatalyst under Visible Light. *APL Materials* **2015**, 3 (10), 104401.
13. Tao Wang, Li Shi, Jing Tang, Victor Malgras, Shunsuke Asahina, Guigao Liu, Huabin Zhang, Xianguang Meng, Kun Chang, Jianping He, Osamu Terasaki, Yusuke Yamauchi, and Jinhua Ye, Co₃O₄-Embedded Porous ZnO Rhombic Dodecahedron Prepared by the Use of Zeolitic Imidazolate Frameworks as Precursors for CO₂ Photoreduction. *Nanoscale* **2016**, 8 (12), 6712-6720.
14. Huabin Zhang, Tao Wang, Junjie Wang, Huimin Liu, Thang Duy Dao, Mu Li, Guigao Liu, Xianguang Meng, Kun Chang, Li Shi, Tadaaki Nagao, and Jinhua Ye, Surface-Plasmon-Enhanced Photodriven CO₂ Reduction Catalyzed by Metal–Organic-Framework-Derived Iron Nanoparticles Encapsulated by Ultrathin Carbon Layers. *Adv. Mater.* **2016**, 28 (19), 3703–3710.

Publications & conferences

15. Tao Wang, Xianguang Meng, Peng Li, Shuxin Ouyang, Kun Chang, Guigao Liu, Zongwei Mei, and Jinhua Ye, Photoreduction of CO₂ over the Well-Crystallized Ordered Mesoporous TiO₂ with the Confined Space Effect. *Nano Energy* **2014**, 9 (0), 50-60.

16. Qing Yu, Xianguang Meng, Tao Wang, Peng Li, Lequan Liu, Kun Chang, Guigao Liu, and Jinhua Ye, A Highly Durable p-LaFeO₃/n-Fe₂O₃ Photocell for Effective Water Splitting under Visible Light. *Chem. Commun.* **2015**, 51 (17), 3630-3633.

Conferences

1. Guigao Liu, Tao Wang, Huabin Zhang, Xianguang Meng, Dong Hao, Kun Chang, Peng Li, Tetsuya Kako, and Jinhua Ye: “Nature-Inspired Environmental “Phosphorylation” for Efficient Photocatalytic H₂ Production over Carbon Nitride Nanosheets”日本化学会 第 96 春季年会, (2016 年 3 月, 同志社大学).

2. Guigao Liu, Tetsuya Kako, and Jinhua Ye: “Efficient Photocatalytic H₂ Production over Carbon Nitride Nanosheets under Visible-Light Irradiation via Environmental “Phosphorylation”Modulation” 第 22 回光触媒シンポジウム「光触媒反応の最近の展開」, (2015 年 12 月, 東京理科大学).

3. Guigao Liu, Tao Wang, Tetsuya Kako, and Jinhua Ye: “BiO(ClBr)_{(1-x)/2}I_x Solid solutions with Controllable Band Gap Engineering as Efficient Visible-light Photocatalysts for Isopropanol Degradation” 日本化学会第 95 春季年会, (2015 年 3 月, 日本大学).

4. Guigao Liu, Tao Wang, Tetsuya Kako, and Jinhua Ye: “BiO(ClBr)_{(1-x)/2}I_x Solid solutions with Controllable Band Gap Engineering as Efficient Visible-light

Publications & conferences

Photocatalysts for Isopropanol Degradation” 国際材料研究学会連合ーアジア国際会議 2014 (IUMRS-ICA2014), (2014 年 8 月, 福岡大学).

5. Guigao Liu, Tao Wang, Tetsuya Kako, and Jinhua Ye. “BiO(ClBr)_{(1-x)/2}I_x Solid solutions with Controllable Band Gap Engineering as Efficient Visible-light Photocatalysts for IPA Degradation”. 第 20 回光触媒シンポジウム「光触媒反応の最近の展開」, (2013 年 12 月, 東京大学).