Functional metal oxide photocatalyst for efficient carbon dioxide reduction

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NANYANG
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**FUNCTIONAL METAL OXIDE PHOTOCATALYST FOR
EFFICIENT CARBON DIOXIDE REDUCTION**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2016

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Abstract

Solar fuels derived from solar energy are envisioned to replace fossil fuels for a sustainable earth and society. Photocatalytic carbon dioxide (CO_2) reduction for gaseous or liquid fuels production is one of the most promising processes to not only solve the energy crisis, but also reduce the environmental issues such as greenhouse effect. However, advancement of CO_2 reduction for solar fuels production is largely hindered by the lack of efficient photocatalysts. In this thesis, the work was focused on surface modification of semiconductor metal oxide photocatalyst to increase the affinity between CO_2 and catalysts as well as preventing the electron hole pair recombination toward optimize the reaction efficiency.

Firstly, methanolamine was utilized to functionalize the TiO_2 surface by a facile one-step solvothermal method. Surface amine group can greatly increases the affinity of CO_2 on TiO_2 surfaces through chemisorption by formation of carbamate. This process can also activate the CO_2 molecules, which allows more efficient charge transfer from TiO_2 . As a results, amine-functionalize TiO_2 can significantly enhances the CO and CH_4 production yield by photocatalytic CO_2 reduction.

Secondly, to further apply this amine group surface modification method, amine-functionalized ZnO was synthesized via a facile one-step hydrothermal method. The CO_2 adsorption ability is greatly increased after surface amine group modification. After activation of CO_2 molecules upon chemisorptions, the photoexcited electrons generated under UV-light irradiation can more efficiently reduce the CO_2 , thus significantly enhance the photocatalytic CO_2 reduction rate.

Finally, to prevent electron-hole pair recombination of semiconductor, Cu was decorated on ZnO nanowire single crystal by photodeposition method. The Cu exists in Cu_2O form and act as a cocatalyst. By trapping the photogenerated electrons, this Cu cocatalyst can effectively reduce electron-hole pair recombination toward efficient CO_2 photoreduction. The selectivity towards CO_2 reduction is also increased by this Cu cocatalst.

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Abbreviations

CB	Conduction Band
VB	Valence Band
UV	Ultraviolet
MEA	Ethanolamine
NHE	Normal Hydrogen Electrode
TCD	Thermal Conductivity Detector
FID	Flame Ionization Detector
FESEM	Field Emission Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

Chapter 1

Introduction

*The depletion of fossil fuels pushed the scientific society to investigate possible alternatives. Photocatalytic CO₂ reduction could be one attractive candidate to solve this energy crisis problem. In this introduction chapter, the background and motivation of the entire thesis work will be elaborated in **section 1.1.1** followed by the statement of hypothesis of the thesis in **section 1.1.2**. Then the statement of objectives and scope of the entire thesis will be illustrated in **section 1.2** while the structure of thesis will be described in **section 1.3**. Finally, the scientific contribution and the originality of this thesis will be demonstrated in **section 1.4**.*

1.1 Hypothesis

1.1.1 Background

1.1.1a Energy supply: from fossil fuels to solar energy

Fossil fuels, such as petroleum, coal, and natural gas are the main energy sources which contribute to more than 80% of the world energy consumption to power the rapidly growing economic and population all over the world.¹ However, the increasing consumption of fossil fuels brings not only energy crisis issues, but also environment concerns. Energy crisis issues originate from the contradiction between rising global energy demands and limited fossil fuel reserves. The global energy consumption is around 15 TW annually, which is 30 times higher than that value in early 1800s.² The oil, coal and gas reserves were estimated about 1688 billion barrels, 891 billion tons and 186 trillion cubic meters. However, humans have consumed 1 trillion barrels of oil in the past 140 years, and the world still demands 1000 barrels of oil, 221 tons of coal, and 93000 cubic meters of natural gas per second.³ As a results, these fossil fuels could only support human society for another 54, 128 and 63 years, respectively (BP, 2014).⁴ In addition, the energy demand is continuously increasing especially in developing countries, which makes the issue much more serious. The estimated energy demand will be 27 TW per year by 2050 and possible 43 TW by 2100.⁵ Hence, it is believed that the depletion age of fossil fuels is inevitably coming soon. It is necessary to think about the transition to other renewable energy resources before the depletion of fossil fuels in the near future.

On the other hand, the combustion of these carbon-based fossil fuels will release enormous amount of CO₂ in the atmosphere, which would lead to serious environmental impacts such as global warming, abnormal climate, sea level rising, acid rain and so on.^{5,6} The concentration of CO₂ in atmosphere will be predicted to be 600 ppm at the end of the century if the consumption rate of fossil fuels persists, which is 2 times of the current value.⁶ The increasing level of CO₂ in the atmosphere will lead to severe greenhouse effect. Global temperature will increase 2-6 °C by greenhouse effect, causing sea level to

increase 6-7 m and the Greenland to melt down.⁷ Coastal cities like New York, Singapore, Amsterdam, Hong Kong, etc. will be submerged under the sea while some small island countries with low sea level will totally disappear.⁸ As a result, the resulted accumulation of CO₂ in the atmosphere must be tackled. It is necessary to think about the transition to other clean energy resources before the global warming becomes irreversible.

Solar energy is an attractive candidate as a sustainable and clean energy resource. While the global energy demand is about 15 TW, the solar power striking the earth ground surface is estimated to be as large as ~90 PW.³ As a result, human civilization needs to harvest only 0.017% solar power to fulfill the global energy consumption. Besides that, solar energy is believed to be clean energy, because it does not involve the combustion of hydrocarbons, which will produce CO₂ in the process. Therefore, solar energy could be treated as a perfect alternative which is inexhaustible, widely abundant, clean and environmental benign.

1.1.1b Solar energy: Problem of capturing and storing efficiently

While solar irradiation is very abundant and almost evenly distributed on the earth planet, it is not easy for human civilization to efficiently capture and store solar energy. In the nature, this process can be accomplished by photosynthesis process as illustrated in **Fig. 1.1**.⁹ Firstly, water was split by sunlight into oxygen and “hydrogen”. The “hydrogen” can be utilized to reduce carbon dioxide to make various types of organic compounds such as glucose, sucrose, etc. The oxygen is released into air, which is very important to maintain the content of oxygen in the atmosphere. However, energy conversion efficiency of natural photosynthesis is low. Under the ideal conditions, the yield of biomass produced from photosynthesis process happened in crop is less than 1%, and often as low as 0.1%.¹⁰ Despite of the low efficiency, it is still a good example of capture and store solar energy into chemical compounds. Instead of producing various and complicated compounds, choosing a suitable energy carrier and redox reactions is one of the key factors to simulate natural photosynthesis efficiently. Thus, artificial photocatalytic CO₂ reduction might be one of the most appropriate solutions. By reduce

CO₂ in the atmosphere to produce hydrocarbons utilize solar energy, photocatalytic CO₂ reduction can not only lower down the CO₂ concentration in the atmosphere to reduce the greenhouse effect, but also generate solar fuels at the same time to provide sustainable energy resources.

Figure 1.1 Schematic illustration of the process of natural photosynthesis, combustion, and respiration.

1.1.1c Carbon dioxide photoreduction

CO₂ capture and storage (CCS) strategies have been well established for preservation of CO₂ in geological forms after many energy consuming steps of separation, purification, compression, transportation and storage.^{11, 12} However, solar-driven CO₂ reduction has a lot of advantages compared with CCS. It produces value-added fuels and chemicals, which represents a long-term solution with more profound environmental and economical impact. The schematic equation of photocatalytic CO₂ reduction for fuels is shown in (eq. 1.1). Under light illumination, CO₂ and H₂O can be converted to valuable fuels such as CH₄, CO, higher hydrocarbons and oxygenates. In this process, choosing a suitable semiconductor photocatalyst is very important since this is one of the key factors for efficient solar-driven CO₂ reduction.

The energy difference between the top of valence band (VB) of a semiconductor and the bottom of conduction band (CB) is referred as its band gap. In the first step of photocatalytic CO₂ reduction, incident photons possess larger energy than the band gap can be induced to the semiconductor photocatalyst to generate electrons and holes in the conduction and valence band, respectively. However, a large proportion of the photoexcited electrons and holes recombine together immediately while the left migrate to the surface. The holes generated from VB oxidize water to produce oxygen and the electrons generated from CB can be utilized to reduce CO₂ to generate hydrocarbons.¹³ To achieve this two half reactions, the CB position and VB position should be appropriate. The location of CB should be more negative than that of CO₂/CH₄ (-0.24 V *vs* NHE) to reduce water, while the location of VB has to be more positive than that of O₂/H₂O (1.23 V *vs* NHE) to oxidize water.¹⁴

1.1.2 Hypothesis statement

Here, we state our hypothesis as following:

Introducing amine group on semiconductor photocatalyst might increase the affinity between CO₂ and photocatalyst. Development of Cu₂O/ZnO heterojunction will prevent electron-hole pair recombination. Investigation of these novel structures might be a feasible approach for achieving more efficient photocatalytic CO₂ reduction.

1.2 Objectives and Scope

The objective of the thesis is to develop efficient semiconductor photocatalyst for CO₂ reduction and understand its working mechanism. To fulfill this objective, the following works have been done:

1. **Fundamental studies to understand mechanism of photocatalytic CO₂ capture and reduction by amine functionalized TiO₂.**

The CO₂ capture is the first step in the CO₂ photoreduction process. Increased affinity between CO₂ and photocatalyst will greatly facilitate the photoreduction process. By surface modification of TiO₂ with amine group, which is frequently used for CO₂ capture, we are able to obtain the first hand information about its photocatalytic behavior. In order to understand the interaction between CO₂ and amine functionlized TiO₂, infrared spectroscopy test was conducted to identify how the surface amine group increase the affinity between CO₂ and photocatalyst. In addition, studies of reaction mechanism and pathway provide us fundamental information of their advantages.

2. Fundamental studies to understand mechanism of photocatalytic CO₂ capture and reduction by amine functionalized ZnO.

ZnO has been well developed for photocatlytic reactions. However, it is rarely used for CO₂ photoreduction since affinity between CO₂ and ZnO is low. Herein, by surface modification of ZnO with amine group, we are able to develop ZnO photocatalyst with high CO₂ affinity. After that, the material was identified by various characterization techniques like XRD and TEM to find out the information of its chemical compositions. Then, the photocatlytic activity was evaluated in a photocatalytic reactor and the results are analyzed by gas chromatography. Finally, detailed reaction mechanism was understood by infrared spectroscopy.

3. Fundamental studies to understand mechanism of Cu₂O/ZnO for efficient CO₂ photoreduction

To suppress the recombination of photoexcited electrons and holes, Cu₂O was loaded as a cocatalyst onto the surface of ZnO by photodeposition method. With Cu₂O cocatalyst, the photocatalytic CO₂ reduction activity increased significantly. The atomic ratios of Cu₂O were adjusted to obtain an optimal performance. Results showed that 1 wt% Cu₂O/ZnO exhibited the highest activity compared with other ratios.

1.3 Dissertation Overview

The thesis consists of 7 chapters in total.

Chapter 1 introduces the background of photocatalytic CO₂ reduction. The motivations and objectives of my research are also illustrated in this chapter.

Chapter 2 summarizes the related works that have been done on photocatalytic CO₂ reduction and especially focuses on the literature of TiO₂ for photoreduction of CO₂.

Chapter 3 discusses the principles underlying the synthesis and characterization techniques.

In *chapter 4*, the experimental results of amine-functionalized TiO₂ for efficient CO₂ photoreduction will be demonstrated.

Then, further development and investigation of amine-functionalized ZnO for efficient CO₂ photoreduction will be illustrated in *chapter 5*.

In *Chapter 6*, the experimental results of Cu₂O decorated ZnO for efficient CO₂ photoreduction will be demonstrated.

Chapter 7 summarizes all the discussions. In addition, the outstanding questions will be stated and recommendations for future works will be displayed.

1.4 Scientific contributions/Originality

The original contributions of the thesis to the scientific society include:

- a) Systematic study of amine-functionalize semiconductor (TiO₂ and ZnO) by understanding the interactions between photocatalyst and CO₂ molecules, followed by the mechanism study of its photocatalytic activity.

b) Investigation and understanding of the photocatalytic CO₂ reduction activity of Cu₂O decorated ZnO in terms of synthesis path ways, photocatalytic activity and their elemental and structural information.

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Chapter 2

Literature Review

Photocatalytic CO₂ reduction for solar fuels production has been explored for more than 40 years. During this period, basic theories have been developed and the corresponded prototypes for proof of the concepts have been created. In this chapter, we will review the theories, recent advances and reaction systems and condition of photocatalytic CO₂ reduction in section 2.1. Section 2.2 and section 2.3 will discuss about two major challenges currently we are facing: fast electron-hole recombination rate of photocatalyst and low affinity between CO₂ and photocatalyst. Then, PhD in context of literature will be illustrated in section 2.4.

2.1 Overview

2.1.1 Mechanism of photocatalytic CO₂ reduction

The energy difference between the top of the valence band (VB) and the bottom of the conduction band (CB) in insulators and semiconductors is referred to as the band gap. Semiconductor photocatalysts with a proper band gap width will enable them to adsorb solar/ultraviolet (UV) light energy and then excite valence band electrons to conduction bands, which can generate electrons and holes in the conduction and valence band, respectively. While a large proportion of the photo-excited electrons and holes recombine together, some will migrate to the surface, which can be utilized for further reactions, like photocatalytic water splitting or CO₂ reduction. As is well known, to achieve the two half reactions for the water splitting, the redox potential of the electrons in the conduction band has to be more negative than that of H⁺/H₂ (0V vs. NHE), while the redox potential of the holes in the valence band has to be more positive than that of O₂/H₂O (0.83V vs. NHE).^{1, 2}

However, for the CO₂ reduction case there is some difference. Since the $E(\text{CO}_2/\text{CO}) = -1.9 \text{ V vs NHE}$ is so high that it is almost impossible to find a suitable semiconductor that has more negative redox potential in the conduction band. This may indicate that CO₂ photoreduction by using semiconductor becomes impossible. However, many researchers reported the successful use of different semiconductor to achieve CO₂ reduction. Early in 1979, Inoue and co-workers³ examined the use of semiconductor powders for CO₂ reduction, including TiO₂, ZnO, CdS, SiC, and WO₃, suspended in CO₂-saturated water under Xe lamp illumination. The product includes methane, carbon monoxide, formic acid, formaldehyde and methanol. The CB and VB position of these semiconductor photocatalyst is shown in **Fig 2.1**.

Multistep reduction process was proposed by Inoue to explain the CO₂ reduction mechanism as shown below:

Figure 2.1. Conduction band and valence band potentials of semiconductor photocatalysts relative to energy levels of the redox couples in water.³ *Reprinted by permission from Macmillan Publishers Ltd: [Nature] (ref 3), copyright (1979)*

The yield of methanol and formaldehyde was highest when SiC was used as photocatalyst. This phenomenon attributed to the relative position of the SiC conduction band with respect to the HCHO/H₂CO₃ redox potential. **Fig 2.1** illustrates band structures of selected semiconductors relative to redox potential of two half reactions of

photocatalytic CO₂ reduction at pH of 5.0. The conduction band of SiC is higher (more negative) than the HCHO/ H₂CO₃ redox potential, which is believed to be responsible for the high rates of product formation. The conduction band of WO₃ is lower than the HCHO/H₂CO₃ redox potential. When WO₃ was used as catalyst, no methanol production was observed. This also further confirms the influence of band-edge positions on CO₂ reduction.

Since multistep reduction process works very well on photocatalytic CO₂ reduction, it is generally accepted by most of the researchers to explain the principles for CO₂ photoreduction. By using this principle, redox potential of the electrons in the conduction band has to be more negative than that CH₄/CO₂ (-0.24V vs. NHE), while the redox potential of the holes in the valence band has to be more positive than that of O₂/H₂O (0.83V vs. NHE).

Path a:

Path b:

Figure 2.2. *The evolution routes CO₂ to CH₄.*

In addition to the evolution route discussed above, there is also another well-established evolution route of CO₂ reduction. Both of these two routes are shown in **Fig 2.2**. In the first route, CO₂ is firstly transformed into formic acid, and then gradually reduced to formaldehyde, methanol and finally methane, as discussed in the previous part of the chapter. 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.

2.1.2 Photocatalytic CO₂ reduction system and condition

Choosing a suitable semiconductor photocatalyst is one of the key steps for photocatalytic CO₂ reduction. However, external environment and operating conditions

includes the quantity of catalyst, type of light, pH of the solution, CO₂ pressure, amount of reductant and temperature will also have significant impact for activity of CO₂ photoreduction. Several strategies can be applied to optimize the photocatalytic CO₂ reduction system and condition. Firstly, photoactivity and selectivity can be greatly affected by light intensity and wavelength. Hou and coworker demonstrated that different products such as CH₄, CO, C₂H₆, CH₃OH, and HCHO can be observed under different light irradiation. They claimed that different photoreduction reaction mechanisms happened when different light was utilized to illuminate on Au loaded TiO₂ photocatalyst.⁴ Secondly, although small variations of temperature don't have much effect on photoactivity because it can't overcome bandgap, it is well known that high temperatures can increase the collision frequency and diffusion rate of the photoreactions.^{5,6} Desorption of the photogenerated product can also be beneficial from the high temperature. Finally, hole-trapping sacrificial reagent. Sacrificial reagent is widely employed in water splitting process to enhance H₂ generations. This strategy can also apply to improve the efficiency of CO₂ reduction, which can increase the lifetime of photoelectrons by consuming the holes generated.⁷⁻⁹ To find the optimum condition for CO₂ photoreduction, two reaction systems were adopted these days. One is aqueous photoreaction system while the other one is gas phase photoreaction systems.

2.1.2a Aqueous photoreaction system

After a pioneering work on the reduction of CO₂ by Inoue *et al* in aqueous solution containing semiconductor powder,³ a lot of researchers start carrying out photocatalytic CO₂ reduction in aqueous solution. Photocatalyst was first dispersed in the aqueous solution, followed by CO₂ degas to make it CO₂ saturated. This method was also known as aqueous photoreaction system.¹⁰ **Table 2.1** summarizes the developments on the CO₂ photoreduction in aqueous photoreaction system. We can find that most of aqueous photoreduction systems give CH₃OH, and some systems can give other products such as C₂H₅OH, HCOOH, CH₄, CO and their mixtures.¹¹⁻¹⁸ Two factors can be responsible for efficiency of photocatalytic CO₂ reduction: CO₂ adsorption condition on the photocatalyst and rate of photogenerated electrons transfer towards CO₂.¹³ In the aqueous

photoreaction system, liquid H₂O might also capture the photogenerated electrons from the semiconductor to produce H₂. This process will compete with CO₂ photoreduction, which make the photocatalytic CO₂ reduction process inefficient as well as lower its selectivity.¹⁹ To solve this problem, increasing the CO₂ pressure to increase the CO₂ concentration in solution is an effective method.^{20,21} Mizuno *et al* reported that hydrocarbons can be obtained from TiO₂ suspension under high CO₂ pressure (2.5 MPa) while no hydrocarbons were observed at ambient CO₂ pressure.²¹

Table 2.1: Summary of various aqueous photoreaction systems..

Photocatalyst	Reaction condition	Light source	Product and Yield	Refs
TiO₂	CO ₂ -saturated NaHCO ₃	500 W Xe-lamp	0.48 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CH ₃ OH	11
Mn, Cu-doped TiO₂	CO ₂ -saturated NaOH and KHCO ₃ solution	200W Hg-lamp; halogen-lamp	238.6 $\mu\text{mol g}^{-1}$ CH ₃ OH	12
Nafion layer on Pd/TiO₂	CO ₂ -saturated Na ₂ CO ₃ solution	300 W Xe-lamp ($\lambda > 300 \text{ nm}$)	10.3 $\mu\text{mol CH}_4$ for 5 h; 1.1 $\mu\text{mol C}_2\text{H}_6$ for 1 h,	13
CdS (or Bi₂S₃)-TiO₂ nanotube	CO ₂ -saturated NaOH and Na ₂ SO ₃ solution	500 W Xe-lamp ($\lambda > 400 \text{ nm}$)	159.5 $\mu\text{mol g}^{-1}$ CH ₃ OH using CdS/TiO ₂ ; 224.6 $\mu\text{mol g}^{-1}$ CH ₃ OH using Bi ₂ S ₃ /TiO ₂	14
Pt/CuAlGaO₄	CO ₂ -saturated FeCl ₂ solution	300 W Xe-lamp	473.3 nmol h^{-1} CH ₃ OH;	15
Enzyme-modified TiO₂ and ZnO	CO ₂ -saturated suspensions	250 W tungsten-Halogen bulb	5.1 $\mu\text{mol CO}$ for 4 h	16
u-g-C₃N₄ derived from urea and m-g-C₃N₄ from melamine	CO ₂ -saturated 1 M NaOH solution	300 W Xe-lamp ($\lambda > 420 \text{ nm}$)	CH ₃ OH + C ₂ H ₅ OH with AQE 0.18%	17
Ag loaded ALa₄Ti₄O₁₅ (A = Ca, Sr, and Ba)	CO ₂ -saturated water	400 W high pressure Hg-lamp	22 $\mu\text{mol h}^{-1}$ CO, 0.7 $\mu\text{mol h}^{-1}$ HCOOH	18

Arai *et al* reported the Z-scheme system to produce HCOOH by combining InP–Ru-complex photocathode with SrTiO₃ photoanode,²² The conversion efficiency was improved by 367% as compared with TiO₂ photoanode reported previously.²³ Barton and coworkers reported photoelectrocatalytic method for CO₂ reduction by using GaP–

pyridine as photoactive material to synthesise CH_3OH and CO .²⁴ These works shows that in order to improve the conversion efficiency, we can both promoting the photogenerated carriers and limiting the H_2 generation during the CO_2 photoreduction process.

The pH of the suspension is also important for aqueous photoreaction system. To increase the solubility of CO_2 , photocatalytic CO_2 reduction is usually carried out under alkaline condition.²⁵⁻²⁹ The OH^- in alkaline solution can accelerate the CO_2 reduction since it can act as a hole scavenger. It is reported that after adding NaOH , the CH_3OH yield was significantly increased.³⁰ The as generated CO_3^{2-} and HCO_3^- in alkaline solution can also increase the activity of the CO_2 reduction.³¹

O_2 is expected to be a major oxidation product of aqueous systems when no hole sacrificial reagent is used. However, it is very difficult to exactly detect the O_2 generation amount since the produced O_2 may dissolve in the solution, adsorb on the catalyst surface or release in outgas. Moreover, the CO_2 photoreduction product such as CH_3OH or $\text{C}_2\text{H}_5\text{OH}$ from an aqueous suspension can act as hole scavenger and be oxidized by photogenerated hole during a long-term reaction. This phenomenon can affect the reaction efficiency and accumulation of photoreduction products.

As described above, there are a lot of problems still existing for aqueous reaction systems. Several methods can be adopted to solve these problems. Firstly, the use of the hole scavenger can increase the photoactivity. Secondly, optimize the reaction condition such as change the pH value of the suspension can further increase the reaction yield. Improving the detection methods is also important for aqueous reaction systems. Finally, we still need to optimize the separation process of photogenerated products from the reaction suspension.

2.1.2b Gas phase photoreaction system

Gas phase photoreaction system utilizes photocatalyst, CO_2 and water vapor under the light illumination to produce hydrocarbons. A summary of developments on gas phase

photoreaction system is shown in **Table 2.2**. As shown below, CH₄ can be obtained from most of gas phase photoreduction systems, while other reduction products such as CO, CH₃OH, C₂H₅OH, HCOOH and their mixtures can also be produced.³²⁻⁴⁷ There are two factors that influence the photoactivity and selectivity of the gas phase system, one is the concentrations of gaseous CO₂/H₂O and the other is the morphology of photocatalysts.

For example, Zhang *et al* reported that while CH₄ yields on Pt-loaded TiO₂ nanoparticle didn't change much with the difference in CO₂/H₂O ratio, the yield of TiO₂ nanotubes increased with more H₂O molecules surrounding the TiO₂ nanotubes.⁴⁸ This suggested the H₂O molecule adsorption plays an important role on photoactivity of the gas photoreaction system. Adsorption of CO₂ and H₂O molecules with active sites largely depend on microstructure and surface property of the photocatalyst.³³⁻⁴⁴ As a result, it is very important to improve the activity and selectivity of a gas phase CO₂ photoreduction system by optimize the semiconductor microstructure and surface property.

Table 2.2: Summary of different gas phase photoreaction systems.

photocatalyst	Reaction condition	Light source	Product and Yield	Refs
Degussa P25	P25 film, CO ₂ pass via a water bubbler	200 W Hg/Xe lamp	CO, CH ₄ , H ₂ , C ₂ H ₆ , CO is formed at a rate of 20 times higher than that of CH ₄	32
Anatase, rutile, and brookite TiO₂	CO ₂ /H ₂ O vapour (H ₂ O 2.3 v/v %)	150 W solar simulator	18.9 $\mu\text{mol g}^{-1}$ CO and CH ₄ using TiB(He);	33
{010} Anatase TiO₂ rods	CO ₂ pass through water bubbler	300 W Xe-lamp	25 $\mu\text{mol g}^{-1}$ CH ₄ ;	34
Hollow {101} TiO₂ mesocrystals	CO ₂ pass through water bubbler	300 W Xe-lamp	17 $\mu\text{mol g}^{-1}$ CH ₄	35
Pt-loaded TiO₂ single crystals	CO ₂ pass through water bubbler	400 W Xe-lamp (250–388 nm)	1361 $\mu\text{mol g}^{-1} \text{h}^{-1}$ CH ₄ using 1 nm Pt/TiO ₂	36
Au-loaded TiO₂	CO ₂ pass through water bubbler	UV-lamp; green laser (532 nm)	CH ₄ , C ₂ H ₆ , CH ₃ OH, and HCHO	37

C-doped TiO₂	CO ₂ and gaseous water were introduced into reactor	Simulated daylight lamp	263.4 $\mu\text{mol g}^{-1}$ HCOOH for 6 h	38
CeO₂-TiO₂	CO ₂ :H ₂ O (95.5%: 4.5%)	300 W Xe-lamp	11 $\mu\text{mol g}^{-1}$ CH ₄ and 66 $\mu\text{mol g}^{-1}$ CO for 320 min	39
(Ti_{0.91}O₂) nanosheets and graphene	CO ₂ and 0.4 mL H ₂ O in reactor	300 W Xe-lamp	8.9 $\mu\text{mol g}^{-1}$ CO 1.14 $\mu\text{mol g}^{-1}$ CH ₄	40
Mesoporous ZnGeON	CO ₂ and 0.5 mL H ₂ O in reactor	300 W Xe-lamp ($\lambda > 400$ nm)	26.8 ppm CH ₄ for 10 h	41
Mesoporous Zn₂GaO₄	CO ₂ and 0.4 mL H ₂ O in reactor	300 W Xe-lamp	5.3 ppm h ⁻¹ CH ₄	42
Cubic and ortho-rhombic NaNbO₃	CO ₂ 80 KPa and 3 mL H ₂ O in reactor	300 W Xe-lamp	0.29 $\mu\text{mol h}^{-1}$ CH ₄ on 0.5 wt % Pt/NaNbO ₃ organic	43
NiO-loaded InTaO₄	CO ₂ pass through water bubbler	Halogen lamp (400–700 nm)	11 $\mu\text{mol g}^{-1} \text{ h}^{-1}$ CH ₃ OH under halogen lamp	44
Sheet-like WO₃	CO ₂ pass through H ₂ O bubbler to reactor	300 W Xe-lamp ($\lambda > 400$ nm)	0.34 $\mu\text{mol g}^{-1} \text{ h}^{-1}$ CH ₄	45
ZnO/C₃N₄	0.25 mL 4M HCl injected into 0.12 g NaHCO ₃	300 W Xe lamp	0.6 $\mu\text{mol g}^{-1} \text{ h}^{-1}$ CH ₃ OH	46
Amine functionalized TiO₂	CO ₂ pass through water bubbler	300 W Xe lamp	66.75 ppm CO 8.61 ppm CH ₄	47

Fig 2.3 shows a typical experimental set up for gas photoreaction system, which is also known as closed-circulation system.⁴⁹ The catalyst was first uniformly dispersed on the bottom of the glass reactor in this set up. After complete evacuation of the reaction system, pure CO₂ gas was followed into the airtight system, and then a small quantity of water was injected into this experimental set up. The catalyst is allowed to equilibrate in the CO₂/H₂O atmosphere for several hours to ensure that the adsorption of gas molecules is complete. To improve the photocatalytic efficiency, optical fibre can be utilized to accelerate the electron transport. The reaction temperature can also be controlled to optimize the reaction yield.⁵⁰

In addition to the CO₂ pressure, pH of the solution and quantity of catalyst, reaction conditions include type of light, amount of reductant and temperature greatly influence the photocatalytic CO₂ reduction yield.

Figure 2.3 Typical reaction setup for gas phase reaction systems. Figure reproduced from ref. 49 with kind permission from the American Chemical Society, 2010.

2.1.3 Recent advances on photocatalytic CO₂ reduction

2.1.3a TiO₂ catalysts

Since the first report on the photocatalytic CO₂ reduction in 1979,³ there have been a large amount of reports focus on the study of the mechanism, activity and selectivity of the photocatalytic CO₂ reduction by using different semiconductors as both UV light or visible light active photocatalysts. Titanium oxide is the most investigated UV light driven catalyst for artificial synthesis because it is highly stable, durable, cheap and non-toxic.^{11-14, 32-40} Rational design and fabrication is important for optimization of TiO₂ for efficient CO₂ reduction. Effect of Crystal phase form, microstructure, surface property and doping should be considered.

Crystal phase controlling

There are three polymorphs of TiO_2 exist in nature. They are anatase, brookite and rutile. Among the three polymorphs of TiO_2 , anatase TiO_2 is often the most active one for photocatalytic reactions since it has the most negative CB position.^{32-40, 47} The desired phase of these three polymorphs can be controlled by changing the pH of the solution via hydrothermal method.¹¹ CO_2 photoreduction was studied on three TiO_2 polymorphs under gas phase photoreaction system.³³ Oxygen-deficient surfaces can be introduced by helium pretreatment of the as-prepared TiO_2 at a moderate temperature. Ti^{3+} sites can be observed on anatase and brookite TiO_2 , while cannot be found on on rutile TiO_2 . Introducing of oxygen defect can significantly enhance the CO and CH_4 yield under UV light irradiation with presence of water vapor. Among then, defective brookite TiO_2 exhibited highest CO_2 reduction activity since it is easier for brookite to generate oxygen vacancy compared with anatase and rutile TiO_2 .³³ Instead of multiple electrons pathway, one electron pathway was proposed to explain the high efficiency on oxygen-deficient brookite and anatase TiO_2 .³³ Although rutile TiO_2 is the least active photocatalyst among these three poly morph, it has the strongest visible light absorption due to it has smallest band gap. The application of mix-phase TiO_2 was more attractive. It has demonstrated an enhanced visible light harvesting ability and the anatase-dominated mixed phase was benefited to CO_2 photoreduction.⁵¹

Microstructure controlling

Morphology and crystal facets of TiO_2 have great impact on photoactivity of TiO_2 . Lots of research work was done to enhance the photoactivity of TiO_2 by utilizing different TiO_2 nanostructure (nanotubes, nanorods and so on).³⁴⁻³⁶ Better electron-hole pair charge separation can be achieved when one-dimensional crystallite (1D) is used since electron transportation along the long axes is very fast. TiO_2 nanotubes synthesized via hydrothermal method were reported by Vijayan and coworkers. The TiO_2 nanotubes exhibited the highest activity for CO_2 photoreduction after calcinate at 400 degree. When

calcinations temperature increased to more than 400 degree, the nanotube can be transformed to nanorods, which possess smaller surface area and showed lower activity. Even in the same crystal, different crystal facets can also exhibit different photoactivities. The surface electronic and atomic structure are determined by crystal facets, which can change the redox potentials of the as generated photoelectrons and create more surface active site.^{34–36} For instance, anatase TiO₂ (110) facets showed a lower photocatalytic activity compared with TiO₂ (100) facets due to it has less active site and produce less CH₄ and CH₃OH.⁵² Another important factor can influence the photoactivity is the particle size of TiO₂. Koċı and coworkers reported that the highest yields were observed for when 14 nmTiO₂ nanoparticles is used.⁵³

Surface property controlling

Surface modification is particularly important for photocatalytic CO₂ reduction since it can affect the form of CO₂ molecules adsorbed on the catalyst surface and increase the affinity between photocatalyst and CO₂ molecules.^{70–71} However, there was little work done on this field. Titanium metal-organic framework was reported for efficient CO₂ photoreduction by introducing NH₂ group.⁷⁰ Zou and coworkers reported that the titanate nanosheet-assembled yolk@shell microspheres synthesized by adding diethylenetriamine.⁷¹ The high CO₂ uptake ability from the amine addition is responsible for the increased activity for photocatalytic CO₂ reduction.

Surface modification can also influence the performance of photogenerated electron conduction.^{36–37} Noble or coinage metal include Pt, Pd, Rh, Ag and Cu loaded on semiconductor surfaces were widely applied to increase its photoactivity.^{36,37} TiO₂ film decorated with Pt synthesized by gas-phase deposition method was reported by Wang *et al.* A unique tilted-target sputtering process is applied to deposit Pt nanoparticles size of 0.5 nm to 2 nm onto TiO₂ single crystals.³⁶ This Pt loaded TiO₂ showed yield as high as 1361 mmol g⁻¹ h⁻¹ with quantum yield of 2.41%. The reaction mechanism is shown in **Fig 2.4**.

Fig 2.4 *CO₂ photoreduction mechanism by using Pt–TiO₂ nanostructured films. Figure reproduced from ref. 67 with kind permission from the American Chemical Society, 2012.*

The Pt particle size can be controlled by deposition time. Pt nanoparticles will be smaller at short deposition time. Due to quantum confinement, these extremely small Pt nanoparticles will have higher energy band separation, which make it very difficult for the photogenerated electrons transfer from the conduction band of TiO₂ to this Pt cocatalyst. If the Pt nanoparticles are too large, its Fermi level will be too low. In this condition, Pt nanoparticles act as bulk Pt and serve as recombination centers. Optimal size of the Pt cocatalyst is determined to be 1 nm.

Doping

Doping is an effective approach to tailor electronic structure and narrow band gap and consequently modify UV light active photocatalysts into visible light responsive counterparts. In addition to that, doping can not only modify the photoactivity of TiO₂, but also change the selectivity of the reaction.^{12,38} Generally, metal ions doping could create impurity levels in the forbidden band, thus enabling the photocatalysts to respond to visible light as shown in **Fig 2.5**.

Mesoporous N-doped TiO₂ was reported to have good activity and selectivity for CO₂ reduction under visible light.⁵⁵ By the sol-gel process, Mn_{0.22}–Cu_{0.78}/TiO₂ sample was obtained and a maximum CH₃OH yield of 238.6 mmol g⁻¹ was observed.¹² Silver-doped

TiO₂ nanoparticles were also prepared by sol–gel method and CH₄ and CH₃OH was found to be the major product.⁵⁵

Figure 2.5 The introduced impurity levels (donor level: A; and acceptor level: B) after doping with metal ions.

2.1.3b other systems

Native CdS has been widely applied on visible light water splitting for H₂ evolution. However, few works have been reported for photocatalytic CO₂ reduction. This may be due to the fact that CdS is highly corrosive and relative low efficiency as reported.^{56,57} It is reported that BiVO₄⁵⁸ and InTaO₄⁵⁹ were utilized for CO₂ reduction with alcohols as the major reduction products. The reaction yield is relatively higher (21.6 mol CH₃CH₂O h⁻¹) by using BiVO₄ compared with other systems. Zou *et al.* used porous Ga₂O₃ for CH₄ evolution. 5 times increased activity for CH₄ production than non-porous gallium oxide was observed, which is mainly due to enhancement of CO₂ adsorption capacity and increasing of surface area.⁶⁰ Similarly, mesoporous or sheaf-like, hyper branched Zn₂GeO₄ were also reported to promote CO₂ reduction.⁶¹ 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.⁶² A pioneer work was done by Li *et al.* using titanium metal-organic framework (MOF) to produce formic acid.⁶³ Enzyme coupled CdS in a biomimic system was also reported for CO₂ reduction, following previous works on enzyme-coupled metal oxides system.⁶⁴ Graphene oxide was also

applied on CO₂ reduction.⁶⁵ Six-fold enhancement for methanol production was achieved compared with pure TiO₂. MgIn LDH was utilized to reduce CO₂ to CO with simultaneous O₂ production.⁶⁶ Enzyme-graphene coupled system was constructed for efficient photocatalytic production of formic acid from CO₂.⁶⁷ Contrast to the heterogeneous CO₂ reduction systems introduced above, there are also many studied homogeneous CO₂ reduction systems. The later can refer to several available reviews.^{68,69}

2.2 Challenges of reducing electron-hole recombination of photocatalyst for efficient CO₂ photoreduction application

Photocatalytic CO₂ reduction is of growing interest because it can not only provide a solution to the current energy crisis, but also solve the environmental threat such as global warming. However, the current efficiency of photocatalytic CO₂ reduction is low. One of the major problems is the fast electron-hole recombination of the semiconductor. As discussed in **section 2.1**, lots of methods such as semiconductor coupling, morphology control, crystal phase control, etc. have been developed to prevent electron-hole pair recombination of the photocatalyst. There will be major challenge in the future research for finding novel materials to reduce electron-hole pair recombination of the photocatalyst.

2.3 Challenges of increasing photocatalyst affinity with CO₂ for efficient CO₂ photoreduction application

As discussed in **section 2.1**, one of the key factors that limit photocatalytic CO₂ reduction rate is the low affinity between CO₂ and photocatalyst. Compared with the electron-hole pair recombination problem, there is little work done for the affinity issue. Increasing affinity between CO₂ and photocatalyst for efficient CO₂ photoreduction is still the major challenges in the future.

2.4 PhD in context of literature

The PhD work will be demonstrated in this thesis is for further development and supplement of the literature work. With the effort of answering the challenges based on literature that have been displayed in **section 2.2**, we presented the development of Cu decorated zinc oxide nanowire array for constructing efficient CO₂ photoreduction. For the challenge raised on **section 2.3**, we developed amine-functionalize TiO₂ and amine functionalized ZnO for efficient CO₂ capture and CO₂ photoreduction.

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Chapter 3

Experimental Methodology

*All the synthesis and characterization techniques for our experiments throughout the entire thesis are summarized in this chapter. This Chapter demonstrates the discussions of the principles underlying the synthesis/characterization employed and the methods of data analysis. The rationale to select the materials and characterization techniques will be demonstrated in **Section 3.1**. The principles of the synthesis method and characterization techniques will be illustrated in **Section 3.2** and **3.3**, respectively.*

3.1 Rationale for selection of methods

This thesis will demonstrate amine-functionalized semiconductor photocatalyst and Cu decorated ZnO nanowire array for efficient CO₂ reduction. For the synthesis of amine-functionalized semiconductors, hydrothermal and solvothermal method was selected to attach the amine group on the surface of oxy-rich semiconductors. Hydrothermal method was also utilized to construct ZnO nanowire array structure followed by photodeposition method to synthesis of Cu/ZnO.

3.1.1 Synthesis

Hydrothermal synthesis method

Hydrothermal synthesis includes the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures. The hydrothermal method, in contrast to other conventional techniques, offers several advantages. Compounds that are usually difficult to be obtained under normal condition can be synthesized in a closed system by the hydrothermal method. In addition, several parameters such as temperature, vapor pressure, composition can be controlled in hydrothermal synthesis to get the desired product. Moreover, hydrothermal method is a scalable method which is applicable for large scale applications.

Solvothermal synthesis method

Solvothermal synthesis method is also used in this thesis. Solvothermal synthesis method has similar mechanism with hydrothermal synthesis. The major difference between solvothermal synthesis and hydrothermal synthesis is that solvothermal usually utilize organic solvent, while hydrothermal syntheses use water as solvent.

Photodeposition method

Photodeposition method was utilized to deposit Cu and Pt nanoparticles on the surface of the ZnO nanowire array. In this method, the noble or coinage metal can be deposited on the semiconductor under illumination of UV light or visible light. The electrons generated from conduction band of the semiconductor under the light illumination can reduce the precursor to metal or metal oxide nanoparticles. The reduced metal or metal oxide will locate at the active site of the semiconductor and usually have higher photoactivity compared with other methods.

3.1.2 Characterizations***Scanning electron microscope (SEM)***

Scanning electron microscope studies the morphology information of a material. It generates images by interacting focused electron beams with atoms in the materials. The secondary electrons emitted by atoms are detected and collected as the signals which could display the topography of the material. Therefore, to obtain surface morphology and cross-section of our materials, a field emission scanning electron microscopy (FE-SEM, JEOL JSM 7600F) was adopted.

X-ray diffraction (XRD)

X-ray diffraction investigated the crystallographic information of a material. By understanding the lattice distance, XRD spectra provides a finger-printer pattern for identify the crystals synthesized.

X-ray photoelectrons spectroscopy (XPS)

X-ray photoelectron spectroscopy is a surface chemical analysis technique that can be used to analyze the surface chemistry of a material in its as-received state. By measuring the kinetic energy and number of electrons that excited by high energy x-rays, XPS is able to reveal the elemental composition, chemical state of the elements within a material.

Photocatalytic CO₂ reduction analysis

For identifying the catalytic and photocatalytic activity of our TiO₂ and ZnO based catalyst, photocatalytic CO₂ reduction analysis is a unique and irreplaceable technique for the activity assay. It is the study of the chemical response of a system under light illumination. These redox reactions can provide information about the type and quantity of the photoreduction product. Therefore, it is selected as the major technique for the activity study of our materials.

3.2 Synthesis and device fabrication

3.2.1 Solvothermal & hydrothermal synthesis

Experimental Set-up

Solvothermal & hydrothermal synthesis are very simple techniques to produce chemical compounds by wet chemistry. It is a method to produce chemical compounds and materials in organic solvent or water solutions at temperatures generally above 90 °C.

The principle of solvothermal synthesis is to make products by decomposition or other chemical reactions, from dissolved precursor in the organic solvent at specific temperature. The main parameters of solvothermal synthesis, which define both the processes kinetics and the properties of the produced materials, are the initial concentration, the reaction duration and temperature of synthesis. The synthesis can be

carried out in a normal glassware (e.g. a flask) coupled with a hot oil bath or an autoclave sealed steel cylinders if high pressure is required for the reaction.

Solvothermal & hydrothermal reaction usually carried out under high temperature and high vapor pressure. In this case, an autoclave sealed steel cylinder is needed to perform the reaction, otherwise there is a danger of leak or explode, which will lead serious safety issues. The reactor is a thick walled stainless steel vessel fitted with a fitting cap (of similar threading) and retainer bolt device. It has an internal cup (liner) and fitting lid, both of which are made of Teflon. The liner can be charged with reagents, and the whole apparatus assembled in accordance to the manufacturer's instructions. Under external heating, the temperature and the pressure of the contents will rise; the pressure developed will depend on the chemical reaction, its charge volume and temperature. Under pressure, the reaction can cause significant damage via explosion, gas leakage or fire.

3.3 Characterizations

3.3.1 Photocatalytic CO₂ reduction analysis

Photocatalytic CO₂ reduction is a process by which photocatalyst can be illuminated under UV light or Visible light illumination to produce hydrocarbons. This process should also be carried out in a closed system to confirm all the produced product can be corrected calculated, as well as prevent the outside contaminations. To maximize the reaction yield, a special designed reaction is used in the reaction. A typical photocatalytic CO₂ reduction reaction set-up is displayed in **Fig3.1**.

Figure 3.1 Digital images of homemade photoreactor and reaction set-up.

The typical photocatalytic CO_2 reduction process have four parts.

1. A special designed reactor. In a typical CO_2 photoreduction test, the reactor was degas with pure CO_2 gas first. After that, the photocatalyst was illuminated under UV-light to produce photoreduction product. The sample gas was taken every hour and inject into the GC for the gas analysis. As a result, the reactor was designed as shown in **Fig 3.1**. For degas and sampling process, there is 2 ports designed at the side of the reactor. The CO_2 gas come in at one port and the air in the reactor come out at another port. The reactor was made of glass, while a quartz window is equipped at the top of the reactor for the UV-light illumination.
2. Degas system. To ensure there is enough water vapor in the reaction system, the CO_2 gas from the gas cylinder pass through a water saturator before entering the reactor. 0.1 M NaOH solution was used to neutralize the exhaust gas.
3. Light source. Light source was use to illuminate the photocatalyst and excite the catalyst to produce hydrocarbons. (MAX-302, Asahi Spectra, USA) was used as the light source for the photocatalytic reaction.

4. Gas chromatography. Gas chromatography was adopted to analyze the gaseous product of the photoreduction reaction. During the reaction, the gas product was analyzed periodically through a gas chromatograph (GC-7890A, Agilent) with a TCD detector. Photocatalytic CO₂ reduction can generate a large amount of different product. CH₄, CO and higher hydrocarbons can be produced in the gas phase. In the liquid phase, alcohols include methanol, carboxylic acid like formic acid and aldehydes can be generated.

Typical reactions happened in the photoreduction of CO₂ was shown in **Table 3.1**.¹ To accurately evaluate the efficiency of the photocatalyst, we need to identify and quantify as many as possible of the CO₂ reduction product. Moreover, the reaction yield of certain product generated in the CO₂ reduction may be very low. This requires the analysis techniques with low detection limits.

Table 3.1 CO₂ reduction products and reduction potential with reference to NHE at pH 7

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

The most common gaseous products of CO_2 photoreduction are CH_4 and CO . H_2 and O_2 can also be generated from the competitive water splitting. In addition to that, the presence of higher alkanes as the photoreduction products of CO_2 are also reported.² Since most of the CO_2 photoreduction are carried out in the CO_2 gas atmosphere, CO_2 will be the main species in the gas phase since the conversion efficiency is low. Infrared spectroscopy (IR) or diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) can be applied to confirm the generation of CO as well as the consumption of CO_2 .³⁻⁵

Gas chromatography (GC) is a type of chromatography used for separating and analyzing compounds that can be vaporized without decomposition. To analyze the gaseous product, GC is the most commonly technique for identification and quantification.⁶⁻⁸ Besides GC, GC-MS can also be applied for detection of CH_4 and CO or for carbon source verification.⁹⁻¹¹ Thermal conductivity detector (TCD) was the only detector used in GC as stated in amine-functionalized semiconductors for efficient CO_2 photoreduction works, while both TCD and flame ionization detector (FID) has been used in GC for Cu decorated ZnO nanowire array work to achieve better sensitivities. FID analysis is a destructive method. As a result, the gas should first be analyzed by TCD for gases quantification followed by FID for the analysis of CO and alkanes. Many types of column have been used, such as molecular sieves, carbon columns, Poraplot Q and Al_2O_3 .¹²⁻¹⁵ It has been noted that molecular sieve column can be damaged if large amount of CO_2 remains in the column. A high concentration of CO_2 can also cause deactivation of the nickel catalyst in the methanizer. As a results, a protect column which adsorbed all water moisture and CO_2 gas is used for the Agilent GC which only equipped with TCD detector, while shincarbon column was used for a Shimadzu GC equipped with both TCD and FID detector for not only alkane and CO , but also quantification of CO_2 .

The analysis of CO₂ and products in the gas phase was performed using Agilent (7890A) GC equipped with a TCD and Shimadzu GC equipped with TCD, FID and a methanizer with Ni catalyst. Argon was used as carrier gas. In a typical analysis, 0.5 mL of the gas sample from the reactor was injected into the column. The gas samples pass through TCD first, then entering the methanizer. CO can be reduced to CH₄ in methanizer catalyzed by the Ni catalyst for further FID analysis, while alkanes remained unaffected. The oven was set to 60 degree during this process, while the FID and TCD temperature was set to 250 and 100 degree, respectively. The quantity of H₂ produced can be measured by TCD. The quantity of O₂ generated in the photoreduction of CO₂ can be also monitored to confirm that water is oxidized by the holes.

3.3.2 Physical and chemical characterizations

Scanning electron microscope (SEM)

Scanning electron microscope (SEM, JEOL 7600F) was adopted to study surface morphology and cross-section view. Focused electron beam was utilized for high-resolution imaging of the surfaces. Compared with conventional light microscopy, the major advantage of SEM is much higher magnification, therefore, making it an important instrument for topography and morphology analysis for nano-sized materials. The resolution of SEM is significantly enhanced according to the Abbes Equation:

$$d = \frac{0.61\lambda}{NA}$$

Where d denotes the minimum resolvable distance, λ is the wavelength of the incident light or electron beam and NA denotes the numerical aperture. Therefore, in principle, higher energy electron beam of SEM was adopted to reduce λ and thus enhance the

resolution. However, higher energy electron beams might charge the less conductive specimen's surface and increase noise signals.

Fig.3.2 schematically demonstrated the basic components of a SEM system. The electron beam is generated by a beam gun and focused by condenser lens. The focused beam can be then shifted by scanning coils electromagnetically to the specific area of the sample. The size of scanning area determines the magnification of the image.

Figure 3.2 *Schematic view of a SEM instrument*

X-ray diffraction (XRD)

The crystallographic analysis of materials was carried out using X-ray diffraction spectroscopy (XRD, Bruker AXS D8 ADVANCE) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). An incident angle of 5° was set to record the XRD spectra, with step size of 0.05° and delay time of 1s for each step.

Fig. 3.3 schematically demonstrates the principle of x-ray diffraction. As shown in **Fig. 3.3**, the x-ray is first scattered by the crystal lattices and creates interference patterns in the reflected waves. After that, the constructive interference is observed on the XRD pattern when the diffraction angle θ meets the Bragg's law:

$$2d\sin\theta = N\lambda$$

Here, d is the lattice distance of the crystal, λ denotes the wavelength of the x-ray, N is a integer number. Therefore, XRD could be treated as a finger-print of a well-known crystal material qualitatively.

Figure 3.3 *Constructive interference of x-ray diffraction on crystal lattices.*

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy characterization were measured in an ultrahigh vacuum (UHV) VG ESCALAB 220i-XL system equipped with a monochromatic Al K α (1486.6eV) source and a concentric hemispherical energy analyzer.

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive spectroscopic technique that measures the chemical state and electronic state of the elements that exist within a material. The spectra can be obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escaped as illustrated in **Fig. 3.4**. The binding energy of a specific element inside the testing sample can be then calculated according to the Ernest Rutherford's equation:

$$E_B = h\nu - (E_K + \phi)$$

Here, $h\nu$ is energy of the absorbed x-ray photons, E_K is the kinetic energy for specific electrons that measured, ϕ is the work function.

Figure 3.4 Relation of binding energy, kinetic energy and photon energy.

Therefore, understanding the binding energy of the electrons that escaped from the surface of a sample, the chemical components and the valence states can be thus understood. In order to reduce the error, the concentric hemispherical energy analyzer in the instrument has to be calibrated with pure gold, silver and copper (polycrystalline) standard samples by setting the Au 4f_{7/2}, Ag 3d_{5/2} and Cu 2p_{3/2} peaks at binding energies of 83.98 ± 0.02 eV, 368.26 ± 0.02 eV and 932.67 ± 0.02 eV.

3.4 Overview of Methodologies

To summarize this chapter, we have demonstrated and discussed the methodologies for synthesizing and characterizing our materials or devices. Among all these techniques, our study mainly relied on electrochemical synthesis and analysis. By understanding the electron's movement (gain or loss), we are able to control the reduction or oxidation of

precursors or solutions. Other techniques would be helpful for understanding the materials from chemical or physical aspects. The results will be demonstrated in *Chapter 4, Chapter 5 and Chapter 6*.

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Chapter 4

Efficient CO₂ Capture and Photoreduction by Amine-Functionalized TiO₂

*In this chapter, we synthesized amine-functionalized TiO₂ for hydrocarbons production in the presence of water vapor. **Section 4.1** will present a general introduction while **section 4.2** will demonstrate the basic experimental procedures involving solvothermal synthesis of the catalyst and photocatalytic CO₂ reduction test. The physical characterizations was performed and its photocativity was confirmed in **section 4.3**. In general, we successfully synthesis the amine-functionalized TiO₂ with enhanced photocatalytic CO₂ reduction activity.*

(This Chapter is adapted from “Yusen Liao, Shaowen Cao, Yupeng Yuan, Quan Gu, Zhenyi Zhang, Can Xue* Efficient CO₂ Capture and Photoreduction by Amine-Functionalized TiO₂, *Chem. Eur. J.* **2014**, 20, 10220 – 10222.” Reproduced with permission of WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)²⁹

4.1 Introduction

TiO₂-based photocatalyst have been most extensively studied for photocatalytic CO₂ reduction since they are stable, non-toxic and low cost. However, its reaction efficiency is generally very low.¹⁻⁸ As described in **Section 2.1**, two factors can be responsible for the low activity of photocatalytic CO₂ reduction: CO₂ adsorption on the catalyst and photogenerated electrons transfer towards CO₂. While most of the research works were focused on the design and fabrication of the TiO₂-based material for better electron-hole pair separation, there was little work done to solve the CO₂ adsorption problem.⁹⁻¹⁶ The chemisorption of CO₂ in TiO₂ is usually realized via weak interaction like “O-C-O-Tiⁿ⁺” (n=3 or 4) with a low bonding strength of 10-20 kcal·mol⁻¹.^{17,18} This weak ability of CO₂ capture on TiO₂ surface can be responsible for the low efficiency of photocatalytic CO₂ reduction.^{19,20}

It is well known that industry widely employed amine groups for CO₂ capture. A lot of efforts have been made to introduce amine-groups on the surface of large variety of different materials for better CO₂ capture.^{21,22} Carbamate (or bicarbamate) that can formed upon interactions between CO₂ and surface amine groups, which can be further transformed to carbonate. As is well known, the amine groups have been widely employed for CO₂ capture in industry. These chemical bond formed in the process provides much strong interaction compared with chemisorptions of CO₂ on TiO₂ surface, which can greatly enhance the CO₂ capture. Herein, we report the preparation of amine-

functionalized TiO₂ by using monoethanolamine (MEA) that possesses a hydroxyl (-OH) group for covalent attachment on TiO₂ and a primary amine (-NH₂) group to endow amine-terminated surface. We firstly demonstrate that the amine groups on TiO₂ surfaces substantially improve the CO₂ adsorption, more importantly, which results in significantly enhanced photocatalytic activity (>8 times) for CO₂ reduction as compared to the TiO₂ without surface amine groups.

4.2 Experimental Methods

4.2.1 Preparation of amine-functionalized TiO₂

All of the TiO₂ based materials were synthesized via a solvothermal method. Amine-functionalized TiO₂ (MEA-TiO₂) was prepared by using 0.18 mL TiCl₄ dissolved in a mixed solution of 2 mL MEA and 28 mL ethanol. For comparison, hydroxyl group functionalized TiO₂ (EG-TiO₂) was synthesized by mixing 28 mL of ethanol and 2 mL of ethylene glycol as solvent. For pure TiO₂ (C-TiO₂), 30 mL of ethanol was used as solvent. The solution was stirred for 10 min, and then transferred into a 40-mL Teflon-lined stainless steel autoclave which was kept at 200 °C for 24 h. After cooling to room temperature, the product was washed with ethanol repeatedly, and then dried in a vacuum oven after centrifugation. All of the chemical compounds were used as received from Sigma Aldrich without further purification.

4.2.2 Photoreduction of CO₂

A special designed reactor with 100-mL volume as described in **Section 3.3** was used to determine the activity of the photocatalyst for CO₂ reduction. In a typical test, the 20 mg of the catalyst was dispersed in 1.5 mL of ethanol. After 15 min sonication, the suspension was then added dropwisely on a 2.5 cm * 2.5 cm glass slide at 60 degree to make a thin film. The glass slide containing catalyst thin film was transferred into the

reactor. The reactor was then degased with high purity CO₂ pass through a water bubbler for 0.5 hour to exclude all the residuals followed by injection of 0.1 mL water to ensure water vapour saturation. The reactor was illuminated from the top quartz window by a xenon lamp (MAX-302, Asahi Spectra, USA). The gaseous product was analyzed every 2 hours through an Agilent 7890A GC equipped with a TCD detector.

4.3 Results

4.3.1 Physical characterizations of amine-functionalized TiO₂

XRD analysis

X-ray diffraction spectroscopy was adopted to confirm the crystal structure of TiO₂. As shown in **Fig 4.1**, all these three samples can be indexed to anatase TiO₂ as indicated by X-ray diffraction (XRD) analysis. We note that the diffraction peaks of MEA-TiO₂ are relatively broader, suggesting smaller crystalline grain, while C-TiO₂ and EG-TiO₂ have larger crystalline grains compared with that of MEA-TiO₂.

Figure 4.1 XRD of MEA-TiO₂, EG-TiO₂ and C-TiO₂. All samples can be indexed as anatase TiO₂.

SEM and TEM analysis

Secondary electron microscope and Transmission electron microscope was performed to get surface morphologies, lattice fringes and selected area diffraction patterns of MEA-TiO₂, EG-TiO₂ and C-TiO₂. For a specific sample to be investigated by SEM, 1-2 drops of prepared MEA-TiO₂ suspension solution was drop-casted on a silicon wafer surface. The top surface analysis was then performed after the sample was dried in air after 1 h. For a specific sample to be investigated by TEM, 7 μ L of the prepared MEA-TiO₂ solution was add to the copper grid, followed by the TEM analysis. As shown in Fig. 4.2, all these three samples are spherical particles (200~500 nm in diameter) assembled by small TiO₂ nanocrystallines.

Figure 4.2 TEM micrographs and diffraction patterns of (a) C-TiO₂, (b) EG-TiO₂ and (c) MEA-TiO₂. The insets show the electron diffraction patterns (left corner) and high-resolution TEM images (right corner). The typical lattice fringe of $d = 0.34$ nm matches with that of the (101) crystallographic plane of anatase TiO₂.

X-ray photoelectron spectroscopy

X-ray Photoelectron spectroscopy (XPS) measurements for the MEA-TiO₂ and EG-TiO₂ samples were performed on a Thermo Scientific Theta Probe XPS with monochromatized Al K α ($h\nu = 1486.6$ eV) source, as shown in **Fig. 4.3** and **Fig. 4.4**. The XPS spectrum of MEA-TiO₂ sample was shown in **Fig. 4.3**. The Ti 2p spectrum can be deconvoluted into four peaks at 457.3 eV, 458.9 eV, 462.7 eV and 464.7 eV. The first (457.3 eV) and third peaks (462.7 eV) are characteristic peaks of Ti (III) in TiO₂.²³ The presence of Ti (III) indicates the existence of surface defect. The second (458.9 eV) and last (464.7 eV) peak typically ascribed to Ti (IV) in TiO₂.²³ The O 1s peak can be separated. The main peak at 530.1 eV confirms the occurrence of Ti-O bond while the peak at 531.9 eV shows the presence of C-O bond.²⁴ The C 1s spectrum can also be deconvoluted into two peaks at 285 eV and 286.2 eV. The former peak can be assigned to C-C and C-H bonding while the latter peak can be assigned to C-O and C-N bonding.²³ The N 1s spectrum can also be separated. The main peak at 399.4 eV confirms the occurrence of C-N bond while the peak at 401.2 eV can be assigned to C-N-H bond, which proves the existence of surface amine group.²⁵

Figure 4.3 XPS spectra of MEA-TiO₂: (a) Ti 2p; (b) O 1s; (c) C 1s; (d) N 1s.⁴

The XPS spectrum of EG-TiO₂ sample was shown in **Fig. 4.4**. The Ti 2p spectrum can be deconvoluted into four peaks at 457.3 eV, 458.8 eV, 463.2 eV and 464.5 eV. The first (457.3 eV) and third peak (463.2 eV) are characteristics peaks of Ti (III) in TiO₂. The presence of Ti (III) indicates the existence of surface defect.²⁴ The second (458.8 eV) and last (464.5 eV) peaks are typically ascribed to Ti (IV) in TiO₂.²⁶ The O 1s peak can also be separated. The main peak at 530.1 eV shows the occurrence of Ti-O bond while the peak at 531.9 eV shows the presence of C-O bond.²⁷

Figure 4.4 XPS spectra of EG-TiO₂: (a) Ti 2p; (b) O 1s.

UV-Vis spectroscopy

UV-vis diffuse reflectance spectra (DRS) were recorded over the spectral range 320–800 nm. BaSO₄ was used as a reflectance standard. As shown in **Fig.4.5**, MEA-TiO₂ and EG-TiO₂ sample showed weak visible-light absorption comparing to C-TiO₂.

Figure 4.5 UV-visible spectra of MEA-TiO₂, EG-TiO₂ and C-TiO₂.

4.3.2 Photocatalytic reduction test of amine-functionalized TiO₂

Photocatalytic reduction of MEA-TiO₂, EG-TiO₂ and C-TiO₂ samples was carried out to examine the photocatalytic activity of the catalyst under the illumination of the UV-light. As shown in **Fig 4.6**, when C-TiO₂ sample was used, very low generation rates of methane (0.91 ppm/h) and CO (10.5 ppm/h) was obtained. The EG-TiO₂ sample shows higher generation rates of methane (2.75 ppm/h) and CO (21.75 ppm/h). The existence of oxygen vacancies and Ti³⁺ on the surface could promote CO₂ activation, which is responsible for the increase of the CO₂ photoreduction yield.²⁸ In comparison, the MEA-TiO₂ sample exhibit the highest production rate (more than 3 times compared with EG-TiO₂) for methane (8.61 ppm/h) and CO (66.75 ppm/h).

Figure 4.6 (a) The amount of generated (a) methane and (b) CO as a function of irradiation time for the samples of MEA-TiO₂, EG-TiO₂, C-TiO₂, control experiment with CO₂ but without irradiation (control 1), and control experiment with illumination but without CO₂ (control 2).

18 h photocatalytic reaction for the MEA-TiO₂ catalyst was performed under the reaction conditions described above to confirm the quantity of O₂ formed during the photoreaction. The amounts of O₂, CO and CH₄ detected were 143.6 ppm, 193.7 ppm and 21.4 ppm. The stoichiometric ratio expected from the photocatalytic conversion of CO₂ with H₂O to CO

and O₂ is 0.5/1 while the stoichiometric ratio expected from the photocatalytic conversion of CO₂ with H₂O to CH₄ and O₂ is 2/1. The expected O₂ generate should be 139.65 ppm. We speculate that the slightly higher O₂ generated may be due to the formation of other reduction products such as H₂. This result also confirmed that the attached MEA on TiO₂ surfaces are stable against O₂ and photogenerated holes on TiO₂.

To evaluate the long-term stability of the prepared MEA-TiO₂ sample, cycling test was performed. The reactor was degassed again and the sample was re-used for the photoreduction of CO₂ after each 6-hour cycle test. As shown in **Fig 4.7**, no obvious decrease of the CH₄ and CO yield was observed after 3 cycles, suggesting a very good stability of the MEA-TiO₂ during the photocatalytic process.

Figure 4.7 The cycling test of photoreduction of CO₂ over 18 hours by using MEA-TiO₂.

4.4 Conclusion

Based on the above results, we report herein a facile one-step solvothermal method to decorate the surface of TiO₂ with amine group. The as-synthesized MEA-TiO₂ is anatase phase. To confirm its photoactivity, CO₂ photoreduction test was carried out. The reaction efficiency is greatly enhanced. The detailed surface properties and reaction mechanisms will be elaborated in *Chapter 7*.

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Chapter 5

Amine Functionalized ZnO for Efficient CO₂ Capture and Photoreduction

*This chapter will demonstrate further application of amine group on other semiconductors for efficient CO₂ reduction. After the general introduction in **section 5.1**, synthesis of this material by hydrothermal method will be introduced in **section 5.2**. Then, the fundamental characteristics as well as their physical and photocatalytic properties will be depicted in **section 5.3**. In general, the amine functionalized ZnO with enhanced CO₂ reduction photoactivity was successfully synthesized via the hydrothermal method.*

5.1 Introduction

Many scientific studies have been devoted to the development of efficient photocatalysts for CO₂ photoreduction.¹⁻¹⁴ *Chapter 4* illustrates that the amine group was effective for CO₂ capture and photoreduction when TiO₂ was used as photocatalyst. To further confirm whether this technique can be applied to other semiconductor photocatalysts, ZnO was selected for CO₂ reduction because it is stable, non-toxic and low cost.¹⁵⁻²⁰

Herein, we demonstrate a new strategy of a facile one-step hydrothermal method for the synthesis of amine-functionalized ZnO nanosheet. Monoethanolamine (MEA) was utilized in this process to endow amine-functionalized surface on ZnO. The surface amine group can significantly enhance the CO₂ adsorption ability. The increased affinity between CO₂ and amine-functionalized ZnO will substantially improve its ability of CO₂ photoreduction (more than 2 times) compared with the pure ZnO.

5.2 Experimental Methods

5.2.1 Preparation of amine-functionalized ZnO (MEA-ZnO)

All of the ZnO based materials were synthesized via a simple one-step hydrothermal method. In a typical procedure, a mixture aqueous solution (20 mL) containing 0.1 M Zn(Ac)₂, 0.2 M NaOH and 0.005 M MEA was first prepared for amine-functionalize ZnO (denoted as MEA-ZnO). For clean ZnO sample (denoted as ZnO), a mixture solution (20 mL) with 0.1 M Zn(Ac)₂ and 0.2 M NaOH was prepared. The solution was then put into a 30 mL autoclave, followed by heating at 90 °C for 12 hours. After cooling to room temperature, the product was then washed with deionized water repeatedly, and dried in a vacuum oven after centrifugation. Since the boiling point of MEA is around 170 °C, the solid product was annealed at 250 °C under Ar atmosphere for 3 hours to remove physisorbed MEA on ZnO surfaces.

5.2.2 Photoreduction of CO₂

A special designed reactor with 100-mL volume as described in **Section 3.3** was used to determine the activity of the photocatalyst for CO₂ reduction. In a typical test, the 20 mg of the catalyst was dispersed in 1.5 mL of ethanol. After 15 min sonication, the suspension was then added dropwisely on a 2.5 cm * 2.5 cm glass slide at 60 degree to make a thin film. The glass slide containing catalyst thin film was transferred into the reactor. The reactor was then degas with high purity CO₂ pass through a water bubbler for 0.5 hour to exclude all the residual air followed by injection of 0.1 mL water to ensure water vapour saturation. The reactor was illuminated from the top quartz window by a xenon lamp (MAX-302, Asahi Spectra, USA). The gaseous product was analyzed every 2 hours through an Agilent 7890A GC equipped with a TCD detector.

5.3 Results

5.3.1 Physical characterizations

XRD analysis

X-ray diffraction spectroscopy was adopted to confirm the crystal structure of ZnO. As shown in **Fig 5.1**, all these two samples can be indexed to wurtzite ZnO as indicated by X-ray diffraction (XRD) analysis. We note that these two samples show almost the same diffraction peaks. This suggests that the MEA modification did not change the crystal structure of ZnO.

Figure 5.1 XRD patterns of MEA-ZnO and clean ZnO. Both samples can be indexed as wurtzite ZnO.

SEM and TEM analysis

To investigate the surface morphologies and lattice fringes of MEA-ZnO and clean ZnO, SEM and TEM was performed. For a specific sample to be investigated by SEM, 1-2 drops of prepared MEA-ZnO suspension solution was drop-casted on a silicon wafer surface. The top surface analysis was then performed after the sample was dried in air after 1 h. For a specific sample to be investigated by TEM, 7 μ L of the prepared MEA-ZnO solution was added to the copper grid, followed by the TEM analysis. As shown in **Fig 5.2a**, MEA-ZnO sample appears as nanosheet morphology. The high-resolution TEM (HRTEM) image shows a lattice fringe of $d=0.28$ nm. This corresponds to the (100) interplanar spacing of wurtzite ZnO.²¹ For clean ZnO sample, irregular nanoparticles are observed. After addition of MEA, the ZnO crystal will be more likely to grow sideways since the intrinsically anisotropic growth of ZnO along the (0001) direction is substantially suppressed. More research is still needed to be done to confirm the exact growth mechanism for these different structures.

Figure 5.2 (a) SEM images of MEA-ZnO; (b) SEM image of clean ZnO; (c) TEM images of MEA-ZnO; The inset is the HRTEM image of a representative ZnO nanosheet; (d) TEM image of clean ZnO.

UV-Vis spectroscopy

The absorbance of MEA-ZnO and clean ZnO at different light wavelength was recorded by UV-Vis spectroscopy (**Fig. 5.3**). The absorption edge was identified at the light wavelength of 376 nm, which is corresponding to the semiconductor's bandgap of 2.6 eV.

Figure 5.3 UV-Vis spectrum of ZnO and MEA-ZnO.

5.3.2 Photocatalytic reduction test of amine-functionalized ZnO

Photocatalytic reduction of MEA-ZnO and ZnO samples was carried out to examine the photocatalytic activity of the catalyst. As shown in **Fig 5.4**, when ZnO sample was used, very low generation rates of methane (2.1 $\mu\text{mol/g}$) and CO (14.8 $\mu\text{mol/g}$) was obtained. The EG-ZnO sample shows higher generation rates of methane (2.75 ppm/h) and CO (21.75 ppm/h). In comparison, the MEA-ZnO sample exhibit highest production rate (more than 2 times compared with ZnO) for methane (4.4 $\mu\text{mol/g}$) and CO (25.3 $\mu\text{mol/g}$).

In order to confirm all the generated hydrocarbons were generated from the photoreaction, Control experiment should be carried out. First experiments were carried out in the absence of CO₂ (in N₂ atmosphere) with UV light irradiation. If MEA on the surface of ZnO was oxidized by the photogenerated holes of ZnO, CO or CH₄ should be observed. If there was any reactive carbon residue, it may also react with H⁺ or H₂ generated based on competitive water splitting and form CO or CH₄. Nether CO or CH₄ was observed in this case, indicate all the hydroncarbon product was generated from photoreduction of CO₂. Another experiment was carried out in the in CO₂ atmosphere but

in the absence of light. Neither CO or CH₄ was formed implying ZnO is the only active catalyst.

Figure 5.4 The amount of generated (a) CH₄ and (b) CO as a function of irradiation time over the sample of MEA-ZnO or clean ZnO. Control experiments without light irradiation (control 1) or without CO₂ (control 2) showed no generation of CO and CH₄.

12 h photocatalytic reaction for the MEA-TiO₂ catalyst was performed under the reaction conditions described above to confirm the quantity of O₂ formed during the photoreaction. The amounts of H₂, O₂, CO and CH₄ detected were 81 ppm, 1145 ppm, 1520 ppm and 146 ppm, respectively. The stoichiometric ratio expected from the photocatalytic conversion of CO₂ with H₂O to CO and O₂ is 0.5/1 while the stoichiometric ratio expected from the photocatalytic conversion of CO₂ with H₂O to CH₄ and O₂ is 2/1. The expected O₂ generate should be 1092.5 ppm. We speculate that the slightly higher O₂ generated may be due to the formation of other reduction products such as CH₃OH, which can't be detected under current experimental set up. This result also confirmed that the attached MEA on ZnO surfaces are stable against O₂ and photogenerated holes on ZnO.

To evaluate the long-term stability of the prepared MEA-ZnO sample, cycling test was performed. The reactor was degassed again and the sample was re-used for the photoreduction of CO₂ after each 4-hour cycle test. As shown in **Fig 5.5**, no obvious

decrease of the CH₄ and CO yield was observed after 3 cycles, suggesting a very good stability of the MEA-TiO₂ during the photocatalytic process.

Figure 5.5 The cycling test of CO₂ photoreduction over 12 hours by using the MEA-ZnO sample.

5.3 Conclusions

Based on the above results, we report herein a facile one-step hydrothermal method to decorate the surface of TiO₂ with amine group. The as-synthesized MEA-ZnO is wurtzite ZnO. To confirm its photoactivity, CO₂ photoreduction test was carried out. The reaction efficiency is greatly enhanced. The detailed surface properties and reaction mechanisms will be elaborated in *Chapter 7*.

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Chapter 6

Cu Decorated ZnO Nanowire Array for Efficient CO₂ Photoreduction

*This chapter will demonstrate the synthesis and application of Cu decorated ZnO nanowire array for efficient CO₂ reduction. After a brief introduction in **section 6.1**, synthesis of this material by hydrothermal method as well as photodeposition method will be introduced in **section 6.2**. Then, the fundamental characteristics as well as their physical and photocatalytic properties will be depicted in **section 6.3**. The Cu cocatalyst showed even higher yield than Pt, indicating it is an efficient method to reduce electron-hole pair recombination in CO₂ photoreduction.*

6.1 Introduction

ZnO-based photocatalyst has attracted considerable interest since it is highly efficient, non-toxic and low cost.¹⁻⁶ ZnO nanostructures have been extensively studied.^{7,8} Among various nanostructures, ZnO nanowires with better photocatalytic activity are ascribed to the increase of surface-to-volume ratio and surface properties such as surface defects and oxygen vacancies.^{9,10} Therefore, ZnO nanowire array have a lot of potential to be a promising material for the CO₂ photoreduction.

Amine group functionalized semiconductor photocatalyst for efficient CO₂ capture and reduction was presented in *chapter 4* and *chapter 5*. The CO₂ reduction activity was greatly enhanced by increasing the interactions between CO₂ and photocatalyst. However, to further increase the efficiency of CO₂ reduction, we also need to prevent electron-hole recombination problem, as mentioned in **section 2.1**. One of the methods to solve this problem is introducing of co-catalysts. It is generally accepted that noble metal co-catalysts such as Pd, Pt, Au and Ag can enhance the photocatalytic CO₂ reduction over semiconductors such as TiO₂.¹² Noble metal co-catalyst can trap the electrons generated in the conduction band of semiconductor, which can facilitate the separation of photogenerated electrons and holes, increasing reaction yield. However, the insight for the rational design of co-catalysts for the efficient reduction of CO₂ is highly deficient. Herein, we demonstrate a new strategy for the design and preparation of efficient Cu/ZnO system for the preferential reduction of CO₂ in the presence of H₂O.

6.2 Experimental methods

6.2.1 Preparation of ZnO nanowire array

Formation of ZnO nanocrystal layers

ZnO nanocrystal layers were first deposited on the FTO surface. In a typical reaction, ZnO layer was loaded on FTO surface by spin coating method. Each coating step refers to spin-coating a volume of 15 μ L precursor solution onto the geometrical 6.25 cm² ZnO surface, the spin rate is 6000 rpm with 90 s. This coating step is repeated five times. The

substrate, now covered with a film of zinc acetate crystallites, is heated to 350 °C in air for 20 min to yield ZnO layer with islands and (0001) planes parallel to the substrate surface.

Formation of ZnO nanowire array

ZnO nanowire array were synthesized via a facile hydrothermal method. Nanowires were grown by immersing seeded substrates in aqueous solutions containing 25 mM zinc nitrate hydrate, 25 mM hexamethylenetetramine at 90 °C for 6 hours. The seeded side of the sample should be face down. After reaction complete, the as-synthesized ZnO nanowire array was then rinsed with water followed by drying under N₂ for the next step analysis.

Photodeposition of Cu₂O on ZnO nanowire array

Cu was deposited on ZnO nanowire array by photodeposition method. The ZnO nanowire array was first immersed in an aqueous solution of CuSO₄ (0.063 mmol dm⁻³). The solution was then exposed to irradiation with the 300 W Hg lamp to deposit Cu species onto the ZnO nanowire array. After a certain irradiation time, the obtained sample was washed thoroughly with deionized water and dried overnight in vacuum. The irradiation time was changed from 5 min to 2 h to regulate the content of Cu in the final sample. A Pt/ZnO was also prepared by the same procedure by using H₂PtCl₆ instead of the CuSO₄.

6.3 Results

6.3.1 Physical characterizations of Cu/ZnO nanowire array

XRD analysis

X-ray diffraction spectroscopy was adopted to confirm the crystal structure of ZnO. As shown in **Fig 6.1**, all these three samples can be indexed to wurtzite ZnO as indicated by X-ray diffraction (XRD) analysis. Pt and Cu concentrations are too small so that there is no Pt or Cu peaks observed in the XRD spectra.

Figure 6.1 XRD of Pt-ZnO, Cu-ZnO and ZnO. All samples can be indexed as wurtzite ZnO

SEM and TEM analysis

Secondary electron microscope was performed to get surface morphology information of Cu/ZnO and ZnO. For a specific sample investigated by SEM, 1-2 drops of prepared MEA-TiO₂ suspension solution was drop-casted on a silicon wafer surface. The top surface analysis was then performed after the sample was dried in air after 1h. As shown in **Fig. 6.2**, diameters of both ZnO nanowire arrays approximately 50 nm were observed. Smooth surface was observed for the ZnO sample, while a lot of small Cu nanoparticles are on the ZnO nanowire for the Cu/ZnO samples.

Figure 6.2 SEM of ZnO and Cu/ZnO.

UV-Vis spectroscopy

UV-vis diffuse reflectance spectra (DRS) were recorded over the spectral range 320–800 nm. BaSO₄ was used as a reflectance standard. As shown in **Fig.6.3**, Cu-ZnO showed weak visible-light absorption comparing to ZnO and Pt-ZnO.

Figure 6.3 UV-visible spectra of Cu/ZnO, Pt/ZnO and ZnO

X-ray photoelectron spectroscopy

To investigate the surface chemical state and composition of Cu/ZnO, X-ray Photoelectron spectroscopy (XPS) measurements were performed. As shown in **Fig. 6.4 (b) and (d)**, the peaks at 1022 eV and 1021.5 eV can be assigned to Zn 2p.¹¹ The XPS spectrum of Cu/ZnO sample with 5 min deposition time was shown in **Fig. 6.4 (a) and (b)**. Only one peak at 932.9 eV was observed and this peak belongs to Cu2p_{3/2} and shows only Cu (I) species existed in the Cu/ZnO sample with 5 min photodeposition time. The composition of Cu(I) species was 0.9% atomic ratio determined by XPS measurement. Cu/ZnO sample with 2h photodeposition time was shown in **Fig. 6.4 (c) and (d)**, spectrum can be deconvoluted into 2 peaks at 932.8 eV and 934.2 eV. The first peak (932.5 eV) is characteristic peaks of Cu (I) species.¹¹ The second peak (934.2 eV) typically ascribed to Cu (II) species.

Figure 6.4 XPS spectra of Cu/ZnO: (a) Cu 2p; (b) Zn 2p. Cu/ZnO: (c) Cu 2p; (d) Zn 2p**6.3.2 Photocatalytic reduction test of Cu/ ZnO**

Photocatalytic reduction of Cu/ZnO, Pt/ZnO and ZnO samples was carried out to examine the photocatalytic activity of the catalyst. As shown in **Fig 6.5**, the ZnO sample exhibits very low generation rates of methane (2.3 ppm/h). The Pt/ZnO sample exhibits higher generation rates of methane (10.7 ppm/h). In comparison, the Cu/ZnO sample with 5 min photodeposition time showed more than 2 times higher production rate for methane (25.6 ppm/h).

Control experiments were carried out in the absence of CO₂ (in N₂ atmosphere) with UV light irradiation. If there is any reactive carbon residue, it may also react with H⁺ or H₂ generated based on competitive water splitting and form CO or CH₄. Nether CO or CH₄ was observed in this case, indicate all the hydrocarbon product was generated from photoreduction of CO₂. Another experiment was carried out in the in CO₂ atmosphere but in the absence of light. Nether CO or CH₄ was formed implying ZnO is the only active catalyst.

Figure 6.5 *The amount of generated methane as a function of irradiation time for the samples of Cu/ZnO, Pt/ZnO and ZnO.*

To measure the amount of O₂ formed during the photocatalytic reaction, we performed a 12 h photocatalytic reaction for the Cu/ZnO catalyst under the reaction conditions described above. The amounts of O₂, and CH₄ detected were 592.3 ppm and 273.7 ppm. The stoichiometric ratio expected from the photocatalytic conversion of CO₂ with H₂O to CH₄ and O₂ is 2/1. The expected O₂ generate should be 547.4 ppm. We speculate that the slightly higher O₂ generated may be due to the formation of other reduction products such as methanol and H₂.

6.4 Conclusion

Cu₂O was successfully deposited on ZnO single crystal by photodeposition method. The reaction efficiency is greatly enhanced. The detailed surface properties and reaction mechanisms will be elaborated in *Chapter 7*.

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Chapter 7

Discussion and Future work

*We have displayed amine-functionalized semiconductor photocatalyst and Cu/ZnO nanowire array for CO₂ reduction applications in chapter 4, 5 and 6. However, certain questions remained during the development or implementation of these catalysts. These questions are not even answered in the literature. Therefore, in **section 7.1.1** and **section 7.1.2**, we would like to investigate the catalytic role of amine functionalized semiconductor photocatalyst. The surface amine group plays an important role in the CO₂ reduction process and the reaction mechanism is also proposed. **Section 7.1.3** demonstrate the effect of Cu cocatalyst for CO₂ photoreduction. The Cu cocatalyst can not only increase the activity, but also enhance the selectivity towards methane. **Section 7.2** will raise some outstanding questions that have been stated in this thesis and future works will be recommended and illustrated in **section 7.3**.*

7.1 General discussions

7.1.1 Understanding the photocatalytic activity of MEA-TiO₂ for photoreduction of CO₂.

7.1.1a Understanding the impact of surface amine group in MEA-TiO₂.

Amine group was introduced to increase the affinity between CO₂ and TiO₂. As discussed in Chapter 4, both TEM and XRD characterization reveals that revealed that the particle sizes of MEA-TiO₂ are smaller compared with C-TiO₂ and EG-TiO₂. Accordingly, the small crystalline size in MEA-TiO₂ offers larger BET surface area ($207 \text{ m}^2 \cdot \text{g}^{-1}$) than that of EG-TiO₂ ($170 \text{ m}^2 \cdot \text{g}^{-1}$) and C-TiO₂ ($106 \text{ m}^2 \cdot \text{g}^{-1}$) based on the N₂-adsorption isotherms. The CO₂ adsorption test was shown in **Fig 7.1**. The CO₂ uptake of MEA-TiO₂ is $15.8 \text{ cm}^3 \cdot \text{g}^{-1}$, which is 4 and 16 times higher than that of EG-TiO₂ ($3.7 \text{ cm}^3 \cdot \text{g}^{-1}$) and C-TiO₂ ($0.9 \text{ cm}^3 \cdot \text{g}^{-1}$). This difference in CO₂ uptake capability indicates that the amine group on the surface significantly enhance the CO₂ adsorption ability compared with the difference in surface area ($207 \text{ vs } 170 \text{ vs } 106 \text{ m}^2 \cdot \text{g}^{-1}$). In addition to that, while the adsorbed CO₂ quantity increased linearly for EG-TiO₂ and C-TiO₂ sample, a dramatic rise in CO₂ uptake is observed at low CO₂ pressure level for MEA-TiO₂. This phenomenon suggests that specific chemical interactions between CO₂ and MEA-TiO₂ might exist during CO₂ adsorption process.

Figure 7.1 CO_2 adsorption isotherm of MEA- TiO_2 , EG- TiO_2 and C- TiO_2 .

FT-IR spectroscopy was utilized to study the nature of covalent attachment of MEA on TiO_2 surface. To exclude the contribution of physisorbed MEA, the prepared MEA- TiO_2 sample was annealed at 250 °C under Ar atmosphere prior to IR test as the boiling point of MEA is around 170 °C. As shown in **Fig 7.2**, the MEA- TiO_2 exhibits most of the signature IR peaks of MEA. The bands at 2947 cm^{-1} and 2871 cm^{-1} are attributed to the C-H stretch of MEA, and the bands at 1074 and 1029 cm^{-1} can be assigned to the C-O stretch and C-N stretch, respectively. The bands at 1596 cm^{-1} and 1627 cm^{-1} correspond to N-H stretch of MEA and the -OH groups on the TiO_2 surface, respectively. These IR results prove the successful covalent attachment of MEA on TiO_2 surfaces.

Figure 7.2 FTIR spectra of MEA- TiO_2 , EG- TiO_2 , C- TiO_2 and liquid MEA

After exposed in pure CO_2 gas for 1.5 h, the MEA- TiO_2 shows characteristic peaks of carbamate ($-\text{OCH}_2\text{CH}_2\text{NHCOO}^-$), HCO_3^- and NH_3^+ containing species in the respective fingerprint region **Fig 7.3**. The difference as (a)-(b) in spectra is shown as **Fig. 7.3 (c)**. The chemisorption of CO_2 leads to the increased intensities at 1322, 1516, 1558, 1616, and 1678 cm^{-1} in the fingerprint region. These peaks correspond to HCO_3^- , NH_3^+ or CNH ,

COO^- , HCO_3^- or NH_3^+ , and C=O in $\text{OCH}_2\text{CH}_2\text{NHCOO}^-$, respectively.^{1,2} This results confirms the chemical adsorption of CO_2 on MEA-TiO_2 .¹

To further confirm the stability of MEA-TiO_2 , the IR spectra of MEA-TiO_2 before and after photocatalytic CO_2 reduction was carried out. As shown in Fig 7.4, there is no obvious change in the IR spectra before and after UV light illumination, which shows that the photocatalyst was stable under UV-light illumination.

Figure 7.3 IR spectra of MEA-TiO_2 (a) with (b) without adsorbed CO_2 .

Figure 7.4 IR spectra of MEA-TiO_2 before and after photocatalytic reaction.

7.1.1b Mechanism study of CO₂ photoreduction in MEA-TiO₂.

Reaction pathway for photoreduction of CO₂ is shown below. Firstly, MEA-TiO₂ capture CO₂ by surface amine group, followed by the electron-hole pairs generation under UV-light illumination. O₂ was produced in the valence band when photooxidation process takes place and water was oxidized by the photogenerated holes. In the conduction band, photoreduction process occurs and CO and CH₄ can be generated from 2 electrons or 8 electrons process, respectively.

Based on the above results, we propose the reaction mechanism of CO₂ photoreduction in TiO₂-MEA as shown in **Fig 7.5**. Firstly, CO₂ molecules can be captured by the surface amine groups to form carbamate. The formation of carbamate acts like an activation process since carbamate is believed to be more reactive than the linear CO₂ molecule.²⁻⁵ Moreover, these activated CO₂ molecules are very close to the TiO₂ surface, and would have high chance to establish direct interactions with surface titanium cations (Ti³⁺ or Ti⁴⁺), which allows for receiving electrons from excited TiO₂ to implement reduction reactions with CO or CH₄ production. As a result, the overall CO₂ photoreduction rate can be promoted through these processes.

Step 1: CO₂ capture by amine group on the TiO₂-MEA surface

Step 2: Photoexcitation (*e-h* Generation & Recombination)

Step 3: CO₂ Reduction Pathways

Valence Band (Photooxidation)

Conduction Band (Photoreduction) $\rightarrow$

Figure 7.5. Proposed mechanism of MEA-TiO₂ capture CO₂ on the TiO₂ surface and then photochemically reduce it to CO and CH₄.

7.1.2 Understanding the photocatalytic activity of MEA-ZnO for photoreduction of CO₂

7.1.2a Understanding the impact of surface amine group in MEA-ZnO

For the MEA-ZnO sample, FT-IR spectroscopy was utilized to study the nature of covalent attachment of MEA on ZnO surface. To exclude the contribution of physisorbed MEA, the prepared MEA-TiO₂ sample was annealed at 250 °C under Ar atmosphere prior to IR test as the boiling point of MEA is around 170 °C. As shown in **Fig 7.6**, the MEA-ZnO exhibits most of the signature IR peaks of MEA. The peaks at 2964, 2919 and 1399 cm⁻¹ are attributed to the C-H stretch of MEA, and the bands at 1073 and 1028 cm⁻¹ can be assigned to the C-O stretch and C-N stretch, respectively. The bands at 1560 cm⁻¹ correspond to N-H stretch of MEA on the ZnO surface. These IR results prove the successful covalent attachment of MEA on ZnO surfaces.¹

Figure 7.6 FTIR spectra of MEA-ZnO, ZnO and liquid MEA

BET surface area of MEA-ZnO sample was determined based on N₂ adsorption isotherms. MEA-ZnO possess larger BET surface area (15.1 m²·g⁻¹) than that of clean ZnO (9.6 m²·g⁻¹). The nanosheet structure of MEA-ZnO is responsible for the increased BET surface area. The CO₂ adsorption test was shown in **Fig 7.7**. The CO₂ uptake of MEA-ZnO is 0.87 cm³·g⁻¹, which is 6 times higher than that of clean ZnO (0.13 cm³·g⁻¹). This

difference in CO₂ uptake capability indicates that the amine group on the surface significantly enhance the CO₂ adsorption ability compared with the difference in surface area (15.1 vs 9.6 m²·g⁻¹). In addition to that, while the adsorbed CO₂ quantity increased linearly for clean ZnO sample, a dramatic rise in CO₂ uptake is observed at low CO₂ pressure level for MEA-ZnO. This phenomenon suggests that specific chemical interactions between CO₂ and MEA-TiO₂ might exist during CO₂ adsorption process.

Figure 7.7 CO₂ adsorption isotherm of MEA-ZnO and clean ZnO.

7.1.2b Mechanism study of CO₂ photoreduction in ZnO-MEA

Based on the above results, we propose the reaction mechanism of CO₂ photoreduction in ZnO-MEA as shown in **Fig 7.8**. Firstly, CO₂ molecules can be captured by the surface amine groups to form carbamate. The formation of carbamate acts like an activation process since carbamate is believed to be more reactive than the linear CO₂ molecule.²⁻⁵ Moreover, these activated CO₂ molecules are very close to the TiO₂ surface, and would have high chance to establish direct interactions with surface Zn²⁺, which allows for receiving electrons from excited TiO₂ to implement reduction reactions with CO or CH₄ production. As a result, the overall CO₂ photoreduction rate can be promoted through these processes.

Figure 7.8 Proposed mechanism of MEA-ZnO capture CO₂ on the ZnO surface and then photochemically reduce it to CO and CH₄.

7.1.3 Understanding the photocatalytic activity of Cu/ZnO for photoreduction of CO₂

As shown in **Table 7.1**, the photocatalytic reduction of CO₂ with H₂O over our catalysts provided CH₄ as major products. The H₂ generation was also observed at the same time. The reaction happened in the photocatalytic process is listed below:

Table 7.1 Photocatalytic conversion of CO₂ with H₂O over ZnO loaded with cocatalyst.

Catalyst	Formation rate of H ₂ (ppm h ⁻¹)	Formation rate of CH ₄ (ppm h ⁻¹)	Selectivity for CO ₂ reduction
ZnO	6.1	2.3	61%
Pt/ZnO	52.7	10.7	43%
Cu/ZnO	10.1	25.6	91%

The photocatalytic reduction of CO₂ with H₂O over our catalysts provided CH₄ as major products (Table 7.1). The H₂ generation was also observed at the same time. The reaction happened in the photocatalytic process is listed below:

As shown in **Table 7.1**, CH₄ evolution rate is significantly enhanced when Cu^I or Pt cocatalyst was loaded onto ZnO nanowire array. The Pt or Cu^I cocatalysts have lower Fermi level energy as compared to CB of ZnO, so that it can effectively “trap” photogenerated electrons. This phenomenon will facilitate electron-hole pair separation.⁶ The electron rich cocatalyst will also favor CH₄ generation since CH₄ evolution is an 8 electron process which needs more electron as compared with CO evolution.⁵ H₂ formation rate was also increased after loading Pt or Cu^I onto TiO₂. This phenomenon was much more significant in the case of Pt cocatalyst. It is well known that the reduction of H₂O for generation of H₂ is a competitive reaction with the reduction of CO₂ for generation of CH₄,⁷ and the selectivity for CO₂ reduction was also shown in **Table 7.1**. It clearly demonstrates that the Pt co-catalyst decreases the selectivity for CO₂ reduction, while Cu^I increase the selectivity from 61 to 91%.

Based on the above results, we proposed the reaction mechanism as shown in **Fig 7.9**. After UV light illumination, the electron from the valance band was excited and transferred to conduction band. The electron generated from the CB of the Cu₂O will migrate to the ZnO, while the hole generated from the VB of ZnO will transferred to that of Cu₂O. This p-n heterojunction will help to separate the electron-hole pairs, which greatly increase the photocatalytic activity of CO₂ reduction.

Figure 7.9 Proposed photocatalytic CO_2 reduction mechanism of Cu/ZnO .

7.2 Outstanding questions

We have demonstrated in our thesis the exploration and investigation of more efficient catalyst for photoreduction of CO_2 . However, there are still some outstanding questions left which will be recommended for the future work. Here, these major questions are summarized based on our thesis and the literature. They are:

1. What is the exact reaction mechanism for MEA-TiO_2 and MEA-ZnO in the process of photoreduction of CO_2 ? Could the catalytic activity be further enhanced?
2. Is there any options to further enhance the Cu/ZnO activity for photocatalytic CO_2 reduction?

To answer these questions, the recommendations for future work will be described in the next section.

7.3 Future work

7.3.1 Further confirmed composition and structure of surface amine group for better understanding of the reaction mechanism between MEA-TiO₂ or MEA-ZnO and CO₂ in the photoreduction process

We have demonstrated in *chapter 4* and *chapter 5* for amine-functionalized semiconductor for efficient CO₂ photoreduction process. However, due to limit of characterization techniques, the detailed mechanism is still unknown. *In-situ* infrared spectroscopy is able to characterize the surface functional groups in the process of photoreaction, which may be an effective method for better understanding of the step-by-step reaction mechanism in the CO₂ photoreduction process. By better understanding of the reaction mechanism, we may further improve the efficiency of photocatalytic CO₂ reduction.

7.3.2 Further exploration of bi-cocatalyst ternary structure for efficient photocatalytic CO₂ reduction

As discussed in *chapter 6*, Cu/ZnO and Pt/ZnO structure was developed. Since both cocatalyst is effective for photocatalytic CO₂ reduction, combining two cocatalyst together for development of bi-cocatalyst ternary structure may be an attractive method for efficient CO₂ photoreduction.

7.3.3 Rational design of MEA-TiO₂/Cu₂O and MEA-ZnO/Cu₂O structure to further optimize the photocatalytic CO₂ reduction yield

To optimize the CO₂ photoreduction yield, we utilize amine group for better interaction between CO₂ and photocatalyst. Cu₂O was also employed to prevent electron-hole pair recombination. These two techniques should be combined together for final optimization to reach the best activity of the photocatalyst. Under the optimized condition, the CO₂ was first capture by amine group on the surface of the photocatalyst, followed by reduction by the photogenerated electrons, which is optimized for prolonged lifetime.

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List of Publications

1. **Yusen Liao**, Shaowen Cao, Yupeng Yuan, Quan Gu, Zhenyi Zhang, Can Xue* Efficient CO₂ Capture and Photoreduction by Amine-Functionalized TiO₂, *Chem. Eur. J.* 20 (2014) 10220 – 10222. **Highlighted as Back Cover.**
2. **Yusen Liao**, Zhaoning Hu, Quan Gu, Can Xue* Amine-Functionalized ZnO nanosheets for Efficient CO₂ Capture and Photoreduction, *Molecules.* 20 (2015) 18847-18855
3. Quan Gu, **Yusen Liao**, Lisha Yin, Jinlin Long, Xuxu Wang, Can Xue* Template-free synthesis of porous graphitic carbon nitride microspheres for enhanced photocatalytic hydrogen generation with high stability, *Appl. Catal. B: Environ* 165 (2015) 502-510.
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6. Yupeng Yuan, Lisha Yin, Shaowen Cao, L. N. Gu, G. S. Xu, P. W. Du*, H. Chai, **Yusen Liao**, Can Xue*, "Microwave-Assisted Heating Synthesis: A General and Rapid Strategy for Large-Scale Production of High Crystalline g-C₃N₄ with Enhanced Photocatalytic H₂ Production", *Green Chem.* 16 (2014) 4663-4668
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