RATIONAL DESIGN AND PREPARATION OF COMPOSITE NANOSTRUCTURES FOR SOLAR WATER SPLITTING

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RATIONAL DESIGN AND PREPARATION OF COMPOSITE NANOSTRUCTURES FOR SOLAR WATER SPLITTING

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ABSTRACT

Artificial photosynthesis, i.e. solar water splitting, has been recognized as a green and promising way to produce clean energy fuel, hydrogen, and solve the fossil fuel shortage problem. My PhD study explores the strategies of improving the efficiency of artificial photosynthesis, and my work mainly focuses on using cheap and abundant materials to design efficient composite photoelectrode and nano-photocatalyst via enhancing light absorption and charge separation.

In my first strategy, a novel design consisting of a sandwich structure of Fe$_2$O$_3$/Au/Fe$_2$O$_3$ was implemented and expected to work as an efficient photoanode for solar water splitting. Fe$_2$O$_3$ is a well-known cheap semiconductor which can utilize visible light energy. However, the efficiency is highly limited due to the poor charge separation. In the new design, the charge separation and photo-response are expected to be significantly improved by inserting one thin intermediate layer of Au within layers of Fe$_2$O$_3$ to form a tandem composite configuration. The SPR absorption from the intermediate Au layer and the resulted Plasmon-excitation induced electron transfer may enable wider light harvesting range and more efficient charge separation. All these may contribute to improve photocurrent response compared to Fe$_2$O$_3$ alone. The tandem layers were constructed by spin-coating of pre-synthesized Fe$_2$O$_3$ nanoparticles and sputtering of the gold intermediate layer. Tests on photo-current response proved that this sandwich structure exhibited much higher photoactivity efficiency as compared to the Fe$_2$O$_3$ photoanode. Mechanism studies on functions of Au intermediate layer well explained this enhancement. The results indicated that the Au intermediate layer was able to contribute in electron transfer as well as visible-light harvesting due to its plasmonic excitation. Such sandwich structure may be applied to other semiconductors to improve their performance in solar water splitting.
In my second strategy, the design on composite material is further explored from photo-electrode towards the powder form of photocatalyst. The strategy of creating nano-heterojunctions would introduce defect/impurity/interfacial states and promote charge separation at the interfaces leading to more efficient photocatalytic reactions. The hybrid nanostructures of ZnS and ZnO could be an ideal model system to explore such strategy. Similar to Fe$_2$O$_3$, ZnO and ZnS are also cheap and abundant materials. However, the wide band gaps of these two semiconductors highly limit their light absorption range within the UV light, and hence they can only utilize less than 4% of the total sun light energy. In order to extend the light absorption to visible light region, a composite photocatalyst in the form of ZnS-ZnO hybrid nanowires was designed and fabricated. It was hypothesized that many well-distributed nanoparticle-heterojunctions were formed within the nanowires and were able to induce high photo-activity for visible-light-driven H$_2$ evolution even without any noble metal co-catalysts. The ZnS-ZnO hybrid nanowires were synthesized through one-step hydrothermal reaction, and then characterized by multiple techniques, such as X-ray diffraction (XRD) measurement, UV–vis diffuse reflectance spectra (DRS), field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDS), and transmission electron microscopy (TEM). The characterization results confirmed the hypothesized nanowire structure and heterojunctions. The ZnS-ZnO hybrid nanowires exhibited active visible-light-driven H$_2$ evolution with a rate of 22 $\mu$mol h$^{-1}$ g$^{-1}$. Despite of the small amount of H$_2$ production, this result was still exciting, since bare ZnS or ZnO had zero H$_2$ evolution under visible-light illumination. The growth process of ZnS-ZnO hybrid nanowires was monitored and ZnS to ZnO molar ratio was manipulated to study the mechanism of the active visible-light photo-activity. The analysis suggested that there may be formation of enriched ZnS-surface-states on the ZnO nanocrystal surfaces and the population of ZnS-surface-states was crucial to the visible-light activity for photocatalytic H$_2$ evolution.
This work provided a meaningful way to develop heterostructured composites as visible-light-active photocatalysts by using wide band gap semiconductors for solar fuels production.

Both of the above two strategies in designing composite photoelectrode and nano-photocatalyst improved the electron transfer and light harvesting, and thus contribute to the efficiency improvement for solar water splitting. This work also provides alternative ways to fabricate composite photocatalytic materials for solar fuel production.
1 INTRODUCTION

1.1 Background

Recently, hydrogen gas has been discussed intensively as a promising clean energy with high energy capacity to meet the increasing energy demand in industry. However, current hydrogen sources, such as fossil fuels and biomass, will generate \( \text{CO}_2 \) in hydrogen production process and thus introducing greenhouse effects and environmental problems. In contrast, hydrogen production via solar splitting water is a clean process without evolving any greenhouse gas. In general, solar water splitting methods require solar light as an external energy to decompose water into hydrogen gas and oxygen gas in the present of photocatalyst.[1] Solar energy is well recognized as an inexhaustible natural resource. It is cheap, abundant and renewable, and thus makes it a realistic and applicable way to produce hydrogen fuel in industry.[2] At present, solar water splitting is considered to be a promising approach to accomplish clean hydrogen/oxygen production so as to meet the global energy demand in the future. And at the same time, it is also considered to be highly desirable to achieve effective solar energy harvesting, conversion and storage.[3]

Currently, semiconductors are the most commonly used photocatalyst for solar water splitting process. With proper band gap energy, semiconductors are able to absorb corresponding solar light energy, and convert this energy to be stored in a form of chemical fuels.[4] Fujishima and Honda reported the first solar water splitting construction involving \( \text{TiO}_2 \) in 1972.[5] They constructed photoelectrochemical cell setup with semiconductor electrodes to achieve electron separation and transfer, and this design was widely applied in solar water splitting thereafter, and named as photoelectrochemical cell (PEC) water splitting. The other approach of solar water splitting simplifies the setup and only involves
Introduction

Seminconductors in the form of powder or pellet in solution, and named as photocatalytic water splitting. Both approaches have advantages and challenges, and attract almost equal attention in this field.

Despite of the different forms of photocatalyst and setup, the basic methodology of the water splitting process is the same for both approaches. Upon absorbing the light energy, electrons within the semiconductors are excited from the valance band (VB) to the conduction band (CB), and then transferred to the surface to participate in water reduction.[6] Although the topic of solar water splitting has been studied for decades, improvement of the solar to hydrogen (STH) efficiency still faces many challenges.

Earth-abundant materials attract an increasing attention and are considered to be more desirable for affordable solar water splitting system. However, the best reported STH efficiencies among these low-cost materials are still below 6 %, far from the goal of 10 % to allow for commercialized production of hydrogen.[7] The first restraint on efficiency improvement comes from light harvesting.[8] Many materials have been intensively studied and applied as photocatalysts, however, most traditional materials are large-band-gap semiconductors.[9] The rationale behind this is to meet the proper CB and VB level for water reduction and oxidation. These large-band-gap semiconductors are only capable of absorbing UV light energy which is less than 4 % of the entire solar energy.[6,10] Therefore, full utilization of solar irradiation energy is extremely limited. Another restraint is the high charge recombination rate owing to inefficient charge separation and transport after electron excitation.[11] It is strongly correlated to many factors, such as particle size, defects, crystal structure, crystallinity and etc. Many efforts have been made to optimize these properties of photocatalysts, however, it cannot be easily achieved by modification of one type of material.
Therefore, it is realized that design and fabrication of photocatalyst is crucial to achieve a cost-effective, stable and efficient water splitting system.

1.2 Objective

This project aims to tackle the above challenges on light harvesting and charge separation, and develop photocatalyst systems with composite structures for efficient solar water splitting. Two strategies were employed to achieve this objective: 1) a composite photoanode is designed with Fe$_2$O$_3$/Au/Fe$_2$O$_3$ sandwich structure for visible-light-driven PEC water splitting; 2) a composite photocatalyst in the form of ZnS-ZnO hybrid nanowires is fabricated for visible-light-driven photocatalytic water splitting.

The following hypotheses have been made to elucidate the ideas:

In the first strategy, a sandwich structure is constructed with two semiconductor layers and an intermediate metallic layer as connection in between. This tandem composite configuration is expected to show stronger photo-response comparing with the single layer of one semiconductor component because it enables wider light harvesting range, tailorable band level matching, and more efficient charge separation. In particular, the SPR absorption from the intermediate gold layers and the resulting Plasmon-excitation induced electron transfer may play an indispensable role to contribute to the high photocurrent responses. The thorough understanding on the photoinduced charge transfer processes between different layers of this sandwich configuration will essentially help to optimize the structure construction towards highly efficient photoelectrodes.

In the second strategy, it is hypothesized that well-distributed nanoparticle-heterojunctions may be developed at the interface of the two large-band-gap semiconductors, i.e. ZnO and ZnS. These heterojunctions may result in overall band-gap reduction and even
allow for visible-light absorption. Possible fast charge transfer across the heterojunctions may promote photo-charge separation and induce high photo-activity even without loading of noble metal co-catalysts. ZnS to ZnO molar ratio may be crucial to the hydrogen evolution performance of this composite photocatalyst, and optimization of this ratio may maximize the production of hydrogen. This work may provide a meaningful way to utilize large-band-gap semiconductors to develop heterostructured composites for visible-light-driven solar fuels production.

1.3 Scope

There are five chapters in this thesis. Chapter 1 is introduction, and it provides background information on solar water splitting, presents the challenges to be addressed and introduces objective and hypothesis. Chapter 2, literature review, is to discuss the undertaken challenges in detail, and review recent studies and progress on solar water splitting. Chapter 3 is the experimental, providing the information of materials, equipment and methodology. Chapter 4 presents the first and second strategy to address the challenge, elaborating the experiment results, analysis and rational discussion. Finally, the conclusions and future recommendations are addressed in Chapter 5.
2 LITERATURE REVIEW

2.1 Global energy demand and hydrogen fuels

Energy has always been the fundamental element of civilization. During the past 150 years, energy that generated by combusting fossil fuels has powered human being to achieve abundant innovations in all aspects of living of the global population. Due to the fast growing population and economic development, the global energy demand is expected to increase from 14.9 terawatt (TW) in 2004 up to 23.4 TW in 2030, which is 57% growth in 26 years.[14] According to the official statistics and prediction as in “World Energy and Economic Outlook 2006”, the global population is going to grow by 36%, up to 8.9 billion in 2050, while the projected global primary energy demand will be increased by a factor of 77% in the same period of time.[15] However, the fossil fuels that supply the global energy usage are extremely limited for such growth of demand. The greedy exploration of the fossil fuels will gradually deplete the precious natural reserves and even threaten the future sustainable development. Moreover, burning of the fossil fuels produces greenhouse gas and causes serious environmental problems such as global warming.[16] Therefore, a revolution in energy is desired so that renewable energy sources can replace the traditional fossil fuel supply.

Solar light energy provides the primary energy input to support the life on the earth. It is considered to be one of the few energy sources that can meet the global scale energy demand. The solar energy that reaches the planet has a rate of ~120 000 TW, which exceeds the global energy consumption in a great scale.[14] If efficient systems can be developed to capture, store and utilize the solar energy, the global energy demand may be satisfied. The solar fuels production is fundamental to concentrate the diffused solar energy to meet higher energy
density requirement and convert this temporary energy source for proper transportation and storage. Hydrogen is one of the most researched solar fuels that available to capture, convert and store the solar energy.[17]

Hydrogen is considered to be an ideal energy fuel base to build up future energy infrastructure to eliminate environmental problems and provide long-term energy supply. First of all, hydrogen is the third most common element on the planet, and it is present in abundant sources such as water, hydrocarbon and biomass.[12] Secondly, it is a clean energy fuel because only water is produced after releasing the chemical energy that stored in the H-H bond.[18] Thirdly, storage can be done in various forms, such as liquid, gaseous and metal hydride, and long-distance transportation is available in tankers or pipelines. Fourthly, hydrogen is the lightest gas and releases 142 MJ kg\(^{-1}\) upon combustion.[19] Thus, the stored energy per unit mass of hydrogen is three times of gasoline and seven times of coal, making it a compatible chemical fuel. Lastly but not the least, direct utilization of hydrogen in internal combustion engines and chemical feed stock have been developed with relative high efficiency.[20]

Therefore, the demand of using hydrogen fuels is projected to further grow in the next a few decades. Current methods of hydrogen production include: (1) Steam Methane Reforming (SMR); (2) Conversion from biomass via thermochemical processes such as pyrolysis, gasification and liquefaction; (3) Solar water splitting.[21] Although SMR is the most widely used method to produce hydrogen, it consumes fossil fuel sources as the input raw material and generates greenhouse gases, i.e. carbon dioxide and carbon monoxide, introducing environmental pollution. Carbon dioxide is also generally emitted during the process of converting biomass to hydrogen. Therefore, the first two methods cannot produce hydrogen with renewable and environmental-friendly process to meet the sustainable goal of
energy fuel development.[22-25] In contrast, solar water splitting can achieve a fully renewable conversion to hydrogen by utilizing the most abundant input energy, i.e. solar energy, cheap source of hydrogen, i.e. water, and earth-abundant materials as the photocatalysts.[26-27] Solar water splitting is frequently referred to as “artificial photosynthesis” because it mimicking the natural photosynthesis process to convert solar energy into chemical energy.[10] Figure 2-1 illustrates a vision of producing and utilizing hydrogen fuel via solar water splitting. This may supply renewable and clean energy power to build a sustainable energy community in the future.[28] In the following sections, aspects of efficient energy transduction systems of the natural photosynthesis will be introduced and fundamental principles, current progresses and future challenges of solar water splitting will be reviewed as well.

Figure 2-1 Illustration of a sustainable hydrogen fuel production and utilization based on solar water splitting.[29]
2.2 Comparisons of natural and artificial photosynthesis

Over the past 3 billion years, an elegant system has been evolved by nature organisms to generate energy by utilizing sunlight. This natural energy system is composed of natural photosynthesis and cellular respiration, providing the blueprints of energy infrastructures for human beings. In this system, the sunlight energy is firstly converted and stored as chemical energy in reduced carbon compounds during natural photosynthesis, and then the stored chemical energy is released for organisms’ usage by reacting with oxygen in cellular respiration.[30]

The heart of the photosynthesis is splitting water into oxygen and ‘hydrogen’ using solar energy. The generated oxygen is released into the atmosphere and support breathing and burning, while ‘hydrogen’ is combined with carbon dioxide to form various organic molecules such as sugars. Basically, photosynthesis is accomplished by generating charge-separated state under sunlight. As shown in Figure 2-2 (a), two systems, photosystem I (PSI) and photosystem II (PSII), are involved in photosynthetic process. Upon irradiation, light energy in forms of actinic photons is captured by chlorophyll and other pigments in light-harvesting complex of PSII and an electron is excited to a higher electronic state within the reaction centre and transferred to the primary electron-acceptor molecule, pheophytin. This process achieves the photoinduced charge separation. Then, electron is shuttled through an electron transport chain, which is composed of a series of electron carriers, and finally reaches the reaction centre of PSI. The electron is excited again and passed down to the electron acceptor, followed by a cascade of electron carriers’ transport to reach ferredoxin-NADP+ reductase (FNR). Finally, hydrogen is produced in the form of NADPH. The holes left in PSII after electron excitation are transferred to oxygen evolving complex (OEC),
where oxygen is produced. The charge separation quantum efficiency of the above natural photosynthetic process is close to 100% under ideal conditions.[31-33]

Figure 2-2 Illustration of charge-separation processes in natural photosynthesis (a) and artificial photosynthesis with single-step reaction (b) and two-step reactions (c).[29]

The success of the natural photosynthesis encourages the researchers to mimic it in the laboratory and develop the biomimetic system, which is called artificial photosynthesis or solar water splitting.[34-35] An illustration of the artificial photosynthesis systems is compared with natural photosynthesis in Figure 2-2. A chromophore, which is usually dye molecule or semiconductor, is employed to achieve photoinduced charge separation similar to natural photosynthesis. The electron donor and electron acceptor are also necessary to accept photo-induced holes and electrons, and participate in water oxidation and reduction to
generate oxygen and hydrogen respectively.\cite{36} Two of such systems can be cascaded together to form more complex two-step reaction system, allowing for various material combination.\cite{37-38} These systems of solar water splitting will be further discussed in the following sections.

2.2.1 Solar water splitting

2.2.2 Hydrogen production via solar water splitting

![Illustration of hydrogen production via solar water splitting.\cite{39}](image)

The basic idea of hydrogen production via solar water splitting is illustrated in Figure 2-3. Upon sunlight irradiation, solar energy is absorbed by the photocatalysts dispersed in water, and water is decomposed to oxygen and hydrogen, which is stored as solar fuels for future usage. This reaction, as in Equation 2-1, is an uphill reaction which has a highly positive standard Gibbs free energy change ($\Delta G$) as $+237\ \text{kJmol}^{-1}$ or 1.23 eV.

$$H_2O(l) \rightarrow \frac{1}{2}O_2(g) + H_2(g);\ \Delta G = +237\ \text{kJ mol}^{-1}$$

Equation 2-1

Since solar water splitting usually involves semiconductors as the photocatalyst, the band gap of the semiconductor need to be larger than 1.23 eV (i.e. wavelength less than 1000 nm) to achieve successful water splitting.\cite{40} Solar water splitting can be categorized into two
approaches: (1) Photocatalytic water splitting using powdered photocatalyst; and (2) Photoelectrochemical (PEC) water splitting. Both of them will be discussed in detail in the following sections.

### 2.2.3 Photocatalytic water splitting

![Diagram of basic principles of photocatalytic water splitting](image)

Figure 2-4 Illustration of basic principles of photocatalytic water splitting. (a) photocatalyst suspension under light irradiation. (b) Photoinduced charge separation process in photocatalyst. (c) Schematic diagram of energy band gap in a semiconductor photocatalyst.

In photocatalytic water splitting, powdered photocatalysts are well dispersed in water, as in Figure 2-4 (a), and there is a three-step reaction processed within the photocatalyst upon light illumination, as illustrated in Figure 2-4 (b). First of all, semiconductors can absorb the light energy when the energy of incident light exceeds its band gap energy, and electron excitation from valence band (VB) to conduction band (CB) can be induced. Simultaneously, holes can be generated in VB after electron excitation. In such a way, electron and hole separation is achieved and they are referred to as photoinduced electrons and holes respectively. After that, these electrons and holes can either migrate to the surface of the photocatalyst or recombine together. The recombination may happen immediately after
excitation within the photocatalyst particles, which is referred to as volume recombination. It can also occur after the electrons and holes migrating to the surface of the particles. The last step is redox reaction of water at the surface of the photocatalyst. Ideally, water molecules are reduced by photoinduced electrons to form hydrogen and oxidized by the photoinduced holes to generate oxygen, respectively. In order to enable these two redox reactions, the minimum level of the conduction band (CB) needs to be higher than the redox potential of \( \text{H}_2/\text{H}_2\text{O} \) (0 V vs NHE at pH=0) while the maximum level of the valence band (VB) needs to be lower than the redox potential of \( \text{H}_2\text{O}/\text{O}_2 \) (1.23V vs NHE at pH=0), as shown in Figure 2-4 (c).[42-43]

The efficiency of the photocatalytic water splitting is usually evaluated by either hydrogen gas evolution or electrons transferred during reaction process. In both cases, rates of gas evolution or electron transfer are normalized to unit time or unit mass of photocatalyst for an easier comparison.[44-45] The overall quantum yield and solar energy conversion are defined as follows:

\[
\text{Overall quantum yield (\%) = } \frac{\text{Number of reacted electrons}}{\text{Number of absorbed photons}} \times 100 \% \quad \text{Equation 2-2}
\]

\[
\text{Solar energy conversion (\%) = } \frac{\text{Output energy of hydrogen evolved}}{\text{Energy of incident solar light}} \times 100 \% \quad \text{Equation 2-3}
\]

Photocatalytic water splitting is an easy and desirable way for massive production in industrial applications. However, its efficiency is limited by many factors, which are discussed as follows:

First of all, single semiconductor which has proper CB and VB energy levels to meet the requirements of redox potentials of both \( \text{H}_2/\text{H}_2\text{O} \) (0 V) and \( \text{H}_2\text{O}/\text{O}_2 \) (1.23 V) together usually possess large band gap energy greater than 3.0 eV. This means only UV light portion of the
sunlight energy (~3 %, as shown in Figure 2-5) can be absorbed, while more than 40 %
energy in visible light range is wasted, and thus limits the light absorption efficiency.[46]
Therefore, photocatalyst absorbing visible light energy can use larger portion of the solar
spectra and thus achieve better solar energy utilization. In order to harvest most light energy,
the band gap energy of the photocatalyst is required to be less than 3.0 eV, and light
scattering or reflection need to be minimized under the illumination. According to Scaife’s
study in 1980, due to the intrinsic limitation, few of the semiconductors can meet these two
requirements of band gap: (1) Band gap energy below 3.0 eV; (2) CB and VB energy levels
suitable for both water oxidation and reduction.[47] Moreover, the photocatalysts should
have an intrinsic property that the light energy absorbed is mostly used to excite electrons
rather than generating heat or phonons.

Figure 2-5 Spectrum of solar energy distribution based on AM1.5 global data.[48]

Secondly, recombination of photo-electrons and holes during migrating can reduce the
number of excited charges and is regarded as a deactivation process. Charge recombination is
strongly correlated to crystal structure, crystallinity, defects and particle size of the powder
photocatalysts. Defects may act as trapping and recombination-centers and thus result in a
stronger suppression on charge separation. Finer crystallinity will reduce the amount of defects in some extend and hence weaken the suppression. Smaller particle size will help in shortening the distances that electrons and holes have to migrate to before reaching the surface reaction sites and thus decrease the possibility of recombination of photo-electrons and holes.[49]

Thirdly, surface back reaction happened on the surface of the photocatalysts may greatly reduce the gas evolution. After water splitting, hydrogen and oxygen may react with each other and reform H₂O on the photocatalyst surface. This reaction is a downhill reaction and frequently referred to as surface back reaction (SBR). Surface properties of the photocatalyst, such as population of surface active sites, may greatly influence the SBR as well.[50]

### 2.2.4 Photoelectrochemical water splitting

![Illustration of basic principles of PEC water splitting](image)

Figure 2-6 Illustration of basic principles of PEC water splitting with an n-type semiconductor photoanode and a metal photocathode.[51]

PEC water splitting, as shown in Figure 2-6, is defined as a water splitting process using light-induced electrochemical setup to convert light energy into chemical energy and store in
hydrogen bond. The setup usually consists of electrolyte solution and two electrodes configuration, including the cathode and the anode. The anode is an electrode made of semiconducting or photoactive materials, which absorbs light energy and initials chemical reaction at its surface. The cathode is working as the counter electrode, and named as photocathode even if it is not irradiated by the light beam.[52-54] Similar to photocatalytic water splitting, photoinduced charge separation can happen at the anode when the light energy is matched to the band gap energy of the semiconductor in the photoanode upon irradiation. In order to drive the water splitting reaction, the electrode potential should be higher than 1.23 V, so that water molecules can be oxidized to oxygen and protons (H⁺). The protons can migrate to the cathode where they are reduced by the photoinduced electrons which are generated and transferred from photoanode.[55-56] Thereby, hydrogen is generated at the photocathode. Due to the slow kinetics, energy will be lost when electron is transferred across the photoanode and electrolyte interface. Therefore, the band gap energy of the semiconductors at photoanode is frequently required to lie between 1.7 eV and 2.4 eV.[51,57]

Usually, a small external bias is employed to work as the driving force to initialize the electron transfer from photoanode to photocathode. Thus, photocurrent and bias potential are both included in calculating of photoconversion efficiency. There are normally two approaches to estimate the efficiency as reported in the literature: one is solar-to-hydrogen conversion efficiency, and the other one is incident photon to current conversion efficiency (IPCE).[58-59]

The solar-to-hydrogen (STH) conversion efficiency (\(\eta\)) can be calculated as follows:

\[
\eta = \frac{J_{mp}(1.23V-V_{app})}{P_{in}}
\]

Equation 2-4
J_{mp} is current density measured externally, V_{app} is the applied bias potential between photoanode and cathode, P_{in} is the light density of illumination. In terms of the hydrogen production, every two electrons contributing to the photocurrent are involved in producing one hydrogen molecule.[60]

The IPCE can be calculated using the following equation:

\[ IPCE(\%) = \frac{J_{mp}(\lambda)}{P_{in}(\lambda)} \]  

Equation 2-5

A 100 % IPCE means that each photon is able to generate one electron-hole pair. However, IPCE is always below 100 % owing to several factors such as the energy loss due to reflection, limit light absorption ability of the semiconductors and possible charge recombination, and etc.[61]

In literatures, either STH or IPCE method is employed to evaluate the PEC performance and the latter one is more frequently used.

The principal difference between photocatalytic water splitting and PEC water splitting is the redox reaction sites. In photocatalytic water splitting, both of the water oxidation and reduction reactions happen at the surface of the photocatalyst particle. In contrast, in PEC water splitting setup, the water oxidation occurs at the photoanode while hydrogen is generated at the photocathode. Therefore, hydrogen and oxygen evolution are physically separated in PEC water splitting, and this greatly suppress the SBR that is inevitable in photocatalytic water splitting. An electrical bias is provided to initialize the electrolysis, improve the electron-hole separation and thus increase the rate of the energy conversion. Besides, PEC water splitting enables the separate modification of anode/cathode and thus allows optimization on single task. Last but not the least, PEC water splitting can provide
easy coupling of semiconductor electrode through serial tandem connections, which is quite challenging in powder form photocatalytic water splitting.[62-63]

Factors that influence the efficiency in photocatalytic water splitting, such as light harvesting ability of the semiconductors and photo-charge recombination can also play an important role in affecting this PEC water splitting efficiency. Besides, semiconductor photo-electrodes are required to possess excellent chemical and thermodynamic stability in electrolyte solution. Resistance of the semiconductor that influences electron transfer within the electrode also needs to be considered. For long term and practical application, cost and readily availability are also the criteria.[64-66]

2.3 Current progress in solar water splitting

2.3.1 Photocatalysts requirements and challenges

Based on the principles of the water splitting, several requirements on the properties of the photocatalysts should be satisfied to achieve efficient water decomposition: (1) Good solar light energy absorption capability, preferred in visible-light range; (2) Proper band gap level positions relative to water reduction/oxidation, as shown in Figure 2-7, the CB level should be more negative than 0 V (vs. NHE, at pH=0) to allow for water reduction and VB level should be more positive than 1.23 V (vs. NHE, at pH=0) to enable water oxidation; (3) Efficient photoinduced charge separation and transport to minimize charge recombination; (4) Good chemical stability to resist photocorrosion in aqueous environment; (5) Low cost.[67-71]
Figure 2-7 Schematic illustration of band gap energy levels of semiconductors relative to water reduction/oxidation potentials.[72]

Over 130 materials have been studied as photocatalysts and some of the most intensively researched materials are schematically illustrated to show their relative band gap levels in Figure 2-8. It can be noticed that some of the semiconductors, such as TiO$_2$, ZnS, GaN have proper CB and VB level for water reduction and oxidation simultaneously, however, they are highly limited due to their large band gap energy over 3.0 eV, which only allows for UV irradiation.[73-74] Most of the visible-light-active semiconductors, such as WO$_3$ and Fe$_2$O$_3$, cannot achieve hydrogen production because they have CB lower than water reduction potential.[75-76] Some of the sulphides and nitrides semiconductors have proper band gap energy, CB and VB band levels for visible light water splitting, such as CdS, however, they are generally unstable in aqueous environment and may undergo photocorrosion under light irradiation.[13] S$^{2-}$ anions in CdS tend to be oxidized by photoinduced holes much more easily than water molecules, eluting toxic Cd$^{2+}$ cations, according to Equation 2-6.

\[
CdS + 2h^+ \rightarrow Cd^{2+} + S \quad \text{Equation 2-6}
\]
Figure 2-8 Relative band gap positions and band gap energy of various semiconductors.[48]

The maximum reported quantum efficiency of visible-light-active photocatalyst, Cr/Rh-GaN/ZnO, is only 2.5 % (at 420-440 nm,) in pure water splitting.[3] The efficiency of PEC water splitting is slightly higher than photocatalytic water splitting due to fewer SBR, as high as 12.4 % for p-/n-GaAs photoanode and GaInP$_2$ photocathode.[77] However, this value is still far below the theoretical efficiency limit of 30 % for practical application.[78] Therefore, developing suitable photocatalyst material still remains a challenge, especially on visible light harvesting and photoinduced charge separation.[79-80] Several approaches can be adopted to explore new photocatalysts and tackle the challenges, as elaborated in the following sections.
2.3.2 Approaches to address challenges on visible light harvesting and charge separation

2.3.2.1 Band gap engineering

Owing to the essential role of band structure on light absorption, band gap engineering is one of the most intensively studied approaches to realize visible-light harvesting. Band gap engineering can be achieved through doping and forming solid solution.

Metal ion doping is frequently used to introduce impurity levels as additional electronic states in forbidden band of the semiconductors, as shown in Figure 2-9 (a) and (b). The impurity level can either work as a completely or partially filled donor level above original VB, or an empty state as an acceptor level below original CB. Since the first reported visible-light-active Cr-doped TiO$_2$,[81] various metal ions, such as Ni, Fe, Mo, Sn and etc., have been studied as the dopant in UV-active semiconductors, such as TiO$_2$ [81-83] and ZnS [84-85], to active it under visible light irradiation. However, enhancement of the photoactivity is invisible in some of the cases because these impurity levels may act as recombination centres for photoinduced electrons and holes.[86] Moreover, these impurity levels are usually discrete, which makes it difficult for photoinduced charges to migrate to the surface, and this will further contribute to an increase in the charge recombination.[87] Therefore, incorporation of metal ions within the photocatalysts needs to be carefully controlled to reduce the side effects on charge recombination.
Figure 2-9 Formation of (a) donor level, (b) acceptor level and (c) new VB by doping.[39]

Non-metal ion doping is also widely used to narrow the band gap to enable visible-light absorption. Instead of introducing impurity levels as metal ion doping, the p states of the non-metal ion dopants (such as C, N, and S) can mix with O 2p states of the oxide photocatalysts, resulting in an upward shift of VB edge and smaller band gap for electron excitation, as shown in Figure 2-9 (c).[88-89] This doping method is more effective to enhance the photoactivity compared to metal ion doping because fewer recombination centres are formed in this way. For example, N-doped TiO$_2$ has been successfully prepared and widely applied to perform visible-light harvesting.[90-91]

Besides doping, the other technique to conduct band gap engineering is to form solid solutions between narrow and wide band gap semiconductors which have similar lattice structure, as illustrated in Figure 2-10. By adjusting the ratio of the solid solution components, the band gap and band position can be customized, and thus visible-light response can be achieved. Many semiconductor alloys are formed in this way, such as ZnS-CdS,[92] CdS-CdSe,[93] ZnS-AgInS$_2$,[94] and ZnS-In$_2$S$_3$-CuS[95] etc.
2.3.2.2 **Sensitization**

Sensitization is an effective strategy to increase the population of electrons in CB of semiconductor photocatalysts.[97-98] The sensitziers, which are capable of visible light excitation, are usually dye molecules, such as Ru(bpy)$_3^{2+}$ [99] and [Ru-(dcbpy)$_2$(dpq)]$^{2+}$[100], or narrow-band-gap semiconductors, such as ZnSe,[101] CdSe,[102] and InP,[103] etc. These sensitizers can be coupled to wide-band-gap semiconductors, such as TiO$_2$, ZnS, and ZnO, to achieve visible light harvesting.[104-105] The principle is illustrated in Figure 2-11, taking dye molecule Ru(bpy)$_3^{2+}$ as an example. Upon light irradiation on dye molecules, electrons can be excited within the dye molecule and these photoinduced electrons can be injected into the CB of the semiconductor soon after excitation. These electrons can then be consumed by water reduction, and the oxidized dye molecules can be subsequently reduced and recovered by receiving electrons from electron donors, such as Ethylenediaminetetraacetic acid (EDTA), triethanolamine (TEA), and $I^3/I^-$, etc.[106]

![Figure 2-10 Band structure controlling by solid solution formation.][96]
Figure 2-11 (a) Basic principle of dye-sensitized visible-light-driven photocatalytic hydrogen evolution, with Ru(bpy)$_3^{2+}$ as dye sensitizer. (b) Illustration of the electron transfer path in dye-sensitized K$_4$Nb$_6$O$_{17}$ nanoscroll.[106]

When a narrow-band-gap semiconductor is used as the sensitizer, the CB of the wide-band-gap semiconductor must be aligned lower than that of the sensitizer for an efficient electron transfer. As illustrated in Figure 2-12, the electron cannot be injected to CB of TiO$_2$ when the CB of the sensitizer PbS locates in a relative lower position. The two semiconductors can form composite by various techniques, such as hydrothermal synthesis,[107] electrospinning,[108] and electrodeposition,[109] and etc.

Figure 2-12 Schematic illustration of relative band gap positions and electron transfer between narrow (PbS) and wide (TiO$_2$) band gap semiconductors in inorganic sensitization.[110]
2.3.2.3 Plasmonic assistance

Recently, some investigations have reported plasmon-enhanced water splitting systems which normally include plasmonic metals and semiconductors.[111] In the concept of the localized surface plasmons, conduction electrons within metal nanoparticles are regarded as harmonic oscillators which are responsive to an oscillating electric field. Upon light irradiation, an external electric field is applied to these electrons, causing redistribution of the electron density and creating an electric field opposite to the external electric field. Thus, a coulombic restoring force is introduced by the displacement of the electron density, and a series of oscillations within the metal nanoparticles is started. Such coherent oscillations of conduction electron density initiated by light irradiation are normally referred to as localized surface plasmons.[112-114] The plasmon resonance frequency, at which the conduction electron oscillation has minimum power dissipation, is associated with particle shape, size and dielectric environment.[115] Most of the metals (Sn, Cd, In, Pb) have plasmon resonance frequency in UV region, while the frequency of Au, Ag and Cu lies within visible light region.[48,116] Concerning the stability, Au is most intensively studied for plasmon-enhanced water splitting.[113,116]

The plasmonic metal can assist solar water splitting in two ways: 1) Sensitizing the semiconductor by injecting photo-excited electrons into CB of semiconductor, as illustrated in Figure 2-13 (a);[117-119] 2) Localizing the optical energy by inducing an electromagnetic field close to the interface, as in Figure 2-13 (b).[120-122] The mechanism of plasmonic electron injection is similar to dye sensitization as mentioned in above section, furthermore, due to the high mobility of charge carriers and $10^5$ times larger absorption cross-sections, the plasmonic metals are considered to be more promising sensitizers than traditional dye sensitizers.[123-124] The possibility to engineer the plasmon resonance frequency via tuning
size and morphology of the nanoparticle adds more advantages to use plasmonic metals to explore visible-light water splitting. Liu et al. also proposed the other plasmonic enhancement mechanism in which a strong electromagnetic field can be induced by Au nanoparticles on TiO$_2$ surfaces.[125] In the optical simulation image, local “hot spots” at the interface can be 1000 times higher than light source electromagnetic field intensity, indicating the much higher charge-carrier generation near the interface.[118,125] These charge-carriers are readily separated under the surface potential and can migrate to the surface with a shorter distance, and thus, the recombination rate can be highly reduced. Therefore, the plasmonic enhancement can contribute to both light harvesting and photo-induced charge separation. Currently, many plasmonic-enhanced photocatalysis were reported, such as Ag/N-TiO$_2$ composite [120], Au-CdS nanorods [126], Au/TiO$_2$ film [125], Au-TiO$_2$ nanocomposites [127], Au-Fe$_2$O$_3$ nanocomposites [128], and etc.

![Figure 2-13](image)

Figure 2-13 (a) Schematic illustration of plasmon-induced charge transfer. (b) Optical simulations of plasmon-enhanced electric fields. The colour bar indicates the electric field intensity after normalized by input light intensity.[118]
2.3.2.4 Co-catalyst loading

Co-catalyst loading is proved to be an effective way to promote charge separation and surface reaction in solar water splitting. Noble metals, such as Pt [129], Au [130], Ru [131], Pd [132], Ag [133], have been reported as efficient co-catalysts for hydrogen evolution via water splitting. These noble metals usually have Fermi energy levels lower than semiconductors, and thus can entrap the photo-induced electrons from the host photocatalyst. Furthermore, they can also play a role as surface reaction centres to reduce water to hydrogen, and subsequently further enhance the photocatalytic efficiency.[39] For example, a quantum yield as high as ~60.34 % at 420 nm was achieved when nanoporous CdS nanostructures were loaded with Pt co-catalyst.[134] Besides noble metal co-catalysts, metal oxides such as RuO$_2$ [135] and NiO [136], metal sulphides such as MoS$_2$ [137] and NiS [138], and Co-based oxygen-evolving complex [139] are widely used as co-catalysts in solar water splitting. Multiple co-catalysts can also co-loaded to single host photocatalysts as illustrated in Figure 2-14. Duonghong et al. co-deposited RuO$_2$ and Pt on TiO$_2$ and a synergistic effect was achieved because photo-induced electrons and holes were directed and trapped by Pt sites and RuO$_2$ sites respectively.[140]

![Figure 2-14 Schematic illustration of Pt and RuO$_2$ as co-catalysts on TiO$_2$.][140]
2.3.2.5 **Semiconductor composites**

Photo-induced charge recombination can be highly inhibited when the electron-hole separation is promoted by efficient charge transfer. Combination of semiconductors or metals to form composite material is one of the promising ways to facilitate charge transfer and prevent charge recombination. There are many approaches to couple two or more semiconductor/metal components, as discussed below.

Combination of suitable p-type and n-type semiconductors to form p-n junction is proved to be an effective way to suppress charge recombination. In general, due to the diffusion of electrons and holes between p-type and n-type semiconductors, a space-charge region is formed at the interface, and such creates a built-in electrical field to drive charge carriers transfer and fast charge separation.[141] Various semiconductor composite materials with p-n junctions, such as p-Cu$_2$O/n-WO$_3$ [142], p-ZnFe$_2$O$_4$/n-SrTiO$_3$ [143], and p-CaFe$_2$O$_4$/n-MgFe$_2$O$_4$ [144], exhibit much higher visible-light driven hydrogen evolution than single p- or n- components.

Direct contact between two semiconductors may lead to formation of heterostructure and three different types of band alignments, as shown in Figure 2-15. Type II alignment is usually considered to be more suitable for semiconductor combination because the energy gradient at the interface can drive electrons and holes to opposite sides of the heterojunction and result in spatial separation.[48] Such heterostructure allows integration of both narrow and wide band gap materials with various combinations.[145] For example, CdS with visible-light absorption band gap has been effectively combined with wide-band-gap semiconductors, such as TiO$_2$ [146] and ZnO [147] to achieve effective charge separation under visible-light irradiation.
Metals can also be involved in forming composite material with semiconductors, however, due to their excellent conductive properties and possible plasmonic effects, the combination effects become more complicated. The role of the metal component may be a combination of co-catalyst, plasmonic assistance and electron transfer mediator.[39,48,51]

Figure 2-15 Illustration of three types of band alignment in semiconductor heterojunctions.[48]
3 EXPERIMENTAL

3.1 Material

Iron (III) chloride (FeCl₃, ACS, 97.0-102.0 %) was purchased from Alfa Aesar. Zinc acetate dehydrate (Zn(CO₂CH₃)₂, puriss. p.a., ACS, 99.0 %), oleic acid (reagent grade, 99 %), Chloroform (for HPLC, >=99.9 % contains amylenes as stabilizer), Potassium phosphate monobasic (KH₂PO₄), Potassium phosphate dibasic anhydrous (K₂HPO₄), Polyethyleneimine (PEI), Ammonium hydroxide solution (NH₄OH, ACS, 28.0-30.0 % NH₃ basis), Hydrogen peroxide solution (H₂O₂, ACS, 30 wt. % in H₂O), Indium tin oxide coated glass slide (ITO glass), zinc acetate (99.0 %), 16-mercaptohexadecanoic acid (MHA, 90 %), isopropyl alcohol (IPA, 99.5 %), Sodium hydroxide (NaOH), ethanol (99.9 %), Zinc sulfide (ZnS, 99.99 %), Zinc oxide (ZnO, 99.999 %) were purchased from Sigma-Aldrich. Deionized water (DI-water, resistance over 18 MΩ) from Nanopure Diamond water system was used in all experiments. All chemicals were used as received without further purification.

3.2 Fabrication of Fe₂O₃/Au/Fe₂O₃ composite electrode

3.2.1 Synthesis of Fe₂O₃ nanoparticles

Fe₂O₃ nanoparticles were synthesized by modifying well-developed hydrothermal method.[148] 15 mL oleic acid, 1.5 g NaOH, 15 mL ethanol and 15 mL DI-water were mixed into a uniform solution, and then added in 15 mL 0.01 M FeCl₃ solution. After 30 min stirring, the mixture were transferred to a 100 mL Teflon-lined autoclave, and heated at 180 °C for 10 h. After cooling down to room temperature, the obtained nanoparticles were washed by ethanol and water repeatedly and dried in vacuum oven.
3.2.2 Preparation of ITO substrate

The ITO glass was cut into small pieces with dimension of 12.5 mm by 25 mm. Then the ITO glass slides were firstly sonicated in DI-water for 5 min. After which the slides were heated at 60 °C for 30 min in the RCA solution (a mixed solution of NH₄OH, H₂O₂ and DI-water, (1:5:20, v/v/v). After cooling down to room temperature, the slides were washed by DI-water and blew dry by nitrogen gas blow.

3.2.3 Construction of composite Fe₂O₃/Au/Fe₂O₃ film

The Fe₂O₃/Au/Fe₂O₃ composite film was constructed through spin-coating and sputtering on ITO glass substrate.

First of all, a Fe₂O₃ layer was prepared by spin-coating on clean ITO glass substrate followed by 40 min Ozone sputtering and annealing at 250 degree in air for 2 h. To prepare the Fe₂O₃ layer by spin-coating, typically, 50 μL Fe₂O₃ suspension in ethanol was dropped onto RCA treated ITO glass substrate and then spin at 200 rpm for 10 sec followed by 1000 rpm for 50 sec. The process was repeated for 30 times.

After that, a second layer of gold with thickness of 30 nm was sputtered on the top of the Fe₂O₃ layer. The sputtering current was 20 mA, and the sputtering speed was 10 nm min⁻¹. The thickness was controlled by sputtering time.

Finally, the top Fe₂O₃ layer was deposited through the same process as the first Fe₂O₃ layer on Au/Fe₂O₃ film. Figure 3-1 illustrates the Fe₂O₃/Au/Fe₂O₃ composite film on ITO substrate in a schematic diagram. Fe₂O₃ double-layer electrode, Fe₂O₃/ITO/Fe₂O₃ composite electrode and Fe₂O₃/Au/Fe₂O₃ composite electrodes with different thickness of Au intermediate layer were prepared following a similar route.
3.2.4 Synthesis of Au nanoparticles

The preparation followed Si’s route.[149] Typically, 1 mL oleic acid solution (40 mM in methanol) was mixed with 8 mL DI water and the pH of the mixture was adjusted to 11. Under constant stirring, HAuCl₄ aqueous solution (0.5 mL, 10 mM) was added, followed by dropwise adding of 0.5 mL freshly prepared NaBH₄ solution (10 mM). The solution was stirred for another 30 min after the color changing from yellow to red. These oleic acid capped Au nanoparticles were kept in 4 °C with Aluminum foil wrap to avoid light exposure.

3.2.5 Photo-current testing using electro-chemical workstation

3.2.5.1 Testing configuration setup

A three electrode configuration was used in testing the photo-current by electro-chemical workstation (CHI852c). 150W Halogen lamp light source (DOLAN JENNER Model 150 Illuminator, light spectrum shown in Figure 3-2) was used to illuminate the samples. The light is mainly visible light with wavelength from 500 nm to 750 nm. Very little intensity lies in UV and NIR range. Oriel Order Sorting Filter (λ > 420 nm) was also inserted into the light source to eliminate the UV light. The photo-current was investigated by measuring photo-current density (j) vs potential (U) and j vs time (t).
Ag/AgCl electrode and Pt-wire electrode was employed as the reference and counter electrode respectively. ITO glass coated with composite film was connected with the system through clamp and used as the work electrode, as shown in Figure 3-3. The area immersed into the electrolyte was 1cm$^2$ so that the current density can be read as the current shown by the software. j-U curve was obtained by scanning in “Linear Sweep Voltammetry” mode with scan rate of 0.1 V s$^{-1}$ and scan interval from 0 to 1.4 V. The j-t curve was obtained by scanning in “Amperometric i-t Curve” mode with initial potential at 1.0 V and sample interval of 0.1 sec.

![Figure 3-2 Light spectrum of DOLAN JENNER Model 150 Illuminator.](image)

![Figure 3-3 Three electrode configuration for photo-current testing.](image)
3.2.5.2 Electrolyte preparation

0.1 M Potassium Phosphate Buffer Solution (PBS) in deionized (18 ΩM) water with pH 7.0 was used as the electrolyte solution during the electrochemical testing. The buffer solution was prepared by mixing the solution of potassium phosphate monobasic and potassium phosphate dibasic. By varying the amount of each component solution, a range of buffer solutions can be prepared with pH differed from 5.8 to 8.0 (as shown in Table 3-1).

Table 3-1 Preparation of 0.1 M Potassium Phosphate Buffer at 25 °C.

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</table>
3.3 **Fabrication of ZnS-ZnO hybrid nanowires**

3.3.1 **Synthesis of ZnS-ZnO hybrid nanowires**

The ZnS-ZnO hybrid nanowires were synthesized by using hydrothermal method. First of all, 0.075 g MHA was dissolved in 30 mL of IPA solution under sonication. Then the solution was mixed with 30 mL of aqueous solution containing 0.44 g zinc acetate and 1.5 g NaOH under stirring. After 40 min strong stirring, the homogeneous mixture was transferred into a 100 mL Teflon-lined autoclave. The autoclave was then sealed and heated at 180 °C for 10 h, and cooled down to room temperature after the heating process. The obtained products were centrifuged at 12000 rpm for 20 min in water and ethanol alternatively to wash off the residual chemicals. Then the samples were dried in vacuum oven at room temperature overnight. The final product was in powder form, and denoted as ZZ-a. Control samples were also synthesized in similar procedure, but with varied zinc acetate or MHA amount. Sample ZZ-b was synthesized with 1.5 times higher quantity of zinc acetate, and ZZ-c was synthesized with fourfold quantity of MHA.

3.3.2 **Photocatalytic hydrogen production**

5 mg ZnS-ZnO powder sample was dispersed in 20 mL aqueous solution of Na$_2$S (0.25 M) and Na$_2$SO$_3$ (0.35 M). The suspension was sealed in a quartz tube with rubber seal and sealing tape. The degas process was conducted with argon gas purged into quartz tube for 1 h to drive away the residual air. Figure 3-4 shows the typical photocatalytic hydrogen production setup. The illumination source was a 300-Watt Xenon lamp (MAX-302, Asahi Spectra, USA) coupled with a UV-cutoff filter ($\lambda > 420$ nm), and the intensity of the lamp was adjusted to 100 mW cm$^{-2}$. The gas product was periodically purged out with a 500 μL syringe and injected into a gas chromatography (Agilent 7890A) with thermal conductivity detector (TCD) detector for quantitative analysis.
3.4 Equipment and Characterization methods

3.4.1 X-ray diffraction

The Fe$_2$O$_3$ nanoparticle and ZnS-ZnO nanowire powders were analyzed by X-ray diffractometer XRD-6000 (Shimadzu, Kyoto, Japan) with Cu Kα source. The accelerating voltage was 40 kV and the applied current was 40 mA. The scanning rate was 1° min$^{-1}$ and the scanning angle ranged from 10 to 80°.

3.4.2 UV/VIS/NIR spectrophotometer

UV–vis diffuse reflectance spectra (DRS) of Fe$_2$O$_3$/Au/Fe$_2$O$_3$ film and ZnS-ZnO nanowire powders were recorded on a Lambda 750 UV/VIS/NIR spectrophotometer (Perkin-Elmer, USA). The ZnS-ZnO nanowire powder was dispersed in ethanol and drop-and-dry on quartz slides before conducting the analysis.
3.4.3 **Field emission scanning electron microscopy**

The field emission scanning electron microscopy (FESEM) images of \( \text{Fe}_2\text{O}_3/\text{Au}/\text{Fe}_2\text{O}_3 \) film and \( \text{ZnS-ZnO} \) nanowire were performed with a JEOL JSM-7600F scanning electron microscope. For the top-view image capture of the \( \text{Fe}_2\text{O}_3/\text{Au}/\text{Fe}_2\text{O}_3 \) film, the film on ITO substrate was adhered on the sample holder using carbon tape while for the side-view images, the ITO substrate with the film was adhered vertically on the half-moon holder. The \( \text{ZnS-ZnO} \) nanowire powders were spread on carbon tape and adhered on the sample holder. The accelerating voltage was 5 kV.

3.4.4 **Energy dispersive X-ray spectroscopy**

Energy dispersive X-ray spectra (EDS) of the \( \text{ZnS-ZnO} \) nanowire were performed with a JEOL JSM-7600F scanning electron microscope which was equipped with energy-dispersive X-ray analysis system. The accelerating voltage was 15 kV.

3.4.5 **Transmission electron microscopy**

Transmission electron microscopy (TEM) images of \( \text{Fe}_2\text{O}_3 \) nanoparticle and \( \text{ZnS-ZnO} \) nanowire were obtained on a JEOL JEM-2100F transmission electron microscope at an accelerate voltage of 200 kV. The sample powder was dispersed in ethanol under sonication and deposited onto a TEM copper grid carbon mesh. The selected area electron diffraction (SAED) patterns were recorded on JEOL JEM-2100F TEM as well.

3.4.6 **Photoluminescence spectroscopy**

The photoluminescence (PL) spectra of \( \text{ZnS-ZnO} \) nanowires were collected on a spectrofluorophotometer (Shimadzu RF-5301). The powder sample was dispersed in water.
under sonication and transferred in quartz cubic cuvette for analysis. The excitation wavelength was 325 nm.
4 RESULTS AND DISCUSSION

4.1 Sandwich Fe$_2$O$_3$/Au/Fe$_2$O$_3$ photoanodes for enhanced photoelectrochemical water splitting

4.1.1 Introduction

Ever since Hardee & Bard’s first report on preparing n-type Fe$_2$O$_3$ electrodes in 1976, α-Fe$_2$O$_3$, as known as hematite, has been intensively studied till now.[150] α-Fe$_2$O$_3$ is known to possess an indirect band gap in the range of 1.9~2.3 eV, which perfectly lies within visible-light range in solar spectrum. It exhibits good stability in most electrolytes, including both acidic and basic pH, and it can hardly undergo photo-corrosion even for prolonged light irradiation. Moreover, cheap and abundant resource of hematite makes it more favourable for long term industry applications. Therefore, α-Fe$_2$O$_3$ is one of the most promising materials for visible-light-driven PEC water splitting.[151] However, several properties of α-Fe$_2$O$_3$ limit its efficiency for desirable photo-electrode applications: 1) Medium light penetration depth (~ 118 nm at wavelength of 550 nm) and the indirect band gap alignment result in a low absorption coefficient of solar light harvesting.[152-153] 2) Short diffusion length ($L_D = 2 \sim 4$ nm) of holes, short lifetime of photo-excitation (~ 10 ps) and poor mobility of charge carriers, lead to a high rate of charge recombination.[154-155] 3) Slow water-oxidation kinetics may result in high possibility of surface back reactions.[156-157] 4) Low electrical conductivity (~ $10^{-14} \Omega^{-1} \text{cm}^{-1}$) can suppress the charge carrier transfer.[151,158]

Many efforts have been made to enhance the photo-response of α-Fe$_2$O$_3$. Nano-α-Fe$_2$O$_3$ is proved to have a better efficiency than bulk due to (i) shorter distance for charge carriers’ migration (ii) high surface-to-volume ratio for more efficient light absorption.[159-160]
Porous-α-Fe₂O₃ is demonstrated to improve the photo-activity by raising the surface area, however, resistivity may also increase with the porosity.[161] Tandem configuration in the form of multilayer thin film is attracting more interest. Semiconductors with different band gap energy can be physically combined together and it may lead to a larger light absorption and better separation of photo-induced charge carriers. This method was first conducted in 1982, using α-Fe₂O₃/TiO₂ composite electrode,[162] and later α-Fe₂O₃/n-Si heterojunction photoanode was constructed and investigated.[163] Recently, WO₃/α-Fe₂O₃ composite structure was proved to have better photo-responses than either WO₃ or α-Fe₂O₃ single-material films.[164] Despite of the limited improvement in photo-current, the tandem water splitting were still considered to be a promising way to fabricate efficient photo-electrodes via multiple combination of raw materials.[165-166]

In this section, a composite photo-electrode is constructed with a thin intermediate layer of plasmonic gold in-between of two layers of α-Fe₂O₃. Thus, a sandwich structure of Fe₂O₃/Au/Fe₂O₃ is fabricated and it is expected to enhance the performance of visible-light-driven photo-activity compared to α-Fe₂O₃ film alone. Modification of the intermediate layer with other conductive material, such as ITO, may assist to understand the essential role of the Au layer. The mechanism of the electron transfer will be studied by altering several factors, such as thickness and layer structures, and thereby explain the enhancement of the photo-activity.

4.1.2 Characterization of Fe₂O₃

To confirm the chemical composition and phase of the as-synthesized nanoparticle, XRD spectrum was obtained and matched with database. The XRD pattern can be assigned to the pure phase of hematite (α-Fe₂O₃) with Joint Committee on Powder Diffraction Standards.
(JCPDS) card number 79-1741 (Hematite, syn), as shown in Figure 4-1. The three most intensive peaks at 33.2°, 35.6° and 54.1° are corresponding to (104), (110) and (116) planes of Rhombohedral α-Fe₂O₃.[167] No more peaks other than those belong to hematite can be observed. Such confirms the synthesized nanoparticles were pure phase of α-Fe₂O₃.

The nanoparticles were then examined by TEM to confirm the size distribution and morphology. As shown in Figure 4-2, the nanoparticles are in cubic shape and the side-length is between 20 and 25 nm. The size distribution is relatively uniform and there is no much difference in shape and size for distinguished nanoparticles. The nanoparticles can be well dispersed in ethanol and chloroform.

Figure 4-1 XRD spectrum of as-prepared Fe₂O₃ nanoparticles. The pattern is compared with standard database JCPDS 79-1741 (Hematite, syn).
Results and Discussion

4.1.3 Characterization of composite film

4.1.3.1 UV-Vis spectroscopy

UV-Vis transmission was obtained while constructing hematite film onto the ITO glass substrate through spin-coating. By repeating the spin-coating program as indicated in experimental section, transmission spectra were obtained after a series number of repeat times to confirm the successful deposition. The transmission percentage is gradually decreased with the number of repeat spin-coating times, as shown in Figure 4-3. The program of spin-coating is fixed as indicated in experimental section to ensure the repeatability of construction with coherent thickness in the following experiments.

After each layer of coating, photo-electrode was examined by diffuse reflectance and the absorbance was calculated by the equation: \( A = \log \left( \frac{100}{R} \right) \), where \( A \) is the absorption and \( R \) is the diffusion reflectance that measured by UV-Vis-NIR photospectrometer. As shown in Figure 4-4, absorption peak around 550 nm after 1st layer deposition is the typical visible light range absorption of Fe₂O₃.[151] The peak position is coherent to the 2.1 eV band gap

Figure 4-2 TEM images of as-prepared Fe₂O₃ nanoparticles.
Results and Discussion

energy of hematite. After 2\textsuperscript{nd} layer construction, the peak position is blue shifted to 480 nm, which is due to the Au plasmonic resonance effect.[125] After 3\textsuperscript{rd} layer construction, there are a significant absorption peak around 480 nm and a small shoulder around 560 nm in the spectrum, which are corresponding to Au and Fe\textsubscript{2}O\textsubscript{3} respectively. Therefore, a broad absorption between 420 nm to 590 nm can be achieved after the construction of the sandwich structure, such confirms the broad visible light absorption ability of the Fe\textsubscript{2}O\textsubscript{3}/Au/Fe\textsubscript{2}O\textsubscript{3} composite film. The color change of the ITO glass slides after each layer coating in Figure 4-5 can also be observed corresponding to the absorption spectra. After the first layer coating of Fe\textsubscript{2}O\textsubscript{3}, the color of the slide is red, the typical color of Fe\textsubscript{2}O\textsubscript{3} nanoparticles. The color of the slides changes to dark green after Au layer deposition, and becomes dark red after the top layer coating of Fe\textsubscript{2}O\textsubscript{3}.

![Transmission spectra of ITO glass spin-coated with hematite nanoparticles.](image)

Figure 4-3 Transmission spectra of ITO glass spin-coated with hematite nanoparticles.
Results and Discussion

Figure 4-4 Absorption spectra of the films after each layer construction (calculated from diffuse reflectance spectra).

Figure 4-5 Photos of (a) Fe$_2$O$_3$, (b) Fe$_2$O$_3$/Au, and (c) Fe$_2$O$_3$/Au/Fe$_2$O$_3$ films on ITO glass substrates. Scale bar is the same for all three images.

4.1.3.2 FESEM imaging

The morphology of the spin-coated Fe$_2$O$_3$ film was examined by capturing images under FESEM. FESEM images of Fe$_2$O$_3$ film after ozone cleaning and annealing was obtained as
shown in Figure 4-6. Compact and full coverage of nanoparticles on the substrate surface can be achieved, although some large Fe$_2$O$_3$ particles with the size around 100 nm can also be observed. These large nanoparticles are not evitable in Fe$_2$O$_3$ synthesis.[167]

![Figure 4-6 FESEM images of spin-coated Fe$_2$O$_3$ layer.](image)

After completing the construction of composite Fe$_2$O$_3$/Au/Fe$_2$O$_3$ film, top-view and side-view FESEM image was obtained. From the top-view image in Figure 4-7, the surface is covered by the cubic nanoparticles, which is the morphology of the outermost layer of Fe$_2$O$_3$. The surface is not perfectly flat due to stacking of some nanoparticles. However, single nanoparticles can still be clearly distinguished and there are no visible cracks or fusion aggregates. The side-view image in Figure 4-8 shows the thickness of the three layers. The bottom solid layer with thickness of 200 nm is the conducting ITO coated on the glass substrate. The subsequent layer with thickness around 200 nm is the bottom layer of Fe$_2$O$_3$. Some imperfection such as holes and large particle can be observed in this layer. The intermediate Au layer is not as clear as the Fe$_2$O$_3$ layer due to significant surface charging between these two layers. The thickness of this Au layer is not easy to distinguished, however, it is still can be estimated less than 50 nm and does not alter the flatness of the bottom layer.
The top \( \text{Fe}_2\text{O}_3 \) layer has a thickness between 500 nm and 550 nm and there is a tight connection between top and bottom layers of \( \text{Fe}_2\text{O}_3 \).

Figure 4-7 FESEM images of spin-coated \( \text{Fe}_2\text{O}_3/\text{Au}/\text{Fe}_2\text{O}_3 \) composite film (top view).

Figure 4-8 FESEM images of spin-coated \( \text{Fe}_2\text{O}_3/\text{Au}/\text{Fe}_2\text{O}_3 \) composite film (side view) and indication of thickness.
4.1.4 Photo-response of composite film

4.1.4.1 Photo-current under visible-light irradiation

The composite electrode was immersed into PBS electrolyte (pH=7) to test the photocurrent under visible-light irradiation with an external potential bias. The measured photo-current density was plotted as a function of applied potential in dark and illumination conditions, as presented in Figure 4-9. The photoconversion performance of the sandwich Fe$_2$O$_3$/Au/Fe$_2$O$_3$ photo-electrode is clearly enhanced compared to $\alpha$-Fe$_2$O$_3$ electrode. The photo-current of the sandwich electrode starts to appear even with applied potential less than 0.1 V, and it rises fast at potential around 0.5 V. In contrast, the photo-current of pure $\alpha$-Fe$_2$O$_3$ can merely be observed before the potential reaches 1.0 V. Such cathodic shift of the onset potential by up to 0.5 V implies that there is much less electric energy input required to initiate the electron transfer in the sandwich electrode. The photo-current density of sandwich electrode increases up to 0.8 mA cm$^{-2}$ compared to pure $\alpha$-Fe$_2$O$_3$ electrode, indicating the excellent visible-light photo-response of the sandwich electrode under low potential bias. The smaller onset potential of sandwich electrode in dark suggests that the Au layer is not fully covered by the top Fe$_2$O$_3$ layer and the exposed Au may catalyse the water oxidation reaction even without light illumination. This is consistent with the fact that the top Fe$_2$O$_3$ layer is porous as shown in the SEM image in Figure 4-8. However, this possibility of Au catalysis effect does not contribute to the photocurrent increment at high potential bias (usually above 1.3 V relative to Reversible Hydrogen Electrode, i.e. RHE), according to previous researchers’ experimental study.[168-169]
Results and Discussion

Figure 4-9 Graphs of current densities of Fe$_2$O$_3$ and Fe$_2$O$_3$/Au/Fe$_2$O$_3$ photoanodes as a function of electrode potential relative to Ag/AgCl reference electrode in PBS buffer electrolyte (pH=7).

By setting the bias potential to 1.0 V relative to Ag/AgCl reference electrode (~ 1.3 V/RHE) to block the Au catalysis effect, the photo-current density was recorded as a function of time with regular switching ON/OFF of light source, as shown in Figure 4-10. A sharp increase of the photo-current can be observed when the light source is ON, while a significant drop can be seen when the light source is OFF. The instantaneous current increase measures the flux of holes to the surface of the electrode and it is usually followed by an immediate decay until a steady state current is reached.[170] The magnitude of the decayed current density, which usually indicates the electron flux due to charge recombination, is small for the sandwich electrode, suggesting the small chance of charge carriers’ recombination upon photo-induced excitation. There is no obvious cathodic current overshoot immediately after the light source is switched off, indicating that the surface electron-hole recombination is retarded as well.[171] The steady state photo-current density saturates at 15 µA cm$^2$, and it is
repeatable after 5 cycles. All these results suggest the photocatalytic performance is significantly improved by using this sandwich photo-electrode.

Figure 4-10 Graph of current density as a function of time for sandwich electrode at 1.0 V relative to Ag/AgCl reference electrode with visible light illumination switching ON and OFF every 30 sec.

4.1.4.2 IPCE evaluation

As mentioned in section 2.2.4, IPCE is a very important approach to evaluate the performance of PEC cells. It measures the effectiveness of energy conversion between incident photon and charge carriers within the flow between cathode and anode electrodes. IPCE is calculated by measuring the generated photocurrent in a PEC cell when illuminated with an incident light in a particular wavelength or a small range of wavelengths. Equation 2-5 shows the calculation of IPCE values by knowing incident power density at certain wavelength $\lambda$ and photocurrent density at the corresponding wavelength $\lambda$. Plotting of the
IPCE value with respect to wavelength is also a useful way to illustrate the wavelength range that is actually absorbed and eventually utilized by certain photo-electrode.[169]

A monochromator (ASAHI SPECTRA, CMS 100) coupled with 300W Xenon lamp (ASAHI SPECTRA, MAX-302) was used as the illumination source. By using the same three-electrode configuration setup as previously mentioned, monochromatic irradiation was varied from 400 nm to 700 nm with an increment of 25 nm. IPCE was calculated accordingly and plotted as a function of incident light wavelength in Figure 4-11. Due to the limitation of the incident light intensity and single side irradiation, the absolute value of IPCE measurement is relatively small. However, a significant improvement can be observed by comparing the results of sandwich electrode and pure Fe$_2$O$_3$ electrode. The increment is more significant between 450 nm to 600 nm, and the IPCE value is doubled at 475 nm. This wavelength range is overlapped to the light absorption peak of Fe$_2$O$_3$ and plasmonic gold nanoparticles. Therefore, a significant enhancement of visible light harvesting capability below 600 nm can be confirmed for the sandwich electrode.
Results and Discussion

Figure 4-11 IPCE measurement of sandwich electrode and pure Fe$_2$O$_3$ electrode at 1.0 V relative to Ag/AgCl reference electrode in PBS buffer (pH=7).

4.1.5 Role of Au intermediate layer

After observing the significant improvement of the photo-current after inserting the Au intermediate layer in between of the two Fe$_2$O$_3$ layers, it can be implied that the Au layer may play an essential role to enhance the photo-response. In order to investigate the role of Au intermediate layer, it was replaced by either conductive layer or Au nanoparticle deposition, and the thickness of Au layer is varied, as discussed as in the following sections.

4.1.5.1 Replacing Au intermediate layer by conductive materials

Considering the metallic nature of Au, the Au intermediate layer was replaced by conductive Pt or ITO to examine whether the Au layer solely plays a role of conductive linkage between two Fe$_2$O$_3$ layers.
Similar to Au, Pt is also a well-known noble metal which has a Fermi energy level lower than that of semiconductor photocatalysts and can entrap the photo-induced electrons from adjacent semiconductors. However, Pt does not possess the plasmonic effect as Au. Therefore, Pt is used to replace the Au intermediate layer via exactly the same sputtering process with Pt target (99.999%). The sandwich structure of Fe$_2$O$_3$/Pt/Fe$_2$O$_3$ was then examined as a photoanode under the same condition as Fe$_2$O$_3$/Au/Fe$_2$O$_3$ electrode. The photo-current of Fe$_2$O$_3$/Pt/Fe$_2$O$_3$ as a function of applied potential bias was plotted in comparison to Fe$_2$O$_3$/Au/Fe$_2$O$_3$ as shown in Figure 4-12. The light and dark current of Fe$_2$O$_3$/Pt/Fe$_2$O$_3$ electrode have onset potential lower than 0.1 V, very close to that of Fe$_2$O$_3$/Au/Fe$_2$O$_3$ electrode. This suggests the conductive Pt intermediate layer contribute in reducing the energy barrier to initiate the electron transfer. However, the photo-current of the Fe$_2$O$_3$/Pt/Fe$_2$O$_3$ electrode is less than 0.1 mA cm$^{-2}$ even when the potential bias is up to 1.0 V, which is 0.7 mA cm$^{-2}$ smaller than that of Fe$_2$O$_3$/Au/Fe$_2$O$_3$ electrode at 0.8 V. This huge difference implies the additional contribution of Au layer in photocatalytic activity. The dark current of Fe$_2$O$_3$/Pt/Fe$_2$O$_3$ electrode also suggests the surface catalytic activity of exposed metallic Pt which is not fully covered by top Fe$_2$O$_3$ layer. Such phenomenon is similar to Au, as mentioned in the previous section.
Figure 4-12 Graphs of current densities of Fe\textsubscript{2}O\textsubscript{3}/Au/Fe\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{2}O\textsubscript{3}/Pt/Fe\textsubscript{2}O\textsubscript{3} photoanodes as a function of electrode potential relative to Ag/AgCl reference electrode in PBS buffer electrolyte (pH=7).

ITO is widely used as a transparent conducting coating in electrode applications. It is an n-type semiconductor with wide band gap energy around 4 eV. Thin ITO layer was prepared by DC sputtering in between of two Fe\textsubscript{2}O\textsubscript{3} layers, following Song’s protocol.[172] The sandwich structure of Fe\textsubscript{2}O\textsubscript{3}/ITO/Fe\textsubscript{2}O\textsubscript{3} was then examined as a photoanode under the same condition as Fe\textsubscript{2}O\textsubscript{3}/Au/Fe\textsubscript{2}O\textsubscript{3} electrode and the resulted photo-current as a function of applied potential bias relative to Ag/AgCl reference electrode was plotted in comparison to Fe\textsubscript{2}O\textsubscript{3}/Au/Fe\textsubscript{2}O\textsubscript{3} as shown in Figure 4-13. Although the onset potential of Fe\textsubscript{2}O\textsubscript{3}/ITO/Fe\textsubscript{2}O\textsubscript{3} electrode at 0.9 V is lower than that of pure Fe\textsubscript{2}O\textsubscript{3} as in Figure 4-9, it is much higher than that of Fe\textsubscript{2}O\textsubscript{3}/Au/Fe\textsubscript{2}O\textsubscript{3} electrode. There is no photo-current observed at 0.8 V. All these results imply that the photocatalytic activity of the sandwich structure is highly reduced when the Au
layer is replaced by ITO conductive layer. Therefore, it is double confirmed that the Au layer does not solely play a role as a conducting linkage between two Fe$_2$O$_3$ layers.

![Graph](image)

Figure 4-13 Graphs of current densities of Fe$_2$O$_3$/Au/Fe$_2$O$_3$ and Fe$_2$O$_3$/ITO/Fe$_2$O$_3$ photoanodes as a function of electrode potential relative to Ag/AgCl reference electrode in PBS buffer electrolyte (pH=7).

4.1.5.2 Effect of varying Au layer thickness

It is proved in last section that Au layer has contribution in photocatalytic activity in addition to the effect of enhancing electron transfer as a conductive layer. As mentioned in section 2.3.2.3, Au has a special plasmonic effect that may assist in light harvesting and energy localization. Since the light harvesting behaviour is closely related to the volume of the plasmonic metal, the thickness of Au layer was varied to investigate its effect on plasmonic light harvesting. Two more samples with Au layer thickness of 5 nm and 10 nm were prepared by varying sputtering time under the same sputtering condition.
Figure 4-14 SEM images of Fe$_2$O$_3$/Au films with varied thickness of Au layers.
The resulted Fe$_2$O$_3$/Au films were examined by FESEM imaging before top layer Fe$_2$O$_3$ deposition, as in Figure 4-14. In the image of 5 nm Au layer, the morphology of cubic Fe$_2$O$_3$ is well maintained and sharp cubic edges can be clearly distinguished. In the image of 10 nm Au layer, the sharp edges can still be observed for large cubic particles, however, the edges of small cubic particles become round. In the image of 30 nm Au layer, round granules instead of cubic particles are present and gaps between adjacent granules can still be distinguished. Therefore, it can be summarized that with the thickness increase, the bottom cubic nanoparticles are gradually capsulated by sputtered Au nanoparticles. In another word, the Au layer is uniformly deposited on single Fe$_2$O$_3$ nanoparticles instead of forming a solid layer on top of the Fe$_2$O$_3$ layer. Thus, it can be implied that the thickness of Au layer may be thinner than the estimated value according to sputtering speed and time.

The sandwich structure of Fe$_2$O$_3$/Au/Fe$_2$O$_3$ with varied Au thickness were examined as photoanodes and the resulted photo-current as a function of applied potential bias relative to Ag/AgCl reference electrode was plotted in Figure 4-15. The photo-current of all the three samples rises rapidly at the same potential bias value (~0.6 V), indicating they have similar effects on electron transfer enhancement. However, by comparing the photo-current at 0.8 V, the values of the current density increase with the thickness. The photo-current of sandwich electrode with 30 nm Au layer is more than twice of the photo-current of the sample with 5 nm Au layer. Thus, the contribution of Au layer on photocatalytic activity is correlated to the thickness, which coincides with the nature of plasmonic effect. Therefore, we may predict that in addition to promoting electron transfer, the plasmonic effect of the Au nanoparticles is responsible for the further enhancement of the photocatalytic activity of the sandwich electrode.
Results and Discussion

Figure 4-15 Graphs of current densities of Fe$_2$O$_3$/Au/Fe$_2$O$_3$ photoanodes with varied thickness of Au layers as a function of electrode potential relative to Ag/AgCl reference electrode in PBS buffer electrolyte (pH=7).

4.1.5.3 Replacing Au sputtering by Au nanoparticle deposition

Oleic acid capped Au nanoparticles were synthesized following Si’s route.[149] The sharp UV-Vis absorption of the Au nanoparticle solution as in Figure 4-16 indicates the successful synthesis of well-dispersed Au nanoparticles with SPR band at around 520 nm. The Au nanoparticles were then spin-coated to Fe$_2$O$_3$ layer and the construction of two Fe$_2$O$_3$ layer remains the same. The resulted sandwich structure was denoted as Fe$_2$O$_3$/Au NP/Fe$_2$O$_3$ and examined as photoanodes. The photo-current as a function of applied potential bias relative to Ag/AgCl reference electrode was plotted in Figure 4-17 and compared with standard Fe$_2$O$_3$/Au/Fe$_2$O$_3$. The onset potential of the photo-current of two samples are similar, however, the enhancement of the current below 0.9 V is highly reduced for the sandwich electrode with Au nanoparticles compared to the standard one. When the potential is raised
up to 1.0 V, the photo-current of the Fe₂O₃/Au NP/Fe₂O₃ electrode is significantly enhanced and become comparable to standard sandwich electrode.

This two-stage performance of the Fe₂O₃/Au NP/Fe₂O₃ electrode may be due to the inefficient electron transfer from plasmonic excited gold nanoparticles to adjacent Fe₂O₃. Since the as synthesized Au nanoparticles are stabilized within the oleic acid micelles, the non-conductive layer of oleic acid may prevent direct charge exchange between Au and Fe₂O₃. This additional energy barrier can be overcome when external potential bias increased to certain level so that the significant enhancement of photo-current can therefore be observed. Although the radiative energy transfer may still take place, the highly reduced photo-current of Fe₂O₃/Au NP/Fe₂O₃ electrode compared to standard Fe₂O₃/Au/Fe₂O₃ electrode implies that the direct plasmonic excited charge transfer may play an essential role in enhancing the photocatalytic activity performance while the near-field energy localization effect may play a minor role in the enhancement. This can be understood because the near-field electromagnetic enhancement of Au plasmonic effect is not homogeneous. It is most intensely localized at the interface between plasmonic metal, semiconductor and water, and decrease exponentially or linearly with distance from the surface.[118] According to Thimsen’s study, the Au nanoparticles that embedded within the semiconductor may induce very limited SPR near-field radiative enhancement on photocatalytic activity.[169] In our system, although the top layer Fe₂O₃ is porous, the interface between Au, Fe₂O₃ and water is quite limited, thus the near-field radiative enhancement is limited as well.
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Figure 4-16 Absorption spectrum of synthesized Au nanoparticles.

Figure 4-17 Graphs of current densities of Fe$_2$O$_3$/Au/Fe$_2$O$_3$ photoanodes with sputtered Au and Au nanoparticle layer (denoted as Au NP) as a function of electrode potential relative to Ag/AgCl reference electrode in PBS buffer electrolyte (pH=7).
4.1.6 Role of bottom and top Fe$_2$O$_3$ layers

In order to investigate the function of bottom Fe$_2$O$_3$ layer, an Au/Fe$_2$O$_3$ electrode was prepared by direct sputtering the Au layer onto ITO substrate followed by Fe$_2$O$_3$ spin coating. The photo-current of Au/Fe$_2$O$_3$ electrode as a function of applied potential bias relative to Ag/AgCl reference electrode was plotted and compared to that of Fe$_2$O$_3$/Au/Fe$_2$O$_3$ electrode in Figure 4-18. The onset potential of Au/Fe$_2$O$_3$ electrode is increased by 0.1 V compared to that of Fe$_2$O$_3$/Au/Fe$_2$O$_3$ electrode, and the photo-current at 0.8 V is less than half of that of Fe$_2$O$_3$/Au/Fe$_2$O$_3$ electrode. Both of the results suggest the decrease of the photocatalytic activity performance. This result confirms that the plasmonic excited electrons need to be fast injected into the conduction band of adjacent semiconductors; otherwise, these hot electrons may not contribute in light energy harvesting. Therefore, besides the possible light harvesting function, the bottom Fe$_2$O$_3$ is necessary to provide appropriate energy level for efficient electron transfer.

Fe$_2$O$_3$/Au film was also constructed to investigate the function of top Fe$_2$O$_3$ layer. By setting the bias potential to 1.0 V relative to Ag/AgCl reference electrode (~ 1.3 V RHE$^{-1}$) to block the Au catalysis effect, the photo-current density was recorded as a function of time with regular switching ON/OFF of light source, as shown in Figure 4-19. Similar to the result of Fe$_2$O$_3$/Au/Fe$_2$O$_3$ electrode, sharp increase/decrease of the photo-current can be observed when the light source is ON/OFF. However, both of the high magnitude of the decayed current density up to 12 µA cm$^{-2}$ and high cathodic current overshoot up to 6 µA cm$^{-2}$ suggest the high rate of charge recombination. The steady state photo-current density is 13 µA cm$^{-2}$, 87% of that of Fe$_2$O$_3$/Au/Fe$_2$O$_3$ electrode. Comparing this photo-current pattern with previous Fe$_2$O$_3$/Au/Fe$_2$O$_3$ electrode, it can be deduced that the top layer Fe$_2$O$_3$ also contributes in minor light harvesting and plays an essential role in reducing surface charge recombination.
Results and Discussion

Figure 4-18 Graphs of current densities of Fe$_2$O$_3$/Au/Fe$_2$O$_3$ and Au/Fe$_2$O$_3$ photoanodes as a function of electrode potential relative to Ag/AgCl reference electrode in PBS buffer electrolyte (pH=7).

Figure 4-19 Graph of current density as a function of time for Fe$_2$O$_3$/Au electrode at 1.0 V relative to Ag/AgCl reference electrode with visible light illumination switching ON and OFF every 30 sec.
4.1.7 Proposed mechanism

Based on the above discussion, an electron transfer mechanism was proposed to explain the significant enhancement of photocatalytic activity of Fe₂O₃/Au/Fe₂O₃ electrode, as illustrated in Figure 4-20. Although the Au plasmonic excitation is responsible for the major visible light harvesting, the contribution in light absorption of bottom and top layer Fe₂O₃ can be observed in previous results. Therefore, upon light irradiation on both sides of the photoanode, the electron excitation happens in all the three layers respectively. The plasmonic excited electrons in Au layer are fast injected to the conduction band of bottom Fe₂O₃ layer under small potential bias. Due to the metallic nature of the Au, photo-induced electrons in top Fe₂O₃ layer are attracted by the Au and direct to transfer to the conduction band of the bottom Fe₂O₃ layer as well. Therefore, under the external driving force of small potential bias, the electrons in the conduction band of Fe₂O₃ are transferred to the ITO substrate and flow to the Pt cathode to participate in water reduction to produce H₂. The photo-induced holes migrate to the surface of the top Fe₂O₃ and participate in water oxidation to produce O₂. Fe₂O₃ has a band gap of 2.13 V and its valence band at + 2.47 V is much more positive than the oxidation level of H₂O/O₂ (+ 0.82 V) and thus can contribute to the O₂ evolution.

By inserting the Au layer, the photoanode can benefit in two ways: On one hand, the plasmonic excitation of Au layer brings the strong light harvesting capability, and all the hot electrons can be injected to Fe₂O₃ due to the low Fermi level of plasmonic Au compared to Fe₂O₃. On the other hand, the Au metallic and highly conductive nature can attract photo-induced electrons from top Fe₂O₃ layer, and contribute in reducing the electron-hole recombination. In addition, although the Au SPR induced near-field radiative energy transfer at the Au, Fe₂O₃ and water interface is limited as mentioned in previous sections, this effect
cannot be excluded. Therefore, the photocatalytic activity performance of the photoanode is highly improved by the Au intermediate layer.

![Illustration of electron transfer mechanism of Fe$_2$O$_3$/Au/Fe$_2$O$_3$ electrode. Arrows show the electron flow direction.](image)

**Figure 4-20** Illustration of electron transfer mechanism of Fe$_2$O$_3$/Au/Fe$_2$O$_3$ electrode. Arrows show the electron flow direction.

### 4.1.8 Short summary

In summary, a sandwich structure of Fe$_2$O$_3$/Au/Fe$_2$O$_3$ photo-electrode was successfully constructed with the purpose of improving the PEC water splitting performance compared to pure $\alpha$-Fe$_2$O$_3$ electrode. The photocatalytic activity tests showed that the onset potential of this sandwich photoanode was reduced to less than 0.1 V and the steady state photo-current at 1.0 V was increased from zero to 15 µA cm$^{-2}$ compared to pure $\alpha$-Fe$_2$O$_3$ electrode. The mechanism study revealed the essential role of Au intermediate layer to enhance light harvesting and electron transfer. The enhancement attribute to the Au plasmonic effect and its conductive nature. The effects can be summarized as follows: (1) Plasmonic excitation of Au under visible light irradiation can generate photo-electrons and inject into conduction band of
bottom Fe₂O₃ layer, and thus contribute in visible light harvesting. (2) The metallic and highly conductive nature of the Au allows the photo-induced electrons and holes to possess relatively high mobility, and thus achieves more efficient electron transfer between top and bottom Fe₂O₃ layers. Such sandwich structure in constructing photo-electrode may be applied to other semiconductors to improve their PEC water splitting performance.
4.2 Nanoparticle Heterojunctions in ZnS-ZnO Hybrid Nanowires for Visible-Light-Driven Photocatalytic Hydrogen Generation

4.2.1 Introduction

Solar water splitting for hydrogen production is a green technique to generate clean energy and a promising way to solve energy shortage and environmental problem caused by fossil fuels.[173] Since the first report of solar water splitting in 1972, many semiconductors have been investigated to work as photocatalyst such as TiO$_2$, ZnO and ZnS.[5,174-175] However, these semiconductors are only capable of absorbing UV light energy due to their large band gap energy. Researchers have found that intermediate states may be created when semiconductors have impurities or defects within their crystal structures. These intermediate states have the potential to induce visible-light activities.[176] However, fast photoinduced charge recombination may be induced when electrons were excited from these intermediate states, and thus the practical usage of such intermediate states excitation is very limited.

It is well known that elaboration of nano-heterostructures allows us to fabricate and optimize material functionalities which may not be easily achieved by modification of single material. Therefore, many efforts have been made to couple two semiconductors with proper band gap energy levels to form nanocomposite in achieving synergetic effect.[177-178] Hetero-nanostructures that combine multiple semiconductors in one hybrid nanoscale structure have appeared to possess synergistically reinforced features, which are otherwise inaccessible in any of the single component or their physical mixture. Interfacial charge transfer within the hetero-nanostructures may retard the photoinduced charge recombination process and contribute in improving the charge separation on both units of semiconductors.[179-181] Furthermore, interfacial states created by coupling two semiconductors may induce visible-light activities and further enhance charge transfer.
Therefore, the strategy of creating nano-heterojunctions via large-band-gap semiconductors coupling may introduce new opportunities of visible-light-driven activities and charge separation enhancement, and finally contribute to higher photocatalytic efficiency.

Among the large-band-gap semiconductors, ZnS-ZnO hybrid nanostructure would be ideally to explore such opportunities. ZnO and ZnS are abundant, stable and cheap semiconductors with wide direct band gap energy ($E_g=3.4$ eV for ZnO and $E_g=3.7$ eV for ZnS) to efficiently absorb UV light.[175,182-187] Recently, various ZnS-ZnO nanocomposites are developed and reported in forms of quantum dots[188], nanorods[189-190], multipods[191], nanotubes[192], nanobelts[193-195] and nanosheets[196] et al. Among these research studies, visible-light activity was discovered in dye degradation experiments and explained by interfacial charge transfer. However, few of them have used ZnS-ZnO composite to explore the hydrogen evolution capability under visible-light irradiation.

In this section, ZnS-ZnO hybrid nanowires which are composed of well-distributed nanoparticle-heterojunctions are fabricated and show significant visible-light-induced hydrogen generation even without loading noble metal co-catalysts. Studies on growth process and electron transfer mechanism reveal the crucial role of ZnS-surface-states which is created by heterojunctions on ZnO nanoparticle surfaces and responsible for the visible-light-driven activities.

**4.2.2 Characterization of the ZnS-ZnO hybrid nanowires**

ZnS-ZnO nanocomposite was synthesized via one-step hydrothermal reaction, as mentioned in Experimental section. Figure 4-21 shows the XRD pattern of the as-synthesized ZnS-ZnO nanocomposite sample ZZ-a. All the diffraction peaks of the sample ZZ-a can perfectly coincide with the standard XRD peaks of ZnS (JCPDS no. 80-0020) and ZnO.
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(JCPDS no. 70-2551). The intense and sharp diffraction peaks shows the high crystallinity of the two components, i.e. ZnO and ZnS. There are no other impurities which do not belong to the two components in the XRD pattern. Such confirms the successful synthesis of the composite material consisting of ZnO and ZnS only.

![XRD pattern of as-prepared ZnS-ZnO nanocomposite sample ZZ-a.](image)

The morphology of the ZnS-ZnO nanocomposite was characterized by capturing SEM images. As shown in Figure 4-22, the as-synthesized ZnS-ZnO nanocomposite product is in the form of nanowires with a uniform diameter less than 200 nm. These nanowires are tangled together and the length can be extended up to several micro meters. The surfaces of these nanowires are smooth and no other shaped morphology can be observed. EDS spectrum of the ZnS-ZnO nanocomposite sample ZZ-a in Figure 4-23 confirms that the nanowire is composed of three elements only: Zn, O and S. The peaks of Al and C elements come from sample holder and carbon tape. In order to further analyse the element distribution within the nanowires, EDS mapping was conducted. The elemental mapping results in Figure 4-23
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indicate that the three elements of Zn, S and O have a homogeneous distribution in the composite nanowires.

Figure 4-22 SEM image of the as-prepared ZnS-ZnO nanocomposite sample ZZ-a. The inset is the image at a higher magnification.

Figure 4-23 EDS mapping of Zn, S and O elements in ZnS-ZnO nanowires.
The microstructure of the ZnS-ZnO nanowires was characterized by TEM imaging. The TEM image in Figure 4-24 (A) confirms the nanowire structure with a diameter between 100 nm to 200 nm, as coherent to that in SEM images. It is also revealed that these nanowires are formed by nanoparticle agglomeration. The inset of Figure 4-24 (A) shows the SAED pattern of the nanowires and suggests the co-existence of ZnS and ZnO diffraction features. Such confirms that both of ZnS and ZnO nanocrystals are present in the nanowire. The high-resolution TEM (HRTEM) image of the nanowire in Figure 4-24 (B) shows the lattice fringes, and an interface can be clearly observed with an interplanar distance of 0.19 nm on the left hand side and 0.31 nm on the right hand side. These two interplanar distances are corresponding to ZnO (102) and ZnS (111) planes respectively. Therefore, it can be revealed that ZnS and ZnO nanocrystals form nanoparticle-heterojunctions within the nanowire structure. Similar ZnS-ZnO nano-heterojunctions can be observed in many other regions in the ZnS-ZnO nanowires, as shown in HRTEM images in Figure 4-25. One ZnS nanocrystal can be observed to form multiple nano-heterojunctions with surrounding ZnO nanocrystals, and vice versa. It can be concluded that the ZnS-ZnO nanocomposite is composed of hybrid ZnS and ZnO nanocrystals, and the nano-heterojunctions in between of the two nanocrystals may play an important role in determining the optical and photocatalytic properties of these ZnS-ZnO hybrid nanowires.
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Figure 4-24 (A) TEM image of the as-prepared ZnS-ZnO nanocomposite, the inset shows SAED pattern of image A. (B) HRTEM of ZnS-ZnO interface region in the nanowire.

Figure 4-25 TEM images of ZnS-ZnO nanoheterostructure in multiple regions within ZnS-ZnO nanowires.
4.2.3 Growth process analysis of the ZnS-ZnO hybrid nanowires

Growth process of ZnS-ZnO hybrid nanowires was monitored by investigating samples with varied reaction time from 2 h to 5 h. The resulted samples were characterized by the same process as for sample ZZ-a. Figure 4-26 shows the XRD patterns of all the samples with reaction time varying. The XRD pattern of 2 h sample has no detectable peaks, and such suggests that no crystallization has happened before 2 h. In the XRD pattern of 4 h sample, peaks that matched to ZnS (JCPDS no. 80-0020) are significant and dominating; while peaks that matched to ZnO (JCPDS no. 70-2551) cannot be observed clearly. This implies that ZnS is formed in the first 4 h reaction and grows to be the major crystallized product while ZnO is the minor one. To further confirm this deduction, TEM images and SAED pattern of 4 h sample were taken and shown in Figure 4-27. The nanowire morphology can be observed again, similar to previous ZZ-a sample. However, diffraction signatures of ZnO is absent in the SAED pattern of the sample at 4 h reaction time, and only diffraction signatures of ZnS can be observed. This result is consistent to the XRD result and double confirms the formation of ZnS nanowires as the major product in the first 4 h reaction time. Therefore, at the early stage of the growth of hybrid nanowire, ZnS nanoparticulated wires are formed first via the reaction between zinc precursor and sulphur precursor, i.e. zinc acetate and SH- group in MHA.

When the reaction time extended from 4 h to 10 h, the XRD signature peaks of ZnO is growing continuously and become evident from 8 h onwards. Combining this observation with the TEM analysis of sample ZZ-a with 10 h reaction time, it can be suggested that the ZnO component in the hybrid nanowires increases with the reaction time. Based on the above results and the absence of free ZnO particles in observation, we can deduced that the ZnO nanocrystals were formed via the reaction between zinc ions (Zn$^{2+}$) and the carboxylate group
(RCOO-) of MHA and then inserted into the pre-formed ZnS nanowire framework. The possibility of forming ZnO from direct oxidation of ZnS is excluded because the intensity of XRD peaks matching to ZnS was not weakened during the growth of the ZnO peaks from 4 h to 10 h.

When the reaction time is further prolonged to 15 h, the intensity of XRD peaks matching to ZnO does not increased further relative to the ZnS peaks, as shown in Figure 4-26. This phenomenon is further confirmed by obtaining the relative molar ratio of ZnS and ZnO in EDS examination. As shown in Table 4-1, the relative molar ratio remains to be 1.3:1 for ZnS vs ZnO when reaction time varying from 10 h to 15 h. Therefore, the composition of ZnS-ZnO hybrid nanowires tends to be stable from 10 h onwards.

![XRD patterns of products with different reaction time varying from 2 h to 15 h.](image)

Figure 4-26 XRD patterns of products with different reaction time varying from 2 h to 15 h.
Results and Discussion

Figure 4-27 TEM image of the product after 4 h reaction, the inset shows SAED pattern of the TEM image.

Table 4-1 EDS elemental ratio of the ZnS-ZnO nanocomposite with different reaction time.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S:Zn Atomic %</th>
<th>ZnS: ZnO molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZZ-10h</td>
<td>0.570</td>
<td>1.3:1</td>
</tr>
<tr>
<td>ZZ-15h</td>
<td>0.568</td>
<td>1.3:1</td>
</tr>
</tbody>
</table>

4.2.4 Photocatalytic activity of ZnS-ZnO hybrid nanowires in hydrogen evolution

In order to check the photocatalytic activity of ZnS-ZnO hybrid nanowires, hydrogen generation was monitored under visible light ($\lambda > 420$ nm) irradiation in mixed aqueous solution of 0.25 M Na$_2$S and 0.35 M Na$_2$SO$_3$ as sacrificial reagent. It is well known that ZnS and ZnO alone can only be activated by UV-light irradiation, owing to their large band gap energy. In our experiments, photocatalytic hydrogen generation of commercial ZnS (99.99 %,
Results and Discussion

denoted as C-ZnS, XRD pattern shown in Figure 4-28 A) and ZnO (99.999 %, denoted as C-ZnO, XRD pattern shown in Figure 4-28 B) were tested and there was no hydrogen evolved under visible light irradiation. In contrast, ZnS-ZnO hybrid nanowire sample ZZ-a shows active photocatalytic hydrogen generation with a rate of 22 µmol·h⁻¹·g⁻¹ under visible light irradiation, as in Figure 4-29. The hydrogen evolution test of sample ZZ-a was repeated for three times with thorough Ar gas purging for 1 h in between of each testing cycle. The sample shows good stability over 12 h photocatalytic reaction and the hydrogen evolution rate remains constant for all the three repeating cycles, as in Figure 4-30. Therefore, the ZnS-ZnO hybrid nanowires exhibit active and stable visible-light-driven hydrogen generation.

To further analyse the factors that may affect the hydrogen evolution, comparison samples were synthesized under the same route with increased quantity of either zinc precursor (denoted as ZZ-b) or sulphur precursor (denoted as ZZ-c). XRD peak positions of these two samples can be identified to be the same as sample ZZ-a, in Figure 4-31. However, the relative peak intensities of ZnS and ZnO components are varied for each sample. The relative molar ratio of ZnS to ZnO was further analysed by EDS, as shown in Table 4-2. The results reveals that ZnS-ZnO molar ratio is 1.3:1 for sample a, while this ratio is increased to 3:1 for sample ZZ-c and decreased to 1:1.33 for sample ZZ-b. Thus, by varying the precursor quantity, ZnS-ZnO hybrid nanowires with different ZnS-ZnO molar ratio were successfully synthesized. The visible-light-driven hydrogen generation was also tested by using the two comparison samples as the photocatalyst. Active hydrogen evolution was observed again, however, the hydrogen evolution rate of ZZ-b and ZZ-c was not as high as that of sample ZZ-a. As shown in Figure 4-29, ZZ-b and ZZ-c have a hydrogen evolution rate of 7 µmol·h⁻¹·g⁻¹ and 16 µmol·h⁻¹·g⁻¹, respectively. The results double confirm the active photocatalytic activity of ZnS-ZnO hybrid nanowires under visible light irradiation. It is also implied that
relative quantity of the two components in the hybrid nanowires has significant influence on the photo-activity.

![XRD patterns](image)

Figure 4-28 XRD patterns of commercial (A) ZnS and (B) ZnO.

![H₂ rate comparison](image)

Figure 4-29 Comparison of visible light H₂ evolution activities of ZnS-ZnO nanocomposite samples in mixed aqueous solution of 0.25 M Na₂S and 0.35M Na₂SO₃ as sacrificial reagent. Light source: 300 W Xenon lamp with an intensity of 120 mW cm⁻².
Figure 4-30 Repeating cycles of H$_2$ evolution in the presence of ZnS-ZnO nanowire sample ZZ-a as photocatalyst in mixed aqueous solution of 0.25 M Na$_2$S and 0.35 M Na$_2$SO$_3$ as sacrificial reagent. Light source: 300 W Xenon lamp with an intensity of 120 mW cm$^2$.

Figure 4-31 XRD patterns of three ZnS-ZnO nanocomposite samples synthesized with different precursor quantities.
Table 4-2 EDS elemental ratio of the ZnS-ZnO nanocomposites with different precursor quantities.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S:Zn Atomic %</th>
<th>ZnS: ZnO molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZZ-a</td>
<td>0.57</td>
<td>1.33:1</td>
</tr>
<tr>
<td>ZZ-b</td>
<td>0.43</td>
<td>1:1.33</td>
</tr>
<tr>
<td>ZZ-c</td>
<td>0.75</td>
<td>3:1</td>
</tr>
</tbody>
</table>

4.2.5 Proposed mechanism of visible-light-driven activity for hydrogen evolution

It is well accepted that both ZnO and ZnS are large-band-gap semiconductors with band gap energy larger than 3.2 eV, and they only can be activated by UV light. Many efforts have been made to extend their absorption in visible light region so as to enhance their capability in utilizing solar energy. Recently, some researchers have reported the possibility of ZnS-ZnO composite materials to exhibit certain photocatalytic activities under visible light irradiation. For instance, Hu et al. demonstrated that ZnO@ZnS core-shell nanostructures could be activated by visible-light irradiation and catalyse dye degradation.[197] They suggested that the band gap energy of the ZnO@ZnS core-shell composite was lowered down compared to individual ZnS and ZnO by creating ZnS-ZnO interfaces. This reduction of band gap energy in ZnS-ZnO composite materials was also reported by Schrier et al.[198] They calculated the strained conduction band minimum (CBM) energies of ZnS and ZnO components in ZnO@ZnS core-shell nanowire model, and found both of them were lowered down. Theoretically, the overall band gap energy could be reduced to 2.07 eV which perfectly lied in visible light region according to their calculation. Moreover, Wang et al.
conducted scanning transmission X-ray microscopy (STXM) analysis on the interface of ZnS-ZnO heterostructures and successfully observed movement of edge energy threshold across ZnS-ZnO interfaces. [199] Although the threshold shift of ZnO in their observation is opposite to Schrier’s calculation, both studies confirm that the alignment of conduction band and valance band of two components may be shifted at the heterostructure interfaces. In addition, Lahiri et al. studied the work function of ZnO before and after forming ZnS monolayer on its surface. [175] An increment of the work function was observed and this was attributed to surface dipole moment and band bending. They explained this by introducing a model of electronic hybridization between ZnO band structure and surface states which was induced by ZnS. With this model, the resulted overall band gap energy is as low as 2.8 eV, which allows visible-light activation.

With the above theoretical support, we proposed the visible-light activation mechanism of the ZnS-ZnO hybrid nanowires as illustrated in Figure 4-32. As mentioned in section 4.2.3, ZnS nanowire was formed first at the early stage of hybrid nanowire growth process and ZnO nanoparticles were generated by intercalating into the ZnS nanowire framework later. In section 4.2.2, the HRTEM images have revealed that numerous heterojunction interfaces were generated between two semiconductor components and each ZnO nanoparticle was surrounded by one or more ZnS nanoparticles via intimate contact. Therefore, it can be proposed that multiple ZnS-surface-states may be created on the surface of ZnO nanoparticle at the interfaces, as in Figure 4-32. At the interface, electrons can be excited from the bended VB energy level of ZnS-surface-states to the CB energy level of ZnO nanocrystal and participate in water reduction. The effective band gap can be narrowed down in this way and excitation by visible light irradiation becomes possible. The photoinduced holes left in ZnS-surface-states can be trapped there and consumed by sacrificial reagent (S²⁻/SO₃²⁻). Therefore, photo-induced electron-hole separation can be further enhanced. The excitation from the
ZnS-surface-states to the CB of ZnS may also be possible and the ZnS acting as active sites cannot be excluded. However, since the CB of ZnS is aligned more positive than that of ZnO, the excited electrons will prefer to transfer from the CB of ZnS to the CB of ZnO through the heterojunction.[195,197,200] Thus the electrons left in the CB of ZnS are quite limited and the chance of ZnS acting as the active sites for proton reduction is much smaller than ZnO. In our mechanism model, higher quantity of ZnS-surface-states can contribute to higher possibility of electron excitation to CB of ZnO under visible light irradiation. Faster electron transfer within the ZnO nanocrystals than across the interface will suppress the photo-induced electron from recombining with the photo-induced holes. Thus photo-induced charge separation can be further enhanced as well. Both of the two effects are responsible for the improvement of hydrogen yield in photocatalytic hydrogen evolution.

![Figure 4-32](image.png) Illustration of proposed mechanism of visible-light-driven hydrogen evolution over ZnS-ZnO hybrid nanowires.

### 4.2.6 Effect of molar ratio of ZnS to ZnO

Experimental analysis on effect of ZnS to ZnO ratio was conducted to further support the proposed mechanism in the above section. Previous photocatalytic tests in section 4.2.4 implied the significant influence of ZnS-ZnO molar ratio on visible light activities. It can be
deduced that the ZnS-ZnO molar ratio may have the essential role to alter the area of ZnS-ZnO interfaces, and thereby affect the visible-light harvesting as well as charge transfer. Therefore, photoluminescence spectra and light absorption spectra were obtained to investigate the above hypothesis.

Photoluminescence spectra were measured with the excitation wavelength at 325 nm to study the effect on charge transfer. As shown in Figure 4-33, all the three ZnS-ZnO hybrid nanowire samples as well as the commercial ZnS powder exhibit a UV emission peak at 360 nm, which is corresponding to the intrinsic band gap emission of ZnS.[201-202] The typical intrinsic band gap emission of ZnO at 380 nm can be observed in the spectrum of the commercial ZnO powder. Both of these two intrinsic emission peaks of ZnS and ZnO were highly quenched in the spectra of ZnS-ZnO hybrid nanowire samples. The peaks of ZnO is even invisible for the samples with ZnS-ZnO molar ratio higher than 1:1, i.e. ZZ-a and ZZ-c. This quenching effect can be ascribed to the photo-induced charge trapping at ZnS-surface-states at the interface of ZnS and ZnO, which act as trapping sites and increase the chance of non-radiative recombination of photo-induced charges. In terms of the sample ZZ-b which have ZnS-ZnO molar ratio less than 1:1, a red-shift on UV emission band up to 390 nm and a broad green emission peak between 450 nm to 500 nm can be observed. It can be deduced that due to the higher ZnO component than ZnS, some of the ZnO nanoparticles may tend to grow larger on the surface of the nanowire rather than being intercalated within the nanowire. Thus, these ZnO nanoparticles have minimum contact with ZnS nanoparticles, and the quantity of ZnS-surface-states at the interfaces do not increase compared to samples with a higher ZnS-ZnO molar ratio. In contrast, intrinsic defects, such as interstitial states and oxygen vacancies in these isolated ZnO nanoparticles may become more evident and responsible for the broad green emission and red-shifted near-band-edge emission with the broad tail.[201,203]
The light absorption spectra of all the above samples were examined and show consistent results. As shown in Figure 4-34, the commercial ZnS and ZnO show the typical excitonic absorption peaks of ZnS and ZnO at 335 nm and 357 nm, respectively.[204-205] Sample “mix” was prepared by physically mixing the two commercial samples with 1:1 molar ratio and this sample exhibits a mixed absorption feature of both ZnS and ZnO in UV region with the absorption edge below 400 nm. However, all the three ZnS-ZnO hybrid nanowire samples exhibit significant light absorption in visible light region. The broad absorption band at ~400 nm is present in the spectra and the absorption edge extends up to 500 nm, which is red-shifted comparing to the absorption feature of ZnO. This observation reinforces the formation of the proposed ZnS-surface-states on ZnO surfaces, which contributes to this broad absorption spectrum in the visible light region.

By comparing ZZ-a with ZZ-c in Figure 4-34, fewer ZnO component reduces ZnS-ZnO interfaces and results in the weaker absorption band near 400nm, and this is also consistent to the result shown in Figure 4-29 that ZZ-a has higher yield of hydrogen evolution under visible-light irradiation than ZZ-c. Although ZZ-b has relative more ZnO component, it still shows much lower photocatalytic hydrogen evolution rate than the other two samples. As mentioned above, the excessive ZnO may grow at the outermost surfaces of the nanowire and thus still lead to relatively less surfaces to form ZnS-ZnO interfaces. In short, all the above observations indicate that the quantity of ZnS-surface-states at the ZnS-ZnO interfaces is directly associated to the visible light activity and thereby influence the photocatalytic hydrogen evolution.
Results and Discussion

Figure 4-33 Photoluminescence spectra of as-prepared ZnS-ZnO nanocomposites with different precursor quantities.

Figure 4-34 UV-Vis absorption spectra of as-prepared nanocomposites with different precursor quantities.
4.2.7 Short summary

In summary, we have successfully fabricated ZnS-ZnO hybrid nanowires with numerous well-distributed nanoparticle-heterojunctions and these hybrid nanowires exhibit good photocatalytic performance in visible-light-driven hydrogen evolution activities even without loading metal co-catalysts. Further studies indicate the crucial role of ZnS-surface-states which are generated at ZnS-ZnO heterojunctions. A mechanism is proposed that these ZnS-surface-states are responsible for effective band gap narrowing down at the interface and thus enable the electron excitation under visible light irradiation. Therefore, the enhancement in light absorption and electron transfer are achieved and thereby improve the hydrogen evolution efficiency. By varying ZnS-ZnO molar ratio in the hybrid nanowires, it is again reinforced that the population of ZnS-surface-states play the essential role in visible-light-driven hydrogen evolution. This section of study demonstrates the possibility of using UV-active large-band-gap semiconductors to achieve visible light photocatalytic hydrogen evolution via generating nanoparticle-heterojunctions and proper interface states. Herein, it may provide an alternative way to construct hybrid photocatalysis systems for efficient solar water splitting and fuel production.
5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this thesis, rational design and preparation of composite materials to enhance light harvesting and photo-induced charge separation in solar water splitting have been studied. Two systems have been developed to realize this objective. Detailed characterization and photocatalytic activity tests have been conducted to investigate the properties and understand the electron transfer mechanisms of the two systems. Based on these studies, the main conclusions can be drawn as follows.

Firstly, a sandwich structure of Fe$_2$O$_3$/Au/Fe$_2$O$_3$ was designed and constructed by spin-coating of pre-synthesized Fe$_2$O$_3$ nanoparticles and sputtering of the gold intermediate layer. This sandwich structure was applied as a photoanode in PEC setup and its photocatalytic activity was investigated. The tests on photo-current response showed that this sandwich structure exhibited much higher photo-activity efficiency as compared to the Fe$_2$O$_3$ photoanode, i.e. the onset potential was reduced from 1.0 V to less than 0.1 V, and the steady state photo-current was increased from zero to 15 µA cm$^{-2}$. The mechanism studies revealed the essential contribution of Au intermediate layer in enhancing visible-light harvesting and electron transfer. Such sandwich structure with plasmonic metallic intermediate layer within two semiconductor layers may be applied to other semiconductors to improve their performance in solar water splitting.

Secondly, a nano-composite photocatalyst in the form of ZnS-ZnO hybrid nanowires was designed and fabricated via one-step hydrothermal reaction. SEM, EDS and TEM studies confirmed the morphology of the nanowire and revealed the well-distributed nanoparticle-heterojunctions within the nanowire. In contrast to the zero hydrogen production of single
material of ZnS or ZnO under visible light, these ZnS-ZnO hybrid nanowires exhibited active visible-light-driven H₂ evolution with a rate of 22 µmol h⁻¹ g⁻¹ without noble metal co-catalyst loading. The growth of ZnS-ZnO hybrid nanowires from 2 h to 15 h was monitored and pre-formed ZnS nanowires were observed and ZnO nanoparticles were formed later then inserted into this framework. ZnS to ZnO molar ratio was manipulated in order to study the mechanism of the active visible-light photo-activity. The mechanism analysis implied the existence of enriched ZnS-surface-states on the ZnO nanocrystal surfaces and suggested the crucial role of ZnS-surface-states population in enabling the visible-light activity for photocatalytic H₂ evolution. This work provided a meaningful way to use UV-active semiconductors to fabricate visible-light-active photocatalysts for solar fuels production via developing heterostructured composites.

The major contribution of this thesis is designing composite photoelectrode and nanophotocatalyst which successfully improved the electron transfer and light harvesting to achieve efficient solar water splitting. This work also provided simple and cost-effective ways to fabricate composite photocatalytic materials.

5.2 Recommendations for future work

In the present work, rational design and preparation of composite materials have demonstrated significant improvement in solar water splitting. Future works are recommended as follows:

1. The sandwich Fe₂O₃/Au/Fe₂O₃ structure in this study has significant enhancement in electron transfer and light absorption compared to bare Fe₂O₃ electrode. However, its efficiency may be further improved if surface co-catalyst, such as Co-Pi can be deposited on the top Fe₂O₃ layer. Co-Pi is a short form of Co-based oxygen-evolving complex and it has
Conclusions and Recommendations

been successfully coupled to Fe$_2$O$_3$ electrode in previous studies.[206] Deposition of Co-Pi on top of the sandwich structure may enhance the surface charge injection into the electrolyte and thus further enhance the photocatalytic activity. Therefore, Fe$_2$O$_3$/Au/Fe$_2$O$_3$/Co-Pi composite electrode can be further investigated as a photoanode in PEC water splitting.

2. In sandwich Fe$_2$O$_3$/Au/Fe$_2$O$_3$ electrode, ITO glass was used as the conductive substrate. Although the ITO glass has the advantage of low cost and transparent properties, it may be replaced by other substrates to achieve a better electron transport between Fe$_2$O$_3$ layer and the substrate. Fluorine doped tin oxide (FTO) glass may be one of the alternative options. FTO glass has a relative higher price and a lower resistivity compared to ITO glass, moreover, some researchers have developed the underlayer modification of FTO with Ga$_2$O$_3$ [207] or Nb$_2$O$_5$ [208], which subsequently improved the crystallinity and uniformity of the Fe$_2$O$_3$ film construction on FTO substrate. Therefore, the oxide-underlayer-modified FTO substrate may be studied to replace ITO substrate to further improve the electron transfer from sandwich film to the substrate.

3. The ZnS-ZnO hybrid nanowire has been demonstrated to be active under visible-light irradiation; however, the hydrogen yield is still limited. Many efforts can be made to improve the hydrogen yield for large-scale production, for example, co-catalyst loading. Noble metal co-catalysts, such as Pt and Au, and non-metal co-catalysts, such as NiS and RuO$_2$, may be loaded on the hybrid nanowire to achieve more efficient photo-induced charge separation, and thus further enhance the hydrogen production yield.


REFERENCES


