Towards solar fuels : photocatalyst development for water splitting and carbon dioxide reduction

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NANYANG
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**TOWARDS SOLAR FUELS: PHOTOCATALYST DEVELOPMENT FOR
WATER SPLITTING AND CARBON DIOXIDE REDUCTION**

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SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

2013

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WATER SPLITTING AND CARBON DIOXIDE REDUCTION**

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LIST OF ABBREVIATIONS

AAD	acetaldehyde-DNPH
ACN	acetonitrile
ACD	acetone-DNPH
BET	Brunauer–Emmett–Teller
BG	band gap
CB	conduction band
CL	column
DMF	dimethylformamide
DNPH	2,4-dinitrophenylhydrazine
DRIFT	diffuse reflectance infrared Fourier transform spectroscopy
EA	elemental analysis
ESI-MS	electrospray ionization mass spectrometry
FAD	formaldehyde-DNPH
FESEM	field emission scanning electron microscopy
FID	flame ionization detector
FTIR	Fourier transform infrared spectroscopy
GC	gas chromatography
GC-MS	gas chromatography-mass spectrometry
HOMO	highest occupied molecular orbital
HPLC	high performance liquid chromatography
ICP	inductively coupled plasma
IEC	ion-exchange chromatography

LC-MS	liquid chromatography-mass spectroscopy
LDH	layered double hydroxide
LUMO	lowest unoccupied molecular orbital
MDL	method detection limit
MV	methyl viologen
MWNT	multi-walled carbon nanotubes
NMR	nuclear magnetic resonance
PAD	propionaldehyde-DNPH
PTFE	polytetrafluoroethylene
PWR	photocatalytic water reduction
RB	rose bengal
TAA	thioacetamide
TCD	thermal conductivity detector
TEM	transmission electron microscopy
TEOA	triethanolamine
TGA	thermal gravimetric analysis
TU	thiourea
UV-Vis	ultraviolet–visible spectroscopy
VB	valence band
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

ABSTRACT

Solar fuels derived from solar energy are envisioned to replace fossil fuels for a sustainable earth and society. Photocatalytic water splitting for hydrogen (H_2) production and photocatalytic carbon dioxide (CO_2) reduction for gaseous or liquid fuels production are two of the most promising but challenging processes. Advancement of these two reactions for solar fuels production is largely hindered by the lack of efficient, stable and low-cost photocatalysts. In this thesis, the work was focused on the development of economical photocatalyst systems toward more efficient and stable solar fuels production via water splitting and carbon dioxide reduction.

Firstly, well-dispersed layered double hydroxide (LDH) nanocrystals were used to immobilize the photosensitizer of rose bengal (RB) and Pt nanoparticles to construct a self-assembled RB-LDH-Pt system for more stable H_2 generation from water. Such a system offers many advantages in photocatalytic water splitting: (i) immobilizing the organic dye photosensitizer for suppressed self-quenching, (ii) close arrangement between photosensitizer molecules and catalyst nanoparticles for efficient electron transfer, (iii) formation of well-dispersed catalysts nanoparticles on the support surface, and (iv) easy recycle of the expensive catalyst.

Secondly, *in situ* sulfur-doped mesoporous graphitic carbon nitride (mpgCNS) was synthesized from a single precursor of thiourea, by using SiO_2 nanoparticles as template. Sulfur group was found to facilitate the condensation of carbon nitride (C_3N_4) polymer. Higher product yield was obtained from thiourea than that from urea as the starting material. The resultant sulfur-doped mesoporous C_3N_4 exhibited 30 times higher activity than the native C_3N_4 for hydrogen evolution. A relatively high apparent quantum efficiency of 5.8% was obtained at 440 nm. The activity enhancement was attributed to 1) stronger and extended light absorption in the visible light region by sulfur doping, 2) more efficient mass and charge transfer in mesoporous structure.

Thirdly, noble metal-free C_3N_4 based photocatalyst was developed for H_2 production by loading nickel sulfide (NiS) cocatalyst on C_3N_4 via a simple hydrothermal method. Both the weight percentage of NiS and the hydrothermal reaction temperature were found to have great influence on the photocatalytic activities. The optimal NiS/ C_3N_4 photocatalyst has 253 times higher activity than the pristine C_3N_4 and is able to retain over 80% of the activity after 4 runs of 24 h.

Fourthly, systematic analysis methods were developed for photocatalytic CO₂ reduction by a combination of gas chromatography (GC) and high performance liquid chromatography (HPLC) methods. The developed methods are able to detect and quantify major products in both gas and liquid phases with low detection limits. The effects of several organic additives including commonly used solvents, photosensitizers and sacrificial reagents in photoreaction were investigated. It has been found that alcohol analysis by GC method is more sensitive to organic additives. In comparison, aldehyde and acid analyses by HPLC method are not affected by most of the organics investigated. The importance of carbon source verification is highlighted and techniques for the verification were proposed.

Finally, self-assembly of carbon nitride (C₃N₄) and LDH was constructed by the electrostatic force based on their opposite surface charges. The immobilized nitrate LDH can easily turn into carbonate LDH *in situ* anion exchange during photocatalytic reduction of CO₂. The CO₃²⁻ anions present in the interlayer space of LDH exhibit much higher reduction efficiency than the free gaseous CO₂ molecules. As a result, 2.6 times higher activity for CH₄ production can be achieved on 10 wt% LDH/C₃N₄ than that without the LDH coating.

In summary, this thesis was devoted to the development of low-cost, stable and efficient photocatalysts for water splitting and carbon dioxide reduction. Different modification on photocatalytic materials such as sensitization, doping, mesoporous structure formation and cocatalyst loading were studied. Carbon nitride was used as the main photocatalytic materials for both water splitting and carbon dioxide reduction. LDH was introduced as a support to enhance the stability in H₂ production and a CO₂ capture medium to improve the activity of CO₂ reduction. Besides, systematic analytical methods based on GC and HPLC were also developed for the analysing the products of CO₂ reduction.

CHAPTER 1 INTRODUCTION

1.1 Background and motivations

The rapid depletion of fossil fuels and deteriorating environment has imposed great urgency in developing technologies to utilize renewable and clean energy sources. Solar energy is one of the most potential renewable energy. The total amount of sunlight that shines on the earth surface for one hour (4.3×10^{20} J) is almost equal to world annual energy consumption (4.1×10^{20} J in 2005).¹ In order to use solar energy efficiently and conveniently, it can be concentrated and turned into electricity or heat. Another feasible method is to capture and store the solar energy directly in the chemical bonds of a material, or ‘fuel’. These chemical fuels, in which energy from the sun has deliberately been stored, are called solar fuels.² Compared with electricity or heat, solar fuels can be more easily stored and used when needed, which can ultimately change the future energy landscape.² In natural photosynthesis, solar energy is stored in the form of chemical bonds by converting H_2O and CO_2 to carbohydrates and O_2 . Inspired by this, scientists have been dedicated to the artificial photosynthesis by mimicking nature’s processes. In practice, the overall photosynthesis reaction can be mimicked by two separated reactions: 1) water splitting to hydrogen and oxygen; 2) carbon dioxide reduction to hydrocarbons and oxygenates. From these two reactions, two main types of solar fuels are produced: 1) carbon-free H_2 and 2) carbon-based fuels like gaseous methane (CH_4), carbon monoxide (CO) or liquid methanol (CH_3OH).

H_2 has long been envisioned as future fuel to replace fossil fuels like coal. The most well-known prediction is in Jules Verne’s science fiction novel *The Mysterious Island* in 1874.³

“And what will they burn instead of coal?” “Water,” replied Harding. “Water!” cried Pencroft, “water as fuel for steamers and engines! Water to heat water!”

“Yes, but water decomposed into its primitive elements... Yes, my friends, I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light... Water will be the coal of the future.”

Although water or H_2 is not truly an energy source, Verne’s predictive description on using water (H_2) as fuel has inspired its worldwide readers including the scientists. To

split H_2O and make H_2 as fuel, energy source like solar energy need to be used for the splitting. As shown in Equation (1), 237 kJ of energy can be stored in the form of H_2 by splitting of one mole H_2O molecules. Based on theoretical calculation, the amount of energy harvested from splitting one standard Olympic swimming pool of water per second is about 33 TJ. This amount is able to supply almost two earths with current global energy consumption rate (18 TW) or the same as the projection value in the year of 2050.⁴ H_2 could be one of most likely future fuels if water splitting photocatalyst can approach the efficiency of splitting a standard Olympic swimming pool of water in one second.

On the other hand, the increasing CO_2 concentration in the atmosphere would lead to serious environmental impacts, such as global warming, sea level rising, abnormal climate and so on.^{5,6} If the consumption rate of fossil fuels persists, the concentration of CO_2 in atmosphere will be doubled to reach around 600 ppm at the end of this century.⁷ As a result, global temperature has been predicted to increase 2-6 °C, causing the Greenland to melt down and sea level to increase 6-7 m.⁸ Coastal cities like New York, Singapore, Shanghai etc. will be submerged under the water while some countries with low sea level will totally disappear. Currently, the fossil fuels still dominate in the world energy consumption. The resulted accumulation of CO_2 in the atmosphere must be tackled. CO_2 capture and storage (CCS) strategies have been developed. These tactics focus on the preservation of CO_2 in geological forms after many energy consuming steps of separation, purification, compression, transportation and storage.^{5,9} Compared with CCS, the solar-driven CO_2 reduction which simultaneously produces value-added fuels and chemicals represents a long-term solution with more profound economical and environmental impact. The schematic equation of CO_2 reduction for fuels production by using solar energy is shown in Equation (2). Driven by sunlight, CO_2 can be converted by reductants (eg. H_2O) to produce valuable fuels such as CH_4 , CO , CH_3OH , HCOOH , higher hydrocarbons and oxygenates.

1.2 Objectives and scope

Both H_2O splitting and CO_2 reduction have been widely studied since the energy crisis

in 1970's.¹⁰ Some start-up companies such as Sun Catalytix, Liquid Light have been founded to scale-up the lab research finding on solar fuels production from H₂O and CO₂. Despite of these efforts, most of research activities in this area are still far from practical applications. Both H₂O splitting and CO₂ reduction are thermodynamically uphill reactions and multi-electrons are involved. It is still a great challenge to achieve efficient, stable and economical reduction of H₂O and CO₂ for solar fuel production. The objectives and scope of this thesis are summarized as following to meet such challenges:

- 1) To improve the stability of dye-sensitized H₂ evolution system. In a typical dye-sensitized system, stability is a main concern, which needs to be improved greatly. Suitable support (like LDH) for the sensitizer was developed to increase the stability of the dye-sensitized system without deteriorating its activity. This work is presented in Chapter 3.
- 2) Besides organic dye photosensitizer, a more stable photo-absorber, polymeric-like C₃N₄ was employed to develop stable, efficient and economical photocatalysts for H₂ evolution and CO₂ reduction. In Chapter 4, C₃N₄ was modified through *in situ* S doping and mesoporous structure formation to enhance the H₂ evolution activity significantly with Pt as the cocatalyst. Noble metal-free cocatalyst NiS was developed to make the C₃N₄-based photocatalyst more economical towards H₂ evolution. On the other hand, the self-assembly of LDH and C₃N₄ was constructed to enhance the efficiency of CO₂ reduction by CO₂ enrichment and fixation in LDH interlayers. These three parts of the work are presented in Chapters 4, 5 and 7, respectively.
- 3) To develop systematic analytical methods for identification and quantification of products from CO₂ reduction. In Chapter 6, systematic methods based on GC and HPLC are presented for the screening of CO₂ reduction products with low detection limits.

In a word, this thesis mainly focuses on the development of more efficient and stable photocatalytic systems for solar fuel production by H₂O splitting and CO₂ reduction. It includes the new modification strategies and investigation of the photoreaction mechanism as well as the setup of analytical methods for CO₂ reduction.

1.3 Major contributions of the thesis

The contributions of this thesis work are summarized as below:

- 1) LDH was found to be a good platform to construct dye-LDH-Pt system by using the electronic static force between positively charged LDH and negatively charged xanthene dyes. The system shows enhanced H₂ production with better stability compared with the LDH free system.
- 2) Modification of carbon nitride by *in situ* S doping and mesoporous structure formation was achieved by using thiourea as the single precursor and SiO₂ as the template. The enhanced light absorption due to S doping and high surface area owing to mesoporous structure result in greatly enhanced photocatalytic activity for H₂ evolution with the highest apparent quantum efficiency among the carbon nitride based photocatalysts at the time of report.
- 3) NiS was developed as noble metal-free cocatalyst on carbon nitride via hydrothermal method. The NiS loading percentage and hydrothermal reaction temperature were found to have great influence on photocatalytic activity. A small loading percentage of NiS on C₃N₄ can lead to remarkable enhancement of H₂ evolution.
- 4) Systematic analytical methods with low detection limits were developed for screening of CO₂ reduction products in both gas and liquid phases. The effects of organic additives on the analysis of liquid oxygenates were investigated.
- 5) Well-dispersed MgAl LDH was found as a novel platform for CO₂ enrichment and fixation by using its anion exchange capacity. This positively charged LDH can be readily self-assembled with the negatively charged C₃N₄ suspension. The photoreduction of concentrated and fixed CO₃²⁻ in LDH interlayer was found to be more efficient than free gaseous CO₂.

CHAPTER 2 LITERATURE REVIEW

2.1 Basic principle of photocatalysis

The basic processes of semiconductor photocatalysis for water splitting and carbon dioxide reduction are shown in Figure 2-1. The energy difference between the top of valence band (VB) and the bottom of conduction band (CB) is referred to band gap (BG). The band gap, position of conduction band and valence band of a semiconductor are three important factors for photocatalysis. Only under irradiation of light with wavelength shorter than certain value ($1240/\text{BG}$, BG in eV), the semiconductor can be excited and electron-hole pairs are generated. The electron can be excited to the CB level and further transported to surface active sites (like Pt, Pd) for H_2O reduction or CO_2 reduction. Meanwhile, the separated hole in the VB can be used for H_2O oxidation. In addition, organic or metal-organic compounds may also be used as non-semiconductor photocatalyst. Unlike the semiconductor photocatalyst, which is usually dispersed in the form of suspension, the organic or metal-organic photocatalyst can be dissolved in either water or certain organic solvent. Such system is called homogeneous photocatalytic system. The basic mechanism of homogeneous photocatalysis is similar to that of semiconductor photocatalysis. In homogeneous system, lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of photocatalyst are used instead of CB and VB. Typical photocatalysts for H_2O splitting and CO_2 reduction are introduced in the section of 2.2 and 2.3.

Figure 2-1 Mechanism of photocatalytic water splitting and carbon dioxide reduction.

2.2 Water splitting

Since the landmark work by Fujishima and Honda in *Nature* in 1972,¹¹ water splitting has been widely studied. As introduced above, either a semiconductor or organic containing compound can be used as photocatalyst. According to the phase of photocatalysts, the photocatalytic water reduction (PWR) can be divided into two major categories: heterogeneous PWR using semiconductor nanoparticle suspension and homogeneous PWR that usually involved a non-semiconductor photocatalyst, a photo-sensitizer and a sacrificial reagent. The other half reaction of water splitting is photocatalytic water oxidation (PWO), which is important to finally construct overall water splitting after coupling with the PWR system. This thesis was mainly focused on the PWR system while advancement of the PWO system will be briefly reviewed.

2.2.1 Homogeneous PWR

Homogeneous or molecular PWR has received great attention in the last three decades,¹²⁻²³ which mainly used the water soluble metal complex, especially the ruthenium complex as photocatalyst. As early as 1978, a binary $\text{Ru}(\text{bpy})_3^{2+}$ - $\text{Co}(\text{bpy})_3^{2+}$ complex has been reported to produce H_2 .²⁴ $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ was also developed by Goldsmith et al. for homogeneous H_2 evolution.¹⁸ A cobalt-based complex was developed as the photocatalyst for molecular H_2 generation, either with the photosensitizer of Pt complex²² or xanthene dyes (Eosin Y¹³ and later element-substituted Rhodamine¹⁵). The turnover number of these systems was reported to be as high as 9000. However, the

activity usually ceased within 4 h.^{13,15,22} Besides, the synthesis procedures of metal complex are usually complicated and costly. Compared with metal complex systems, another kind of homogeneous system using xanthene dyes as photosensitizer is more economically practical considering that xanthene dye is cheaper than the precious metal complex. A system using one of xanthene dyes, rose bengal, as photosensitizer and Pt as photocatalyst was constructed to produce H₂ with an apparent quantum efficiency of 11.3% at 420 nm but deactivated quickly.²³ In general, the homogeneous systems suffer from the photo-degradation of either metal complex or the photosensitizer which limits their application. Further examination on the degradation process and search for a suitable platform for stability enhancement without deteriorating activity are necessary and crucial.

2.2.2 Heterogeneous PWR

Among the over 130 heterogeneous photocatalysts that have been investigated, TiO₂ is the most widely studied one.^{10,25-29} TiO₂-based photocatalysts have many advantages, such as easy preparation, low cost, high photo-stability, and non-toxicity, etc. Native TiO₂ is not visible-light-responsive due to its wide band gap between 3.0 to 3.2 eV. Although doping (metal or non-metal) and sensitization (by using dye or other semiconductors) can induce visible light absorption for TiO₂, their activity and quantum efficiency are usually inefficient.^{25,26,30-32} Another well-studied system is the solid solution of CdS-ZnS which combined the advantages of CdS (visible light response) and ZnS (high conduction band).^{29,33-37} However, the application is limited due to its photocorrosion and the toxicity.²⁹ GaN-ZnO is another typical and efficient photocatalyst which was developed by Domen's group.^{10,38} The synthesis of such materials usually requires rather high temperature which needs to consume additional energy. Considering practical application, novel photocatalysts still need to be developed and designed to meet the following requirements: 1) high activity under visible light; 2) long durability; 3) economically acceptable. The new emerging graphitic C₃N₄, which is composed of earth-abundant carbon and nitrogen elements, is likely to meet these challenges.

C₃N₄ is one kind of diamond-like polymeric semiconductors. The derivatives of C₃N₄ have been synthesized by Berzelius and named by Liebig as "melon" in 1834 which is regarded as the oldest polymer that has been synthesized in history.³⁹ However,

it is not until last decades that many works dedicated to the synthesis and applications of this polymer. Many methods including thin layer deposition,⁴⁰ solvothermal method,⁴¹ solid state reaction^{42,43} and thermal decomposition⁴⁴⁻⁴⁶ have been developed to prepare C_3N_4 ; different kinds of applications including metal free catalyst for Friedel-Crafts reaction,^{39,47} nitriles and alkynes cyclisation^{39,48} and photocatalyst for H_2 evolution,⁴⁹⁻⁵⁶ O_2 evolution^{49,54} and dye pollutant degradation^{46,50,57-60} have been studied.

The application of C_3N_4 in photocatalysis was discovered very recently.⁵⁴ Graphitic C_3N_4 as reported to be able to produce H_2 and O_2 by using different sacrificial reagents in 2008.⁵⁴ Since then, many works have been done for the further study of this material in photocatalysis. The up-to-date reports of C_3N_4 for H_2 evolution were summarized in Table 2-1. Several techniques have been developed and employed to improve the performance of this material:

1) Creating mesoporous structure in C_3N_4 . The mesoporous C_3N_4 with open crystalline pore wall and larger surface area can facilitate mass transfer and strengthen light harvest capacity, thus enhancing the H_2 production rate.^{37, 38}

2) Doping with non-metal element, such as sulphur^{49,50} or phosphorus⁶¹. The doping can introduce new electronic level to change electron mobility and therefore leads to enhanced performance in H_2 evolution,^{49,50} O_2 evolution⁴⁹ as well as dye pollutant degradation.⁵⁰

3) Incorporation with organic molecules⁶² or other semiconductors.^{51,59} Zhang et al reported that around $30 \mu\text{mol h}^{-1}$ rate of H_2 evolution can be achieved after copolymerization for C_3N_4 .⁶² Another work combined the C_3N_4 with N-doped $H_2Ta_2O_6$ reached an apparent quantum efficiency up to 4.8% at 420 nm.⁵¹ Besides, poly(3-hexylthiophene) (P3HT) was used to form the polymer composite of C_3N_4 -P3HT and 300 times enhancement of H_2 production was achieved compared with that of C_3N_4 .⁶³ The composite of CdS quantum dot/ C_3N_4 was reported to increase the light absorbance and electron transfer efficiency.⁶⁴ As a result, 9 times higher activity for H_2 evolution was obtained over native C_3N_4 without CdS quantum dot.

4) Sensitization with organic dyes. Takanable et al. employed magnesium phthalocyanine (MgPc) to broaden the light absorption spectrum of mesoporous C_3N_4 . However, MgPc only works when 640 nm cutoff filter was used, but deteriorates the H_2 evolution rate when using 420 nm cutoff filter.⁶⁵

Despite these aforementioned achievements, the activity of C_3N_4 is still quite low compared with other well-known photocatalysts such as TiO_2 and $CdS-ZnS$.^{25,66} Therefore further studies are necessary to make it an efficient photocatalyst. On the other hand, as summarized in Table 2-1, noble metal like Pt is usually used to make C_3N_4 active. Without Pt, native C_3N_4 barely produces not more than $1 \mu\text{mol h}^{-1} \text{H}_2$. The introduction of noble metals will increase the cost of this system greatly. Hence, noble metal-free cocatalysts need to be developed to make C_3N_4 based photocatalyst more economical.

Table 2-1 Summary of C_3N_4 based photocatalysts for H_2 evolution.

Systems	H_2 , $\mu\text{mol h}^{-1}$	Notes	Ref.
C_3N_4	0.1-4	-	54
Pt/ C_3N_4	18	-	52
Pt/ $C_3N_{4-x}F_x$	12	fluorinated C_3N_4	62
Pt/ C_3N_4B	29.4	Incorporated with barbituric acid	62
Pt/ C_3N_4/KT	20	KT: N-doped $H_2Ta_2O_6$	51
Pt/ $C_3N_{4-x}S_x$	35	sulfur doped C_3N_4	50
Pt/ $C_3N_{4-x}S_x$	140.5	sulfur mediated C_3N_4	49
Pt/ $C_3N_4/P3HT$	560	P3HT: poly(3-hexylthiophen)	63
mp C_3N_4	0.2	mesoporous C_3N_4	52
Pt/mp C_3N_4	149	-	52
MgPc/Pt/ C_3N_4	4.5	MgPc: magnesium phthalocyanine	65
Pt/ CdS/C_3N_4	17.3	-	64
Ni(OH) ₂ / C_3N_4	7.6	-	67
Pt/HCNS	224	HCNS: hollow carbon nitride nanosphere	68
Pt/polypyrrole/ C_3N_4	15.4	In pure water	69

2.2.3 Water oxidation and overall water splitting

Compared with PWR, which only involved the transfer of 2 electrons, the oxidative side of water splitting i.e. PWO requires 4 electrons to participate in the reaction thus it is more complicated and difficult. The importance of PWO is recently recognized owing to its bottleneck role to construct a Z-scheme water splitting system. Increasing attention has been paid to this emerging area recently. For example, a special forum focused on PWO was highlighted in the *Inorganic Chemistry* journal.⁷⁰ Some of the

typical results on PWO are summarized in Table 2-2. WO_3 is the most well studied photocatalyst for PWO, and it is also often used for comparison when developing new PWO photocatalyst.⁷¹⁻⁷⁴ So far, the record of O_2 evolution under visible light is $636 \mu\text{mol h}^{-1}$ by using Ag_3PO_4 as photocatalyst and AgNO_3 as sacrificial reagent with an apparent quantum efficiency of around 90% at 420 nm.⁷³ However, the activity quickly ceased after 2 h. Hence, PWO catalysts with better stability still need to be developed.

Table 2-2 Summary of typical photocatalytic water oxidation systems.

Photocatalysts	Sacrificial Reagent	O_2 , μmol	Ref.
WO_3	AgNO_3	13.7/1 h	⁷⁴
WO_3	AgNO_3	12/2 h	⁷¹
Co^{2+}	KPi^c	95/10 h	⁷⁵
$\text{Co}_3\text{O}_4/\text{SBA}^a$	$\text{Na}_2\text{S}_2\text{O}_8$	150/3 h	⁷⁶
ZnCr LDH	AgNO_3	64.4/3 h	⁷²
$\text{IrO}_2\text{-ZnO/ZnGeON}$	AgNO_3	225/1 h	⁷⁷
Ag_3PO_4	AgNO_3	636/1 h	⁷³
$\text{IrO}_2\text{-ZnDPEG}^b$	$\text{Na}_2\text{S}_2\text{O}_8$	28/1 h	⁷⁸
CaMn_2O_2	Ce^{4+}	413/5 h	⁷⁹
$[\text{Co}_4(\text{H}_2\text{O})(\text{PW}_9\text{O}_{34})_2]^{10-}$	$\text{Ru}(\text{bpy})_3^{3+}$	-	⁸⁰

^a SBA: SBA-15 zeolite; ^b ZnDPEG: Zinc deuteroporphyrin IX bis- ethylene glycol; ^c KPi: potassium phosphate.

Although a few semiconductors like GaN-ZnO system do show the ability to split the water directly over single photocatalyst (as shown in Figure 2-2A), the activity is extremely low ($0.06 \mu\text{mol h}^{-1} \text{ H}_2$ and $0.03 \mu\text{mol h}^{-1} \text{ O}_2$) under visible light.³⁸ It is difficult to find such semiconductors that both 1) have suitable band edge to produce H_2 and O_2 simultaneously and 2) response to visible light (band gap narrower than 3 eV).⁸¹ In comparison, it is more promising to construct a Z-scheme water splitting (as shown in Figure 2-2B) by combining a H_2 evolution system with an O_2 evolution system using a pair of electron mediator. Typical systems of Z-scheme overall water splitting are summarized in Table 2-3. These Z-scheme water splitting systems show higher activity than direct water splitting. To develop more efficient Z-scheme water splitting systems, great efforts are needed to search for suitable PWR and PWO photocatalysts and their corresponding cocatalysts as well as electron mediators.

Sacrificial reagents are generally needed to evaluate the half reaction of water reduction or water oxidation.²⁸ The common sacrificial reagents for water reduction are alcohols (methanol, ethanol, etc), sulfides/sulfites (sodium sulfide, sodium sulfite or

mixture of both), amines (triethanolamine, triethylamine, etc.), and acids (lactic acid, ascorbic acid, etc.). The common sacrificial reagents for water oxidation are silver salt, iron salt and persulfate salt, etc. The purpose of adding sacrificial reagent is to serve as electron donors and hole scavengers, thus the thermodynamic possibility and kinetic affecting parameters can be studied for particular systems. The evaluation of half reaction photocatalyst is important to sort out those promising ones and can be finally tested for overall water splitting. However, a good half-reaction photocatalyst using sacrificial reagent cannot guarantee a good overall water splitting photocatalysts. In the current work, sacrificial reagents were used for the study of water reduction photocatalyst but they should be avoided in the future work on overall water splitting.

Figure 2-2 Schematic diagrams of direct water splitting system (A) and Z-scheme water splitting system (B).

Table 2-3 Summary of typical Z-scheme water splitting systems.

H ₂ photocatalyst	O ₂ photocatalyst	Mediator	H ₂ , μmol h ⁻¹	O ₂ , μmol h ⁻¹	Ref.
Pt/SrTiO ₃ :Cr, Ta	Pt/WO ₃	IO ₃ ⁻ /I ⁻	16	8	82
Pt/TaON	Pt/WO ₃	IO ₃ ⁻ /I ⁻	24	12	83
Pt/CaTaO ₂ N	Pt/WO ₃	IO ₃ ⁻ /I ⁻	6.6	3.3	84
Ru/SrTiO ₃ :Rh	BiVO ₄	-	40	19	85
Pt/ZrO ₂ /TaON	Ir/R-TiO ₂ /Ta ₃ N ₅	IO ₃ ⁻ /I ⁻	3	1	86
Pt/ZrO ₂ /TaON	Pt/WO ₃	IO ₃ ⁻ /I ⁻	52.1	26.7	87
Ru/SrTiO ₃ :Rh	BiVO ₄	[Co(bpy) ₃] ^{3+/2+}	100	47	88
Pt/BaZrO ₃ -BaTaO ₂ N	TiO ₂ rutile	Fe ³⁺ /Fe ²⁺	21.3	9.5	89

2.2.4 Summary

From the above literature review, the stability is one major problem for homogeneous PWR system which needs to be solved. Heterogeneous PWR system is generally more stable but the efficiency under visible light is another concern. From literature study, C₃N₄ would be an ideal candidate for photocatalyst although its study is still in the early state. Modification including doping and structure tuning may make C₃N₄ more efficient while non-noble metal cocatalyst need to be developed to make C₃N₄ based photocatalyst more economical. The PWR systems studied in this thesis can be possibly employed to construct Z-scheme water splitting system after coupling with suitable water oxidation photocatalyst.

2.3 Carbon dioxide reduction

Compared with water splitting, the study of photocatalytic carbon dioxide reduction is still limited. The reaction of CO₂ reduction is more complicated than water splitting. It is a multi-electron reaction and several kinds of compounds including gaseous CH₄, CO, etc. or liquid oxygenates (alcohol, aldehyde, acid, etc.) may exist in reduction products. Currently, no systematic analytical method has been studied and proposed for this reaction. The efficiency of CO₂ reduction is still very low especially under visible light.

2.3.1 Reaction paths and product analysis

There are two main evolution routes of CO₂ reduction as indicated in Figure 2-3. In the first route, CO₂ is firstly transformed into formic acid, and then gradually reduced to

formaldehyde, methanol and finally methane; in the other route, CO₂ is gradually reduced to CO, C, CH₂ and finally CH₄. Both of these two paths involve 8 electrons in the total reduction of CO₂ to CH₄. These multi-electrons chain reactions make it very difficult to reduce the CO₂ efficiently.

Path a:

Path b:

Figure 2-3 The evolution routes from CO₂ to CH₄.

The reaction path as well as products generated from CO₂ reduction is largely affected by the band structure of semiconductor photocatalyst used. As early as 1979, Inoue et al. have shown that SiC, CdS, ZnO, TiO₂ and WO₃ can reduce CO₂ to formic acid (HCOOH), formaldehyde (HCHO), CH₃OH and CH₄, depending on the used photocatalyst.⁹⁰ The HCHO and CH₃OH concentrations were higher when SiC was used, while no CH₃OH was obtained when WO₃ was used.⁹⁰ These results are consistent with the relationship of band position with redox potential of CO₂ reduction reactions. The conduction band of SiC is higher than all the redox couples in water, while that of WO₃ is lower than that of CH₄/CO₂ and close to that of CH₃OH/H₂CO₃.

The band position of typical semiconductors and the redox potential of several CO₂ reduction involved reactions were summarized in Figure 2-4. As shown in Figure 2-4, different reaction paths and products exist, based on different photocatalyst used and their conduction band versus the redox potential of CO₂ reduction reactions. Currently, many groups practically adopted the routine analysis of one or two products in either gas or liquid phase for evaluation of the photocatalytic efficiencies. Only a few works have paid attention to the screening of CO₂ reduction products. Alonso-Vante et al. reported the screening of C1-C3 compounds from CO₂ photoreduction.⁹¹ In their work, products including CH₄, CH₃CH₃, CH₃OH, ethanol (CH₃CH₂OH) and acetone (CH₃COCH₃) were analyzed by GC with two different columns while formic acid (HCOOH) and formaldehyde (HCHO) were analyzed by Nash's method. In another work by Yui et al, hydrocarbons, CO, CH₃OH, CH₃CH₂OH, HCHO and acetaldehyde (CH₃CHO) were analyzed by GC while HCOOH and acetic acid (CH₃COOH) were detected by ion-exchange chromatography (IEC).⁹² Over 16 CO₂ reduction products over Cu electrode were identified and quantified using combined methods of GC, ¹H

nuclear magnetic resonance (NMR) spectroscopy and ^{13}C NMR.⁹³ Despite these works, the accuracy of different used methods may be varied and some techniques like NMR may not be suitable for routine quantification. To evaluate the performance of photocatalyst properly and effectively, more systematic methods for CO_2 reduction products analysis need to be set up.

Figure 2-4 The correlation of semiconductor band position and redox potential of carbon dioxide reduction.⁹⁰ [Reprinted by permission from Macmillan Publishers Ltd: \[Nature\] \(ref 12\), copyright \(1979\).](#)

2.3.2 Recent advances on CO_2 reduction

Up to date, it is still a big challenge to develop an efficient photocatalyst for CO_2 reduction. Lots of semiconductors have been examined for possible photocatalyst to reduce CO_2 . The recent reported TiO_2 -based and non TiO_2 -based photocatalyst systems were summarized in Table 2-4 and Table 2-5, respectively.

TiO_2 -based systems. Similar to water splitting, TiO_2 and its derivatives are the most widely studied systems for CO_2 reduction. Halmann et al. examined several TiO_2 based semiconductors including TiO_2 , SrTiO_3 and CaTiO_3 for CO_2 reduction using sunlight.⁹⁰ The highest energy conversion efficiency of 0.016% can be achieved by using SrTiO_3

in the medium of LiHCO_3 and 518.8 nmol HCOOH , 9.4 nmol HCHO , 4.4 nmol CH_3OH and 8.4 nmol CH_3CHO can be obtained.⁹⁴ KTiO_3 was also used as a photocatalyst for reducing CO_2 to CH_4 , HCOOH and HCHO together with the reduction of water into H_2 .⁹⁵ When a dealuminated Y-type zeolite was used to form a hybrid together with KTiO_3 , additional CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ were produced besides the above products.⁹⁶ Zinc-phthalocyanine (ZnPc),⁹⁷ cobalt-phthalocyanine (CoPc),⁹⁸ tris (2,2'-bipyridyl) ruthenium(II) chloride hexahydrate ($\text{Ru}(\text{bpy})_3^{2+}$)⁹⁹ and N3 dye¹⁰⁰ were used also to construct sensitized- TiO_2 photocatalyst, respectively.

Morphology control of both TiO_2 and its loaded cocatalyst are another research focuses. Engineering the crystal structure,¹⁰¹ fabricating periodically modulated multiwalled nanotube arrays,¹⁰² coating Pt nanoparticle¹⁰³ or Pt- Cu_2O core/shell as cocatalyst¹⁰⁴ were reported for TiO_2 based photocatalysts. Nanocomposite of rutile TiO_2 nanoparticles decorated anatase TiO_2 nanorods,¹⁰¹ Pt-Cu decorated TiO_2 nanotube array,¹⁰² and ordered mesoporous CeO_2 - TiO_2 composites¹⁰⁵ were prepared respectively. All these modifications can enhance the CO_2 reduction over pristine TiO_2 . Hybrid CuO-N-doped TiO_2 with a hollow nanocube structure was designed and twice higher CH_4 production activity over traditional impregnated CuO/ TiO_2 can be obtained.¹⁰⁶ Wang et al. coated the TiO_2 film with ultrafine Pt nanoparticle of controllable size through a sputtering system and found that Pt with diameter of 1 nm as cocatalyst can give highest CH_4 production while the CO production was inhibited.¹⁰³ Based on the commercial P25 TiO_2 , Choi and co-workers found that simply coating a layer of proton conducting Nafion can make the Pd/P25 more active towards CO_2 reduction for CH_4 production.¹⁰⁷ High activity of 3 $\mu\text{mol h}^{-1}$ CH_4 can be achieved, which was mainly attributed to more efficient proton-coupled electron transfer facilitated by the Nafion layer.¹⁰⁷ By a step-by-step *in situ* photoreduction method, Pt- Cu_2O with core/shell structure was loaded on TiO_2 as binary cocatalyst leading to a higher activity and a better selectivity for CH_4 production.¹⁰⁴

Table 2-4 Summary of TiO_2 based photocatalyst for CO_2 reduction.

Semiconductor system	Reaction medium	Light source	Product/Rate ($\mu\text{mol h}^{-1}$)	Ref.
CdSe/Pt/ TiO_2	CO_2 and H_2O in gas phase	300 W Xe lamp, >420 nm	CH_4 /0.18, CH_3OH /0.01	77
Cu, Pt/N- TiO_2 nanotube array film	CO_2 and H_2O	Natural outdoor sunlight	CH_4 , $\text{C}_n\text{H}_{2n+2}$, C_nH_{2n} /total: 32 $\text{nmol cm}^{-2} \text{h}^{-1}$	108

		The above with a filter, >400 nm	3% of the above rate	
Enzyme-TiO ₂	CO ₂ and H ₂ O	45 mW.cm ⁻² , > 420 nm	CO/1.25	109
Cu/TiO ₂	CO ₂ and H ₂ O	2.4mW/cm ⁻²	CO/6.0, CH ₄ /0.85	110
AgBr/TiO ₂	CO ₂ (75 atm) and H ₂ O	150 W Xe lamp, > 420 nm	CH ₄ /12.9, CH ₃ OH/7.9, CH ₃ CH ₂ OH/1.3, CO/3.2	111
N-Ni/TiO ₂	CO ₂ and H ₂ O	15 W lamp, 400-780 nm	CH ₃ OH/6.0	112
CuO/TiO ₂	CO ₂ and CH ₃ OH	250 W Hg lamp, UV-vis ^a	HCOOCH ₃ /48.0	113
TiO ₂	CO ₂ and H ₂ O in gas phase	100 W UV lamp, $\lambda = 365$ nm	CH ₄ /0.002, QE ^c = 10 ⁻³ at 365 nm	114
Pt/TiO ₂	CO ₂ and H ₂ O in gas phase	AM 1.5G sunlight (100 Mw cm ⁻²)	CH ₄ /1.6	115
Au/TiO ₂	CO ₂ and H ₂ O	UV-vis	CH ₄ /22.5	116
TiO ₂	CO ₂ and H ₂ O	500 W Hg lamp, >310 nm	CO/0.05	92
Pd/TiO ₂			CH ₄ /0.06	
Rutile TiO ₂ / Anatase TiO ₂	CO ₂ and H ₂ O	300 W Hg lamp	CH ₄ /2.36	101
Pt-Cu/TiO ₂	CO ₂ and H ₂ O	AM1.5	CH ₄ /0.02 mL h ⁻¹	102
Nafion/TiO ₂	CO ₂ in Na ₂ CO ₃	300 W Xe lamp, > 300 nm	CH ₄ /3	107
Pt-Cu ₂ O/TiO ₂	CO ₂ and H ₂ O	200 W Xe lamp, 320-780 nm	CH ₄ /0.66 CO/0.16 H ₂ /0.5	104

^a UV-vis: Ultraviolet-visible light

Other systems. Native CdS has been well studied for H₂ evolution under visible light, but only few papers have been reported for CO₂ reduction. This may be due to the fact that CdS is highly corrosive and relative low efficiency as reported.^{117,118} Some metal oxides such as BiVO₄¹¹⁹ and InTaO₄¹²⁰ were also examined for CO₂ reduction with the major products composed of alcohols. Compared with other systems, the rate is relatively higher (21.6 $\mu\text{mol CH}_3\text{CH}_2\text{O h}^{-1}$) by using BiVO₄. SiC is another promising photocatalyst for CO₂ reduction due to its high conduction band. However, most of reports so far are mainly focused on its application as photochemical electrode using UV light as source usually.^{97,142} Porous gallium oxide (Ga₂O₃) was found to have 5 times higher activity for CH₄ production than non-porous gallium oxide which is

mainly due to the increasing of surface area and enhancement of CO₂ adsorption capacity.¹²¹ Similarly, mesoporous or sheaf-like, hyperbranched Zn₂GeO₄ were also reported to promote CO₂ reduction.¹²² Mesoporous ZnAl₂O₄ was used to modify the ZnGaNO solid solution aiming to increase both physical adsorption and chemisorption of CO₂ as well as light absorption.¹²³ Titanium metal-organic framework (MOF) was synthesized and used for CO₂ reduction to produce formic acid for the first time.¹²⁴ Chaudhary et al. used biomimic system, enzyme coupled CdS, for CO₂ reduction following their previous works on enzyme-coupled metal oxides system.¹²⁵ Graphene oxide was also reported active for photocatalytic CO₂ reduction.¹²⁶ Six-fold enhancement for methanol production was achieved compared with pure TiO₂. MgIn LDH was also reported to reduce CO₂ to CO with simultaneous O₂ production.¹²⁷ Enzyme-graphene coupled system was constructed for efficient photocatalytic production of HCOOH from CO₂.¹²⁸ Contrast to the heterogeneous CO₂ reduction systems introduced above, there are also many studied homogeneous CO₂ reduction systems. The later was not covered in this thesis but can refer to several available reviews.^{129,130}

Table 2-5 Summary of non-TiO₂ based photocatalyst for CO₂ reduction.

Semiconductor system	Reaction medium	Light source	Product/Rate (μmol h ⁻¹)	Ref.
Pt/ZnAl ₂ O ₄ /ZnGaNO	CO ₂ and H ₂ O in gas phase	300 W Xe lamp, >420 nm	CH ₄ /2.5	131
Micro/mesoporous Zn ₂ GeO ₄	CO ₂ and H ₂ O in gas phase	UV-vis, 300 W Xe lamp	CH ₄ /1.9	132
N-Ta ₂ O ₅ /Ru complex	CO ₂ saturated ACN/TEOA solution	500 W Xe lamp, >410 nm	HCOOH/3.5	133
Cu ₂ O/SiC	CO ₂ and H ₂ O	500 W Xe lamp, >400 nm	CH ₃ OH/7.6	134
ZnCuAl LDH	CO ₂ , H ₂ O and H ₂	500 W Xe lamp, UV-vis	CH ₃ OH/0.02, CO/0.058	135
Pt/ZnAl ₂ O ₄ /ZnGaNO	CO ₂ and H ₂ O in gas phase	300 W Xe lamp, >420 nm	CH ₄ /0.5	136
Pt/meso-ZnGaON	CO ₂ and H ₂ O in gas phase	300 W Xe lamp, >400 nm	CH ₄ /0.06	123
Ag/BaLa ₄ Ti ₄ O ₁₅	CO ₂ and H ₂ O	400 W Hg lamp	H ₂ /10; O ₂ /7; CO/4.3; HCOOH/0.3	137

Pt/NaNbO ₃	CO ₂ and H ₂ O	300 W Xe lamp	CH ₄ /1.7	138
Enzyme-CdS	CO ₂ and MES ^a	250 W Tungsten Halogen lamp, >420 nm	CO/0.75	125
MgIn LDH	CO ₂ and H ₂ O in gas phase	200 W Xe(Hg) lamp	CO/0.3	127
Graphene/porphyrin	CO ₂ /TEOA	450 W Xe lamp, > 420 nm	HCOOH/60	128
Graphene oxide	CO ₂ and H ₂ O	300 W Halogen lamp	CH ₃ OH/0.03	126

^a MES: 2-(N-morpholino)ethanesulfonic acid.

2.3.3 Summary

Presently, two major challenges are existent for CO₂ reduction: 1) the accurate detection of reduction products; 2) the low efficiency of reduction. Unlike water splitting which only have products of H₂ and O₂, several different compounds like gaseous CH₄, CO etc. or liquid oxygenates (alcohol, aldehyde, acid etc.) may exist in reduction products of CO₂ reduction. Systematic methods need to be developed for accurate analysis for CO₂ reduction products. More importantly, new strategies need to be designed to achieve more efficient CO₂ reduction.

2.4 Summary of literature review

From literature review, it is still a great challenge to make a stable homogeneous PWR system. The work presented in Chapter 3 was dedicated to meet this challenge to improve the stability by employing LDH as supports.

The newly developed C₃N₄ photocatalyst would be an ideal candidate for either water splitting or CO₂ reduction due to its suitable band structure. The efficiency of C₃N₄ was still low and several affecting parameters like morphology, electronic structure and cocatalyst etc. have not been well studied. In Chapter 4, 5 and 7, we focused on the modification of C₃N₄ including doping and structure tuning to make C₃N₄ more efficient. Meanwhile, non-noble metal cocatalyst would be developed to make C₃N₄ based photocatalyst more economical. Moreover, the possibility of using C₃N₄ to reduce CO₂ was investigated through the self-assembly with LDH.

The accurate detection of reduction products and low efficiency of reduction were

two main problems for CO₂ reduction. Systematic methods developed in Chapter 6 were to tackle the first problem. Meanwhile, the investigation of C₃N₄ for CO₂ reduction was presented in Chapter 7.

CHAPTER 3 SELF-ASSEMBLED DYE-LAYERED DOUBLE HYDROXIDE-Pt NANOPARTICLES: A NOVEL H₂ EVOLUTION SYSTEM WITH REMARKABLY ENHANCED STABILITY

(This Chapter is adapted from “Hong, J. D.; Wang, Y. B.; Pan, J. S.; Zhong, Z. Y.; Xu, R., Self-assembled dye-layered double hydroxide-Pt nanoparticles: a novel H₂ evolution system with remarkably enhanced stability. *Nanoscale* **2011**, *3* (11), 4655-4661.” Reproduced with permission of The Royal Society of Chemistry)¹³⁹

3.1 Introduction

As introduced in Chapter 2, increasing research efforts have been spent on the homogeneous (or molecular) H₂ evolution systems which usually involve a non-semiconductor photocatalyst, a photosensitizer (e.g., dye molecules) and a sacrificial reagent.^{12-15,21-23,140,141} Photoexcitation of dye molecules results in the generation of excitons (bound electron-hole pairs) which are separated into the free charge carriers. The electrons are injected into the photocatalysts causing reduction of water to H₂, while the reaction between the sacrificial donor and oxidized dye brings the dye back to its ground state. Eisenberg and co-workers have reported a series of homogeneous H₂ evolution systems.^{13,15,22,142,143} For example, cobalt-based complex was developed as the photocatalyst for molecular H₂ generation, together with the photosensitizers of Pt complexes²² or xanthene dyes.^{13,15} The turnover number of these systems was reported to be as high as 9000, however, the activity usually ceased within a few hours. Okeyoshi and Yoshida reported the condensation of Ru(bpy)₃²⁺ photosensitizer and loading of Pt photocatalyst in a polymer gel. A higher quantum efficiency at 460 nm was reported compared with the homogeneous solution system.¹⁶ Despite these achievements, the molecular H₂ generation systems reported so far still suffer from either the instability of the metal complex catalysts or the fast degradation of photosensitizers which limit their applications. Very few works have paid attention to the stability issue to date. For example, Abe et al. reported that the stability of Eosin Y can be significantly improved by covalently grafting it on TiO₂ but consequently the activity was reduced to half.¹⁴⁴ Therefore, it remains a great challenge to develop both active and stable H₂ production systems involving photosensitizers. Major challenges are to achieve maximum exciton generation in dye molecules followed by dissociation,

and efficient electrons injection into the photocatalysts followed by a rapid electrochemical reaction of water splitting. Hence the interfacial properties between the photosensitizer and photocatalyst could be important factors in controlling these processes.

LDHs, also known as anionic clay, have attracted considerable attention due to their interesting physicochemical properties such as large surface areas, positively charged surface and compositional flexibilities.^{145,146} LDHs consist of positively charged brucite-like layers which are intercalated with anions and water molecules in the interlayer space.¹⁴⁵ The general formula of LDHs can be expressed as $[M(II)_{1-x}M(III)_x(OH)_2]^{x+} (A^{n-})_{x/n} mH_2O$ (where M = metal, and A = interlayer anion).¹⁴⁵ LDHs have been widely studied in catalysis,^{145,147} adsorption,^{148,149} biomedical areas^{150,151} and so on. In particular, LDHs have been demonstrated as potential materials in photocatalysis.^{72,152-154} For example, hierarchically nanostructured metal oxides generated from the LDH precursors were used in photocatalytic degradation of dyes.¹⁵⁴ Zn-Cr-LDHs were found be able to produce O₂ under visible light.⁷² LDHs prepared by conventional methods usually consist of loose powders of irregular aggregates.^{145,146} It has been reported that hydrothermally treated LDHs can be present in the form of colloidal nanosheets dispersible in the liquid phase.¹⁵⁵ Thus the colloidal LDH sheet-like nanocrystals can be utilized as the building blocks for self-assembly of functional nanomaterials.^{149,156}

In this Chapter, well-dispersed LDH nanocrystals were used to construct a photocatalytic H₂ evolution system with remarkably enhanced activity and stability. The multi-component colloidal system consists of LDHs as the support, immobilized Pt nanoparticles as the photocatalyst and adsorbed rose bengal (RB) as the photosensitizer.

3.2 Experimental

3.2.1 Preparation of samples

The aqueous suspension of well-dispersed LDH was prepared as following. Briefly, 8 mL of the mixed aqueous solution of Mg(NO₃)₂ 6H₂O and Al(NO₃)₃ 9H₂O (0.4 M and 0.1 M, respectively) was dropwise added into 32 mL of 0.15 M NaOH aqueous solution under vigorous stirring. After aging for a short period of 10 min, the gel was collected by centrifugation at 20,000 rpm for 5 min, washed with deionized water three times, and then re-dispersed in 40 mL of deionized water. The resulting mixture was

transferred into an autoclave for hydrothermal treatment at 100 °C for 16 h. The density of white colored LDH solid in the resulting suspension was determined to be 3.05 mg mL⁻¹ (average of three measured values with $\pm 4\%$ error) by drying 40 mL of the LDH suspension at 60 °C overnight and measuring the weight of dry powder. To immobilize RB on the surface of LDH, RB (sodium salt, 10 μ mol) was added into a desired volume (20, 40, 60, 80 or 90 mL) of LDH suspension and the mixture was stirred for 15 min. At this step, the color of LDH changed from white to dark red which is similar to that of RB, indicating the adsorption of RB on the surface of LDH. Then the aqueous solution of triethanolamine (TEOA) with a desired concentration and volume was added into the RB-LDH suspension to make the total volume to be 100 mL and the concentration of TEOA 5 v%. The mixture was stirred for another 15 min. To determine the amount of immobilized RB on LDH, the final suspension (200 μ L) was withdrawn and centrifuged at 20,000 rpm for 5 min. The concentration of RB in the supernatant solution was measured by UV-visible absorbance spectroscopy (UV-2450, Shimadzu).

3.2.2 Materials characterizations

The powder X-ray diffraction (XRD) patterns were recorded with Bruker AXS D8 X-ray diffractometer equipped with monochromatized Cu K α radiation ($\gamma = 1.54056$ Å, 40 kV and 20 mA). Zeta potential of the RB-LDH suspensions in aqueous solutions of TEOA (5 v% TEOA, pH = 8.5) was measured at room temperature on ZetaPALS Zeta Potential Analyzer Brookhaven Instruments Corporation. Field emission scanning electron microscopy (FESEM, JEOL JSM 6700F) and transmission electron microscopy (TEM, JEOL 3010) were used to obtain the particle size and morphology of the samples. The surface area of LDH was obtained from the adsorption isotherms of nitrogen at -196 °C in a Quantachrome Autosorb-6B apparatus by using the Brunauer–Emmett–Teller (BET) method. The absorption spectra of RB-LDH-Pt and Free systems (RB-Pt without LDH) after photoreaction for 0, 10 and 120 min were obtained by UV-visible absorption spectroscopy (UV-2450, Shimadzu) after dissolving LDH and/or Pt by using 5 wt% of HCl aqueous solutions. Electrospray ionization-mass spectrometry (ESI-MS) was used to analyze the photobleached products of RB in the reaction solution. Mass spectra were recorded on a Thermo Finnigan LCQ Deca XP Max (San Jose, CA) ultra high sensitivity quadruple ion trap mass spectrometer fitted with Surveyor LC Auto Sampler and MS Pump. Acquisition mass range was typically

with m/z 15-4000. Data were recorded and processed using X-Calibur software (Thermo Scientific, MA, USA).

3.2.3 Photocatalytic activity evaluation

Photocatalytic reaction was carried out in a closed circulation system using a Pyrex cell (total volume about 300 mL with a top irradiation area of around 28 cm²). The as-prepared RB-LDH suspension (100 mL with 5 v% of TEOA) was added into the reaction cell under stirring and the cell was kept at room temperature with cooling water. The pH was adjusted to 8.5 by adding the dilute HNO₃ solution and monitored with a digital pH meter (Lab 850 Set, Schott, Germany). A certain amount of H₂PtCl₆ · xH₂O (2, 6, 10, 15 or 20 μmol) was added into this mixture before the photocatalytic reaction. A 300 W Xeon lamp equipped with a 420 nm cut-off filter (Newport) was used as the visible light source. The amount of produced H₂ was determined using an online gas chromatography (Agilent 6890N, Argon as carrier gas, 5 Å molecular sieve column, TCD detector). The photocatalytic reaction for the Free system was carried out under the same conditions except in the absence of LDH. For comparison, the above well-dispersed LDH was replaced by two other substrates. One was LDH synthesized by a conventional co-precipitation method as described in our earlier work which consisted of aggregated particles.²⁹ This sample was denoted as LDH-control. The other substrate was multi-walled carbon nanotubes (CNano Technology Ltd, purity > 95%), MWNT. Certain amounts of these substrates were used to keep their total surface area the same as that of well-dispersed LDH. Other photocatalytic reaction conditions were also kept the same. Recycle study was carried out for both RB-LDH-Pt and Free systems. After each run (6 h and 2 h for RB-LDH-Pt and Free, respectively), the suspension was centrifuged at 20,000 rpm for 30 min. The solid samples collected were washed with deionized water twice and then re-dispersed in 100 mL of fresh TEOA solution (5 v%, pH = 8.5). After ultrasonication for 15 min, fresh RB (10 μmol) was added into the suspension for the next run. The turnover number (TON) was calculated using the following equation:

$$TON = \frac{n(H_2)}{n(Pt)},$$

Where $n(H_2)$ was the amount of H₂ produced (μmol) and $n(Pt)$ was the amount of initial added Pt (in μmol).

3.3 Results and discussion

The surface of the as-prepared LDH nanocrystals is positively charged with a zeta potential measured to be +47.3 mV. Hence the negatively charged RB species in the aqueous solution can be adsorbed on the external surface of LDH by electrostatic interaction.¹⁴⁹ As shown in Figure 3-1, the zeta potential of the RB-LDH suspensions decreases along with the increasing ratio of RB:LDH (i.e., decreasing the amount of LDH while fixing that of RB) as the surface of LDH is more extensively covered with RB. The percentage of RB adsorbed on LDH was determined and the data are also presented in Figure 3-1. It can be seen that RB is difficult to be completely adsorbed on LDH in the aqueous solution of TEOA. Even at a RB:LDH mass ratio of 1:27, there is still about 1.5% of RB not adsorbed. RB can be fully immobilized on LDH even at a RB:LDH ratio of 1:6 in the absence of TEOA.¹⁴⁹ The TEOA solution may compete with the positively charged LDH surface leading to the distribution of RB in the two phases. At a RB:LDH ratio of 1:18, 76% of RB is adsorbed on the surface of LDH. The measured specific surface area of LDH is about 90 m² g⁻¹. RB could be adsorbed on the surface of LDH in a monolayer since the adsorption is by electrostatic interaction. Based on the estimated molecular size of RB of about 10.9 Å by the ChemOffice software, around 26% of LDH surface is covered with RB when the mass ratio of RB:LDH is 1:18. The remaining surface is available for the deposition of Pt nanoparticles.

Figure 3-1 Zeta potential of the RB-LDH suspensions in aqueous solutions of TEOA

with different mass ratio of RB:LDH (5 v% TEOA, pH = 8.5, amount of RB = 10 μ mol, the amount of LDH was varied, total vol. = 100 mL).

Figure 3-2 shows the XRD patterns of LDH, RB-LDH and RB (sodium salt). The as-prepared LDH sample exhibits a typical rhombohedral LDH structure (Figure 3-2A).¹⁵⁵ The weak diffraction peaks observed at around 20° (marked with *) correspond to a small percentage of Al(OH)₃ impurity phase.^{148,149} The impurity of Al(OH)₃ could be due to the imperfect mixing of the suspension during the synthesis. As Al(OH)₃ has a much lower solubility than that of Mg(OH)₂,¹⁵⁷ the Al(OH)₃ phase inevitably forms during the co-precipitation process.¹⁴⁹ Comparing the diffraction patterns of LDH (Figure 3-2A) and RB-LDH (Figure 3-2B), it can be seen that the negatively charged RB ions are not intercalated in the interlayer space of LDH since the position of the (003) basal peak is unaltered. It is also noted that no extra peaks can be observed, indicating that RB does not form crystals on the surface of LDH. However, RB-LDH exhibits much weaker diffraction intensities than LDH due to the formation of organic-inorganic hybrids.¹⁵⁸ After photocatalytic reaction for 24 h, the LDH structure still can be observed (Figure 3-2C) and the intensity recovered to the same as pristine one due to that most of RB was degraded after light irradiation for 24 h and the peak intensity of Al(OH)₃ is much lower which may gradually dissolved during the reaction.

Figure 3-2 XRD patterns of (A) LDH, (B) RB-LDH (RB:LDH = 1:18) before irradiation, (C) RB-LDH-Pt after irradiation for 24 h, and (D) RB (sodium salt).

The FESEM images of LDH and RB-LDH are displayed in Figure 3-3. The particle size of pristine LDH nanocrystals is around 50-100 nm and their surface are quite smooth. It can be observed that the surface of LDH turns rough after adsorption of RB (Figure 3-3B). A higher magnification image (Figure 3-3B inset) shows that RB forms well distributed amorphous nanoparticles on the surface of LDH upon drying. Compared to LDH, RB-LDH has a lower specific surface area of 72 m² g⁻¹. Such observations and results are in good agreement with those discussed earlier indicating that RB photosensitizer is adsorbed on the surface of LDH nanocrystals.

Figure 3-3 FESEM images of (A) LDH and (B) RB-LDH (RB:LDH = 1:18).

Platinum has been reported as an efficient catalyst for hydrogen production from water because of its high work function and high redox potential.¹⁵⁹ The precursor of the platinum catalyst used in this study (H₂PtCl₆ · xH₂O) was dissolved in the solution of RB-LDH suspension before photoreaction. Upon light irradiation, [PtCl₆]²⁻ was gradually reduced to well-dispersed Pt nanoparticles (2-5 nm) and deposited on the surface of LDH as evidenced by the TEM images (Figure 3-4A and B insets) after 2 h and 24 h of irradiation, respectively. In contrast, Pt nanoparticles formed in the Free system are severely aggregated (Figure 3-4C and D insets), indicating that LDH not only functions as the support but also leads to better dispersed Pt catalyst nanoparticles. The specific surface area of Pt-LDH is around 96 m² g⁻¹ which is slightly higher than that of LDH alone due to a good dispersion of Pt nanoparticles.

Figure 3-4 TEM images of RB-LDH-Pt after (A) 2 h and (B) 24 h of photoreaction, and Free after (C) 2 h and (D) 24 h of photoreaction. The d -spacing of 0.198 nm corresponds well with that of Pt⁰ (200) planes.¹⁶⁰

The above results suggest that in our RB-LDH-Pt system, a self-assembled H₂ generation system with RB as the photosensitizer and Pt as the photocatalyst immobilized on LDH nanocrystals are formed, as schematically shown in Figure 3-5. RB is a large and rigid molecule. Upon being immobilized on the surface of LDH, energy loss due to self-quenching of RB can be minimized by suppressing the random collision of RB molecules in solution.^{16,161} Furthermore, the close arrangement between RB and Pt nanoparticles on the surface of LDH is expected to favor the electron transfer from RB to Pt nanoparticles leading to more efficient H₂ generation.¹⁶

Figure 3-5 Schematic diagram of self-assembled H₂ generation system, RB-LDH-Pt.

The effects of the RB:LDH ratio (by varying the amount of LDH) and Pt concentration on H₂ production were investigated. Figure 3-6 shows the time course of H₂ production over the RB-LDH-Pt and Free systems. The optimum pH for photoreaction in our systems was found around 8.5, which is consistent with other dye-sensitized H₂ evolution systems.^{22,23} As shown in Figure 3-6A, the optimum mass ratio of RB:LDH is 1:18 (Figure 3-6A-d). At this ratio, RB-LDH-Pt is significantly more active and stable than the Free system. A much higher H₂ production rate was achieved within the initial 4 h. Similar to other molecular H₂ systems reported,^{13,15,16,22,23} the activity of the Free system almost ceased after a short period of around 4 h. However, H₂ can still be generated at a reaction time longer than 20 h in the RB-LDH-Pt system with the optimum ratio of RB:LDH. The total amount of H₂ produced from RB-LDH-Pt (RB:LDH = 1:18) is about 4.4 times of that from the Free system. Similar observations are made when a higher concentration of RB at 1.0 mM was used (Figure 3-6B). The total amount of H₂ produced reached nearly 4 mmol, which is 2.5 times of that from the Free system. At higher RB:LDH ratios of 1:12 and 1:6, lower amounts of H₂ were produced as shown in Figure 3-6A. This is because that since the total amount of RB is fixed, only about 55% and 35% of RB are immobilized on LDH (Figure 3-1), respectively, while the remaining free RB molecules dissolved in the solution are less stable, leading to fast photobleaching and loss of activity (to be discussed shortly). On the other hand, a lower RB:LDH ratio (i.e., a higher amount of LDH at a fixed amount of RB) resulted in a lower initial H₂ generation rate (Figure 3-6A-e). Such a phenomenon can be associated to the light scattering effect due to a higher concentration of LDH nanocrystals in the reaction mixture.¹⁶²

Figure 3-6 The effect of RB:LDH mass ratio on H₂ production, (A) Free (a), 1:6 (b), 1:12 (c), 1:18 (d), and 1:24 (e), [RB] = 0.1 mM; (B) Free (a), and 1:1.8 (b), [RB] = 1.0 mM. Other conditions: 5 v% TEOA, pH = 8.5, [Pt] = 0.1 mM, the amount of LDH was varied.

As shown in Figure 3-7, the optimum Pt concentration is 0.1 mM when the overall concentration of RB is 0.1 mM for both RB-LDH-Pt and Free systems. At lower Pt concentrations, the electron transfer from RB to Pt is not efficient enough, which could result in quick photobleaching of RB. Similar to other systems, at higher Pt concentrations, Pt nanoparticles may catalyze the hydrogenation of RB, leading to its accelerated photobleaching as well as consumption of H₂.^{23,140} The enhanced fold of H₂ production by comparing the RB-LDH-Pt and Free systems with equivalent amounts of RB and Pt is also shown in Figure 3-7. It can be seen that generally, more than 4-fold enhancement can be achieved at the Pt concentrations studied. Compared to the earlier study in which Eosin Y was covalently grafted to the surface of TiO₂,¹⁴⁴ our work presented here demonstrates that via a simple method of dye immobilization on LDH, both the activity and stability of the system can be greatly enhanced.

Figure 3-7 The effects of Pt concentration on H₂ production, (A) RB-LDH-Pt, (B) Free, and (C) enhanced fold of RB-LDH-Pt vs Free. [RB] = 0.1 mM, RB:LDH (mass) = 1:18.

RB is a heavy halogen-substituted xanthene dye. It has a high intersystem crossing yield which facilitates the formation of long-lived $3\pi\pi^*$ triplet state for electron transfer to the catalyst.^{163,164} However, the C-X (X = halogen) bonds in RB cleavage very fast often through reductive quenching leading to its photobleaching and the loss of activity.^{13,163} When RB was replaced by the halogen-free fluorescein dye in our system, a very low amount of H₂ was formed under the same conditions. Therefore, to achieve a more stable system, it is imperative to have a favourable electron transfer from the excited state of the photosensitizer to the catalyst. The progressive photobleaching of RB in both the RB-LDH-Pt and Free systems was monitored during the photoreaction. As shown in Figure 3-8, RB in the self-assembled system is much more stable than that in the Free system. Initially, both systems had the same concentration of RB with a maximum absorption at 554 nm and a shoulder of 520 nm.¹⁶⁵ Upon irradiation for only 10 min, RB in the Free system degraded quickly as indicated by the drastic color change of the reaction solution (Figure 3-8B). The main absorption peak was shifted to 504 nm and also turned much weaker (Figure 3-8A). Herein, the peak shifts are in accordance with the losing of chloride and iodide of RB.¹⁶³ Correspondingly, the major components in the solution were determined to be RB-Cl-2I and RB-2Cl-4I dehalogenated analogues based on our MS analysis. In contrast, the absorption peak in the case of RB-LDH-Pt was much stronger and the peak shift was not so obvious (at 528 nm) at 10 min. The dominant species were RB and the less dehalogenated species,

RB-Cl and RB-Cl-I. At 2 h of photoreaction, the peaks were further shifted to lower wavelength of 505 nm and 497 nm for RB-LDH-Pt and Free, respectively. Upon this time, RB was totally dehalogenated to fluorescein in the Free system leading to the substantial loss of activity, while RB-Cl, RB-Cl-I and RB-Cl-2I analogues were still present in the RB-LDH-Pt system. The color of the latter at 2 h was even stronger than that of the Free system at 10 min (Figure 3-8B). Based on the above results, it is suggested that the self-assembled RB-LDH-Pt system functions like a nanoreactor which facilitates the electron transfer path while suppressing the self-quenching of RB. In addition, the presence of LDH leads to better dispersed Pt nanoparticles as evidenced in TEM images (Figure 3-4), which can certainly result in more efficient H₂ production on their surfaces.

Figure 3-8 Analysis of reaction solutions after different photoreaction time, (A) UV-vis spectra, (B) photo images (Left: RB-LDH-Pt after dissolving LDH and Pt; Right: Free after dissolving Pt), (C) dominant species of the photobleached products based on MS analysis (e.g. RB-Cl refers to RB with one C-Cl bond cleaved), and (D) the molecular structure of RB.

Figure 3-9 shows the hydrogen production when different substrates were used. It is clear that the well-dispersed LDH nanocrystals (Figure 3-9A) exhibit an advantage over the other two substrates, LDH-control (Figure 3-9B) and MWNT (Figure 3-9C). The LDH-control sample which is comprised of aggregated particles cannot be dispersed well in water. As a result, less efficient immobilization of RB and Pt is expected which leads to the lowered photocatalytic activity. On the other hand, the surface of MWNT is not positively charged as its zeta potential was measured to be -10.9 mV. Hence MWNT has no advantage in adsorbing the negatively charged RB ions. In fact, the photocatalytic activity obtained using MWNT as the substrate is even

slightly lower than that of the Free system as shown in Figure 3-9. The above results indicate that the positively charged surface and the colloidal dispersion of LDH nanocrystals are key factors contributing to the activity enhancement of the dye-sensitization H₂ production system.

Figure 3-9 Comparison of H₂ production using different substrates for RB and Pt immobilization, (A) well-dispersed LDH nanocrystals, (B) LDH-control, (C) the Free system, and (D) MWNT. RB:LDH (mass) = 1:18, [RB] = 0.1 mM, [Pt] = 0.1 mM, the surface area of the substrates was kept the same.

In our system, Pt catalyst is the expensive component and hence reusability of Pt after termination of H₂ production is an important factor to make such a system potentially economical. Recycle study was carried out for RB-LDH-Pt after 6 h of photoreaction in each run. At the end of each run, the reaction mixture was centrifuged and the solid particles were collected to be re-dispersed in the fresh solution of RB and TEOA for the subsequent run. The same procedure was applied to the Free system but the reaction duration of each run was only 2 h due to its lower stability. Figure 3-10 shows that the catalyst in the RB-LDH-Pt system can be repeatedly used for at least six runs and around 64% of the activity was still retained at the sixth run. However, the Free system lost all the activity at the fourth run. Unlike the free-standing Pt nanoparticles in the Free system, Pt catalyst nanoparticles deposited on LDH surface can be easily collected and recycled by centrifugation. The total TON obtained after six

runs for RB-LDH-Pt was calculated to be 304 based on Pt, which gave at least 13 fold of enhancement compared to that from the Free system.

Figure 3-10 H₂ production in the recycle study over the RB-LDH-Pt and Free systems. [Pt] = 0.1 mM, [RB] = 0.1 mM, RB:LDH = 1:18.

3.4 Conclusions

In summary, we have demonstrated a simple method for the construction of the self-assembled RB-LDH-Pt H₂ generation system. Well-dispersed LDH nanocrystals act as support for immobilizing RB photosensitizer and Pt nanoparticles. Such a system offers many advantages in photocatalytic water splitting: (i) immobilizing the dye photosensitizer to suppress self-quenching, (ii) close arrangement between photosensitizer molecules and catalyst nanoparticles for efficient electron transfer, (iii) formation of well-dispersed Pt nanoparticles on the support surface, and (iv) easy recycle of the expensive catalyst. The strategy demonstrated in this Chapter may be extended to other photosensitizer/catalyst/support systems to achieve efficient and stable photocatalytic H₂ generation.

CHAPTER 4 MESOPOROUS CARBON NITRIDE WITH *IN SITU* SULFUR DOPING FOR ENHANCED PHOTOCATALYTIC HYDROGEN EVOLUTION FROM WATER UNDER VISIBLE LIGHT

(This Chapter is adapted from “Hong, J. D.; Xia, X.; Wang, Y.; Xu, R., Mesoporous carbon nitride with *in situ* sulfur doping for enhanced photocatalytic hydrogen evolution from water under visible light. *Journal of Materials Chemistry* 2012, **22**, 15006-15012.” Reproduced with permission of The Royal Society of Chemistry)¹⁶⁶

4.1 Introduction

From the work in Chapter 3, the homogeneous H₂ evolution usually suffers from instability, which has been improved greatly through the introduction of LDH as physical support. However, other intrinsic stable semiconductor systems still need to be developed for practical application. As introduced in Chapter 2, C₃N₄, a metal-free, stable and inexpensive polymeric semiconductor, has received increasing attention among the carbon nitride family due to its interesting electronic properties and promising catalytic activities.^{39,46,47,58,167,168} It has been shown that C₃N₄ has a direct band gap of around 2.7 eV with its conduction band sufficiently negative for water reduction to produce hydrogen.⁵⁴ More importantly, the thermal-stability and photo-stability of C₃N₄ are much better than homogeneous system and metal sulfide photocatalyst.³⁹ However, the C₃N₄ still has limited activity towards H₂ evolution currently.

In general, the adoption of artificial photosynthesis to meet future fuel demand is largely hampered by limited light absorption and inefficient charge transfer in the current photocatalytic systems. Doping, especially anion doping, in semiconductor photocatalysts is an effective way to extend light absorption range.^{30,169-171} On the other hand, it has been reported that photocatalysts with mesoporous structures benefit light absorption and charge transfer due to high surface areas and short bulk-to-surface distances compared to their bulk counterparts.^{172,173} The combination of the above two approaches may enhance the performance of C₃N₄. Besides, the synthesis of C₃N₄ involves the pyrolysis of nitrogen-rich organic precursors during which condensation of C-N bond occurs to form two dimensional tri-s-triazine (melem) sheets connected via tertiary amines.^{174,175} It has been shown that the type of precursors affects the

properties of C_3N_4 , such as surface area and porosity, and its photocatalytic performances due to different reaction pathways and degree of condensation.^{49,176,177} The most commonly used precursors so far include cyanamide^{47,52-54,167,178,179}, dicyandiamide^{50,57,62,168} and melamine^{46,63,180}, etc. Besides employing different precursor compounds, there have been other attempts in morphological and compositional modifications to improve the photocatalytic activities of C_3N_4 .^{49,50,52,53,63,178,179,181-183} For example, to attain efficient light absorption and charge transfer, Wang and co-workers synthesized mesoporous graphitic C_3N_4 (mpgCN) of high surface areas by condensation of cyanamide or ammonium thiocyanate precursor using SiO_2 nanoparticles or ordered mesoporous SiO_2 as hard templates.^{52,53,182} It has been found that the photocatalytic activities for hydrogen evolution can be improved remarkably compared to those obtained using the bulk C_3N_4 . On the other hand, both *ex situ* and *in situ* sulfur doping at small percentages of sulfur (<1.0 wt%) have been demonstrated effective in enhancing the photocatalytic activities of C_3N_4 .^{49,50} Herein, we combined both strategies in one material by forming *in situ* sulfur-doped mesoporous C_3N_4 (mpgCNS) using a sulfur containing precursor, thiourea (TU), and SiO_2 nanoparticles as the template. Although being a simple organic compound, TU exhibits rich dynamic behaviour during its thermal decomposition and several intermediate compounds could form by oxidation including cyanamide, ammonium thiocyanate and trithiocyanuric acid.¹⁸⁴ These compounds have all been used as the starting materials for the synthesis of C_3N_4 or sulfur-doped C_3N_4 .^{49,50,182} Zhang et al. synthesized C_3N_4 using TU as the precursor. It was proposed that the role of sulfur species as leaving groups was to facilitate the condensation process of C_3N_4 and no sulfur was doped in the resultant C_3N_4 products obtained by heating TU in air above 500 °C.¹⁷⁶

In the work of this Chapter, we found that when TU was employed as the precursor to synthesize mesoporous C_3N_4 in the presence of SiO_2 nanoparticle template, the presence of sulfur was detected in the end products, leading to modification of the electronic band structures and enhancement of photocatalytic performances for hydrogen evolution from water splitting under visible light.

4.2 Experimental

4.2.1 Preparation of C_3N_4 samples

Sulfur-doped mesoporous carbon nitride (mpgCNS) was prepared as following: thiourea ($\text{CH}_4\text{N}_2\text{S}$, 10 g, Alfa Aesar, 99%) was dissolved in deionized water (20 mL) and the solution was mixed with a certain amount (0, 1, 2, 3, 4 and 6 mL) of SiO_2 gel solution (Ludox® HS40, Aldrich, diameter: 12 nm, 40 wt% suspension in water). After stirring for 30 min, the mixture was heated at 60 °C for 16 h in an open system to remove water. The resultant dry sample was ground to fine powder and calcined in static air (with the crucible covered by the lid) at different temperatures in the range of 400-600 °C for 4 h with the heating rate of 2.5 °C min⁻¹. SiO_2 template was removed from the calcined sample (1.5 g) by treatment in hydrofluoric acid solution (HF, 5 wt%, 40 mL, Alfa Aesar; **CAUTION**: HF is highly toxic and should be used with extreme care!) for 24 h with continuous shaking, followed by centrifugation and washing with deionized water several times until pH of supernatant solution reached around 7.0. For comparison, native graphitic carbon nitride (CN) was prepared by pyrolysis of melamine ($\text{C}_3\text{H}_6\text{N}_6$, Alfa Aesar, 99%) at 550 °C for 4 h.^{46,49} Sulfur doped nonporous carbon nitride was synthesized by two methods: 1) native CN prepared above was further treated at 450 °C for 1 h with a heating rate of 2.5 °C min⁻¹ in H_2S (12 mL min⁻¹, 10% H_2S with balance N_2), denoted as CNS(H_2S); and 2) direct pyrolysis of TU in static air at 550 °C for 4 h with a heating rate of 2.5 °C min⁻¹, denoted as CNS(TU). Mesoporous C_3N_4 (mpgCN) was prepared using urea (Alfa Aesar, 99%) as the precursor and Ludox SiO_2 as the template.⁵² The procedure and experimental conditions were similar to those described for mpgCNS. The optimum mass ratio of SiO_2 :urea and pyrolysis temperature were found to be 0.16 and 550 °C, respectively.

4.2.2 Materials characterizations

The TEM and BET characterization are similar to those performed in Chapter 3. The desorption isotherms in BET analysis were used to determine the pore size distribution by using Barret-Joyner-Halender (BJH) method. The XRD patterns of the as-prepared samples were obtained on a X-ray diffractometer (Bruker D2 Phaser, Cu K α , $\lambda = 1.5406$ Å, 30 kV and 10 mA) in the range of 10 °-70 °. The chemical state and percentage of sulfur were measured by X-ray photoelectron spectroscopy (XPS) analysis in a VG Escalab 220i XL and the binding energies were calibrated using C 1s peak at 285.0 eV. The UV-vis diffused reflectance spectra (DRS) were obtained on a UV-vis spectroscopy (Shimadzu UV2450) using BaSO_4 as reference. Fourier transform infrared (FTIR)

spectra were collected on a Digilab FTS 3100 FTIR in the range of 400 - 4000 cm^{-1} by using a standard KBr disk technique. Elemental analysis (EA) for carbon and nitrogen were performed on a Vario EL III Element analyzer. Photoluminescence (PL) spectra were collected from FluoroMax-3 spectrofluorometer (Horiba Jobin Yvon) at room temperature with the excitation wavelength of 365 nm and the excitation/emission slit widths both of 5.0 nm. Mott-Schottky plots were recorded on CHI660D electrochemical workstation (CH Instrument Inc., USA) by using Impedance-Potential technique. Measurement was performed on a conventional three-electrode cell: cleaned Fluoride-tin oxide (FTO) deposited with sample film as working electrode, Pt wire as counter electrode and saturated calomel electrode (SCE) as reference electrode respectively. The aqueous solution of 0.2 M Na_2SO_4 purged with nitrogen gas was used as the electrolyte.

4.2.3 Photocatalytic activity evaluation

Photocatalytic reaction was carried out on the same system described in Chapter 3. Typically, photocatalyst (100 mg) was dispersed in TEOA aqueous solution (15 vol%, pH = 8.5, 100 mL) followed by adding certain amount (0, 1.0, 2.0, 3.0, 4.0 or 5.0 wt% in metal basis) of H_2PtCl_6 (Acros Organics, 99.9%). The used light source and GC analysis method are same to those used in Chapter 3. The apparent quantum efficiency was measured for mpgCNS at 420 nm, 440 nm, 460 nm, 480 nm, 500 nm and 550 nm, respectively. The measurement was under the same photoreaction conditions except that an additional long band pass interference filter centered at their respective wavelength was equipped during the 2nd and 3rd hour of the reaction.

4.3 Results and discussion

The mixture of TU and SiO_2 nanoparticles in water formed a homogeneous suspension. Upon a series of straightforward steps of drying, pyrolysis in static air and removal of SiO_2 by etching with HF solution, sulfur-doped mesoporous carbon nitride (mpgCNS) was readily formed. To study the effect of sulfur, a control mesoporous C_3N_4 sample was prepared using urea as the non-sulfur containing compound analogous to TU. This sample was denoted as mpgCN. Three additional control samples including sulfur-doped bulk C_3N_4 prepared from TU without SiO_2 template (CNS(TU)), native C_3N_4 (CN) prepared from condensation of melamine, and CN treated by H_2S

(CNS(H₂S)) were prepared. The synthesis conditions of these samples are briefly summarized in Table 4-1.

Table 4-1 Synthesis conditions of mpgCNS and control samples.

Sample ^a	Precursor	Template	S-doping method
mpgCNS	thiourea	SiO ₂ ^b	<i>in situ</i>
mpgCN	urea	SiO ₂ ^c	-
CNS(TU)	thiourea	-	<i>in situ</i>
CN	melamine	-	-
CNS(H ₂ S)	melamine	-	H ₂ S, 450 °C, 1 h

^a the pyrolysis condition for all these samples: 550 °C, 4 h, static air; ^b at optimum mass ratio of SiO₂:TU of 0.16; ^c at optimum mass ratio of SiO₂:urea of 0.16.

Figure 4-1 (A) XRD patterns and (B) XPS spectra of S 2p of mpg(CNS) prepared from TU precursor and various control samples.

Figure 4-1 shows the XRD patterns of mpgCNS and control samples. The typical interlayer-stacking (002) peak can be observed at 27.2° ($d_{002} = 3.28 \text{ Å}$) and in-planar peak at 13.1° ($d = 6.78 \text{ Å}$) for mpgCNS, indicating that the unique graphitic structure of carbon nitride^{50,167} was obtained when TU was used as the precursor. Different microstructure and morphological properties of C₃N₄ can be resulted when employing different precursors. Based on the XRD results, it can be seen that samples obtained from condensation of TU and urea exhibited lower diffraction intensities and broader peaks, compared with the native CN prepared from melamine. Among the two analogous precursors, it was found that TU resulted in a higher yield than urea. A relatively good yield of 31% (based on carbon) was obtained for mpgCNS, while only 9.4% for mpgCN when using urea as the precursor. Similarly, as reported in the

literature, when urea was used as the precursor for synthesis of bulk C_3N_4 , the yield was 7.8 wt% (based on carbon).¹⁷⁷ Compared to the oxygen species in urea, sulfur groups in TU better facilitated the condensation process to form the polymer network.

The presence of sulfur in our TU derived samples was clearly evidenced from the high-resolution XPS results (Figure 4-1B). The binding energy of S 2p was found at around 165.8 eV and 166.0 eV for mpgCNS and CNS(TU), respectively. Compared to the binding energy of 163.9 eV reported by Cheng and co-workers for sulfur doped in the position of nitrogen,⁵⁰ the higher binding energies obtained in our samples suggested that sulfur could be doped in the position of carbon instead of nitrogen to give rise to S-N bond. Although there is not prior report on sulfur doping at carbon sites of carbon nitride, phosphorus (P) doping at such a position to form P-N bond was confirmed when P-containing additive was poly-condensed with the precursor for carbon nitride.⁶¹ The broad S 2p peak of mpgCNS is likely due to the existence of sulfur oxide species which formed from the capturing of S by surface oxygen (5.8 at%) of mpgCNS.⁵⁰ After reaction for 72 h, the sulfur oxide species are more or less dissolved which make the S 2p peak narrower (Figure 4-10C). The weight percentage of sulfur estimated from the XPS results was 0.80% and 0.62% in mpgCNS and CNS(TU), respectively as shown in Table 2. Prior to this work, sulfur mediated condensation of C_3N_4 has been reported when trithiocyanuric acid was used as the precursor.⁴⁹ However, when ammonium thiocyanate and TU precursors were employed by the same group, sulfur was not doped in the resultant C_3N_4 .^{176,182} In another recent work, when TU was used as the precursor to prepare melon/ TiO_2 composites at a relative lower temperature of 400 °C, sulfur residue was detected in the composite products.¹⁸⁵ In view of the complicated reaction pathways and only a small percentage of sulfur (< 1 wt%) doped, it is possible that the doping of sulfur is very sensitive to the pyrolysis condition. During the pyrolysis step in the muffle furnace in this work, the crucible was covered by the lid to create a static environment. The control experiment in which the crucible was not covered resulted in a very low product yield of below 2%. In addition, the pyrolysis step was also carried out in nitrogen environment at 550 °C. Similarly, a low yield (<2%) was found when the crucible was not covered, while a dark-grey sample was obtained without photocatalytic activities if the crucible was covered by the lid.

The FTIR spectra shown in Figure 4-2 further confirmed the formation of C_3N_4 phase in all the samples by the absorption peak at 800 cm^{-1} (breathing mode of triazine) and absorption bands in the range of 1200-1600 cm^{-1} (stretching mode of C-N

heterocycles).⁴⁹ The broad bands in the range of 3000-3700 cm^{-1} region can be attributed to the adsorbed H_2O molecules and N–H vibration possibly due to uncondensed amine groups.⁴ The excess nitrogen was confirmed by the elemental analysis. As shown in Table 4-2, the C:N atomic ratio in our samples was measured to be 0.65-0.67 which was lower than the theoretical value (0.75) of C_3N_4 .

Figure 4-2 FTIR spectra of mpgCNS and control samples.

Table 4-2 Physicochemical properties and photocatalytic activities of mpgCNS and the control samples.

Sample	S% [wt%] ^a	C:N ^b	S.S.A. [m^2g^{-1}]	H_2 Evol. rate [$\mu\text{mol h}^{-1}$] ^c
mpgCNS	0.80	0.65	128.4	136.0
mpgCN	-	0.66	131.0	100.2
CNS(TU)	0.62	0.65	27.9	43.3
CN	-	0.67	12.1	4.5
CNS(H_2S)	0.49	0.67	12.8	7.1

^a obtained from XPS analysis; ^b atomic ratio obtained from elemental analysis; ^c average value of first 4 h photoreaction.

Based on the above results, the formation mechanism of sulfur doped C_3N_4 was proposed in Figure 4-3. Upon heating, TU can be partially converted to its isomer, ammonium thiocyanate. These two precursors can form cyanamide (or melamine) and trithiocyanuric acid, respectively after a series of decomposition and transformation.¹⁸⁴ During the co-polymerization, –SH group in trithiocyanuric acid can react with the amine group of cyanamide (or melamine) to join the C–N network and form the S–N bond.⁶¹ While trithiocyanuric acid was used as single precursor, sulfur species only

acted as leaving groups rather than doping elements since no amine group present in this precursor.⁴⁹

Figure 4-3 Proposed formation mechanism of sulfur-doped C_3N_4 from condensation of thiourea.

Figure 4-4 TEM images of (A) mpgCNS, (B) mpgCN, (C) CNS(TU), (D) CN and (E) SiO_2 template.

Figure 4-5 (A) Adsorption isotherms of various C_3N_4 samples. The isotherms are offset by 100, 200, 300 and 400 $cm^3 g^{-1}$ for CNS(H_2S), CNS(TU), mpgCN, mpgCNS respectively. (B) BJH pore size distribution of mpgCNS.

In the TEM image of sample mpgCNS (Figure 4-4A), well-distributed pores of 10-20 nm in diameter can be observed. A similar observation was made for sample mpgCN (Figure 4-4B) prepared with the SiO_2 template from urea. As expected, the bulk carbon nitride samples, CNS(TU) and CN, exhibit a typical nonporous and platelet-like structure (Figure 4-4C and D). Correspondingly, the specific surface areas (S.S.A.) of mpgCNS ($128.4 m^2 g^{-1}$) and mpgCN ($131.0 m^2 g^{-1}$) are much higher than those of CNS(TU) ($27.9 m^2 g^{-1}$) and CN ($12.1 m^2 g^{-1}$). Compared to CN, CNS(TU) was found with a slightly less dense structure, which was in agreement with its broader and less intense XRD peaks shown in Figure 4-1 and a higher surface area. The N_2 adsorption isotherms are shown in Figure 4-5A. The type I hysteresis loop observed for samples mpgCNS and mpgCN confirmed the existence of mesoporous structure.¹⁸⁶ The pore size distribution of mpgCNS obtained from its absorption isotherm (Figure 4-5B) is consistent with the observed pore sizes from the TEM image.

Figure 4-6 (A) UV-vis DRS, and (B) PL spectra of mpgCNS and the control C₃N₄ samples under excitation wavelength of 365 nm at 298 K.

Figure 4-7 Mott-Schottky plots of (A) mpgCN and (B) mpgCNS samples. (C) Band structure of CN, mpgCN and mpgCNS.

It is expected that the open pore structure and high surface area are beneficial for mass transfer as well as the dispersion of co-catalyst nanoparticles. In addition, the scattering sites of the pore walls can enhance light harvesting as evidenced by the upshift of absorbance comparing the UV-vis diffuse reflectance spectra (DRS) of porous and nonporous C₃N₄ samples in Figure 4-6A. Sulfur doping further enhanced the light absorption in both UV and visible light regions by comparing the spectra of mpgCNS

and mpgCN. In overall, the absorption edge of mpgCNS was red shifted from 460 nm of native sample CN to 475 nm together with a stronger light absorption. Figure 4-6B shows the PL spectra under excitation wavelength of 365 nm. Emission peaks centred around 430-440 nm can be found for all samples. It was remarkable that the PL intensity of mpgCNS was the lowest among all the samples and in particular was greatly suppressed compared to that of native CN, indicating the electron relocation on surface terminal sites.⁵² Such optical properties are important for promotion of photocatalytic activities. Furthermore, the effect of sulphur doping on the electronic band structure of mesoporous C_3N_4 was investigated. The Mott-Schottky curves shown in Figure 4-7 indicate a typical n-type plot for mpgCN and mpgCNS. Based on these plots, the flat band potentials of mpgCN and mpgCNS were determined to be -1.05 eV and -0.80 eV, respectively. Their band gaps obtained from UV-vis DRS curves were 2.69 and 2.61 eV, respectively. Hence, sulfur doping not only narrowed the band gap slightly but also caused a down shift of the conduction band. Similar phenomena were also reported for *in situ* sulfur doped C_3N_4 ,⁴⁹ while an up shift of conduction band in *ex situ* sulfur doped C_3N_4 was reported.⁵⁰ This could be due to the difference in position of sulfur doping. As discussed earlier, sulfur was likely doped at the carbon site based on our XPS study, hence causing a different effect on the band structure compared to the case where sulfur was doped at the position of nitrogen.⁵⁰ Although a slight down shift in conduction band (0.25 eV) for mpgCNS may cause the lower reduction ability of electrons, its narrower band gap and enhanced light absorption (Figure 4-6A) could be more critical in promoting the photocatalytic activities.

Figure 4-8 (A) The effects of Pt loading percentage on H₂ evolution rate (average of the first 4 h photoreaction, (B) Time course of hydrogen evolution for mpgCNS and control samples. Reaction condition: 100 mg of catalyst loaded with 3 wt% of Pt co-catalyst, 100 mL of 15 vol% triethanolamine, 300 W Xe lamp with 420 nm cut-off filter, and (C) stability test for mpgCNS under the same conditions of (B) in continuous reaction with evacuation at every 12 h.

The loading Pt weight percentage on mpgCNS was optimized to be 3 as shown in Figure 4-8A. Figure 4-8B shows the photocatalytic activities of mpgCNS and various control samples under visible light. The experimental conditions for the preparation of mpgCNS were optimized. As shown in Table 4-3, the optimum SiO₂:TU mass ratio was 0.16 and the optimal pyrolysis temperature was 550 °C. The hydrogen evolution rate obtained over mpgCNS prepared under such optimized conditions was 136 μmol h⁻¹ which was 214% and 36% higher than those of CNS(TU) and mpgCN control samples, respectively (Figure 4-8B and Table 4-2). Such data indicated promotional effects of both mesoporous structure and sulfur doping. Moreover, it was found that the activity of mpgCNS was promoted almost 30 times against that of native CN, although the surface increase was only 10 fold. Doping of sulfur in mesoporous carbon nitride resulted in additional promotional effect due to the change in its optical properties. On the other hand, *ex situ* sulfur doping alone was found less effective in activity enhancement. It was reported that doping of boron and nitrogen in mesoporous TiO₂¹⁸⁷ and doping of boron and fluorine in mesoporous C₃N₄¹⁸⁸ have also led to better catalytic activities.

Table 4-3 Physicochemical properties and photocatalytic activities of mpgCNS synthesized under different conditions.

Condition	C:N ^b	S.S.A. [m ² g ⁻¹]	H ₂ Evol. Rate [μmol h ⁻¹] ^c
r = 0.16, ^a 400 °C	0.62	14.4	0
r = 0.16, 450 °C	0.63	13.9	10.9
r = 0.16, 500 °C	0.64	69.2	43.9
r = 0.16, 550 °C	0.65	128.4	136.0
r = 0.16, 600 °C	0.65	125.3	94.7
r = 0.00, 550 °C	0.65	27.9	43.3
r = 0.05, 550 °C	0.65	77.4	87.1
r = 0.10, 550 °C	0.65	99.6	89.5
r = 0.21, 550 °C	0.65	54.4	77.1
r = 0.31, 550 °C	0.65	83.0	80.9

^a r = mass ratio of SiO₂:TU; ^b obtained from CHN elemental analysis; ^c average value of first 4 h photoreaction.

Figure 4-9 Apparent quantum efficiency at different wavelength and the UV-vis DRS curve of mpgCNS.

Apparent quantum efficiency was measured for mpgCNS at 420, 440, 460, 480, 500, 550 nm, respectively. As shown in Figure 4-9, it was interesting to note that the highest quantum efficiency of 5.8% was obtained at 440 nm. Even at 550 nm, a quantum efficiency of 1.9% was still obtained. The quantum efficiency of mpgCNS at 440 nm (5.8%) is much higher than that of CN reported (0.1% at 420-460 nm),⁵⁴ and slightly higher than those of more complicated systems such as the composites of carbon nitride/conducting polymer¹⁶ and carbon nitride/graphene.¹⁸⁰ The stability of mpgCNS was investigated by running the photoreaction for 72 h with evacuation at every 12 h. As shown in Figure 4-8C, mpgCNS was quite stable. Except around 10% drop in the activity during the second run, there was no further deactivation of activity in the long

run. The total amount of hydrogen evolved in 72 h was as high as 7.9 mmol, corresponding to a turnover number of 513.5 on the basis of Pt co-catalyst. Figure 4-10 displays the XRD, XPS and TEM result of the sample collected after 72 h of photoreaction. It can be seen that there exhibited no obvious changes in materials properties, except that nanoparticles of Pt co-catalysts were detected by XRD (Figure 4-10B) and TEM (Figure 4-10D) analyses.

Figure 4-10 (A) XRD and (B) high resolution XRD patterns, (C) XPS spectra of S 2p of mpgCNS before and after 72 h of photoreaction, and (D) TEM image of mpgCNS after 72 h of photoreaction (the black dots indicate the Pt nanoparticles).

4.4 Conclusions

In summary, *in situ* sulfur-doped mesoporous C_3N_4 was synthesized from a single precursor, thiourea, by using SiO_2 nanoparticles as template. Sulfur group was found to facilitate the condensation of C_3N_4 polymer, as a higher product yield was obtained from thiourea than that from urea as the starting material. The resultant sulfur-doped mesoporous C_3N_4 has been found 30 times more active than the native C_3N_4 for hydrogen evolution from photocatalytic water splitting. A relatively high apparent

quantum efficiency of 5.8% was obtained at 440 nm. The activity enhancement was attributed to the stronger and extended light absorption in the visible light region by sulfur doping and more efficient mass and charge transfer in mesoporous structure. Our findings could offer useful insights for development of better photocatalysts toward practical solar fuel production

CHAPTER 5 NOBLE METAL-FREE NiS/C₃N₄ FOR EFFICIENT PHOTOCATALYTIC HYDROGEN EVOLUTION FROM WATER

(This Chapter is adapted from “Hong, J. D.; Wang, Y. S.; Wang, Y. B.; Zhang W. and Xu, R. Noble metal-free NiS/C₃N₄ for efficient photocatalytic hydrogen evolution from water, *ChemSusChem* **2013**, *6*, 2263-2268.” Reproduced with permission of WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)¹⁸⁹

5.1 Introduction

In the work of Chapter 4, the H₂ evolution activity of C₃N₄ has been enhanced significantly through the mesoporous structure formation and *in situ* S doping. Besides our work, the H₂ evolution activity of C₃N₄ can also be greatly enhanced by introducing various metals as cocatalysts,⁵⁵ doping metal or nonmetal elements,^{50,61,166} creating hollow structure,⁶⁸ and forming composite with other semiconductors.^{51,63,64} However, to date, the precious metals such as Pt, Pd and Ru or their oxides were often used as cocatalysts both in literature and our work in Chapter 4, without which the activity of C₃N₄ is typically lower than 1 μmol h⁻¹ for H₂ evolution.^{50,52,54,55,61,64,166,180} Therefore, it is of both scientific and economic importance to investigate cocatalysts containing earth-abundant elements only. Sun and coworkers reported the use of [Ni(TEOA)₂]Cl₂ complex as a stable and efficient catalyst for H₂ evolution while C₃N₄ functions as the light harvesting material.¹⁹⁰ It is worthwhile to further explore the use of inorganic earth-abundant cocatalysts in such a system. Recently, thin layers of MoS₂ was loaded on C₃N₄ and better activity for H₂ generation than Pt as cocatalyst can be obtained under identical reaction conditions.¹⁹¹

In previous studies from our lab, it has been demonstrated that nickel is an important transition element to develop efficient and low cost photocatalyst systems. For example, NiS loaded CdS was found to be highly efficient to produce H₂ by using lactic acid as a sacrificial reagent.¹⁹² Ni²⁺ doping in Zn_xCd_{1-x}S photocatalysts results in 86% enhancement in H₂ evolution activity.¹⁹³ Later on, nickel-thiolate complex catalyst was *in situ* assembled for efficient H₂ evolution with low-cost xanthene dyes as sensitizer.¹⁹⁴ In another work, Ni based inorganic nanoparticles including Ni, NiO, NiS, NiSe were synthesized as catalysts for xanthene dye-sensitized H₂ evolution.¹⁹⁵ In all these

systems, noble metals like Pt can be avoided but high activity can still be achieved. Meanwhile, there are still limited works on the development of noble metal-free cocatalyst for C₃N₄ and expensive Pt is widely used. We expect that the nickel based cocatalyst may also replace the expensive Pt in C₃N₄ system. In this Chapter, we tried to employ NiS as the cocatalyst in C₃N₄-based photocatalyst system for efficient and stable H₂ evolution. NiS loaded C₃N₄ was prepared via a facile hydrothermal treatment of C₃N₄ with nickel acetate (NiAc) and thioacetamide (TAA) at various temperature and time. The loading conditions of NiS were systematically investigated and optimized. The as-obtained NiS/C₃N₄ can be used directly for efficient photocatalytic H₂ evolution without adding any noble metals.

5.2 Experimental

5.2.1 Preparation of NiS/C₃N₄

Mesoporous C₃N₄ was prepared according to the method described in Chapter 4.¹⁶⁶ The precursor of urea (10.0 g, Alfa Aesar, 99%) was firstly dissolved in 20 mL of deionized water, which was added with 3.0 mL of SiO₂ gel solution (Ludox® HS40, Aldrich, diameter: 12 nm, 40 wt% suspension in water, 1.3 g mL⁻¹) at a mass ratio of SiO₂: urea of 0.16. Water was removed by heating the mixture at 60 °C for 16 h in an open system and the resultant dry mixture was ground to fine powder and calcined at 550 °C in a chamber furnace for 4 h without purging gas. The crucible to hold the precursor was covered with a lid so that the calcination was maintained in a static air atmosphere. SiO₂ template in the product after calcination was removed by treatment with hydrofluoric acid solution (HF, 5 wt%, 40 mL, Alfa Aesar; **CAUTION**: HF is highly toxic and should be used with extreme care!) for 24 h, followed by centrifugation and washing with deionized water several times, until pH of the supernatant solution reached around 7.0. The resulting sample was dried at 50 °C in a vacuum oven.

NiS loaded C₃N₄ was prepared by a hydrothermal method. Typically, 300 mg of the as-prepared C₃N₄, a certain amount (16.5, 33.1, 41.3, 66.2, 82.7 μmol) of nickel (II) acetate (NiAc, Alfa Aesar, 99%) and thioacetamide aqueous solution (TAA, Alfa Aesar, 99%) with a molar ratio of TAA:Ni²⁺ fixed at 20 were mixed to make a total volume of 40 mL. This mixture was transferred into a 45 mL autoclave and further treated at various temperatures (120, 140, 160, 180 and 200 °C) and durations (4, 8, 12, 18 and 22 h). The theoretical weight percentages of NiS in the resultant products are 0.5%, 1.0%,

1.25%, 2.0% and 2.5%, respectively, based on the added amount of NiAc. The obtained products were washed with deionized water thoroughly and dried in vacuum at 50 °C overnight. For comparison, CoS loaded C₃N₄ was prepared by the same method using cobalt (II) acetate (Alfa Aesar, 99%) as the precursor.

5.2.2 Characterizations

The XRD, BET, TEM, XPS, UV-vis DRS and EA (for C, N, S) characterization are similar to those described in Chapter 4. Energy-filtered TEM analysis was performed on the same TEM microscope equipped with a Gatan imaging filter to obtain elemental mappings. The percentage of nickel in NiS/C₃N₄ was measured using inductively coupled plasma (ICP) optical emission spectroscopy in a Perkin Elmer ICP Optima 2000DV.

5.2.3 Photocatalytic activity evaluation

Photocatalytic reaction was carried out in the same system used in Chapter 3 and Chapter 4. The light source, H₂ analysis method and apparent quantum efficiency measurement are same as those used in previous chapters. In each run, 100 mg of NiS/C₃N₄ was dispersed in 100 mL of TEOA aqueous solution (15 vol%, pH = 11). During the stability study, the photocatalyst was filtrated, washed with deionized water and re-dispersed in fresh TEOA solution (15 vol%, pH = 11) after each run.

5.3 Results and discussion

As shown in Figure 5-1, by loading a small percentage of NiS on the surface of C₃N₄, the photocatalytic H₂ evolution activity can be greatly enhanced. C₃N₄ in the absence of any cocatalysts only gave rise to a very low H₂ evolution rate of 0.2 $\mu\text{mol h}^{-1}$. Upon loading of 0.5 wt% NiS, the rate was increased to 9.2 $\mu\text{mol h}^{-1}$. The H₂ evolution rate reached the maximum of 48.2 $\mu\text{mol h}^{-1}$ at 1.25 wt% of NiS loading and decreased to 32.1 $\mu\text{mol h}^{-1}$ and 13.5 $\mu\text{mol h}^{-1}$ upon further increasing of the loading to 2.0 wt% and 2.5 wt%, respectively. The actual percentages of NiS determined from ICP and elemental analyses are found generally different from the calculated values by $\pm 10\text{--}15\%$. This is expected due to a low concentration of NiS in the samples. In the case of the optimum sample with 1.25 wt% of theoretical loading, the actual percentage of NiS is around 1.1 wt%. For the sake of convenience, the samples are named

according to their theoretical weight percentage of NiS, e.g. NiS(1.25%)/C₃N₄.

Figure 5-1 The effects of NiS loading percentage (theoretical) on H₂ evolution rate (average of the first 4 h photoreaction). Hydrothermal condition for NiS loading: 160 °C, 18 h. Photoreaction conditions: 100 mg of photocatalyst, 100 mL of aqueous solution of TEOA (15 v%, pH = 11.0), 300 W Xe lamp with 420 nm cutoff filter.

Although the XRD pattern of NiS loaded C₃N₄ (Figure 5-2A b) does not display any obvious diffraction peaks of NiS phase probably due to the low percentages and small particle sizes for the entire series of the samples, the successful deposition of NiS on C₃N₄ can be evidenced by the combined UV-vis DRS, TEM, elemental mapping, and XPS results (Figure 5-3, Figure 5-4, and Figure 5-5). It can be observed in the UV-vis DRS curves (Figure 5-3) that the absorbance intensity of sample NiS(1.25%)/C₃N₄ beyond 420 nm is much enhanced compared to that of the pristine C₃N₄. The color of the sample correspondingly changed from light yellow of C₃N₄ to grey of NiS(1.25%)/C₃N₄ (Figure 5-3 inset). The absorbance edge of C₃N₄ after loading NiS did not shift, indicating that neither Ni nor S doping in C₃N₄ occurred during the hydrothermal process.^{166,196} As a result, the enhanced H₂ evolution activity should be attributed to the presence of NiS cocatalyst as the active reaction sites.

Figure 5-2 XRD patterns (A) of (a) pristine C₃N₄, (b) NiS(1.25%)/C₃N₄ with NiS loaded at 160 °C and 18 h, and (c) Ni/C₃N₄ (conditions same as except the absence of thioacetamide); FTIR spectra (B) of (a) pristine C₃N₄, (b) NiS(1.25%)/C₃N₄ with NiS loaded at 160 °C and 18 h and (c) NiS(1.25%)/C₃N₄ with NiS loaded at 160 °C and 72 h and (C) Zoom-in view of (B) in the range of 400 – 800 cm⁻¹.

Figure 5-4A shows the TEM image of the pristine mesoporous C₃N₄ prepared using SiO₂ nanospheres as the hard template. The average pore diameter determined from N₂ physisorption is 18.7 nm which is consistent with the pore size observed from the TEM image. The specific surface area of C₃N₄ was measured to be 94.1 m² g⁻¹. After loading of NiS, both the surface area and average pore size decreased to 76.8 m² g⁻¹ and 14.4 nm, respectively, indicating that the mesopores of C₃N₄ are partially blocked by NiS nanoparticles. In addition, hydrothermal treatment of C₃N₄ may also cause some aggregation and partial collapse of the pore structure. Figure 5-4B and Figure 5-4C shows the TEM and HRTEM images of NiS(1.25%)/C₃N₄. During our TEM study, it was generally difficult to locate NiS nanoparticles. Nevertheless, some lattice fringes of NiS can be observed on top of those of C₃N₄ as shown in Figure 5-4C, suggesting a good interface between C₃N₄ and NiS. The *d* spacing of 1.98 Å and 3.24 Å can be assigned to (102) and (002) planes of NiS (JCPDS 77-1624) and C₃N₄, respectively.

More importantly, the energy-filtered elemental mapping image of Ni (green), S (orange) and N (blue) displayed in Figure 5-4D suggests a good dispersion of NiS on the surface of C₃N₄.

Figure 5-3 UV-vis DRS results and photo images (inset) of (A) NiS(1.25%)/C₃N₄, (B) C₃N₄-TAA and (c) C₃N₄.

Figure 5-4 (A) TEM image of C₃N₄, (B) TEM and (C) HRTEM images of

NiS(1.25%)/C₃N₄, and (D) energy-filtered elemental mapping image of NiS(1.25%)/C₃N₄ (Ni: green, S: orange, N: blue).

Finally, XPS results obtained for Ni 2p and S 2p (Figure 5-5) are in agreement with the formation of surface NiS. The binding energies of the main and satellite peaks of Ni 2p_{3/2} are found at 852.1 and 858.7 eV, respectively, which are consistent with those of Ni 2p_{3/2} in NiS.¹⁹⁷ The minor peak of S 2p at 162.9 eV is close to that of NiS, which accounts for only a small fraction of the sample, while the major peak at 164.1 eV is most likely from the elemental S, trapped on surface of C₃N₄.^{50,198} During hydrothermal treatment, the excess H₂S from the decomposition of TAA which is not incorporated into NiS would be further decomposed and trapped by C₃N₄.⁵⁰ When C₃N₄ was hydrothermal treated with TAA under the identical conditions of NiS(1.25%)/C₃N₄, similar content of S (0.435 wt%) can be detected in the resulted sample. As evidenced by the constant of absorbance edge from UV-vis DRS spectra (Figure 5-3), this S was not doped but trapped on surface of C₃N₄. Furthermore, this surface trapped S can raise the H₂ evolution of C₃N₄ from 0.20 $\mu\text{mol h}^{-1}$ to 0.71 $\mu\text{mol h}^{-1}$. The measured Ni:S ratio using ICP and elemental analyses are close to 1.0 when the percentage of NiS is higher than 1.25 wt%. For samples of lower NiS loading, the measured ratio may not be reliable due to the detection limit in S measurement.

Figure 5-5 XPS spectra of (A) Ni 2p and (B) S 2p of sample NiS(1.25%)/C₃N₄.

It is interesting to find that the yield of NiS/C₃N₄ product after hydrothermal process strongly depends on the hydrothermal temperature. As shown in Figure 5-6, the yield varies from 93.3% to 2.6% when the temperature was increased from 120 °C to 200 °C, respectively. During the hydrothermal treatment, Ni²⁺, as a transition metal cation, may

act as a catalyst for decomposition of C₃N₄, and higher reaction temperature can accelerate the process. At 200 °C, almost all C₃N₄ was decomposed. As shown in Figure 5-2A(b), an obvious peak at 10.6 ° can be observed. It may be attributed to the in-planar pattern of C-N networks containing triazine rings formed due to partial decomposition of C₃N₄.¹⁹⁹ When TAA was absent during the hydrothermal treatment, the same XRD peak can also be found (Figure 5-2A(c)), indicating the role of Ni²⁺ alone in decomposition of C₃N₄. FTIR spectra in Figure 5-2B and C showed that new major peaks appeared at 440, 528, 593 and 768 cm⁻¹ for NiS/C₃N₄ which cannot be observed for the pristine C₃N₄. So the new XRD peak at 10.6 ° does not belong to C₃N₄, but from the fragments of C₃N₄ which may contain C-N aromatic rings. In addition, the (002) peak of C₃N₄ is shifted slightly from 27.3 ° to 27.5 ° indicating the decreasing of the stacking distance of the aromatic units after the hydrothermal treatment with d_{002} changed from 0.326 nm to 0.324 nm. All samples obtained at temperatures lower or higher than 160 °C gave very low or even no activities as shown in Figure 5-6. On the other hand, when the hydrothermal treatment duration was increased from 4 h to 22 h at the fixed temperature of 160 °C, the sample yield decreased only slightly from 77.2% to 70.2% and also less significant change was resulted in the H₂ evolution rate, as shown in Figure 5-7.

Figure 5-6 The effects of hydrothermal treatment temperature during loading of NiS (1.25%) on C₃N₄ with a reaction time of 18 h (sample yield refers to the percentage of NiS/C₃N₄ product obtained versus to the initial C₃N₄ added before hydrothermal treatment).

Figure 5-7 The effects of hydrothermal treatment duration during loading of NiS (at 1.25%) on C₃N₄ with the reaction temperature of 160 °C.

To illustrate the advantage of loading NiS cocatalyst on the surface of C₃N₄, photocatalytic H₂ evolution reaction was conducted over several control systems with the equivalent metal nickel and C₃N₄ contents as those in the optimal sample. In the first control, [Ni(TEOA)₂]Cl₂ complex sensitized by C₃N₄ was prepared according to the procedure reported in the literature, while the reaction scale was kept at 100 mL, which is the same as that for NiS/C₃N₄.¹⁹⁰ To this system, Na₂S (0.1 M, 10 mL) was added in order to precipitate the Ni complex to NiS as the second control ([Ni(TEOA)₂]Cl₂-Na₂S). NiS was also *ex situ* prepared by mixing NiAc and Na₂S at room temperature and the precipitate was physically mixed with C₃N₄ as the third control (NiS/C₃N₄-mixed). As shown in Figure 5-8, the activity of NiS/C₃N₄ (Figure 5-8D) is about 3 times of that of C₃N₄-sensitized [Ni(TEOA)₂]Cl₂ hybrid system (Figure 5-8A). After addition of Na₂S into this system, the activity is about doubled, indicating NiS precipitated out serves as a better cocatalyst than the pristine nickel complex. On the other hand, the activity of the sample NiS/C₃N₄-mixed is about half of that of NiS/C₃N₄. It is well expected that NiS loaded by hydrothermal treatment has a better interface with C₃N₄, which should promote the electron transfer from the excited C₃N₄ to the active sites of NiS. In comparison, the contact between the physically mixed NiS and C₃N₄ is more random and electron-hole separation is less efficient.

Figure 5-8 Time course of H₂ evolution over NiS(1.25%)/C₃N₄ (D) and several control systems, (A) Ni[(TEOA)₂]Cl₂/C₃N₄: NiCl₂ and C₃N₄ were mixed and dispersed in 15v% TEOA (pH = 11.0), (B) NiS/C₃N₄-mixed: NiS prepared from precipitation of NiCl₂ by Na₂S was mixed with C₃N₄, and (C) Ni[TEOA]/C₃N₄-Na₂S: 10 mL 0.1 M Na₂S was added into A to precipitate the Ni²⁺. Photoreaction conditions were the same as those in Figure 5-1.

Besides NiS, CoS was also investigated as the possible noble metal-free cocatalyst and loaded by the same method. The results (not shown) indicate that NiS is about 1.5 times more active than CoS as the cocatalyst of C₃N₄ for H₂ evolution. The activity of NiS/C₃N₄ also reaches around 70% of that of Pt/C₃N₄ under the same reaction conditions, but NiS is at a much lower cost.

The stability test results of NiS/C₃N₄ are shown in Figure 5-9. Although the H₂ evolution rate decreased gradually over time within each run, the activity can be almost restored in the following run after adding fresh TEOA. The total amount of H₂ generated at the fourth run is around 84% of that from the first run, which is slightly lower than that of Pt/C₃N₄ (around 90%).¹⁶⁶ The elemental analysis of the sample after four cycles of photoreaction indicates that S% decreased from 0.42% to 0.36% while C:N is increased from 0.67 to 0.70. Compared with our lab's previous work on NiS/CdS photocatalyst,¹⁹² NiS in this system is more stable most probably because that the optimal photoreaction condition is under an alkaline environment with a pH value of 11.0 (Figure 5-10A). Furthermore, when acid sacrificial reagents including lactic, oxalic and ascorbic acids were used, almost no H₂ was evolved (Figure 5-10B). The higher of C:N ratio after photoreaction may be due to the fact that the pristine C₃N₄ has

rich amine groups, which are decomposed during the photoreaction.³⁹ When Pt(1wt%)/C₃N₄ (500 mg) was irradiated in pure H₂O, around 11 μmol of H₂ over 45 h was evolved while no O₂ detected (Figure 5-11). Such a finding indicates that the rich amine group on the surface of C₃N₄ can possibly function as self-sacrificial reagent.

Figure 5-9 Time course of H₂ evolution in the recycle study using NiS(1.25%)/C₃N₄ as catalyst. Photoreaction conditions were the same as those in Figure 5-1. After each run of 6 h, the solid sample was collected by filtration and re-dispersed in 100 mL fresh TEOA solution.

Figure 5-10 The effects of (A) pH of the photocatalytic reaction medium and (B) the type of sacrificial reagent on H₂ evolution over NiS(1.25%)/C₃N₄.

Figure 5-11 Time course of H₂ evolution over Pt(1wt%)/C₃N₄. Photoreaction conditions: 500 mg of photocatalyst, 100 mL of deionized water, 300 W Xe lamp with 420 nm cutoff filter.

Figure 5-12 Dependence of QE on the wavelength over NiS(1.25%)/C₃N₄.

Apparent quantum efficiency (QE) of NiS/C₃N₄ at various wavelength is plotted with its UV-vis DRS spectrum (Figure 5-12). The highest QE is 1.9% at 440 nm, which is relatively lower than that in Chapter 4 (5.8% at 440 nm)¹⁶⁶ and literature for Pt/C₃N₄. However, this QE is the highest among C₃N₄ based photocatalyst system in the absence of the noble metal cocatalyst.^{63,67}

5.4 Conclusions

In conclusion, we have developed a noble metal-free C₃N₄-based photocatalyst for H₂ evolution by loading NiS on C₃N₄ via a simple hydrothermal method. Both the weight percentage of NiS and the hydrothermal reaction temperature have great influence on the photocatalytic activities. The resultant optimal NiS/C₃N₄ photocatalyst is 253 times more active than the pristine C₃N₄ and is able to retain over 80% of the activity after 4 runs of 24 h. This study demonstrates that the intrinsically stable C₃N₄ polymeric semiconductor could potentially serve as a stable earth-abundant system for photocatalytic water splitting when a small fraction of transition metal based cocatalyst is properly loaded.

CHAPTER 6 DEVELOPMENT OF PRODUCT ANALYSIS METHODS FOR PHOTOCATALYTIC CARBON DIOXIDE REDUCTION

(This Chapter is adapted from “Hong, J. D.; Zhang, W.; Ren, J.; Xu, R., Photocatalytic reduction of CO₂: A brief review on product analysis and systematic methods. *Anal. Methods* **2013**, 5, 1086-1097.” Reproduced with permission of The Royal Society of Chemistry)²⁰⁰

6.1 Introduction

Compared with water splitting as presented in above three Chapters, the research on photocatalytic reduction of CO₂ is still at its early stage, despite the recent renewed interest from the scientific community and certain progresses attained in the directions of CO₂ reduction and utilization.^{5,129,130,201-204} It is notorious that the efficiencies of photocatalytic CO₂ reduction reported so far are very low. This certainly exerts stress in product identification and quantification. Hence, many groups practically adopted the routine analysis of one or two products in either gas or liquid phase for evaluation of the photocatalytic efficiencies.

Unlike water splitting that only involves the analysis of two products H₂ and O₂, CO₂ photoreduction involves multi-electron processes, which can lead to a large variety of products ranging from CO, CH₄ to higher hydrocarbons in gas phase, and various oxygenates in liquid phase such as alcohols, aldehydes and carboxylic acids. A few representative reactions leading to gas and liquid products are shown in Table 6-1. The identification and quantification of as many as possible of such products are essential for more accurate evaluation of the photocatalytic performance for design of better photocatalysts. Furthermore, at the current stage of research, analysis techniques with low detection limits are also important to identify the influence of carbon residues originated from photocatalyst synthesis, which can possibly contribute to the reduction products.²⁰⁵ As a simple illustration, if 0.1 g of photocatalyst, which contains 1% of carbon residues (in the form of organic species), is irradiated, the amount of carbon containing products formed from these carbon residues could be in a magnitude of a few tens of micromoles, which are far greater than many of those reported values attributed to photoreduction of CO₂ in the current literatures. In a recent review by Izumi, it was concluded that those reduction products with relative high yields without

careful verification may not be totally produced from CO₂.²⁰⁶ While our research efforts are devoted to developing efficient photocatalyst systems (presented in Chapter 7), several important issues with regards to the product analysis of CO₂ reduction need to be urgently addressed:

(1) Can the most likely occurred reduction products be detected accurately? A reliable conclusion on photocatalytic activities can only be drawn after accurate quantification of the products and elimination of the contribution from carbon contamination.

(2) Will the presence of organic additives affect the product analysis? Organic additives are often used as sacrificial reagents, solvents, photocatalysts or photosensitizers especially in homogeneous molecular systems. Their effects on the analysis of CO₂ reduction products need to be investigated.

(3) Do the detected products truly originate from the reduction of CO₂? Techniques like ¹³C NMR and gas chromatography-mass spectroscopy (GC-MS) can be used for verification.

Table 6-1 CO₂ reduction products and corresponding reduction potential with reference to NHE at pH of 7.

Product	Reaction	E ⁰ _{redox} (V vs NHE) ^a
Oxygen	H ₂ O → 0.5O ₂ + 2H ⁺ + 2e ⁻	0.82
Methane	CO ₂ + 8H ⁺ + 8e ⁻ → CH ₄ + 2H ₂ O	-0.24
Ethane	2CO ₂ + 14H ⁺ + 14e ⁻ → C ₂ H ₆ + 4H ₂ O	-0.27
Carbon monoxide	CO ₂ + 2H ⁺ + 2e ⁻ → CO + H ₂ O	-0.51
Methanol	CO ₂ + 6H ⁺ + 6e ⁻ → CH ₃ OH + H ₂ O	-0.39
Ethanol	2CO ₂ + 12H ⁺ + 12e ⁻ → C ₂ H ₅ OH + 3H ₂ O	-0.33
1-Propanol	3CO ₂ + 18H ⁺ + 18e ⁻ → CH ₃ CH ₂ CH ₂ OH + 5H ₂ O	-0.31
2-Propanol	3CO ₂ + 18H ⁺ + 18e ⁻ → CH ₃ CH(OH)CH ₃ + 5H ₂ O	-0.30
Formaldehyde	CO ₂ + 4H ⁺ + 4e ⁻ → HCHO + H ₂ O	-0.55
Acetaldehyde	2CO ₂ + 10H ⁺ + 10e ⁻ → CH ₃ CHO + 3H ₂ O	-0.36
Propionaldehyde	3CO ₂ + 16H ⁺ + 16e ⁻ → CH ₃ CH ₂ CHO + 5H ₂ O	-0.32
Acetone	3CO ₂ + 16H ⁺ + 16e ⁻ → CH ₃ COCH ₃ + 5H ₂ O	-0.31
Formic acid	CO ₂ + 2H ⁺ + 2e ⁻ → HCOOH	-0.58
Acetic acid	2CO ₂ + 8H ⁺ + 8e ⁻ → CH ₃ COOH + 2H ₂ O	-0.31

^a Reduction potentials are calculated by using the Gibbs free energy of formation from tabulated thermodynamic data.²⁰⁷

In this Chapter, we focus on the product analysis for photocatalytic reduction of CO₂. Several analysis techniques based on both literatures and our work are discussed and

compared. One set of methods is proposed for analysis of a wide range of photoreaction products in gas and liquid phases with low detection limits. The effects of most commonly used organic additives were also investigated. Though the analysis methods discussed and proposed here are in the context of photocatalytic reduction of CO₂, they are also applicable for other CO₂ reduction processes, such as electrochemical reduction, chemical conversion and biological transformation.

6.2 Analysis of gas phase products

6.2.1 Brief review of literature methods

CH₄ and CO are the major gaseous products of CO₂ photoreduction while H₂ and/or O₂ may also be produced as by-products from water splitting.^{137,202,204} In addition, Varghese et al. reported the presence of higher alkanes as the photoreduction products of CO₂.¹⁰⁸ Besides the products, CO₂ as the main species in the gas phase due to a low conversion needs to be quantified to determine the reaction progress and/or the extent of CO₂ dissolution in the liquid phase.²⁰⁸ Infrared spectroscopy (IR) or diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) has been occasionally employed to verify the consumption of CO₂ and the generation of CO.^{77,205,209-211} GC is by far the most commonly used method for quantification of these gas species.^{91-93,96,97,109,131,133,135,137,208,212,213} Besides GC, GC-MS was also used for routine analysis of CH₄ and CO^{111,214,215} or for carbon source verification.^{92,127,216} Although thermal conductivity detector (TCD) was the only detector used in GC as stated in some reports, it is suggested that flame ionization detector (FID) should be used in order to achieve higher sensitivities for detection of low concentrations of CO and hydrocarbons.²¹⁷ FID analysis is a destructive method. Therefore, the gas should be first analyzed by TCD for gases quantification followed by FID for analysis of CO and alkanes. Many types of columns have been used such as molecular sieve,^{90,92,93,96,97,119,121,124,135,137,216,218-235} carbon column,^{77,109,127,133,236-244} Poraplot Q^{119,218-220,235,245-249} and Al₂O₃.⁹¹ It has been noted that if a high concentration of CO₂ remains in the gas product stream, it can cause deactivation of nickel catalyst in methanizer and certain types of columns including the most commonly used molecular sieve column to make frequent column regeneration necessary.⁹² A better design of GC configuration is proposed in this Chapter to separate and detect all the gases including CH₄, CH₃CH₃, CO, CO₂, O₂, N₂ and H₂ with low detection limits as well as to avoid

regular column regeneration and achieve longer lifetime of methanizer and detector.

6.2.2 Methods developed in this thesis

The analysis of CO₂ and products in gas phase was performed using an online GC equipped with a TCD, FID and a methanizer, which contains a Ni catalyst. Standard gases (CO₂, H₂, N₂, CH₄, CO and CH₃CH₃) of high purities and gas mixtures prepared from these standard gases were charged to the photoreactor system as the gas samples. Figure 6-1 shows the simplified configuration of our GC. Helium (99.9995%) was used as the carrier gas. The back channel of GC is equipped with two packed columns, Hayesep Q and MolSieve 5Å, and three gas switch valves, V1-V3. During the analysis, 0.25 mL of gas sample in the sample loop of V1 was introduced to Hayesep Q column where CO₂ was separated from the remaining gases. The remaining gases are ahead of CO₂ and can totally enter MolSieve column at certain time (before 2.5 min here). At the time of 2.5 min, V2 is switched to bypass (the loop at V2) for CO₂ to pass while skipping MolSieve column and further sent to TCD for analysis. The analyzed CO₂ can be vent out by the switch of V3 (during 3-7 min). The rest of the gases after Hayesep Q column were further separated by MolSieve 5Å column. At the time of 10 min, V2 is switched back to mainpass for the separated gases to pass and be detected by TCD and then CH₄, CO and CH₃CH₃ were further detected by FID with higher sensitivities. The role of methanizer (nickel catalyst) is to convert CO to CH₄ for FID analysis while alkanes remained unaffected. During this process, the GC oven was held at 60 °C for 15 min and increased to 180 °C for 5 min for the post-run. The detailed program can be found in Table 6-2.

Figure 6-1 The flow chart of gas chromatography for gas phase product analysis and liquid phase analysis of alcohols. V1-V3: gas switch valves, and CL1-3: separation columns.

Table 6-2 Analytical conditions for gas products.

Equipment	Agilent 7890A GC
Valve box heater	100 °C
Inlet	Heater (250 °C) Split ratio (2:1) total flow of 15 mL min ⁻¹ septum purge flow of 3 mL min ⁻¹
Sample volume	0.25 mL
Column	Hayesep Q 80-100 (2.74 m L × 2.0 mm ID × 1/8 in OD) MolSieve 5 Å 80-100 (2.74 m L × 2.0 mm ID × 1/8 in OD)
Carrier gas	He, constant flow of 20 mL min ⁻¹
Oven	60 °C (15 min), post-run at 180 °C (5 min)
Methanizer	Ni Catalyst (350 °C)
Detector	FID-Front, off, He makeup flow of 10 mL min ⁻¹ FID-Back, 250 °C, H ₂ flow of 40 mL min ⁻¹ , Air flow of 350 mL min ⁻¹ TCD-Third, 200 °C, Reference flow of 30 mL min ⁻¹
Aux Heater	375 °C
Events	0.01 min: Valve 1 on (start of sampling) 0.25 min: Valve 1 off (finish of sampling) 2.5 min: Valve 2 on (switched to bypass for CO ₂ to pass) 3 min: Valve 3 on (Start of CO ₂ vent) 7 min: Valve 3 off (finish of CO ₂ vent) 10 min: Valve 2 off (switched to mainpass for separated remaining gases from MolSieve column to pass)

The volume of photoreactor circulation system is around 1.0 L. The calibration lines

of individual gases (CH_4 , CH_3CH_3 , CO and CO_2) are shown in Figure 6-2A-D. All these data points are well fitted to a straight line as indicated by the R^2 values of close to unity. Typical GC chromatographs from TCD and FID for analysis of a gas mixture containing N_2 , O_2 , CH_4 , CH_3CH_3 , CO and CO_2 are shown in Figure 6-2E. It can be seen that a good separation was achieved. Furthermore, the method detection limit (MDL) in our system was obtained by following the procedures described in US EPA method.²⁵⁰ The obtained MDLs for CO_2 , CO , CH_4 and CH_3CH_3 are as low as 2.6, 0.07, 0.03 and $0.004 \mu\text{mol L}^{-1}$, respectively.

Figure 6-2 GC calibration lines of gas standards, (A) CH_4 , (B) CH_3CH_3 , (C) CO , (D) CO_2 , and (E) GC curves (bottom: TCD signal with Peaks 1-5; top: FID signal with Peaks 6-8) of standard gas mixture, (1) CO_2 ($2989.0 \mu\text{mol L}^{-1}$), (2) O_2 ($198.2 \mu\text{mol L}^{-1}$), (3) N_2 ($499.2 \mu\text{mol L}^{-1}$), (4) CH_4 ($33.0 \mu\text{mol L}^{-1}$) and (5) CO ($44.0 \mu\text{mol L}^{-1}$), (6)

CH₃CH₃ (1.1 μmol L⁻¹), (7) CH₄ (33.0 μmol L⁻¹) and (8) CO (44.0 μmol L⁻¹).

The automatic sampling system has several advantageous features: (1) the auto-sampling loop in the first switch valve can realize online product analysis and ensure a consistent volume of gas introduced to the column, (2) the use of second switch valve protects MolSieve 5Å column from the high concentration of CO₂ to avoid frequent regeneration of the column, and (3) the third switch valve protects the methanizer from the high concentration of CO₂. CO₂ if not vented can also be converted to CH₄ by the methanizer. However, a high concentration of CO₂ will lead to quick deactivation of Ni catalyst. Unlike other systems without the vent valves, this design can greatly enhance the lifetime of both the column and methanizer.

Some research groups such as Anpo,^{133,214,251-253} Zou^{131,136,254} and Ye^{132,255,256} adopted gas phase reaction for CO₂ photoreduction. In a typical gas phase reaction, solid photocatalyst was first dispersed well at the bottom of the reactor, which contains CO₂ gas followed by injecting a small amount of liquid water (e.g. 1 mL) as the reducing reagent. Under a low pressure condition, liquid water vaporizes and mixes with CO₂ gas. In these cases, analysis methods proposed above can be used for accurate analysis of gas products. Gas phase reduction was also carried out using H₂²⁴¹⁻²⁴³ or CH₄^{257,258} instead of water to reduce CO₂. For these water free gas-solid systems, GC-based method is widely used for the quantification of products. It is worth noting that *in situ* DRIFT coupling with isotopically labeled ¹³CO₂ is superior to monitor the intermediates or products adsorbed on the solid surface.^{77,205,211} For example, in Yang et al.'s work, a cell equipped with three windows (two for IR transmission and one for light irradiation) is used to hold the photocatalyst and a spectrometer with liquid N₂ cooled mercury cadmium telluride (MCT) detector is used to record the spectrum.²⁰⁵ Real-time spectra can be collected at different irradiation time to verify the intermediates during CO₂ reduction. The limitation of DRIFT is difficult to quantify the final products, which can be solved by GC methods as proposed.

6.3 Analysis of liquid phase products

6.3.1 Brief comparison of various techniques

Although GC with TCD/FID is still the main technique used for analysis of different types of liquid oxygenates (mainly

alcohols),^{77,90-92,94-96,111,112,120,135,208,218,219,224,225,228,245,259-271} several other methods have been utilized, include GC-MS,^{113,119,214} HPLC,^{208,216,229-231,236,265,272,273} IEC,^{92,118,124,133,137,208,226,238,247,274-278} ultraviolet–visible (UV-Vis) spectroscopy (colorimetric assay) after reacting with chromotropic acid^{218-220,222,225} or Nash reagent^{91,97,117,263,264,279,280} and NMR.^{93,281} The compounds that can be analyzed and their detection limits of various techniques together with the associated limitations are summarized in Table 6-3.

Table 6-3 Comparison of techniques used for liquid phase analysis in CO₂ photoreduction.

Technique	Compounds	Detection limit	Limitations
GC	Alcohols	3 µmol L ^{-1a}	Much higher detection limits
	Aldehydes	100 µmol L ⁻¹⁹²	for aldehydes
HPLC	Carboxylic acids ²⁷³	5 µmol L ^{-1a}	Aldehydes need to be
	Aldehydes ^{208,282}	0.07 µmol L ^{-1a}	derivatized before analysis
IEC	Carboxylic acids	0.1 µmol L ⁻¹ for HCOOH ⁹² 10 µmol L ⁻¹ for CH ₃ COOH ⁹²	For acids only
UV-Vis	HCHO after reaction with Nash' reagent or HCOOH	0.17 µmol L ^{-1 a} 0.08 µmol L ^{-1 a}	Not applicable for other aldehydes and acids; HCOOH can only be analyzed when no other organics are present
¹ H or ¹³ C NMR	All oxygenates ⁹³	Not available	High cost, difficult for quantification although some work demonstrated quantification, ⁹³ mainly for product qualification, carbon source verification
GC/LC-MS	All oxygenates	Not available	Mainly for product qualification, carbon source verification

^a Approximately the average value of the MDLs obtained for standard samples analyzed in this work following US EPA method. MDL of individual compounds can be found in Figure 6-9.

6.3.2 Alcohols analysis

Based on the literature, alcohols especially methanol are the frequently detected products from CO₂ photoreduction in liquid phase. GC with a FID works well for analysis of alcohols and several kinds of columns have been used such as HP-5,^{111,218,219,225} Porapak Q,^{91,94,120,259} DB-WAX^{92,260} and PEG column.^{112,135,245} In this work, alcohols up to C₃ including methanol, ethanol, 1-propanol and 2-propanol in liquid phase were analyzed by GC with a FID, a DB-wax column and helium as carrier gas. The liquid sample was first filtered with a PTFE filter to remove solid particles

before auto-injection of 1.0 μL of the clear solution into GC. It was found that the filter membrane has no effect on the concentrations of chemical species in liquid phase.

The GC oven was initially held at 40 $^{\circ}\text{C}$ for 5 min, then ramped to 180 $^{\circ}\text{C}$ with a heating rate of 20 $^{\circ}\text{C min}^{-1}$ and held at this temperature for 3 min to eliminate the water vapor in the liquid sample from the column. Detailed conditions can be found in Table 6-4. Figure 6-3A-D shows the calibration lines of methanol, ethanol, 1-propanol and 2-propanol standards in aqueous solutions. The data points can be well fitted to a straight line with the R^2 values close to unity. A typical GC graph from analysis of an aqueous mixture of the four alcohols is shown in Figure 6-3E. Using the current method, 2-propanol (Peak 2) and ethanol (Peak 3) signals are overlapped due to their similar polarities and boiling points (82.5 $^{\circ}\text{C}$ and 78 $^{\circ}\text{C}$). This problem can be overcome by using a longer column or reduced carrier gas flow (data not shown). The MDLs obtained by the current method for methanol, ethanol, 1-propanol and 2-propanol in aqueous solutions were 3.5, 3.3, 2.3 and 1.7 $\mu\text{mol L}^{-1}$, respectively.

Table 6-4 Analytical conditions for alcohols in liquid phase.

Equipment	Agilent 7890A GC
Inlet	Heater (125 $^{\circ}\text{C}$), Splitless, total flow of 43 mL min^{-1} , septum purge flow of 3 mL min^{-1}
Injection volume	1.0 μL
Column	DB-Wax (30 m $\times$ 0.53 mm ID $\times$ 1 μm thickness film)
Carrier gas	He, constant flow of 20 mL min^{-1}
Oven	40 $^{\circ}\text{C}$ (5 min), 40-180 $^{\circ}\text{C}$ (20 $^{\circ}\text{C min}^{-1}$), 180 $^{\circ}\text{C}$ (3 min)
Detector	FID-Front, 200 $^{\circ}\text{C}$, H_2 flow of 40 mL min^{-1} , Air flow of 350 mL min^{-1} , He makeup flow of 25 mL min^{-1} , column+makeup of 45 mL min^{-1} FID-Back, off, He makeup flow of 10 mL min^{-1} TCD-Third, off, He reference flow of 10 mL min^{-1}

Figure 6-3 GC calibration lines of alcohol standards in aqueous solution, (A) methanol, (B) ethanol, (C) 1-propanol, and (D) 2-propanol, and (E) a typical GC curve of an aqueous mixture of alcohol standards, (1) methanol ($24.8 \mu\text{mol L}^{-1}$), (2) 2-propanol ($13.1 \mu\text{mol L}^{-1}$), (3) ethanol ($17.2 \mu\text{mol L}^{-1}$), and (4) 1-propanol. ($13.4 \mu\text{mol L}^{-1}$).

In many studies, organic compounds have been engaged in photoreduction of CO_2 for various reasons such as sacrificial reagents (e.g., methanol, triethanolamine),^{124,216,230,265} solvents (e.g., acetonitrile, dimethylformamide (DMF)),^{216,283} photocatalysts (e.g., Ru complexes)^{129,130} or photosensitizers (e.g., N3 dye, Rose bengal).¹⁰⁰ The presence of such organic compounds in the reaction systems may affect the product analysis in liquid phase. In this study, the influence of several commonly used organic species was investigated for liquid phase analysis. Table 6-5 lists the effects of the organic additives on alcohol analysis including acetonitrile (ACN), DMF, TEOA, triethylamine (TEA), methyl viologen (MV), RB and $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$. In addition, the effect of alkaline condition as adjusted by NaOH was investigated. The concentrations of alcohols were kept at $1 \mu\text{L L}^{-1}$. The results shown in Table 6-5 and Figure 6-4 indicate that alcohol analysis is very sensitive to most of the organics in terms of peak areas. In addition, as shown in Figure 6-4, many extra peaks

can be detected due to the presence of the organic compounds in the case of MV, ACN, DMF, TEOA and TEA. The interaction of these compounds with the column and their interference with alcohols cause the complicated spectra of GC signals. In fact, to the best of our knowledge, there is rare example of alcohol quantification when organics are involved in CO₂ reduction. GC-MS and/or NMR technique may be used for qualitative analysis of alcohols when the use of organics is unavoidable. When only a simple alkaline condition was applied by adding NaOH, the peak positions and areas for all the four alcohols remained almost unchanged, except around 10% increase in the peak area of 1-propanol.

Table 6-5 Effects of various organic compounds and alkaline condition on the GC peak areas of alcohols (1 $\mu\text{L L}^{-1}$).^a

Medium	Methanol	Ethanol	1-propanol	2-propanol
H ₂ O	5.7	9.0	9.0	8.6
ACN ^b	45.1	9.6	15.3	8.6
DMF ^b	36.9	11.0	5.0	8.3
TEOA ^b	14.1	10.4	8.9	9.6
TEA ^b	58.6	21	4.6	9.1
MV ^c	93.9	6.2	7.2	8.2
RB ^c	6.1	14.0	10.3	8.4
[Ru(bpy) ₃]Cl ₂ ^c	4.9	7.4	9.4	7.9
NaOH ^d	5.4	9.2	10.0	8.9

^a Equivalent to 24.8 $\mu\text{mol L}^{-1}$ of methanol, 17.2 $\mu\text{mol L}^{-1}$ of ethanol, 13.4 $\mu\text{mol L}^{-1}$ of 1-propanol and 13.1 $\mu\text{mol L}^{-1}$ of 2-propanol; ^b 15 v%; ^c 0.1 mM; ^d 0.1 M.

Figure 6-4 GC peaks of methanol, ethanol, 1-propanol in (A) 0.1 M NaOH, 0.1 mM MV, 0.1 mM RB, 0.1 mM $\text{Ru}(\text{bpy})_3\text{Cl}_2$, and (B) 15 v% ACN, 15 v% DMF, 15 v% TEA, 15 v% TEOA; GC peaks of 2-propanol in (C) 0.1 M NaOH, 0.1 mM MV, 0.1 mM RB, 0.1 mM $\text{Ru}(\text{bpy})_3\text{Cl}_2$, and (D) 15 v% ACN, 15 v% DMF, 15 v% TEA, 15 v% TEOA.

6.3.3 Aldehydes analysis

Aldehydes are another group of possible reduction products. Although less frequently detected and reported in literatures, analytical techniques need to be developed for CO_2 reduction products screening. Besides Nash's colorimetric method,^{224,284} others also used GC with either TCD/FID with a Porapak T column^{91,96} or FID with a DB-WAX column⁹² and BX-10 column²¹⁶ to quantify aldehydes. However, the detection limits ($\sim 100 \mu\text{mol L}^{-1}$) are about 2 orders of magnitude higher than those of alcohols. Hence, only relatively concentrated aldehydes can be analyzed by the GC method while the concentrations of aldehydes in liquid phase of CO_2 photoreduction are usually much lower than such detection limits. In this work, C_1 - C_3 aldehydes (formaldehyde, acetaldehyde, propionaldehyde and acetone) were analyzed by HPLC after derivatization with 2,4-dinitrophenylhydrazine (DNPH). Although this derivatization method has been widely used for aldehydes analysis in ambient air, cigarette smoke, drinking water, etc.,²⁸² only one recent work has adopted it for the quantification of

aldehydes in CO₂ reduction and more detailed investigation like the effect of organics has not been studied yet.²⁰⁸ Herein, the DNPH derivatization was performed according to a modified US EPA method 8315A.²⁸⁵

Briefly, 50 mL of the liquid sample was added with 10 mL of citrate buffer (pH = 5) followed by the addition of 2 mL of DNPH (5 mM in methanol). The mixture was shaken at 40 °C for 2 h followed by adding 20 mL of methylene chloride to extract the derivatized aldehyde-DNPH product for three times. A rotary evaporator was used to remove the solvent of collected methylene chloride layers. The dried solid was then dissolved in 5 mL of ACN and analyzed by HPLC with an Eclipse Plus C18 column, a variable wavelength detector (VWD) at 360 nm and 60 v% ACN in H₂O as the mobile phase. More details about the method can be found in Table 6-6. The calibration lines of various aldehydes after derivatization with DNPH are shown in Figure 6-5A-D with their R² values very close to unity. A typical HPLC curve of the mixture of these four derived compounds (Figure 6-5) shows well separated peaks. The MDLs of this method were found to be very low at around 0.03-0.08 µmol L⁻¹.

Table 6-6 Analytical conditions for aldehyde-DNPH in liquid phase.

Equipment	Agilent 1260 HPLC
Column	Eclipse Plus C18 (ID: 4.6 mm × 100 mm, particle size: 3.5 µm)
Injection volume	3 µL
Mobile phase	60 v% acetonitrile in H ₂ O
Flow rate	1.5 mL min ⁻¹
Temperature	40 °C
Detector	VWD (360 nm)
Analysis time	5 min

Figure 6-5 HPLC calibration lines of aldehydes after 2,4-dinitrophenylhydrazine (DNPH) derivatization, (A) formaldehyde, (B) acetaldehyde, (C) acetone, (D) propionaldehyde, (E) UV-Vis calibration curve for formaldehyde after reaction with Nash's reagent, and (F) HPLC curve of $5 \mu\text{mol L}^{-1}$ aldehydes-DNPH standards with various peaks, (1) formaldehyde-DNPH, (2) acetaldehyde-DNPH, (3) acetone-DNPH and (4) propionaldehyde-DNPH.

The DNPH derivatization method discussed above is relatively time consuming. As a result, it is suggested that this method could be applied mainly to verify whether aldehydes are produced in liquid phase. If formaldehyde is the only product verified by this method, Nash's method is much more convenient for routine analysis.²⁸⁴ Nash reagent was prepared by adding 25 g of ammonium acetate, 2.1 mL of acetic acid and 0.2 mL of acetylacetone into water and making the total volume of the solution to be 100 mL. Then 2 mL of liquid sample was mixed with 2 mL of Nash reagent and kept shaking for 1 h. The final solution was analyzed by UV-Vis spectroscopy and the absorbance at 414 nm was used for quantification. The calibration line of formaldehyde by this method is shown in Figure 6-5E and the MDL obtained is $0.17 \mu\text{mol L}^{-1}$. Another colorimetric method similar to Nash's method uses chromotropic acid (4,5-dihydroxynaphthalene-2,7-disulfonic acid, disodium salt dehydrate) as color

reagents and the absorbance at 577 nm was monitored. Detailed method can be found in the literatures.^{260,286}

As discussed above, organics may affect the analysis of oxygenates. Several organics were added during the preparation of derived aldehydes-DNPH for HPLC analysis. As shown in Table 6-7 and Figure 6-6, most of these additives did not affect the aldehyde analysis, with both retention time and peak area remained unchanged. In the case of TEA and NaOH, as shown in Figure 6-6B, only acetone-DNPH in TEA still can be identified with a slightly smaller peak area and shorter retention time than those in H₂O. No matching peaks can be found for all the other three aldehydes. Low concentrations of TEA (around 20-30 mM) were often used as the modifier for the mobile phase of HPLC, which typically do not affect the analysis of organic compounds. However, if TEA concentration is relatively high such as 15 v% (equivalent to 1.1 M in this work), the peak shape and retention time can be affected.²⁸⁷ On the other hand, higher pH (0.1 M NaOH, pH=13) also leads to the risk of matrix dissolution of some columns packed with silica.²⁸⁸

Table 6-7 Effects of various organics and alkaline condition on the HPLC peak areas of aldehydes (10 $\mu\text{mol L}^{-1}$).

Medium	FAD ^d	AAD ^e	ACD ^f	PAD ^g
H ₂ O	21.8	20.9	22.1	25.7
Methanol ^a	21.4	20.6	22.0	25.6
Ethanol ^a	21.3	20.4	22.2	25.8
1-Propanol ^a	21.1	20.3	21.7	25.3
2-Propanol ^a	20.2	19.3	20.9	24.3
DMF ^a	20.4	19.5	21.1	24.5
MV ^b	20.8	20.3	22.2	25.8
RB ^b	22.7	21.6	24.3	26.3
[Ru(bipy) ₃]Cl ₂ ^b	22.1	21.5	22.0	25.8
TEOA ^a	20.5	20.3	22.1	25.4
NaOH ^c	-	-	18.2	-
TEA ^a	-	-	18.6	-

^a 15 v%; ^b 0.1 mM; ^c 0.1 M; ^d Formaldehyde-DNPH; ^e Acetaldehyde-DNPH; ^f Acetone-DNPH; ^g Propionaldehyde-DNPH.

Figure 6-6 HPLC peaks of FAD, AAD, ACD, PAD in (A) 15 v% methanol, 15 v% ethanol, 15 v% 1-propanol, 15 v% 2-propanol, 15 v% DMF, 15 v% TEOA and 0.1 mM MV, and (B) 0.1 mM RB, 0.1 mM Ru(bpy)₃Cl₂, 15 v% TEA and 0.1 M NaOH.

6.3.4 Carboxylic acids analysis

Carboxylic acids (formic acid and acetic acid) have been found as the photoreduction products of CO₂ in liquid phase. In a recent work by Cao et al., formic acid was produced from CO₂ reduction and ¹H NMR was used for quantification by using CH₃COONa as an internal standard.²⁸¹ However, for routine analysis especially the mixture of carboxylic acid in the liquid sample, IEC^{92,118,124,133,137,208,226,238,247,274-278} or HPLC method^{208,216,229-231,236,265,272,273} is recommended. Herein, we used HPLC method with a PL Hi-Plex H column and VWD (210 nm) for carboxylic acids analysis.

The mobile phase used was 5 mM H₂SO₄. The temperature was set at 55 °C and injection volume was 20 μL. More details about the method can be found in Table 6-8. The calibration lines of formic acid and acetic acid are shown in Figure 6-7A and 7B,

respectively with well fitted straight lines. A typical HPLC curve is shown in Figure 6-7D indicating a good separation of these two acids. In HPLC curve, the water solvent peaks (marked by asterisks) are also present. The obtained MDLs for HCOOH and CH₃COOH in the aqueous solution were 3.9 and 6.3 $\mu\text{mol L}^{-1}$, respectively. When HCOOH is the only organic species present in liquid phase, UV-Vis spectroscopy can be used for quantification. The liquid sample after being removed with the solid particles can be directly analyzed by measuring the UV absorbance at 210 nm.

Table 6-8 Analytical conditions for carboxylic acid in liquid phase.

Equipment	Agilent 1260 HPLC
Column	PL Hi-Plex H (ID: 7.7 mm $\times$ 300 mm, particle size: 8 μm , Varian)
Injection volume	20 μL
Mobile phase	5 mM H ₂ SO ₄
Flow rate	0.6 mL min ⁻¹
Temperature	55 $^{\circ}\text{C}$
Detector	VWD (210 nm)
Analysis time	17 min

Figure 6-7 HPLC calibration lines of (A) formic acid and (B) acetic acid, (C) UV-Vis calibration line of formic acid and (D) HPLC curve of a mixture containing 109 $\mu\text{mol L}^{-1}$ formic (Peak 1) and 83 $\mu\text{mol L}^{-1}$ acetic (Peak 2) acid; * denotes water solvent peaks.

The calibration curve obtained by this method is shown in Figure 6-7C with a low detection limit of 0.08 $\mu\text{mol L}^{-1}$. Although this method is simple for HCOOH analysis, it has a limitation since it can only be used for quantification of HCOOH in water in the

absence of other organic species. Alternatively, when HCOOH is only carboxylic acid product, colorimetric method can also be used after reducing HCOOH to HCHO²⁸⁶ and then react with chromotropic acid²⁶⁰ or Nash reagent.^{224,289} Briefly, 0.5 mL of liquid sample was added into magnesium powder (50 mg) following by drop-wise adding of 0.5 mL 37% hydrochloric acid (10 M) at 0 °C bath and then 3 mL 1 M NaOH. The resultant suspension was centrifuged at 13000 rpm for 5 min and 2 mL of supernatant was mixed with 2 mL of Nash reagent for UV-Vis analysis (see Section 6.3.3) to determine the total amount of HCHO. HCOOH can be determined after subtracting the amount of HCHO in product (Nash's method). Care should be taken that the accuracy of HCOOH quantification by this method is largely affected by the yield of reduction. Hence, this method is not suitable for accurate routine analysis but may be used for a quick qualitative check when the identification of HCOOH by other techniques is obscure. The effects of organics and alkaline condition on acid analysis were also studied. The results in Table 6-9 and Figure 6-8 show that only DMF, TEA and TEOA affected the analysis of acids. In the case of TEOA, the effect was mainly due to the up-shift of baseline caused by the tail of TEOA peak. Therefore, baseline correction needs to be carried out during the quantification of HCOOH and CH₃COOH when TEOA is present. When TEA was present, the analysis of HCOOH was not affected while the peak area of CH₃COOH was greatly enhanced. In the presence of DMF, the baseline upshifted after HCOOH signal with the peak area of HCOOH enhanced and CH₃COOH unchanged. The retention time in all cases was kept constant. The interaction of amine group in TEA and DMF with the column materials may cause such abnormality.

Table 6-9 Effects of various organics and alkaline condition on the HPLC peak areas of acids (10 µL L⁻¹).^a

Medium	Formic acid	Acetic acid
H ₂ O	229	135
Methanol ^b	229	134
Ethanol ^b	227	134
1-Propanol ^b	230	137
2-Propanol ^b	228	135
ACN ^b	232	136
MV ^c	231	138
[Ru(bpy) ₃]Cl ₂ ^c	231	139
RB ^c	226	136
NaOH ^d	230	136
DMF ^b	451	131
TEA ^b	234	306

TEOA^b 229^e 138^e
^a Equivalent to 217 $\mu\text{mol L}^{-1}$ of formic acid and 167 $\mu\text{mol L}^{-1}$ of acetic acid; ^b 15 v%;
^c 0.1 mM; ^d 0.1 M; ^e After baseline correction.

Figure 6-8 HPLC peaks of formic acid and acetic acid in (A) 15 v% methanol, 15 v% ethanol, 15 v% 1-propanol, 15 v% 2-propanol, 15 v% ACN, 0.1 M NaOH, 0.1 mM MV, 0.1 mM Ru(bpy)₃Cl₂ and 0.1 mM RB, and (B) 15 v% DMF, 15 v% TEA and 15 v% TEOA.

6.4 Carbon source verification and O₂ monitoring

The contribution of carbon residues on the photoreduction products was recently reported.²⁰⁵ The *in situ* DRIFT study indicated that ¹²CO was the main product when ¹³CO₂ gas was used during surface photoreaction over the Cu(I)/TiO₂ catalyst. The ¹²C source was proven to be from the carbon residue on the photocatalyst originated from the organics used during photocatalyst preparation. Based on this, the photocatalytic activities reported for CO₂ reduction in the literature may need to be verified if there

was no tracking of carbon source or enough evidences for photocatalytic events.²⁰⁶ Thus, either carefully and systematically designing control experiment or carbon source tracking by NMR, GC-MS or LC-MS with isotope ^{13}C labeled CO_2 as the reactant is necessary. The carbon source in gas products like methane and carbon monoxide can be verified by spectroscopic method (e.g. DRIFT) or GC-MS and in liquid oxygenates by ^{13}C NMR, GC-MS or LC-MS. For example, Liu et al. studied the solvent effect on photocatalytic CO_2 reduction by using $^{13}\text{CO}_2$ with GC-MS and ^{13}C NMR to identify the source of carbon in CO and liquid products, respectively.²¹⁶ Yui et al. reported the use of TiO_2 (P25) for methane production. The carbon source of methane was confirmed from CO_2 based on a signal at $m/e = 17$ ($^{13}\text{CH}_4$) on GC-MS when $^{13}\text{CO}_2$ was used.⁹² The photocatalytic activity of titanium metal–organic framework in CO_2 reduction to produce formic acid was confirmed by using ^{13}C NMR.¹²⁴ The signal at 165.30 ppm can be found, which was assigned to HCOO^- , while such a signal was not found when $^{12}\text{CO}_2$ was used. In another report, ^{13}C -labeled HCOOH in product was found to be easily detected by ^{13}C NMR to confirm that the product was from the reduction of CO_2 rather than from other carbon sources on the used carbon nanoparticles.²⁸¹ Using LDH as photocatalyst, carbon source of CO and oxygen source of O_2 were also confirmed from CO_2 and H_2O respectively by using $^{13}\text{CO}_2$ and H_2^{18}O with GC-MS method.¹²⁷

Finally, when water is used as the reducing agent for CO_2 , O_2 evolution is an important indicating factor to support photocatalytic CO_2 reduction.¹⁰³ Kudo and co-workers¹³⁷ reported that the production of H_2 , O_2 and CO are stoichiometric over Ag loaded $\text{ALa}_4\text{Ti}_4\text{O}_{15}$ (A = Ca, Sr, and Ba) photocatalysts. The ratio of the mole of reacted electrons to that of holes was found almost unity indicating that the CO_2 reduction occurred photocatalytically with water as the reducing agent. To ascertain that O_2 is generated from the reaction rather than from air contamination, the volumetric (molar) ratio of O_2 to N_2 over reaction time shall be monitored. In a recent study, the molar ratio of O_2/N_2 was found gradually increased from 0.26 (the ratio in air) to 0.40 after light irradiation. In addition, the trend of this ratio was found similar to that of CH_4 production, indicating O_2 was produced by photoreaction.¹⁰³

6.5 Conclusions

Based on the above results, major products in both gas and liquid phases from CO_2 photoreduction can be detected accurately with low detection limits by a combination

of GC and HPLC methods. Figure 6-9 summarizes the analysis methods and the detection limits of the major chemical species in both gas and liquid phases in the absence of organic additives. The effects of several organic additives including commonly used solvents, photosensitizers and sacrificial reagents in photoreaction were investigated. It has been found that alcohol analysis by GC method is more sensitive to organic additives while aldehyde and acid analyses by HPLC method are not affected by most of the organics investigated. The importance of carbon source verification is highlighted and several techniques like DRIFT, NMR and GC-MS can be used.

Figure 6-9 Summary of analysis methods for gas and liquid phase samples. Derivatization: aldehydes were derivatized with DNPH before performing HPLC analysis. The detection limits ($\mu\text{mol L}^{-1}$) are shown in brackets.

CHAPTER 7 PHOTOCATALYTIC REDUCTION OF CARBON DIOXIDE OVER SELF-ASSEMBLED CARBON NITRIDE AND LAYERED DOUBLE HYDROXIDE: THE ROLE OF CARBON DIOXIDE ENRICHMENT

7.1 Introduction

Despite of vast materials screening including TiO_2 ,^{90,102-104,107} Zn_2GeO_4 ,^{131,132} $\text{BaLa}_4\text{Ti}_4\text{O}_{15}$,¹³⁷ Ga_2O_3 ,¹²¹ LDH ^{127,135} for CO_2 reduction photocatalysts, the current efficiency is still limited. This is mainly due to the fact that CO_2 is a rather inert molecule. The insufficient contact of CO_2 molecules with the active sites of photocatalyst imposes further limits on the reduction efficiency. Alkaline additives like MgO have been used to create CO_2 adsorption sites on the surface of P25 TiO_2 for enhanced CO_2 adsorption and reduction.^{290,291} Sodium carbonate was used as a reduction medium to dissolve more CO_2 than pure H_2O .¹⁰⁷ The pre-enrichment of CO_2 on the surface of photocatalyst is critical for subsequent CO_2 activation and reduction. Better candidate to concentrate CO_2 during photoreaction need to be developed for further reduction efficiency enhancement.

As introduced in Chapter 3, LDH has received great interest due to their interesting physicochemical properties such as large surface areas, positively charged surface and compositional flexibilities.^{145,146} In particular, LDH has been used to assemble organic-inorganic hybrids through the electrostatic force with negatively charged materials for different applications.^{139,149,292} As presented in Chapter 3, xanthene dye immobilized on LDH was found more stable towards H_2 production from water than the free xanthene dye¹³⁹ while 2D LDH/graphene nanosheet showed enhanced O_2 evolution.²⁹³ Native LDH has been applied for CO_2 reduction to produce methanol or CO .^{127,135} Besides, LDH has a unique interlayer structure and shows high affinity towards CO_2 molecules to form carbonate LDH. It may be advantageous to employ CO_2 -rich LDH with other narrow-band-gap semiconductor for CO_2 reduction than to use it as photocatalyst.

C_3N_4 was found active for water splitting under visible light⁵⁴ and modification work (eg. doping and creating mesoporous structure) to improve its activity and NiS loading as noble metal-free cocatalyst have been presented in the work of Chapter 4 and Chapter 5, respectively. Mesoporous C_3N_4 were also used as catalyst for CO_2 activation

to produce CO after coupling with the reaction of benzene oxidation.²⁹⁴ C₃N₄ has a relative narrow band gap of 2.7 eV and has significant light absorption in the range of 200-450 nm. Its conduction band is around -1.1 eV¹⁶⁶, which is more negative than most of CO₂/CO₂ reduction product redox potential.²⁰⁰ Based on the above facts, it could serve as another candidate for photocatalytic CO₂ reduction. In addition, the template free synthesized C₃N₄ usually has a sheet-like structure in the scale 1-10 μm and carries plentiful negative charge, which is ideal for the assembly with positive LDH nanosheets.

In this Chapter, we presented the construction of self-assembled MgAl LDH/C₃N₄ with Pd as cocatalyst for photocatalytic CO₂ reduction. To investigate the role of LDH, carbonate-free LDH and carbonate-rich LDH were synthesized and compared. Besides MgAl LDH, three other kinds of LDH, i.e. ZnAl, NiAl and ZnCr LDH were also studied.

7.2 Experimental

7.2.1 Preparation of C₃N₄ and LDH

To prepare C₃N₄, the precursor of urea (10g, Alfa Aesar, 99%) was calcined in 550 °C chamber furnace for 4 h without purging gas. The crucible to hold precursor was covered with lid carefully to make sure the calcination was undergoing in static air atmosphere. The obtained yellow powder was washed and filtrated, dried in 50 °C vacuum oven for further usage.

LDH suspension was prepared according to those in Chapter 3.¹³⁹ Typically, 8 mL mixed solution of Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O with a ratio of Mg:Al = 0.3 : 0.1 (M/M) were added into 32 mL of 0.15 M NaOH solution under vigorously stirring. The obtained suspension after stirring for 10 min was centrifuged at 20,000 rpm for 5 min and washed thoroughly with deionized water 3 times to remove free electrolyte like nitrate and hydroxide ion. The final wet precipitate was re-dispersed in 40 mL water and transferred into 45 mL vessel. The vessel in autoclave was undergoing hydrothermal treatment at 100 °C for 16 h. To reduce the contamination of carbonate in LDH, N₂ was purged during the coprecipitation of mixed metal nitrates and NaOH, the obtained LDH was denoted as LDH(N₂). Carbonate LDH was prepared by anion exchanged of LDH suspension with 0.15 M Na₂CO₃ (v/v=1:1) at room temperature under stirring for 30 min. The LDH suspension after this treatment was centrifuged at

20,000 rpm for 5 min to remove excess CO_3^{2-} anion and then re-dispersed in H_2O to form LDH suspension, denoted as $\text{LDH}(\text{CO}_2)$. For ZnAl LDH, NiAl LDH, ZnCr LDH, same procedures were followed except changing the metal precursors to their corresponding metal nitrate salts.

C_3N_4 (200 mg) was dispersed in 100 mL deionized water and ultrasonicated for 30 min to get the C_3N_4 suspension. For the assembly of $\text{LDH}/\text{C}_3\text{N}_4$, different volumes of LDH suspension were added into the suspension of C_3N_4 with a weight ratio of LDH to $\text{C}_3\text{N}_4 = 0, 5\%, 10\%, 15\%, 20\%$, respectively. The final total volume of $\text{C}_3\text{N}_4/\text{LDH}$ suspension was made to 200 mL by adding extra H_2O .

7.2.2 Characterizations

The Zeta Potential, BET, FESEM and TEM characterizations are similar to those used in Chapter 3. The XRD, FTIR, BET, EA (for C, H, N), UV-vis DRS characterization are similar to those described in Chapter 4. ICP analysis for the content of Mg, Al is similar to those performed in Chapter 5. The thermogravimetric analysis (TGA) was carried out on a Perkin Elmer Thermal Analyzer with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ in air up to $800\text{ }^\circ\text{C}$.

7.2.3 Photocatalytic activity evaluation

Photocatalytic reaction was carried out in a closed circulation system (with total volume around 1000 mL) using a Pyrex cell, which is same to that in Chapter 6 for analysis method establishment. Certain amount of Na_2PdCl_4 (0.5 wt% Pd of total catalyst) was added in x wt% $\text{LDH}/\text{C}_3\text{N}_4$ as source of Pd cocatalyst. A 500 W Mercury (Xenon) lamp (Newport) was used as the light source. The reaction cell was kept at room temperature with cooling water. The photocatalyst suspension was irradiated for 2 h under vacuum to remove dissolved oxygen before charging with 200 Torr CO_2 (99.995%, SOXAL). The amount of gaseous reactant (CO_2) and products (CH_4 , CH_3CH_3 , CO , O_2 etc.) at different time of photoreaction was determined using an online GC. These compounds were firstly separated through Haysep Q and MolSieve $5\text{ \AA}$ column and three switch valves, then detected by a thermal conductivity detector (TCD) and a flame ionization detector (FID). The liquid oxygenates were analyzed separately at the end of photoreaction (24 h). The alcohols in liquid phase were analyzed by another channel of the same GC through manual injection, using a DB-wax

column for separation and a FID for detection. The aldehydes (after derivatization) and acids were analyzed by high performance liquid chromatography (HPLC) using a VWD detector. An Eclipse Plus C18 column and a PL Hi-Plex H column were used respectively for the separation of aldehyde derivatives and acids. More details on the analysis methods like valve switch and aldehydes derivatization can be found in Chapter 6.²⁰⁰

7.3 Results and discussion

The Zeta Potential results in Figure 7-1 show that C_3N_4 suspension carries a negative charge of -27.3 mV and LDH has a positive charge of +52.7 mV. After adding 1 wt% of LDH into C_3N_4 suspension, the charge of the system quickly shifted to +24.9 mV and increased further if more LDH was added. The shift of zeta potential from negative to positive indicates the successful self-assembly of LDH with C_3N_4 . The peaks in Figure 7-2a at 12.7° and 27.3° are corresponding to the in-planar pattern and interlayered stacking pattern of C_3N_4 .¹⁶⁷ Typical XRD patterns of MgAl LDH can be found in Figure 7-2e. Similar to work in Chapter 3,¹³⁹ two weak peaks at around 20° can be found and are corresponding to small percentage of $Al(OH)_3$ impurity.²⁹⁵ As shown in Figure 7-2b, the major peaks of LDH (003) and (012) along with those of C_3N_4 can be identified for the 5 wt% LDH/ C_3N_4 . With weight percentage of LDH increases from 5 wt% to 20 wt%, the intensity of LDH characteristic peaks of LDH also increased.

Figure 7-1 Zeta Potential of LDH/ C_3N_4 with different weight percentages of LDH.

Figure 7-2 XRD patterns of C_3N_4 (a), 5 wt% LDH/ C_3N_4 (b), 10 wt% LDH/ C_3N_4 (c), 15 wt% LDH/ C_3N_4 (d), 20 wt% LDH/ C_3N_4 (e) and LDH (f).

As shown in Figure 7-3A, the FTIR absorption peak at 800 cm^{-1} and absorption bands in the range of $1200\text{--}1600\text{ cm}^{-1}$ can be well identified in both C_3N_4 and LDH/ C_3N_4 assembly, which are attributed to the breathing mode of triazine and stretching mode of C–N heterocycles in C_3N_4 .⁴⁹ The peaks at 1383.8 cm^{-1} and 447.3 cm^{-1} in line **f** of Figure 7-3A are corresponding to the interlayer NO_3^- vibration and metal-oxygen (M–O) lattice vibration in LDH.²⁹⁶ Due to the strong vibration of C–N heterocycles of C_3N_4 in LDH/ C_3N_4 assembly from 1200 to 1600 cm^{-1} , the characteristic peak of interlayer NO_3^- cannot be observed clearly. However, the M–O lattice vibration of LDH can be found in all LDH containing samples and intensity of this peak increases with LDH coating amount as shown in the magnified FTIR spectra in Figure 7-3B.

Figure 7-3 FTIR spectra with wavenumber range of $4000\text{--}400\text{ cm}^{-1}$ (A) and $800\text{--}400\text{ cm}^{-1}$ (B) for samples of C_3N_4 (a), 5 wt% LDH/ C_3N_4 (b), 10 wt% LDH/ C_3N_4 (c), 15 wt% LDH/ C_3N_4 (d), 20 wt% LDH/ C_3N_4 (e) and LDH (f).

As observed in Figure 7-4A, the obtained C_3N_4 has a large sheet-like structure in the

scale of micrometer. Hexagonal LDH sheets with diameters between 50-100 nm are shown in Figure 7-4B. As indicated in Figure 7-4C, the LDH nanosheets are well dispersed on the surface of C_3N_4 , demonstrating the successful self-assembly of LDH and C_3N_4 . After photoreaction for 24 h, LDH nanosheets are still attached to the surface of C_3N_4 as shown in Figure 7-4D, indicating the stability of LDH/ C_3N_4 during photoreaction. Besides, 5-10 nm of Pd nanoparticles are produced and well deposited on the LDH/ C_3N_4 assembly. The self-assembly of LDH with C_3N_4 as well as close attachment of LDH on C_3N_4 can also be supported by TEM images with higher magnification and FESEM images in Figure 7-5 and Figure 7-6, respectively.

Figure 7-4 TEM images of C_3N_4 (A), LDH (B), 10 wt% LDH/ C_3N_4 before (C) and after photoreaction of 24 h (D).

Figure 7-5 TEM images with higher magnification for C_3N_4 (A), LDH (B), 10 wt% LDH/ C_3N_4 (C) and 10wt% LDH/ C_3N_4 after photoreaction for 24 h (D).

Figure 7-6 FESEM images of C_3N_4 (A), LDH (B), 10 wt% LDH/ C_3N_4 (C) and 10wt% LDH/ C_3N_4 after photoreaction for 24 h (D).

Figure 7-7 shows several control studies to verify the CO_2 reduction event. Under the reaction conditions of curve a, $3.7 \mu\text{mol}$ of CH_4 , $0.1 \mu\text{mol}$ of CO and $0.06 \mu\text{mol}$ of CH_3CH_3 are produced after 24 h irradiation. No oxygenates like alcohol, aldehyde or acid can be detected in the liquid phase from our products screening. Due to the negligible activity of CO and CH_3CH_3 , the major product CH_4 was taken for activity comparison and discussion in the following study. In the absence of photocatalyst or light, no CH_4 or other compounds can be detected, indicating both light and catalyst are

compulsory for the CH₄ production. To examine whether CH₄ was produced from CO₂ reduction or from degradation of other possible carbon source, He gas was charged in the system instead of CO₂. Surprisingly, 1.3 μmol of CH₄ can still be produced when He is used. The possibility of CH₄ production from the degradation of C₃N₄ can be eliminated because no CH₄ was detected when Pd/C₃N₄ was irradiated under He atmosphere. It is well known that the affinity of CO₃²⁻ to LDH is much stronger than the other anions like NO₃⁻.¹⁴⁶ Therefore, the synthesized nitrate LDH can be easily contaminated with some of CO₃²⁻ although it is not reflected either in XRD patterns (Figure 7-2f) or in FTIR spectra (curve f in Figure 7-3A) due to the low percentage of CO₃²⁻.¹⁴⁹ From the EA analysis (Table 7-1), there is still 0.73 wt% of C in the sample of nitrate LDH, which is likely due to this contamination of CO₃²⁻ since no any carbon containing precursors were used during the LDH synthesis. Based on this, the interlayered CO₃²⁻ was calculated to be 12.2 μmol. When He was charged, the system is not truly CO₂ free but contains CO₂ in the form of interlayered CO₃²⁻ in LDH, which was responsible for the CH₄ production.

Figure 7-7 CH₄ production under different control conditions: a) 10% LDH/C₃N₄; b) He was charged instead of CO₂; c) without light irradiation and d) without photocatalyst. Reaction conditions of a): 10 wt% LDH/C₃N₄ (200 mg) in 200 mL H₂O, 0.5% Pd was loaded as cocatalyst, 200 Torr CO₂ charged. Hg(Xe) lamp (500 W) without filter was used as light source.

Table 7-1 Elemental analysis of LDHs and their activity for CH₄ production after assembly with C₃N₄.

Samples	Formula ^a	C wt% ^b	CO ₂ , μmol ^c	CH ₄ , μmol	Yield % ^d
LDH	Mg _{0.689} Al _{0.311} (OH) ₂ (NO ₃) _{0.133} (CO ₃) _{0.048} ·0.657H ₂ O	0.73	12.2	1.3	10.8
LDH(N ₂)	Mg _{0.693} Al _{0.307} (OH) ₂ (NO ₃) _{0.274} (CO ₃) _{0.019} ·0.846H ₂ O	0.22	3.7	0.25	6.7
LDH(CO ₂)	Mg _{0.656} Al _{0.344} (OH) ₂ (NO ₃) _{0.031} (CO ₃) _{0.118} ·0.624 h ₂ O	2.34	39	1.8	4.6

^a The formula of LDH was estimated based on the following experiment and assumptions. Mg, Al were determined by ICP and number of Al atom was taken as unit. N and C were measured by EA and assumed only from the interlayered NO₃⁻ and CO₃²⁻. Water amount was determined from TGA by calculating weight loss of LDH from room temperature to temperature of 1st endothermic peak.; ^b Measured by EA; ^c Assuming all the C measured are due to the CO₃²⁻ in LDH interlayers; ^d The yield was obtained from the division of produced CH₄ to the converted CO₂ amount in the LDH interlayer.

Two more control experiments were conducted to study the role of interlayered CO₃²⁻. N₂ gas was purged during the co-precipitation of LDH precursors to reduce CO₂ contamination and the obtained LDH was denoted as LDH(N₂). The nitrate LDH was exchanged with Na₂CO₃ to obtain CO₂-rich LDH, which denoted as LDH(CO₂). The FTIR peaks at around 1384 cm⁻¹ (Figure 7-8A) for both LDH and LDH(N₂) were found indicating the presence of NO₃⁻ in these two LDHs. EA analysis (Table 7-1) shows that the C wt% in LDH(N₂) has been reduced to 0.40, indicating that less CO₂ was contaminated but it cannot be totally avoided. The C content is corresponding to 6.7 μmol of CO₃²⁻ while 0.25 μmol CH₄ over 24 h can be produced. As evidenced by FTIR spectra in Figure 7-8A, peak shifted from 1384 cm⁻¹ to 1367.4 cm⁻¹ in LDH(CO₂) indicating that the interlayered NO₃⁻ has been exchanged by CO₃²⁻. As a result, the C wt% in LDH(CO₂) increased to 2.35 and 1.8 μmol CH₄ in total can be produced. Overall, the yield of CH₄ from interlayered CO₃²⁻ among these three LDHs was calculated to be 5-10 %. In the absence of LDH, only 1.4 μmol CH₄ can be produced from around 8000 μmol free gaseous CO₂ in the system with a yield of 0.02%, while no CH₄ was produced when the free CO₂ decreased to the scale of 10 μmol. The much higher CO₂ reduction efficiency can be attributed to the fact that CO₂ was concentrated in the interlayer of LDH in the form of CO₃²⁻, which can be more easily reduced due to its close contact with Pd and C₃N₄ in the LDH/C₃N₄ assembly.

Figure 7-8 FTIR spectra (A) for LDH (a) , LDH (N_2) (b), LDH (CO_2) (c); TGA weight loss curves (B) for LDH (a) , LDH (N_2) (b), LDH (CO_2) and TGA heat flow curves (B) for LDH (d) , LDH (N_2) (e), LDH (CO_2) (f).

The effect of LDH coating percentage on CH_4 production was studied and shown in Figure 7-9. The optimal LDH wt% was found at 10. When LDH wt% was at 5, only part of C_3N_4 was assembled with LDH (Figure 7-10A and B), thus not all active sites can be employed for CO_2 reduction. By increasing the loading amount of LDH from 5 wt% to 10 wt%, more LDH can be assembled, therefore, more CO_3^{2-} sources would be present and lead to higher activity. After further increasing weight percentage, excess free LDH was found nearby the C_3N_4 (Figure 7-10C and D), indicating that LDH may over cover the surface of C_3N_4 as well as Pd and block the light irradiation, hence the activity was decreased.

Figure 7-9 The optimization of LDH weight percentage in LDH/ C_3N_4 assembly for CH_4 production.

Figure 7-10 TEM images of 5 wt% LDH/C₃N₄ (A & B), 15 wt% LDH/C₃N₄ (C) and 20 wt% LDH/C₃N₄ (D).

Figure 7-11 shows the comparison of different components for CO₂ reduction. LDH alone and LDH after loading Pd show almost no activity towards CO₂ reduction. Although some LDHs have been reported active for CO₂ reduction to CH₄,¹²⁷ it would be difficult for the present MgAl LDH to be used as photocatalyst directly considering its wide band gap and weak light absorption even in the UV range. As shown in Figure 7-12, the UV-vis DRS spectra of LDH/C₃N₄ were close to that of C₃N₄, indicating that only C₃N₄ serves as a light-harvesting photocatalyst. Native C₃N₄ without modification can produce 0.4 μmol CH₄ and the activity can be increased to 1.4 μmol after loading 0.5 wt% Pd as the cocatalyst. After assembly with LDH, the CH₄ production can be further increased to 3.7 μmol, which is 2.6 times of that without LDH coating. After self-assembly, the LDH was closely attached to the surface of C₃N₄. After charging with CO₂ in the system, the nitrate LDH can easily change to carbonate LDH due to the higher affinity of CO₃²⁻ to LDH than NO₃⁻. As discussed previously, the resulted interlayered carbonate has a higher concentration than aqueous CO₃²⁻. Besides, comparing with aqueous CO₃²⁻, the interlayered CO₃²⁻ is strongly attached to the surface of C₃N₄ thus it can be more easily reduced. Meanwhile, the consumed interlayered CO₃²⁻ in LDH during photoreaction can be compensated by the aqueous CO₃²⁻ and gaseous CO₂. When running in He, there is no more CO₂ to compensate the interlayered CO₃²⁻, which is the reason for why the CH₄ production for this case drops

significantly after 24 h (Figure 7-7b).

Figure 7-11 CH₄ production over different components of photocatalyst. The amount of component when used is 200 mg for C₃N₄, 20 mg for LDH, 0.5 wt% in total catalyst for Pd. Reaction medium: 200 mL H₂O, 200 Torr CO₂ charged. Hg(Xe) lamp (500 W) without filter was used as light source.

Figure 7-12 UV-vis DRS spectra of C₃N₄, LDH, 10 wt% LDH/C₃N₄ before and after 24 h photoreaction.

Besides MgAl LDH, other LDHs including ZnAl, NiAl and ZnCr LDH were also synthesized and employed for self-assembly of LDH/C₃N₄. The successful synthesis of these LDHs can be evidenced by their corresponding typical XRD patterns as shown in Figure 7-13A. The major peaks in FTIR spectra (Figure 7-13B) at 427 cm⁻¹, 512 cm⁻¹ and 430 cm⁻¹ are attributed to the vibration modes of metal-oxygen in the interlayer of

ZnAl, ZnCr and NiAl LDHs, respectively.²⁹⁷⁻²⁹⁹ UV-vis DRS spectra in Figure 7-14A show that ZnAl LDH has similar light absorption behaviour to MgAl LDH and these two white color samples have a very limited light absorption even in the UV range (200-400 nm). In comparison, NiAl and ZnCr LDHs show different types of UV-vis spectra. Two major peaks at 400 and 570 nm can be found for brown ZnCr LDH, while two more broad and intense peaks at 370 and 640 nm are shown for green NiAl LDH. The late two LDHs have stronger light absorption in both UV and visible light range, which may be favourable for CO₂ reduction. However, the activity comparison in Figure 7-14B shows that ZnAl and ZnCr LDHs have only half activity for CH₄ production, compared with MgAl LDH. Compared with C₃N₄ without LDH coating, ZnAl and ZnCr LDHs still give a slight enhancement for CH₄ production. Interestingly, NiAl LDH, which has strongest light absorption, shows the lowest activity. These results clearly indicate that the LDHs in the assembly of LDH/C₃N₄ do not play the role of either photocatalyst or light absorber, hence do not relate to their UV-vis spectra. In our work, the LDH simply serves as CO₂ enrichment and fixation platform for subsequent CO₂ reduction. The main reason leading to the activity difference may be ascribed to the different dispersion among these LDHs. The MgAl LDH suspension has very good dispersion, which can last for at least for 3 months without settling down. In comparison, the dispersion of ZnCr and NiAl LDH is worse. In particular, most of NiAl LDH settles down within 5 min and part of ZnCr LDH also settles down gradually (Figure 7-15). The Zeta Potential measurement of ZnAl, ZnCr and NiAl LDHs suspension showed values of +58.0, +37.6 and +30.8 mV, respectively, while +52.7 mV was obtained for MgAl LDH (Figure 7-15). The worse dispersion of ZnCr and NiAl LDHs may be unfavourable for the good assembly of LDH/C₃N₄. As a result, these two LDHs did not improve much on activity and the activity was even decreased for NiAl LDH. The obtained ZnAl LDH also has a high zeta potential. However, unlike the transparent MgAl LDH suspension, it is a flocculent suspension, which may not be good for the self-assembly.

Figure 7-13 XRD patterns (A) and FTIR spectra (B) of ZnAl LDH (a), ZnCr LDH (b) and NiAl LDH (c).

Figure 7-14 UV-vis DRS spectra (A) of MgAl, ZnAl, ZnCr and NiAl LDHs; CH_4 production over different LDH/ C_3N_4 assemblies. Reaction conditions are the same as those in Figure 7-7a.

Figure 7-15 Photos of MgAl LDH (A), ZnAl LDH (B), ZnCr LDH (C) and NiAl LDH (D) suspension at different time intervals. Their zeta potential values (mV) of initial suspension were shown on top.

As shown in Figure 7-16, the activity of CH₄ production is quite stable within 24 h and gradually decreased after that. This is possibly because LDH is possible to dissolve slightly in the weak acidic environment in the presence of CO₂ and H₂CO₃ formed. The pH measured was 5.3. Based on ICP analysis of Mg and Al in the samples after photoreaction for 72 h, 22.9 wt% of LDH has lost thus leading to the drop of CO₂ reduction activity.

Figure 7-16 Stability study of photocatalytic CO₂ reduction by using 0.5 wt% Pd loaded 10 wt% LDH/C₃N₄.

As shown in the schematic diagram in Figure 7-17, MgAl LDH and C₃N₄ can be readily self-assembled through the electronic static force and Pd nanoparticles can be *in situ* loaded during light irradiation. In the environment of CO₂, the nitrate LDH can easily turn into carbonate DH, hence the aqueous random CO₂ molecules can be enriched and fixed. Due to the close attachment of LDH on C₃N₄ nanosheets and Pd cocatalyst, the concentrated CO₃²⁻ in the interlayers can be reduced more efficiently, compared with the surrounding moving CO₂ or CO₃²⁻. Meanwhile, the consumed CO₃²⁻ can be readily compensated by the surrounding free CO₂ or CO₃²⁻, hence, a high activity of CO₂ reduction can be sustained. Beyond work presented in this Chapter, LDH is also proposed as CO₂ storage materials but under high temperature up to 200 °C.^{300,301} Due to the higher affinity of CO₂ to LDH, CO₂ in atmosphere tends to be exchanged with the interlayered anions even at room temperature. Based on this, the diluted atmospheric

CO₂ may be concentrated and stored in the LDH interlayers. By combining with the CO₂ reduction work as presented above, a continuous system based on photocatalyst/LDH for CO₂ capture, storage and reduction may be practically possible if better CO₂ reduction efficiency can be obtained in the near future.

Figure 7-17 Schematic diagram of self-assembled LDH/C₃N₄ for photocatalytic reduction of CO₂.

7.4 Conclusions

In conclusion, we have demonstrated the well-dispersed MgAl LDH as a novel platform for CO₂ enrichment and fixation by using its anion exchange capacity. This positive charged LDH can be readily self-assembled with the negative charged C₃N₄ suspension. The assembly LDH/C₃N₄ shows 2.6 times activity for reducing CO₂ to CH₄ over that without LDH. The enhancement is mainly due to the enrichment of CO₃²⁻ by using LDH. The concentrated and fixed CO₃²⁻ is readily to be reduced with a much higher yield than free gaseous CO₂ due to the close attachment of LDH to the C₃N₄. It was expected that the findings here may offer new insights for future CO₂ reduction improvement.

CHAPTER 8 CONCLUSIONS AND OUTLOOK

8.1 Conclusions

The research work presented in this thesis mainly focused on the development of stable, efficient and low-cost photocatalyst for water splitting and carbon dioxide reduction towards solar fuels production. The major conclusions and findings are summarized as following:

- 1) Well-dispersed LDH nanocrystals act as supports for immobilizing RB photosensitizer and Pt nanoparticles to construct a self-assembled RB-LDH-Pt system for H₂ evolution. Such a system offers many advantages for photocatalytic water splitting: (i) immobilizing the dye photosensitizer for suppressing self-quenching, (ii) close arrangement between photosensitizer molecules and catalyst nanoparticles for efficient electron transfer, (iii) formation of well-dispersed catalysts nanoparticles on the support surface, and (iv) easy recycle of the expensive catalyst. As result, TON of RB-LDH-Pt can reach 304 based on Pt after six recycled runs, which gave at least 13-fold enhancement, compared with that from the Free system without the use of LDH. The expensive Pt can be easily recycled and reused for at least 6 times (still maintaining 64% of the activity after the 6th run) by a simple method of centrifugation, which makes this system more economical.
- 2) *In situ* sulfur-doped mesoporous C₃N₄ was synthesized from a single precursor, thiourea, by using SiO₂ nanoparticles as templates. Sulfur group was found to facilitate the condensation of C₃N₄ polymer, as a higher product yield was obtained from thiourea than that from urea as the starting material. The resultant sulfur-doped mesoporous C₃N₄ has been found to be 30 times more active than the native C₃N₄ for hydrogen evolution from photocatalytic water splitting when Pt was used as the cocatalyst. A relatively high apparent quantum efficiency of 5.8% was obtained at 440 nm. The activity enhancement was attributed to the effect of stronger and extended light absorption in the visible light region by sulfur doping and more efficient mass and charge transfer in mesoporous structure.
- 3) Noble metal-free C₃N₄-based photocatalyst for H₂ production was constructed by loading NiS on C₃N₄ via a simple hydrothermal method. The C₃N₄ after loading a small fraction of NiS (1.07 wt%) is 253 times more active than native C₃N₄ and can keep over

80% activity after 4 runs for 24 h. These results demonstrate that the intrinsically stable C_3N_4 polymeric semiconductor could potentially serve as a stable earth-abundant system for photocatalytic water splitting, when a small fraction of transition metal based cocatalyst is properly loaded.

4) A combination of GC and HPLC methods was developed for detection of major products in both gas and liquid phases from CO_2 photoreduction. The effects of several organic additives including commonly used solvents, photosensitizers and sacrificial reagents in photoreaction were investigated. It has been found that alcohol analysis by GC method is more sensitive to organic additives, while aldehyde and acid analyses by HPLC method are not affected by most of the organics investigated. This work provides the comprehensive and standard methods for analysis of CO_2 reduction products with low detection limits.

5) Well-dispersed MgAl LDH was found as a novel platform for CO_2 enrichment and fixation owing to its anion exchange capacity. The positively charged LDH can be readily self-assembled with the negatively charged C_3N_4 in the suspension. The assembled LDH/ C_3N_4 shows a 2.6-fold enhancement to CO_2 reduction to CH_4 , compared to that without LDH. The enhancement is mainly due to the enrichment of CO_3^{2-} by using LDH. This concentrated and fixed CO_3^{2-} is readily to be reduced with a much higher yield than free gaseous CO_2 due to the close attachment of LDH to C_3N_4 .

8.2 Outlook

Although a lot of work including ours have been conducted to improve the solar fuel production efficiency, there is still a long way to go from the lab scale system to practical applications. Moreover, the mechanism of some photocatalytic processes is still unclear, which needs further investigation. Besides, the H_2 evolution reaction studied in this work should be ultimately coupled with water oxidation to construct overall water splitting. Some suggestions for future work are proposed as following:

- 1) **Investigation of nanoscaled C_3N_4 for H_2 evolution and CO_2 reduction.** As presented in Chapter 4 and 7, the C_3N_4 obtained from template-free calcination usually has a large sheet-like structure in the scale of micrometers. Learning from other inorganic semiconductors studies, great enhancement of photocatalytic activity can be achieved after reducing the bulk particles into nanoscale. It is expected that nanoscaled C_3N_4 can also perform better photocatalytic activity than

the current bulk C_3N_4 sheet. In the future work, nanoscaled C_3N_4 can be synthesized and evaluated for photocatalytic reactions. In the work of this thesis, it has been already found that C_3N_4 networks can be partially decomposed under the hydrothermal treatment in the presence of Ni^{2+} . More systematic work can be carried out to investigate the effect of metal catalysts (like different metal types, concentration etc.) on the morphology, size and photo-physical properties of the C_3N_4 fragments.

- 2) **Development of overall water splitting systems.** C_3N_4 could be a possible candidate to construct an overall water splitting system. In future work, more efficient H_2 evolution catalyst based on C_3N_4 should be developed though investigating several aspects like the morphology and the cocatalyst. Meanwhile, O_2 evolution based on C_3N_4 should be studied by loading O_2 evolution cocatalyst like C_3O_4 . It may be possible to develop an overall water splitting system simply based on C_3N_4 with two different optimized cocatalysts. Besides, the C_3N_4 -based H_2 evolution photocatalyst can also be used to couple with other O_2 evolution photocatalysts like $BiVO_4$, PtO_x/WO_3 to construct a Z-scheme water splitting system.
- 3) **Study of correlation between size of cocatalyst particle and C_3N_4 mesopores and their effect on photocatalysis.** The introduction of mesoporous structures into C_3N_4 is able to improve H_2 production effectively based on the literature reports and our work presented in Chapter 4. However, when the mesoporous C_3N_4 was employed for photocatalytic reduction of CO_2 , lower activity for CH_4 evolution than that obtained from the native C_3N_4 . The results are unexpected and interesting. Generally, the introduction of mesoporous structure can largely increase the surface area and facilitate the mass and electron transfer, thus leading to enhanced photocatalytic activity. Photo-deposited Pd has the particle size close to the pore size of mesoporous C_3N_4 (10-20 nm), which may block the pore of the later after reduction. This could be the reason of lower activity towards CO_2 reduction. Detailed experiments need to be designed to study this. Chemical reduction methods can be developed to prepare Pd nanoparticle with particle size smaller than 5 nm and then these smaller sized Pd can be loaded on mesoporous C_3N_4 for CO_2 reduction study.
- 4) **Control of selectivity to CO_2 reduction products.** Multiple compounds existing in products will cause extra steps for separation. In the preliminary study of CO_2

reduction, pH-dependent formation of reduction products was found when Pd/P25 TiO₂ catalyst was used (not covered in this thesis). A lower pH tends to result in a higher CH₄ selectivity, while a higher pH favors CO production. In the future work, detailed study of underlying mechanism is needed for selectivity control of CO₂ reduction.

- 5) ***In situ* monitoring of CO₂ reduction progress.** Currently, most of CO₂ reduction work including those presented in this thesis was mainly focused on the photocatalyst development and reduction efficiency enhancement. To better understand the progress and mechanism of CO₂ reduction and offer guidance on optimal photocatalyst development, real time monitoring of CO₂ reduction products and intermediates certainly needed. In the future work, the *in situ* analysis of both gas and liquid products can be carried out through more regular sampling via GC and HPLC methods. For intermediate characterizations, *in situ* NMR or spectroscopy is needed to be coupled with our current photoreactors. the exfoliation of bulk C₃N₄ into two-dimensional one could offer chance for the efficiently loading of H₂ and O₂ evolution cocatalyst
- 6) **Two-dimensional materials for water splitting and CO₂ reduction.** The new emerging two-dimensional materials have opened up great opportunities because of their high accessible surface area and easily tuning electronic structure. In particular for photocatalysis application, two-dimensional photocatalyst can offer more space for cocatalyst loading and may introduce more active sites. Besides, higher surface area with alkaline property tuning can absorb more CO₂ molecules for subsequence reduction. In the future work, two-dimensional photocatalysts can be synthesized and evaluated for possible photoactivity enhancement.

LIST OF PUBLICATIONS

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