Photocatalytic systems for visible light driven H₂ production from water

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**Photocatalytic Systems for Visible Light
Driven H₂ Production from Water**

Zhang Wei

School of Chemical and Biomedical Engineering

2011

**Photocatalytic Systems for Visible Light
Driven H₂ Production from Water**

**By
Zhang Wei**

**A thesis submitted in fulfillment of the requirements
for the degree of
DOCTOR OF PHILOSOPHY**

**School of Chemical and Biomedical Engineering
Nanyang Technological University
Singapore**

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Abstracts

Water splitting from sunlight is a clean and recyclable way to provide H₂ as an alternative choice for increasing energy demands. The photocatalytic splitting of water using solar energy represents one of the attractive processes to solve the global energy problem. The solar light driven photocatalytic H₂ production process can mainly be realized through water splitting systems heterogeneously containing semiconductor photocatalysts, and also homogeneously on molecular systems with light absorbing photosensitizers. The research work in this thesis was focused on the development of four types of low-cost and efficient photocatalytic systems for H₂ production from water splitting by visible light.

In the first part of the project work, a series of solid solutions between Zn_{0.95}Cu_{0.05}S and CdS with a cubic structure were synthesized through a simple coprecipitation method at room temperature. The band structures of these semiconductors have been well controlled to optimize their photocatalytic activities for visible light driven water splitting. The Zn and Cd sulfide solutions contribute to obtain a proper band gap while maintaining relatively high conduction band potential, and Cu²⁺ impurity levels in the forbidden band facilitate the charge transportation and thus increase the photocatalytic activity. It has been found that the solid solution sample (Zn_{0.95}Cu_{0.05})_{1-x}Cd_xS with x value of 0.33 gives the highest H₂ production rate of 508 μ mol/h even without the expensive Pt co-catalyst. After the Pt loading, sample with x value of 0.50 leads to the highest H₂ production rate of 1.09 mmol/h. The apparent quantum efficiencies (QE) are 15.7% and 31.8%, respectively. Further work was carried out by controlling the position of copper doping in the solid solution of Zn and Cd sulfides. A series of CuS(y)-Zn_xCd_{1-x}S photocatalysts were synthesized in ethylene glycol using thiourea as the sulfur source. Due to the different chelating and solubility properties among the metal species, the obtained nanospheres are found surface enriched with Zn and Cu, which is beneficial for electron separation/transport and

hence surface reduction of water to H_2 in the absence of noble metal co-catalysts. The one-step synthesis method developed is simple and effective for generation of the nanostructured semiconductor photocatalysts with a gradient distribution of constituting metal ions. The activity, which can only be increased by four times by a traditional Pt co-catalyst for the as-prepared $Zn_{0.65}Cd_{0.35}S$ sample, can be enhanced by around 20 times to 550 $\mu\text{mol/h}$ and 624 $\mu\text{mol/h}$ after adding 5.9 mol% and 11.1 mol% (metal basis) of Cu during the synthesis to form a Cu-rich surface. It is believed that the surface Cu^{2+} 3d impurity levels can function as the same role of the noble metal co-catalysts as charge accommodation sites for more efficient charge separation, and hence increase the photocatalytic performance for water splitting.

Inspired by the above co-catalyst effect of CuS, a novel and low-cost NiS/CdS photocatalyst system was synthesized and evaluated. Nickel sulfides were reported as good electrocatalysts for cathodic H_2 evolution in water electrolysis. The use of NiS as a co-catalyst for photocatalytic water splitting had not received prior investigation in literature. In this work, NiS nanoparticles were loaded on CdS surface via a simple hydrothermal route by precipitating nickel acetate in the presence of a large excess of thiourea. An intimate contact between NiS and CdS lattices was formed during the hydrothermal loading process of NiS. The photogenerated electrons in the conduction band of CdS can be easily transferred to the surface NiS nanoparticles due to heterojunction formed between the two phases. Photocatalytic reactions were conducted in aqueous solutions containing lactic acid as the sacrificial reagent. The H_2 evolution rate obtained using the optimized photocatalyst was as high as 2.18 mmol h^{-1} ($\lambda > 420 \text{ nm}$) and the QE was 51.3%, which is the highest ever reported for H_2 production photocatalysts without noble metals co-catalysts.

In the last part of this thesis work, economic and efficient noble-metal-free molecular systems consisting of xanthene dyes as photosensitizers and Ni^{2+} (or Co^{2+}) coordinating to small sulfur-containing organic chemicals as catalysts were developed. The photocatalytic reactions were conducted in TEOA aqueous solutions without

adding toxic solvents. This work provides significant contribution towards the finding of low-cost H₂ production molecular systems and insights towards the reaction mechanism understanding. Among those systems employed, molecular system containing Erythrosin B, Ni²⁺ and mercaptoethanol is found to be the best combination for photocatalytic H₂ production with outstanding QEs of 26% - 11% in visible light range of 460 nm – 550 nm, respectively.

It is believed that the findings from this thesis work greatly contribute towards a better understanding of the controlling factors of the photocatalytic hydrogen system for generation of more efficient photocatalysts.

Keywords: water splitting, H₂ evolution, semiconductor, molecular system, visible light, quantum efficiency, photocatalysts.

Nomenclature

ΔE	Band Gap Energy
ΔG	Gibbs Free Energy Change
λ	Photon Wavelength
ν	Photon Frequency
ATR-IR	Attenuated total reflectance Infrared
BE	Binding Energy
BET	Surface Area Measurement Method
DI	Deionized
dmgH ₂	Dimethylglyoxime
DRS	Diffuse Reflectance Spectroscopy
EB	Erythrosin B
EDX	Energy-dispersive X-ray Spectroscopy
ESI-MS	Electrospray Ionization Mass Spectrometry
eV	Electron Voltage
FTIR	Fourier transform infrared spectroscopy
GC	Gas Chromatography
h	Plank Constant
HAADF	High Angle Annular Dark Field
HRTEM	High Resolution Transmission Electron Microscopy
ICP	Inductively Coupled Plasma
ICP-OES	Inductively Coupled Plasma Atomic Emission Spectroscopy
LMCT	Ligand to Metal Charge Transfer
MA	Mercaptoacetic Acid
ME	Mercaptoethanol
NHE	Normal Hydrogen Electrode
QE	Quantum Efficiency
STEM	Scanning Transmission Electron Microscopy

TCD	Thermal Conductivity Detector
TEM	Transmission Electron Microscopy
TEOA/TEA	Triethanolamine
TON	Turnover Number
TU	Thiourea
UV	Ultra Violet
UV-vis	Ultra Violet – Visible
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

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Chapter I Introduction

1.1 Background

With an increasing concern on the depletion of fossil fuels and the serious environmental problems caused by burning fossil fuels, the utilization of solar energy has become an important subject over the last few decades. At a power level of 1000 W/m^2 , the solar energy incident on the earth's surface by far exceeds the energy needs of all human beings. Besides the photoelectrochemical cells, which are of high fabrication costs, photocatalytic water splitting by sunlight into hydrogen is a promising alternative way to convert solar energy to chemical energy. Hydrogen, being considered as a next-generation energy carrier with increasing demands, contains energy of high density and causes minimal environmental pollution. The photocatalytic splitting of water using solar energy represents one of the attractive processes to solve the global energy problem.¹⁻⁴ The solar light driven photocatalytic H_2 production process can mainly be realized through water splitting systems heterogeneously containing semiconductor photocatalysts,⁵⁻¹¹ and homogeneously on molecular systems with light absorbing photosensitizers.¹²⁻²³

1.2 Semiconductor Photocatalysts for Water Splitting

1.2.1 Overall Introduction

Semiconductors with a proper band gap can be used as the photocatalysts to absorb solar energy for water splitting.⁵⁻¹¹ A brief scheme is shown in Figure 1-1. Photons from sunlight with a certain level of energy can activate the electrons from the valence bands to the conduction bands of semiconductors with appropriate band gap energies. The photo-generated electrons in the conduction bands and the positively charged holes left in the valence bands can be transferred to the material surface, and subsequently reduce/oxidize the H^+/OH^- respectively.

As shown in Figure 1-1, to produce H₂ and O₂ from water, the conduction band minimum should be low enough to reduce H⁺ and the valence band maximum should be high enough to oxidize OH⁻. Secondly, the photogenerated electrons and holes need to be separated and transported efficiently to the surface without recombination.

Figure 1-1 Scheme of visible light photocatalytic water splitting on semiconductor photocatalysts.

With the development of electrochemical solar cells, researchers have realized that light energy can be converted and stored in terms of electrical energy from photon activated electrons in semiconductor materials.²⁴⁻²⁶ The advancement in photoelectrochemical process has inspired the development of semiconductor materials as photocatalysts for harvesting solar energy to directly drive chemical reactions of industrial and environmental importance, such as organic dye degradation, exhaust gas detoxification and the water splitting reaction (Reaction 1-1).

TiO₂ was the first semiconductor photocatalyst used for water splitting, which was discovered in 1971 by Fujishima and Honda.²⁷ However, it has no wide practical applications since its requirements of strong UV light due to its wide band gap and noble metal like Pt as the co-catalyst for H₂ formation. Over the past few decades, increasing efforts have been spent on developing catalysts that are responsible to visible light as it composes the most part of solar spectrum. Since the beginning of

photocatalytic water splitting research, the important goal is to construct highly active visible light driven water splitting photocatalysts and systems with comparable efficiencies to solar electrochemical cells. Meanwhile, cost factor is another consideration as conventional photocatalysts always consist of noble metals or their oxides as co-catalysts towards better activity.²⁸⁻³⁰ Today, hundreds of materials and their derivatives have been developed and evaluated towards the water splitting.³ However, only a few are known to catalyze the overall water splitting into H₂ and O₂ in pure water (NiO surface loaded, La doped KTaO₃;³¹ Cr/Rh loaded GaN/ZnO solid solutions^{3,10,11}), and others can only reduce or oxidize water in the presence of sacrificial reagents to consume photon generated charges. Since only H₂ is the target gas as the clean energy source, water reduction into H₂ in aqueous solutions containing low-cost sacrificial reagents continues to attract wide attention. Currently the well-known photocatalysts with best performances are NiO surface loaded, La doped NaTaO₃ (QE = 56%, pure water, UV light),³¹ ZnS (QE = 90%, aqueous Na₂S/Na₂SO₃, light with $\lambda > 300$ nm) with other metal sulfides solution derivatives,³²⁻⁴¹ Pt and PdS co-loaded CdS (QE = 93%, aqueous Na₂S/Na₂SO₃, light with $\lambda > 420$ nm),⁴² and Cr/Rh loaded GaN/ZnO solid solutions (QE = 5.6%, pure water, visible light).^{3,10,11}

Figure 1-2 photocatalytic water splitting on different type semiconductors.³

In general, an active semiconductor for water splitting must bear a proper band structure in two different aspects. In the first place, the band gap must be narrow enough to absorb visible light for electron activation. On the other hand, the band position for both valence and conduction band should be potentially enough to oxidize and reduce water respectively, shown in Figure 1-2A. However, these rigid conditions can seldom be satisfied in one material system. Electron acceptor and donor reagents are hence widely used in order to achieve half reactions (reduction or oxidation of water) using certain efficient catalysts, shown as Figure 1-2B and 1-2C. In addition, the combination of two catalysts for half reactions on different sites can be adopted to form a Z scheme for the overall water splitting, as shown in Figure 1-2D.³

1.2.2 Titania and Titanates

Among numerous semiconductor photocatalysts, titania is the first found photocatalyst for water splitting under UV light with a very low efficiency.²⁷ Under UV light, Pt loaded anatase TiO_2 was found to tendentiously reduce water for H_2 generation in sacrificial solution containing iodide anion as the electron donor to counteract the positive charged holes; while water oxidation conducted dominantly on rutile TiO_2 in the presence of iodate anion as the electron acceptor for activated electrons. It was generally believed that water reduction and oxidation occurs on different crystalline surface of TiO_2 . However, the exact mechanism is not fully understood yet due to the difficulty in in-situ monitoring of gas evolution. Theoretically, these two kinds of reactions can be combined for overall water splitting using I^-/IO_3^- as the external redox couple. To reduce the band gap of TiO_2 and make it responsible to visible light, N and some transition metal doping have been widely reported. However, the efficiencies for those derivatives are still quite low due to the limited doping strategies and uncontrollable doping processes.^{43,44}

When TiO_2 is calcinated with metal oxides (SrO , PbO , La_2O_3), solid solutions in terms of metal titanates with adjusted band gaps can be obtained.⁴⁵⁻⁴⁹ Inspired by its photocatalytic CO_2 reduction ability, SrTiO_3 powder was found to be able to split

water stoichiometrically under UV light, and its performance can be largely exaggerated by surface modification of NiO and noble metal co-catalysts.⁴⁷ Since then, researchers focused on the co-catalyst effects on water splitting reaction towards a better understanding of the whole reaction scheme.^{50,51} It is recognized that co-catalyst usually functions as electron trap to accelerate the charge transfer and minimize charge recombination, and also can provide separate surface reaction sites for oxidation or reduction to prevent the back reaction between H₂ and O₂. Recent research on titania and titanates has been focused on the relationship between the activity and crystal structure due to the successful synthesis of titania with desired surface facets. Yang and coworkers studied the enhanced photocatalytic abilities on nanosized anatase TiO₂ and anatase TiO₂ nanosheets with dominant (001) facets.^{52,53}

1.2.3 Ta and Nb System

In 1990s, Japanese researchers began to study the Ta and Nb family as photocatalysts since both Ta₂O₅ and Nb₂O₅ have proper band positions. In this series, surface layered structure was found to have important role in their catalytic performance, and it is acknowledged that layered structure can efficiently separate surface reaction sites as the same role of noble metal co-catalysts to avoid back reaction between generated gases.^{54,55} In this Ta and Nb family, the first layered structures of A₄Ta_xNb_{6-x}O₁₇ (A=Rb, K; x=1-4) were synthesized by doping K₄Nb₆O₁₇ with Ta₂O₅ by Domen and coworkers in 1990s.⁵⁵ The band gap can be elaborately adjusted by varying the Ta content, and also the activity can be affected by the Ta concentration. Later, Kudo and coworkers developed similar tantalates ATaO₃ (A= Li, Na, K) with much a simpler structure, which was also capable to split water under UV light.^{56,57} In 2003, Kudo and coworkers optimized their tantalates system and reported that NaTaO₃, doped with 2 mol % La and loaded with NiO as the co-catalyst on the surface, can overall split water with a high quantum efficiency of 56% under UV light.³¹ This photocatalytic system is regarded as a milestone in the development of photocatalysts for water splitting.

In order to facilitate more practical applications of this series of photocatalysts, great attention had been paid on the control of the band gap to be responsive under visible light irradiation. Foreign alkaline earth elements doping and synthesis methods refining were emphasized to control the band positions and surface morphology. However, the efficiency under visible light is still low for this series.⁵⁸ Until recent few years, Domen and coworkers studied the N doped Ta oxides as photoanode for overall water splitting and also Ta nitrides for photocatalytic H₂ evolution under visible light irradiation, respectively.^{59,60}

1.2.4 Other Transition Metal Oxides

Several transition metal oxides can catalyze partial water redox reactions with the presence of suitable electron donors or acceptors as sacrificial reagents. Among them, materials involving VO₄ and WO₆ clusters attract the most attention.

BiVO₄ and Ag₃VO₄ consist of VO₄ tetrahedral units separated by cations have narrow band gaps and can thus absorb visible light of wavelength even up to 600 nm. Under visible light irradiation, O₂ can be evolved over these materials from an aqueous solution containing AgNO₃ as the electron accepting sacrificial reagent. More interestingly, these O₂ generation photocatalysts usually can be combined with some partial water splitting catalysts with good H₂ evolution performance to form a Z-scheme system for overall water splitting. However, such systems usually result in low efficiencies since the slower reaction in the redox couple is the rate-determining step.^{61,62}

Similar as VO₄ clusters, Pt loaded WO₃ can produce O₂ at a high rate in NaIO₃ solution. Recently, Domen and coworkers successfully applied Pt/WO₃ photocatalyst together with a H₂ production photocatalyst Pt/ZrO₂/TaON to form a Z-scheme for the overall water splitting in an IO₃³⁻/I⁻ redox shuttle.⁶³ In comparison to the Pt/WO₃, a complicated tungsten system in a form of Keggin structure with a formula of [Si(W₃O₁₀)₄]⁴⁻, acting as a homogeneous catalyst, produces high rate of H₂ from

aqueous methanol. However, no O_2 was produced even when $AgNO_3$ is present.⁶⁴ It is generally quite difficult to find suitable overall water splitting catalysts with good activities.

1.2.5 Ga and Ge system

In the past decade, nitrogen doping into metal oxide semiconductors through high temperature annealing under NH_3 atmosphere was reported to be an efficient method to lower the band gaps and achieve suitable band positions for overall water splitting. In this process, part of the O atoms is replaced by N, and N 2p orbits contribute to the valence band configuration for a higher energy level. Among those metal oxides, Ga and Ge are the most successful examples investigated by Domen and coworkers.^{4,10,11,65,66}

GaN:ZnO solid solution system is another milestone in the development of water splitting photocatalysts. It is basically synthesized through high temperature NH_3 gas treatment of physical mixture of Ga_2O_3 and ZnO. Due to the repulsion between Zn 3d and N 2p orbits, the resulting products have a smaller band gap (around 2.4 eV) than both individual components of GaN (3.4 eV) and ZnO (3.2 eV). Domen's group systematically examined the effects of several parameters including the Ga to Zn ratio, the N doping level which can be controlled by the NH_3 treatment time and temperature, the crystallinity and the types of surface co-catalysts on this system.^{10,11} Up to date, photocatalysts with Cr/Rh mixed oxides as the surface co-catalyst in this family holds the best record of quantum efficiency for overall water splitting under visible light (2.5% at 420 nm). Later, the half redox reactions in the presence of common electron acceptors and donors were carried out attempting to elucidate the rate determining step in overall water splitting over this system.⁶⁷ More recently, Mn_3O_4 has been found to be an efficient co-catalyst on GaN:ZnO surface to generate O_2 , and the Mn_3O_4 -Rh/ Cr_2O_3 co-loaded GaN:ZnO system exhibits improved water splitting activity.⁶⁸ Similar to the Ga-Zn system, the Ge-Zn system prepared using a

similar method has been also explored comprehensively. However, it has a much lower efficiency.⁶⁹

1.2.6 Metal Sulfides

Besides the metal oxides and nitrides, metal sulfides are attractive as light driven water splitting photocatalysts due to their narrow band gaps that absorb visible light. However, their main disadvantages lie in the poor photochemical stability and the requirement of the use of sacrificial donors for H₂ evolution from aqueous solutions. Nonetheless, in the presence of S²⁻ and SO₃²⁻ anions as sacrificial reagents, the photochemical corrosion of metal sulfides can be largely inhibited while maintaining high H₂ evolution rate even under visible light. Among this large family, ZnS and CdS are the best studied metal sulfide photocatalysts ever since the early 1980s.

Among the metal sulfides, CdS and ZnS are the two major semiconductors attracting frequent research interest for H₂ production from water either on their individual basis^{28,32-41} or after forming solid solutions²⁸⁻³⁰ between the ZnS and CdS. CdS is a semiconductor with a relatively narrow band gap of 2.4 eV and therefore can absorb visible light efficiently. The flat-band potential of CdS is -0.87 V (vs NHE) which is sufficiently high to reduce H₂O to H₂.⁷⁰ The deposition of Pt as a co-catalyst on CdS surface is essential to ensure a good electron transfer and at the same time maintain its photo-corrosion resistance under prolonged irradiation. Hence, Pt-CdS has been intensively studied as visible light photocatalysts for producing H₂ from aqueous solutions containing sacrificial reagents.^{34,36,40,70} In recent studies from Li's group, MoS₂/CdS photocatalyst interestingly showed compatible activity for photocatalytic H₂ evolution from lactic acid aqueous solution, which suggested the possibility of employing low cost co-catalysts other than noble metals on the surface of metal sulfides.⁷¹ In a later time, results on CdS system from the same group convinced the highest QE for visible light photocatalytic H₂ evolution ever since reported. The QE at 420 nm is up to 93% on a Pt/PdS co-loaded CdS photocatalyst for H₂ production from solution containing S²⁻ and SO₃²⁻ anions.⁴²

ZnS with a wide band gap of 3.5 eV is found highly active for H₂ production under UV light even without co-catalysts due to its high conduction band potential.^{33,72} To make use of ZnS under visible light, doping of Cu or Ni into ZnS has been reported by Kudo and co-workers.^{32,73} In particular, Cu doped ZnS with a composition of Zn_{0.957}Cu_{0.043}S was reported to be an efficient photocatalyst for H₂ evolution from water in the absence of any co-catalysts.⁷³ The result indicates that although the band gap is narrowed by forming donor levels in the forbidden band, the high conduction band potential of ZnS host semiconductor remains effective for separation of charges and reduction of water. However, in this system, the absorption edge is around 500 nm with an estimated band gap of 2.5 eV indicating that there is still great room for further tuning of the band to improve the photocatalytic activities.

To better combine the advantages of different types of metal sulfides, several metal sulfide solid solutions, such as Zn_xCd_{1-x}S, (AgIn)_xZn_{2(1-x)}S₂, (CuIn)_xZn_{2(1-x)}S₂ and ZnS-CuInS₂-AgInS₂ have been widely studied and showed very good H₂ productivity under visible light in solution containing sacrificial reagents S²⁻ and SO₃²⁻.^{6-8,28-30} For those sulfides, surface Pt co-catalyst can usually increase their performance greatly.

Till today, metal sulfides possess the highest efficiency for H₂ production under visible light, and are promising for future industrial application since the sacrificial sulfur source used in this reaction is a low-cost byproduct in petrochemical process.

1.2.7 Summary on Semiconductor Photocatalysts

In conclusion, hundreds of semiconductors are known to catalyze the light driven water splitting with or without the presence of sacrificial reagents. Metal oxides and transition metal salts, metal nitrides with metal sulfides compose this family. Researchers are eager to find materials with proper band positions, limited charge recombination and separated surface reaction sites for reduction and oxidation of water. Firstly, proper band positions are the predominant factors to determine whether

a semiconductor is competent or not, and the band potentials will be directly related to the driven force for redox reactions. Secondly, charge recombination will tremendously decrease the photon efficiency. It happens during the charge transfer to the catalyst surface after irradiation since only surface can be the reaction sites. Fewer defects in the crystal and shorter transfer distance are preferred for less recombination. However, fewer defects mean better crystallinity which in turn infers a larger particle size. It is of critical importance to balance and optimize among these factors. Finally, the back reaction at the surface should be avoided, and it can happen easily since the minus Gibbs free energy change in this reaction. Thus co-catalyst and special surface morphology that can separate charge for different reaction usually contribute dominantly to the water splitting performance.

The whole reaction mechanism and the controlling aspects from materials are still not totally clear. Researchers are currently focused on the reaction scheme study to get a deeper knowledge, and hopefully can design efficient catalysts on molecular level for any industrial interest. With the consideration of catalyst composition, morphology and crystallinity, the synthesis of new photocatalysts towards high activity and low cost will be of great interest in H₂ production.

1.3 Molecular Systems for Water Splitting

1.3.1 Overall Introduction

Besides the heterogeneous photocatalyst system employing semiconductors for water splitting, another promising scheme for the visible light driven water splitting consists of the use of photosensitizers and molecular catalysts.¹²⁻²³ Typically used photosensitizers are transition metal complexes or organic dyes with strong absorption to the visible light. Besides a few organic cobalt complexes, the catalysts used in these molecular systems are mainly based on noble metals in the form of either colloids or complexes.^{12-19,74-76} Molecular H₂ evolution from water under visible light has been

considered as the artificial photosynthesis. This half water splitting process can be illustrated with a schematic as shown in Figure 1-3.

Figure 1-3 Reaction scheme of H_2 evolution from water in a molecular production system under visible light in solutions containing sacrificial reagents.

In a typical H_2 evolution molecular system, the photosensitizer (PS) is supposed to absorb specific visible light efficiently forming long-lived triplet excited state, and subsequently photon emission from the photosensitizer can sensitize the catalyst towards forming its excited triplet state for the H^+ reduction. Meanwhile, during the energy transfer, an electron immigrates from photosensitizer to the catalyst leaving oxidized photosensitizer. Provided with the energy and the electron from the sensitization, negative charges can be transferred to the catalyst core resulting in the reduction of the metal center. Reductive metal center plays the final role in electron transfer to H^+ for H_2 production. The oxidized photosensitizer can be quenched by the sacrificial reagents functioning as the electron donor in the reaction.⁷⁶

Comparing to the heterogeneous semiconductor system, the molecular system usually provides homogeneous reaction environment towards maximal availability of active catalytic sites. In recent decades, H_2 production molecular systems have been developed in laboratory from the inspiration of nature photosynthesis.

1.3.2 Metalloporphyrin Complexes

Metalloporphyrin complexes used by green plants in photosynthesis attracted great interests as PS in molecular systems.²¹⁻²² However, the low yield in photocatalytic H₂ production based on those complexes due to difficulties in their structural modification largely limited their practical applications. Meanwhile, the porphyrin synthesis could be challenging although it provides fantastic visible light absorption when coordinated to Zn²⁺ and Mg²⁺. Studies on porphyrin in the application of photocatalytic H₂ evolution are so far limited on systems employing porphyrin as photosensitizer and a diiron catalyst.²¹ A recent report described a porphyrin photosensitizer linked to a cobaloxime catalyst covalently as single molecular device for photocatalytic H₂ production.²² Nonetheless, it is known that the efficiencies of molecular H₂ system usually highly depend on the presence of noble metals. Among numerous types of PS molecular systems studied, precious noble metals have been employed in the chromophore and/or the catalyst towards better efficiency and robustness.

1.3.3 Nobel Metal Complexes

A variety of molecular systems containing Ir, Ru and Pt complexes as efficient PS had been well designed and examined as substitutes of metalloporphyrins in artificial photosynthesis.^{12-19,74-76} Bernhard and coworkers systematically studied a series of Ir complexes from different ligands for the photocatalytic H₂ production using parallel synthetic techniques. [Co(bpy)₃]Cl₂ complex was used as the homogeneous catalyst and TEOA as the sacrificial reagent.¹² Sakai's group developed a single-component system consisting of a Ru(bpy)₃²⁺ derivative and a Pt²⁺ complex,¹⁴ and a Ru-Rh-Ru complex capable for H₂ production was reported by Brewer's group.¹⁷ Lu and coworkers studied the Rose Bengal-Pt system using TEA as electron donor under visible light. The QE for this system at 420 nm was calculated to be 11.3%.¹⁹ Besides the high costs, noble metal complexes exhibit poor stability under strong light irradiation, which largely limits their potential industrial application. On-going research efforts are paid on developing low cost molecular systems consisting earth

abundant elements and also designing complexes that show excellent robustness under light irradiation.

1.3.4 Xanthene Dyes

Systems consist of xanthene dyes and Pt catalyst exhibit as a possible efficient system for photocatalytic H₂ production.¹⁹ To reduce the cost, catalysts containing cobalt have been considered to replace the Pt complexes. In their recent studies, Eisenberg and coworkers reported great progress employing xanthene dyes or their derivatives after S/Se modification as the PSs with Co based [Co^{III}(dmgH)₂pyCl] organic complexes as the catalyst.^{20,23} A system consisting of Eosin Y as the photosensitizer and [Co^{III}(dmgH)₂pyCl] as catalyst exhibits good H₂ production efficiency. In the presence of TEOA as sacrificial reagent and excessive dmgH₂ ligand, the TON of H₂ is up to 900 and the QE is 4% at 520 nm.²⁰ Later, researchers from the same group reported the enhanced system employing S/Se modified rhodamine dye as the PS aiming to increase the photodecomposition resistance and H₂ production activity. The TON was incredibly increased to 9000 at 8 h of irradiation, and the QE was increased up to 32.8% at 520 nm over the best photosensitizer used.²³

1.3.5 Summary on Molecular Systems

In the past few decades, numerous molecular systems have been developed and examined for photocatalytic H₂ production. A few of them employed the low cost metal complexes and others are mainly based on noble metal complexes. Compared to the heterogeneous photocatalytic H₂ generation systems, molecular systems provide optimal active catalytic reaction sites and offer distinct electronic configurations towards mechanism understanding. The challenges remain on the cost reduction and stability improvement. It is still highly desirable to develop low cost molecular systems for photocatalytic H₂ production with quantum yields and better stabilities.

1.4 Photocatalytic Systems Developed in This Thesis

The photocatalytic systems developed for H₂ production from water in this work are discussed in the following four chapters. Chapter II describes a series of solid solutions between Zn_{0.95}Cu_{0.05}S and CdS with a cubic structure. The band structures of these semiconductors have been well controlled to optimize their photocatalytic activities for visible light driven water splitting. The Zn and Cd sulfide contribute to obtain a proper band gap while maintaining relatively high conduction band potential, and Cu²⁺ impurity levels in the forbidden band facilitate the charge moving and thus increase the photocatalytic activity. By forming solid solutions between Zn_{0.95}Cu_{0.05}S and CdS, we successfully controlled both the conduction band and valence band positions. The activity has been optimized through carefully adjusting the composition of the solid solutions. Moreover, Cu rich surface of the solid solutions increased the H₂ production activity.

Since CuS on the surface of Zn, Cd, Cu ternary metal sulfide solid solution can increase the activity, a series of CuS(y)-Zn_xCd_{1-x}S photocatalysts with CuS rich surface were synthesized in ethylene glycol using thiourea as described in Chapter III. Due to the different chelating and solubility properties among the metal species, the obtained nanospheres are found surface enriched with Zn and Cu, which is beneficial for electron separation/transport and hence surface reduction of water to H₂ in the absence of noble metal co-catalysts. The one-step synthesis method developed is simple and effective for generation of the nanostructured semiconductor photocatalysts with a gradient distribution of constituting metal ions. The activity for the Zn_{0.65}Cd_{0.35}S sample can be enhanced by around 20 times after the adding of Cu during the synthesis to form a Cu-rich surface. It is believed that the surface Cu²⁺ 3d impurity levels can function as the same role of the noble metal co-catalysts as charge accommodation sites for the charge separation, and hence increase the photocatalytic performance for water splitting. This work provides insight studies of the CuS

co-catalyst effect in the $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ photocatalyst, which can contribute towards the finding of low-cost photocatalyst systems.

As inspired by the CuS co-catalyst effect from the $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ photocatalyst, the synthesis and evaluation of a novel and low-cost NiS/CdS photocatalyst system is followed in Chapter IV. The use of NiS as a co-catalyst for photocatalytic water splitting has not received prior investigation. In this work, NiS nanoparticles were loaded on CdS surface via a simple hydrothermal route by precipitating nickel acetate in the presence of a large excess of thiourea. The H_2 evolution quantum efficiency from the NiS/CdS photocatalyst is among the highest QEs for visible light driven water splitting photocatalysts, and is the highest so far reported for photocatalysts without noble metals co-catalysts. In this work, NiS as a low-cost co-catalyst on CdS surface is proved highly efficient in H_2 production from lactic acid sacrificial solution, which is a great progress for developing economical photocatalytic systems.

Since the discovery of NiS as efficient co-catalyst on CdS surface, a study of employing NiS in homogeneous photocatalytic H_2 production systems is followed in Chapter V. A variety of noble-metal-free molecular systems consisting of xanthene dyes as photosensitizers and Ni^{2+} (or Co^{2+}) coordinating to small sulfur-containing organic chemicals as catalysts were developed and examined thoroughly. The photocatalytic reactions were conducted in TEOA aqueous solutions without adding the commonly used toxic solvents such as acetonitrile and toluene. Among those systems employed, molecular system containing Erythrosin B, Ni^{2+} and mercaptoethanol is found to be the best combination for photocatalytic H_2 production with outstanding QEs in visible light range. This work provides significant contribution towards the finding of low-cost H_2 production molecular systems and insights towards the reaction mechanism understanding.

Chapter II (Zn_{0.95}Cu_{0.05})_{1-x}Cd_xS Solid Solution Nanocrystals for H₂ Evolution from Water under Visible Light

(This chapter is reproduced with permission from Zhang, W., Zhong, Z. Y., Wang, Y. S. and Xu, R., Doped Solid Solution: (Zn_{0.95}Cu_{0.05})_{1-x}Cd_xS Nanocrystals with High Activity for H₂ Evolution from Aqueous Solutions under Visible Light, J. Phys. Chem. C, 112, 17635-17642, 2008. Copyright 2008, The American Chemical Society)

2.1 Background Introduction

As introduced in Chapter I, photocatalytic splitting of water into H₂ and O₂ using solar energy is a process of great economic and environmental interest. Numerous materials have been reported as photocatalysts for visible light driven water splitting in order to utilize visible light which composes more than 60% of the solar energy.³ However, it remains a challenging task in finding photocatalysts that are highly active even under light with wavelength up to 600 nm, thus providing a high solar energy conversion efficiency comparable with photoelectrochemical cells.⁴ To achieve this goal, it is required that semiconductors for the water splitting process must have narrow band gaps to absorb visible light. Furthermore, proper band positions are essential to provide high potential for reduction of water to H₂. Meanwhile, better crystallinity of the semiconductor as a photo-catalyst is usually preferred to avoid the recombination of photo generated electrons and holes since better crystallinity can result in less defects in the crystal. However, better crystallinity is commonly achieved through high temperature thermo treatment, and thus large particle size and small surface area can seldom be avoided. As we know, larger particle size means longer transfer time for the charge carriers from the bulk to surface, and the recombination possibility will increase dramatically. Also, smaller surface area will bring fewer reaction sites since the water splitting reaction can only happen on the semiconductor surface. This paradox requires very fine control during the material synthesis procedure to get optimized photocatalytic capability. In summary, these

rigid conditions and requirements can seldom be satisfied with those familiar commercial chemicals. Thus the band structure control and materials property optimization of semiconductors are crucial towards developing active photocatalysts for water splitting under visible light.

Regarding band structure control, foreign elements doping and forming solid solutions between wide and narrow band gap semiconductors are the two promising methods.^{28,32,73,77-80} Foreign element doping into a wide band gap material can possibly decrease the band gap for visible light absorption. On the other hand, the band gap can be adjusted by varying the composition in the solid solution formed by a narrow and a wide band gap semiconductor. Among numerous semiconductors, metal sulfides have been widely reported as photocatalytic water splitting catalysts in sacrificial solutions due to their high activity and the easiness in the formation of solid solutions. As stated in Chapter I, metal sulfides possess the highest efficiency for H₂ production under visible light, and are promising for future industrial application since the sacrificial sulfur source used in this reaction is a cheap byproduct in petrochemical process.

Cu doped ZnS with a composition of Zn_{0.957}Cu_{0.043}S was reported to be an efficient photocatalyst for H₂ evolution from water in the absence of any co-catalysts.⁷³ It would be interesting to investigate the solid solutions formed between this system and CdS for a finer band structure control, while taking the advantage of high conduction band potential of ZnS. Since CdS and ZnS were reported to be able to form solid solutions with a wide range of Zn and Cd composition,^{28,29,81} it is thus possible to form solid solutions between the Zn_{1-x}Cu_xS system and CdS. The research reported in this chapter was focused on the synthesis and evaluation of the solid solutions between Zn_{0.95}Cu_{0.05}S and CdS with a wide range of compositions through a simple co-precipitation method at room temperature. A series of (Zn_{0.95}Cu_{0.05})_{1-x}Cd_xS solid solutions with different compositions ($x = 0, 0.17, 0.27, 0.33, 0.50, 0.67, 1$) were synthesized and evaluated. At the optimized composition, excellent photocatalytic

activity and stability were obtained. The high activities of the solid solution nano-crystals have been attributed to their efficient visible light absorption due to the presence of cadmium sulfide, relatively high conduction band potentials contributed by zinc sulfide, and the accommodation sites of charge carriers provided by Cu^{2+} impurity levels.

2.2 Experimental Section

2.2.1 Reaction Apparatus and Analytical Systems

Our reaction system is composed mainly by a closed gas circulation and evacuation system fitted with a top window Pyrex cell and connected to on-line gas chromatography (GC) analytical system. The sketch is shown in Figure 2-1.

Figure 2-1 Water splitting reaction system.

The light source is a 300 W Xenon lamp from the top of the reaction cell, and it can be equipped with cut-off filters or band pass filters to provide light with certain wavelength required. The reaction cell locates in a water jacket which was kept at room temperature with cooling water. The whole system can be vacuumed by the connected pump to provide a non-oxygen environment for the H₂ production, and the vacuum level inside the circulation system can be monitored by the pressure gauge. The circulator in the loop route is helpful for the gas diffusion, and thus the results from GC can be identical to the real value. The whole system has a sampling system, which is connected to the on-line GC through a 4-way valve. At each time, only a small amount of gas is sampled, hence it has a negligible effect on the accumulative quantity of H₂ produced.

Figure 2-2 H₂ calibration line.

Figure 2-3 O₂ calibration line.

On the GC analysis part, we use argon gas as the carrier, 5A molecular sieve column for the products separation, and TCD at 150 °C as the detector. The column oven temperature is set at 35 °C with a gas rate of 13 mL/min inside the column. The calibration lines of H₂ and O₂ were obtained by injecting pure gas into the circulation system at certain pressure. Thus we can relate the GC peak area with gas pressure inside the circulation system. As the volume inside the reaction system was accurately measured, the amount of gas generated can be calculated from the pressure and volume. Figure 2-2 and 2-3 are the calibration lines of H₂ and O₂ respectively. All the photocatalytic H₂ production reactions studied in this thesis work were conducted on the above described system.

2.2.2 Synthesis of (Zn_{0.95}Cu_{0.05})_{1-x}Cd_xS Solid Solution

The reagents were all analytical grade and used without further purification. In a typical synthesis, 90 mL of 0.1 M Na₂S (Na₂S·9H₂O, Acros Organics, extra pure) solution was added to 30 mL of 0.1 M (metal basis) M(NO₃)₂ mixture solution with different molar ratios of Zn²⁺ (Zn(NO₃)₂·6H₂O, Fluka, >99.0%), Cu²⁺ (Cu(NO₃)₂·

3H₂O, Acros Organics), and Cd²⁺ (Cd(NO₃)₂·4H₂O, Fluka, >99.0%) under rigorous stirring. The resulting precipitates were aged in the mother liquors for 8 h under continuous stirring. The precipitates were then collected and centrifuged, followed by washing with deionized water for several times. The solid samples were dried in an oven overnight at 60 °C. The compositions of the prepared samples are listed in Table 2-1.

2.2.3 Characterization

The powders were characterized by X-ray powder diffraction (XRD) analysis, which was carried out in a Bruker D8 Advance X-ray diffractometer equipped with graphite monochromatized Cu K α radiation ($\lambda=1.54056$ Å). The BET surface areas were measured in Autosorb-6B (Quantachrome instruments) using the liquid nitrogen adsorption method. The UV-visible diffuse reflectance spectra (DRS) were obtained from an UV-visible spectrophotometer (UV-2450, Shimadzu). The morphology, nano-crystals size and lattice fringes were measured by TEM and high resolution TEM (Tecnai-G², FEI) with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was conducted in an Axis Ultra spectrometer (Kratos Analytical) using a monochromated Al K α X-ray source (1486.7 eV) operating at 15 kV. The binding energies were calibrated with the position of C 1s peak (284.8 eV) arising from adventitious hydrocarbon.

2.2.4 Photocatalytic Activity Measurement

Visible light driven H₂ evolution from aqueous solutions of sulfide and sulfite was conducted in a closed gas circulation and evacuation system fitted with a top window Pyrex cell. In each run, 0.3 g of the as-prepared metal sulfide sample was well dispersed with constant stirring in a 200 mL of aqueous solution containing 0.35 M Na₂SO₃ (Sodium Sulfite Anhydrous, Alfa Aesar, 98%) and 0.25 M Na₂S (Na₂S·9H₂O, Acros Organics, extra pure). The system was evacuated and refilled with argon gas for several times to remove the air inside and finally filled with approximately 30 torr of argon before the reaction. Deposition of Pt co-catalyst was carried out using an in

situ reduction method. The reaction mixture was added with 0.75 wt% (metal basis) of $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ (Hydrogen hexachloroplatinate hydrate, 40% Pt, Acros Organics), and irradiated under Xenon lamp for half an hour before the reaction. The light source was a 300 W Xenon lamp with a cut-off filter ($\lambda \geq 420$ nm). The reaction cell was kept at room temperature with cooling water. The produced H_2 was detected using an online gas chromatography (argon carrier, 5A molecular sieve column, TCD detector).

The quantum efficiency were measured under the same reaction conditions except a band pass interference filter (Newport, centre wavelength 420 nm, band width 10 nm) and a long pass cut-off filter (cut on 420 nm) were equipped to provide photons with wavelength between 420 and 425 nm. The number of photons from irradiation was measured using a photodiode.

$$\text{QE} = \frac{2 \times \text{the number of evolved hydrogen molecules}}{\text{the number of incident photons}} \times 100\% \quad (2-1)$$

In a typical calculation of the quantum efficiency, irradiation intensity was measured by the photodiode in terms of Watts per unit area. Thus we can get the whole irradiation efficiency by multiplying the average value of photodiode with the light spot area. In one hour irradiation, the total energy and number of incident photons can subsequently be known since the wavelength of photons and Planck constant are identified.

2.3 Results and Discussion

2.3.1 The Crystal Structure and Morphology

Figure 2-4 shows the XRD patterns of samples with different compositions. All the samples obtained under the present synthesis condition exhibit a cubic zinc blend structure with broad diffraction peaks of (110), (220) and (311). Sample a is Cu doped

ZnS with a stoichiometric composition of $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{S}$. The XRD result for this sample is consistent with that reported by Kudo and co-workers in terms of crystal phase and peak broadness.⁷³ At a low concentration, Cu atoms can be incorporated into the ZnS lattice, since Zn and Cu have similar ionic radius (0.74 and 0.72 Å, respectively) and can both form cubic structured sulfides. The peak position of (111) plane for Sample g, CdS, is located at 26.9° , which is lower than that of Sample a at 29.2° . The shift towards the lower angle for CdS is in agreement with the larger radius of Cd^{2+} cation (0.97 Å). For Samples b-f, $(\text{Zn}_{0.95}\text{Cu}_{0.05})_{1-x}\text{Cd}_x\text{S}$, with an increasing x value, it can be observed that there is a successive shift of the (111) peak from higher to lower angles between those of Samples a and g. Such a phenomenon clearly indicates that solid solutions were formed between $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{S}$ and CdS for all the compositions, rather than their mixtures.^{6,82} Therefore, the room-temperature coprecipitation in the presence of excess S^{2-} anions results in the successful formation of solid solutions, cubic structured $(\text{Zn}_{0.95}\text{Cu}_{0.05})_{1-x}\text{Cd}_x\text{S}$, with controllable compositions. Another commonly encountered crystal structure of CdS, ZnS and their solutions is hexagonal wurtzite structure, which is often obtained via high temperature synthesis or thermal treatment.^{30,35,37,83}

The TEM and HRTEM images of a typical solid solution sample, $(\text{Zn}_{0.95}\text{Cu}_{0.05})_{0.67}\text{Cd}_{0.33}\text{S}$ (Sample d), are shown in Figure 2-5a and 2-5b, respectively. It can be found that the solid solution sample is comprised of nanocrystals with very small particle sizes in a range of 2–5 nm, which are consistent with the average grain sizes obtained from XRD results between 2.2 nm to 3.0 nm.

Figure 2-4 XRD patterns for $(\text{Zn}_{0.95}\text{Cu}_{0.05})_{1-x}\text{Cd}_x\text{S}$ samples with different compositions. Composition for the samples: a, $x=0$; b, $x=0.17$; c, $x=0.27$; d, $x=0.33$; e, $x=0.50$; f, $x=0.67$; g, $x=1$.

The reason for the formation of nanosized crystals may be due to the extremely small solubility product of these metal sulfides. Upon the adding of sulfide anions into the solutions containing the metal cations, the formation of nuclei is very rapid, resulting in the formation of a high concentration of nuclei and hence the small crystal sizes. Aggregation of nanocrystals happened to the solid solution particles, which can be seen from the HRTEM images of the nanoparticles shown in Figure 2-5. Aggregates of nanocrystals without long-range order will still show a broad XRD peak. The HRTEM image shows the short ranged lattice fringes of individual nanocrystals, indicating a generally poor crystallinity for this sample. The HRTEM images of Sample a ($\text{Zn}_{0.95}\text{Cu}_{0.05}\text{S}$) and Sample g (CdS) are displayed in Figure 2-5c and 2-5d, respectively. The crystallinity of these two samples appears slightly better than that of

the solid solution sample as longer ranges of lattice fringes can be observed. Such difference is understandable by considering that distorted lattice could be introduced during the formation of the solid solutions due to the large difference in ionic radii of Cd^{2+} and Zn^{2+} , thus resulting in poorly crystallized particles.^{84,85} As a result, the specific surface areas of the solid solution samples are generally quite high in a range of 128–156 m^2/g as shown in Table 2-1. CdS alone has the lowest specific surface area at around 74 m^2/g , which corresponds to its relatively larger particle sizes.

Figure 2-5 TEM (A) and HRTEM (B) images of Sample d with a composition of $(\text{Zn}_{0.95}\text{Cu}_{0.05})_{0.67}\text{Cd}_{0.33}\text{S}$, and HRTEM images of Sample a, $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{S}$ (C), and Sample g, CdS (D).

Figure 2-6 The XPS wide and narrow scan spectra of Sample d, $(\text{Zn}_{0.95}\text{Cu}_{0.05})_{0.67}\text{Cd}_{0.33}\text{S}$.

The XPS spectra of Sample d were shown in Figure 2-6. The spectrum of the survey scan indicates the presence of Zn, Cd, Cu and S in the sample. The C signal should be attributed to adventitious hydrocarbon.^{86,87} The spectra of Zn 2p, Cu 2p and Cd 3d are also displayed in Figure 2-6. The binding energies of these metal cations as indicated in Figure 2-6 are in agreement with the literature data for Zn^{2+} in ZnS ,⁸⁸ Cu^{2+} in CuS ,⁸⁹ and Cd^{2+} in CdS ⁹⁰ with only slight difference. A very low signal-to-noise ratio observed in the spectrum of Cu 2p is due to its low percentage in the sample.

2.3.2 Photophysical Properties and Band Structures

Figure 2-7 shows the UV-visible diffuse reflectance spectra of different samples. The band gap energy estimated based on the onset of the absorbance edge is listed in Table 2-1.

Table 2-1 Summary of materials properties and photocatalytic activities of $(\text{Zn}_{0.95}\text{Cu}_{0.05})_{1-x}\text{Cd}_x\text{S}$ solid solution samples.

Sample ID	Composition (x)	BET S.S.A. (m^2/g)	Band gap ^a (eV)	H_2 production rate without Pt ^b ($\mu\text{mol/h}$)	H_2 production rate with 0.75 wt% Pt ^b ($\mu\text{mol/h}$)
a	0	149	2.30	46	28
b	0.17	156	2.01	320	682
c	0.27	152	1.99	430	1012
d	0.33	141	1.97	508	1050
e	0.50	137	1.97	205	1086
f	0.67	129	1.96	156	847
g	1	74	2.14	8	82

^aThe band gap values were calculated based on the onset of the absorbance from UV-vis DRS.

^bReactions were conducted under a 300 W Xenon lamp with a cut-off filter ($\lambda \geq 420 \text{ nm}$); 0.3 g of catalyst was dispersed in a 200 mL aqueous solution containing 0.35 M Na_2SO_3 and 0.25 M Na_2S .

Figure 2-7 UV-visible diffuse reflectance spectra of $(\text{Zn}_{0.95}\text{Cu}_{0.05})_{1-x}\text{Cd}_x\text{S}$ solid solutions with different composition. Y-axis is absorbance unit treated by Kubelka-Munk Function. Composition for the samples: a, $x=0$; b, $x=0.17$; c, $x=0.27$; d, $x=0.33$; e, $x=0.50$; f, $x=0.67$; g, $x=1$.

An almost horizontal line was drawn with superposition to the spectra at 700-800 nm. Another tangent line was drawn from the reflection point of the spectra, intersecting with the former line. The x value (wavelength) of this intersection point was converted to band gap energy by equation $\Delta E = h\nu$. CdS (Sample g) showing an intense absorption band with a steep edge in the visible light region has a band gap of 2.14 eV. On the other hand, $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{S}$ (Sample a) with a band gap of ca. 2.30 eV has both UV and visible light absorption with an extended long tail in the visible region. The visible absorption by this sample is attributed to the transition from Cu^{2+} impurity levels to the conduction band of ZnS.⁷³ The bandgap we measured is from the Cu dopant level to the minimum of conduction band for $(\text{Zn}_{0.95}\text{Cu}_{0.05})_{1-x}\text{Cd}_x\text{S}$. In this case, it is possible to have a narrower bandgap for $(\text{Zn}_{0.95}\text{Cu}_{0.05})_{1-x}\text{Cd}_x\text{S}$ than both CdS (2.14 eV) and $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{S}$ (2.30 eV). Because ZnS has bandgap of 3.5 eV, Cu doping narrowed the gap by 1.2 eV. Figure 2-8 shows the band structures of CdS and $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{S}$ samples.

Figure 2-8 The band structures of CdS, $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{S}$ and $(\text{Zn}_{0.95}\text{Cu}_{0.05})_{1-x}\text{Cd}_x\text{S}$ solid solutions.

For the solid solution samples, it can be observed that the absorption in the UV region gradually decreases from Samples b to f (Figure 2-7) with an increasing Cd^{2+} percentage in the solid solution. Such observation is consistent with the drop of the conduction band potential away from that of ZnS, which provides another strong evidence for the formation of solid solutions. The band structure of the solid solution samples is also indicated in Figure 2-8. The conduction band potential of the solid solution samples lies between those of CdS and ZnS. It has been reported that the band gap of $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ can be adjusted in a range of 2.35–2.71 eV by varying the composition of the solid solution.²⁹ Remarkably, the band gap energy of our $(\text{Zn}_{0.95}\text{Cu}_{0.05})_{1-x}\text{Cd}_x\text{S}$ solid solution samples is in a lower and much narrower range of 1.96–2.01 eV. Firstly, the lower band gap energies obtained for our samples compared with those of $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ should be due to the presence of Cu^{2+} donor levels in our solid solutions. Cu3d orbitals will hybrid with S2p orbitals to form the valence band of the solid solutions. Secondly, the significant decrease of UV absorbance edge from Samples b to f indicates the shift of the conduction band potential to be less negative as x increases (Figure 2-8). On the other hand, it is to be noted that the percentage of Cu^{2+} (metal basis) decreases from 4.15% to 1.65% as x increases from 0.17 to 0.67 in the solid solutions (Table 2-1). Therefore, by taking into account of the almost constant band gap at around 2.0 eV for our solid solution samples, it can be interestingly deduced that a lower doping percentage of Cu^{2+} leads to more positive donor levels as indicated in Figure 2-8. In fact, the larger band gap of a similarly prepared Cu doped ZnS, $\text{Zn}_{0.99}\text{Cu}_{0.01}\text{S}$ (2.5 eV), by Liu et al.⁸⁰ compared with that of our sample, $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{S}$ (2.3 eV), further confirms this speculation. It is also noteworthy that the absorbance of our solid solution samples even extends to 650 nm due to Cu doping. These donor levels can possibly accommodate the photogenerated charge carriers to suppress electron/hole recombination.^{91,92} The extent of such a promotional effect could be affected by both the potential of the Cu^{2+} donor levels and the Cu^{2+} doping concentration. Moreover, the impurities in nanocrystals often lead to phenomena not found in the bulk because their electronic states are confined to a small volume.⁹³ It would be interesting to investigate the effect of the doping

concentration of the impurities in nanocrystals on the photocatalytic activity for H₂ evolution.

2.3.3 Photocatalytic Activity for H₂ Evolution

To achieve efficient H₂ evolution from the photocatalytic water splitting process under visible light, it is essential to have a photocatalyst that absorbs visible light efficiently, has a sufficiently high conduction band potential, and promotes charge separation and transportation to the surface reaction sites. By forming the solid solutions between Zn_{0.95}Cu_{0.05}S and CdS, our samples with narrow band gap energies of ca. 2.0 eV have their absorption bands effectively red-shifted up to 650 nm. The high conduction band potential of ZnS results in relatively high conduction band potentials of the solid solutions. Moreover, the particle sizes of our samples are quite small (2–5 nm) due to the room temperature synthesis condition. As a result, photo generated electrons and holes can move to the surface of the nanocrystals in short distance. Table 2-1 summarizes the H₂ production rate using different samples as photocatalysts under visible light. The amounts of H₂ produced versus the irradiation time for samples without and with the Pt co-catalyst are plotted in Figure 2-9 and Figure 2-10, respectively.

Figure 2-9 Photocatalytic H₂ production rate using different (Zn_{0.95}Cu_{0.05})_{1-x}Cd_xS solid solutions without Pt under visible light ($\lambda \geq 420$ nm). 0.3 g of catalyst in a 200 mL aqueous solution containing 0.35 M Na₂SO₃ and 0.25 M Na₂S. Composition for the samples: a, x=0; b, x=0.17; c, x=0.27; d, x=0.33; e, x=0.50; f, x=0.67; g, x=1.

Figure 2-10 Photocatalytic H₂ production rate using different (Zn_{0.95}Cu_{0.05})_{1-x}Cd_xS solid solutions loaded with 0.75 wt% Pt under visible light ($\lambda \geq 420$ nm). 0.3 g of catalyst in a 200 mL aqueous solution containing 0.35 M Na₂SO₃ and 0.25 M Na₂S. Composition for the samples: a, $x=0$; b, $x=0.17$; c, $x=0.27$; d, $x=0.33$; e, $x=0.50$; f, $x=0.67$; g, $x=1$.

Among the samples without the Pt co-catalyst, Sample d ($x = 0.33$) gives the highest H₂ evolution rate of ca. 508 $\mu\text{mol/h}$ under the irradiation of a 300 W Xe lamp ($\lambda \geq 420$ nm). To the best of our knowledge, based on the previously obtained results by other researchers using various metal sulfide solutions without co-catalysts,^{6,8,29,30,82} the highest H₂ production rate reported under visible light was around 350 $\mu\text{mol/h}$ (350 W Xe lamp, $\lambda \geq 430$ nm) using the same amount of photocatalyst as ours (0.3 g).⁸⁰ The measured apparent quantum efficiency for our Sample d is 15.7% at 420 nm which is among the highest reported. Therefore, our solid solution sample with a

composition of $(\text{Zn}_{0.95}\text{Cu}_{0.05})_{0.67}\text{Cd}_{0.33}\text{S}$ represents one of the most highly active metal sulfide photocatalysts in the absence of noble metal co-catalysts. It is also interesting to point out that unlike the previous claim that only hexagonal phased CdS are active for H_2 evolution,^{35,41} our samples have a cubic structure.

Table 2-1 and Figure 2-9 show that the H_2 production rate is sensitive to the composition of the solid solution samples. When x is lower at 0.17 and 0.27 (Samples b and c), the average H_2 production rate obtained is lower at 320 and 430 $\mu\text{mol/h}$, respectively. Upon increase of x to 0.50 and 0.67 (Samples e and f), the production rate dropped quickly to 205 and 156 $\mu\text{mol/h}$, respectively. The particle size, surface area, and band gap among our solid solution samples are quite similar. Therefore, the difference in their photocatalytic activities could be explained by the combined effect of several important factors including the conduction band potential, Cu^{2+} impurity level potentials, and Cu^{2+} concentration. Based on the band structure proposed in Figure 2-8, Samples b and c should have higher conduction band potentials than Sample d. However, due to their relatively higher Cu^{2+} doping concentrations, the donor level potentials of Cu^{2+} impurities are less positive, i.e., further away from the maximum of the valence band. As a result, the photoelectrons generated in these two samples could less easily move to the impurity levels than those in Sample d. On the other hand, the much lower activities obtained for Sample e and f is due to their less negative conduction band potentials and lower Cu^{2+} concentrations. For comparison, samples without Cu doping but with a similar composition as Sample d ($\text{Zn}_{0.67}\text{Cd}_{0.33}\text{S}$) gave lower H_2 evolving rates of 344 and 693 $\mu\text{mol/h}$ without and with Pt loading, respectively under the same reaction conditions. Since the doping level of Cu^{2+} is critical, we have attempted to vary the Cu^{2+} concentration slightly based on the composition of the most active sample (Sample d). However, both increasing and decreasing of Cu^{2+} doping resulted in lower activities. Therefore, doping of Cu^{2+} at an optimum level provides enhanced photocatalytic efficiency for H_2 evolution compared to the undoped sample. Trapping of charge carriers is one of the methods to suppress electron/hole recombination. It has been reported that some transition metal

dopants can act as the trapping sites to inhibit the electron/hole recombination.⁹¹ It is likely that the Cu^{2+} dopants here similarly act as the accommodation sites for charge carriers. More systematic investigation on the catalyst composition, the surface Cu^{2+} effects and mechanism study is presented in the next chapter. Finally, Sample a ($\text{Zn}_{0.95}\text{Cu}_{0.05}\text{S}$) and Sample g (CdS) give very low H_2 production rates of ca. 46 and 8 $\mu\text{mol/h}$, respectively.

The Pt co-catalyst loaded on the surface of the nano-crystals promotes electron transfer. As shown in Table 2-1 and Figure 2-10, the H_2 production rates have been greatly increased after loading of about 0.75 wt% Pt for all the samples, except $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{S}$ based on which the H_2 production rate was reduced from 46 to 28 $\mu\text{mol/h}$ after Pt loading. For this sample, it has been reported that the high conduction band potential of ZnS is effective for reduction of H_2O to H_2 without co-catalysts.^{33,72} Coating of Pt nanoparticles could block the surface reaction sites and thus leads to a lower activity. CdS (Sample g) shows the highest factor of increase in activity (almost 10 times) after Pt loading, and such observation is consistent with the literature data.^{35,40,41,94} The difference in H_2 evolution activity among the solid solution samples is reduced with the Pt co-catalyst. Samples c ($x = 0.27$), d ($x = 0.33$) and e ($x = 0.50$) exhibit improved activities with almost a similar H_2 production rate of 1.01–1.09 mmol/h. A high quantum efficiency was obtained with the value of 31.8% for Sample d loaded with 0.75 wt% Pt. It is concluded that the Pt co-catalyst further increases the electron mobility and the $\text{Pt}/(\text{Zn}_{0.95}\text{Cu}_{0.05})_{1-x}\text{Cd}_x\text{S}$ photocatalyst system prepared in our work is highly effective for H_2 evolution from aqueous solutions of sulfide and sulfite. The stability of Sample d loaded with the Pt co-catalyst was investigated in three consecutive runs of accumulatively 12 h. As shown in Figure 2-11, no significant decrease in the photocatalytic activity is observed. The slight drop in the H_2 production rate could be due to the consumption of the sacrificial reagents (S^{2-} , SO_3^{2-}) in the reaction mixture over the time, since the concentrations of sacrificial reagents affect the performance largely.³⁹ The initial concentrations of the sacrificial reagents in our reactions were optimized. They are quantitatively sufficient, but the

decrease in concentrations will result in lower photocatalytic productivity. The scheme of photocatalytic H₂ evolution using metal sulfide semiconductors in aqueous solution containing sulfide and sulfite anions can be represented by eqs 2-2 to 2-6.³⁹

The disulfide ions S₂²⁻ produced in eq (2-5) act as optical filters and compete with the reduction of proton. However, this can be greatly suppressed by the addition of SO₃²⁻ as shown in eq (2-6). The thiosulfate ions S₂O₃²⁻ product formed are colorless and do not compete with the catalyst for light absorption. It can be seen from the above reaction scheme that the presence of S²⁻ anions not only stabilizes the catalyst surface by suppressing the surface sulfur defects, but also together with SO₃²⁻ ions consumes the photon generated holes.

Figure 2-11 Stability study using Sample d loaded with 0.75 wt% Pt under visible light ($\lambda \geq 420 \text{ nm}$).
0.3 g of catalyst in a 200 mL aqueous solution containing 0.35 M Na₂SO₃ and 0.25 M Na₂S.

To further investigate the stability of our catalyst, Sample d (without Pt) was recollected after 12 h of photocatalytic reaction under visible light, then washed thoroughly and dried at 60 °C. The UV-vis diffuse reflectance spectrum, XRD pattern, TEM and HRTEM images of this recovered sample are shown in Figure 2-12. The UV-vis diffuse reflectance spectrum and XRD curves of the same sample before reaction are also shown for comparison. No significant difference can be observed from these results, except that the nanocrystals after reaction are slightly more aggregated. The pH of the reaction solution varied only in a small range from 12.0 before reaction to 12.2 after 12 h reaction.

Figure 2-12 The UV-vis diffuse reflectance spectrum (A), XRD pattern (B), TEM (C) and HRTEM (D) images of Sample d (without Pt) after 12 h reaction under visible light. The UV-vis DRS and XRD curves obtained for the same sample before reaction are shown in (A) and (B) for comparison.

To further evaluate the performance of the samples under irradiation of longer wavelength, long pass cut-off filters cutting on 455 nm and 475 nm were equipped during the photocatalytic reactions. As shown in Figure 2-13, the drop in activity is evident with light of longer wavelength. However, the performances at 475 nm are still quite good with or without Pt. In the presence of Pt co-catalyst, the hydrogen production rate is still as high as 800 $\mu\text{mol/h}$.

Based on the above results, it is obvious that surface modification by Pt can prominently increase the photocatalytic performance. However, Pt is a costly noble metal, thus it is worthwhile to develop alternative surface functional sites that can also effectively promote charge separation and accommodation. In this regard, ion exchange with Cu and Ag cations that can provide d orbitals as electron traps was conducted.

Figure 2-13 Performance of sample d under different light source. Reaction conditions remained the same.

Figure 2-14 and 2-15 show the results of surface modification by ion exchange method. Typically, 0.1 g of sample d was mixed with 100 mL of Cu(II) or Ag(I) nitrate solution containing 1/6 of the Cu in the solid and stirred for 24 h at room temperature. The resulting solids were collected and carefully washed. Since Ag₂S and CuS both have much smaller dissociation constants compared to those of ZnS and CdS, the surface Zn and Cd ions can possibly be replaced by Ag and Cu ions in the solution. As shown in Figure 2-14, it can be observed that Ag modification has no effect on the performance (compared to none) and it causes a slight drop when the sample was loaded with Pt. On the other hand, Cu modification leads to enhanced performance with or without Pt by about one third of the original results. To better evaluate the surface Cu effects, different Cu concentrations in the exchange solution were applied, and results are shown in Figure 2-15. The copper concentration refers to the equivalent of the amount present in the original solid sample before ion exchange. Higher Cu loading on the surface leads to a drop in the activity with or without Pt, and more systematic study is presented in the next chapter for the surface modification and the surface charge separation mechanism.

Figure 2-14 Surface modification effects by Ag and Cu ion exchange.

Figure 2-15 Surface modification by different amount of Cu.

Finally, it is noteworthy that the room temperature synthesis of the semiconductor nanocrystals in our work represents a low energy route. No thermal treatment at elevated temperatures is required to achieve good photocatalytic activities. Furthermore, only a straightforward precipitation process in aqueous solutions using simple inorganic precursors (metal nitrates and sodium sulfide) is engaged. No organic solvents or toxic gases (e.g., H_2S) are involved. Therefore, the photocatalysts in the current work are obtained via a “green” pathway, which should be considered as an important factor for practical applications.

2.4 Conclusion

We synthesized a series of solid solutions between $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{S}$ and CdS with a cubic structure through a simple coprecipitation method at room temperature. The crystallite sizes of the solid solution samples are in a range of 2–5 nm and they have large specific surface areas of 128–156 m^2/g . The band structures of these semiconductors have been well controlled to optimize their photocatalytic activities for visible light driven H_2 evolution from aqueous solutions of sulfide and sulfite. The Zn and Cd

sulfide contribute to obtain a proper band gap while maintaining relatively high conduction band potential, and Cu^{2+} impurity levels in the forbidden band could accommodate the photogenerated charge carriers and thus increase the photocatalytic activity. It has been found that the solid solution sample $(\text{Zn}_{0.95}\text{Cu}_{0.05})_{1-x}\text{Cd}_x\text{S}$ with $x = 0.33$ gives the highest H_2 production rate of 508 $\mu\text{mol/h}$ even without the Pt co-catalyst. After the Pt loading, sample with $x = 0.50$ leads to the highest H_2 production rate of 1.09 mmol/h. The apparent quantum efficiencies obtained are 15.7% and 31.8% for the samples without and with Pt, respectively. The surface ion exchange with Cu^{2+} ions can improve the activity slightly, which inspired the idea of enriching the surface of this ternary metal sulfide system with Cu as presented in the next chapter.

Chapter III Surface Engineered Photocatalysts without Noble Metals: CuS-Zn_xCd_{1-x}S Nanospheres

(This chapter is reproduced with permission from Zhang, W., and Xu, R., Surface Engineered Active Photocatalysts without Noble Metals: CuS-Zn_xCd_{1-x}S Nanospheres by One-Step Synthesis. *Int. J. Hydrog. Energy*, 34, 8495-8503, 2009. Copyright 2009, Elsevier)

3.1 Background Introduction

It is understood that the efficiency of a certain semiconductor photocatalyst system depends on many materials factors such as crystal structure, crystallinity, particle size, surface feature, impurity doping, etc., which can all be affected by its synthesis pathway. During the past decade, many advanced synthetic techniques have been developed for the fabrication of a vast variety of semiconductor nanomaterials. However, coupling of the success in nanomaterials syntheses to that in practical applications is not so straightforward, especially for a complicated process like photocatalysis. It is known that the activities of the photocatalysts can often be enhanced by the surface co-catalysts due to their promotional effect on charge separation and/or function as separated redox reaction sites. Efficient charge separation can resist the charge recombination, and meanwhile separated redox reaction sites can reduce the possibility of the back reaction between produced H₂ and O₂.^{54,55} Noble metals and their oxides are the most widely used co-catalysts, such as the Pt in TiO₂⁹⁵⁻⁹⁸ and CdS systems,^{35,37,41,94} and RuO₂ and the mixed oxides of Cr and Rh in GaN-ZnO solid solutions.^{10,11} However, in consideration of the high costs and limited availabilities of these noble metals, efficient photocatalysts without the presence of noble metals have become very attractive. It can be found from the literature that there are two general strategies to achieve this task. Firstly, photocatalysts with alternative surface modifying species that play the same role as

the noble metals could be used. For example, the enhanced activities of CdS by surface Ag₂S prepared through a cation-exchange or coprecipitation process were reported by Reber and Rusek.²⁸ Kudo and coworkers optimized their tantalate systems by surface loading with NiO as co-catalyst.³¹ Another successful attempt is the coating of MoS₂ on CdS surface by impregnation of molybdenum precursor and subsequent thermal treatment in H₂S.⁴⁰ In these cases, the surface modifying species exhibited intimate contact with the base semiconductors by forming heterojunctions which resulted in easier charge transfer and better separation efficiency. Besides this approach, the use of a semiconductor with a high conduction band potential has also been found effective. In particular, ZnS was reported to be active for H₂ production without co-catalysts.^{33,34} However, ZnS only absorbs UV light due to its wide band gap of 3.5 eV.⁹⁹ To make use of ZnS under visible light, formation of solid solutions between ZnS and other metal sulfides of narrower band gaps, and/or doping of transition metal ions such as Cu²⁺, Ni²⁺ are the feasible ways.^{28-30,32,73,80,100-102} Promising quantum efficiencies in a range of 9.6%–19.8% at 420 nm were achieved using Cd_{1-x}Zn_xS, ZnS-In₂S₃-Ag₂S, Cu-doped Cd_{1-x}Zn_xS, Cu-doped ZnIn₂S₄ photocatalysts without noble metals by our and other groups.^{30,80,100-102}

According to the results presented in Chapter II, a Cu rich surface of the (Zn_{0.95}Cu_{0.05})_{1-x}Cd_xS solid solution can increase its photocatalytic activity, which inspired the research of surface engineered photocatalysts in this chapter. ZnS-CdS solid solutions with or without doping of Cu in literatures were mostly prepared by co-precipitating the metal ions in an aqueous environment using inorganic sulfides such as Na₂S and H₂S. Such a preparation method resulted in a homogeneous distribution of the three metal ions.^{28,29,80,100} Herein, a one-pot synthesis of Cu-Zn-Cd sulfide nanospheres of 20-30 nm in ethylene glycol in the presence of excess thiourea is described. Due to the different reactivity of the constituent metal species in the organic solvent, the surface of the nanospheres was found enriched with Zn and Cu sulfide layers. It is suggested that a compositional gradient due to uneven distribution of metal ions in semiconductor nanoparticles is beneficial for charge separation and

transfer. The resulting nanosphere photocatalysts of optimized compositions are highly active for H₂ production in the absence of noble metal co-catalysts. The synthesis strategy used in this work may be applied for the fabrication of other semiconductor systems with compositional gradient for tailored applications. .

3.2 Experimental Sections

3.2.1 Synthesis of CuS-Zn_xCd_{1-x}S Samples

In a typical synthesis, a total 4 mmol of zinc acetate (Zn(Ac)₂·2H₂O, >99.0%, Chemicod) and cadmium acetate (Cd(Ac)₂·2H₂O, >99.0%, Kanto Chemical) with a Zn:Cd molar ratio of 0.65:0.35, 0.25 mmol of copper acetate (Cu(Ac)₂, extra pure, Alfa Aesar) and 60 mmol of thiourea (99%, Alfa Aesar) were mixed together in a flask containing 100 mL of ethylene glycol (>99.5%, Fisher Chemical). The mixture was heated to 90 °C under continuous stirring, and kept at this temperature for 0.5 h to form a clear solution. The temperature of the mixture was then increased to 160 °C with a heating rate of 5 °C/min. After that, the mixture was aged at 160 °C for another 2 h. The precipitate was then collected and centrifuged, followed by washing with deionized water for several times. The solid was dried in an oven overnight at 60 °C. Samples with different Zn:Cd molar ratios and a fixed Cu composition of 5.9% (CuS(5.9%)-Zn_xCd_{1-x}S, where 0.3 ≤ *x* ≤ 0.8), or different Cu compositions with the same Zn:Cd molar ratio of 0.65:0.35 (CuS(*y*)-Zn_{0.65}Cd_{0.35}S, where 0% ≤ *y* ≤ 15.8%) were prepared under the same conditions. The %CuS refers to the relative mole percentage of Cu²⁺ among the three metal cations in the precursor solution. Samples without Cu (Zn_xCd_{1-x}S, where 0.3 ≤ *x* ≤ 0.8) were synthesized under the same conditions for comparison.

3.2.2 Characterization

The XRD, UV-vis, BET and XPS characterization of the samples are similar to those described in Section 2.2.3. The morphology and nanocrystal sizes were measured by

TEM (JEOL 2010) with an accelerating voltage of 200 kV. The metal compositions were measured using inductively coupled plasma - optical emission spectroscopy (ICP-OES) in a Prodigy High Dispersion ICP (Leeman Teledyne).

3.2.3 Photocatalytic Activity Measurement

The H₂ production reaction apparatus can be referred in Section 2.2.1. The photocatalytic reaction details, the Pt loading method and the QE calculation method are similar to those described in Section 2.2.4.

3.3 Results and Discussion

Figure 3-1 displays the XRD pattern, TEM and HRTEM images of sample CuS(5.9%)-Zn_{0.65}Cd_{0.35}S. Such characterization results of other samples with different compositions are quite similar (data not shown). The XRD pattern (Figure 3-1a) indicates that the samples obtained under the present synthesis conditions have a cubic zinc blend crystal structure.^{6,73,82} The weak and broad pattern suggests that the samples are not well crystallized. The estimated grain size based on the (110) peak is approximately 5 nm using Scherrer equation. For Cu-free samples, the XRD peak position of (111) plane shifts slightly toward higher angle (27.24° - 27.56° - 28° - 28.4°) as the increase of Zn concentration ($x = 0.5, 0.6, 0.7, 0.8$), which suggests the formation of solid solutions between ZnS and CdS in general. While the UV-vis DRS results to be discussed shortly indicate that Zn_xCd_{1-x}S samples prepared by this method are not totally homogeneous solid solutions and single metal sulfides may be formed. The TEM image (Figure 3-1b) shows that hollow nanospheres of 20-30 nm in diameter were formed. It can be observed that the nanospheres consist of clustered nanoparticles of about 5 nm in size, which is consistent with the grain size estimated from the XRD result. The nanospheres are polycrystalline with lattice fringes of different orientations clearly observed on the HRTEM image (Figure 3-1c). The formation of metal sulfide hollow nanospheres in the presence of excess thiourea could be due to the Ostwald ripening process as discussed in our previous work.⁸³

Figure 3-1 (a) XRD pattern, (b) TEM, (c) HRTEM images of sample CuS(5.9%)-Zn_{0.65}Cd_{0.35}S.

Figure 3-2 UV-vis diffuse reflectance spectra of (a) samples $\text{Zn}_x\text{Cd}_{1-x}\text{S}$, (b) samples $\text{CuS}(5.9\%)\text{-Zn}_x\text{Cd}_{1-x}\text{S}$. Y-axis is the absorbance unit treated by Kubelka-Munk function.

Figure 3-2 shows the UV-visible diffuse reflectance spectra of samples $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ and $\text{CuS}(5.9\%)\text{-Zn}_x\text{Cd}_{1-x}\text{S}$. It can be generally observed that as the mole fraction of Cd increases (x decreases), the absorption edge is red-shifted since CdS has a narrower band gap (2.4 eV) than ZnS (3.7 eV). The absorption edges of samples without Cu (Figure 3-2a) are not smooth, especially of samples with larger mole fractions of Zn ($\text{Zn}_{0.7}\text{Cd}_{0.3}\text{S}$ and $\text{Zn}_{0.8}\text{Cd}_{0.2}\text{S}$). In addition, distinct ZnS absorption feature can be observed in the spectra of these samples. Such phenomena indicate that $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ samples prepared by this method are not homogeneous solid solutions between ZnS and CdS. A composite system of the solid solution and the single metal sulfides, in particular, ZnS, may be formed. It has been noticed from previous investigations that the formation of solid solution between these two sulfides may not be very straightforward. White and co-workers showed that separate phases of ZnS and CdS were formed on SiO_2 support by a wet impregnation and precipitation method, although $\text{Zn}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2$ were co-impregnated on the support.¹⁰³ $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ samples synthesized by Zhang et al.³⁰ through a thermal sulfuration method and Wang et al.¹⁰⁴ by precipitation using thioacetamide also showed similar absorption features. After doping of Cu (Figure 3-2b), the absorption edges of the samples are all

red-shifted with respect to their counter parts without Cu. In addition, the absorption edges become much smoother and no obvious feature from ZnS can be observed any more. As the ionic radius of Cu^{2+} is very close to that of Zn^{2+} but much smaller than that of Cd^{2+} , it is energetically favorable for Cu^{2+} to be doped in the lattice of ZnS. The band gap can be effectively narrowed by the donor levels of Cu 3d in the forbidden band.^{73,80} Thus, the seemingly smooth absorption curves of $\text{CuS}(5.9\%)\text{-Zn}_x\text{Cd}_{1-x}\text{S}$ samples shown in Figure 3-2b may not necessarily arise from the solid solutions among the three metals. The actual materials system could be quite complicated and will be further discussed based on other characterization results shortly. The apparent band gap energies estimated from the onset of the absorption edges vary from 2.1 eV to 2.5 eV for $\text{CuS}(5.9\%)\text{-Zn}_x\text{Cd}_{1-x}\text{S}$ samples ($0.3 \leq x \leq 0.8$), indicating that these semiconductors absorb visible light. In addition, the absorbance is extended to longer wavelength of 800 nm due to Cu doping.

The photocatalytic H_2 production was conducted in aqueous solutions containing Na_2SO_3 and Na_2S as sacrificial reagents under visible light ($\lambda \geq 420$ nm). As shown in Table 3-1, the specific surface areas of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ samples increase from around 70 to $190 \text{ m}^2/\text{g}$ as x increases from 0.3 to 0.8. Doping of Cu did not affect the surface area much ($< 10\%$). However, a distinct comparison of the H_2 evolution rates is observed among the as-prepared samples with or without Cu doping. Very low activities were resulted from samples without Cu doping (Figure 3-3a and 3b). Among them, the optimal composition is found to be $\text{Zn}_{0.65}\text{Cd}_{0.35}\text{S}$ which gives a H_2 evolution rate at about $29 \mu\text{mol/h}$. For comparison, the solid solution sample, $\text{Zn}_{0.67}\text{Cd}_{0.33}\text{S}$, reported in our earlier work produced H_2 at a rate of $344 \mu\text{mol/h}$ under the same reaction conditions.¹⁰⁰ The lower photocatalytic activities incurred for the Zn-Cd sulfides in this work are mainly because that no homogeneous solid solutions were formed, as discussed earlier based on the UV-vis diffuse reflectance spectra. After loading of 1 wt% Pt co-catalyst, the H_2 production rates can be increased by around 2-4 times as shown in Figure 3-3b and Table 3-1. Nevertheless, the activity is still quite low and the highest H_2 rate obtained is only $114 \mu\text{mol/h}$ for $\text{Pt}(1 \text{ wt}\%)/\text{Zn}_{0.65}\text{Cd}_{0.35}\text{S}$.

Figure 3-3 H_2 production rates under visible light irradiation ($\lambda \geq 420$ nm, 300 W Xe lamp), (a) samples $\text{Zn}_x\text{Cd}_{1-x}\text{S}$, (b) samples $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ with 1 wt% of Pt, (c) samples $\text{CuS}(5.9\%)\text{-Zn}_x\text{Cd}_{1-x}\text{S}$, (d) samples $\text{CuS}(5.9\%)\text{-Zn}_x\text{Cd}_{1-x}\text{S}$ with 1 wt% of Pt.

Table 3-1 BET surface areas and H₂ production rates of the as-prepared Zn_xCd_{1-x}S and CuS(5.9%)-Zn_xCd_{1-x}S samples with or without Pt co-catalysts.

Samples	Without Cu			With Cu		
	BET	H ₂ evolution	H ₂ evolution	BET	H ₂ evolution	H ₂ evolution
	surface area(m ² /g)	rate(umol/h) without Pt	rate(umol/h) with 1wt%Pt	surface area(m ² /g)	rate(umol/h) without Pt	rate(umol/h) with 1wt%Pt
X=0.3	71.8	15.7	60.1	64.8	36.2	206
X=0.5	82.5	15.5	40.7	81.5	225	589.5
X=0.6	116	24.6	68.6	106	456.3	703.4
X=0.65	125	29	114.2	123	549.7	739.5
X=0.7	141	26.2	116	132	497.1	632.7
X=0.8	190	18.9	80.1	181	253.9	316.1

Reactions were conducted under 300W Xenon lamp with a cut-off filter ($\lambda \geq 420$ nm); 0.3g of catalyst was dispersed in 100 mL aqueous solution containing 0.1 M Na₂SO₃ and 0.1 M Na₂S.

It is remarkable that doping of a small percent of Cu results in significant improvement in the photocatalytic H₂ evolution performance. The H₂ production rates are increased by nearly 20 times for samples with $0.6 \leq x \leq 0.7$ (Figure 3-3c), which is much better than the enhancement brought by Pt co-catalyst without Cu doping. A H₂ production rate of about 550 $\mu\text{mol/h}$ is obtained from sample CuS(5.9%)-Zn_{0.65}Cd_{0.35}S, which is about 10% higher than that from the solid solution sample (Zn_{0.95}Cu_{0.05})_{0.67}Cd_{0.33}S in our previous work.¹⁰⁰ However, the apparent quantum efficiency of sample CuS(5.9%)-Zn_{0.65}Cd_{0.35}S at 420 nm is 8.1%, which is only around half of that (15.7%) of the latter. Such a difference could be most probably due to that the samples synthesized in this work utilize light of longer wavelength more efficiently. The H₂ production rate can be further increased to 740 $\mu\text{mol/h}$ after loading of 1 wt% Pt co-catalyst, corresponding to a quantum efficiency of 19.1%. As mentioned above, a co-catalyst like Pt can efficiently separate photogenerated electrons and holes in the photocatalyst through providing accommodation levels for the negative electrons. Thus it can reduce the chance of the electron/hole recombination, and also function as active sites for proton reduction. Charge recombination greatly lowers the efficiency of water splitting photocatalysts. Co-catalyst loading is one promising way to suppress the recombination, while those most popular and efficient co-catalysts are noble metals with high price and limited

supply. Thus it is highly desired to employ cheap transition metal sulfides/carbides as co-catalysts on common metal sulfide photocatalysts. The d orbitals of Cu are generally considered as impurity levels in semiconductor materials. Donor levels from Cu 3d orbitals trap the photogenerated holes, and thus suppress the charge recombination in the same role of that from Pt co-catalyst. Subsequently, CuS will act as oxidation sites for the reactions from those sacrificial reagents to consume the positive holes. In this research, a cheap and efficient co-catalyst was realized.

To further understand the properties of the nanosphere photocatalysts, the bulk and surface compositions were analyzed by ICP and XPS methods. XPS spectra of Cd 2p, Zn 2p and Cu 2p of sample CuS(5.9%)-Zn_{0.65}Cd_{0.35}S are shown in Figure 3-4a-c. The binding energies of the core level electrons of these metal ions are consistent with literature data with small variations.⁸⁸⁻⁹⁰ The bulk and surface metal compositions of this sample are displayed in Figure 3-4d (bars labeled with “2 h”, where 2 h refers to the reaction time at 160 °C). The compositions of the intermediate sample obtained when the reaction temperature just reached 160 °C was also analyzed and the results are shown by the bars labeled with “0 h”. As shown in Figure 3-4d, for the sample collected when the reaction temperature just reached 160 °C, the composition of Zn at the surface (73.1%) is higher than its overall composition (60.2%), while that of Cu is similar (3.2% vs 3.8%). After 2 h, there were no substantial changes for Zn and Cd compositions both in the bulk and on the surface. However, both the bulk and surface Cu composition increased along with the reaction time. In particular, there is a remarkable increase of surface Cu composition from 3.8% to 8.5%. It is known that thiourea is a chelating reagent which forms complexes with metal cations through metal-S coordination.¹⁰⁵ In a typical synthesis for a sample containing Cu, a clear solution was formed after stirring at 90 °C for half an hour, indicating that the three metal ions formed the complexes with thiourea. Among these three metal ions, Cu²⁺ has the strongest coordination ability due to its electronic configuration.¹⁰⁶ As a result, the precipitation of copper sulfide would be retarded due to the ligand protection effect. Secondly, upon increasing of the reaction temperature, the release of S²⁻ anions

due to the breaking of C=S bond by the attack of the nucleophilic O atoms of ethylene glycol molecules could be a slow process.¹⁰⁷ Under such a condition, Cd²⁺ ions precipitated more rapidly than Zn²⁺ ions due to the thermodynamic solubility product difference.¹⁰⁸ As such, nanospheres with a Cd-rich core and Zn-rich surface were formed when the reaction temperature was increased from 90 °C to 160 °C, and the solids appeared yellowish in color. There could be a separate ZnS phase present on the surface, as supported by the absorption spectra presented earlier (Figure 3-2a). Based on the ICP results, it is found that only part of Cu²⁺ was precipitated and doped in the solids, and the remaining still existed in the form of complex in the solution. While the reaction was continued at 160 °C, the color of the solids turned to light orange due to the sufficient decomposition of thiourea to release the remaining Cu²⁺ ions and also to provide sulfur anions for the precipitation of Cu²⁺ on the surface of the solids. Copper is believed to be doped into the Zn-rich surface layers based on the observation of the disappeared ZnS absorption feature (Figure 3-2b). The relative Cu concentration in the final sample is close to that added at the beginning of synthesis, suggesting that almost all the Cu²⁺ ions was precipitated. The proposed formation process is schematically displayed in Figure 3-5.

Figure 3-4 XPS spectra of (a) Cd 2p, (b) Zn 2p, (c) Cu 2p, and (d) the bulk and surface metal compositions of CuS(5.9%)–Zn0.65Cd0.35S measured by ICP and XPS methods, respectively. The sample was collected when the reaction temperature just reached 160 °C (bars labeled with “0 h”) and after reaction at 160 °C for 2 h (bars labeled with “2 h”).

Figure 3-5 Proposed formation process of surface Zn and Cu enriched Cu-Zn-Cd sulfide nanospheres.

Figure 3-6 H₂ production rates under visible light irradiation ($\lambda \geq 420$ nm, 300 W Xe lamp) using samples CuS(y)-Zn_{0.65}Cd_{0.35}S ($0\% \leq y \leq 15.8\%$, which is the relative mole percentage of Cu²⁺ among the metal ions).

Similar to Ni and Ag, the d orbitals of Cu are generally considered as impurity levels in semiconductor materials. Cu doped into the lattice of some semiconductor materials can narrow their wide band gaps, and increase the absorbance of visible light for better water splitting performance.^{78,100,101} The donor levels of transition metal ions can possibly accommodate the photogenerated charge carriers to suppress electron/hole recombination and lead to more efficient photocatalysts.^{91,92} It has been demonstrated here that the enriched Cu doping on the surface is another way to achieve better photocatalytic activity. We further investigated the effect of Cu composition with the optimized Zn:Cd ratio of 0.65:0.35. Figure 3-6 shows the H₂ production rates on CuS(y)-Zn_{0.65}Cd_{0.35}S photocatalysts with different Cu compositions. It can be seen that even with a small percentage of 3.0%, Cu-doped catalyst already gives rise to a remarkably higher H₂ production rate compared to Cu-free catalyst. The activity increased with the Cu concentration till reaching a maximum H₂ production rate of 624 μmol/h at 11.1% of Cu doping. Further increase of Cu concentration results in lower activities. CuS on the photocatalyst surface acted

as surface co-catalyst. It will provide charge accommodation and H^+ reduction sites on the surface. With the increasing of surface CuS under a certain limit, more surface active sites will bring higher expected activity. Meanwhile, further increased surface CuS will consumable the photons to be absorbed by the ZnCdS solid solution as CuS has good absorption of photons in visible light range. All Cu-doped catalysts without Pt co-catalyst provide better performance than Cu-free catalysts loaded with 1 wt% Pt on the surface. In our previous study of the ternary Zn-Cd-Cu sulfide system, Cu is homogeneously doped into the bulk to form a solid solution with Zn and Cd. It was found that only 2 to 3 times of improvement can be attained by the optimized Cu doping in the bulk.¹⁰⁰ In the present synthesis environment, the reactivity difference of the three ions following the order of $Cd^{2+} > Zn^{2+} > Cu^{2+}$ allowed controlled precipitation to generate a compositional gradient of metal ions. The Zn-Cu sulfide rich surface likely induces a more efficient charge separation and transfer of electrons towards the surface, hence increases the photocatalytic performance. Furthermore, compared to the traditional way of loading noble metals by impregnation or in situ reduction, this method could produce a more homogeneous surface with fewer defects.

For metal sulfide semiconductor photocatalysts, surface corrosion could occur during the light driven water splitting reaction. The stability of samples CuS(5.9%)-Zn_{0.65}Cd_{0.35}S and CuS(11.1%)-Zn_{0.65}Cd_{0.35}S without Pt co-catalyst were investigated. As shown in Figure 3-7 line a, no significant decrease in the photocatalytic activity is observed. However, the H_2 evolution rate of the sample bearing a higher Cu concentration dropped obviously after around 2-3 h reaction, as shown in Figure 3-7 line b. The Cu-rich surface of this sample is less stable and prone to anodic corrosion. Therefore, it is found that the sample with a moderate doping concentration of Cu results in the best H_2 evolution performance with good stability.

Figure 3-7 Stability study for (a) sample CuS(5.9%)-Zn_{0.65}Cd_{0.35}S, (b) sample CuS(11.1%)-Zn_{0.65}Cd_{0.35}S under visible light irradiation ($\lambda \geq 420$ nm, 300 W Xe lamp).

3.4 Conclusions

In conclusion, we synthesized a series of CuS(y)-Zn _{x} Cd_{1- x} S (where $0.3 \leq x \leq 0.8$, $0\% \leq y \leq 15.8\%$) nanospheres with a Zn and Cu-rich surface were synthesized via a one-step method in ethylene glycol. The cubic phased nanospheres of approximately 20-30 nm in diameter are comprised of nanocrystals of about 5 nm. Due to the reactivity difference among the metal ions in the organic solvent, the surface of the nanospheres was found enriched with Zn and Cu sulfide layers. In the absence of Cu, sample Zn_{0.65}Cd_{0.35}S gives a H₂ production rate of 29 $\mu\text{mol/h}$ under the irradiation of a 300 W Xenon lamp with a cut-off filter ($\lambda \geq 420$ nm) in aqueous solutions containing S²⁻ and SO₃²⁻. The activity, which can only be increased by four times by a traditional Pt co-catalyst for the as-prepared Zn_{0.65}Cd_{0.35}S sample, can be enhanced by around 20 times to 550 $\mu\text{mol/h}$ and 624 $\mu\text{mol/h}$ after adding 5.9 mol% and 11.1 mol% (metal basis) of Cu during the synthesis to form a Cu-rich surface. It is believed that the surface Cu²⁺

3d impurity levels can function as the same role of the noble metal co-catalysts as charge accommodation sites for the charge separation, and hence increase the photocatalytic performance for water splitting. The one-step synthesis method developed is simple and effective for generation of the nanostructured semiconductor photocatalysts with a gradient distribution of constituting metal ions. The effectiveness of the co-catalyst CuS on the photocatalyst surface prompted us to search more efficient and low cost co-catalyst, and such work is presented in the next chapter.

Chapter IV Highly Efficient and Noble Metal-Free NiS/CdS Photocatalysts for H₂ Evolution under Visible Light

(This chapter is reproduced with permission from Zhang, W., Wang, Y. B., Wang, Z., Zhong, Z. Y., Xu, R.*, Highly Efficient and Noble Metal-Free NiS/CdS Photocatalysts for Hydrogen Evolution from Lactic Acid Sacrificial Solution under Visible Light, *Chem. Commun.*, 46, 7631-7633, 2010. Copyright 2010, Royal Society of Chemistry)

4.1 Background Introduction

Studies on semiconductor-type photocatalysts have indicated that co-catalysts loaded on the surface of semiconductor particulates play important roles in promoting the photocatalytic activities.^{1,3,110,11,31,109-111} An appropriate co-catalyst can accommodate the photogenerated charge carriers, suppress charge recombination and provide designated redox reaction sites to avoid back reactions.^{10,31} Among the numerous types of semiconductor systems studied, metal sulfides have demonstrated promising activities towards H₂ production from water containing sacrificial reagents under visible light.^{6,32-42,100,102,112} In particular, CdS has been most frequently investigated for its efficient absorption of visible light and sufficient conduction band potential for reduction of H⁺ to H₂.³⁵⁻⁴² However, CdS alone exhibits very low photocatalytic activities and its good performance was mainly achieved in the presence of noble metal co-catalysts, such as Pt, Pd, etc.³⁹⁻⁴² To reduce the cost of renewable H₂ production, it is necessary to explore alternative co-catalysts based on transition metals. In a recent study, MoS₂ was found a potential co-catalyst for CdS and the optimized MoS₂/CdS photocatalyst resulted in a H₂ evolution rate of 0.54 mmol h⁻¹ under visible light ($\lambda > 420$ nm) with the same lamp power.⁴⁰ In the Chapter III, a metal sulfide system with Cu rich surface was discussed. Low-cost transition metal

sulfides that can provide empty d orbitals have been demonstrated to play the same role as the noble metals as co-catalysts on photocatalyst surface.

Herein, the synthesis and evaluation of a novel and low-cost NiS/CdS photocatalyst system is presented in this chapter. Nickel sulfides were reported as good electrocatalysts for cathodic H₂ evolution in water electrolysis.¹¹³⁻¹¹⁶ The use of NiS as a co-catalyst for photocatalytic water splitting had not been studied before, although Ni and NiO were used as co-catalysts for oxide semiconductor photocatalysts.^{1,31} In this work, NiS nanoparticles were loaded on CdS surface via a simple hydrothermal route by precipitating nickel acetate in the presence of a large excess of thiourea. The H₂ evolution rate obtained from a 30 vol% of L-(+)-lactic acid sacrificial solution using the optimized photocatalyst was as high as 2.18 mmol h⁻¹ ($\lambda > 420$ nm) and the quantum efficiency (QE) was 51.3%. Based on our knowledge, this is among the highest QEs for visible light driven water splitting photocatalysts, and is the highest so far reported for photocatalysts without noble metals co-catalysts.

4.2 Experimental Sections

4.2.1 Synthesis of NiS/CdS Samples

CdS was synthesized according to the literature method⁴² without undergoing the final drying step before the loading of NiS. Typically, the CdS solids were prepared through adding Na₂S (400 mL, 0.14 M) aqueous solution drop by drop into Cd(Ac)₂ aqueous solution (500 mL, 0.14 M) under vigorous stirring. The yellow suspension was stirred for 24 h and kept for an additional 24 h. The resulting yellow slurry was filtered. The wet solid was hydrothermally treated in a Teflon-lined stainless steel autoclave (150 mL) with 120 mL of pure water at 473 K for 72 h. The yellow solid was filtered, washed with DI water before the loading of NiS.

In a typical synthesis of NiS/CdS photocatalyst, around 0.5 g of CdS (in a wet state, weight estimated on a dry basis), 30 mmol of thiourea (99%, Alfa Aesar) and 75 μ mol

of nickel acetate (>99%, Alfa Aesar) were dispersed in 100 mL of deionized water in a Teflon-lined autoclave with 120 mL in capacity. The mixture was subjected to ultrasonication for 2 h followed by hydrothermal treatment at various temperatures for 4 h. The dark green solids were collected by centrifugation and washed with deionized water for several times, followed by drying overnight at 60 °C. Different loading concentrations of NiS were achieved by using different amounts (75-380 μ mol) of nickel acetate precursor during the hydrothermal treatment at 140 °C, while keeping other conditions the same.

The loading of CoS, CuS and Ag₂S was performed with the same procedure using cobalt nitrate (>99%, cobalt nitrate hexahydrate, Fluka Chemika), copper acetate (99.999%, Alfa Aesar) and silver acetate (99%, Alfa Aesar) precursors, respectively.

4.2.2 Characterization

The XRD, UV-vis characterization of the samples are similar to those described in 2.2.3. The morphology, particle size, lattice fringes and Energy-filtered TEM analysis was performed on a TEM (JEOL 2010) equipped with a Gatan imaging filter. The High-Angle Annular Dark Field Scanning-TEM (HAADF-STEM) studies, energy dispersive X-ray spectroscopy (EDX) scan and line scan were carried out on a FEI Titan 80-300 electron microscope operated at 300 kV, which is equipped with an electron beam monochromator, an EDX and a Gatan electron energy loss spectrometer. The probing electron beam size of EDX measurement was around 0.3 nm with the dwell time of 20 seconds. Elemental profile was obtained by recording EDX spectrum at 2 nm steps along 50 nm line on one particle. The ICP analysis was similar to those described in 3.2.2. Energy-filtered TEM analysis was performed on a TEM (JEOL 3010) equipped with a Gatan imaging filter to obtain elemental maps.

To investigate the oxidation products in the reaction solution, electrospray ionization-mass spectrometry (ESI-MS) and attenuated total reflectance (ATR) techniques were used to analyze the reaction solutions. The solution after 24 h

reaction was subjected to the ESI-MS analysis, and standard solution containing lactic acid and pyruvic acid at a mole ratio of 13.6:1 (based on theoretical conversion of lactic acid to pyruvic acid) was also examined for comparison. Mass spectra were recorded on a Thermo Finnigan LCQ Deca XP Max (San Jose, CA) ultra high sensitivity quadruple ion trap mass spectrometer fitted with Surveyor LC Auto Sampler and MS Pump. Acquisition mass range was typically with m/z 15-200. Data were recorded and processed using X-Calibur software (Thermo Scientific, MA, USA). ATR-IR was conducted on a Perkin-Elmer Spectrum One FTIR Spectrometer from using the reaction solutions before and after reaction of 24 h. The ATR crystal was fully covered by the solution during the analysis.

4.2.3 Photocatalytic Activity Measurement

The H_2 production reaction apparatus can be referred in Section 2.2.1. The photocatalytic reaction details and the QE calculation method are similar to those described in Section 2.2.4. In each run, 0.3 g of the as-prepared photocatalyst was well dispersed with constant stirring in a 100 mL of aqueous solution containing 30 vol% of L-(+)-lactic acid (85-90% aqueous solution, Alfa Aesar). Deposition of 1 wt% of Pt co-catalyst for the generation of Pt/CdS photocatalyst was carried out using an in-situ reduction method according to method stated in Chapter II. Photocatalytic reaction was also conducted in D_2O dissolved with lactic acid anhydrous crystals. Helium gas was used as GC carrier in this case to distinguish H_2 and D_2 .

4.3 Results and Discussions

As it can be seen from Figure 4-1, there is a distinct colour change from yellow to dark green before and after loading of NiS on CdS. The XRD results are shown in Figure 4-3. CdS used in this work has a hexagonal crystalline structure (Figure 4-2a). The signals of NiS were very weak for all the NiS/CdS samples prepared, indicating highly dispersed and ultrafine NiS nanoparticles formed. Based on the XRD result of NiS(1.2mol%)/CdS (Figure 4-2b), NiS could possibly adopt a rhombohedral structure.

The UV-vis DRS results of CdS and NiS(1.2mol%)/CdS are shown in Figure 4-3a. The absorption edge of CdS is not shifted, but the absorption level in the visible light region after 550 nm is substantially enhanced. This indicates that Ni^{2+} ions were not doped into the CdS lattice by $\text{Ni}^{2+}/\text{Cd}^{2+}$ cation exchange but were rather precipitated on the surface of CdS. Such a phenomenon is expected as NiS has a much larger solubility product than CdS.¹⁰⁸

The presence of NiS nanoparticles on CdS surface are further evidenced by the HRTEM images (Figure 4-3c and d), XPS (Figure 4-4) and EDX results (Figure 4-5). The lattices with a distance of 0.270 nm on the surface of CdS particle could be assigned to the (300) plane of rhombohedral NiS. Although the interface between NiS and CdS can be observed in Figure 4-3d, a distinct boundary is not shown. An intimate contact between NiS and CdS lattices was formed during the hydrothermal loading process of NiS in this work. The binding energies (BEs) of the main and satellite peaks of Ni $2p_{3/2}$ are at 853.9 and 860.3 eV, respectively, which are close to the reported values for NiS.¹¹⁷ In addition, the BEs of the two subpeaks of S 2p at 161.5 and 162.8 eV can be assigned to S in CdS and NiS, respectively.¹¹⁸

Figure 4-1 Picture of samples before and after loading of NiS. (a) CdS and (b) NiS(1.2mol%)/CdS.

Figure 4-2 XRD patterns of (a) CdS, (b) NiS(1.2mol%)/CdS, and the line pattern of rhombohedral NiS (PDF #86-2281). Star labels indicate the possible presence of very weak signal from NiS.

Figure 4-3 Characterization of the sample NiS(1.2 mol%)/CdS. (a) UV-vis diffuse reflectance spectra; (b)-(d) TEM and HRTEM images.

Figure 4-6 shows the H_2 evolution rates on NiS/CdS photocatalysts with different NiS concentrations (measured by ICP method) loaded at 140°C . In the absence of NiS, CdS had a very low activity as usual with a H_2 evolution rate of $0.063 \text{ mmol h}^{-1}$. Loading of a small amount of NiS significantly improved the performance. At 0.18 mol% of NiS loading, the H_2 production rate was increased approximately 10 times to 0.66 mmol h^{-1} . When the NiS loading was increased to 0.63–1.87 mol%, the H_2 production rates obtained were remarkably high. The sample with 1.2 mol% of NiS gave the highest H_2 production rate of 2.18 mmol h^{-1} , which is about 35 times of that obtained on the NiS-free CdS sample. The QE was measured to be 51.3% at 420 nm for NiS(1.2mol%)/CdS. ICP analysis of the reaction solutions showed that the acidic

corrosion occurred to the surface NiS. After 2, 4 and 8 h of the reaction time, the percentage of Ni^{2+} leached into the solution was 6.7%, 21% and 24.8%, respectively. This could be due to that the fine NiS nanoparticles present on the surface can be partially dissolved at the acidic condition (pH at ~ 1.9) due to the presence of lactic acid. Nevertheless, it was found that the activity only dropped slightly after 8 h (Figure 4-7), which indicated that the ultrafine NiS nanoparticles remained on the surface of CdS still function as the efficient co-catalyst for H_2 evolution. On the other hand, the concentration of Cd^{2+} leached into the solutions was found insignificant. The hydrogen evolution rates obtained at different wavelengths are shown in Table 4-1. It can be seen that our photocatalyst can still provide good photocatalytic activities at the wavelength greater than 475 nm with a H_2 evolution rate of 1.28 mmol h^{-1} .

Table 4-1 Photocatalytic activities of NiS(1.2mol%)/CdS with the reaction conducted using cut-off filters at different wavelengths

Cut-off wavelength (nm)	Hydrogen evolution rate (mmol/h)
400	2.56
420	2.18
455	1.97
475	1.28

Figure 4-4 XPS results of the sample NiS(1.2 mol%)/CdS. (a) Ni 2p, and (b) S 2p.

Figure 4-5 (a) HAADF-STEM image of NiS(1.2mol%)/CdS, (b) the corresponding EDX results of the sample area shown in (a), and (c) EDX scan results of Cd, Ni and S along the line indicated in (a).

Similar to the mechanism of cathodic H_2 evolution reactions (HER) in electrolysis, it is proposed that the NiS co-catalyst in our photocatalysts plays important roles in electron transfer (Reaction 4-1) and electrochemical desorption (Reaction 4-2) for H_2 evolution.¹¹⁵

Figure 4-6 Photocatalytic activities of NiS/CdS photocatalysts with different NiS contents loaded at 140 °C. Reaction condition: 0.3 g catalyst in 100 mL of 30 vol% lactic acid aqueous solution, 300 W Xenon lamp with a cut-off filter, $\lambda > 420$ nm.

Figure 4-7 The amount H₂ evolved on NiS(1.2mol%)/CdS in 12 h of continuous reaction.

The photogenerated electrons in the conduction band of CdS can be easily transferred to the surface NiS nanoparticles due to the intimate contact between the two phases. The formation of the hydride on NiS catalysts was well reported both experimentally and computationally in hydrotreating processes.¹¹⁹⁻¹²² Lactic acid in the reaction mixture served as the sacrificial electron donor. The H₂ generation scheme is illustrated in Figure 4-8.

Figure 4-8 H₂ generation scheme and band position alignment from the NiS/CdS photocatalyst in a lactic acid sacrificial solution under visible light.

In addition, the solution was maintained acidic due to the presence of lactic acid. The pH before and after reaction was measured to be 1.85 and 1.90, respectively. Thus both forward reactions in Reactions (4-2) and (4-3) are favoured under such conditions. ESIMS analysis of the solution after 24 h (Figure 4-9) showed that the only product in the solution was pyruvic acid with *m/z* signal at 87 (lactic acid signal is at 89). The ATR result (Figure 4-10) indicated that there was no noticeable change in the concentration of –COOH group in the solution before and after reaction. These results suggest that the oxidation of lactic acid to pyruvic acid is the only pathway for consumption of photogenerated holes from the photocatalyst in the current system. When the photoreaction was conducted in the presence of the frequently used Na₂SO₃ and Na₂S pair as the sacrificial reagents while keeping other conditions the same, the activity of the photocatalyst was much lower (Figure 4-11, the topmost bar). This should be due to a basic medium (pH at 12.0 caused by Na₂SO₃ and Na₂S electrolytes) which suppresses the forward reactions. The more detailed mechanism study is underway.

Pt is regarded as an efficient co-catalyst for CdS because of its high work function and high redox potential.³⁶ However, the Pt(1wt%)/CdS photocatalyst can only produce 0.4 mmol H₂ per hour under the same reaction conditions in this work. We also studied other transition metal sulfides that can provide similar d orbitals as NiS. As shown in Figure 4-11, loading of a proper amount of CoS can increase the activity of CdS by about 5 times, while CuS and Ag₂S both deactivated CdS (data not shown).

To ensure that the H₂ is from water, while not from lactic acid, photocatalytic reaction was also conducted in D₂O dissolved with lactic acid anhydrous crystals. Helium gas was used as GC carrier to distinguish H₂ and D₂ gases, since their thermal conductivities obey the relation: H₂ > He > D₂.^{18,123} In Figure 4-12, the negative GC signal confirmed the generation of D₂ gas. And the D₂ evolution rate (~2.2 mmol/h for first 4 hours) was almost the same as that for H₂ when reaction was conducted in H₂O solution with other conditions remained the same. Hence it is clear that the H₂ evolved is from the splitting of water in this system, and lactic acid acts just as sacrificial reagent.

Figure 4-9 ESI-MS spectra of (A) the standard solution prepared from lactic acid and pyruvic acid with a mole ratio of 13.6:1 (this ratio was calculated based on the amount of hydrogen produced at 24 h and assuming that all photogenerated holes reacted with lactic acid to pyruvic acid), (B) the reaction solution at 24 h of photocatalytic reaction. The signals with m/z at 89 and 87 are assigned to lactic acid and pyruvic acid, respectively.

Figure 4-10 The ATR spectra of solutions before and after 24 h of photocatalytic reaction.

Figure 4-11 Activity comparison of different photocatalysts. NiS/CdS**: reaction was conducted in Na₂S (0.25 M) and Na₂SO₃ (0.35 M) solution, and NiS + CdS*: physical mixture of CdS and NiS.

Finally, the effect of the loading temperature of NiS nanoparticles was studied. The same amount of nickel acetate was used for the hydrothermal reaction to obtain these NiS/CdS photocatalysts for comparison. The actual NiS concentrations for NiS/CdS samples loaded at 140, 160, 180 and 200 °C varied a little from 1.2 to 1.66 mol%. While due to a much slower thiourea decomposition rate, the NiS/CdS loaded at 120 °C had a lower NiS concentration at 0.57 mol%. Longer hydrothermal reaction time (24 h) at 120 °C led to a slightly higher NiS surface concentration (0.63 mol%) but a decreased activity. This is possibly due to the NiS aggregation under long duration of hydrothermal environment, as poor dispersion of Ni can be observed in Figure 4-13 (B) for the elemental mapping. As shown in Figure 4-14, samples with NiS loaded at 120, 140 and 160 °C had similar photocatalytic activities and all provided a H₂ evolution rate of more than 2 mmol h⁻¹. Higher loading temperatures of 180 and 200 °C resulted in poorer photocatalytic performance. The H₂ evolution rate was reduced to 1.4 and 1.2 mmol h⁻¹, respectively. Similarly, higher hydrothermal temperature will bring a faster NiS formation rate, and thus cause a poorer dispersion on CdS surface. As shown in the elemental mapping, the Ni dispersion from sample under 200 °C (Figure 4-13, D) is much worse than that from sample under 140 °C (Figure 4-13, C).

Figure 4-12 (A) GC signals obtained using He (instead of Ar) as the carrier gas. (a) H₂ peak when reaction was carried out in H₂O, and (b) D₂ peak when the reaction was carried out in D₂O dissolved with lactic acid anhydrous solids. Catalyst: NiS(1.2mol%)/CdS, other reaction conditions were kept the same as that described in Experimental details. (B) D₂ evolution rate on NiS(1.2mol%)/CdS. The calibration was done using D₂ gas and a linear equation was obtained with R² close to 1.0.

Figure 4-13 Energy filtered TEM elemental mapping images of Cd (in orange) and Ni (in green) from samples synthesized hydrothermally at (A) 120 °C, 4h, (B) 120 °C, 24h, (C) 140 °C, 4h, and (D) 200 °C, 4h.

Figure 4-14 Effect of the loading temperature of NiS on photocatalytic activities.

4.4 Conclusions

In conclusion, the hydrothermally loaded NiS was found as a highly efficient and low-cost co-catalyst on CdS surface for photocatalytic H₂ evolution from an aqueous solution containing lactic acid under visible light. The conventional activation treatment such as thermal oxidation and photo-reduction is not required. The QE of 51.3% obtained on the optimized NiS/CdS photocatalyst at 420 nm is the highest so far reported for photocatalysts without noble metal co-catalysts. NiS co-catalyst developed in this work inspired us to explore Ni-sulfur complexes as the catalyst in homogeneous photocatalytic H₂ production molecular systems, which is detailed in the next chapter.

Chapter V Novel Low-cost Molecular Systems for Photocatalytic H₂ Evolution from Water under Visible Light

5.1 Background Introduction

Photocatalytic hydrogen production from water using sunlight can mainly be realized through semiconductor photocatalyst system¹ and photosensitizer (PS) molecular system.¹²⁻²³ Comparing to the former heterogeneous system, the latter molecular system usually provides homogeneous reaction environment towards optimal availability of active catalytic sites. In recent decades, H₂ production molecular systems have been developed in a few research groups from the inspiration of natural photosynthesis.

As shown in our earlier chapter, a highly active NiS/CdS photocatalyst in heterogeneous H₂ evolution from sacrificial solution has been developed. NiS and CoS were found capable of replacing Pt in the well-known Pt/CdS semiconductor photocatalyst. This phenomenon inspired us towards employing these low cost transition metal sulfides or metal-sulfur complexes in molecular systems as catalysts for H₂ production. Herein, a variety of noble-metal-free molecular systems consisting of xanthene dyes as PSs and Ni²⁺ (or Co²⁺) coordinating to small sulfur-containing organic chemicals as catalysts is evaluated in this chapter. The photocatalytic reactions were conducted in TEOA aqueous solutions without adding toxic solvents such as acetonitrile, which was commonly used in molecular H₂ production systems as solvent for better dissolution of both PSs and catalysts.^{20,23}

5.2 Experimental Sections

5.2.1 Chemicals Used in the Experiments

All the chemicals used are analytical grade without further purification: Erythrosin B, Erythrosin Yellowish, Rose Bengal, Eosin Y and Fluorescein are all from Alfa Aesar; Nickel Acetate (>99%, Alfa Aesar); Cobalt Nitrate (> 97%, Fluka Chemika); 2-Mercaptoethanol (>98%, Alfa Aesar); Mercaptoacetic Acid (>97%, Alfa Aesar); Thiourea (99%, Alfa Aesar); Triethanolamine (>99%, Acros Organics); Nitric Acid (69%, Honeywell); Hydrogen Hexachloroplatinate (40% Pt, Acros Organics); D₂O (99.9 atom% D, Aldrich).

5.2.2 Characterization

The UV-vis and XPS characterizations are similar to those described in Section 2.2.3. The TEM analysis is the same as described in Section 3.2.2. The ESI-MS analysis of the dye molecules and Ni-ME complex is similar as described in Section 4.2.2. Cyclic voltammetry experiments were performed on CHI 660D electrochemical station under a three-electrode cell system consisting of a glassy carbon working electrode, a Pt wire counter electrode and a saturated calomel reference electrode. Ni-ME complex in the solution was formed by adding 30 mM of nickel(II) acetate and 60 mM of ME in water. All measurements were carried out in aqueous solutions after purging of nitrogen thoroughly. The scan started at reduction with a rate of 100 mV/s for all measurements. All redox potentials are reported versus SCE.

5.2.3 Photocatalytic Activity Measurement

In a typical reaction, certain amounts of nickel acetate, 2-mercaptoethanol and Erythrosine B were added in sequence into a 100 mL of aqueous solution containing 15 vol% of TEOA under vigorous stirring. The pH value of TEOA solution had been previously adjusted to 8.5 using concentrated HNO₃. Different longpass filters ($\lambda \geq 420, 455, 475, 500$ nm) and bandpass filters (centered at 420, 460, 530, 550 nm) were equipped when conducting reactions under irradiation of different wavelengths and

collecting QE results, respectively. The reaction solutions were irradiated under $\lambda \geq 420$ nm for 1 h before switching to bandpass filters for QE tests about the H_2 production in the following first 5 h.

5.3 Results and Discussions

The photocatalytic H_2 production reactions were performed in 100 mL of 15 vol% TEOA aqueous solutions with pH = 8.5 (adjusted by concentrated HNO_3). Figure 5-1 shows the H_2 evolution rates against the reaction time from molecular systems containing different xanthene dyes (2.25 mM), $Ni(Ac)_2$ (3mM) and 2-mercaptoethanol (30 mM) under visible light irradiation ($\lambda \geq 420$ nm). The dye content, catalyst amount, nickel to sulfur ratio and the TEOA concentration together with pH have been optimized in a systematic way, as shown in Figure 5-2. The structure and UV-Vis DRS of all the examined xanthene dyes can be referred in Figure 5-3 and 5-4. Among those dyes with differences in halogen elements bonding to the xanthene ring, Erythrosin B (EB) outperforms the others in activity. The EB system can efficiently generate around 10 mmol of H_2 gas in the first 12 h irradiation. Major slowdown happened after 16 h of reaction and the total amount of H_2 produced in 24 h is 12.1 mmol. Rose Bengal with 4 more chlorine substitutions compared to EB showed only half the activity of EB. Compared to EB, Erythrosin Yellowish has two less iodine substitution which brings a slightly lower overall activity and a more rapid activity cessation after 16 h reaction. Meanwhile, lowered activity can be observed by replacing the iodines to bromines on the xanthene ring when comparing EB to Eosin Y. Different halogenations affect the ground and excited states of xanthene dyes resulting in harvesting photons with different wavelengths. The halogen-free Fluorescein exhibits a much lower H_2 evolution rate compared to other xanthene dyes examined. This is consistent with some theoretical studies indicating that heavy I and Br atoms can facilitate the formation of triplet states of xanthene dyes from their excited singlet states through intersystem crossing.¹²⁵ Based on the spin conservation rule (Wigner Rule), the photosensitizer in its long-lived excited triplet state can

sensitize the catalyst towards forming its own long-lived excited triplet state, and thus enhance the photocatalytic activity due to the longevity of the triplet excited state.

Figure 5-1 H₂ evolution rates against reaction time from molecular systems containing different xanthene dyes (2.25 mM), Ni(Ac)₂ (3mM) and 2-Mercaptoethanol (30 mM) in 100 mL 15 vol% TEOA aqueous solutions (pH = 8.5), 300 W Xenon lamp with filter, $\lambda \geq 420$ nm.

Figure 5-5 shows the H₂ evolution rates on molecular systems containing EB as PS, Ni²⁺ or Co²⁺ with different sulfur-containing capping reagents (ME: SHCH₂CH₂OH; MA: SHCH₂COOH; TU: NH₂CSNH₂) as catalysts. Ni-ME complex is found to be the best combination as the catalyst for H₂ production when EB is the PS. In an overall comparison, Ni-S complexes have better activities than Co-S complexes for H₂ production. Typically, Ni-ME is 4 times better than Co-ME in H₂ production ability. Unlike the homogeneous Ni-ME complex in the reaction solution, Co²⁺ can

easily form solids with ME, and thus decreases its accessibility to the PS during reaction. Among Ni-S complexes, ME is the best capping reagent for Ni^{2+} for H_2 production performing almost 3 times better than MA. ME is widely used in the synthesis of water-soluble ZnS nanoparticles for its excellent capping ability,¹²⁶ while excess amount of MA can precipitate Ni^{2+} easily in aqueous solutions. Within these combinations examined, Ni^{2+} capped with ME homogeneously in solution is shown to be an efficient catalyst for generating H_2 with EB as the PS.

Figure 5-2 H_2 evolution results in 24 h irradiation under $\lambda \geq 420$ nm. (a) 3mM of Ni^{2+} , 30mM of ME and different amount of EB; (b) 2.25mM of EB and different amount of Ni-ME (Ni to S ratio in the solutions was fixed at 1:10.); (c) 2.25mM of EB, 3mM of Ni^{2+} and different amount of ME (Ni to S ratio in the solutions varies from 1:8, 1:10 to 1:12.).

Figure 5-3 Molecular structures of xanthene dyes investigated.

Figure 5-4 UV-Vis DRS of xanthene dyes (50 $\mu\text{mol/L}$ in water) investigated.

Under different frequency ranges of the visible light, the EB-Ni-ME molecular system can generate H_2 efficiently even under photons with wavelength longer than 500 nm (Figure 5-6). The QEs for this system at different wavelengths were collected and displayed in Figure 5-7. The highest QE of 24.5% was obtained at 460 nm, which is shorter than the wavelengths of photons from the highest absorption position of the PS in the visible light range. To best of our knowledge, the QEs at visible light range from 450 to 550 nm are among the highest reported for all the photocatalytic H_2 production molecular systems.

Figure 5-5 H₂ evolution rates from molecular systems containing Erythrosin B (2.25 mM), Ni²⁺ or Co²⁺ (3mM) with different sulfur capping reagents (30 mM). ME: SHCH₂CH₂OH; MA: SHCH₂COOH; TU: NH₂CSNH₂

Figure 5-6 H₂ evolution results in 24 h irradiation under photons with different wavelengths in EB-Ni-ME molecular system.

To further demonstrate the advantages of the EB-Ni-ME molecular system, solution containing the same amount of EB and 1 mM of Pt (Pt concentration has been optimized in this system towards the highest H₂ evolution rate.) was irradiated for H₂ generation for comparison. Pt is widely considered as an efficient component not only as co-catalyst on heterogeneous semiconductor photocatalyst but also as catalyst in molecular systems.^{15,19,74,75} The plots shown in Figure 5-8 suggest that the overall H₂ production is 4 times better when Ni-ME is used as catalyst comparing to Pt catalyst. In Pt system, the PS degrades rapidly, and after 4 h of irradiation the activity is almost lost. This is due to the poor stability of dye molecules in the Pt system as demonstrated in the analysis of the reaction solutions by UV-vis DRS as shown in

Figure 5-9. The dye concentration in Ni-ME system after 24 h reaction is still much higher than that in Pt system with only 6 h reaction. The halogen to carbon bond can be broken easily thus leading to the photodecomposition of the PS under light irradiation. The strong absorption ability of Ni-ME complex at the peak absorption range of the PS (460 to 560 nm) can not only quench the excited electrons in the PS efficiently, but also can function as a natural filter partially avoiding the PS to be exposed under strong irradiation. Thus the self-oxidation of the dyes during reactions can be retarded leading to more stable PS. The difference in UV absorption between Ni-ME catalyst and Pt catalyst are shown in Figure 5-10. With the same concentrations as those used for the H₂ evolution reactions, Pt complex exhibits much poorer absorption than Ni-ME complex in the visible light range.

Figure 5-7 The H₂ evolution QEs of EB-Ni-ME molecular system under photons with different wavelengths. (300 W Xenon lamp with different bandpass filters centered at 420, 460, 530 and 550 nm.)

Figure 5-8 H₂ evolution comparison between Ni (3 mM) - ME (30 mM) catalyst and Pt (1 mM) catalyst in TEOA solutions containing 2.25 mM EB.

Furthermore, to exclude any possibility that the H₂ is from the sacrificial reagent or the decomposition of the PS/catalyst, reaction in a D₂O solution was conducted based on similar procedures presented in the previous chapter. The negative signal of D₂ in helium gas carrier and nearly the same amount of gas as H₂ from H₂O generated in 24 h of reaction confirm that the only hydrogen source in the generated H₂ gas is water.

Figure 5-9 Real time analysis of the UV-vis spectra of the reaction solutions (centrifuged, filtered and diluted by 20 times after certain hours of reaction.) (a) Ni-ME as catalyst. UV-vis DRS peaks of EB at 0h, 0.5h, 1h, 2h, 4h, 8h, 16h and 24h reaction. (peak position at around 520nm shifts from right to left.); (b) Pt as catalyst. UV-vis DRS peaks of EB at 0h, 1h, 2h, 4h, 6h reaction (peak position at around 520nm shifts from right to left.).

Figure 5-10 UV-vis DRS of Ni-ME complex (3 mM Ni^{2+} and 30 mM ME), H_2PtCl_6 (1 mM) and Erythrosin B (50 ppm) in 15 vol% TEOA solution. (15 vol% TEOA as reference.)

Our Ni-ME complex has also been shown as an efficient electrocatalyst for the reduction of protons to molecular hydrogen based on the cyclic voltammetric study. As shown in Figure 5-11A, similar to other Ni-complexes,^{127,128} the Ni-ME complex displays an irreversible reduction wave at around -0.69 V (vs SCE) which should be associated with the reduction of Ni(II) to the reactive Ni(I) center. After adding acetic acid (HAc) to the solution, the current was greatly enhanced and the electrocatalytic proton reduction potential was shifted slightly more negative to -0.73 V. Similar observations were reported by other groups for transition metal complexes of nickel and iron.¹²⁷⁻¹²⁹ The oxidation and reduction potentials of EB obtained by the cyclic voltammetric studies are $+0.88$ V and -1.05 V, respectively. The reduction potential of TEOA was measured to be -0.55 V. By comparing these redox potentials, it is suggested that an oxidative quenching pathway of the photosensitized EB by TEOA is supported. Without the presence of electron relay, the charge and energy transfer from

photosensitizer to catalyst will happen when molecular collision happened between the two. As in our case, the photosensitizer is negatively charged and the Ni-ME complex is positively charged, the attractive force between opposite charges will facilitate their contact for the electron transfer. To directly perceive the H₂ production mechanism, a reaction scheme of the EB-Ni-ME molecular system for photocatalytic H₂ production in TEOA sacrificial solution is proposed and illustrated in Figure 5-11B. EB is supposed to absorb specific visible light efficiently forming long-lived triplet excited state, and subsequently photon emission from the EB can sensitize the Ni-ME complex towards forming its excited triplet state for the H⁺ reduction. Meanwhile, during the energy transfer, an electron is immigrated from EB to Ni complex leaving EB⁺. With ligand containing S (high energy lone electron pairs) and Ni²⁺ metal center (4s⁰ empty orbital), Ni-ME complex is believed to be a typical ligand to metal charge transfer (LMCT) type complex. After the energy and the electron transfer from the sensitized EB, negative charges from sulfur can be transferred to the nickel core resulting in the reduction of the Ni(II) to Ni(I). Reductive nickel center plays the final role in electron transfer to H⁺ for H₂ production. In the whole scheme, H⁺ obtains the electron from the reductive nickel. The oxidized EB⁺ is then quenched by TEOA which functions as the electron donor in the whole reaction scheme.

Figure 5-11 (A) Cyclic voltammogram of Ni-ME complex formed between nickel(II) acetate (30 mM) and ME (60 mM) in water; a glassy carbon working electrode; scan rate at 100 mV/s. (B) Proposed reaction scheme of the photocatalytic hydrogen production over the EB-Ni-ME molecular system.

Several reports can be found from the literature dealing with the structures of the complexes between Ni(II) and primary thiolates.¹³⁰⁻¹³⁴ De Brabander et al. proposed a linear “core + link” polymeric complex between Ni(II) and ME in dilute aqueous solutions based on a titration method.¹³⁰ On the other hand, Gould and Harding precipitated the crystal from alkaline solution of concentrated Ni(II) and ME. Their X-ray diffraction data indicated a cyclic hexameric complex with six Ni(II) ions forming a planar ring and the Ni(II) centers bridged by twelve ME groups.¹³¹ A few other groups also proposed the hexagon structure between Ni(II) and ME or other thiolate.¹³²⁻¹³⁴ In order to determine the structure of Ni-ME complex formed in our work and to investigate the influence of TEOA, UV-vis absorption and electrospray ionization-mass spectrometry (ESI-MS) analyses were carried out. Figure 5-12 shows the UV-vis absorption spectra of Ni-ME complex in DI water (pH=8.5, adjusted by NaOH) and TEOA (pH=8.5). In both cases, four characteristic charge transfer bands can be observed at nearly the same wavelength of 258, 330, 408 and 525 nm, indicating that TEOA does not affect coordination between Ni(II) and ME ligand. Nevertheless, the absorption intensities of Ni-ME in TEOA solution were slightly lower than those in DI water. We further diluted both solutions and compared their absorption intensities as shown in Figure 5-13 and Table 5-1. The concentration of

Ni-ME complex in TEOA solution was estimated to be around 90% of that in DI water when $[\text{Ni}^{2+}]$ was in the range of 0.3-1.0 mM (Table 5-2). To elucidate the structure of Ni-ME complex and understand why the UV-vis absorption intensity of Ni-ME in TEOA is lower than that in water, positive ion electrospray ionization-mass spectrometry (ESI-MS) analysis was carried out for the following mixtures and the MS spectra are shown in Figure 5-14: A) Ni-ME in water (pH adjusted to 8.5 by NaOH), dark brown color; B) Nickel acetate in TEOA solution (pH = 8.5), colorless; C) Ni-ME in TEOA solution (pH adjusted to 8.5 by NaOH), dark brown color. It was found that the Ni-ME complex formed in DI water has a formula of $[\text{Ni}(\text{SCH}_2\text{CH}_2\text{OH})_2]_6$ (Figure 5-14A and Table 5-3). The results from Experiments 1-3 as shown in Table 5-3 indicate that acetate is not involved in the formation of Ni-ME complex. The difference in m/z value (16) from 1 and 4 in Table 5-3 coincides with the difference in the atomic weight of Na and K. Hence it is suggested that Na^+ or K^+ is associated with the complex. Based on the above results, the Ni-ME complex in System A is $[\text{Ni}(\text{ME})_2]_6\text{Na}^+$ ($m/z = 1298.06$). The signal at 1220 shall correspond to the complex with one ME (M.W. = 78) less, which could be most likely due to fragmentation of the complex under the harsh condition of ESI-MS. The MS spectrum of nickel acetate in TEOA solution shows a dominant peak at 823 (Figure 5-14B) which shall correspond to the colorless tetramer formed between Ni(II) and TEOA. Finally, the spectrum of Ni-ME in TEOA solution suggests the presence of both Ni-ME ($m/z = 1298$) and the tetramer Ni-TEOA ($m/x = 823$) complexes (Figure 5-14C). In addition, a peak at 1448 was observed, which can be assigned to Ni-ME associated with one TEOA ($1448-1298 = 150$, M.W. of TEOA = 149). Although the peak of Ni-TEOA complex (823) is rather strong compared to those of Ni-ME complexes, such results are not reliable for quantitative analysis due to i) ESI process may not be efficient to produce charged ions for all complexes, and ii) fragmentation of molecules is another issue under the harsh environment of ESI. Combining our quantitative UV-vis and qualitative MS results, it can be concluded that the presence of TEOA does not affect the structure of Ni-ME complex, although TEOA can partially associate with Ni-ME complex. Nevertheless, TEOA does compete with ME

to form the colorless tetramer with Ni(II). This complex is not active since in our control experiment in the absence of ME, no hydrogen was produced. As mentioned above based on the UV data, it could be estimated that about 10% of Ni(II) forms complex with TEOA, and 90% of Ni(II) remains in the complex with ME as $[\text{Ni}(\text{SCH}_2\text{CH}_2\text{OH})_2]_6$. Based on the above results and literatures,¹³⁰⁻¹³⁴ it is proposed that Ni-ME complex formed in TEOA solution adopts a cyclic structure (Figure 5-15A), although we could not exclude the possibility of a liner structure (Figure 5-15B). TEOA can also coordinate with Ni(II) but does not affect the coordination between Ni(II) and ME.

Figure 5-12 UV-vis DRS of Ni-ME complex in DI water (solid line, pH was adjusted to 8.5 using NaOH) and 5 vol% TEOA solution (dashed line, pH = 8.5). In both solutions, $[\text{Ni}^{2+}] = 1 \text{ mM}$, Ni:ME = 1:10. DI water and 5 vol% TEOA solution were used as references, respectively. Compared to the reaction condition ($[\text{Ni}^{2+}] = 3 \text{ mM}$, Ni:ME = 1:10, 15 vol% TEOA), the solution was 3 times diluted in order to avoid the oversaturation of the UV absorption peaks.

Figure 5-13. UV-vis spectra of Ni-ME complex in DI water (A) and in TEOA solution (B). Concentration of Ni^{2+} along the direction of arrow in both spectra: 1.0, 0.7, 0.5, 0.3, 0.1 mM.

Table 5-1 UV-vis absorption intensities of Ni-ME complex in DI water and TEOA solution with different Ni^{2+} concentrations (see Figure 5-13).

Solution		DI water				TEOA solution			
Peak Position		258 nm	330 nm	408 nm	525 nm	258 nm	330 nm	408 nm	525 nm
Ni Concentration (mM)	1	3.503	3.423	1.291	0.428	3.108	3.026	1.261	0.386
	0.7	2.751	2.472	0.93	0.306	2.402	2.14	0.894	0.272
	0.5	2.003	1.775	0.624	0.214	1.774	1.566	0.626	0.192
	0.3	1.172	1.078	0.372	0.128	1.111	0.969	0.38	0.115
	0.1	0.308	0.299	0.102	0.034	0.35	0.293	0.114	0.035

Table 5-2 The percentages of Ni-ME complex concentration in TEOA solutions against those in DI water at the same Ni^{2+} concentration.

Nickel Concentration (mM)	[Ni-ME] in TEOA/[Ni-ME] in DI H_2O *
1.0	87.1%
0.7	87.9%
0.5	89.9%
0.3	92.4%
0.1	82.1%

*A calibration line was obtained based on the absorption intensities at 330 nm of Ni-ME prepared in DI H_2O . The absorption intensities at 330 nm were used for calculation.

Figure 5-14A ESI-MS spectrum of Ni-ME in water (pH adjusted to 8.5 by NaOH).

Table 5-3 Positive ion ESI-MS signals of Ni-ME complex prepared from different nickel sources in NaOH aqueous solution (pH=8.5), $\text{Ni}^{2+}:\text{ME} = 1:10$, $[\text{Ni}^{2+}] = 3 \text{ mM}$.

Experiment	Nickel source	ESI-MS signal of the complex (m/z)
1	$\text{Ni}(\text{Ac})_2$	1220.11, 1298.06
2	$\text{Ni}(\text{NO}_3)_2$	1220.09, 1298.04
3	NiCl_2	1220.23, 1297.78
4	$\text{Ni}(\text{Ac})_2$ (KOH for pH adjust)	1237.09, 1314.01

(Atomic weight of H: 1.01, C: 12.01, O: 16.00, Na: 22.99, S: 32.06, Ni: 58.69)

Figure 5-14B ESI-MS spectrum of nickel acetate in TEOA solution (pH = 8.5).

Figure 5-14C ESI-MS spectrum of Ni-ME in TEOA solution (pH adjusted to 8.5 by NaOH).

Figure 5-15 Proposed structure of cyclic hexameric Ni-ME complex (A) in aqueous TEOA solution, and the possibility of a linear structure (B) cannot be completely excluded. Based on MS results, TEOA can be associated with the complex as shown in (B).

5.4 Conclusions

In summary, a variety of noble-metal-free molecular systems consisting of xanthene dyes and Ni^{2+} (or Co^{2+}) coordinating to small sulfur-containing organic chemicals as catalysts have been developed and analyzed for the photocatalytic H_2 production. This work provides significant contribution towards the finding of low-cost H_2 production molecular systems and insights towards the mechanistic understanding. Among the systems investigated, the EB-Ni-ME molecular system is found to be the best combination for photocatalytic H_2 production with outstanding QEs obtained in visible light range.

Chapter VI Conclusions and Outlook

6.1 Conclusions

The photocatalytic splitting of water driven by solar energy represents one of the most attractive processes to solve the global energy problem. To contribute to this great project, several successful photocatalytic systems towards H_2 evolution from water have been developed and evaluated in this thesis work systematically.

Firstly, a series of solid solutions between $Zn_{0.95}Cu_{0.05}S$ and CdS were synthesized. The band structures of these semiconductors have been well controlled to optimize their photocatalytic activities for visible light driven H_2 evolution from aqueous solutions of sulfide and sulfite. In addition, it was found that the surface ion exchange with Cu^{2+} from the $(Zn_{0.95}Cu_{0.05})_{1-x}Cd_xS$ ternary metal sulfide slightly improved the activity. Following this, a series of $CuS(y)-Zn_xCd_{1-x}S$ nanospheres with a Zn and Cu-rich surface were synthesized via a one-step method. The activity of the $Zn_{0.65}Cd_{0.35}S$ sample can be enhanced by around 20 after adding of Cu during the synthesis to form a Cu-rich surface. Subsequently, the hydrothermally loaded NiS was found as a highly efficient and low-cost co-catalyst on CdS surface for photocatalytic H_2 evolution from an aqueous solution containing lactic acid under visible light. The QE of 51.3% obtained on the optimized NiS/ CdS photocatalyst at 420 nm is the highest so far reported for photocatalysts without noble metal co-catalysts. NiS as a low-cost co-catalyst on CdS surface is proved highly efficient in H_2 production from lactic acid sacrificial solution, which is a great progress for developing economical photocatalytic systems. NiS as a co-catalyst on the surface of CdS inspired the application of Ni-Sulfur complexes as catalyst in homogeneous photocatalytic H_2 production molecular systems, which was also introduced in this thesis.

Subsequently, a variety of noble-metal-free molecular systems consist of xanthene dyes and Ni^{2+} (or Co^{2+}) coordinating to small sulfur-containing organic chemicals as catalysts have been developed and analyzed for the photocatalytic H_2 production. Among those systems employed, the EB-Ni-ME molecular system was found to be the best combination for photocatalytic H_2 production with outstanding QE in visible light range. This work provided significant supplements towards the finding of low-cost H_2 production molecular systems and insights towards the reaction scheme understanding.

6.2 Outlook

Aiming to solve the global energy problem, the photocatalytic H_2 production must be efficiently and economically acceptable for industrial application. Thus the developing of highly active and low cost photocatalytic systems will be the focus for any researchers in this project. Several research directions are suggested and elaborated in the following sections. .

6.2.1 Bulk to Surface Element Distribution Control

Zn-Cd binary sulfides with core-shell structures have been reported with special optical properties different from their solid solution counterparts. Thus the element distribution of the Zn-Cd-Cu sulfide ternary system will be worth studying, and their catalytic performance can be possibly controlled by adjusting the element distribution in the solid solution. Furthermore, doping of foreign elements like Cu, Ni, and Mn at controlled locations and concentrations could be another strategy to enhance the photocatalytic performance.

6.2.2 P-N Junction Scheme Design

Efficient charge separation is considered as one of the most important factors towards achieving improvement in photocatalyst activity since charge recombination affects

the efficiency largely. A p-n junction scheme for efficient charge separation in heterogeneous photocatalysts can be proposed. In p-type semiconductors, positively charged holes are the main charge carrier as they have a better mobility in the lattice and the same applies for electrons in n-type semiconductors. If a p-type semiconductor can be combined with n-type semiconductor with proper band positions shown in Figure 6-1 to form a p-n junction on the interface, the photo excited electrons can become more stable when they transfer to the n-type semiconductor, and at the same time holes will be enriched in the p-type semiconductor. Thus charges can be separated efficiently and the p- and n-semiconductors act as the different reaction sites for the two half reactions of water, which can avoid the back reaction between hydrogen and oxygen.

Figure 6-1 P-n junction scheme for the design of water splitting catalysts.

Besides forming the heterojunctions between two semiconductors, it is also possible to design charge junctions between dye molecules and semiconductors for efficient charge separation. For example, a system combining certain xanthene dye and NiS/CdS could be investigated in more details.

6.2.3 Develop Overall Water Splitting Systems

Besides systems producing H_2 in the presence of electron donors, overall water splitting to produce H_2 and O_2 using solar energy represents a more sustainable process. Instead of developing new efficient overall water splitting systems, it will be more promising to design a Z-scheme between the H_2 evolution systems developed in this thesis with other efficient O_2 generation systems.

It is expected that with continuous research efforts from the scientific communities around the world, photocatalytic H_2 production will reach satisfactory efficiencies for practical applications to meet our future energy needs.

Publications Related to This Thesis

Journal Papers

- (1) **Zhang, W.**, Zhong, Z. Y., Wang, Y. S. and Xu, R.*, Doped Solid Solution: $(\text{Zn}_{0.95}\text{Cu}_{0.05})_{1-x}\text{Cd}_x\text{S}$ Nanocrystals with High Activity for H_2 Evolution from Aqueous Solutions under Visible Light, Journal of Physical Chemistry C, 112, 17635-17642, 2008.
- (2) **Zhang, W.**, and Xu, R.*, Surface Engineered Active Photocatalysts without Noble Metals: $\text{CuS-Zn}_x\text{Cd}_{1-x}\text{S}$ Nanospheres by One-Step Synthesis. International Journal of Hydrogen Energy, 34, 8495-8503, 2009.
- (3) **Zhang, W.**, Wang, Y. B., Wang, Z., Zhong, Z. Y., and Xu, R.*, Highly Efficient and Noble Metal-Free NiS/CdS Photocatalysts for Hydrogen Evolution from Lactic Acid Sacrificial Solution under Visible Light, Chemical Communications, 46, 7631-7633, 2010.
- (4) **Zhang, W.**, Hong, J. D., Zheng, J. W., Huang, Z. Y., Zhou, J. R., and Xu, R.*, Nickel-Thiolate Complex Catalyst Assembled in One Step in Water for Solar H_2 Production, Journal of American Chemical Society, DOI: 10.1021/ja208555h.

Conference

- (1) Wang, Y. B., **Zhang, W.**, and Xu, R. Synthesis of Uniform Zn-Cu-Cd Sulfide Nanospheres and Their Photocatalytic Activity Evaluation Under Visible Light, The International Symposium on Advanced Bio, Nano, and Pharmaceutical Science and Technology, May, 2009, China.
- (2) **Zhang, W.**, Wang, Y. B. and Xu, R. Development of Efficient Photocatalysts for H_2 Production from Water Using Visible Light, 16th Regional Symposium on Chemical Engineering, Dec. 2009, Philippines.
- (3) **Zhang, W.**, Xu, R. Highly Efficient and Noble Metal-Free NiS/CdS Photocatalysts for H_2 Evolution from Water under Visible Light, 17th Regional Symposium on Chemical Engineering, Nov. 2010, Thailand

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