Deposition of economic cocatalysts on graphitic carbon nitride for efficient photocatalytic hydrogen generation

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NANYANG
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**DEPOSITION OF ECONOMIC COCATALYSTS ON
GRAPHITIC CARBON NITRIDE FOR EFFICIENT
PHOTOCATALYTIC HYDROGEN GENERATION**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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fulfillment of the requirement for the degree of
Doctor of Philosophy

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ABSTRACT

Energy crisis and environmental issues are two most severe problems faced by all human beings on this planet. In order to solve the two problems, researchers are seeking for alternative energies other than fossil fuels. The alternative energies should be abundant, clean as well as sustainable. From this point of view, hydrogen is a good candidate. Hydrogen could be generated from a clean process, photocatalytic water splitting, in which semiconductor photocatalyst is a key factor. Polymeric graphitic carbon nitride (g-C₃N₄), which could respond to visible light with a proper band gap of 2.7 eV and suitable conduction band (CB) of -1.1 eV to reduce protons, is demonstrated to be able to achieve photocatalytic H₂ generation. However, pristine g-C₃N₄ exhibits a poor performance for photocatalytic H₂ generation due to the fast recombination of photoexcited electrons and holes. Whereas loading of noble metal cocatalysts such as Pt could enhance the performance. This project aims at suppressing the charge carrier recombination and thus enhancing the photocatalytic activity of g-C₃N₄ by depositing earth abundant and low-cost cocatalysts, e.g. bimetallic alloy, PtCo, and noble metal free NiS₂.

Firstly, the noble metal Pt cocatalyst was partially replaced with Co and a series of PtCo alloys with different compositions were loaded on to the surface of g-C₃N₄ *via* the solvothermal method. Different amounts of Pt and Co precursors were added to adjust the compositions and the H₂ evolution results indicated the highest activity was obtained at an atomic ratio of 2.5 to 1 (Pt to Co). This Pt_{2.5}Co/ g-C₃N₄ with 1wt% cocatalyst loading exhibited an even higher activity than that of Pt (1 wt%) loaded g-C₃N₄ prepared under same conditions. The constant H₂ evolution

rate of 1wt% Pt_{2.5}Co/ g-C₃N₄ under continuous 25-hour illumination under visible light suggested this alloy is highly stable on g-C₃N₄. The photoluminescence spectra and photoelectrochemical properties measurements imply that PtCo alloy could efficiently inhibit the recombination of photogenerated electrons and holes and therefore enhance the photocatalytic H₂ production activity of g-C₃N₄.

Secondly, the noble metal Pt cocatalyst was fully replaced with earth abundant and noble metal free cocatalyst, NiS₂. NiS₂/g-C₃N₄ composite with different weight percentages were synthesized *via* the hydrothermal method using thiourea and nickel acetate tetrahydrate as precursors. The presence of NiS₂ was confirmed by X-ray diffraction pattern (XRD), transmission electron microscope (TEM) and X-ray photoelectron spectra (XPS). The H₂ evolution test indicates that NiS₂ loading could increase activity of g-C₃N₄ dramatically and 2 wt% loading of NiS₂ on g-C₃N₄ shows the best performance, even better than 1 wt% Pt/g-C₃N₄ from photodeposition. Photoluminescence (PL) spectra of the samples suggest that the enhancement is associated with the more effective charge carrier separation as well.

In summary, this thesis is devoted to developing earth abundant, low-cost, stable and more importantly, effective g-C₃N₄ based composites for photocatalytic H₂ evolution. Studies on PtCo/g-C₃N₄ and NiS₂/g-C₃N₄ reveal PtCo alloy and NiS₂ as cocatalysts are effective in suppressing the charge carrier recombination to enhance the photocatalytic activities as well as reducing the cost on photocatalyst systems. Therefore, this thesis demonstrates PtCo alloy and NiS₂ are excellent and promising cocatalyst candidates.

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Chapter 1 Introduction

1.1 Background

For centuries, fossil fuels, such as coal, petroleum, and natural gas are the main energy source to power the rapidly growing population and economic all over the world. However, the increasing consumption of fossil fuels brings two significant issues, energy crisis and environment concerns. Energy crisis comes from the contradiction between limited fossil fuel reserves and rising global energy demands. The global energy demands are estimated to be 27 TW per year by 2050 and possible 43 TW by 2100 from 13.5 TW in 2001.¹ The fast consuming speed implies the fossil fuel reserves can only support human beings for as long as several centuries assuming the rate keeps at 25 TW-30 TW per year.² On the other hand, severe environment concerns such as acid rain, air and earth pollution and global warming owing to the increasing atmospheric CO₂ from combustion of these carbon-based fossil fuels are threatening health of human beings and balance of ecosystems. Therefore, it is urgent to discover or develop an alternative energy supply, which is abundant, clean, and sustainable. In this case, hydrogen is a promising candidate and an ideal energy carrier in the future since water is the only product after hydrogen combustion. Furthermore, hydrogen possesses an even higher gravimetric energy density (140 MJ Kg⁻¹ at 700 atm) than other known fuels (e.g. ~50 MJ Kg⁻¹ for liquid fuels).³ Consequently, the studies on hydrogen generation and storage have attracted tremendous attention. Since then, many methods have been applied to hydrogen generation such as steam reforming of

hydrocarbon materials,⁴⁻⁹ electrolysis of water,¹⁰⁻¹² gasification of biomass^{13,14} and solar water splitting¹⁵⁻¹⁷ (Figure 1-1). The former techniques all rely on fossil fuels directly or indirectly, suggesting that they cannot completely solve the energy and environment issues. To this end, solar water splitting stands out as it can generate hydrogen in a renewable and continuous way.¹⁸

Solar water splitting (as shown in Figure 1-2), which mimics the photosynthesis of plants in the nature, could be conducted in the presence of sunlight, semiconductor photocatalysts with or without cocatalyst and water.^{19,20} In this process, sunlight provides the energy source and semiconductor photocatalysts act as the light absorber and energy converter. After all, solar energy are converted and stored in the form of chemical bonds in hydrogen.

Figure 1-1 Conventional strategies to generate hydrogen and its applications.²¹

Suppose that the conversion efficiency from solar energy to chemical bonds could reach 5%, then the energy received from the sun (only 600 TW of solar energy are

estimated to be available for conversion) would be as high as 30 TW, which is far more than enough for the current energy demands.²²

Figure 1-2 Circulation of hydrogen generation and hydrogen utilization in which the consumption product water would be further involved in photocatalytic water splitting for hydrogen generation.¹⁹

1.2 Solar water splitting

Solar water splitting, also called artificial photosynthesis, can be achieved via two approaches, photoelectrochemical water splitting (PEC water splitting) and powdered photocatalytic water splitting (the so-called photocatalytic water splitting), as shown in Figure 1-3 (a) and (b), respectively.²³ PEC water splitting was first introduced by Fujishima and Honda using TiO₂ electrode in 1972.²⁴ Since then, PEC water splitting using semiconductor electrodes has been extensively studied (Figure 1-3 (a)). Different from PEC water splitting, photocatalytic water splitting takes place in a powdered photocatalyst system (Figure 1-3 (b)). When

sunlight irradiates at water pool containing photocatalysts with or without cocatalysts, photocatalysts are excited. In this way, the solar energy is converted to chemical energy by electronic processes and surface/interface reactions. The chemical energy is further utilized to split water and generate H_2 and O_2 . Generally, both PEC water splitting and photocatalytic water splitting have advantages and disadvantages and attract enormous attentions in this field. However, PEC water splitting requires applied bias to initiate the reactions, and high-cost Pt electrode in the three-electrode setup. Moreover, the area of the exposed electrodes is limited. All these factors restrict the application of PEC water splitting for large scale production of H_2 in the future. Compared with PEC water splitting, photocatalytic water splitting is totally bias free and electrode free. The simple setup makes it available to large-scale production of hydrogen. At the same time, it is sustainable and a good strategy to solve energy and environmental issues. These properties will lead photocatalytic water splitting to an energy revolution.

Figure 1-3 Schematic illustration of photoelectrochemical water splitting in which oxygen is produced at n-type semiconductor photoanode (a)²⁵ and powdered photocatalytic water splitting (b).²³

1.3 Processes of photocatalytic water splitting

The energy difference between the top of valence band (VB) of a semiconductor and the bottom of conduction band (CB) is referred as its band gap. When the incident photons possess larger energy than the band gap, the semiconductor photocatalysts are induced to generate electrons and holes in the conduction and valence band, respectively. This is the first step of photocatalytic water splitting. However, a large proportion of the photoexcited electrons and holes recombine together immediately while the left migrate to the surface. Finally, the holes on the surface oxidize water to produce oxygen and the electrons reduce water to generate hydrogen (Figure 1-4).²⁶ To achieve the two half reactions, the conduction band (CB) position and valence band (VB) position should be appropriate. The location of CB should be more negative than that of H^+/H_2 (0 V vs NHE) to reduce water, while the location of VB has to be more positive than that of O_2/H_2O (1.23 V vs NHE) to oxidize water, indicating that the minimum band gap for water splitting is 1.23 eV theoretically (as shown in Figure 1-5).²⁷ As visible light accounts for 46 % of the solar light, it is advantageous if the semiconductor photocatalysts could absorb light in the range of 400 nm-700 nm, corresponding to band gap of 3.10 eV-1.77 eV (calculated from equation 1). Therefore, an ideal photocatalysts should occupy a band gap between 3.10 eV-1.77 eV to absorb visible light and a CB lower than 0 eV for water reduction and a VB band higher than 1.23 eV for water oxidation.

$$\text{Band gap energy (eV)} = 1240/\lambda \text{ (nm)} \quad (\text{eqn 1})$$

Figure 1-4 Main processes involved in photocatalytic water splitting, in which the photocatalyst is loaded with H₂ and O₂ evolution cocatalysts.²⁶

Figure 1-5 Schematic illustration of photocatalytic water splitting using semiconductor photocatalysts.²⁷

1.4 Efficiency evaluation

Usually, the rate of photocatalytic H₂ or O₂ evolution is presented in the form of mole amount like 1 μmol·h⁻¹. However, it is unreasonable to compare the activities

of photocatalysts on the basis of mole amount as the activities are highly dependent on the real experimental conditions like light source, distance from the light source to the reactor, type of reactors, sacrificial reagents and so on. Therefore, quantum efficiency is calculated for comparisons. Quantum efficiency is defined as the percentage of the incident photons that are absorbed. In a dispersed system, a large amount of the incident photons are scattered and it is difficult to determine this part. Therefore apparent quantum efficiency (AQE) instead of quantum yield is defined for evaluation. The apparent quantum yield is defined as follows: ²⁸

$$\begin{aligned} \text{AQE [\%]} &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \\ &= \frac{\text{number of evolved H}_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100 \quad \text{eqn 2} \end{aligned}$$

Considering the process of photocatalytic water splitting, the AQE is mainly affected by four factors. They are light absorption and photoexcitation, charge separation and migration, back reaction, and stability.

First of all, light absorption and photoexcitation. Photocatalytic water splitting starts from absorption of sunlight and excitation of semiconductor photocatalysts. Thus photocatalysts should be able to absorb as much sunlight as possible. Since visible light accounts for 46% of the whole sunlight, it is reasonable to conclude that visible light responsive photocatalysts are more favorable for photocatalytic water splitting. Figure 1-6 illustrates band structures of selected semiconductors relative to redox potential of two half reactions of water splitting at pH of 7.¹ It

indicates that some semiconductors for example, g-C₃N₄, TaON own suitable band structures to achieve overall water splitting, not only water reduction to produce H₂ but also water oxidation to generate O₂. Whereas semiconductors such as CuInS₂ and Cu₂O could only achieve water reduction due to the limitation of VB position and others for instance, WO₃ and Fe₂O₃ are only able to generate O₂.

Secondly, charge separation and migration. Even if the photocatalysts are able to be excited by sunlight to generate electron/hole pairs, the generated charge carriers may recombine immediately or during the migration process. Defects, crystal structure, crystallinity, particle size and surface area all play significant roles in recombination. Defects sometimes serve as the trapping and recombination centers, where electrons and holes neutralize in the process of migration. Considering this, a shorter distance from the excitation sites to the active sites is beneficial. Therefore, smaller particle size and more active sites on the surface are preferred. Particle size can be tuned by preparation conditions. For example, bulk g-C₃N₄ prepared via polycondensation method can be as large as tens of micrometers while g-C₃N₄ quantum dots synthesized by exfoliating and breaking bulk structure into quantum dots.^{29,30} Besides, the active sites may also be introduced and increased by loading cocatalysts such as Pt, NiO and MoS₂.

Figure 1-6 Band position of selected semiconductors and redox potential of two half reactions of water splitting (pH=7).¹

Thirdly, backward reaction. The evolved H_2 , O_2 and intermediates from water splitting easily react back to form water again due to the downhill reaction. Good photocatalysts and cocatalysts should be capable of inhibiting back reaction.

Finally, stability. Some metal oxides and most metal sulfides are unstable during photocatalytic water splitting. They are feasible to be oxidized by photoexcited holes compared with water. This phenomenon is called photocorrosion. CdS and ZnO are two examples that undergo photocorrosion as well as photocatalytic water splitting at the same time. As shown in eqn 3 and eqn 4, CdS and ZnO are slowly dissolved into solution under irradiation and lose their photocatalytic activities.²³ Therefore, the photocatalytic performances of CdS and ZnO continue dropping during photocatalytic water splitting under light illumination.

1.5 Objectives and scope

H₂ production from photocatalytic water splitting has been studied for decades. However, the large scale production in industry is still under way. The key factors here is to develop ideal photocatalyst which is abundant, clean, non-toxic, stable and particularly, efficient. Polymeric g-C₃N₄ could cover all the requirements except high efficiency. The low efficiency of g-C₃N₄ is ascribed to poor visible light absorption and fast recombination of photogenerated electrons and holes after irradiation and excitation. The objectives here concentrated on solving the fast recombination problem and thereby enhancing the photocatalytic performance of g-C₃N₄. Detailed objectives and scope are listed as follows:

- i) To suppress the recombination of photoexcited electrons and holes as well as control the total cost on g-C₃N₄ based photocatalyst system, a bimetallic alloy, PtCo, was loaded as a cocatalyst onto the surface of g-C₃N₄. PtCo nanoparticles were prepared via reduction of Pt and Co precursor by ethylene glycol under solvothermal conditions. With PtCo cocatalyst, the activity of g-C₃N₄ increased significantly. The atomic ratios of Pt to Co were adjusted to obtain an optimal performance. Results showed that 1 wt% Pt_{2.5}Co/g-C₃N₄ exhibited the highest activity compared with other ratios including pure 1 wt% Pt/g-C₃N₄ prepared from the same method.
- ii) To enhance the photocatalytic activity of g-C₃N₄ in a more economical way, noble metal free, transition metal sulfide, NiS₂ was synthesized as a cocatalyst via

hydrothermal method. The photocatalytic H_2 evolution test over different weight percentages of NiS_2 and 1wt% Pt indicated that, NiS_2 was an efficient cocatalyst in enhancing the photocatalytic activity of g- C_3N_4 , in which 2 wt% NiS_2 /g- C_3N_4 even revealed a higher activity than 1 wt% Pt/g- C_3N_4 from photodeposition. The enhancement in photocatalytic performance is proposed to be a consequence of efficient electrons and holes separation.

In summary, this thesis concentrate on enhancing the photocatalytic activity of g- C_3N_4 by suppressing the fast recombination and reducing the cost at the same time. To achieve the goals, earth abundant, low-cost and effective PtCo and NiS_2 cocatalysts were deposited on g- C_3N_4 . The works involve synthesis of composite nanomaterials, measurements of photocatalytic performances, and investigation of mechanisms.

1.6 Organization of the thesis

This thesis includes five chapters. Chapter 1 describes the urgency to produce clean and renewable H_2 energy from photocatalytic water splitting. Chapter 2 provides the literature reviews about photocatalyst materials for photocatalytic water splitting, mainly g- C_3N_4 , and the challenges faced by g- C_3N_4 as well as potential solutions. Chapter 3 presents an enhanced photocatalytic activity over g- C_3N_4 by loading bimetallic PtCo alloy as cocatalyst. Chapter 4 demonstrates noble metal free NiS_2 /g- C_3N_4 could exhibit good performance as well. Finally, Chapter 5 addresses a conclusion on the project and recommends several possible research areas in the future.

Chapter 2 Literature Review

2.1 Photocatalyst materials for water splitting

Considering the processes of photocatalytic water splitting described in Chapter 1.3, we can conclude that an excellent photocatalyst material should meet the following requirements: (i) appropriate band gap to absorb sunlight, especially visible light, to produce photoexcited electrons and holes; (ii) good charge separation and charge carrier transport ability; (iii) suitable CB and/or VB positions to reduce and/or oxidize water effectively. In addition, a good photocatalyst should also be stable in contact with water, non-toxic, abundant, and easy to obtain desired morphology.

However, for a majority of semiconductor photocatalysts, it is impossible to reduce water and oxidize water at the same time due to the limitation of CB or VB position. In this case, only half reaction, water reduction (H_2 evolution) or water oxidation (O_2 evolution), is available and a sacrificial reagent is required to consume the left photogenerated holes or electrons, respectively. Sacrificial reagents play important roles in the half reactions and different sacrificial reagents are applied to different materials. For examples, methanol is employed to most metal oxide photocatalysts like TiO_2 and $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ is present in metal sulfide photocatalysts and triethanolamine in $\text{g-C}_3\text{N}_4$ during H_2 evolution. On the other hand, when it comes to O_2 evolution, AgNO_3 is commonly applied as an electron scavenger.

Generally speaking, the materials used in photocatalytic water splitting can be classified into metal oxides, metal (oxy) sulfides, metal (oxy) nitrides, g-C₃N₄ and other materials.

2.1.1 Metal Oxides

Since the first report on PEC water splitting using TiO₂ electrode by Fujishima and Honda in 1972,²⁴ metal oxides have been extensively studied as photocatalysts. Metal oxides for instance, TiO₂ and ZnO, have lots of advantages. They are abundant, facile to be prepared, cheap, non-toxic. However, most metal oxides have wide band gaps that can only utilize UV light which accounts for 4% of the solar energy. To enhance their light absorption ability and visible light harvesting, doping,³¹⁻⁴⁴ sensitization,⁴⁵⁻⁴⁷ fabrication of heterojunctions,⁴⁸⁻⁵⁹ plasmonic coupling with metal nanoparticles⁶⁰⁻⁶² and so on are applied. In the system of Au/TiO₂, Tian *et al* observed not only the visible light absorption at around 550nm due to plasmon resonance of gold nanoparticles but also the charge transfer from gold to TiO₂.⁶³

Several other metal oxides such as WO₃⁶⁴ and BiVO₄⁶⁵⁻⁶⁸ have rather narrow band gaps of below 3 eV. But the less negative CB positions make them unable to reduce water to produce H₂.

2.1.2 Metal (oxy) sulfides

Metal (oxy)sulfides such as ZnS and CdS are another category of photocatalysts that are widely studied. Similar to TiO₂ and ZnO, ZnS has a wide band gap of 3.66

eV, limiting its application in visible light driven photocatalytic water splitting.⁶⁹ CdS has a proper band gap to absorb visible light up to 600 nm and proper CB to reduce water, suggesting it is a promising visible light responsive photocatalyst.⁷⁰ CdS alone could catalyze H₂ evolution at a rather low rate due to fast charge carrier recombination. In order to improve its photocatalytic activity, various noble metal and non-noble metal cocatalysts are employed to suppress the recombination, including Pt, Pd, Au, Rh, MoS₂, NiS, WS₂, graphene and so on.⁷⁰⁻⁷⁴ Yan *et al* reported the highest quantum efficiency so far at 420 nm over CdS co-loaded with 0.30 wt% Pt and 0.13 wt% PdS.²⁸ Zhang *et al* reported a noble metal free NiS/CdS photocatalyst could evolve 2.18 mmol h⁻¹ H₂ ($\lambda > 420$ nm) with an extreme high quantum yield of 51.3%, which is the highest quantum yield for noble metal free system under visible light.^{28,75} However, the high activity cannot be maintained under long-term irradiation due to severe photocorrosion of CdS as previously mentioned.^{76,77} To inhibit the deactivation after long-time irradiation, the mixture of Na₂S and Na₂SO₃ is applied as electron donor since the free and rich S²⁻ in the solution are more feasible to be oxidized by photogenerated holes.

2.1.3 Metal (oxy)nitrides

UV light driven photocatalyst metal (oxy)nitrides like GaN and visible light responsive metal (oxy)nitrides such as Ta₃N₅, TaON and LaTiO₂N were also reported for photocatalytic water splitting.⁷⁸⁻⁸⁰ Among them, GaN is the most interesting one. It is reported that the band gaps of GaN and ZnO are 3.4 eV and 3.2 eV, respectively. However, the band gap of GaN:ZnO solid solution is

estimated to be 2.58 eV, indicating its visible light response.⁸¹ After modification with cocatalyst RuO₂, Madea *et al* even observed stoichiometric H₂ and O₂ evolution over GaN:ZnO solid solution under visible light.

2.1.4 Other materials

Besides three categories mentioned above, some other materials are also found to be active in photocatalytic water splitting.

GaP is a narrow band gap semiconductor (2.25 eV). But it is not stable due to photocorrosion of GaP during H₂ evolution. Qiu *et al* improved the stability by building a p-n junction between n-type TiO₂ and p-type GaP and thus enhanced the photocatalytic performance.⁸²

α -S crystals are promising candidate for visible light driven photocatalytic water splitting as well although its experimental band gap is 2.79 eV, much larger than the calculated from density functional theory (DFT) (1.63 eV).⁸³

Red phosphor is another example of elemental photocatalysts. Red phosphor has a strong absorption in the visible range as long as 700 nm.^{84,85} Pure red phosphor could produce 22 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ H₂ under visible light illumination. When 30 wt% g-C₃N₄ was loaded onto red phosphor, the H₂ evolution rate was increased to 1000 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, almost 50 times enhancement.⁸⁶

Polymeric g-C₃N₄ is a metal free polymeric photocatalyst that discovered recently. g-C₃N₄ has appropriate band structure that enables it to respond to visible light as well as to reduce and oxidize water. Besides, g-C₃N₄ is non-toxic and stable at ambient temperature. These properties attracted tremendous attention towards g-

C₃N₄ and make it an ideal candidate for photocatalytic water splitting. More details about this material will be provided as follows.

2.2 g-C₃N₄ for photocatalytic H₂ evolution

2.2.1 Preparation of g-C₃N₄

The synthesis of polymeric carbon nitride, melon, by Liebig could be dated back to 1834.⁸⁷ Since then, several allotropes of carbon nitrides with various properties have been prepared. Among them, g-C₃N₄ is considered to be the most stable phase under ambient conditions. Polymeric g-C₃N₄ is reported to be thermal stable under high temperature up to 873 K in the air and chemical stable against acid, base and organic solvents.

Generally, g-C₃N₄ could be obtained from polycondensation method from nitrogen rich organic compounds. Other approaches, such as template method,^{88,89} hydrothermal approach, solvothermal approach are also applied to develop g-C₃N₄ material.

One example of polycondensation method using cyanamide as precursor is shown as in Figure 2-1.⁹⁰ The reaction starts from condensation of cyanamide into melamine, following with elimination of ammonia. As a result, melamine based compounds are the main products as investigated by Thermoanalytical methods (TGA, DSC) and XRD patterns. At this stage, the temperature is no higher than 350°C. When the temperature increases to around 390 °C, these melamine based compounds would further rearrange into tri-s-triazine. The tri-s-triazine units would condense into the final polymeric g-C₃N₄ at around 520 °C. Beyond this

temperature, the as-prepared g-C₃N₄ is still stable until it reaches 600 °C, at which the decomposition occurs. Besides cyanamide,⁹¹ many other compounds containing carbon and nitrogen are introduced as precursors, including dicyanamide,⁹² melamine,^{93,94} ammonium thiocyanate,^{95,96} trichloromelamine,⁹⁷ guanidinium chloride,⁹⁸ trithiocyanuric acid,⁹⁹ urea^{100,101}, thiourea¹⁰²⁻¹⁰⁴ and so on. Polycondensation of these precursors could obtain g-C₃N₄. One important thing here is the band gap of g-C₃N₄ is highly dependent on the degree of condensation because condensation process may have effect on the polymerization, defects and surface termination of g-C₃N₄. Besides this solid state reaction, Thomas *et al* also successfully synthesized g-C₃N₄ from liquid phase precursor like cyanamide(CN-NH₂) or dicyandiamine((CN-NH₂)₂) under normal pressure.^{91,92}

Figure 2-1 The synthetic path for g-C₃N₄ with precursor of cyanamide.⁹⁰

For template method, the template can be soft template as well as hard template. Both template methods can result in mesoporous g-C₃N₄. In a case of soft-template method, amphiphilic surfactant molecules are added and the reaction is taken place under hydrothermal conditions. This method is restricted by the limitation of the soft template choices. Shen *et al* prepared mesoporous g-C₃N₄ via this method using Titon X-100¹⁰⁵ as a template and melamine and glutaraldehyde as precursors. For hard-templating method, the templates are usually silica spheres, 2D hexagonal SBA-15 and 3D cubic KIT-6 mesoporous silicas.^{106,107} Antonietti *et al* synthesized disordered mesoporous g-C₃N₄ using silica nanospheres. The resulted products has a pore size of 12 nm and surface areas varied from 86 to 439 m² g⁻¹ with different precursor to silica weight ratios. The precursor they used is cyanamide.¹⁰⁸

Despite of varying precursors and synthesis methods, all the obtained g-C₃N₄ are estimated to be comprised of one of the two building blocks shown below (Figure 2-2).¹⁰⁹ The first type is consist of condensed s-triazine with a periodic array of single carbon vacancies, while the other one is condensed tri-s-triazine subunits linked by planar tertiary amino groups with larger periodic vacancies in the matix. The density functional theory (DFT) calculations confirm that the second structure is more stable.^{110,111} Therefore, researchers agree that the basic unit for g-C₃N₄ is tri-s-triazine nucleus instead of s-triazine. Here we assume g-C₃N₄ talked in this project possesses the second type as well. Like graphite, g-C₃N₄ has a stacked 2D structure and π -conjugated graphitic planes via hybridization of carbon and nitrogen atoms. Its stacking distance between two layers is 0.326 nm, slightly smaller than that of crystalline graphite (d=0.335 nm).

Figure 2-2 Schematic illustration of two types of building blocks of g-C₃N₄: s-triazine (top) and tri-s-triazine (bottom).¹⁰⁹

2.3.2 Challenges and solutions

Since the synthesis centuries ago, g-C₃N₄ has been applied to gas sensor design,^{112,113} oxidation of hydrocarbons,¹¹⁴⁻¹¹⁷ degradation of organic pollutants,¹¹⁸⁻¹²⁷ hydrogen storage,¹²⁸⁻¹³⁰ and particularly, photocatalytic water splitting. Photocatalytic water splitting over g-C₃N₄ was first reported in 2009 by Wang *et*

*al.*¹³¹ According to their work, the moderate band gap of g-C₃N₄ (2.7 eV) and appropriate band positions enable it to achieve both H₂ and O₂ evolution under visible light. In the presence of proper sacrificial reagents (electron donor or scavenger), g-C₃N₄ could generate H₂ or O₂ with or without cocatalysts. Calculation indicates that the reduction sites for H⁺ to H₂ are C atoms while the oxidation sites for H₂O to O₂ fall onto the N atoms.¹³¹

Although it is attractive for H₂ and O₂ evolution, pure g-C₃N₄ exhibits a low photocatalytic activity. The reasons for the low efficiency are listed as follows: First, its light absorption is restricted to 460 nm and below, no visible light longer than 460 nm could be absorbed, which means a large proportion of visible light is ineffective. Second, as shown above (Figure 2-2), g-C₃N₄ is composed of aromatic systems connected by tertiary amino group, resulting in a clear surface and lack of active sites for photocatalytic H₂ and O₂ evolution. Thirdly and most importantly, photoexcited electrons and holes are rapidly recombined before migrating to the active sites and involving in photocatalytic reactions,¹³² which is the key factor affecting its activity.

To solve the problems, strategies including texture modification, elemental doping, and copolymerization are employed to tune the intrinsic properties of g-C₃N₄ such as electronic structure, size, morphology, defects and so on. For example, metal or non-metal doping could adjust the band gap and introduce impurity levels between CB and VB and thus extend the visible light absorption range. And micro/nanostructure modification through exfoliation or precursors producing gas bubbles during polymerization could increase the surface area of g-

C₃N₄ and thus increase the active sites on the surface. Besides, the modification in micro/nanostructure may extend the light absorption as well. As a result, this treatment could also promote H₂ generation over g-C₃N₄. In addition, hybridization with another semiconductor photocatalyst with proper band position and especially, deposition of cocatalysts on the surface are also investigated and results indicate the two strategies are efficient in suppressing electron-hole recombination and thus enhance the performance. For cocatalysts deposition, it can introduce H₂ reduction sites or O₂ oxidation sites as well, which makes it highly efficient in facilitating photocatalytic reactions. Following are the details about the strategies to enhance the photocatalytic activity, mostly, photocatalytic H₂ evolution of g-C₃N₄.

Doping

Doping is an effective approach to tailor electronic structure and narrow band gap and consequently modify UV light active photocatalysts into visible light responsive counterparts. For example, after doping with metal ions such as Ni³⁺ and V⁵⁺ and non-metal ions like C, N, S, TiO₂ shows good visible light absorption ability and excellent photocatalytic performance under visible light.

Generally, metal ions doping could create impurity levels in the forbidden band, thus enabling the photocatalysts to respond to visible light (Figure 2-3). Therefore, it is also possible to adjust the band structure and enhance visible light absorption of g-C₃N₄, which in turn would promote photocatalytic H₂ evolution. So far, a few dopants have been incorporated to g-C₃N₄ to tune the electronic structure, texture, morphology and surface property. Polymeric g-C₃N₄ possesses ideal building

blocks for doping since its six lone-pair electrons of nitrogen are perfect sites for metal inclusion (as shown in Figure 2-4). For instance, Wang and co-workers modified g-C₃N₄ with iron by co-polycondensation of both g-C₃N₄ precursors and iron chloride.¹¹⁴ After the modification, its visible light absorption is extended from 450 nm to almost 650 nm and as a result, Fe/g-C₃N₄ exhibits a better performance in photodegradation of a series of organic dyes (rhodamine B (Rh B), methylene blue, methyl orange, and p-hydroxyazobenzene) in the presence of H₂O₂. Similar band gap narrowing and enhanced visible light harvesting ability are observed in zinc-doped and boron-doped g-C₃N₄.^{133,134} However, the metal precursors should be carefully selected as the dopant residues may act as the recombination center and spoil the electronic structure if they are incompatible with g-C₃N₄.

Figure 2-3 The introduced impurity levels (donor level: A; and acceptor level: B) after doping with metal ions.¹⁹

Figure 2-4 The unit in the circle is a preferred site for metal incorporation.¹³⁴

Similar to metal ions doping, doping of non-metal ions are able to adjust surface property and electronic structure of photocatalysts and to enhance the photocatalytic performance. However, the hypotheses on non-metal anions doping are more complicated. Besides the theory of formation of localized states in the band gap, the valence band edge is proposed to be shifted upwards in some cases. Up to now, various non-metal elements such as carbon, hydrogen, sulfur and phosphorus are *ex situ* or *in situ* introduced into g-C₃N₄. Dong *et al* prepared carbon self-doped g-C₃N₄ from absolute ethanol treated melamine as precursor.¹³⁵ The carbon self-doping could lead to substitution of bridging N atoms by C atoms and a narrowed band gap from 2.72 eV to 2.65 eV. The enhanced visible light absorption results in a 1.42 times higher H₂ evolution rate compared with pristine g-C₃N₄. Zhang and co-workers reported an obvious color change from yellow to brown after doping phosphorus onto g-C₃N₄, corresponding to the whole absorption of visible light.¹³⁶ They also found that the band gap energy continues

dropping with increasing phosphorus content. Besides carbon and phosphorus, the study on sulfur doping into bulk or mesoporous $g\text{-C}_3\text{N}_4$ is conducted by various groups and the results are slightly different. Zhang *et al* and Hong *et al* prepared and modified $g\text{-C}_3\text{N}_4$ from different precursors and synthesizing techniques, in which some of C atoms are substituted by sulfur atoms.^{99,103} The substitution gives rise to the downshift of CB and VB positions as illustrated in Figure 2-5. The less negative CB and more positive VB suggest a weaker water reduction ability and stronger water oxidation capacity. However, the narrower band gap and wider visible light absorption after sulfur doping still contribute to enhanced photocatalytic H_2 evolution, as revealed by experiments.

Figure 2-5 Band structures of $g\text{-C}_3\text{N}_4$, mesoporous $g\text{-C}_3\text{N}_4$ and S-doped mesoporous $g\text{-C}_3\text{N}_4$.¹⁰³

On the contrary, in the study of Liu and co-workers, the band gap is observed to be broadened. The authors proposed two mechanisms to explain the effect of sulfur doping on widening band gap of $g\text{-C}_3\text{N}_4$ (Figure 2-6).¹³⁷ If the anions (sulfur) are

only doped onto the surface, localized states can be introduced between the CB and VB and behave as the new “VB”. If the anions (sulfur) are homogeneously incorporated, the VB would be elevated and widened. In both cases, the band gap is narrowed after doping, same as other works on sulfur doping. In Liu’s work, they first fabricated g-C₃N₄ from thermal polycondensation of dicyandiamide and then treated the as-obtained g-C₃N₄ under H₂S gas to reach homogeneous S-doping. In

Figure 2-6 Schematic illustration of band structure modification after surface and homogeneous anion doping.¹³⁷

this case, VB position is elevated and band gap is narrowed according to the mechanism. However, it was observed the bulk g-C₃N₄ was broken into quantum dots after the treatment and the surface area increased remarkably, simultaneously with S-doping. The quantum size effect here works in the opposite direction and widens the band gap. The S-doping effect and quantum size effect compete and give a broader band gap and more negative CB position, as depicted in Figure 2-7. The synergistic consequence of superior photoreduction capability by upshift of CB and increased surface area results in an enhanced photocatalytic H₂ evolution by a factor of 8 under visible light.

Figure 2-7 Schematic of modified band structures of g-C₃N₄ by S doping effect and subsequent quantum size effect.¹³⁷

Different from the non-metal ions doping by C, P, and S, protonation has led to a wider band gap. The doped protons in g-C₃N₄ could localize electrons and thus adjust the electronic band structures to display a larger band gap.¹³⁸ Although the band gap was enlarged and the color lightened (from the original yellow to white), the protonated g-C₃N₄ indicated a 2-fold enhancement in H₂ evolution after treatment with HCl (37%).¹³⁹ The enhancement comes from higher solubility, larger surface area as well as better ionic conductivity.

Micro/nanostructure modification

Compared with bulk structures, micro/nanostructures usually exhibit higher photocatalytic H₂ evolution rate because of higher surface areas and/or better light harvesting. Surface area plays a significant role in the photocatalytic activity as a large surface area could provide more reactive sites. Normally, bulk g-C₃N₄ displays very low surface area ($< 10 \text{ m}^2 \cdot \text{g}^{-1}$), whereas the similarity with graphite in structure implies the surface area of g-C₃N₄ could be extended. Theoretically, the surface area of single-layered g-C₃N₄ could reach $2500 \text{ m}^2 \cdot \text{g}^{-1}$. The theoretical surface area of $2500 \text{ m}^2 \cdot \text{g}^{-1}$ implies many efforts could be done to increase the

surface area and consequently to improve its performance in photocatalytic water splitting.

Generally speaking, fabrication of micro/nano g-C₃N₄ with higher surface could be achieved by two approaches: template directing syntheses and exfoliation of bulk g-C₃N₄. Template directing syntheses including hard template method and soft template method have been highlighted by several works to give mesoporous and nanoporous g-C₃N₄ with surface area ranging from 68 to 517 m² g⁻¹. For hard-template method, porous silica or porous aluminum oxides act as the hard templates to guide the growth of mesoporous g-C₃N₄.^{96,108,140-149} The template is subsequently removed by sodium hydroxide (NaOH), ammonium bifluoride (NH₄HF) , or hydrogen fluoride (HF), which are all environmental unfriendly. Chen *et al* reported a typical synthesis from nanoporous SBA-15 template and cyanamide by mixing the two in water before thermal treatment. In this case, water or other solvents would compete with cyanamide in absorption onto the template, causing poor mass diffusion of cyanamide in the pore channels of SBA-15. The resulted mesoporous g-C₃N₄ (ompg-CN-1) showed an increased surface area of 239 m² g⁻¹ but suffered from considerable structural defects. To address the problem, Zhang and co-workers optimized the protocol and designed a new synthetic strategy as shown in Figure 2-8 (b).¹⁴⁹ The template, SBA-15, was pre-treated with 1 M HCl to strengthen the interaction with -NH₂ abundant cyanamide. No solvent was added in this process and liquid cyanamide was pumped to the nanochannels by sonication under vacuum condition. After thermal condensation and template removal, the surface area of newly obtained mesoporous g-C₃N₄

(ompg-CN-2) could reach $517 \text{ m}^2 \text{ g}^{-1}$. The photocatalytic H_2 evolution rate of ompg-CN-2 reached $243 \text{ } \mu\text{mol h}^{-1}$, almost twice of that of ompg-CN-1, and the apparent quantum yield arrived 6.77 % at 455 nm, over twice compared with ompg-CN-1(2.96 %). The better photocatalytic activity is ascribed to larger specific surface area, highly ordered mesoporous channels and less textural defects, in which the ordered mesochannels endow photogenerated electrons and holes to move rapidly to the reaction sites before recombination.

Although hard template is effective in guiding the growth of mesoporous g- C_3N_4 , the removal process using ammonium bifluoride or hydrogen fluoride is highly dangerous. Compared with hard template method, soft template could be self-decomposed during thermal treatment, which makes it attractive. Moreover, soft template method is rather simple and usually one pot synthesis. Yan *et al* reported synthesis of mesoporous g- C_3N_4 from Pluronic P123 surfactant and melamine.¹⁵⁰ During the process of thermal polycondensation, P123 was decomposed and left some carbon atoms incorporating into the structure of mpg- C_3N_4 . As melamine was rather inactive, the doped carbon content was low and the as-prepared mpg- C_3N_4 exhibited an excellent photocatalytic H_2 evolution activity in the whole visible light range. Furthermore, Zhang *et al* and Jiang *et al* synthesized mpg- C_3N_4 by direct polymerization of urea,¹⁵¹ in which urea behaves not only the precursor but also the soft template. In the process of polymerization, the structure of urea is broken, releasing some gas bubbles. These bubbles are the so-called soft template that creates the pores in the structure of mpg- C_3N_4 .

Figure 2-8 Illustration for the synthesis process of ompg-CN.¹⁴⁹

Bulk g-C₃N₄ is connected by Van der Waals force between tri-s-triazine built layers. The weak Van der Waals force implies it is possible to break the bonding force between the layers and to exfoliate the bulk structure into thin nanosheets, which usually displays high surface area as graphene. Inspired by the success of graphene, much interest has been dedicated to exfoliation of bulk g-C₃N₄. Niu *et al* found that g-C₃N₄ nanosheet could be easily achieved by heating bulk g-C₃N₄ at 500 °C in the air because the high temperature thermally oxidized the hydrogen bonds and broke the bonding force between layers (Figure 2-9 (a)).¹⁵² After the thermal oxidation, the thickness was reduced to around 2 nm, indicating the presence of nanosheets. Similarly, Zhang *et al* and Yang *et al*^{153,154} exfoliated bulk

g-C₃N₄ into ultrathin nanosheets by liquid sonication (Figure 2-9 (b)). The interaction between the liquid solvent molecules and g-C₃N₄ could break the bonds and liberate the layers. Unlike the previous works, Xu *et al* employed the highly dangerous concentrated H₂SO₄ to chemically oxidize the bonds (Figure 2-9 (c)).¹⁵⁵ When concentrated H₂SO₄ was added to g-C₃N₄ aqueous solution during sonication, the temperature of the solution increased rapidly. Simultaneously, some H₂SO₄ molecules were inserted into the interlayers of g-C₃N₄. Consequently, the interlayer bondings were broken by the intercalated H₂SO₄ at high temperature.

Figure 2-9 Exfoliation of g-C₃N₄ by different approaches: thermal oxidation (a);¹⁵² liquid oxidation (b)¹⁵³ and chemical oxidation (c).¹⁵⁵

In conclusion, no matter it is creating mesopores or exfoliating to nanosheet, the

surface area of g-C₃N₄ is increased dramatically. At the same time, the photocatalytic H₂ evolution rates are enhanced in all cases. The enhancement is as high as 10 fold in some cases.

Heterogeneous composites

The low efficiency of g-C₃N₄ is mainly restricted by fast recombination of photogenerated electrons and holes before taking part in photocatalytic H₂ evolution. One of the solutions is to build heterogeneous junction between g-C₃N₄ and another semiconductor with suitable band positions. The band alignment allows the electrons and holes to migrate in opposite directions and separates the two in different sides spatially, and consequently suppresses the charge recombination and enhances the performance. For example, two kinds of g-C₃N₄/CdS heterogeneous composites were reported.¹⁵⁶⁻¹⁵⁹ According to Ge *et al*, the composite was prepared by chemisorption and calcination of g-C₃N₄ and CdS quantum dots.¹⁵⁸ The composite with 30 wt% CdS loading displayed 9.1 times higher H₂ evolution rate compared with pure g-C₃N₄ and more than twice enhancement compared with CdS quantum dots. Besides, the stability of CdS during H₂ evolution was highly improved. No photocorrosion was observed during 28 hours irradiation under visible light because the photoexcited holes were transferred to g-C₃N₄. Despite of the enhanced photocatalytic activity, CdS quantum dots on g-C₃N₄ experienced severe aggregation. Cao and coworkers advanced the preparation by adopting a solvothermal method.¹⁵⁶ The photocatalytic performance is further improved and the H₂ evolution rate under visible light over

12 wt% CdS/g-C₃N₄ increased by a factor of 60 compared with bare g-C₃N₄. Recently, Zhang and coworkers synthesized core/shell CdS/ g-C₃N₄ nanowires by a two-step self-assembly method.¹⁵⁹ First, bulk g-C₃N₄ was obtained and exfoliated in methanol. Second, well-prepared CdS nanowires were added and sonicated. After the sonication, CdS nanowires were coated with g-C₃N₄ shells. The core-shell structure also showed a higher photocatalytic efficiency and good stability.

TiO₂, as a super star in the field of photocatalyst, is selected to form heterojunctions with g-C₃N₄ from various approaches and precursors.¹⁶⁰⁻¹⁶⁹ Chai *et al.* fabricated the composite of (g-C₃N₄)-Pt-TiO₂ by calcination method.¹⁶⁰ Yang *et al.* reported the design of N-doped TiO₂/g-C₃N₄ composite from impregnation method using TiCl₄ and g-C₃N₄.¹⁶⁷ Zhou *et al.* reported the construction of the composite consisted of g-C₃N₄ and TiO₂ nanotube arrays from anodic oxidation and electrodeposition method.¹⁶⁹ All these TiO₂/ g-C₃N₄ composites indicated an enhanced photocatalytic performance and quenched photoluminescence intensity, suggesting the recombination of photoexcited electrons and holes was suppressed.

Besides CdS and TiO₂, many other photocatalysts have been coupled with g-C₃N₄. Pan and coworkers prepared BiPO₄/g-C₃N₄ core-shell structure via self-assembly similar to the CdS/ g-C₃N₄ core-shell nanowire structure.¹⁷⁰ Wang and coworkers reported an effective ZnO/g-C₃N₄ composite by the calcination method.¹⁷¹ Other composites reported in the past few years includes multi-walled carbon nanotubes/g-C₃N₄,¹⁷²⁻¹⁷⁴ ZnWO₄/ g-C₃N₄,¹⁷⁵ DyVO₄/ g-C₃N₄,¹⁷⁶ TaON/ g-C₃N₄,¹⁷⁷ Co₃O₄/ g-C₃N₄,^{178,179} BiVO₄/ g-C₃N₄,¹⁸⁰ and so on. All the g-C₃N₄ based composites showed excellent photocatalytic H₂ evolution performance under

visible light irradiation. This is due to the more negative CB of g-C₃N₄ compared with the other semiconductor in the composites. A mechanism illustration is shown in Figure 2-10 based on CdS/g-C₃N₄ composite.¹⁵⁶ Under visible light illumination, the more negative CB of g-C₃N₄ enables the transfer of photoexcited electrons from g-C₃N₄ to CdS, whereas the more positive VB of CdS promotes the migration of photoexcited holes to g-C₃N₄. As a consequence, photoexcited electrons and holes are separated in space and distributed in two different sections of the composite. That is why photocorrosion of CdS is inhibited after coupling with g-C₃N₄. The movement of electrons and holes in two opposite directions and thus more efficient charge carrier separation are supported by the quenched photoluminescence after hybridization.

Figure 2-10 Band structure configuration and the photoexcited electron and hole transfer between g-C₃N₄ and CdS.¹⁵⁶

Cocatalysts

Cocatalyst loading is the most common and effective strategy to suppress charge carrier recombination and thereby to enhance the photocatalytic activity. Besides, the deposited cocatalysts sometimes could act as reactive sites on the surface of photocatalysts and may inhibit the backward reaction of water formation from active H_2 and O_2 . Therefore, in the long history of photocatalytic water splitting, various cocatalysts are extensively loaded onto semiconductor photocatalysts to boost the reaction rate.

Noble metal like Pt, Pd, Au and Ag are widely applied as cocatalysts to a majority of semiconductor photocatalysts to achieve a higher efficiency. Particularly, Pt has been demonstrated to be an excellent cocatalyst working on almost all semiconductors. Take Pt as an example, the role of noble metal cocatalysts in photocatalytic reactions are depicted as Figure 2-11. In the presence of Pt, the lower Fermi energy level compared with photocatalysts drives electrons to migrate to Pt cocatalyst, leaving holes on the semiconductor. To this end, electrons and holes are spatially separated on two parts and then participate in water reduction and water oxidation, respectively. As a result, the efficiency increases with cocatalyst loading. It is notable that Pt particles on the surface may also serve as the active sites for proton reduction and accelerate the redox reactions by inhibiting backward reaction. In most cases, Pt is loaded via photodeposition method since it is convenient to reduce Pt cations by photoexcited electrons onto photocatalysts in aqueous solution and the photocatalytic H_2 evolution can be then started without further purification. Furthermore, the Pt particles are deposited on the sites where

photoexcited electrons accumulate, which undoubtedly would facilitate accumulation of photoexcited electrons on Pt particles and later water reduction. However, Pt particles prepared from photodeposition may aggregate. The large nanoparticles from aggregation and relatively poor deposition drive researchers to seek for other methods that allow Pt to be loaded homogeneously. Maeda *et al* reported that Pt loaded g-C₃N₄ from impregnation method using bis (1,5-cyclooctadiene) platinum complex [Pt(cod)₂] as precursor and obtained twice photogenerated H₂ under same conditions in comparison with Pt/g-C₃N₄ from photodeposition.¹⁸¹ The high efficiency is attributed to the good dispersion of Pt nanoparticles on g-C₃N₄ surface. Ag and Au loaded g-C₃N₄ via impregnation method were reported by Ge *et al*¹⁸² and Cheng *et al*,¹¹⁸ respectively, and both showed enhancement in photocatalytic activity. The high activity of Ag or Au loaded g-C₃N₄ may be due to wider visible light absorption compared with pure g-C₃N₄. The absorption over 450 nm in the visible range comes from the surface plasmon resonance of Ag and Au. Nevertheless, noble metals are expensive as well as rare, which means they are not suitable for large scale production of H₂. Therefore, researchers attempts to discover noble metal free and highly efficient cocatalysts which are stable and facile to be prepared.

Figure 2-11 Process of migration path of photoexcited electrons and holes in the presence of Pt as a cocatalyst on the surface of semiconductor photocatalyst.¹⁹

Besides noble metals, some metal oxides and metal sulfides are also found to be highly effective as cocatalysts in enhancing photocatalytic H₂ evolution on various semiconductors. Some metal sulfides, for instance MoS₂,¹⁸³⁻¹⁹¹ NiS,¹⁹²⁻¹⁹⁴ Ag₂S¹⁹⁵⁻¹⁹⁸ are especially attractive since they perform even better than Pt as cocatalysts in some cases. Zong *et al* demonstrated CdS loaded with MoS₂ as cocatalyst exhibited higher photocatalytic H₂ evolution activity in comparison with other noble metals including highly efficient Pt and Au nanoparticles.^{190,191} They found that the intimate contact between CdS and MoS₂ and formation of junction would facilitate electron and hole separation and be responsible for the good performance. Motivated by this work using transition metals as cocatalysts, the works on NiS/CdS,^{192,194} MoS₂/ g-C₃N₄,¹⁹⁹ and NiS/ g-C₃N₄²⁰⁰ are reported one after another. For example, Zhang *et al* revealed that NiS/CdS displayed the highest quantum

efficiency (51.3%) over noble metal free systems under visible light ($\lambda > 420$ nm) with sacrificial reagent of lactic acid.¹⁹⁴ Hou *et al* found that the heterojunction could be fabricated between MoS₂ and g-C₃N₄ due to the similarity of layered structures, as depicted in Figure 2-12. The heterojunction would be beneficial for the charge transportation in the interface of g-C₃N₄ and MoS₂ and thereby suppress electron and hole recombination before photocatalytic reactions.¹⁹⁹ Consequently, the photocatalytic H₂ evolution rate over MoS₂/g-C₃N₄ is enormously increased, even exceeding that of Pt/g-C₃N₄ under the same conditions.

Figure 2-12 Layered nanojunction formed between MoS₂ and g-C₃N₄ for photocatalytic H₂ evolution under visible light.¹⁹⁹

2.3 Summary

Since the first demonstration of TiO₂ in photocatalytic water splitting in 1972, photocatalytic water splitting or photocatalytic H₂ evolution has been proven to be a promising strategy to solve the energy crisis and environmental issues by generating renewable and clean H₂ fuel. Over the past several decades, a large

amount of semiconductors have been employed to photocatalytic H₂ evolution including metal oxides, metal sulfides, metal nitrides and non-metal materials. Among these metal and non-metal based materials, polymeric g-C₃N₄ stands out for the following reasons: (i) proper band gap of 2.7 eV to absorb visible light up to 460 nm; (ii) suitable CB and VB positions that enable both reduction and oxidation of water; (iii) composed of abundant elements of C and N and facile to be synthesized; (iv) good stability under ambient conditions; and (v) non-toxic. Despite of the advantages aforementioned, g-C₃N₄ shows some drawbacks towards photocatalytic H₂ evolution under visible light and the poor photocatalytic performance is mainly ascribed to fast recombination of photogenerated electrons and holes. To suppress the recombination and increase the utilization rate of photoexcited charge carriers and finally to enhance the photocatalytic activity of g-C₃N₄ through economic approaches, herein a bimetallic alloy cocatalyst, PtCo, and a noble metal free cocatalyst, NiS₂, are deposited via feasible solvothermal and hydrothermal method, respectively.

Chapter 3 : Enhanced photocatalytic activity over PtCo alloy decorated g-C₃N₄ under visible light

3.1 Introduction

As described in Chapter 2, bulk g-C₃N₄ could be synthesized by various approaches from several nitrogen abundant precursors. For example, Yan *et al* reported a facile synthetic method of directly heating the economic precursor, melamine, in a semiclosed system.²⁰¹ The heating process took two steps, first maintaining at 500 °C for 2 hours and then keeping at 520 °C for another two hours. However, Cao *et al* claimed the as-obtained g-C₃N₄ exhibited poor performance towards photocatalytic H₂ evolution, which was attributed to severe recombination of photogenerated electrons and holes after initiation and during transportation.²⁰² One feasible and effective strategy to suppress the charge carrier recombination is cocatalyst (Pt, Au, NiO, NiS, etc) deposition.

Noble metals, for example, Pt, Au, Ru and Rh, are excellent candidates for cocatalysts since noble metal cocatalysts are effective in trapping electrons and facilitating charge carrier recombination. Besides, these noble metals on the surface of photocatalysts could serve as active sites for protons reductions.²³ In order to explore the mechanism, researchers further explore and elucidate the relationship between physical properties of a surface and

the chemical reactivity. Trasatti found that the relationship between catalytic activities and M-H (M stands for metal) bond strength was in a volcano shape. Pt, which shows a moderate bond strength (locates at the peak of the “volcano”), exhibits the best performance.²⁰³ This is in good accordance with Sabatier principle, that is, the highest catalytic activity is obtained at proper binding energies.²⁰⁴ Weak M-H bond strength implies high activation energy, e.g. it is difficult to initiate the reaction. On the other hand, when the M-H bond is too strong, the hydrogen atoms would be absorbed to all the reactive sites, resulting in catalyst poisoning. Therefore, the proper bond strength between Pt and H enables Pt good catalytic property, which has been demonstrated by tremendous literatures. For instance, Pt deposited TiO₂, CdS, and g-C₃N₄, *etc.* and has led to remarkable enhancement in photocatalytic performances compared with pristine photocatalysts.

Although Pt is an effective cocatalyst, the high cost and rareness restrict its future application in large scale photocatalytic H₂ generation. One alternative way is to alloy Pt with other cheap, abundant as well as efficient transition metals, for instance Co, Mo, Sn, Cr and Fe. Pt based alloys have received extensive attentions and revealed superior performance compared to pure Pt in photocatalytic hydrogen evolution²⁰⁵ and in various catalytic reactions, including oxygen reduction reaction (ORR),²⁰⁶⁻²¹⁸ methanol oxidation.^{219,220} Significantly, very recently, Hu *et al* applied the Pt₃Co alloy into photocatalytic H₂ evolution by loading Pt₃Co onto CdS and TiO₂ nanoparticles.²²¹ The results indicated Pt₃Co deposited photocatalysts

showed enhanced photocatalytic performances in both cases compared with noble metal Pt cocatalyst due to efficient charge carrier recombination (Figure 3-1). Hence, it is possible and promising to develop the Pt based alloy loaded g-C₃N₄ photocatalyst for enhanced photocatalytic hydrogen evolution. Herein for the first time, we loaded PtCo alloy with different compositions and various amounts onto g-C₃N₄ to improve the electron-hole separation ability and thus to enhance the photocatalytic H₂ evolution.

Figure 3-1 photocatalytic H₂ evolution rate of Pt based alloy cocatalysts on CdS ((a)) and TiO₂ ((b)), respectively.²²¹

3.2 Experimental section

3.2.1 Sample preparation

All chemicals were used without further purification.

Preparation of g-C₃N₄

Bulk g-C₃N₄ powder was prepared by thermal polycondensation method according to the literature.²⁰¹ In a typical experiment, Melamine was chosen to be the precursor. 6.0 g of melamine (Sigma-Aldrich) was weighted and placed in an alumina crucible with a cover. Firstly, it was heated at 773 K for 2 h with a heating rate of 20 K/min, and then the temperature was increased to 793 K (5 K/min) and the crucible was kept at 793K for another 2 h. The product was finally ground with a mortar and pestle to get bulk g-C₃N₄ powder.

g-C₃N₄ loaded with Pt based alloy cocatalyst

g-C₃N₄ with 1wt% Pt_xCo alloy cocatalyst was synthesized *via* the reduction of Pt and Co precursors together in ethylene glycol. In a typical experiment, a certain amount of H₂PtCl₆ (Sigma-Aldrich) and Co(NO₃)₂ 4H₂O (Sigma-Aldrich) were dissolved in 20 mL ethylene glycol (Sigma-Aldrich) (pH was adjusted to 11 by 1M NaOH) to form a homogeneous and light yellow solution, following with the addition of 297 mg g-C₃N₄. The total amount of Pt and Co in the precursors is exactly 3 mg to obtain the theoretical loading content of 1 wt%. The solution was then stirred and sonicated for 30 mins before transferring to a 40 mL Teflon-lined stainless steel autoclave and heating at 473 K for 10 hrs. The resulted brown precipitate was centrifugated and washed with deionized water, and absolute ethanol to remove soluble species before being dried in a vacuum oven. For comparison, g-C₃N₄ with pure Pt nanoparticles was also prepared using the same method, but without

addition of $\text{Co}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and g- C_3N_4 with pure Co metal was prepared without the addition of H_2PtCl_6 . For other loading amount of Pt_xCo alloy, reduced g- C_3N_4 was added while the total amount of Pt and Co was kept at 3 mg.

Pt and Pt based alloy loaded g- C_3N_4 were prepared and labelled as in Table 1.

Characterization techniques

After preparation, the materials were characterized by a series of equipments. XRD patterns were measured with a Shimadzu XRD-6000 X-ray diffractometer (Cu $\text{K}\alpha$ source) under 2 theta mode from 10° to 80° at a scan rate of $1^\circ/\text{min}$. The morphologies were captured by A JEOL JSM-7600F field emission scanning electron microscope (FESEM), JEOL JEM-2010 and JEOL JEM-2100F transmission electron microscope (TEM). Energy-dispersive X-ray spectra (EDX) were taken from JEOL JEM-2100F TEM at an accelerating voltage of 200 kV. UV-vis absorption spectra and diffuse reflectance spectra (DRS) were detected using Lambda 750 UV/vis/NIR spectrophotometer (Perkin-Elmer, USA). The photoluminescence (PL) spectra were recorded on Shimadzu RF-5310PC fluorometer and the excitation wavelength here was 325 nm. X-ray Photoelectron spectroscopy

Table 1 Samples prepared in this work and detailed preparation parameters about these samples.

Sample	Cocatalyst content (wt%)	Pt/Co (at.)	Cocatalyst loading method
Pt(ph)/CN ^a	1 wt%	1/0	photodeposition
Pt(ph)/CNEG ^b	1 wt%	1/0	photodeposition
PtCN ^b	1 wt%	1/0	solvothermal
Pt ₃ CoCN ^b	1 wt%	3/1	solvothermal
Pt _{2.5} CoCN ^b	1 wt%	2.5/1	solvothermal
Pt ₂ CoCN ^b	1 wt%	2/1	solvothermal
PtCo ₆ CN ^b	1 wt%	1/6	solvothermal
CoCN ^b	1 wt%	0/1	solvothermal
Pt _{2.5} FeCN ^b	1 wt%	2.5/1	solvothermal
Pt _{2.5} NiCN ^b	1 wt%	2.5/1	solvothermal
Pt _{2.5} CoCN ^b -0.5 wt%	0.5 wt%	2.5/1	solvothermal
Pt _{2.5} CoCN ^b -3 wt%	3 wt%	2.5/1	solvothermal
Pt _{2.5} CoCN ^b -10 wt%	10 wt%	2.5/1	solvothermal

Pt(Ph)/CN^a represents the sample in which 1wt % Pt was photodeposited onto pristine g-C₃N₄.

Pt(ph)/CNEG^b represents the sample in which 1wt % Pt was photodeposited onto ethylene glycol treated g-C₃N₄ under solvothermal environment.

$\text{Pt}_x\text{Co}_y\text{CN}^b$ represents the sample in which 1 wt% cocatalyst was deposited onto $\text{g-C}_3\text{N}_4$ *via* solvothermal method and x and y indicates the atomic ratio of Pt to Co in the cocatalyst.

$\text{Pt}_x\text{Co}_y\text{CN}^b$ -A wt% represents $\text{Pt}_x\text{Co}_y\text{CN}^b$ with A wt% of cocatalyst loading.

(XPS) measurements were performed on a Thermo Scientific Theta Probe XPS with monochromatized Al K α ($h\nu = 1486.6$ eV) source and a calibration binding energy at 284.6 eV of C 1s peak. The Brunauer–Emmett–Teller (BET) surface areas were collected on a Micro-meritics ASAP 2020M+C system. Fourier transform infrared spectrum (FTIR) was obtained from an IR Affinity-1 FTIR spectrometer between 4000 and 400 cm^{-1} .

Photocatalytic hydrogen evolution

All photocatalytic H_2 evolutions were conducted using a 45-mL closed glass reaction tube reactor septa (Sigma–Aldrich), sealing with Suba Seal rubber septa (Sigma–Aldrich). Typically, 10 mg of the as-prepared photocatalysts were suspended in 10 mL 15 vol% triethanolamine (TEOA) aqueous solution. The suspension was sonicated and then degassed with nitrogen gas for 30 mins to drive away the O_2 in the reactor. After degassing, the reactor was irradiated under 300-W xenon lamp (MAX-302, Asahi Spectra, USA) coupled with a UV cut-off filter ($\lambda > 420$ nm). During the irradiation, the suspension was stirred at a speed of 750 rpm to ensure the solution as well as photocatalysts anywhere in the reactor were

irradiated at equal possibility. The gas product was detected each hour manually by a gas chromatograph (GC-7890A, Agilent) with a TCD detector.

Photoelectrochemical Measurements

Photocurrent measurements were carried out with a standard three-electrode configuration on an electrochemical analyzer (Solartron Instruments SI 1287), in which Pt wire worked as counter electrode and Ag/AgCl (in saturated KCl) as reference electrode. The light source here was a Xe arc lamp. And the electrolyte was potassium phosphate buffer (KPi, 1M) solution at PH value of 7. To assemble the working electrodes, a solution consisted of 50 μ l nafion (Sigma-Aldrich), 1 ml ethanol and 4 ml DI water was prepared, followed with ultra-sonication for 2 hrs. Then 8 mg of as-prepared samples were added to 2 ml of above solution and sonicated for another 2 hrs to obtain homogeneous mixture. Finally, the mixture was gently dropped onto the fluorine-doped tin oxide (FTO) glass surface with a pipette. The FTO glass surface was covered by thermal tape with a hole of 0.25 cm². Therefore the areas of all working electrode were all exactly 0.25 cm².

The electrochemical impedance spectra (denoted as EIS) were measured using the same three electrode configuration and light source. The perturbation signal was set at 20 mV and the frequency changed from 100 kHz to 10 mHz.

3.3 Results and discussion

3.3.1 Characterizations of the as-synthesized g-C₃N₄

The as-prepared g-C₃N₄ was first characterized by XRD diffraction pattern. Two obvious peaks (Figure 3-2 (a)) are revealed, consistent with that reported in literatures for g-C₃N₄.^{131,201} The strong peak at 27.6° is assigned to (002) facet, similar to that in graphite. This peak corresponding to a lattice fringe distance of 0.326 nm, is formed by inter-planar stacking of the conjugated aromatic system. The other weak peak at 13.2° can be ascribed to (100) facet. This peak associated with a distance of 0.681 nm, represents the more oriented tri-s-triazine. Thus, the XRD pattern indicates the successful preparation of g-C₃N₄.

The FTIR spectrum further confirms the presence of g-C₃N₄ since the breathing mode of triazine at 807 cm⁻¹ is evident as indicated in Figure 3-2 (b). Besides, the stretching mode of C-N heterocycles is observed between 1200 and 1600 cm⁻¹. Furthermore, N-H stretching vibration mode is indicated in the broad band in the range of 3000-3700 cm⁻¹.

The SEM and TEM images of as-prepared g-C₃N₄ were displayed in in Figure 3-2 (c) and (d), respectively. SEM image confirms that g-C₃N₄ possesses a layered structure and rough surface with irregular morphology and size due to the rough grounding after polycondensation. The TEM image of as-prepared g-C₃N₄ is in good accordance with the SEM result. The size of layered g-C₃N₄ is over 1 μm.

Figure 3-2 Characterization of as-prepared g-C₃N₄: (a) XRD patterns; (b) FTIR spectrum; (c) SEM image and (d) TEM image.

The surface compositions and chemical states of as-prepared g-C₃N₄ were evaluated by XPS measurements as shown in Figure 3-3. The elemental survey reveals the presence of C, N and O. A trace amount of oxygen element is detected because melamine is polymerized in the air and atmospheric oxygen is unavoidable to be inserted into the surface of g-C₃N₄. Both the C 1s spectrum and N 1s

spectrum are deconvoluted into three peaks with Gaussian-Lorentzian shapes. The binding energy at 288.2 eV for C 1s and 398.7 eV for N 1s are assigned to carbon and nitrogen, respectively, in the triazine rings (N-C=N and C-N=C, respectively), providing another evidence of presence of g-C₃N₄. The other two peaks at 286.2 and 285.0 eV for C 1s reveal the existence of carbon atoms in the forms of C-O bonds and the sp₂ C-C bonds. The other two peaks for N 1s at 401.1 eV and 400.0 eV correspond to nitrogen atoms in the amino group (C-N-H) and in the N-(C)₃ bonds.

Figure 3-3 Elemental survey and chemical states of C, N, and O element of as-prepared g-C₃N₄.

The UV-vis absorption spectrum was indicated in Figure 3-4. The absorption edge is around 460 nm, corresponding to a band gap of 2.7 eV, which is exactly the same as reported by Wang *et al.*¹³¹ The spectrum also indicates that as-prepared g-C₃N₄ could respond to visible light.

Figure 3-4 Diffuse reflectance spectrum of as-prepared g-C₃N₄.

3.3.2 Effect of preparation parameters

Three different Pt/g-C₃N₄ samples were prepared under different conditions, and photocatalytic H₂ evolution tests over the three samples were carried out to optimize the reaction conditions. The photocatalytic H₂ evolution rates as shown in Figure 3-5 are in the order of Pt(ph)/CN < Pt(ph)/CNEG < Pt CN. Therefore, the optimal Pt/g-C₃N₄ sample could be achieved *via* a hydrothermal method by ethylene glycol reduction. It is noteworthy that g-C₃N₄ treated by ethylene glycol also shows a higher activity, implying that g-C₃N₄ undergoes some changes after the hydrothermal treatment.

Figure 3-5 Time courses of H₂ evolution under visible light over PtCN (Pt/g-C₃N₄ from ethylene glycol reduction), Pt(ph)/CN (photodeposited Pt on pristine g-C₃N₄), and Pt (ph)/CNEG (photodeposited Pt on ethylene glycol treated g-C₃N₄).

To investigate the enhancement, SEM, UV-vis absorption spectra and PL spectra were conducted on pristine g-C₃N₄ and g-C₃N₄ after ethylene glycol treatment. No obvious changes in morphology, roughness and size are indicated from SEM images (Figure 3-6) before and after treatment. However, after treatment, a slightly stronger absorption (Figure 3-7 (a)) between 450 nm and 550 nm is given and a dropped PL intensity (Figure 3-7 (b)) is exhibited. So the treatment does not change the bulk structure of g-C₃N₄. Instead, its microstructures might be tailored by removing surface

oxygen species through ethylene glycol reduction or forming more surface defects, which leads to a stronger absorption and suppressed photoexcited electron-hole recombination and as a result, the activity is improved.

Figure 3-6 SEM images of g-C₃N₄ before (a, b) and after treatment (c, d). The scale bar as shown in the image is 1 μm.

Figure 3-7 UV-vis absorption spectra (a) and Photoluminescence (PL) spectra (b) of g-C₃N₄ (g-C₃N₄) before and after treatment (g-C₃N₄-EG).

3.3.3 PtCo alloy loaded g-C₃N₄: characterization and photocatalytic H₂ evolution

PtCo alloy was deposited onto as-prepared g-C₃N₄ by solvothermal method using ethylene glycol as solvent and reductant. The XRD patterns after modification were displayed in Figure 3-8. For the three samples (Pt/g-C₃N₄, Pt₃Co/ g-C₃N₄ and Co/ g-C₃N₄) with 1 wt% loading (Figure 3-8(a)), no other peaks except the two for g-C₃N₄ are observed although two possible peaks are shown between 40 ° and 60 ° in the former two peaks. This might be ascribed to the low loading amounts. Therefore, higher contents of PtCo alloy were deposited (Figure 3-8 (b)) and a clear peak at around 40.5 ° is evident. The peak slightly shifts towards a higher degree compared with (111) facet of Pt (JCPDS 70-2431), consistent with that reported by Hu *et al.*²²¹

Pt atom is larger than Co atom so that the substitution of Co atoms in Pt structure led to a contraction in lattice fringe and higher diffraction peak. Antolini *et al* claimed that the geometric changes after alloying Pt with Co, mainly decrease of Pt-Pt bond distance was one of the two reasons that caused enhanced electrocatalytic activity towards oxygen reduction reaction.²⁰⁶ In our case, the geometric variation from substitution of Co atoms in the crystal structure and followed contraction induced decreased Pt-Pt bond distance would most likely have positive impact on the photocatalytic H₂ evolution.

Figure 3-8 XRD patterns of (a):1wt% loaded Pt, Pt₃Co and Co on g-C₃N₄ and (b) Pt₃Co (3 wt%)/ g-C₃N₄ and Pt_{2.5}Co(10 wt%)/g-C₃N₄.

In order to investigate the composition and chemical states of Pt and Co, XPS measurements were performed on Pt (1 wt%) /g-C₃N₄ (Figure 3-9), and

Pt_{2.5}Co(20 wt%)/g-C₃N₄ (Figure 3-10). A comparison of the Pt 4f peaks between Pt (1 wt%) /g-C₃N₄ and Pt_{2.5}Co(1 wt% and 20 wt%)/g-C₃N₄ is made and shown in Figure 3-11. All samples reveal the presence of C, N and O, which are ascribed to g-C₃N₄. The same binding energies of C 1s, and N 1s confirm that g-C₃N₄ is stable under current solvothermal conditions.

For Pt (1 wt%) /g-C₃N₄ (Figure 3-9), despite of the noises, Pt 4f_{7/2} and Pt 4f_{5/2} peaks are still obvious, locating at 71.0 eV and 74.0 eV , respectively. The two peaks are typical for metallic Pt, confirming that the precursor, H₂PtCl₆, is reduced to Pt under experimental conditions.

For Pt_{2.5}Co/g-C₃N₄, we first analysed the sample with 1 wt% loading amount. But the noise is too loud so that we increased the content of Pt_{2.5}Co to 20 wt% and did the analyses. Notably, similar Pt 4f_{7/2} and Pt 4f_{5/2} peaks are observed in Pt_{2.5}Co (20 wt%)/g-C₃N₄(Figure 3-10), as shown below. But the locations shift to 71.6 eV and 74.8 eV. We expected to see clear Co peaks with this high content. Unfortunately, Co signals are unable to be deconvoluted due to the low intensity.

The Pt 4f signals are also collected and compared between Pt (1 wt%) /g-C₃N₄ and Pt_{2.5}Co(20 wt%)/g-C₃N₄ (Figure 3-11). Remarkable shifts towards higher binding energies for both Pt 4f_{7/2} and Pt 4f_{5/2} are observed for Pt_{2.5}Co with 20 wt% loading, in consistent with the observations reported by Choi *et al.*²⁰⁸ They also indicated that this shift would lead to shift of d band center and thus affect the catalytic activities. This is supported by Wakisaka *et al.*, as indicated in Figure 3-1.²²² In their opinion, the shift to a smaller binding

energy suggests the downshift of d band center, which in turn affects photocatalytic H₂ evolution as a cocatalyst. The shift of d band center is the other reason for enhanced oxygen reduction reaction activity, and might be another reason for enhanced photocatalytic performance as well.

Figure 3-9 XPS measurements of PtCN: a) survey; b) binding energy of C 1s; c) binding energy of N 1s; d) binding energy of Pt 4f.

Figure 3-10 XPS measurements of Pt_{2.5}CoCN-20 wt%: a) survey; b) binding energy of C 1s; c) binding energy of N 1s; d) binding energy of Pt 4f; e) binding energy of Co 2p.

Figure 3-11 Comparison of binding energy of Pt 4f: A, PtCN; B, Pt_{2.5}CoCN-20 wt%.

The TEM and HRTEM images and TEM-EDS spectrum for Pt (1 wt%)/g-C₃N₄ were shown in Figure 3-12. Panel (a) apparently indicates that Pt nanoparticles synthesized from polyol reduction randomly deposit on the surface of g-C₃N₄. Panel (b) with a higher magnification further demonstrates the Pt nanoparticles on g-C₃N₄ are around 3-5 nm. The HRTEM image (c) shows the lattice fringe distance of Pt nanoparticle is 0.224 nm, corresponding to (111) facet. TEM-EDS spectrum also verifies the as-synthesized sample is composed of element Pt, C and N. The peak for Cu is from the copper grid supporting the materials in TEM tests.

Figure 3-12 (a)-(b) TEM images, (c) HRTEM image and (d) EDS spectrum of the as-synthesized Pt (1 wt%)/g-C₃N₄.

Similar TEM and HRTEM analyses were also conducted on Pt_{2.5}Co (1 wt%)/g-C₃N₄ sample shown in Figure 3-13. The bright field and dark field TEM images in (a) and (b) show that the alloy nanoparticles are not randomly deposited on the surface of g-C₃N₄ as Pt nanoparticles. And

HRTEM images in c) and d) confirm the lattice fringe distances of $\text{Pt}_{2.5}\text{Co}$ are also around 0.222 nm, assigned to (111) facet, which is smaller than that in Pt loaded sample, in good accordance with higher degree shift of XRD pattern.

Figure 3-13 Bright field (a) and dark field (b) TEM images and HRTEM images (c, d) of $\text{Pt}_{2.5}\text{Co}$ (1 wt%)/ $\text{g-C}_3\text{N}_4$.

The UV-vis absorption spectra of pristine g-C₃N₄, Pt/ g-C₃N₄, Pt_{2.5}Co / g-C₃N₄ and Co/ g-C₃N₄ (all loading amount are 1 wt%) are shown in Figure 3-14. Compared with pristine g-C₃N₄, Pt/ g-C₃N₄ and Pt_{2.5}Co / g-C₃N₄ reveal a weak absorption in the whole visible range with a wavelength larger than 460 nm due to the deposition of noble metal nanoparticles, in accordance with colour change from yellow to the brown after deposition. While for Co loaded sample, an additional absorption between 500 nm and 600 nm is observed.

Figure 3-14 The UV-vis absorption spectra of pristine g-C₃N₄, Pt/ g-C₃N₄, Pt_{2.5}Co / g-C₃N₄ and Co/ g-C₃N₄ (all loading amount are 1 wt%).

The photocatalytic H₂ evolutions over PtCo alloy loaded g-C₃N₄ samples with different atomic ratios and pure Pt and pure Co loaded sample are exhibited in Figure 3-15. All samples here are loaded with 1 wt% cocatalysts. For reference, H₂ evolution experiments were also carried out in the absence of photocatalyst or illumination. In these cases, no H₂ was detected, suggesting all H₂ produced from photocatalytic H₂ evolution over photocatalysts. It is found that Pt/ g-C₃N₄ exhibits a moderate photocatalytic H₂ evolution activity (2.95 $\mu\text{mol h}^{-1}$). When a small proportion of Pt is replaced with Co, enhanced photocatalytic performances are observed. The photocatalytic H₂ evolution rate over Pt₃Co/ g-C₃N₄ is increased to 3.91 $\mu\text{mol h}^{-1}$ and the rate continued rising to 4.63 $\mu\text{mol h}^{-1}$ for Pt_{2.5}Co/ g-C₃N₄, about 1.6 times of pure Pt loaded sample prepared from same conditions. Further increasing the content of Co in the alloy results in a decreased activity of 3.27 $\mu\text{mol h}^{-1}$ for Pt₂Co/ g-C₃N₄, which is still slight higher than that of Pt/ g-C₃N₄. When the majority of Pt is replaced with Co and the atomic ratio of Pt:Co reaches 1:6, the activity drops dramatically to 0.49 $\mu\text{mol h}^{-1}$. Pure Co loaded sample only produces H₂ at a negligible rate of 0.05 $\mu\text{mol h}^{-1}$. All these results indicate that the optimal composition for PtCo alloy as cocatalyst on g-C₃N₄ at current conditions is Pt_{2.5}Co. A comparison between pure Pt loaded sample and pure Co loaded sample confirmed that the performance of Pt as a cocatalyst is much better, in accordance with previous reports.

Figure 3-15 Photocatalytic H₂ evolution tests over Pt, Co and PtCo alloy with different compositions loaded g-C₃N₄.

To further investigate the effect of cocatalyst contents, different loading percentages of Pt_{2.5}Co were deposited onto g-C₃N₄ and H₂ evolution analyses over these samples are shown in Figure 3-16. Sample with 0.5 wt% loading amount shows a slight lower activity compared with that of Pt_{2.5}Co (1 wt%)/g-C₃N₄. While 3 wt% loaded and 10 wt% loaded sample reveal continued and significant drop in photocatalytic activity. The decreased activity is caused by shading effect as excessive coverage of cocatalysts on g-C₃N₄ blocks its absorption of visible light.

Figure 3-16 Photocatalytic H₂ evolution analyses over Pt_{2.5}Co/g-C₃N₄ with different loading amount.

To check if other transition metals are able to be alloyed with Pt to show high efficiency, Pt_{2.5}Ni and Pt_{2.5}Fe were synthesized and deposited onto g-C₃N₄ through the polyol reduction method under the same conditions. All Pt_{2.5}M (M= Co, Ni, Fe) loaded samples (as shown in Figure 3-17) exhibits higher photocatalytic H₂ evolution rates than that of pure Pt loaded sample. Among the three alloy samples, Pt_{2.5}Co performs the best, while Pt_{2.5}Fe is in the middle. Pt_{2.5}Ni shows a comparable performance as Pt although slightly better.

Based on the above-mentioned experiments, we could conclude that $\text{Pt}_{2.5}\text{Co/g-C}_3\text{N}_4$ with 1 wt% loading showed the highest efficiency in visible light driven photocatalytic H_2 evolution using TEOA as sacrificial reagent.

Figure 3-17 Photocatalytic H_2 evolution over $\text{Pt/g-C}_3\text{N}_4$, $\text{Pt}_{2.5}\text{Co/g-C}_3\text{N}_4$, $\text{Pt}_{2.5}\text{Ni/g-C}_3\text{N}_4$ and $\text{Pt}_{2.5}\text{Fe/g-C}_3\text{N}_4$.

To evaluate the stability of the highly effective $\text{Pt}_{2.5}\text{Co}$ (1 wt%)/ $\text{g-C}_3\text{N}_4$, the photocatalyst system was kept irradiating for 25 hours under visible light (Figure 3-18). A linear H_2 production versus irradiation time is observed, indicating the H_2 evolution rate is constant and $\text{Pt}_{2.5}\text{Co}$ (1 wt%) / $\text{g-C}_3\text{N}_4$ is

stable under current reaction conditions. The effectiveness and durability provide evidences that $\text{Pt}_{2.5}\text{Co}$ is a promising cocatalyst on $\text{g-C}_3\text{N}_4$.

Figure 3-18 Stable photocatalytic H₂ evolution over $\text{Pt}_{2.5}\text{Co}/\text{g-C}_3\text{N}_4$ under long-term irradiation.

To investigate the effect of electronic structure change, mainly d band centre shift, photoluminescence (PL) spectrum, photocurrent response and electrochemical impedance spectroscopy (EIS) were carried out on samples before and after alloying with Co.

A comparison of PL spectra over PtCN , CoCN and $\text{Pt}_{2.5}\text{CoCN}$ reveals that the PL intensity is quenched over $\text{Pt}_{2.5}\text{CoCN}$, implying that $\text{Pt}_{2.5}\text{Co}$ is more effective in inhibiting the electron hole recombination compared with Pt

and Co (Figure 3-19). Larger photocurrent density is also observed over $\text{Pt}_{2.5}\text{CoCN}$ working electrode compared with the other three electrodes when light is turned on, supporting more effective electron and hole separation on the surface of PtCo alloy loaded $\text{g-C}_3\text{N}_4$ (Figure 3-20). However, the photocurrent density over $\text{Pt}_{2.5}\text{CoCN}$ tends to decrease and becomes almost the same as PtCN after 200s, suggesting the alloy is not stable in the presence of bias under current conditions. This effective charge separation also happens to $\text{Pt}_3\text{Co}/\text{CdS}$ and $\text{Pt}_3\text{Co}/\text{TiO}_2$,²²¹ which might be corresponded to the electronic change and d band centre shift.

Figure 3-19 PL spectra of PtCN, CoCN, and $\text{Pt}_{2.5}\text{CoCN}$ with excitation wavelength at 325 nm.

Figure 3-20 Transient photocurrent responses over g- C_3N_4 working electrode, PtCN working electrode, CoCN working electrode, and $\text{Pt}_{2.5}\text{CoCN}$ working electrode at voltage of 0.3 V (vs RHE).

Moreover, the EIS spectra (shown in Figure 3-21) using the typical three electrode system at 0.3 V (vs RHE) were employed to explore the mechanism. The smaller diameters over pure g- C_3N_4 , PtCN and $\text{Pt}_{2.5}\text{CoCN}$ when light turns on suggest photoelectrons could be produced for all three samples under light irradiation. Whereas the smaller diameter from pure g- C_3N_4 to PtCN and finally $\text{Pt}_{2.5}\text{CoCN}$ under the same conditions (all light on

or all light off) demonstrates more efficient electron transfer over $\text{Pt}_{2.5}\text{CoCN}$ and from $\text{Pt}_{2.5}\text{CoCN}$ to the electrolyte. The more effective electron mobility also implies a higher photocatalytic H_2 evolution activity.

Figure 3-21 Nyquist plots of electrochemical impedance spectra with $\text{g-C}_3\text{N}_4$ (red), PtCN (black) and $\text{Pt}_{2.5}\text{CoCN}$ (blue) working electrodes at voltage of 0.3 V (vs RHE).

Therefore, PL spectra, photocurrent responses and EIS spectra all indicate the enhanced photocatalytic H_2 evolution could be explained by more

effective electron and hole separation and migration. Why are PtCo alloy more effective in inhibiting charge carrier recombination and in promoting their transportation? Hu *et al* conducted a series of electrochemical measurements on pure CdS, Pt/CdS, Pt₃Co/CdS and Co/CdS and found Co was more effective in trapping photogenerated electrons on surface.²²¹ This might be due to the emptier d orbital of Co. Thus, after alloying, electrons from photoexcitation are more feasible to be transferred rather than recombine with holes.

In addition of the more effective electron and hole separation and transportation, the enhancement can also be explained from surface electrochemical reactions. The activity of photocatalytic H₂ evolution highly depends on two processes: H⁺ absorption on active sites and H₂ desorption after generating. Greeley and coworkers pointed out the absorption properties of transition metals were depended on local d band center.²⁰⁵ After alloying Pt with Co, the d band centre would be shifted positively as illustrated in Figure 3-22.²²² Consequently, the absorption abilities after alloying are tailored, which lead to the modification of activity in photocatalytic H₂ evolution. On the other hand, Greeley *et al* found weaker hydrogen binding and easier hydrogen desorption in alloys, implying the hydrogen generated are immediately released and the back reaction of hydrogen with oxygen is inhibited.²²³

Figure 3-22 Schematic illustration of CL shift and d band center shift of Pt after alloying with Co. The binding energy shown in XPS measurement is indicative of E_F .²²²

Therefore, the Pt_xCo alloy would promote charge transfer from excited $g-C_3N_4$ and reduce the rate of back reaction (H_2 oxidation), thereby enhancing the efficiency of photocatalytic H_2 generation. Certainly, excessive Co in the alloy is not good since Pt is the major part to lower down the energy barrier of H^+ reduction into H atoms. As such, there is an optimal ratio of Pt/Co. In our studies, the optimal ratio ratio ($Pt_{2.5}Co$) is based on the experimental observation.

3.4 Conclusion

In summary, we have successfully synthesized $Pt_xCo/g-C_3N_4$ for the first time by ethylene glycol reduction of metal salts under hydrothermal conditions. H_2PtCl_6 and $Co(NO_3)_2$ were co-reduced and alloyed onto the

surface of g-C₃N₄. In this process, ethylene glycol works not only as a solvent and reductant but also as a stabilizer of the as-prepared Pt_xCo alloys. XRD patterns confirmed that Pt had been substituted by Co with a shift towards higher degree. TEM indicated the lattice fringe distances of Pt nanoparticles and Pt_{2.5}Co were between 0.223 nm and 0.234 nm, all assigned to (111) facet of Pt (JCPDS 70-2431). UV-vis absorption spectra displayed stronger absorption peaks in Pt_xCo/g-C₃N₄ in the visible light range, which was in consistent with color changes from the initial light yellow of g-C₃N₄ to the dark brown of Pt_xCo/g-C₃N₄. The photocatalytic H₂ evolution over Pt_xCo/g-C₃N₄ with different compositions and various loading amount revealed that Pt_{2.5}Co (1 wt%) /g-C₃N₄ exhibited the highest activity under visible light using 15 % TEOA aqueous solution as hole scavenger. Besides Pt_xCo/g-C₃N₄, Pt was also alloyed with transition metals, Fe and Ni from the same hydrothermal method. Pt_{2.5}Fe (1 wt%) /g-C₃N₄ and Pt_{2.5}Ni (1 wt%) /g-C₃N₄ both showed higher activity than that of Pt (1 wt%) /g-C₃N₄ but lower activity than that of Pt_{2.5}Co (1 wt%) /g-C₃N₄. The stability test suggested Pt_{2.5}Co (1 wt%) /g-C₃N₄ held high durability during photocatalytic H₂ evolution as the rate did not slow down during 25-hour illumination under visible light. The high efficiency and good stability of Pt_{2.5}Co (1 wt%) /g-C₃N₄ demonstrated that Pt_{2.5}Co was an effective and durable cocatalyst on g-C₃N₄. Furthermore, PL spectra, photocurrent responses and electrochemical impedance spectroscopy implied an efficient and fast charge transfer between Pt_{2.5}Co and g-C₃N₄, which promotes photocatalytic H₂ evolution.

Additionally, the decreased Pt-Pt bond distance caused by alloying Pt with Co would also enhance the photocatalytic performance.

Chapter 4 : Enhanced photocatalytic H₂ evolution over noble metal free NiS₂/g-C₃N₄ composite

(This Chapter is adapted from “Lisha Yin, Yu-Peng Yuan, Shao-Wen Cao, Zhenyi Zhang and Can Xue*, Enhanced visible-light-driven photocatalytic hydrogen generation over g-C₃N₄ through loading the noble metal-free NiS₂ cocatalyst. *RSC Adv.*, **2014**, 4, 6127-6132.” Reproduced with permission of The Royal Society of Chemistry)

4.1 Introduction

The work presented in Chapter 3 demonstrates that PtCo alloy is an effective and promising Pt based alloy cocatalyst, which could reduce cost since less Pt is applied in the photocatalyst system. However, PtCo alloy still requires the utilization of expensive and rare Pt metal. Thus, noble metal free cocatalysts which have high activity in photocatalytic reaction would be potential substitution of noble cocatalysts. Recently, noble metal free transition metal based materials including MoS₂, Ni(OH)₂, Ag₂S, IrO₂, WS₂, *etc.* received tremendous attentions. Among those transition metal based materials, molybdenum and nickel based nanostructures are most studied for their good performances. Jaramillo and co-workers found that MoS₂ fell slightly below Pt in the volcano plot which describes the relationship between exchange current density and Gibbs free energy of adsorbed atomic hydrogen on electrocatalysts calculated from density functional theory

(DFT).²²⁴ The position of MoS₂ indicates it possesses a low overpotential and suitable bonding strength with atomic hydrogen, comparable to Pt, which suggests it could show a similar activity to Pt as a cocatalyst towards photocatalytic H₂ evolution. This is supported by a large number of works on MoS₂ cocatalyzed photocatalytic H₂ evolution.²²⁵⁻²²⁷ Zong and co-workers reported that under the same conditions, MoS₂ loaded CdS exhibited higher activity than all the noble metals, e.g. Pt, Ru, Rh, Pd, Au, loaded samples as displayed in Figure 4-1.¹⁹¹ CdS loaded with 0.2 wt% MoS₂ even showed 36 times enhancement in photocatalytic H₂ evolution compared with pure CdS. Moreover, Hou and co-workers fabricated a layered nanojunction between MoS₂ and g-C₃N₄.¹⁹⁹ 0.5 wt% MoS₂ loaded mesoporous C₃N₄ also performed better than Pt based sample with same loading amount since the nanojunction could facilitate the electron transfer across the interface and thus promoted the photocatalytic H₂ evolution.

Figure 4-1 Photocatalytic H₂ evolution over various cocatalysts loaded CdS.

The loading amounts are all 0.2 %.¹⁹¹

Driven by the high efficiency of MoS₂ cocatalyst, WS₂, which shows a similar electronic and layered structure, attracts intensive attention as well. Wu *et al*, Chen *et al* and Voiry *et al*, all claimed WS₂ nanosheets showed very low overpotential which was comparable to that of Pt and even lower than that of MoS₂.²²⁸⁻²³⁰ The overpotentials of the three materials are compared and described as in Figure 4-2. The low overpotential suggests WS₂ with nanosheet structure is a good electrocatalyst towards H₂ evolution reaction.²³¹ Zong and coworkers deposited WS₂ cocatalyst onto CdS nanoparticles through an impregnation-sulfidation approach.²³² The as-prepared composite with only 1 wt% WS₂ increases the photocatalytic H₂ evolution by a factor of 28 in comparison with pure CdS nanoparticles. The enhanced photocatalytic performance was also observed on WS₂ loaded mesoporous g-C₃N₄ reported by Hou *et al*.²³³ However, in both cases, the photocatalytic H₂ evolution rate continued decreasing with increasing illumination time. Further XRD and XPS analyses on fresh composites and composites after photocatalytic reactions revealed WS₂ was partially oxidized or corroded under irradiation.

Figure 4-2 Tafel plots of WS₂, WS₂ nanosheets(NS), MoS₂ and Pt.²³⁰

The studies on nickel based materials are more diverse. NiO is a good H₂ evolution cocatalyst on various photocatalysts and has been studied for years.²³⁴⁻²³⁹ In addition of NiO, Ni(OH)₂ is also an excellent cocatalyst.²⁴⁰⁻²⁴² Yu *et al* prepared Ni(OH)₂ loaded g-C₃N₄ by a facile precipitation method. The optimal Ni(OH)₂/g-C₃N₄ composite with 0.5 mol% Ni(OH)₂ displayed a similar activity with that of 1 wt% Pt loaded sample.²⁴² Furthermore, NiS is discovered to be effective as a cocatalyst on photocatalysts such as CdS and g-C₃N₄. Xu's group synthesized both NiS/CdS and NiS/g-C₃N₄ composites via hydrothermal method and demonstrated NiS to be a good and noble-metal free cocatalyst.^{194,200} Chen *et al* developed NiS/g-C₃N₄ as well and the growth was achieved via *in situ* template-free ion-exchange process, which also revealed high photocatalytic H₂ evolution rate.²⁴³

Other metal sulphides such as Ag₂S^{195,197} and CoS₂ also showed good performance as cocatalysts, suggesting transition metal based materials, especially metal sulphides are good candidates and substitution of Pt for photocatalytic H₂ evolution.

The aforementioned MoS₂, NiS, Ag₂S and WS₂ all have been employed to g-C₃N₄ in the past years due to the specific structure of g-C₃N₄. The tri-s-triazine building blocks of g-C₃N₄ connected by triple bonded nitrogen atoms are the ideal sites to coordinate with transition metals and to construct heterojunctions between g-C₃N₄ and transition metal based materials.

Despite of these works, more transition metal sulphide cocatalysts which are abundant and economic for practical application should be explored. For

this purpose, we prepared $\text{NiS}_2/\text{g-C}_3\text{N}_4$ for the first time through hydrothermal method using nickel acetate and thiourea as nickel and sulphur source, respectively.

4.2 Experimental Section

All chemicals are used without further purification.

4.2.1 Preparation of $\text{NiS}_2/\text{g-C}_3\text{N}_4$

All $\text{NiS}_2/\text{g-C}_3\text{N}_4$ samples were synthesized through a one-step hydrothermal process. $\text{g-C}_3\text{N}_4$ was prepared via the same polycondensation method as described in Chapter 3. $\text{NiS}_2/\text{g-C}_3\text{N}_4$ samples with NiS_2 loading of 0 wt%, 1 wt%, 2 wt%, and 5 wt% were labelled as CN0, CN1, CN2, and CN5, respectively. Typically, 456.0 mg of thiourea (Strem), 67.2 mg of $\text{g-C}_3\text{N}_4$, and 1.87 mg of nickel acetate tetrahydrate (Strem) for CN1 were added into 20 mL ultrapure water, and treated with ultrosonication for 2 h. Then the mixture was poured into a 40-mL Teflon-lined autoclave and heated at 413 K for 6 h. After cooling down to room temperature, the resulting samples were washed with ultrapure water and absolute ethanol for three times and then dried in the vacuum oven for 12 h.

4.2.2 Characterization techniques

After preparation, the materials were characterized by a series of equipments. XRD patterns were measured with a Shimadzu XRD-6000 X-ray diffractometer (Cu $\text{K}\alpha$ source) under 2 theta mode from 10° to 80° at a

scan rate of 1°/min. The morphologies were captured by A JEOL JSM-7600F field emission scanning electron microscope (FESEM), JEOL JEM-2010 and JEOL JEM-2100F transmission electron microscope (TEM). Energy-dispersive X-ray spectra (EDS) were taken from JEOL JEM-2100F TEM at an accelerating voltage of 200 kV. UV–vis absorption spectra and diffuse reflectance spectra (DRS) were detected using Lambda 750 UV/vis/NIR spectrophotometer (Perkin-Elmer, USA). The photoluminescence (PL) spectra were recorded on Shimadzu RF-5310PC fluorometer and the excitation wavelength here was 325 nm. X-ray Photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific Theta Probe XPS with monochromatized Al K α ($h\nu = 1486.6$ eV) source and a calibration binding energy at 284.6 eV of C 1s peak.

4.2.3 Photocatalytic H₂ production

In a typical photocatalytic H₂ evolution, 10 mg sample was dispersed in a glass reactor at room temperature and irradiated under the same 300 W xenon lamp (MAX-302, Asahi Spectra, USA) assembled with a UV cut-off filter ($\lambda > 420$ nm). 10 mL triethanolamine (TEOA, 15 vol%) aqueous solution was used as hole scavenger as well. The photogenerated H₂ gas was detected by the same gas chromatograph (Agilent 7890A) with TCD detector at a regular interval.

Photodeposition of Pt/g-C₃N₄: 125 μ L of 0.16 wt% H₂PtCl₆ was injected into 10 mL 15 vol% TEOA aqueous solution with 10 mg g-C₃N₄ inside. After illumination for 1 h, Pt nanoparticles were *in-situ* deposited onto the g-C₃N₄ with a theoretical loading amount of 1 wt%.

4.3 Results and discussion

XRD patterns of pure g-C₃N₄ and NiS₂/g-C₃N₄ composites with different NiS₂ loading amounts were displayed in Figure 4-3. All samples show two peaks at 13.2° and 27.6°, which are respectively assigned to (100) and (002) facet of g-C₃N₄, in consistent with previous literature.¹³¹ Besides the two peaks, new peaks at 31.4° and 53.4° appear on 1 wt% and 2 wt% NiS₂/ g-C₃N₄ and more peaks at 35.3°, 45.1° and 48.0° are identified when NiS₂ loading amount was increased to 5 wt%. These new XRD peaks are well matched with NiS₂ (JCPDS 73-0574), indicating NiS₂/g-C₃N₄ samples with nickel sulphide composition of NiS₂ were successfully prepared through the above-mentioned hydrothermal approach. Since the two peaks for g-C₃N₄ are both located at the same positions, no shift towards either direction, we could conclude no nickel or sulphur is present in the form of dopant in the lattice of g-C₃N₄. This is an evidence that g-C₃N₄ is extremely stable even under high temperature and high pressure.

Figure 4-3 XRD patterns of pure g-C₃N₄ and NiS₂/ g-C₃N₄ composites: CN0 (a), CN1 (b), CN2 (c) and CN5 (d).

TEM and HRTEM analyses were carried out on 2 wt% NiS₂/g-C₃N₄ to further characterize and confirm the distribution and composition of NiS₂ on g-C₃N₄ (Figure 4-4). As displayed in Figure 4-4 (a), polymeric g-C₃N₄ shows a multi-layered structure with irregular morphology and size, in accordance with previous reports. While after deposition (Figure 4-4 (b)), NiS₂ nanoparticles are introduced onto the surface of g-C₃N₄. The size of resulting NiS₂ nanoparticles are below 10 nm. The magnified HRTEM images (Figure 4-4 (c)) indicates a lattice fringe distance of 0.335 nm, corresponding to (-111) facet of NiS₂, confirming the composition of NiS₂ as the XRD patterns. The followed energy dispersive X-ray (EDX) analysis conducted on the selected area (Figure 4-4 (d)) reveals the atomic ratio of Ni to S is close to 2, providing

another evidence for the nickel sulfide species of NiS_2 .

Figure 4-4 TEM image (a) of CN0 and TEM (b), HRTEM (c) images of CN2, and EDS result (d) of CN2.

XPS measurements were performed on 5 wt% $\text{NiS}_2/\text{g-C}_3\text{N}_4$ to verify the chemical states of C, N, Ni and S in the composite sample (Figure 4-5). The same binding energies and deconvoluted peaks for C 1s and N 1s suggest that $\text{g-C}_3\text{N}_4$ does not change after hydrothermal treatment and deposition of

NiS₂, verifying the stability of g-C₃N₄ under harsh environment and implying the possibility to modify g-C₃N₄ in the future. The binding energies for N 2p and S 2p in this work are similar to those of N 2p and S 2p peaks based on NiS₂ material reported by Zhu *et al* and Vanderheide *et al*, respectively.^{196,244} The binding energy of Ni 2p_{3/2} at 853.6 eV is typical of Ni²⁺. The binding energies locate at 162.5 eV for S 2p_{3/2} peak and 163.7 eV for S 2p_{1/2}, respectively, are in good agreement with S₂²⁻ in NiS₂. Thus, the XPS measurements further provide the evidence for the presence of NiS₂ in the as-prepared samples.

Figure 4-5 XPS measurements showing the binding energies for C 1s (a), N 1s (b), Ni 2p (c), and S 2p (d).

The optical absorption spectra of pure $\text{g-C}_3\text{N}_4$ and NiS_2 loaded $\text{g-C}_3\text{N}_4$ samples are shown in Figure 4-6. Polymeric $\text{g-C}_3\text{N}_4$ alone is able to absorb visible light and the absorption edge is around 460 nm, corresponding to the

band gap of 2.7 eV, same as reported in literatures. After the introduction of NiS_2 , all the composite samples maintain the absorption edge at 460 nm, while these samples display obvious absorption between 460 nm and 800 nm. Moreover, the absorption in the range is gradually enhanced with increasing content of NiS_2 , consistent with the color change from green-yellow for 1 wt% loading to green-grey for 5 wt% (as shown in Figure 4-7) ,which could be attributed to the visible light response of NiS_2 nanoparticles.

Figure 4-6 UV-vis absorption spectra of CN0, CN1, CN2 and CN5.

Figure 4-7 Color changes of the as-prepared samples. From left to right: CN0, CN1, CN2 and CN5.

Photocatalytic H_2 evolution over pure $g-C_3N_4$ and different $NiS_2/g-C_3N_4$ samples were performed under visible light as shown in Figure 4-8. Triethanolamine (TEOA) was chosen to be sacrificial reagent to consume photoexcited holes after irradiation. For comparison, 1 wt% Pt was *in-situ* photodeposited onto $g-C_3N_4$ in TEOA aqueous solution with H_2PtCl_6 as Pt source. The obtained 1 wt% Pt/ $g-C_3N_4$ was evaluated for photocatalytic H_2 evolution under the same conditions as the others. Negligible H_2 is generated in the absence of either photocatalyst or visible light irradiation, indicating the following generated H_2 gas is from photocatalytic water reduction reaction. The H_2 production for pure $g-C_3N_4$ could not be detected, suggesting pure $g-C_3N_4$ is inactive under experimental conditions. When cocatalysts (e.g. Pt and NiS_2) are loaded, H_2 productions are dramatically increased with a considerable photocatalytic H_2 evolution rates. 1wt% Pt/ $g-C_3N_4$ shows a moderate H_2 production rate of $\sim 1.07 \mu mol h^{-1}$. While $NiS_2 / g-C_3N_4$ with the same NiS_2 loading amount exhibits a slightly higher rate of $\sim 1.14 \mu mol h^{-1}$. Besides, a significant impact of NiS_2 loading amounts is found as revealed by Figure 4-8 (b). 2wt% NiS_2 loading reveals a remarkable

H₂ production rate of 4.06 $\mu\text{mol h}^{-1}$, about 3 times enhancement compared with that of 1 wt% NiS₂ loaded or 1 wt% Pt loaded sample.

This remarkable H₂ production rate decreases to 0.65 $\mu\text{mol h}^{-1}$ when NiS₂ content is risen to 5 wt%. High content of NiS₂ facilitates the electron transfer from g-C₃N₄ to NiS₂, however, excessive NiS₂ dispersion on g-C₃N₄ would block light absorption of g-C₃N₄ and thus result in less photogenerated electrons and holes and deactivate photocatalytic H₂ evolution. Moreover, excessive NiS₂ nanoparticles may cover the active sites on the surface of g-C₃N₄, which is another drawback.

Figure 4-8 Time course photocatalytic H₂ evolution (a) and photocatalytic H₂ evolution rate (b) over CN0, CN1, CN2, CN5, CNPt.

Figure 4-9 Stability test over CN₂ under visible light for 20 h. The reactor was purged with N₂ at an interval of 4 h to drive away the newly produced H₂ gas.

Prolonged irradiation over 2 wt% NiS₂/g-C₃N₄ under visible light was carried out to investigate the stability or durability of NiS₂ as a cocatalyst. At the end of each cycle, N₂ was purged into the reactor to remove produced H₂ gas. No TEOA aqueous solution was added in the process. As shown in Figure 4-9, the H₂ generation rate gradually slows down when recycled, and drops to $\sim 2.46 \mu\text{mol h}^{-1}$ in the fifth cycling reactions, only 61% of the first cycle. The decreased activity might be corresponded to the slow fall-off of the NiS₂ nanoparticles from g-C₃N₄ surfaces or photocorrosion of NiS₂ under illumination. The photocorrosion caused deactivation of photocatalytic H₂ evolution occurs in all photocatalyst composites containing transition metal sulphides including MoS₂/g-C₃N₄, WS₂/g-C₃N₄, Ag₂S/C₃N₄.^{187,199,200,243,245}

The way of improving the stability of NiS_2 cocatalyst is still under exploration at current stage. Nevertheless, the activities in five cycles are all higher than that of 1 wt% Pt loaded g- C_3N_4 , demonstrating NiS_2 is a potential cocatalyst for economic and large-scale H_2 evolution in the future.

Figure 4-10 Proposed mechanism for enhanced photocatalytic H_2 evolution over $\text{NiS}_2/\text{g-C}_3\text{N}_4$ under visible light. TEOA is the sacrificial reagent.

A possible mechanism is proposed to illustrate the enhancement in photocatalytic H_2 generation by NiS_2 loading (Figure 4-10). When NiS_2 loaded g- C_3N_4 is irradiated by visible light, the electrons at valence band (VB) of g- C_3N_4 would be excited to move to conduction band (CB), whereas the holes left on VB would be consumed by TEOA in solution. The excited electrons are then capable to be trapped by NiS_2 . The electron-hole pair

separation rather than recombination is supported by the dropped PL intensity of CN2 sample as compared with CN0 (as indicated in Figure 4-11). Therefore, the presence of NiS₂ cocatalyst on g-C₃N₄ would efficiently inhibit the recombination of photogenerated charge carriers, resulting in an increased H₂ production rate. The effective charge transportation from cocatalyst to photocatalyst is also observed in NiS loaded CdS sample.¹⁹⁴

In addition, as a cocatalyst, NiS₂ should be able to serve as reactive sites for H₂ evolution, as presented in cathodic H₂ evolution reactions during electrolysis.^{246,247} Xu *et al* reported that NiS on the surface of CdS would form an intermediate, HNiS, which not only promote electron transfer but also accelerate hydrogen desorption ($\text{NiS} + \text{e}^- + \text{H}^+ \rightarrow \text{HNiS}$; $\text{HNiS} + \text{e}^- + \text{H}^+ \rightarrow \text{NiS} + \text{H}_2$).¹⁹⁴ Similarly, NiS₂-hydride may also be formed during H₂ evolution reactions to accelerate hydrogen production under visible light over NiS₂/g-C₃N₄ composite. Detailed mechanism over NiS₂/g-C₃N₄ composite is still unclear and to be explored in the future.

Figure 4-11 Photoluminescence spectra of CN0 and CN2, excited at a wavelength of 325 nm.

4.4 Conclusion

One-step hydrothermal method was employed to the synthesis of $\text{NiS}_2/\text{g-C}_3\text{N}_4$. XRD patterns indicate the presence of NiS_2 in the samples while TEM images show the deposited NiS_2 nanoparticles disperse randomly on $\text{g-C}_3\text{N}_4$ surface. In some areas, the nanoparticles aggregate to appear as large particles. HRTEM image displays the lattice fringe distance of 0.335 nm which could be corresponded to (-111) facet of NiS_2 , further confirming

NiS₂/g-C₃N₄ was successfully prepared. XPS measurements show the binding energy for Ni²⁺ and S₂²⁻ as well, well matching with the XRD and HRTEM results.

The samples are further characterized by UV-vis absorption spectra. NiS₂ loaded samples show strong absorption in the whole range due to the absorbance of NiS₂ nanoparticles.

The following photocatalytic H₂ evolution demonstrates that NiS₂ could dramatically improve the activity of g-C₃N₄, in which the optimal loading amount is 2 wt%. 2 wt% NiS₂/g-C₃N₄ exhibits an enhancement in activity by a factor of 3 compared with 1 wt% Pt/g-C₃N₄. Besides, 1 wt% and 5 wt% NiS₂/g-C₃N₄ display comparable activity to 1 wt% Pt/g-C₃N₄.

In order to study the mechanism, PL spectra were obtained for g-C₃N₄ and 2 wt% NiS₂/g-C₃N₄. The decreased PL intensity of the latter suggests more effective electron transfer from g-C₃N₄ to NiS₂ is achieved than to Pt. Furthermore, the facile absorption of H⁺ and desorption of H₂ on NiS₂ surface may be another reason for the enhancement.

Chapter 5 : Conclusions and proposed future work

5.1 Conclusions

Photocatalytic H_2 production from water reduction that mimics photosynthesis process of the natural plants is a promising strategy to supply an alternative and clean energy to human beings. To achieve photocatalytic H_2 evolution, photocatalyst systems, solar light, especially, visible light, and holes scavengers are necessary. Photocatalyst systems involve at least one semiconductor that can absorb light and generate photoinduced electrons and holes. In many cases, cocatalysts are also involved to enhance charge separation.

In this thesis, all works are based on a polymeric noble metal free semiconductor photocatalyst, g- C_3N_4 . Native g- C_3N_4 shows low photocatalytic activity, corresponding to the fast recombination of photoexcited electrons and holes. Our works mainly focus on enhancing the photocatalytic performance of g- C_3N_4 through cocatalyst depositions because cocatalysts could suppress the recombination by decreasing the overpotential for water reduction and attracting photoexcited electrons from the photocatalyst, as well as could provide active sites for proton reduction. Good cocatalyst should meet the requirements of high effectiveness in photocatalytic H_2 evolution when deposited onto some certain photocatalysts,

low-cost and earth abundance to allow large scale application. The major findings and contributions are listed as follows.

Pt is believed to be the most effective cocatalyst working on various photocatalysts since it can attract electrons from photocatalysts, decrease the overpotential for water reduction reaction and offer active sites for photocatalytic H₂ production. Despite of its excellent efficiency, Pt is limited by the high cost and rare sources. In order to maintain the efficiency whereas reduce cost, Pt based alloys rather than bare Pt were designed and deposited on g-C₃N₄ surfaces using a facile one-step solvothermal method in which metal cations were reduced by ethylene glycol under high temperature and pressure. Firstly, we prepared PtCo cocatalyst. Different compositions of PtCo were employed to g-C₃N₄ with 1 wt% loading. It is found that Pt_{2.5}Co/g-C₃N₄ exhibits the highest photocatalytic H₂ evolution rate and 1.6 times enhancement compared with Pt/g-C₃N₄. Then different amounts of Pt_{2.5}Co were loaded onto g-C₃N₄, in which 1 wt% sample appears to be the most effective. Besides, the stability test over 1 wt% Pt_{2.5}Co/g-C₃N₄ indicates no activity lost within 25 h irradiation. Therefore, it is concluded that 1 wt% Pt_{2.5}Co/g-C₃N₄ is the sample with optimal composition and loading amount for photocatalytic H₂ production. Secondly, other transition metals, Fe and Ni were also alloyed with Pt to develop Pt based cocatalysts. It is interesting to find that Pt_{2.5}Fe/g-C₃N₄ and Pt_{2.5}Ni/g-C₃N₄ both display better performances for photocatalytic H₂ evolution than Pt/g-C₃N₄ prepared and measured under the same conditions. Hence, the work demonstrates that Pt-

transition metal alloys ($\text{Pt}_{2.5}\text{Co}$, $\text{Pt}_{2.5}\text{Fe}$, and $\text{Pt}_{2.5}\text{Ni}$) are effective cocatalysts on $\text{g-C}_3\text{N}_4$ as they show comparable activity with bare Pt during photocatalytic H_2 evolution. Since they are earth-abundant and more economic, Pt-transition metal alloys are good alternative cocatalysts to Pt.

To further develop earth-rich and cheap cocatalyst, $\text{NiS}_2/\text{g-C}_3\text{N}_4$ composites were synthesized through hydrothermal method from nickel acetate and thiourea as nickel and sulphur precursors. The composites were first examined by XRD and XPS analyses to confirm the NiS_2 composition. XRD patterns reveal several peaks that could all be assigned to NiS_2 and XPS measurements confirm the sulphur is presented in the form of S_2^{2-} , not S^{2-} . Then $\text{NiS}_2/\text{g-C}_3\text{N}_4$ samples were characterized by TEM and HRTEM and UV-vis absorption spectroscopy. According to TEM and HRTEM results, NiS_2 nanoparticles are between 10 nm and 20 nm, dispersing randomly on the surface of $\text{g-C}_3\text{N}_4$. According to UV-vis absorption spectra, the composites samples all indicate enhanced visible light absorption at the wavelength longer than the absorption edge of $\text{g-C}_3\text{N}_4$ (460 nm). The photocatalytic H_2 evolution test suggests that NiS_2 despite of the contents is excellent in enhancing the performance of pure $\text{g-C}_3\text{N}_4$. 1 wt% $\text{NiS}_2/\text{g-C}_3\text{N}_4$ exhibits comparable H_2 generation rate and 2 wt% $\text{NiS}_2/\text{g-C}_3\text{N}_4$ gives the highest enhancement in which the rate is enhanced by a factor of 3, comparing with 1 wt% Pt/ $\text{g-C}_3\text{N}_4$ from photodeposition in TEOA aqueous solution. The enhancement is then studied by PL spectra. 2 wt% $\text{NiS}_2/\text{g-C}_3\text{N}_4$ sample shows a quenched PL intensity compared with $\text{g-C}_3\text{N}_4$, implying

introduction of NiS_2 could inhibit the recombination of photogenerated electrons and holes in $\text{g-C}_3\text{N}_4$. Therefore, the rapid electron transfer between the interfaces is the reason for the enhanced photocatalytic H_2 evolution in $\text{NiS}_2/\text{g-C}_3\text{N}_4$ sample.

In summary, economic and efficient cocatalysts, PtCo alloy and NiS_2 are developed in this project and demonstrated to be able to enhance photocatalytic H_2 evolution reaction based on polymeric noble metal free $\text{g-C}_3\text{N}_4$.

5.2 Proposed future work

The USA Department of Energy (DOE) predicts that to enable the economic viability of industrial production of H_2 through photocatalytic water splitting, the minimum efficiency that required under visible light should be 10 %.^{21,248} Only when the efficiency is beyond this threshold, it is possible to produce H_2 commercially. Since the first example of photocatalytic H_2 evolution based on TiO_2 , tremendous studies and efforts have been dedicated to enhance the efficiency. Despite of some promising works of high efficiencies reported recently, the majority of photocatalyst systems are still far below the target. It is still a huge challenge to develop high efficient, earth-abundant and economic photocatalysts to achieve the target. Following are some suggestions given to reach the goal.

- 1) **Fabrication of effective and low-cost cocatalysts.** As described in Chapter 3 and Chapter 4, both PtCo alloy and NiS_2 are demonstrated

to be effective cocatalysts in enhancing the photocatalytic H₂ evolution of g-C₃N₄ under visible light illumination. However, studies on effective and cheap cocatalysts like the two are still limited. More works should be done. Further systematic studies on Pt based alloys and transition metal sulphides as cocatalysts are urgently needed.

PtM (M=Co, Fe, Ni) alloys show enhanced performances as cocatalysts on g-C₃N₄ compared with pure Pt, implying that Pt based alloys may be excellent alternative cocatalysts of Pt. The rich sources and low cost also encourage researchers to put more attention on Pt based alloy cocatalysts. According to literatures as in Chapter 3, Pt based alloys are feasible to be prepared by various reduction methods under different environments. Moreover, Pt free cocatalysts consist of cheap and abundant transition metals such as Co, Ni, Fe, Mo are extremely attractive. If such kind of cocatalysts are synthesized and proven to be effective towards photocatalytic H₂ evolution, commercial H₂ production from this technology should take a step.

Besides PtM cocatalysts, NiS₂ is also a good choice for photocatalytic H₂ evolution based on g-C₃N₄ as shown in Chapter 4. In addition, MoS₂, NiS and WS₂ are also reported to be able to act as cocatalysts on a variety of photocatalysts. However, no systematic studies have been employed on universal cheap and abundant transition metal sulphides and their performances as cocatalysts. Therefore, it is necessary and significant to discover and screen the

whole transition metal sulphides and build a library. This library should guide researchers the effectiveness of each transition metal sulphide on an individual photocatalyst.

- 2) **Mechanism study on PtCo/ g-C₃N₄ and NiS₂/ g-C₃N₄.** Although photocatalytic H₂ evolution rate of g-C₃N₄ has been increased a lot by loading PtCo alloy and NiS₂ as cocatalysts, respectively, detailed mechanisms on how they enhance the activity are still not fully understood.

For PtCo/g-C₃N₄, we know the geometric and electronic structures of Pt are changed after alloying with Co. But how the changes would affect photocatalytic performance is still unclear. Wang *et al* demonstrated the ordered intermetallic platinum-cobalt core-shell nanoparticles were consist of Pt₃Co ordered bimetallic core and Pt shells with 2-3 atomic layers from annular dark-field (ADF)-scanning transmission electron microscope (STEM) images associated with simulation.²⁴⁹ Stamenkovic *et el* determined the surface electronic structure (d band centre) of Pt₃M (M=Ni, Co, Fe, Ti, V) through ultraviolet photoemission spectroscopy (UPS).²⁵⁰ We may try these tools to figure out the mechanism of enhanced photocatalytic H₂ evolution over PtCo loaded g-C₃N₄ in the future.

For NiS₂/ g-C₃N₄, as we described in Chapter 4, NiS₂ behaves as a metal and shows a narrow band gap. However, investigation on exact

band structures and CB positions of NiS_2 is required to conduct to explain how electrons and holes transfer between NiS_2 and $\text{g-C}_3\text{N}_4$.

- 3) Introduction of reduced graphene oxide (rGO) into $\text{NiS}_2/\text{g-C}_3\text{N}_4$ composites.** According to the XPS results in our study (Chapter 4) and other evidences from literatures, the surface of $\text{g-C}_3\text{N}_4$ prepared from thermal polycondensation of melamine is clean, which means few functional groups or bonds are present. The lack of functional groups or bonds makes it difficult to anchor nanostructures on the surface. As shown in the chapter 4, the distribution of deposited NiS_2 nanoparticles is random. Besides, the deposited NiS_2 nanoparticles are prone to aggregate together to irregular and larger particles. In order to achieve a better dispersion of NiS_2 , rGO could be introduced. The functional groups like $-\text{COOH}$, $-\text{OH}$ on the surface of rGO could anchor NiS_2 . Additionally, rGO itself is a good cocatalyst facilitating the transfer of photoexcited electrons and holes. Therefore, homogeneous distribution of NiS_2 nanoparticles on rGO would be observed and photoexcited electrons could be transported from $\text{g-C}_3\text{N}_4$ to rGO for direct H_2 evolution or electrons would be transferred again from rGO to NiS_2 and participate in water reduction reaction on the surface of NiS_2 . As a result, both rGO and NiS_2 are advantageous for photocatalytic H_2 evolution of $\text{g-C}_3\text{N}_4$.
- 4) Extension of visible light absorption.** Restricted by its intrinsic electron structure, $\text{g-C}_3\text{N}_4$ could only be excited by visible light no

longer than 460 nm, experimentally and theoretically, which is one of the reasons that lead to low photocatalytic activity. Doping with metal or non-metal elements is one strategy to tune the electronic structure, thus narrowing the band gap and extending the light absorption. Dye sensitization is another strategy to achieve this goal. Eosin Y (EY) - sensitized g-C₃N₄ showed a strong absorption at around 550 nm due to the absorption of EY and the maximum apparent quantum yield of 18.8%.^{251,252} Magnesium phthalocyanine could even extend the photoresponse of g-C₃N₄ to the whole visible light range.²⁵³ However, dyes in the photocatalytic systems tend to be decomposed under irradiation, resulting in a deactivation of dye-sensitized photocatalysts. So development of stable and wide-absorption dye sensitizers is equally urgent. Besides doping and dye-sensitization, the absorption of g-C₃N₄ could also be improved by introducing plasmonic metal nanoparticles like Au and Ag.^{118,254} Samanta and co-workers prepared Au/g-C₃N₄ via deposition–precipitation method and obtained an absorption peak at around 550 nm owing to the plasmon resonant absorbance of Au nanoparticles.²⁵⁴ In a word, the visible light responses of g-C₃N₄ could be enhanced by several approaches.

- 5) **Overall water splitting based on g-C₃N₄ composites.** Sacrificial reagents, for example, TEOA in this thesis and ethanol, Na₂S/Na₂SO₃ mixture are unavoidable in photocatalytic H₂ evolution because they are able to consume photogenerated holes. However, for practical

application, sacrificial reagents are not favourable in terms of recovery of photocatalysts and reclamation of clean water. This could be solved by overall water splitting in which photocatalytic water reduction and oxidation take place at the same time on a single or combined photocatalyst system in the absence of sacrificial reagents. Overall water splitting has an extremely strict requirement on the CB and VB positions of photocatalysts. g-C₃N₄ is the one that could meet the requirement whose CB is more negative than the reduction potential of water and VB is more positive. As we have described in this thesis, by loading proper photocatalytic H₂ evolution cocatalysts, g-C₃N₄ could exhibit excellent H₂ production performance. Similar to H₂ evolution, g-C₃N₄ could also display a great activity towards photocatalytic O₂ evolution by depositing of O₂ evolution cocatalysts, for instance, Co₃O₄, and RuO₂. Maeda *et al*¹⁸¹ reported RuO₂ loaded g-C₃N₄ could evolve O₂ from water under visible light and Han *et al*¹⁷⁸ in 2014 reported Co₃O₄-g-C₃N₄ heterojunction could degrade methyl orange efficiently under visible light. Based on our work on H₂ generation of cocatalyst deposited g-C₃N₄, we can further introduce O₂ evolution cocatalyst on to NiS₂/g-C₃N₄ or PtCo/g-C₃N₄. As a result, the system may achieve overall water splitting without adding sacrificial reagents.

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