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**Earth-abundant, Visible-light Activated Photoelectrodes for
Photoelectrochemical Water Splitting**

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Abstract

Water splitting utilizing solar energy is an attractive way to produce clean and sustainable energy. Among various approaches, photoelectrochemical cell (PEC) has proven to be a promising route to achieve highly efficient artificial photosynthesis. In general, there are three types of PEC: single absorber PEC, dual-absorber PEC and Photovoltaic (PV)-assisted PEC. Between these three types, dual-absorber PEC has the most advantages as it has higher photon absorption efficiency compared to single absorber PEC. Meanwhile, it also has simpler configuration and lower manufacture cost compared with PV-assisted PEC.

The performance of a PEC depends on the photocatalytic performance of its photoelectrodes. Hence, fabricating photoelectrodes with high photocatalytic efficiencies is the most important objective.

In this work, high performance WO_3 photoanode was achieved through optimizing the nanostructure. A triple layered WO_3 was prepared using a one-step controllable anodizing method. The anodization was carried out in a heated acidic solution containing NH_4F as the surfactant for morphology control. Results show that with this unique triple layer structure, light generated charge carriers can be efficiently separated and migrated to the electrode surface for the chemical reactions. This triple layered WO_3 is able to generate photocurrent as high as $0.9 \text{ mA}\cdot\text{cm}^{-2}$ at 1.2 V vs RHE . By the time we reported this work, this was the highest photocurrent achieved by pure WO_3 photoanode without any cocatalyst deposition. Moreover, it has been greatly reported that the stability of WO_3 is a main limiting factor in its photoelectrochemical application, even in neutral electrolyte. Thus, an ultrathin (10 nm) TiO_2 protective overlayer was added on top of triple layered WO_3 enhanced the stability of the triple-layer WO_3 photoanodes considerably.

Meanwhile, efficient Cu_2O photocathodes have been prepared through depositing a thin layer of NiFe layered double hydroxide (LDH) co-catalyst on top of Cu_2O . Both materials were prepared using simple electrodeposition methods without any post treatment. Through modifying Cu_2O with NiFe-LDH co-catalyst,

the photocurrent of Cu₂O photocathode has been greatly improved, especially in the low bias range. It is observed that under as low as -0.2 V vs Ag/AgCl applied voltage, photocurrent increases almost seven times with the assist of NiFe-LDH co-catalyst. The origin of such a pronounced effect is the improved electron transportation towards the electrolyte as the NiFe-LDH overlayer induces an appropriate energy level alignment. LDH are known to be used as oxygen evolution cocatalyst, and it was the first time for NiFe-LDH to be reported as a photocathode cocatalyst. Moreover, It is well known that the electrochemical instability of Cu₂O poses a serious challenge to its PEC application. The stability of Cu₂O has shown great improvement after coating with NiFe-LDH. Results show that there is almost zero photocurrent loss after 40 hours continuous illumination at -0.2 V vs Ag/AgCl condition.

To explore other semiconductor oxide systems, BiVO₄ was also prepared as an alternative photoanode in the current work. Results indicate that an ultra-thin layer of NiCo-LDH improves the photocurrent by three-folds.

Finally, by combining the synthesized photoelectrodes (*i.e.* WO₃-based photoanode, Cu₂O-based photocathode and BiVO₄-based photoanode) with commercially available semiconductors (*i.e.* p-type Si, and p-type GaP) and another commonly used photoanode ($\alpha\text{-Fe}_2\text{O}_3$), the mechanisms behind the voltage generation of a dual-absorber PEC was investigated. It is clear that the important factors for the overall voltage generation are the photoanode and photocathode photocurrent, especially under low bias conditions.

In conclusion, modification of the nanostructure and deposition of a co-catalyst are two efficient approaches in improving the photoelectrode activities. In general, the nanostructure increases the light harvesting efficiency and reduces the charge recombination rate; the co-catalyst improves the reaction kinetics and increases the charge transportation and inject rate towards the electrolyte. Meanwhile, in order to achieve high efficiency dual-absorber PEC, the voltage generated within the integrated dual-absorber PEC upon illumination is very important. This can be improved by increasing the efficiencies of the photoelectrodes especially their charge separation and injection rate.

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Abbreviations

PEC	Photoelectrochemical Cell
LDH	Layered Double Hydroxide
PV	Photovoltaics
STH	Solar-To-Hydrogen
IPCE	Incident Photon-To-Current Efficiency
SEM	Scanning Electron Microscope
FESEM	Field Emission Scanning Electron Microscope
HRTEM	High Resolution Transmission Electron Microscopy
EDX	Energy Dispersive X-ray Analysis
XRD	X-ray Diffraction
LSV	Linear Sweep Voltammetry
EIS	Electrochemical Impedance Spectroscopy
NRs	Nanorods
NPs	Nanoparticles
NFs	Nanoflakes
AFM	Atomic Force Microscopy
NHE	Normal Hydrogen Electrode
RHE	Reversible Hydrogen Electrode
FTO	Fluorine-doped Tin Oxide
AM	Air Mass
Ag/AgCl	Silver Chloride Electrode
OCV	Open Circuit Voltage
CB	Conduction Band
VB	Valence Band

Abbreviations

Chapter 1

Introduction

Environmental issues and energy crisis have driven researchers to lay massive efforts in developing clean and sustainable energies in the past decades. Amongst the various approaches, the PEC is the most promising because it utilizes earth abundant resources – solar energy and water to produce hydrogen and oxygen gases. In order to achieve an efficient PEC, both photoelectrodes performance and the PEC configuration are vital. This work targets the design and fabrication of high performance photoelectrodes and seeks to understand the dual-absorber PEC mechanisms with an aim to achieve visible light activated, low cost and highly efficient PEC for water splitting. This chapter focuses on the overview of this work and provides an evaluation of its importance in both environmental and economic aspects. This is followed by the objectives, scope and detailed plans.

1.1 Background

With the exhausting of fossil fuels, the energy crisis has become a major obstacle for the sustainable development of humankind. According to research study, we consume the equivalent of over 11 billion tons of oil in fossil fuels each year; and crude oil reserves are vanishing at the rate of 4 billion tons per year.^[1] To compound the problem, the usage of fossil fuels also leads to numerous environmental pollution such as CO₂ emissions.^[2] Thus, the search for an alternative energy source is an exigent mission. There has been a growing global interest for clean renewable energy over the past decades as a result of increased energy demand, combined with depleting natural reserves and the environmental consequences of their use. In this regard, hydrogen is most commonly touted as a promising clean energy source. As an ultimate replacement of the fossil fuels, hydrogen gas has drawn a lot of attention in recent years. It has numerous advantages such as zero-emission and renewability, and thus holds great promise as a future energy source. As the 8th most abundant element on earth, with 6,700,000 ppb compared with a “mere” 1,600,000 ppb of carbon, hydrogen is significantly more available than any other energy sources on earth.^[3]

Furthermore, a kilogram of hydrogen can be harnessed to yield an impressive 123 MJ energy. In comparison to today’s conventional fossil fuels such as propane (46.44 MJ/kg) or gasoline (~46 MJ/kg), hydrogen can generate significantly higher amount of energy, surpassed only by nuclear energy sources. Thus, there is a momentous environmental advantage in research focus towards utilizing hydrogen from water as a source for clean energy.

There are various tactics to harvesting hydrogen from water. Among them, the use of solar energy for hydrogen production has emerged as the most viable and cost effective approach. Since solar energy is the most abundant and inexhaustible energy source, with the magnitude of available solar power striking the earth’s surface at any one instant equal to 130 million 500 MW power plants.^[4]

Nature has its own magnificent way to harvest solar energy – through natural photosynthesis, which is essential to the global carbon cycles and organisms. Scientists have been inspired from this natural process, and delegated themselves into building a system to mimic this process, which is so-called “artificial photosynthesis”. There are various systems attempting to achieve artificial photosynthesis. Traditional “artificial

photosynthesis” approach – water splitting is carried out with powdered materials such as TiO_2 dispersed in an aqueous media which generates hydrogen or oxygen upon receiving light energy. This method has proved to be efficient and promising, but it suffers from enormous limitations, such as difficulties in oxygen and hydrogen gas separation and collection. Comparatively, PEC is more applicable owing to its advantages including higher gas generation rate and easy gas separation and collection procedures.

1.2 Objectives and Scope

With the arising needs in clean and renewable energy, the scope of this research is to fabricate an efficient PEC that can potentially be used for water splitting, utilizing earth abundant, low cost and visible light responsive photocatalysts. Although PEC has been extensively studied in the past years, most of the highly efficient systems being explored still consists either expensive materials such as single crystal silicon or wide band gap materials such as TiO_2 . Moreover, the expensive materials usually require extreme fabricating methods involving environmental harming chemicals or costly instrumentations. This compromises the environmental and commercial advantages of PEC-based water splitting. Meanwhile, wide band gap material (*e.g.* TiO_2) can only utilize the UV range of the solar spectrum. This dramatically limits the PEC theoretical efficiencies. Thus, the search for alternative materials is an urgent and crucial task. Consequently, the objective of this work is to fabricate high performance photoanode and photocathode for PEC water splitting using low cost, earth abundant and visible light responsive materials through these progressions:

1) Synthesis of materials using low cost production approaches

This step is to develop methods to fabricate high performance photoelectrodes with reasonable fabrication cost and suitability for large scale manufacture while seeking to understand the formation and growth mechanisms of WO_3 photoanode and Cu_2O photocathode and learning the limiting factors in their synthesis and PEC performances.

a. For WO_3 photoanode, the first task is to understand the relationship between morphologies and photocatalytic properties, following which a structure that optimizes its PEC performance through improvement in photocurrent can be designed by adjusting the morphologies of pristine WO_3 .

b. For Cu_2O and BiVO_4 photoelectrodes, after optimizing the pristine photoelectrode preparation conditions, deposition of an appropriate co-catalyst will be carried out to improve their PEC performance. An effort will be made to understand the function of the co-catalyst and explore the mechanisms behind the improvement in photocurrent brought by the co-catalyst deposition.

2) Establish basic understandings in voltage generation within a dual-absorber PEC. As achieving a self-biasing PEC for efficient water splitting is still a long term goal for researchers, the current work hopes to achieve certain basic understandings in the voltage generation mechanism behind a dual-absorber PEC as a foundation for a working prototype in the future.

1.3 Dissertation Overview

This thesis will be divided into 9 chapters divides into 4 sections:

It starts with a detailed literature review on PEC, including the popular photocatalytic materials for both photoanode and photocathode. This includes the mechanism of PEC water splitting; the potential approaches to achieve an efficient PEC; as well as current research progress on several promising photocatalysts that can be used as efficient, low cost and visible light responsive photoelectrodes. Afterward, appropriate synthesis and characterization methods are designed and planned carefully for both photoanode and photocathode materials.

The second section will cover the results and discussions of the WO_3 photoanode; Cu_2O photocathode and BiVO_4 photoanode photocatalytic properties; strategies for improving their activities, along with the outcomes.

The third section will be focused on the open circuit voltage (OCV) generation mechanisms of a dual-absorber PEC. As OCV is a very important factor in achieving zero bias PEC water splitting, the elements that play the most important roles in OCV generation will be investigated by combining and testing different photocatalysts.

Lastly, a conclusion of all the results, complications from the research and future recommendations will be described comprehensively.

The detailed dissertation is as below:

Chapter 1 provides a rationale for the research and outlines the goals and scope.

Chapter 2 reviews the literature on PEC and photocatalysts.

Chapter 3 describes the experimental methodologies.

Chapter 4 describes the results and discussions on WO_3 -based photoanode.

Chapter 5 describes the results and discussions on Cu_2O -based photocathode.

Chapter 6 describes the results and discussions on BiVO_4 -based photoanode.

Chapter 7 describes the integration of dual-absorber PEC, especially on its OCV generation mechanisms.

Chapter 8 Reconnaissance studies – WO_3/TiO_2 tandem photoanode

Chapter 9 draws a conclusion on the results of the whole project. Future recommendations will be discussed on how to further improve the PEC performance.

1.4 Findings and Outcomes

This research led to several novel outcomes by:

1. Synthesizing a novel triple-layer structured WO_3 photoanode and study of the correlations between the nanostructure and the photoelectrochemical performance.
2. Fabricating high performance photocathode by coupling Cu_2O with NiFe-layered double hydroxide (LDH) co-catalysts. The mechanism of the NiFe-LDH co-catalyst function has been studied in depth.
3. Producing high performance BiVO_4 -based photoanode by depositing a very thin layer of NiCo-LDH co-catalyst on top of the plain BiVO_4 . The function of the LDH structure has been explored by comparing it with $\text{Ni}(\text{OH})_2$ co-catalyst and $\text{Co}(\text{OH})_2$ co-catalyst.
4. Through testing and analyzing different pairs of photoelectrodes for dual-absorber PEC, the mechanism of voltage generation and limiting factors on the OCV before and after illumination have been explored.

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Chapter 2

Literature Review

The increasing needs for clean and renewable energy have attracted great attention from researchers towards artificial photosynthesis. Among the existing research approaches, the PEC has proven promising in achieving efficient water splitting. This chapter will be focused on the current research status on PEC. It will start with an overview on PEC including its development history. It is evident that high quality photocatalysts play the upmost important role towards an efficient PEC. Thus, the second section will be a detailed literature studies on the promising photocatalysts, including WO_3 as a photoanode candidate and Cu_2O as a photocathode candidate, as these photocatalysts have been demonstrated in various systems to be efficient and favorable. It is also worth noticing that both of them have very attractive properties such as nontoxic, low cost and most importantly, can be activated using visible light. In conclusion, it is possible to build an efficient dual-absorber PEC via careful selection of photocatalysts and conscientious optimization.

2.1 Artificial photosynthesis via photoelectrochemical method

Artificial photosynthesis is a process that mimics the natural photosynthesis. It harvests the solar energy and produces hydrogen, which can be used as clean fuels, from water. As water is composed of two hydrogen atoms and one oxygen atom, this process is also called “water splitting”. A great advantage of this process is that it has absolutely zero emission, with no waste or pollution. This advantage renders artificial photosynthesis great potential in solving current energy crisis and environmental pollution problems. Water splitting can be achieved through various systems. Among those, a direct photocatalysts/liquid contact system is the most attractive path because it is the most undeviating approach and does not involve complicated fabrication process. When a semiconductor is brought into direct contact with a liquid, an electric field forms instantly at the interface. This electric field is essential in allowing the water splitting reactions to occur.

There are several types of water splitting systems that allow direct contact of semiconductor with liquid. In one, the photocatalysts are directly dispersed in the liquid like that reported for the very first time with TiO_2 by Frank and Bard.^[1] Basically, electrolysis occurs through the following two reactions:

The energy required for both reactions under standard state condition is $\Delta E = -1.23 \text{ V}$. Considering the limited photon flux and the energy lost during charge transportation, a minimum total energy of 1.6 V must be generated in order to achieve artificial photosynthesis.

PEC is another system that allows direct contract of semiconductor with liquid. It has several advantages such as flexible device designs and easy gas separation and collection processes. Furthermore, with the assistance of external bias, PEC can achieve higher gas production rate compared to other systems.

2.1.1 Semiconductor/electrolyte interface

As mentioned, a system where photocatalyst directly contacts liquid is the most convenient and effective approach for water splitting. The schematic illustrations of energy

level adjustment happening at the semiconductor and electrolyte interface before they are in contact, after they have interaction and once the semiconductor is illuminated are shown in Figure 2.1. In this scheme, E^0 is the Nernst potential of the redox pair of the electrolyte. For water splitting reaction, the redox reaction is H^+/H_2 for the photocathode (like the one shown in Figure 2.1) and O_2/H_2O for the photoanode. Usually the photocathode is composed of a p-type semiconductor and the photoanode is an n-type semiconductor. When the material and electrolyte first come in contact, a charge transfer process happens. This is because of the difference between the energy level of the semiconductor (*i.e.* fermi level) and the energy level of the electrolyte (*i.e.* redox level). After a short period of time, an equilibrium is reached, at which point the electrochemical potential is the same everywhere. At the moment when the semiconductor is illuminated, charge carriers (*i.e.* electrons and holes) will be generated within the photoelectrode. Thus, in the case of photocathode, it will immediately be negatively charged. Meanwhile, the electrolyte is positively charged. Vice versa for photoanode material. Because of the difference in the type of charge carrier, the band bending directions of p-type semiconductor and n-type semiconductor are opposite. In this case of a p-type semiconductor photocathode as shown in Figure 2.1, the negative charges are spread out over the depletion width, W . Where the positive charges are spread over a much narrower region in the electrolyte, called “Helmholtz layer”. These two layers form a double layer, which is the most important electric phenomenon at the photoelectrode/electrolyte interface. Although the depletion width in a semiconductor is very thin, typically on the order of hundreds of nanometers, the electric field generated in this layer in a photoelectrode can be as large as 10^5 V cm^{-1} .^[2]

Figure 2.1 The p-type semiconductor/electrolyte interface (a) before equilibrium; (b) after equilibrium in the dark condition and (c) quasi-static equilibrium under illumination.

It is worth noticing that the difference between the photoanode and photocathode in a PEC is the difference in electric field that is developed during equilibrium phase. This causes the different band bending direction in the photoelectrodes, like the difference between n-type semiconductor and p-type semiconductor. Upon illumination, there will be uneven number of photogenerated electrons and holes in the photoelectrodes. This causes an electron quasi-fermi level $E_{f,n}$ and hole quasi-fermi level $E_{f,p}$. In theory, the amount of voltage generated by an electrode is given by the difference between the $E_{f,p}$ and $-qE(A/A^-)$ for photocathode and $E_{f,n}$ and $-qE(A/A^-)$ for photoanode. Whereas, when combining a photoanode and a photocathode into a PEC, the amount of voltage generated by the PEC upon illumination is not only decided by the voltage generation within each semiconductor. It is also directly affected by the band position difference of both photoelectrodes.

2.1.2 Photoelectrode engineering

The efficiency of PEC depends on the independent performance of photoelectrodes and the design of the cell. Thus, photoelectrode engineering is the most important strategy in achieving high performance PEC water splitting. Basically, the photocurrent of PEC is dependent on the number of active charge carriers generated by the photoelectrode. In order to increase the number of charge carriers, photoelectrode engineering is often necessary.

The commonly used photoelectrode engineering strategies include morphology control,^[3] doping,^[4] and second layer deposition which includes but not limited to second photocatalyst deposition, co-catalysts deposition and passivation layer coating.^[5]

a. Morphology control

The most popular and well-recognized approach to photoelectrode engineering is morphology manipulation through nanostructure engineering. Nanoscience has a slightly shorter history than photoelectrolysis, which starts in 1974 when Dingle discovered the quantum size effect in thin films.^[6] Within a short period of time, nanoscience has become tremendously popular as it opens a new era in material engineering. The first important benefit of nanostructure in photocatalysts is the improved light harvesting efficiency. Obviously, a hierarchically constructed micro/nano surface has much more surface area and higher surface roughness than a flat surface. Thus, more photons can reach the surface and be absorbed and utilized by the photoelectrode. Moreover, a structured surface also reduces the light scattering loss during absorption. Another important effect brought by nanostructure is a shorter charge carrier collection pathway.^[3] As mentioned before, the photocatalyst suffers from severe energy loss through the charge recombination process in the bulk and the nanostructure of a photocatalyst is able to reduce this charge carriers' recombination, as illustrated in Figure 2.2. Photon-generated electrons and holes have very limited mobility, which leads to their short diffusion lengths and subsequently increased charge recombination. For instance, some semiconductors such as hematite ($\alpha\text{-Fe}_2\text{O}_3$) suffers greatly from this disadvantage, as its hole diffusion length of hematite is less than 4 nm.^[7] However, it has been reported that by creating nanoporous structure through acid treatment, the limitation caused by the short hole diffusion length can be largely overcome.^[8] The optimized nanoporous sample shows photocurrent density of 1.41 mA cm⁻² at a 1.23 V vs RHE, 1.7 times higher than that of pristine hematite.

Figure 2.2 Charge separation and collection processes of (a) a photoelectrode with flat surface and (b) a structured photoelectrode. L : electron diffusion length; d : photoelectrode thickness

Compared with suspended nanoparticles system, it is much harder to achieve efficient photoelectrode by adjusting the thickness and morphologies. To achieve both high charge carriers' generation and good separation and collection efficiencies, the thickness of the photoelectrode has to be optimized. It is clear that the thickness of the film directly relates to the number of electrons and holes generated. If the film is very thin, that its thickness, d is less than the diffusion length, L , although the charge recombination rate will be greatly diminished, there will also be very limited total number of charge carriers produced. This will greatly compromise the PEC photocurrent. It is challenging to find the middle ground to achieve the best efficiencies, especially when it comes to a more complicated multi-layer system. Thus, approaches other than morphologies manipulation are to be considered in order to achieve higher performance photoelectrodes.

b. Doping

Another strategy to improve the charge collection and separation efficiency is doping. Fundamentally, doping is a way to induce impurities into a semiconductor to increase the charge carriers' concentration. The induced impurities will reduce the electrons and holes recombination rate. A right concentration of dopant can greatly enhance the performance of the photoelectrode. For example, research has shown that a non-isovalent substitutional dopant such as Mo can improve the BiVO_4 photoanode

photocurrent greatly. It has been reported that using 3% Mo doping into the site of V in BiVO_4 , its IPCE increases from 9% to 41% at 420 nm.^[9] Doping can also increase the light harvesting efficiencies by changing the morphology of a photoelectrode. In one report, the surface area of NaTaO_3 increases by 8 times by doping with 2% La.^[10] This amount of surface area increase improves the photocurrent dramatically. There are great number of works focusing on doping of photoelectrode. Whereas, doping also significantly complicates the synthesis process for PEC electrodes. Compared with suspended powder system, it is more difficult to achieve a homogenous doping throughout the entire thin film. This complication dramatically increases the cost of a photoelectrode.

c. Second layer deposition

Another well-recognized approach is to deposit a second material on top of the main photocatalyst. This material can work as a second photocatalyst, co-catalyst or a surface passivation layer. There exist a very blurred distinction between co-catalyst, second photocatalyst and passivation layer. As some semiconductors have both photocatalytic and electrocatalytic properties such as NiO .^[11] Thus, it can work both as a second photocatalyst or a co-catalyst. And materials like NiO may also work as a surface passivation layer because of its good stability. Overall, the final goal of this second layer deposition is to improve the photocurrent of photoelectrode and its stability from chemical or photon corrossions.

Overall, the deposition of a second layer improves the performance through one of the following effects:

(1) Increase in photon absorption efficiencies

Some combinations of the main and second photocatalyst can configure into a tandem cell, which splits and utilizes the light spectrum independently. The top photocatalyst absorbs the higher energy photons, leaving the lower energy photons to be exploited by the lower main photocatalyst;

(2) Decrease in charge recombination rate

This can be achieved by both the second photocatalyst and co-catalyst. Usually, semiconductors with different band energies form a heterojunction at the interface where they contact. This heterojunction between the second photocatalyst and the main

photocatalyst introduces band bending at the interface, which subsequently improves the charge separation efficiencies.

The co-catalyst decreases the charge recombination rate for the main photocatalyst by improving the reaction kinetics and optimizing interfacial energetics at the semiconductor/electrolyte interface. The interface energetics are greatly influenced by the redox reaction level of the electrolyte. Although the redox couple in water splitting is fixed, chemically controlling and optimizing the interfacial barrier height by fine tuning the redox reaction potential is still possible.^[12] Beside changing the electrolyte, the semiconductor/electrolyte interface can be adjusted by adding a passivation or co-catalyst layer;

(3) Improved photoelectrode stability.

Typically, this is achieved by depositing a passivation layer on the top of the main photocatalyst. In chemistry, the passivation layer is a layer of shield material, which is created to protect against corrosion. In photoelectrolysis, a passivation layer on top of the photocatalyst is commonly used to reduce the charge carriers' recombination at the semiconductor/electrolyte interface.^[13] It often contributes to band position shifts by changing their charge distribution.^[14] The passivation layer can be catalytic or noncatalytic thin film. If the passivation layer material is a catalytic thin film, it can promote facile charge carrier transfer across the interface; if it is noncatalytic thin film, it will passivate defect states, suppressing surface recombination. Ultimately, both catalytic and noncatalytic films improve the photoelectrochemical properties of a photoelectrode.

As illustrated in Figure 2.3, there are three main charge recombination processes happening in an activated photoelectrode. The majority of charge recombination happens through bulk recombination J_{br} . This is due to the limited charge transportation length. One way to reduce this recombination is through doping, like that in Mo doped BiVO_4 . A point worth to mention is doping has a negative effect of creating lattice defects which may act as traps that promote charge recombination. Second layer deposition is used to reduce the charge recombination through minimizing depletion region recombination J_{dr} and surface charge recombination J_{ss} . Through catalytic passivation layer deposition or co-catalyst deposition, the second layer favors the charge carriers' transport towards the electrode. This improves charge transportation in the depletion layer, and consequently reduces J_{dr} .

A noncatalytic passivation layer is able to diminish the surface defects, and therefore reduces J_{ss} . The examples of combining photoelectrode with a second photocatalyst, co-catalyst or thin passivation layer will be given in the next section where potential photoelectrode materials for PEC are discussed in detail.

Figure 2.3 Charge recombination pathways in a p-type photoelectrode in contact with electrolyte upon illumination. The photogenerated electrons and holes recombine through: bulk recombination (J_{br}); depletion-region recombination (J_{dr}) and surface recombination (J_{ss}).

Despite the potential benefit, all second layers have to be adjusted carefully to achieve the best performance. The most important factor that affects the second layer performance is the thickness of the layer. Apparently, if the film is too thin, the second layer will not be sufficient to either promote the charge separation or improve the reaction kinetics. But if the thickness of the second layer is excessive, then it will also bring several drawbacks such as (1) blocking the active sites on the photoelectrode; (2) excessive light absorption, which results in insufficient light reaching the main photocatalyst; (3) inducing negative effects on the surface area and (4) decreasing the charge recombination within the second layer itself. Thus, careful plan for the second layer deposition is very important in order to achieve high performance PEC.

2.1.3 PEC development history

The first photoelectrochemistry study was reported in 1955 with Brattain's work.^[15] This gives PEC more than 60 years history. After that, Fujishima and Honda first reported a PEC system for water splitting based on TiO_2 photocatalysts.^[1] Successively, huge varieties of designs and materials were developed for achieving higher water splitting efficiencies. Overall, PEC development has undergone three main stages until now. The first stage was from 1970 until early 1990s. In that period of time, PEC research was mainly focused on the traditional semiconductors such as GaP, GaAs, InN etc., which have very good photocurrent but suffers from poor stability and complicated manufacturing processes. The first outstanding work was published in 1975. Yoneyama et al. demonstrated a p-GaP/n- TiO_2 tandem combination that is able to generate H_2 and O_2 without an external voltage.^[16] It is also worth noticing that ever since Yoneyama's work, tandem cell has become very popular. By using a tandem cell, the theoretical maximum efficacies could increase from 32% for single photocatalyst PEC to 42% for tandem solar PEC.^[17] Other tandem systems were also reported during that time such as n-GaP/p-GaP system, p-GaP/n- SrTiO_3 system.^[18]

The second stage was from late 1990s to late 2000s. During this time, a lot of attention was focused on silicon based systems, especially for multi-junction silicon cell. As demonstrated by Licht's group, 18.3% solar-to-hydrogen conversion efficiency was achieved using an AlGaAs/Si/RuI₂/Pt_{black} system for both H_2 and O_2 evolution.^[19] However, the systems created at that time are rather complicated and expensive.

The third stage is from 2010 until now. Vast amount of efforts are focused on replacing noble-metal electrocatalysts with affordable elements, such as metal oxides; improving the stability of the system and demonstrating fully integrated devices.^[20] A great number of metal oxide photocatalysts are also playing important roles in current stage, such as WO_3 , Fe_2O_3 , Cu_2O , BiVO_4 and so on. A detailed literature review on the selected photocatalysts will be given in the next section.

2.1.4 PEC configuration

Other than photoelectrode engineering as mentioned above, the PEC configuration is also a very important factor to consider in order to achieve high performance water

splitting. The configurations and working principles of three types of PEC are illustrated in Figure 2.2. Traditional PEC consists of a working photoanode and a counter electrode immersed in an electrolyte (Figure 2.4a). The photoanode is usually an n-type photocatalyst and the most commonly used counter electrode is Pt electrode. When the photoanode absorbs incident light, it generates electrons and holes. As the photoanode is the only light absorber, this type of PEC is also called single-absorber PEC. Ideally, the photon-generated holes are used to generate oxygen from water, and electrons will transfer to the counter electrode to produce hydrogen. This type of PEC requires external voltage to direct the charge carriers' separation and transportation. It also has limited photon absorption efficiencies as the light absorption is exclusively dependent on the absorption of the photoanode.

Compared with single-absorber PEC, a better way to utilize the incident light would be a dual-absorber PEC. In a dual-absorber PEC, the counter electrode is another photocatalyst - photocathode (Figure 2.4b). Upon illumination, both photoanode and photocathode absorb photons and generate charge carriers. The electrons generated by photocathode will migrate to the photocathode surface and reduce water to hydrogen and the holes generated by photoanode will evolve oxygen from water. Ideally, the unwanted photogenerated electrons in the photoanode will transport through the external conducting wire and recombine with unwanted holes in the photocathode. The advantages of a dual-absorber PEC are: (1) more charge carriers can be generated compared with single-absorber PEC; (2) higher light harvesting efficiencies, especially for tandem designs; and (3) better charge separation under very low bias or even zero bias condition because there is an external electric field generated between the two photoelectrode upon activation. Ideally, this light-generated voltage is enough to drive electrons in photoanode transport to photocathode without external voltage. This results in a self-biasing or non-biasing PEC. But it requires highly optimized photoelectrodes and very good match of the electrode band positions and currents. Thus, the challenges for this type of dual-absorber PEC, especially to achieve zero biasing are: (1) both photoanode and photocathode material need to be optimized, having very good photoelectrochemical performance and (2) these two photoelectrodes have to match with each other, in terms of band gap and band position.

Figure 2.4 Basic set up schemes and working principles of a (a) single absorber PEC; (b) dual absorber PEC and (c) PV assisted PEC

Another type of PEC, photovoltaics (PV)-assisted PEC has drawn extensive attentions in recent years (Figure 2.4c). Different from the two types of PEC above, PV-assisted PEC utilizes the voltage generated by PV cell instead of adding an external voltage source. Therefore, it is possible to achieve a standalone system with 100% light activated device, without external electric input. The pros for PV-assisted PEC is very clear, which is high utilization of solar energy and no extra energy input. Whereas, the cons beneath are also aplenty: (1) in order to build a fully functionalized PV-assisted PEC, all the components need to be in perfect match with each other, in terms of band gap and band position. For example, if the voltage generated by the PV cell is too large, then the photoelectrode materials have to be able to withstand and function under such high voltage. Materials such as Cu_2O which suffers from electric-corrosion will not be suitable; (2) the use of a PV cell dramatically increases the cost and difficulties of the whole setup assembly in view of material synthesis as most efficient inorganic PV cells such as Si-PV cell and GaP-PV cell are expensive and difficult to manufacture. Nevertheless, successful examples have been reported with PV-assisted electrochemical water splitting utilizing two electrocatalysts instead of photocatalysts.^[21] However, these reported devices do not fall in our regime of PEC, given consideration that no photocatalyst is directly involved in the water splitting reaction in their systems.

In conclusion, the dual-absorber PEC has the biggest potential and advantages compared with single-absorber PEC and PV-assisted PEC.

2.1.5 PEC efficiencies

The efficiencies of a PEC are important indicators for its catalytic performance. One of the most common ways to quality the efficiency of a single-absorber system with a two-electrode configuration is by its Faradaic efficiency (η) using equation 3.

$$\eta = \frac{J_{mp} \times (1.229V - V_{app})}{P_{in}} \quad (2.3)$$

where V_{app} is the applied voltage; J_{mp} is the externally measured current density and P_{in} is the illumination power. For a cell with no external connection, V_{app} and J_{mp} are not applicable. Thus, there is another way to calculate Faradaic efficiency, which is through measuring the final production volume (hydrogen gas or oxygen gas).^[22]

Another well recognized efficiency measurement for PEC is solar-to-hydrogen (STH) efficiency, where only sunlight and water are considered as input energy. STH efficiency can be calculated with equation 4:

$$STH = \frac{J_p \times 1.229V}{I_o} \times 100\% \quad (2.4)$$

In this efficiency calculation, the applied voltage $V_{app} = 0$ V. The theoretical STH and photocurrent of a photoelectrode under AM 1.5 G irradiation are displayed in Figure 2.5a. A single semiconductor with a band gap of 1.6 eV has an ideal maximum conversion efficiency at 1 Sun of 30%.

By independently measuring the performance of photoanode and photocathode, an integrated system's expected performance can be directly calculated, as shown in Figure 2.5b. Overall water splitting efficiency can be estimated by overlapping the individually tested J-V data for each photoelectrode.^[23] The red shaded area illustrates the power generated for each components and blue shaded area indicates the power generated at the maximum operating current density.^[24] If there is no cross point for photoanode and photocathode, then the combination of these two materials will not be able to achieve water splitting. Thus, the careful selection of the photoanode and photocathode materials is vital to constructing a dual-absorber PEC.

Figure 2.5 Dependence of theoretical STH and solar photocurrent density of (a) single photocatalyst PEC system^[25] and (b) dual absorber PEC system under AM 1.5G irradiation.^[24]

2.2 Current state of some promising photoelectrodes

2.2.1 WO₃ photoanode

Due to its multiple oxidation states, high coloration efficiency and good cyclic stability, WO₃ is one of the most well-known working electrodes available for electrochromic devices.^[26] Furthermore, WO₃ exhibits a good oxygen evolution performance. It is reported to have a band gap of 2.6 - 2.8 eV, which can be activated under the blue-UV region of the light spectrum. The theoretical maximum conversion efficiency of WO₃ is about 6.3% for the absorption of photons with energies higher than 2.6 eV.^[27] Compared with TiO₂ and Fe₂O₃, which are both popular oxygen evolution catalysts, WO₃ exhibits longer hole diffusion length (150 nm).^[28] All of these properties make it an excellent candidate for photoanode in PEC water splitting.

The first time that WO₃ is used as a photoanode material was in 1976 by Gary Hodes, David Cahen and Joost Manassen.^[29] At that time, the most popular metal oxide photoanode material was TiO₂. They demonstrated the possibility of using WO₃ as a photoanode since it has a shorter bandgap compared with the commercial available TiO₂ photoanode. They simply sprayed a layer of ammonium tungstate on conducting glass and heated it at 500 °C. It rendered crystalized WO₃ with photocurrent of ~0.2 mA cm⁻² at 1 V vs NHE and onset voltage shift of 1.4 V upon illumination. However, they also pointed out a serious drawback of WO₃ as photoanode, which is the instability of WO₃ against photocorrosion and chemical corrosion. Nevertheless, this work demonstrated the vast potential of WO₃ in the field of PEC water splitting.

The photoactivity of WO₃ is greatly influenced by the crystal phases and morphology of the material. These properties are greatly influenced by the synthesis methods, particularly the annealing conditions. There are five common forms of WO₃: tetragonal (α -WO₃),^[30] orthorhombic (β -WO₃),^[31] monoclinic I (γ -WO₃),^[32] triclinic (δ -WO₃)^[33] and monoclinic II (ϵ -WO₃).^[34] Out of these five crystal structures, monoclinic is the most stable phase in room temperature. The comparison of these five forms of WO₃ are listed in Table 2.1. It is reported that in most solution-based synthesis, the as-prepared WO₃ exhibits an orthorhombic structure. After post annealing in temperatures greater than 400 °C, orthorhombic WO₃ will start to convert to hexagonal WO₃. When the temperature further increases to above 500 °C, it will transform to the most stable monoclinic WO₃.^[28]

Another thing worth noticing is that out of these five forms, studies have proven that monoclinic WO_3 has the highest photocatalytic performance.^[35]

Table 2.1 List of WO_3 phases and stable temperature

WO_3 crystal structure	Temperature required	Properties
tetragonal ($\alpha\text{-WO}_3$)	$> 740\text{ }^\circ\text{C}$	Second most stable phase
orthorhombic ($\beta\text{-WO}_3$)	$330\text{ }^\circ\text{C}$ to $740\text{ }^\circ\text{C}$	as-prepared WO_3
monoclinic I ($\gamma\text{-WO}_3$)	$17\text{ }^\circ\text{C}$ to $330\text{ }^\circ\text{C}$	Most stable phase, with highest photocatalytic properties
triclinic ($\delta\text{-WO}_3$)	$-43\text{ }^\circ\text{C}$ to $17\text{ }^\circ\text{C}$	
monoclinic II ($\varepsilon\text{-WO}_3$)	$< -43\text{ }^\circ\text{C}$	

As for obtaining the maximum surface to volume ratio, various morphologies of WO_3 photoanode have been reported such as nanoflakes;^[36] nanoparticles;^[37] nanorods;^[28] nanowires;^[38] nanoplatelet^[39] and some special morphologies including wormlike structures^[40] and wedge-like structure^[41]. Among these morphologies, nanoflake is the most favorable structure because it has both large surface area and good structural continuity. These properties render both good charge carrier transportation and increased photon absorption and charge separation efficiencies. Numerous methods are available for the synthesis of WO_3 photoanodes. The most popular techniques are chemical vapor deposition,^[42] thermal vapor deposition,^[43] anodization of W foil, hydrothermal method,^[26] heat treatment of metal W film or filament / wire in both air or oxygen atmosphere^[44]. Some representative WO_3 photoanode with various morphologies and different preparation methods are summarized in Table 2.2.

Another important way to achieve high performance WO_3 photoanode is by combining it with a second photocatalyst. In this way, the double layer can achieve higher

Table 2.2 Selected examples of nanostructured WO₃ photoanodes

Morphologies	Preparation method	Crystal phase	Electrolyte used	Photocurrent (mA cm⁻²)	Ref
Nanoflakes	Hydrothermal	Monoclinic	0.1M Na ₂ SO ₄	2.3 (1.2 V <i>vs</i> Ag/AgCl)	[45]
Nanoparticles	Sol-gel	Monoclinic	1 M H ₂ SO ₄	1.6 (1.4 V <i>vs</i> SCE)	[46]
Wormlike structure	Anodization	Monoclinic	1 M H ₂ SO ₄	3.5 (1.5 V <i>vs</i> SCE)	[40]
Column Structure	Sputtering	Monoclinic	0.33 M H ₃ PO ₄	2.7 (1.6 V <i>vs</i> SCE)	[47]
Nanorods	Hydrothermal	Monoclinic	0.5 M Na ₂ SO ₄	2.26 (1.23 V <i>vs</i> RHE)	[28]
Nanoporous	Anodization	Monoclinic	0.5 M Na ₂ SO ₄	1.4 (0.8 V <i>vs</i> SCE)	[48]

light absorption rate. Moreover, the second layer can also form a heterojunction with WO₃, increasing the charge separation efficiencies. BiVO₄ thin layer has been used widely for this purpose.

With a very thin BiVO₄ absorber layer, the optimized WO₃ nanorod photoanode, modified with cobalt-phosphate (Co-Pi) co-catalyst, achieved as high as 5.1 mA cm⁻² photocurrent at 1.23 V *vs* RHE.^[49] Liu et al. has also demonstrated a novel WO₃/TiSi₂ nanonet structure for PEC water splitting. This core-shell nanostructure reduced the diffusion length for minority carriers and achieved a maximum photo-conversion efficiency of 1.1% at 0.8 V *vs* RHE.^[50] It has also been demonstrated that when combined with a dye-sensitized solar cell, WO₃-based photoanode can achieve up to 3.1% STH conversion efficiency.^[51]

Additionally, co-catalyst deposition has also proven to be helpful in reducing the charge recombination rate. Successful silver nanoparticle co-catalyst deposition has been demonstrated on WO₃ photoanode for PEC application. It is reported that with 2 mol% Ag deposited, the IPCE of WO₃ photoanode reaches as high as 20% at 360 nm wavelength.^[52]

Another very popular co-catalyst for WO₃ photoanode is Co-Pi. Oxygen evolution result shows that Co-Pi increases the theoretical O₂ conversion efficiency from 62% (bare WO₃ photoanode) to approximately 100% (WO₃/Co-Pi photoanode) at 0.8 V *vs* Ag/AgCl.^[53]

Although WO₃ show great potential in achieving high efficiency PEC, it suffers from a major drawback – poor electrochemical stability. WO₃ is known to be not stable in electrolyte solution with pH > 4 due to OH⁻ induced chemical dissolution as shown in equation 5 ^[36]

In order to improve WO₃ stability, several methods have been explored, including doping^[54] and co-catalyst protection layer.^[53]

2.2.2 Cu₂O photocathode

Generally speaking, the requirements for photocathode are more difficult to meet compared with photoanode because of limited number of suitable materials. Basically, a photocathode's conduction band (CB) should be higher (more cathodic) than water reduction level. Meanwhile, it must also have a suitable band bending direction at the electrode/electrolyte interface. Photocathode materials are typically p-type semiconductors, however, there are not a lot of p-type semiconductor oxides with appropriate band gaps and positions available, especially material that also meet the requirements of low cost and earth abundance. All these features render p-type Cu₂O a popular choice as a visible light active photocathode for PEC water splitting.

As one of the most simple and abundant p-type oxide photocatalysts, Cu₂O has a theoretical STH conversion efficiency of 18%, with band gap of 2.0–2.2 eV (Figure 2.6).^[55] It has been reported that the conductive band of Cu₂O is as negative as -0.7 eV *vs* NHE. Thus a strong driving force of charge carriers is expected, induced by the strong band bending in the electrode/electrolyte interface.

Figure 2.6 The relationship between photocathode band gap and the theoretical photocurrent and STH conversion efficiencies under AM 1.5G illumination.^[56]

Cu₂O is most-known as a reddish dye and antifouling paints in daily life. It is usually found as the reddish mineral cuprite. The synthesis of Cu₂O is rather simple and straightforward. It is usually prepared through simple oxidation of copper metal. But the condition for synthesis is tricky. As shown in the Pourbaix diagram in Figure 2.7, Cu can transform into Cu₂O only under alkaline conditions, which is why most of the synthesis reaction of Cu₂O are carried out in alkaline solutions. Similar with other photoelectrodes, the morphology plays an important role in photoelectrochemical activity. In order to control the nanostructure, various preparation methods have been explored.^[57] Comparatively, electrodeposition has been proven to be the most convenient and promising method. Furthermore, through altering the deposition conditions (*e.g.* current density, deposition solvent type, solvent pH value and deposition temperature), various morphologies and crystallization orientation have been achieved.^[58] Graezel's research group has a great number of reported work on optimizing electrodeposited Cu₂O photocathode.^[58] They found that the best deposition conditions for Cu₂O photocathode should be a solution pH value at 12, temperature at 30 °C and current density -0.1 mA cm^{-2} . On one hand, it results in the most uniform morphologies and on the other hand, it is

found that a strong (111) orientation of Cu_2O was found at this deposition condition, which has been proven to be the crystal orientation with the best photoelectrochemical properties.

Figure 2.7 Pourbaix diagram for copper in uncomplexed media.^[59]

Although Cu_2O appears to be a very promising photocathode, it suffers greatly from instability resulting from self-reduction to Cu and self-oxidation to CuO .^[60] This property has significantly hindered the application of Cu_2O in any type of aqueous solution including water splitting. Various attempts have been made to improve the stability of Cu_2O . It has been demonstrated that by tuning the morphology and crystal orientation, the stability can be improved to some extent. The crystallinity of Cu_2O affects its performance as a photocathode in several aspects:

- Type of semiconductors. Cu_2O can be either a p-type or n-type semiconductor and this can be altered by its crystallinity (vacancy type). It has been reported that with different synthesis condition, a different type of Cu_2O can be easily fabricated and differentiated.^[61]
- Band gap and band position. Similar with other semiconductors, the crystallinity difference leads to band gap and band position difference.
- Stability. As for stability, it is a big problem hinders Cu_2O to be used in water splitting. Some work has demonstrated that improved crystallinity can improve the stability of Cu_2O .^[62]

It has been reported that polycrystalline Cu_2O which is predominated by Cu^+ terminated (111) on its surface is more stable than other orientations. In the meantime, the single crystal of (211) or (311) with an O^{2-} terminated surface has also been proven much more stable. But these differences are minor, which cannot render a stable enough Cu_2O photocathode for long-term application in PEC.^[63] Thus, a better strategy is urgently needed.

Other than morphologies control and crystallization manipulation, the heterojunction is also a very popular area for improving both photocurrent and stability of Cu_2O photocathodes. The most commonly used semiconductor to form heterojunction with Cu_2O is CuO .^{[64] [65]} As CuO is also an earth abundant p-type photocatalyst, with a known narrow band gap of 1.2 eV. It has been reported that with a CuO top layer, almost two times photocurrent is achieved compared with bare Cu_2O (1.54 mA cm^{-2} at 0 V vs RHE).^[66] This effect is induced by better charge separation efficiency brought by the $\text{Cu}_2\text{O}/\text{CuO}$ heterojunction. Upon illumination, the photogenerated electrons transfer from Cu_2O to CuO , then inject into the electrolyte and photogenerated holes transfer from CuO to Cu_2O . Meanwhile, CuO also improves the stability of Cu_2O photocathode. Compared with bare Cu_2O , $\text{Cu}_2\text{O}/\text{CuO}$ system enhanced the stability for more than two times. It has also been reported that $\text{Cu}_2\text{O}/\text{CuO}/\text{TiO}_2$ triple layer shows better photocurrent (0.84 mA cm^{-2}), compared with $\text{Cu}_2\text{O}/\text{TiO}_2$ bi-layers (0.45 mA cm^{-2}).^[58]

In summary, WO_3 and Cu_2O have been proven to be two efficient photocatalysts for PEC water splitting. Considering their drawbacks such as poor stability, our first target is to improve their stabilities as well as achieving higher photocurrent. Followed by integrating these two photoelectrodes and studying their PEC performance.

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Chapter 3

Experimental Methodology

This chapter is focused on the experimental details and rationales behind the selected fabrication methods. The characterization techniques are explained too. For material synthesis, there are great number of synthesis methods available to prepare photocatalysts. Out of those, the most cost effective, easy-to-synthesize approaches were selected, such as anodization, electrodeposition etc. After the synthesis, various material characterizations were carried out to study the material properties. These include the morphologies and crystallization studies using equipment such as FESEM, XRD etc. As for material and device performance testing, photocurrent measurement is the most straightforward to examine the performance of a photoelectrode. Impedance study is used to inspect the electrode/electrolyte interface dielectric properties. Efficiencies tests (i.e. IPCE, Faradaic efficiencies) are also used to evaluate the PEC performance.

3.1 Material preparation

When selecting the production method for a photoelectrode, the most important parameters to consider are simple processing and low fabrication cost. It is well known in the semiconductor industry that costly preparation processes are always big hindrance to the commercial development of many promising materials. The commonly used semiconductors such as single crystal silicon, GaP, CdTe and so on all involve special instruments and harsh reaction atmospheres in their fabrication processes. Thus, it is necessary to avoid these materials and seek easy-to-fabricate semiconductors as an alternative. Simultaneously, we also want to develop facile fabrication methods, which have possibilities for large scale fabrication for future PEC commercial applications.

3.1.1 Fabrication of triple layered WO₃ photoanode

As mentioned in the last chapter, WO₃ has been well studied for more than 40 years. Along the way, there are various methods reported for producing WO₃ photoanode. Several commonly used methods are:

1. *Sol-gel*

Sol-gel is a process well-known for fabricating metal oxides. It involves the conversion of monomers into colloidal solution that acts as the precursor for an integrated network (gel), thus the so-called “sol-gel” method.^[1] This method to prepare thin film usually starts with spraying the prepared gel on a conductive substrate (*e.g.* FTO conductive glass), follow by drying and annealing. For example, Wang et al. prepared a nanostructured WO₃ film using sol-gel process with Na₂WO₄ as precursor, with addition of carbowax and triton as the surfactants.^[2]

The advantages of sol-gel method are: speedy process, low cost and ease of preparation. Moreover, by controlling the synthesis condition (*e.g.* precursors, surfactants, heating temperature and annealing environments), morphologies and crystal structures of the synthesized WO₃ photoanode can be easily adjusted.^[3] In the meantime, the disadvantages of this method are also unneglectable: (1) the films are not uniform when fabricating the material in medium-to-large scale, especially when simple methods such as spray coating or dip coating are used to prepare the gel on conductive substrate; and (2) the

thickness of the material is limited. By using this method, films more than 1 μm thickness film with good catalytic properties can scarcely be prepared.

2. Hydrothermal

Hydrothermal crystallization of metal oxide was first introduced by Adschiri et al. This method involves heating of aqueous acidified metal salt solution to a supercritical state of 400 °C and 35 MPa.^[4] This high temperature and high pressure environment allows rapid and simple formation of crystallized metal oxide. Using hydrothermal method to prepare WO_3 has been very popular.^[5] For example, Hong et al. synthesized WO_3 photoanode with hydrothermal method using ammonium metatungstate as a precursor, followed by calcination at 500-800 °C.^[6]

The advantage of this preparation method is similar with the sol-gel method, which is having the ability to adjust the final material properties. Through changing the hydrothermal conditions (*e.g.* the precursors, reaction solvents, synthesis temperature and duration), WO_3 with various morphologies can be achieved. For example, it has been reported that plate-like, wedge-like, and sheet-like nanostructured WO_3 films on FTO glasses could be selectively prepared by a crystal seed-assisted hydrothermal method using $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ as a tungsten source and Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, and $\text{CH}_3\text{COONH}_4$ as capping agents, respectively.^[5c] Followed by calcination in air at 500 °C for 30 min, amorphous WO_3 turns into crystallized WO_3 . Technically, the morphologies are controlled by altering the crystal seeds layer. It is worth noticing that with different WO_3 morphologies, different photocatalytic properties have been achieved.

Generally, the disadvantages of using hydrothermal method to prepare WO_3 photoanode are: (1) a seed layer on the conductive glasses prior to hydrothermal reaction is compulsory in order to prepare a continuous WO_3 film with good affinity, (2) prolonged synthesis duration. In some cases, more than 24 hours is required to synthesize a sample. (3) difficulty in scaling up. The hydrothermal reaction requires a special hydrothermal reactor to maintain the pressure throughout the crystal formation process. The volume of such reactor is limited. Thus, to achieve a large sample size, the cost will be dramatically increased.

3. *Sputtering*

Sputtering has been used in recent years as an easy and convenient method to prepare WO₃ photoanode. Sputtering is a process whereby particles are ejected from a solid target material due to bombardment of the target by energetic particles, particularly in the laboratory, gas ions.^[7] Physical sputtering is driven by momentum exchange between the ions and atoms in the target materials due to collisions.^[7] The commonly used sputtering technique for WO₃ photoanode preparation is magnetron sputtering.^[8] The advantages of magnetron sputtering are: (1) easy to control the thickness of the material. The thickness of the film is in direct relation with the combination of sputtering power and time. With very short sputtering duration, less than 10 nm thin film can be prepared. (2) ability to fabricate thick WO₃ film when necessary. As mentioned above, some methods limit the thickness of WO₃ photoanode. However, with magnetron sputtering, films thicker than 3 μm or more can be easily achieved by simply increasing the sputtering duration; (3) sputtered films are uniform and dense, and easy to scale up and (4) very short preparation time, usually only few minutes are required for the actual sputtering process, excluding the preparation of the machine (few hours). While, the disadvantages of this technique are (1) expensive equipment, magnetron sputtering requires a high vacuum chamber with extreme cleanliness in order to deposit a high quality film; and (2) limited control over morphology. The sputtered films are usually uniform dense layers without nanostructural features, due to the nature of this fabrication method.

4. *Anodization*

Anodizing is an electrochemical process that is typically utilized to convert a metal surface into a decorative, durable, corrosion-resistant, anodic oxide finish.^[9] The process is called anodizing because the surface to be treated forms the anode electrode of an electrical circuit. Anodization is also a popular method to fabricate metal oxide film. Anodizing changes the microscopic texture of the surface and changes the crystal structure of the metal near the surface. The advantages of this methods are: (1) easy control in the fabrication process. By adjusting the temperature, voltage, solution pH value, the morphologies of WO₃ can be easily controlled; (2) low cost, as no expensive equipment is involved; (3) possible to achieve thick film (more than 3 μm). This is very important as the

thickness is essential in achieving high photocurrent as the number of charge carriers is directly related to the film thickness. and it remains a challenge to form a thick and stable film for WO_3 using other methods such as hydrothermal and direct annealing metallic tungsten. The anodization method reported in this thesis utilizes W metal as the substrate and WO_3 is grown in situ from the metallic layer. In this way, WO_3 film with thickness higher than 3 μm has been achieved, with surprisingly good mechanical stability.

The WO_3 photoanode was synthesized via a simple time-controlled anodization method of tungsten foils with the assistance of fluorine and nitric acid co-etching effect at high temperature. The successive anodization steps of W foils lead to WO_3 nanostructured overlayers.

The actual preparation processes are as below:

Anodization of the tungsten foils was carried out by applying 30 V between a platinum cathode and a $2 \times 2 \text{ cm}^2$ metallic tungsten foil (GoodFellow, 99.95%, 0.2 mm) in an acidic electrolyte consisting 25 ml 1.5M HNO_3 and 40 mg NH_4F . The anodization time was precisely controlled and set to be in the range between 1-4 hours, resulting in WO_3 overlayers of increasing thicknesses in the range 1.4-3.0 μm . During anodization, the electrolyte temperature was maintained at 50°C. After anodization, samples were washed carefully with distilled water and blow dried by a stream of nitrogen gas, followed by annealing in air at 550°C for 4 hours. A 10 nm-thick TiO_2 layer was finally deposited on selected samples by atomic layer deposition (ALD, Beneq TFS 200) using TiCl_4 and H_2O as the precursors.

3.1.2 Fabrication of $\text{Cu}_2\text{O}/\text{NiFe}$ -layered double hydroxide (LDH) photocathode

Due to the unstable nature of Cu_2O , there are not a lot of methods available to fabricate Cu_2O thin film.

1. Thermal oxidation

The first developed fabrication method was thermal oxidation, which is by far the most widely used method for Cu_2O in the fabrication of solar cells.^[10] The fabrication process is essentially an annealing process. By heating copper at an elevated temperature (1000 – 1500 °C) for various duration in either oxygen or air condition, a Cu_2O film can

be formed. During this process, CuO will also form as a most stable state among different types of copper oxides, which can be removed later using an etching solution such as FeCl_3 , HCl and NaCl.^[11] This process may lead to a good quality polycrystalline Cu_2O , whereas the properties of the film is also greatly dependent on the starting material and heating atmosphere. Thus, samples may exhibit batch variability even with the same preparation conditions. Another point of note is that there is no control over the film morphology, thus, the photoelectrochemical properties is far from ideal when applying those films in PEC.

2. *Sputtering*

Another method is sputtering, similar with the fabrication process of WO_3 photoanode. The advantages and disadvantages of this method have been described earlier. In short, this method provides limited structural control for the photoelectrode surface.

3. *Reduction*

Other novel methods have also been brought up in recent years such as the novel reduction route reported by Zheng et al.^[12] They used polyethylene glycol as a surfactant at room temperature to synthesize Cu_2O nanowires. The method is very simple, but it is difficult to apply this same route for thin film fabrication.

4. *Electrodeposition*

So far, the best fabrication method developed for Cu_2O thin film synthesis is electrodeposition. Essentially, electrodeposition is a long-established way to deposit thin film on a conducting substrate. This process is carried out using a two or three electrode configuration with an external voltage/current applied. Ions in the solutions are deposited onto the negatively/positively charged electrode. The advantages of this preparation method are: (1) low cost and short preparation time. Only electricity is used as an energy input and the deposition time is usually short. In the current experiment, the deposition durations are 1500 s for Cu_2O and 20 s – 300 s for NiFe-LDH co-catalyst; (2) easy to control. By controlling the deposition conditions (*e.g.* current/voltage value, solution type and pH, and deposition duration), the morphologies and performance of as-synthesized photoelectrode can be tuned easily.

In the current preparation process, both Cu₂O and NiFe-LDH co-catalyst were deposited using the electrodeposition method. The detailed preparation conditions for both materials are:

a. Preparation of Cu₂O photocathodes

Prior to the deposition, 50 nm Au was deposited on FTO glasses via e-beam deposition to ensure the conductivity and reproducibility of the samples. Electrodeposition of Cu₂O was carried out in a basic solution of lactate-stabilized copper sulfate consisting 0.2M CuSO₄ (Sigma Aldrich) and 3M lactic acid (Fisher Scientific) solution in deionized water. Afterwards, 1M NaOH was added to adjust the solution pH to 12. The basic environment ensures that deposited Cu₂O is of p-type conduction. During deposition, the temperature was kept constant at 40°C using a hot plate. The Cu₂O thin films were deposited at a constant current density of $-1 \text{ mA} \cdot \text{cm}^{-2}$ vs Ag/AgCl reference electrode using a three-electrode system (galvanostatic mode, Gamry Instruments, Inc.)

b. Electrodeposition of the NiFe-LDH co-catalyst

Electrodeposition of NiFe-LDH is realized using Cu₂O as the working electrode, together with a Pt counter-electrode and Ag/AgCl as the reference electrode. The solution for electrodeposition of NiFe-LDH consists a mixture of 0.2M Ni(NO₃)₂·6H₂O and 0.1M Fe(NO₃)₃·9H₂O in 50 ml of deionized water. A constant potential of -1.0 V vs Ag/AgCl is applied for various periods of time ranging from 20-300 s, leading to different morphologies. For deposition time less than 60 s, the NiFe-LDH does not reveal a clear nanoflake morphology, although photocurrent is improved as compared with bare Cu₂O.

3.2 Material characterization

3.2.1 Morphologies

As mentioned in chapter 2, compared with a flat surface, nanostructured morphologies greatly improve photoelectrode performance by increasing the light absorption efficiency and reducing the charge recombination rate. The most important technique used to study the morphologies of synthesized photoelectrodes is the scanning

electron microscope (SEM). Through SEM, a photoelectrode's morphologies can be observed, and the thickness of the layer can be obtained from a cross section view.

The principle of SEM is similar with that of a light microscope, the latter uses light source but the former uses energetic electron beams as energy source. Compared with the light microscope, SEM is not limited by the light wavelength because of the short wavelength of the accelerated electrons. The basic working principle of SEM is shown in Figure 3.1. Electrons from a thermionic, Schottky or field-emission cathode are accelerated through a voltage difference between cathode and anode that may be as high as 50 keV.^[13] Tungsten is usually used as cathode material because of its high melting temperature, low vapor pressure and low cost. When electron beams interacts with the sample, the electrons lose energy by interacting with the surface. This interaction results in reflection of electrons by elastic scattering, emission of secondary electrons and radiation.^[14] As the main purpose of SEM is for imaging, the secondary electrons emitted by atoms were detected to map the target surface. Secondary electrons are electrons ejected from the k-shell of the sample atoms by inelastic scattering upon the electron beam interaction. Due to their low energy, these electrons originate within a few nanometers from the sample surface.^[15] Using the signal of secondary electrons, it is possible to image sample features less than 0.5 nm.

In the current experiments, we use field emission SEM (FESEM) to study the morphologies. The difference between FESEM and SEM are: (1) the work function barrier of FESEM is much narrower; (2) external potential applied against source, voltage controls the emission current without heating the source and (3) electrons are “extracted”, thus emission diameter is constant. FESEM usually gives better resolution compared with SEM. The resolution of a SEM is basically given by the minimal spot size. This probe is formed by demagnifying the image of the emission gun. A field emission gun emits the electrons from a much smaller area. Additionally, the coherency is much higher, so the energy spread is smaller. This again allows better focus of the beam.

Figure 3.1 Principle of SEM. Aberrations in the image: BSE = backscattered electrons, SE = secondary electrons, SC = specimen current, EBIC = electron-beam-induced current, X = x-rays, CRT = cathode-ray tube.^[13]

3.2.2 Crystallization

Ever since Max Von Laue discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in crystal lattice in 1912, X-ray Diffraction (XRD) has become an essential technique for the study of crystal structures.^[16] In this work, XRD was used to study the crystallinity of the synthesized materials. As mentioned in chapter 2, different crystallized semiconductor has different photoelectrochemical properties. Thus, in order to achieve high performance PEC,

a certain type of crystal structure of the as-synthesized photoelectrode is preferred and this should be confirmed by XRD.

XRD works by generating X-ray in a cathode ray tube through several steps: (1) heating a filament to produce electrons; (2) accelerating electrons by a voltage and (3) electrons hitting on the target materials, generating characteristic X-ray spectra. Atoms scatter X-ray through atoms-electrons interaction upon incoming electrons waves. They scattered constructively in a few specific directions, determined by Bragg's law:

$$2d \sin \theta = n\lambda \quad (3.1)$$

where d is the spacing between diffracting planes, θ is the incident angle, n is any integer, and λ is the wavelength of the beam. These specific directions appear as spots on the diffraction pattern, which is the XRD spectra we obtained and used to analyze the crystallization of the materials.

Figure 3.2 The incoming beams causes the scattering when interacting with a crystal.^[17]

3.2.1 Light absorption

Another very important properties of photoelectrode is its light absorption efficiency. Using ultraviolet–visible spectroscopy (UV-vis), we can obtain the information about its absorption and reflectance response towards the incident light. UV-vis refers to the absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region.^[18] This technique can be complemented by fluorescence spectroscopy, which is a technique relates to transitions from the excited state to the ground state, while UV-vis absorption measures transitions from the ground state to the excited state.^[19]

The working mechanism of UV-vis shows in Figure 3.3. A beam of light from a visible (wavelength 400-800 nm) and/or UV light (wavelength 200-400 nm) source is separated into its component wavelengths by a prism or diffraction grating. Each monochromatic beam split into two equal intensity beams by a half mirrored device. One beam passes through a control sample, which can be a transparent solution or transparent substrate; another beam passes through the sample to be tested. The intensities of the light beams are measured and compared. The intensity of beam passed by the transparent sample (control) is defined as I_0 , the intensity of the beam passed by the sample is I .

Figure 3.3 Working principle of a UV-vis spectrometer.^[20]

Absorption of the sample can be presented as transmittance ($T=I/I_0$) or absorbance ($A=\log I_0/I$). The information can be derived from UV-vis spectra are:

- (1) Light absorption. The most straightforward information that can be extracted from the UV-vis spectra is the ability of a photoelectrode to utilize light energy. Through comparing the light absorption of photoelectrode before and after modification (*i.e.* morphologies changes, co-catalyst deposition, surface passivation layer and second photocatalyst deposition), the effect of the photoelectrode modification can be analyzed.

For example, although co-catalyst enhances the photocatalytic properties of the photoelectrode, it does not necessarily enhance the light absorption. Some co-catalyst may even reduce the light absorption performance of the photoelectrode. Meanwhile, catalytic surface passivation layer and second photocatalyst will increase the light absorption by either broadening the absorption wavelength range or increasing the absorption ratio.

(2) Band gap of the photoelectrode. A semiconductor absorbs photons from light and generate electron – hole pairs. The minimum photon energy required for this charge carrier generation directly relates to the band gap of this semiconductor. Thus, by observing from the UV-vis spectra, the minimum required light wavelength λ (nm) can be obtained. The minimum required photon energy (E_{PH} , eV) can be calculated accordingly using equation 2. This photon energy corresponds to the band gap of the photoelectrode.

$$E_{PH} = \frac{1240}{\lambda} \quad (3.2)$$

(3) Surface roughness. The incident light will experience one of the three processes after interacting with the photoelectrode surface: absorption, transmission or reflection. Through measuring the light reflection ratio, surface roughness can be comparatively evaluated. This information is especially useful for nanostructured photoelectrode.

3.3 Photoelectrochemical tests

3.3.1 Photocurrent measurement

Photoelectrochemical tests are the most important methods in assessing the performance of aPEC. The most basic photoelectrochemical test is the photocurrent measurement. By directly measuring the current passing through the external conducting wire before and after photoelectrode illumination, a photoelectrode's charge generation performance can be observed directly. In order to evaluate the photoelectrode's performance under different voltage, external bias can be added when testing the photocurrent. There are two modes that can be used for the measurements: (1) chronoamperometry, wherein the voltage is set to a certain value, and current is measured periodically between the photoelectrode in dark condition and the photoelectrode under light; and (2) Linear sweep voltammetry (LSV), wherein the current is measured while the potential between a working electrode and a reference electrode is swept linearly over time.

LSV can also be measured with intermittently illumination. In this way, almost all the photocurrent information can be extracted from the LSV data as shown in Figure 3.3, these information includes:

- (1) Redox peaks such as oxidation/reduction process, or certain non-faradaic process such as cation absorption. In the example shown in Figure 3.4, this peak results from the insertion of protons into the WO_3 film. ^[22]
- (2) Light current. This is the current detected when the photoelectrode is illuminated with a light source at a certain voltage value.
- (3) Dark current. This is the current detected with the photoelectrode under dark condition at a certain external bias.
- (4) Photocurrent. The difference between light current value and dark current value is the value of photocurrent. The photoelectrode generates electrons and holes with the incident light energy. These charge carriers increase/decrease the current value upon illumination compared with the cell under dark conditions. This difference in current value reflects the ability of a photoelectrode to generate charge carriers. Overall, this is the most important information for a photoelectrode as it gives direct information about the material's photocatalytic abilities. The advantage of using LSV to observe photocurrent is that it also gives information about the photocurrent generated under different external voltage. When increasing the voltage, it provides stronger driving force for the charge carriers generated within the photocatalyst towards the counter electrode. Thus, with increasing external bias, the photocurrent usually increases, up to a certain point (saturated photocurrent).
- (5) Saturated photocurrent. This is the point at which there is no more increase in photocurrent with increasing voltage. As the total number of charge carriers generated by a photocatalyst is fixed, the external voltage can only drive this amount of generated charge carriers towards the counter electrode. When theoretically all the generated carriers contribute to the photocurrent, there will be no further increase in the photocurrent no matter how much more voltage is applied. Overall, the saturated photocurrent reflects the maximum number of charge carriers the photoelectrode can generate.
- (6) Turn on voltage in dark ($V_{\text{on-dark}}$). $V_{\text{on-dark}}$ is the turn on voltage of the photoelectrode under dark conditions. As the photoelectrode is a semiconductor, it has a turn on voltage

similar to a diode. $V_{\text{on-dark}}$ represents the barrier potential of the material. When the voltage increases above this value, the current voltage curve starts to be dominated by the ohmic resistance of the bulk semiconductor.^[22] The turn on voltage of a photoelectrode in dark exclusively relates to its band gap and band position.

(7) Turn on voltage under light ($V_{\text{on-light}}$). Similar with $V_{\text{on-dark}}$, $V_{\text{on-light}}$ is the turn on voltage of a photoelectrode under illumination. The difference between $V_{\text{on-light}}$ and $V_{\text{on-dark}}$ is induced by the band position shift arising from charge carrier generation after incident light activates the photoelectrode. This difference results in reduced barrier potential of the material, thus $V_{\text{on-light}}$ is usually smaller compared with $V_{\text{on-dark}}$.

Figure 3.4 Selected example of linear sweep voltammetry data of WO_3 photoanode to illustrate the information can be extracted from LSV graph.

3.3.2 Dielectric properties

a. Impedance

While LSV gives information about the photocurrent generation, electrochemical impedance spectroscopy (EIS) provides information about the dielectric properties of the photoelectrode as a function of frequency. In simple term, impedance is the frequency domain ratio of the voltage to the current, similar to that of electrical resistance in an ideal

resistor. The term was coined by Oliver in 1886 and firstly represented by Arthur in 1893.^[23-24] In general, impedance is usually measured by applying an AC potential to an electrochemical cell and measuring the current. Assuming that we apply a sinusoidal potential excitation, the response to this potential is an AC current signal, which can be further analyzed as a sum of sinusoidal functions (a Fourier series) like that shown in Figure 3.4.^[25]

Figure 3.5 Sinusoidal current response in a linear system.⁹

The excitation signal (voltage) expresses as a function of time:

$$E_t = E_0 \sin(\omega t) \quad (3.3)$$

where E_t is the potential, E_0 stands for the amplitude of the signal, ω is the radial frequency, which relates to the frequency in the relationship of:

$$\omega = 2\pi f \quad (3.4)$$

The response signal (current) is shifted in phase (ϕ):

$$I_t = I_0 \sin(\omega t + \phi) \quad (3.5)$$

Then the impedance will be:

$$Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \quad (3.6)$$

By plotting this impedance we can get an oval, known as “Lissajous figure” (shown in Figure 3.6). Analysis of this Lissajous figure using EIS instrumentation will result in EIS data.

Figure 3.6 Origin of Lissajous figure. ^[9]

b. EIS data interpretation

EIS has been used in electrochemical measurement for a long time. Recently, Macdonald raised the issue about electrical equivalent circuits (EECs), which he describes as an analog of the reactions taking place at the electrode/electrolyte interface. ^[25] As illustrated in Figure 3.7, the electron is transferred from electrode to electrolyte through several electrified interface. This charge transfer process results in both faradaic and nonfaradaic components: (1) the faradaic component arises from the electron transfer occurring via an electrochemical reaction across the interface, namely polarization resistance (R_p) shown in Figure 3.7b, along with the solution resistance (R_s); (2) the nonfaradaic component arises from the double layer (IHP, inner Helmholtz plane and OHP, outer Helmholtz plane, shown in Figure 3.7a). This results in a double-layer capacitor (C_d). For photoelectrode, the number of charge carriers generated and the rate of the charge carriers transfer from electrode to electrolyte determines the dielectric properties of the materials, which is illustrated by impedance (Z_w) in the model shown in Figure 3.7b. Usually, the difference in Z_w before and after illumination reflects the photocatalytic ability of a photoelectrode. While, the frequency-dependent impedance Z_w at the interface is rather complex especially when chemical reactions are involved.

Figure 3.7 (a) electrified interface in which the electrode is negatively charged, at bottom are the electrical circuit elements corresponding to each interface components; (b) an idealized electrical equivalent circuit for the interface.^[27]

Through testing and interpretation of the graphs, several pieces of information can be extracted from the EIS data:

- (1) Electrolyte resistance. This usually depends on the ionic solution concentration, type of ions, and geometry of the area and so on.
- (2) Double layer capacitance. As mentioned in chapter 2, a double layer exists at the interface between an electrode and electrolyte. The double layer of the photoelectrode is contributed by the ions from the solution absorbed on the electrode surface and the charge generated and transferred to the electrode surface. The double layer capacitance information extracted from EIS is mainly contributed by the solution ion concentrations.
- (3) Charge transfer resistance. This is usually the most important information that is to be extracted from an EIS data. Charge transfer resistance is formed by a single, kinetically-

controlled electrochemical reaction. In a photoelectrochemical reaction, electrons are generated by photoelectrode and diffuse into the electrolyte, forming a charge transfer process. The general relation between potential and current is:

$$Zi = i_0 \left(\frac{C_0}{C_0^*} \exp \left(\frac{\alpha n F \eta}{RT} \right) - \left(\frac{C_R}{C_R^*} \exp \left(\frac{-(1-\alpha) n F \eta}{RT} \right) \right) \right) \quad (3.7)$$

where i_0 = the exchange current density; C_0 = concentration of oxidant at the electrode surface; C_0^* = concentration of oxidant in the bulk; C_R = concentration of reductant at the electrode surface; η = overpotential; F = Faradays constant; T = temperature; R = gas constant; α = reaction order; n = number of electrons involved.

When $C_0 = C_0^*$, $C_R = C_R^*$, equation (3.7) is simplified into:

$$Zi = i_0 \left(\exp \left(\frac{\alpha n F \eta}{RT} \right) - \exp \left(\frac{-(1-\alpha) n F \eta}{RT} \right) \right) \quad (3.8)$$

When η is very small and system is at equilibrium, the charge transfer resistance can be expressed with:

$$R_{ct} = \frac{RT}{n F i_0} \quad (3.9)$$

This equation can be used to calculate the exchange current density when R_{ct} is obtained from the EIS measurement and modelling.

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Chapter 4

Nanostructured WO₃ photoanode

Unique nanorods/nanoparticles/nanoflakes (NRs/NPs/NFs) WO₃ triple-layers are grown on a metallic W foil by a simple one-step anodization method. The triple-layer structure is formed through a self-organization process, the film thickness (up to 3 μm) being controlled by the anodization time. A first layer made of an array of WO₃ densely-packed vertically-aligned NRs (1.2-1.4 μm in height) grow atop the tungsten foil, followed by a second layer of small NPs (50-80 nm) and finally a third layer made of rectangular NFs (200-300 nm). When irradiated by white light in a photoelectrochemical cell these WO₃ triple-layers generate a photocurrent as high as 0.9 mA.cm⁻² at 1.2 V vs RHE. Moreover, it is shown that the stability of the triple-layer WO₃ photoanodes can be considerably enhanced by adding an ultrathin (10 nm) TiO₂ protective overlayer.

4.1 Introduction

It has long been a dream for mankind to efficiently convert sunlight into clean and readily usable fuels such as hydrogen and methane on a large scale.^[1-5] Over the past decades intensive research efforts have been devoted to this challenge and various materials and technologies have been explored in view of solar light conversion and storage.^[6-9] One of the most promising technologies consists in splitting water into hydrogen and oxygen through solar irradiation of semiconductor-based devices. Ever since the first work on a TiO₂-based system,^[10] metal oxide semiconductors have become a promising arsenal of materials for water splitting applications, particularly in photoelectrochemical (PEC) systems.^[11-15] Though TiO₂ is the most commonly used material in PEC applications, its wide band-gap (3.0-3.2 eV) hinders its light harvesting efficiency within the visible range of the solar spectrum. Various approaches to extend TiO₂ absorption into the visible range have been investigated, prominently 3d-metal doping, dye sensitization and quantum dots. However these approaches reveal to be costly thus limiting their commercial applications.^[16-17] Therefore, the quest for alternative visible-light photosensitive and earth-abundant semiconductors is focusing the attention of researchers worldwide.

Among the promising novel energy-related materials, WO₃ recently proved to be a very attractive photoanode material in PEC architectures for the following reasons. First, WO₃ possesses a band-gap of ≈ 2.6 eV,^[18] thus allowing its utilization in part of the visible range of the solar spectrum. Then, the theoretical maximum conversion efficiency of WO₃ is $\approx 6.3\%$ for photons having energies higher than 2.6 eV.^[19] Moreover, WO₃ exhibits an important hole diffusion length (≈ 150 nm),^[20] as compared to other semiconducting metal oxides. All these properties render WO₃ a suitable candidate as a photoanode material in PEC applications.

Here a new type of nanostructured WO₃ photoanode is reported constituted of a nanorods/nanoparticles/nanoflakes (NRs/NPs/NFs) triple layer architecture. The triple-layer WO₃ films are fabricated by a simple time-controlled anodization method of tungsten foils with the assistance of fluorine and nitric acid co-etching effect at high temperature. After annealing, the WO₃ triple-layers are monoclinic. The PEC performances of several WO₃ photoanodes having either one, two or three layers obtained with different

anodization times are systematically investigated, revealing the superior photocurrent generation of triple-layers over single- and double-layers. Finally it is shown that the stability of the triple-layer WO₃ in a neutral electrolyte can be considerably enhanced after deposition of a thin (10 nm) TiO₂ top coat by means of atomic layer deposition. Nevertheless, PEC testing results demonstrated that the synthesized WO₃ photoanode has excessive application in strong acidic environment, which is a clear advantage over other photoanode candidates such as Fe₂O₃ and BiVO₄.

4.2 Results and Discussion

4.2.1 Morphologies

The successive anodization steps of W foils leading to WO₃ nanostructured overlayers are illustrated in Figure 4.1. Within the first hour the starting tungsten foil is first anodized into a densely-packed array of vertically-oriented WO₃ NRs along an oxidation reaction. One of the advantages of this packed NRs layer is to preserve good structural continuity between tungsten and WO₃. Such a structural continuum will allow to efficiently transfer photocarriers from the oxide surface to the W substrate in PEC experiments. In a second step, the fluorine/nitric acid co-etching effect produces a porous NPs layer followed by a loose NFs layer. Such a nanostructured triple-layer morphology provides an optimized surface area to harvest a maximum number of incident photons as well as more sites for hole injection.

Figure 4.1 Scheme of the three-step growth of a NRs (1.4 μm)/NPs (1.0 μm)/NFs (0.5 μm) WO₃ triple-layer by anodization of a W foil. The growth times of the NRs, NPs and NFs layers are 1, 2-3 and 3-4 hours respectively.

Figure 4.2 shows the top and cross-sectional morphologies of the WO₃ layers as observed by FESEM. By fine-tuning the parameters of the W oxidation such as in particular the fluorine concentration, temperature and anodization voltage, the thickness and nanostructure of the NRs/NPs/NFs triple-layer structure can be adjusted. After one hour, an array of vertically-aligned WO₃ NRs grow on top of the W foil according to the chemical process below:^[9]

These reactions occur under relatively high voltage (30 V) and in a fluorine-free electrolyte, which means NH₄F does not involve in this reaction for nanorod growth disregard its existence. The effect of fluorine starts from the growth of nanoparticle. In the first step of anodization, W is oxidized into W⁴⁺/W⁶⁺ due to the high voltage. Then W⁴⁺/W⁶⁺ react with penetrated O²⁻ into WO₂²⁺ close to the surface of the W foil (equation 1). Subsequently, WO₂²⁺ is oxidized into W₂O₅ (equation 2) which further oxidizes into the

more stable WO₃ (equation 3).

Figure 4.2 FESEM cross-sectional micrographs of WO₃ layers after anodization of a W foil during (a) 1 hour: NRs layer, (b) 2-3 hours: NRs/NPs bilayer, and (c) 3-4 hours: NRs/NPs/NFs triple layer. (d) FESEM cross-sectional view of nanoparticles NPs and (e, f) FESEM top view of nanoflakes NFs after anodization for 4 hours (f) The scale bars represent 1 μm for a-c, f and 100 nm for d, e.

Because oxidization is a self-limiting process due to the poor penetration of oxygen atoms inside the W foil, the addition of fluorine ions can increase the thickness of metal oxide and act as a capping agent for crystal growth.^[21] Meanwhile, the F⁻ anions dissolve the metal oxide to form fluorine complexes according to equation 4-5.^[22] A porous NPs layer are resulted from the following reaction is also spotted on top of the NRs array (Figure. 4.2b).

The outermost layer of the WO₃ thin film is composed of nanoflakes NFs. These flakes arise from the etching effect of the HNO₃/NH₄F acidic electrolyte at high temperature.^[23] Acid etching is a reaction based on Pourbaix diagram (potential vs pH) in pH=1 environment, first forming WO₄²⁻ species that convert into WO₃.^[24]

During such a chemical process both temperature and pH play important roles in the final WO₃ morphology, according to equation 6.

However, acid etching is usually a very slow process with etching speed in the range 0.5-1.0 μm.h⁻¹ at 50°C (which is the temperature used here), and the flake size is quite large

(diameter >500 nm).^[25] In comparison, in our process the F⁻ anions induce a faster etching that results in flakes of substantially smaller size (diameter ≈ 200-300 nm). Co-etching by both HNO₃ and NH₄F leads to the NPs/NFs bilayer nanostructure whose high roughness, inducing high surface area, is favorable to an efficient photon absorption (see Figure 4.3). The surface roughness and the surface morphology of the triple-layer WO₃ thin film were analyzed by the atomic force microscopy DI-3100. The mode working was tapping mode through the use of probe in a radius of 15 nm. From the AFM image, Surface roughness Rms value of 114.41 nm is calculated. This roughness provides a large surface area, thus improving considerably light absorption of WO₃ photoanodes.

Another advantage provided by the unique NR/NP/NF triple layers is that the density gradually evolves from densely-packed NRs to porous NPs and to disconnected NFs. Such a surface morphology results in a reduced reflectance and an increased photon absorption and charge carrier generation.

Figure 4.3 AFM of a tungsten foil after an anodization time of 4 hours.

The photon absorption of the WO₃ triple layers was evaluated through the reflectance spectra (Figure 4.4). UV-visible optical absorption and photoluminescence (PL) were used to further investigate the light harvesting capability of WO₃ triple layers. After anodization times of 1-4 hours the PL spectra show no peak shift. WO₃ is an in-direct

Figure 4.4 (a) UV-visible reflectance and (b) photoluminescence ($\lambda_{\text{ex}}=300$ nm) spectra of W after anodization during 1h, 2h, 3h and 4h respectively.

bandgap semiconductor, of which the electron-hole recombination loss is only through photon emission or absorption for the wave vector compensation.^[24] The photon emission is measured through photoluminescence spectra, which is corresponding to the electron-

hole recombination efficiency. With different excitation wavelength, the peak position can be varied. In this case, under 300 nm as excitation light, there are two peaks observed in 360 nm and 465 nm, of which 465 nm is corresponding to the band gap value anodization time up to 4 hours, thus indicating an improved charge separation induced by the nanostructured NR/NP/NF triple-layer.

The spectra show that the samples prepared under anodization times in the range 1-3 hours exhibit similar absorption features. However, after 4 hours of anodization the samples exhibit a lower reflectance, hence a higher absorbance, induced by the unique NF structure. These loose NFs layers ensure an optimized photon absorption because of an important area, which then give rise to photocarriers, while the NPs and NRs layers ensure transport of photogenerated electrons toward the metallic W foil.

Figure 4.5 XRD spectra of (a) a tungsten foil before anodizing, (b) as-anodized WO₃, and (c) WO₃ after annealing at 550 °C for 4 hours.

The XRD patterns of an anodized W foil before and after annealing are shown in Figure 4.5. Before annealing (Figure 4.5b) the diffraction pattern is essentially similar to that of tungsten, showing the amorphous character of WO₃ at this stage. In sharp contrast, after annealing at 550°C for 4 hours (Figure 4.5), amorphous WO₃ turned into a crystalline monoclinic phase, as revealed by the appearance of two intense XRD peaks at 24.3° and

75.3°, attributed to the (200) and (040) planes respectively.

Figure 4.6 a-c shows typical HRTEM images of individual monoclinic WO₃ nanoflake, nanoparticle and nanorod. High-resolution reveals that NRs grow along the [200] crystallographic direction. In turn, NPs grow along the [400]. Finally NFs grow along both [022] and [020] with lattice spacings of 0.27 and 0.37 nm respectively. Meanwhile, TEM images reveal the diameter of NRs is ≈ 50 nm (see Figure 4.6d). The HRTEM results correspond with the XRD data, and further prove the good crystallinity property (monoclinic) of as prepared WO₃ thin film.^[26]

Figure 4.6 HRTEM images of (a) an individual WO₃ nanorod, (b) a nanoparticle NP and (c) a nanoflake. The crystallographic growth directions and lattice spacings are indicated.

The scale bar represents 5 nanometers (a and c) or 2 nanometers (b). (d) TEM images of WO₃ nanoparticles NPs (dark) and nanorods NRs (light).

We have also measured the Mott-Schottky of the anodized WO₃, as shown in Figure 4.7. Combined with the absorption data it can be safely calculated that the conduction band of WO₃ photoanode is at 0.359V vs NHE and valance band is at 2.959V vs NHE. The band alignment of WO₃ with other photoelectrodes can be found in Chapter 9.

Figure 4.7 Mott-Schottky of WO₃ after an anodization time of 4 hours.

4.2.2 Photocurrent

The PEC properties of as-prepared triple-layer WO₃ thin films were evaluated using pulsed linear sweep voltammetry (LSV). Figure 4.8a shows that the highest photocurrent density (0.9 mA.cm⁻² at 1.2 V vs RHE) is observed after a 4 hour anodization time. For shorter anodization periods (1-3 hours) the photocurrents are considerably lower, thus

Figure 4.8 (a) LSVs of WO₃ photoanodes under incident chopped light ($f=0.2$ Hz) for anodization times of respectively 1, 2, 3 and 4 hours. (b) Respective linear sweep voltammograms of hydrothermal single layer (red) and anodized triple layer (black) performed on samples having similar thickness.

revealing the importance of having a triple layer structure. To better evaluate the advantage of the triple-layer morphologies, single layer WO₃ with similar thickness is prepared, by hydrothermal method. The WO₃ photoanode after hydrothermal reaction has similar

nanoflake surface morphology but much larger flake size ($>2\ \mu\text{m}$) (Figure 4.9) The hydrothermal conditions are as below: 150°C , 4 hours in 25ml solution mixture of 1.5M HNO₃ and 50mg NH₄F. The LSV comparison between triple-layer WO₃ and single-layer WO₃ with similar thickness further proved the superior PEC properties of as prepared triple-layer WO₃ (see Figure 4.8b).

Figure 4.9 FESEM image of WO₃ photoanode on W metal using the hydrothermal method. Resulted film thickness is about $\sim 3.5\ \mu\text{m}$. The scale of the image is $1\ \mu\text{m}$

The superior performances of WO₃ anodized during 4 hours arises from a more efficient charge separation and a faster interfacial charge transfer,^[27] as revealed by

Figure 4.10 Nyquist experimental data and fitting plots after anodization during (a) 1h, 2h, 3h and 4h under illumination and (b) 4h either in the dark (blue dots) or under illumination (black dots).

electrochemical impedance spectroscopy (Figure 4.10). The EIS plots in Figure 4.8b show that the difference in Nyquist arc of as-prepared WO₃ in dark and illumination conditions, which shows the light-generated electron improves the conductivity of WO₃ photoanode.

Equivalent circuit modelling is based on the impedance experimental data, which is plotted as real admittance vs. imaginary admittance. The data configuration in Figure 4.10 is within the first quadrant, thus implying that no inductance is needed.^[28]

(a)

(b)

Sample	R ₁ (ohms)	R ₂ (ohms)
WO ₃ -1h	3.484	2398
WO ₃ -2h	2.069	1126
WO ₃ -3h	2.049	910.1
WO ₃ -4h	1.833	799.2

Figure 4.11 Proposed equivalent circuit consisting in a constant phase element (CPE) working as a non-ideal capacitor, an interface resistance R₁ and an internal electron-hole recombination resistance R₂. (b) Resistance values R₁ and R₂ as obtained from the EIS measurements.

The model is shown in Figure 4.11a, whereas other models have also been used in PEC cell studies. It consists in two resistances R_1 and R_2 and one constant phase element (CPE) working as a non-ideal capacitor.^[29] R_1 represents the material resistive loss predominantly at the interface of the material surface and the electrolyte, and R_2 represents the internal electron-hole recombination resistance including the recombination happening within the depletion layer. The R_1 and R_2 values derived from the impedance data are summarized in Figure 4.11b. It can be observed that the samples anodized during 4 hours possess both the smallest interface and internal resistances, thus explaining the origin of its higher PEC capability.

4.2.3 Stability

However, although the WO₃ triple layers exhibit excellent PEC properties, they suffer from chemical dissolution in pH value greater than 5 solutions, thus affecting the photocurrent.^[30] In order to prevent this drawback, a 10 nm-thin TiO₂ layer is coated on top of the WO₃ NRs/NPs/NFs triple-layer.

Comparative PEC stability tests on WO₃ triple layers with and without a TiO₂ protective layer are conducted in pH=7 buffer solutions under a constant bias of 0.8 V vs RHE (Figure 4.12). During PEC tests, the samples are illuminated during 50 seconds with periods in the dark of varying duration in the range 0.5-4.0 hours.

Figure 4.12 shows that unprotected WO₃ loses 50% of its original photocurrent within the first hour. In sharp contrast, there is no significant photocurrent loss detected for the TiO₂-protected WO₃ samples within the first 10 hours. Furthermore, when the PEC test is realized after an additional 24 hours, the recorded photocurrent remains as high as 83% of the initial one. This clearly demonstrates that the PEC photocurrent is three times higher with nanostructured NR/NP/NF WO₃ triple layers as compared to single WO₃ layers and can also be stabilized under illumination by an ultrathin TiO₂ protective overlayer.

Figure 4.12 PEC stability tests of (upper) an as-grown WO₃ triple-layer, and (lower) a WO₃ triple-layer coated by a 10 nm-TiO₂ overlayer. Tests are conducted in a pH=7 buffer solution under constant voltage 0.8V vs RHE. The inset is the chronoamperometry scan with periodic on/off light cycles. Incident light intensity: 100 mW.cm⁻²; illuminated sample area: 0.76 cm².

4.3 Summary

In summary, we describe here a new and simple strategy to fabricate well-defined nanostructured WO₃ NR/NP/NF triple- layers acting as efficient photoanodes in PEC systems. The preparation of these WO₃ triple-layers consists in the anodization of a starting

metallic W foil under control of time. For short anodization times (1 hour) the surface of the W foils oxidizes into a highly-ordered array of vertically-oriented WO₃ nanorods. For longer times (2-3 hours) a second layer made of nanoparticles grow atop the nanorods. Finally for anodization time of 4 hours a third layer made of nanoflakes appears, while longer times do not induce any further modification. After annealing, the WO₃ triple-layer exhibits a photocurrent of 0.90 mA cm⁻² under 1.2 V bias vs RHE, which is three times higher than that obtained with a single-layer made of nanorods (0.32 mA cm⁻²). With a 10 nm-thin TiO₂ protective coating, the WO₃ triple layer photoanodes exhibit a superior stability without any significant loss in photocurrent over 10 hours of continuous illumination. As a perspective, further improvement in PEC stability can probably be achieved by increasing slightly the thickness of the TiO₂ protective layer. With such optimized morphological and PEC properties, we believe that these novel nanostructured WO₃ NR/NP/NF triple-layers can be very useful in other PEC systems, especially in view of artificial photosynthesis.

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Chapter 5

Cu₂O/NiFe-LDH photocathode

LDHs are bimetallic hydroxides that currently attract considerable attention as co-catalysts in PEC systems in view of water splitting under solar light. A wide spectrum of LDHs can be easily prepared on demand by tuning their chemical composition and structural morphology. We describe here the electrochemical growth of NiFe-LDH overlayers on Cu₂O electrodes and study their PEC behavior. By using the modified Cu₂O/NiFe-LDH electrodes we observe a remarkable seven-fold increase of the photocurrent intensity under an applied voltage as low as -0.2 V vs Ag/AgCl. The origin of such a pronounced effect is the improved electron transfer towards the electrolyte brought by the NiFe-LDH overlayer due to an appropriate energy level alignment. Long-term photostability tests reveal that Cu₂O/NiFe-LDH photocathodes show no photocurrent loss after 40 hours of operation under light at -0.2 V vs Ag/AgCl low bias condition. These improved performances make Cu₂O/NiFe-LDH a suitable photocathode material for low voltage H₂ production. Indeed, after 8 hours of H₂ production under -0.2 V vs Ag/AgCl the PEC cell delivers a 78% faradaic efficiency. This unprecedented use of Cu₂O/NiFe-LDH as an efficient photocathode opens new perspectives in view of low bias PEC water splitting under sunlight illumination.

5.1 Introduction

Cu₂O is a promising photocathode material due to its suitable band gap (1.9-2.2 eV) and high absorption coefficient in the visible region.^[1-4] Its CB is located above the reduction potential of water, making it suitable for mediating H₂ production with little or no external bias in a PEC cell. Among different methods, electrodeposition has proven to be the most convenient and reliable to prepare nanostructured Cu₂O.^[1, 5] Recent studies show that the Cu₂O morphology and orientation can be controlled by judiciously tuning the deposition parameters such as the electrolyte pH, temperature, applied potential and current density.^[1, 5] The morphology and crystal structure determine the material performances through their role in light absorption and charge transport.

Although Cu₂O possesses an intrinsic potential as a photocathode, the reported photocurrents remain well below the theoretical values in particular under low external biases. These poor performances arise essentially from structural defects at the semiconductor-electrolyte interface. It has been reported that at low external voltages, Cu₂O does not transfer electrons efficiently towards the electrolyte due to an inappropriate band bending.^[6] In order to improve the photocurrent of Cu₂O electrodes, various approaches have been recently developed. For example Cu₂O can be combined with another photocatalyst such as TiO₂,^[7] or by depositing a protective layer on its surface such as Cu₂S,^[8] RuO₂,^[9] or polyoxometallates.^[10]

LDHs attract a growing attention as co-catalysts due to several advantages. LDHs constitute a group of two-dimensional materials of general formula $[M_1-x^{2+}M_x^{3+}(\text{OH})_2][A_{x/n}] \cdot m\text{H}_2\text{O}$ in which a fraction of a divalent metal cation M^{2+} coordinated octahedrally by hydroxy groups is replaced isomorphously by a trivalent metal cation M^{3+} .^[11] The variety in chemical composition and structural morphology of LDH materials make them suitable for a wide range of applications as electrocatalysts.^[12-15] In particular, LDHs can act as efficient photocatalysts for improving the charge separation of photogenerated electrons and holes.^[16] Moreover, the hierarchical morphology of LDHs provides convenient charge transfer at the electrolyte interface in PEC systems. Several types of LDHs such as CoNi,^[16] or ZnCo,^[17] have been widely investigated to enhance PEC water splitting.

We describe here the fabrication of Cu₂O/NiFe-LDH via a facile two-step electrodeposition method and the use of NiFe-LDH to enhance the performances of Cu₂O photocathodes. The NiFe-LDH layers grow as nanoplatelets that are uniformly anchored onto the Cu₂O surface. Our Cu₂O/NiFe-LDH exhibits greatly improved photocurrent intensities particularly at low applied voltages. Moreover we demonstrate that modified Cu₂O/NiFe-LDH photocathodes allow more efficient H₂ production at low applied voltages. The Cu₂O/NiFe-LDH photocathodes reveal to be highly stable with no degradation under low bias after 40 hours of illumination, making Cu₂O/NiFe-LDH an excellent photoelectrode for low bias PEC water splitting.

5.2 Results and Discussion

5.2.1 Morphology of Cu₂O/NiFe-LDH materials

Images recorded by FESEM show that electrodeposited Cu₂O consists in compact and highly homogeneous layers made of cubic particles having ~400 nm in size (Figure 1a) and thicknesses of ~1 μm after 1,500 s of deposition time (Figure 5.1b). NiFe-LDH overlayers are then grown on the Cu₂O samples using different deposition times (Figure 5.1b-c). After 60 seconds, the NiFe-LDH material adopts a uniform nanoflake morphology (Figure 5.1d) with individual flakes of size ~5 nm. After 300 s it self-assembles into sponge-like structures (Figure 5.1f). Besides, the XRD pattern of NiFe-LDH after 150 s exhibits typical (003), (006), and (104) reflection peaks, while Cu₂O shows the known dominant (111) reflection.^[18, 19] NiFe-LDH (20 s) does not show visible XRD peaks, while EDX images confirm the existence and uniformity of Ni and Fe elements in the Cu₂O layer (Figure 5.2). The elements that have been tested are Cu (red spots), O (white spots), Ni (green spots) and Fe (white spots). The images reveal the low density of Ni and Fe atoms detected as compared to O and Cu, which is consistent with the reduced thickness of the NiFe-LDH overlayer after only 20 s of electrochemical deposition.

Figure 5.1 FESEM images of (a) bare Cu₂O; (b) cross-sectional image of bare Cu₂O; (c) Cu₂O/NiFe-LDH (20 s); (d) Cu₂O/NiFe-LDH (60 s); (e) Cu₂O/NiFe-LDH (90 s) and (f) Cu₂O/NiFe-LDH (300 s). Scale bars: 1 μm.

Figure 5.2 EDX of a typical Cu₂O/NiFe-LDH (20 s) sample. The area under study is indicated by a yellow square on the morphology FESEM image (top).

5.2.2 PEC measurements

a. Linear sweep voltammetry

The PEC properties of Cu₂O with and without NiFe-LDH were investigated under chopped light by linear sweep voltammetry (LSV) (Figure 5.3). Before deposition of NiFe-LDH the photocurrent density is 1.27 mA.cm⁻² under -0.6 V vs Ag/AgCl. For deposition times shorter than 20 s the photocurrent of bare Cu₂O does not improve significantly. After deposition of NiFe-LDH for 20 s, the photocurrent density exhibits a twofold increase to reach 2.42 mA.cm⁻². An even more important relative photocurrent increase is observed in the low bias range from 0.0 V to -0.3 V vs Ag/AgCl. For example, Cu₂O/NiFe-LDH (20 s) exhibits a photocurrent density of 0.36 mA.cm⁻² under -0.2 V vs Ag/AgCl, that is more than seven times that of bare Cu₂O (-0.05 mA.cm⁻², Figure 5.4). It shows that the introduction of the NiFe-LDH layer induces a more efficient separation of photogenerated charges on one side and an effective electron injection into the electrolyte on the other side.^{13, 16} Prolonged deposition of NiFe (more than 20 seconds) shows less or no improvement in photocurrent. This is due to absorption of light by NiFe-LDH, which results in reduced charge carriers generation by Cu₂O.

Figure 5.3 LSV under light-chopped illumination of bare Cu₂O and Cu₂O/NiFe-LDH (20 s) electrodes in the voltage ranges +0.1/-0.8 V vs Ag/AgCl.

Figure 5.4 LSV under light-chopped illumination of bare Cu₂O and Cu₂O/NiFe-LDH (20 s) electrodes in the voltage ranges $-0.3/-0.05$ V vs Ag/AgCl. ΔJ_{ph} denotes the photocurrent density after subtraction of the dark current. At -0.25 V vs Ag/AgCl, the ΔJ_{ph} value for bare Cu₂O is $\Delta J_{ph1}=0.07$ mA.cm⁻² while for Cu₂O/NiFe-LDH it is $\Delta J_{ph2}=0.49$ mA.cm⁻².

Furthermore, whereas bare Cu₂O generates a *positive* photocurrent when illuminated under positive low voltages (Figure 5.5a), the Cu₂O/NiFe-LDH (20 s) electrodes generates a *negative* photocurrent under *negative* voltages (Figure 5.5b). For example, under $+0.1$ V the Cu₂O electrode produces a weak *positive* photocurrent ($+0.1$ mA.cm²) while under -0.1 V the Cu₂O/NiFe-LDH (20 s) generates a *negative* photocurrent (-0.3 mA.cm²). Note that for reversed voltages (that is negative for bare Cu₂O and positive for Cu₂O/NiFe-LDH) both types of electrodes do not produce any significant photocurrent. This photocurrent reversal is another evidence of the profound modification brought by the NiFe-LDH (20 s) overlayer on the PEC behaviour of Cu₂O electrodes.

Figure 5.5 Zoom-in of the photoresponse of Cu₂O and Cu₂O/NiFe-LDH electrodes in the -0.2/+0.1 V vs Ag/AgCl low voltage range.

Results show that NiFe-LDH itself generates very limited charge carrier upon illumination. This excludes the possibilities that the photocurrent enhancement of Cu₂O/NiFe-LDH photocathode is induced by the increased number of photon-generated charge carriers induced by NiFe-LDH.

Another point worth notice is that the difference in photocurrent of Cu₂O photocathode and Cu₂O/NiFe-LDH photocathode becomes smaller with increased bias voltage. This is because the increased high applied voltage is able to efficiently separate the majority of photon-generated charge carriers. The effects of NiFe-LDH become less pronounced. As there is no difference for the total number of charge carriers as Cu₂O is the only photon absorber. Thus, the maximum photocurrent of both electrodes have very little difference.

In order to eliminate the possibilities that this photocurrent enhancement is induced by the metal valence state changes in NiFe-LDH, investigated the cyclic voltammetry behavior of NiFe-LDH (Figure 5.6). Results indicate that at the low bias condition (less than -0.2 V vs Ag/AgCl), there is no reduction/oxidation behavior on NiFe-LDH. This eradicates the likelihoods of metal valence state changes induced photocurrent enhancement of Cu₂O/NiFe-LDH photocathode in low bias condition.

Figure 5.6. Cyclic voltammetry of NiFe-LDH (60 s)

b. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) provides information about the interfacial property of the synthesized photocathode, which further reveals the efficient

charge separation effect and improved electron injection property brought by NiFe-LDH layer (Figure 5.8). The semi-circular diameter of the measured EIS stands for the charge

Figure 5.7 EIS of Cu₂O/NiFe-LDH (20 s) under dark and light conditions

carrier transfer resistance (R_{ct}) that controls the electron transfer kinetics at the electrode/electrolyte interface.^[20] The resistance of Cu₂O/NiFe-LDH in the dark is much larger than that under illumination, indicating a higher number of charge carriers at the electrode interface. (Figure 5.8). In addition, as compared with bare Cu₂O, the radius of the semicircle of Cu₂O/NiFe-LDH is smaller under all the conditions (Figure 5.9).

An interesting observation is that by increasing the applied bias from -0.02 V to -0.12 V vs Ag/AgCl, the interface resistance increases for bare Cu₂O but decreases for the Cu₂O/NiFe-LDH samples. This phenomenon arises from the difference between the

Figure 5.8 EIS of (a) Cu₂O and (b) Cu₂O/NiFe-LDH (20 s) electrodes under different external biases.

electrode/electrolyte interfaces with either Cu₂O or NiFe-LDH. Under illumination over the voltage range $-0.02/-0.12$ V vs Ag/AgCl, the surface of bare Cu₂O is predominantly charged with holes essentially because of the blockage of the electron transfer path from Cu₂O to the electrolyte (see Figure 5.11). At more negative voltages, the number of holes

decreases, thus resulting in a resistance increase of bare Cu₂O. This is evidenced by the larger semi-circle diameter in the EIS (Figure 5.8). In contrast, deposition of a NiFe-LDH overlayer induces an appropriate energy level alignment with respect to the electrolyte redox levels so that electrons are efficiently transported towards the surface where they reduce water into H₂ (Figure 5.1b). Electrons become predominant and the NiFe-LDH surface is negatively charged. The number of electrons increases with increasing negative voltage, as confirmed by the smaller semi-circle diameter in Figure 5.3b. This demonstrates the key role of NiFe-LDH in introducing appropriate energy levels at the interface and the subsequent higher electron injection rate into the electrolyte.

Figure 5.9 (left) Voltage dependence of the resistance R_{ct} of Cu₂O and Cu₂O/NiFe-LDH electrodes using the equivalent circuit (right).

Figure 5.10 Schematics of photogenerated electron transfer occurring in a PEC system using (a) bare Cu₂O and (b) modified Cu₂O/NiFe-LDH (20 s) electrodes. The reversal of the electron flow at low voltages is indicated as well as the corresponding band diagrams (red dots denote electrons).

Overall, the misalignment of energy levels when using bare Cu₂O induces an overwhelming number of photogenerated electrons in the bulk because of an insufficient transfer towards the electrolyte. On the contrary, after coating by NiFe-LDH, electrons are able to transfer from electrode to electrolyte under very low external bias (Figure 5.9). This results in a reduced number of electrons in the Cu₂O layer, driving electrons from the counter-electrode to the Cu₂O photocathode. As a result, the sample with and without NiFe-LDH have different electron flow directions for a given bias (Figure 5.9). This superior property makes Cu₂O/NiFe-LDH an excellent candidate for photocathode in low or non-bias PEC systems. The alignment with accurate energy level data of Cu₂O and NiFe-LDH is shown in Figure 5.11. Tafel plots of Cu₂O and Cu₂O/NiFe-LDH (20 s) have been added in Figure 5.12. The results indicate that the Cu₂O/NiFe-LDH shows lower slope than Cu₂O.

Figure 5.11. Mott-Schottky measurements of (a) Cu₂O and (b) Cu₂O with NiFe-LDH (20 s) and band alignment of Cu₂O and NiFe-LDH (20s) base on the measurements of (a) and (b).

Figure 5.12. Tafel plots of Cu₂O and Cu₂O/NiFe-LDH (20 s)

c. Photostability

In order to evaluate the potential of Cu₂O/NiFe-LDH photocathodes for H₂ production, we tested their long-term stability under illumination at low voltages. It is well-known that Cu₂O suffers from poor stability under illumination. The photogenerated electrons reduce Cu₂O into Cu and photogenerated holes oxidize Cu₂O into CuO, the illuminated area rapidly turning black.

Various attempts have been made to solve this problem,^[21-24] but the stability of Cu₂O under low bias is rarely mentioned because of too low photocurrents. However, in the presence of the NiFe-LDH co-catalyst, the photostability of Cu₂O under low bias can be explored. Observations indicate that Cu₂O instability is mostly caused by the highly negative applied voltage, under which electrons that accumulate at the photocathode reduce Cu₂O into metallic copper (Figure 2.7). The testing conditions in the literature are usually under ~0V vs RHE, under which environment Cu₂O tends to be reduced to a most stable state – metallic Cu. Whereas, our testing condition is -0.2V vs Ag/AgCl under pH 6.5, which fell exactly in its stable condition range. This is supported by the fact that Cu₂O samples under -0.2 V vs Ag/AgCl is also surprisingly stable after 40 hours of continuous illumination (Figure 5.14). The stability tests of Cu₂O with and without NiFe-LDH under -0.6 V vs Ag/AgCl show that NiFe-LDH also lengthens the stability of Cu₂O under relatively high voltage (Figure 5.14).

Figure 5.13 Long-term photostability of bare Cu₂O (black curve) and Cu₂O/NiFe-LDH (20 s) (red curve) electrodes under white light illumination and -0.2 V vs Ag/AgCl external voltage.

Figure 5.14 Stability test of bare Cu₂O and Cu₂O/NiFe-LDH for various deposition times (20, 40 and 60 s) recorded under -0.6 V vs Ag/AgCl. The table on the right provides the residual current ratio I_b/I_a (indicated by the green arrows) obtained after 15 minutes of illumination.

d. H₂ production

H₂ evolution tests using Cu₂O/NiFe-LDH (20 s) photocathodes have been conducted in a 25% methanol solution as a sacrificial reagent under visible light irradiation according to literature.^[25] The faradaic efficiency is calculated according to $\rho = nH_2 / (Q/2F)$ where nH_2 is the amount of hydrogen generated, and F is the faraday constant. As shown in Figure 5.15, under low bias -0.2V vs Ag/AgCl, the initial faradaic efficiency is 61%, which increases with time up to 78% before decreasing slowly after 800 minutes of illumination. There is no significant decrease in the performances during the first 12 hours. Over the following 10 hours the efficiency slightly decreases to 59%. When a higher bias of -0.8V vs Ag/AgCl is applied, it shows good H₂ evolution in the first 40 minutes. However, after 60 minutes H₂ stops evolving and a progressive decrease of the faradaic efficiency takes place to reach less than 5% after 1,000 minutes of illumination.

Figure 5.15 (a) Hydrogen production and (b) faradaic efficiency of a PEC system using Cu₂O/NiFe-LDH (20 s) as the working electrode under applied voltages of -0.2 V vs Ag/AgCl (red curves) and -0.8 V vs Ag/AgCl (black curves).

5.3 Summary

The growth of an ultrathin NiFe-LDH co-catalyst on Cu₂O electrodes by electrodeposition during 20 s induces a remarkable seven-fold increase of the photocurrent density under low applied voltages (typically 0.49 mA.cm⁻² at -0.25 V *vs* Ag/AgCl, as compared to 0.07 mA.cm⁻² for bare Cu₂O). Electrochemical impedance spectroscopy reveals that NiFe-LDH (20 s) considerably reduces the Cu₂O surface resistance thus allowing photogenerated electrons to be efficiently transported and injected into the electrolyte. Both results are induced by the appropriate band alignment induced by NiFe-LDH. When coated with NiFe-LDH (20 s) as a co-catalyst, the Cu₂O photocathodes generate negative photocurrents with an excellent stability over 40 hours of continuous visible illumination under an external bias of -0.2 V *vs* Ag/AgCl. In Cu₂O/NiFe-LDH (20 s) photocathodes, the combination of high photocurrents and long-term stability under low voltage allow hydrogen evolution. After 8 hours of continuous illumination, Cu₂O/NiFe-LDH photocathodes exhibit a 78% Faradaic efficiency under -0.2 V *vs* Ag/AgCl, while the efficiency drops down to only 5% under -0.8 V *vs* Ag/AgCl. These results demonstrate that modified Cu₂O/NiFe-LDH photoelectrodes are well-adapted to low-biased or self-biased PEC systems in view of artificial photosynthesis.

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Chapter 6

BiVO₄/NiCo-LDH photoanode

BiVO₄-based photoanode has been prepared as a second option in addition to the WO₃ photoanode for investigating dual-absorber PEC mechanisms. BiVO₄ is a well-studied photoanode candidate with a suitable band gap (~2.4 eV) and band position for visible light water oxidation (valance band ~ 2.67 eV vs SHE). However, it suffers from substantial recombination loss of its photogenerated charge carriers. The current results demonstrate that with a very thin layer of NiCo-LDH co-catalyst deposited on the top, BiVO₄'s photoelectrochemical performance has been greatly enhanced. Plain porous BiVO₄ generates 0.57 mA·cm⁻² photocurrent under 0.4V vs Ag/AgCl external bias. In sharp contrast, BiVO₄/NiCo-LDH (deposited for 15 s) exhibits a near threefold increase in photocurrent under the same condition. Furthermore, it is demonstrated that this co-catalyst deposition strategy induces a considerable cathodic shift in the photocurrent onset potential of BiVO₄.

6.1 Introduction

In order to achieve artificial photosynthesis with affordable cost, numerous photocatalysts have been developed.^[1-3] Among these materials, n-type BiVO₄ has recently been established as a promising photoanode candidate for PEC water splitting.^[4-6] BiVO₄ has been widely used as a pigment, having bright yellow color with slight green tint. Electronic properties investigation reveals that it has a band gap of ~2.4 eV, which enables it to absorb a substantial portion of the visible spectrum. Meanwhile, the valence band (VB) of BiVO₄ is in a favorable position for oxygen production. Therefore, it can be used as a photoanode material for visible light activated PEC water splitting. However, plain BiVO₄ photoanode generates very low photocurrent especially under low voltage range due to its poor charge separation efficiency. Thus, researchers have been trying to develop different approaches to improve its charge separation rate.^[7-11] Among these techniques, co-catalyst deposition (*e.g.* Co-Pi, Co₃O₄), has been proven to be efficient and promising to achieve high performance BiVO₄ photoanode.^[6, 12-13]

co-catalystLDHs have drawn a lot of attention in recent years as co-catalyst materials. They have been reported with good electrochemical activities. Meanwhile, they also have the advantages of low cost and are easy to synthesize.^[14-16] Additionally, the hierarchical morphology of LDHs provides efficient charge transfer at the electrode/electrolyte interface. In consequence, the charge carriers generated by the main photocatalyst (*e.g.* BiVO₄) can be efficiently driven towards the electrolyte by LDH cocatalysts. Several types of LDHs have been applied as co-catalyst to improve photocatalysts' efficiencies.^[17-19] The function and properties of NiFe-LDH have been investigated on Cu₂O photocathode as a hydrogen evolution catalyst as shown in Chapter 5.

Here, another LDH will be prepared as oxygen evolution catalyst – NiCo-LDH. A novel BiVO₄/NiCo-LDH photoanode is fabricated by simple electrochemical deposition method. Results demonstrate that the deposition of NiCo-LDH cocatalyst greatly enhance the photoelectrochemical performance of BiVO₄ photoanode. The optimized NiCo-LDH co-catalyst has the functions of both Ni(OH)₂ co-catalyst and Co(OH)₂ co-catalyst. Thus, it improves the photoelectrochemical performances of BiVO₄ in both the photocurrent and the onset potential.

6.2 Sample preparation

a. BiVO₄ photoanode production

Mo doped BiVO₄ photoelectrodes were synthesized by metal-organic decomposition method. We used 0.2M Bi(NO₃)₃·5H₂O in glacial acetic acid (Sigma Aldrich), 0.04M vanadyl acetylacetonate in acetylacetone (Sigma Aldrich) and 0.01M molybdenyl acetylacetonate in acetylacetone (Sigma Aldrich) as the starting solutions. Proper amount of these solutions were mixed according to the stoichiometric ratio of Bi:V:Mo as 100:97:3. 60 μ l of the precursor were dropped on the FTO substrates (1 cm $\times$ 2 cm). The samples were then dried properly and heated at 470 $^{\circ}$ C in a muffle furnace for 30 min.

b. Electrodeposition of NiCo-LDH co-catalyst

Electrodeposition of NiCo-LDH on BiVO₄ was carried out in a solution that consists of 0.1M CoCl₂·6H₂O (Sigma Aldrich) and 0.15M Ni(NO₃)₂·6H₂O (Sigma Aldrich) in 50 mL distilled water. The potentiostatic deposition was performed through a three electrode system using BiVO₄ as working electrode, for various duration (15 s to 300 s). The voltage was maintained at -1.0 V vs Ag/AgCl throughout the deposition process (Gamry Instruments, Inc.). For comparison, Co(OH)₂ and Ni(OH)₂ co-catalysts were deposited under the same electrochemical conditions using solutions that contains 0.1M CoCl₂·6H₂O or 0.15M Ni(NO₃)₂·6H₂O, respectively. After the deposition, the sample was rinsed carefully with distilled water and dried with nitrogen gas under room temperature.

6.3 Results and discussions

The FESEM images show the morphologies of pristine BiVO₄ and BiVO₄ with different co-catalyst deposited on its top. Bare BiVO₄ has uniform morphology with nanoporous structure (Figure 6.1a). The porosity of BiVO₄ enables higher photon absorption efficiency and better charge separation rate compared with unstructured surface.^[20] From the FESEM images of BiVO₄ with NiCo-LDH co-catalysts, we can clearly observe that NiCo-LDH co-catalyst is visible after a very short electrochemical deposition duration. After as short as 15 s, NiCo-LDH nanoflakes already appear on top of

the BiVO₄ surface (Figure 6.1b). With increasing of deposition time, more and more nanoflakes are deposited until the bottom BiVO₄ layer is fully covered with NiCo-LDH (after 90 s, Figure 6.1c-e). Prolonged deposition renders flower-like NiCo-LDH microspheres (Figure 6.1f). In order to analyze the function of the LDH structure, both Co(OH)₂ and Ni(OH)₂ have been deposited separately as co-catalysts. FESEM images of BiVO₄ after Co(OH)₂ and Ni(OH)₂ deposition are shown in Figure 6.1g-h. Both Co(OH)₂ and Ni(OH)₂ have similar flake morphologies. Nevertheless, Co(OH)₂ nanoflakes are much bigger in size (~500 nm) than NiCo-LDH nanoflakes (~100 nm) and Ni(OH)₂ nanoflakes are much smaller size (20-30 nm).

The photoelectrochemical properties of BiVO₄ with and without NiCo-LDH co-catalyst were first investigated with photocurrent measurement through LSV, as shown in Figure 6.2. Plain porous BiVO₄ generates 0.57 mA·cm⁻² photocurrent under 0.4V *vs* Ag/AgCl voltage. In sharp contrast, BiVO₄/NiCo-LDH (15 s) exhibits a near threefold increase in photocurrent at the same condition (1.51 mA·cm⁻² at 0.4V *vs* Ag/AgCl). However, with further increase of the deposition time, the photocurrent of BiVO₄/NiCo-LDH decreases dramatically (Figure 6.2). BiVO₄/NiCo-LDH (30 s) shows even lower photocurrent than bare BiVO₄; and BiVO₄/NiCo-LDH (60 s) exhibits only half the photocurrent of BiVO₄. This photocurrent reduction is caused by the reduced photon absorption of BiVO₄ because of the light absorption of thick co-catalyst layer, as BiVO₄ is the charge carriers generator. The dramatic difference in photocurrent with the slight increase in co-catalyst deposition duration is partially induced by the fast speed of NiCo-LDH formation. As indicated in FESEM images, 60 s deposition already renders near 80% coverage on BiVO₄. When NiCo-LDH fully covered the BiVO₄ (after 90 seconds deposition, as shown in figure 6.1e), the photons reach BiVO₄ photocatalyst reduces dramatically. Moreover, as BiVO₄ is not stable in the NiCo-LDH deposition solution (alkaline condition), prolonged deposition time reduces the thickness of BiVO₄. This material loss reduces the charge carriers' number even further. Whereas, considering the significant photocurrent enhancement induced by a very short deposition duration (15 s), the unstable nature of BiVO₄ under this circumstances can be neglected.

In order to further investigate the function of NiCo-LDH co-catalyst, especially the advantage of LDH structure, we also tested BiVO₄ with Ni(OH)₂ co-catalyst and BiVO₄

Figure 6.1 FESEM images of (a) bare BiVO₄; (b) BiVO₄/NiCo-LDH (15 s); (c) BiVO₄/NiCo-LDH (30 s); (d) BiVO₄/NiCo-LDH (60 s); (e) BiVO₄/NiCo-LDH (90 s); (f) BiVO₄/NiCo-LDH (120 s); (g) BiVO₄/Co(OH)₂ (15 s) and (h) BiVO₄/Ni(OH)₂ (15 s).

Scale bars: 100 nm.

Figure 6.2 Photoresponses of (upper) BiVO₄ with and without NiCo-LDH (15 s) under dark and illumination; and (lower) LSV of BiVO₄ with different NiCo-LDH deposition durations.

Figure 6.3 LSV of BiVO₄ with different co-catalysts

Figure 6.4 Nyquist data of BiVO₄ with and without NiCo-LDH under dark and illumination

with Co(OH)_2 co-catalyst (Figure 6.3). It is clearly observed that after depositing Ni(OH)_2 , the photocurrent of BiVO₄ photoanode has been improved. BiVO₄/Ni(OH)₂ (15 s) generates as high as 1.3 mA cm⁻² photocurrent at 1V vs RHE, which is more than twofold increase compared with bare BiVO₄ (0.57 mA·cm⁻²). At the same time, after depositing

Co(OH)₂, the key improvement lies on the onset potential shift. The BiVO₄/Co(OH)₂ (15 s) shows ~0.1V cathodic onset potential shift compared with bare BiVO₄. As LDHs are compounds with the highly organized mixture of two hydroxide in the composition of [M²⁺_{1-x}M³⁺_x (OH)₂]^{q+}(Xⁿ⁻)_{q/n}·yH₂O^[21-22] (M²⁺ = Ni²⁺, and M³⁺ = Co³⁺), the NiCo-LDH shares the co-catalyst properties of both Ni(OH)₂ and Co(OH)₂. This structure advantage leads BiVO₄/NiCo-LDH (15 s) exhibiting both photocurrent and onset voltage improvements.

LDHs are proven to be efficient electrocatalysts.^[21-23] This is also confirmed by EIS results. The EIS plots in Figure 6.4 show the difference in the Nyquist of BiVO₄ with and without NiCo-LDH (15 s) under both dark and illumination conditions. The results first demonstrate that the light-generated electron improved the conductivity of the BiVO₄, which reflexed in the reduced resistance after illumination compared with BiVO₄ under dark condition. Additionally, the comparison between BiVO₄ with and without NiCo-LDH (15 s) indicates the improved conductivity induced by NiCo-LDH thin layer. The equivalent circuit modelling is conducted based on the impedance experimental data.

The carrier transport was evaluated by comparing the photocurrent measured with and without sacrificial agent H₂O₂. Studies have shown that the efficiency of hole injection into the electrolyte is ~100% in the presence of H₂O₂.^[24] The photocurrent ratio of BiVO₄/NiCo-LDH (15 s) to bare BiVO₄ is 2.9 without H₂O₂ and reduced to 1.9 when the sacrificial agent is added. This sharp comparison demonstrated the effect of NiFe-LDH is to improve the carrier transportation and injection towards the electrolyte when no sacrificial agent involved

IPCE data of pure BiVO₄ and BiVO₄/CoNi-LDH (15 s) are measured at 1.0 V vs Ag/AgCl (Figure 6.5) Upon the deposition of CoNi-LDH, the IPCE of the BiVO₄ photoanode is greatly improved at wavelengths shorter than 480 nm.

Gartner's model is a convenient starting point for the description of the photocurrent produced under depletion condition in a semiconductor junction; it can be used to fit the behavior of semiconductor / electrolyte systems. Using his model, carrier concentration N_D and hole diffusion length can be calculated.:

$$\ln(1 - \eta') = - \left(\frac{2\epsilon\epsilon_0}{qN_D} \right)^{\frac{1}{2}} (V - V_{fb})^{\frac{1}{2}} - \ln(1 + \alpha L_d),$$

where η' represents the quantum efficiency.

Through plotting $\ln(1 - \eta')$ vs $(V - V_{fb})^{1/2}$, the slope $\left(\frac{2\epsilon\epsilon_0}{qN_D}\right)^{1/2}$ can be obtained and an intercept of $-\ln(1 + \alpha L_d)$ from which N_d and L_d can be calculated.^[25]

The calculated hole diffusion lengths of synthesized BiVO₄ when $\lambda=420$ nm is around 117 nm for bare BiVO₄, and the calculated N_d at 0.3V vs RHE is $1.7 \times 10^{19} \text{ cm}^{-3}$. This value is comparable with what have been reported in the literature, where the undoped BiVO₄ is reported a hold diffusion length of 68nm and after Mo doping, the hole diffusion lengths increased to 183 nm.^[26]

Figure 6.5 IPCE spectra of bare BiVO₄ and BiVO₄ with NiCo-LDH (15 s)

6.4 Summary

In summary, BiVO₄ photoanode has been developed as a second option other than WO₃ photoanode. Through depositing a very thin layer of NiCo-LDH co-catalyst (15 s), the photocurrent has been improved greatly. This efficiency enhancement is induced by the improved charge separation and injection efficiencies. The reduced surface resistance is further proven by impedance studies. With this BiVO₄/NiCo-LDH photoanode, the mechanisms behind the dual-absorber PEC's OCV generation will be explored next.

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Chapter 7

Dual-absorber PEC integrations

The integrations of different photoelectrodes into several dual-absorber PECs and their OCV generation performance comparison have been carried out. As per OCV is the most important parameter to achieve self-biasing PEC for water splitting. Several photoanode candidates are used, viz: the synthesized triple layered WO_3 and the synthesized BiVO_4 . In addition, another commonly used n-type material hematite $\alpha\text{-Fe}_2\text{O}_3$ is also employed in the study. Meanwhile, the photocathode is chosen among the electrochemical deposited Cu_2O and two commercial available p-type semiconductors: Si and GaP. OCV measurement results demonstrate that the performance of $\text{WO}_3\text{-Cu}_2\text{O}$ system is limited by the poor charge separation efficiencies of WO_3 . This is reflected in WO_3 's limited photocurrent under low voltage (less than 0.1 mA under voltage < 0.4 V vs NHE). Nevertheless, OCV results also indicate that BiVO_4 and Cu_2O coupled PEC is very promising for self-biasing water splitting. $\text{BiVO}_4\text{-Cu}_2\text{O}$ dual-absorber PEC generates as high as 250 mV voltage upon illumination. In addition, by depositing two type of LDHs on both photoelectrodes (NiFe-LDH onto Cu_2O photocathode and NiCo-LDH onto BiVO_4 photoanode), the OCV generates by $\text{BiVO}_4\text{-Cu}_2\text{O}$ system increases further to 410 mV.

7.1 Dual-absorber PEC integration

Self-biasing PECs have been attempted in several systems in the goal of 100% solar water splitting without external electric input. In the past years, vast amount of attention has been focused on silicon-based systems.^[1-3] One of the reasons might be that different types of silicon semiconductor materials have been developed and most of them are commercially available. Moreover, by adjusting the type and concentration of the dopant, silicon with different electronic properties can be achieved. Nevertheless, it is known that in order to attain a high quality silicon cell, it requires particular harsh synthesizing conditions which dramatically increases the cost of production.^[4] Consequently, alternative cost-effective materials or systems are in urgent need. At this point, research work on metal oxide photocatalysts based self-biasing systems starts to merge and will be the focus in the near future. Whereas, in order to design an efficient dual-absorber self-biasing PEC for potential water splitting application, understanding the key factors affecting the PEC overall performance is the most important task. Several aspects were considered affecting the PEC's ultimate efficiency in the goal of achieving low cost, earth abundant, visible light activated dual-absorber PEC for solar water splitting. Among which, OCV is no doubt an important parameter, as it reveals the systems' potential to drive the redox reactions.

The objective of the current study is to reveal the mechanisms behind the OCV generation, in order to design an efficient dual-absorber PEC. Thus, PEC with different photoelectrodes were combined and tested. The photoanode is chosen among the synthesized triple layered WO_3 , BiVO_4 , $\text{BiVO}_4/\text{NiCo-LDH}$ and another popular photoanode material $\alpha\text{-Fe}_2\text{O}_3$. At the same time, the photocathode material is chosen among commercial available p-type Si, p-type GaP and the synthesized Cu_2O , and $\text{Cu}_2\text{O}/\text{NiFe-LDH}$. In order to analyze the performance of integrated dual-absorber PEC, OCV measurements were conducted with different systems. By comparing the OCV values, a detailed scheme of OCV generation before and after both photoelectrodes are under illumination has been revealed. From where, key factors for high OCV generation within a dual-absorber PEC have also been proposed. This work aims to provide a preliminary guideline for designing dual-absorber PEC for water splitting.

7.2 Experiments

7.2.1 Sample preparation

α -Fe₂O₃ photoanodes were synthesized according to the literature:^[4]

An aqueous solution (33.3 mL) containing of 0.15 M ferric chloride (FeCl₃·6H₂O, Sigma) and 1 M sodium nitrate (NaNO₃, Sigma) was sealed in a 40 mL Teflon liner container. The fluorine-doped tin oxide (FTO)-coated glass of 1×2.5 cm was cleaned with deionized water, ethanol, acetone, ethyl acetate and placed in the liner with the FTO side facing the wall of the liner. The liner was put into an autoclave and heated at 100°C for 12h. After the reaction, the yellow films formed on the FTO substrates were thoroughly rinsed with deionized water and transferred to a furnace. Then the yellow films coated substrates were annealed at 550°C for 2 h with a ramp rate of 2°C/min to convert yellow Fe(OH)_x into red α -Fe₂O₃.

P-type silicon wafers were purchased from Latech, Inc with thickness of 280 μ m with 10-20 Ω ·cm resistivity. P-type GaP wafers were purchased from Semiconductor Wafer, Inc with the thickness of 400 μ m. Prior to testing, both wafers were cut to 1cm × 1cm size and washed with DI water and ethanol for 3 times then dried with nitrogen gas. After that, a thin layer of Au was deposited through magnetron sputtering machine to serve as a conductive layer. In order to prevent conductive layer (Au) directly contract with the electrolyte which will result in current leakage during testing, a layer of epoxy was applied carefully to ensure the full coverage of the back of the electrode and then dried in room temperature toughly for 12 hours.

7.2.2 PEC measurements

LSV measurements were carried out under both dark and illumination conditions with a scan rate of 5 mV s⁻¹. All the tests were conducted in a 0.5M Na₂SO₄ electrolyte using a three-electrode configuration with synthesized sample as the working electrodes, Pt and Ag/AgCl electrodes being used as the counter and reference electrodes, respectively. The inter-electrode spacing was ~1 cm. Currents were recorded using a PCI4/300™ potentiostat equipped with PHE200™ software (Gamry Instruments, Inc.). The working electrodes were exposed to the AM 1.5 light from a solar simulator equipped with a 300 W

Xe-lamp (HAL-320, Asahi Spectra Co., Ltd.). The incident light intensity was 100 mW cm^{-2} and the sample illumination area 0.28 cm^2 .

OCV measurements were conducted in $0.5 \text{ M Na}_2\text{SO}_4$ electrolyte using a two-electrode configuration with selected photoanode as the working electrodes, selected photocathode electrode as the counter electrode. Both photoelectrodes were exposed to AM 1.5 light from a solar simulator equipped with a 300 W Xe-lamp (HAL-320, Asahi Spectra Co., Ltd.). The incident light intensity was 100 mW cm^{-2} and the sample illumination area was 3 cm^2 .

7.3 WO_3 -based system

7.3.1. WO_3 -Si

The first tested system is WO_3 -Si dual-absorber PEC. Although Si based systems have the limitation of high cost and complicated manufacture procedures, semiconducting Si is still included to study the mechanisms of OCV generation by comparing with other photocathode materials. Seeing that it is indeed an efficient photocatalyst which has been utilized in a lot of semiconductor applications. In these measurements, the commercial available p-type Si wafer is used as the photocathode after coated with a 20 nm thick Au conduction layer by magnetron sputtering. The coated Si was then coupled with the synthesized triple layered WO_3 photoanode to form a dual-absorber PEC.

First of all, the band gap and band position of the as-prepared Si photocathode are measured prior to PEC integration performance testing. The band position alignment of both photoelectrode may plays an important role in the generated OCV value. Mott-Schottky measurement is used to determine the CB edge of the Si (Figure 7.1a). Meanwhile, UV-vis absorption spectroscopy is used to measure its band gap (Figure 7.2b). Combine with the study results of our triple layered WO_3 , we then draw a schematic illustration for the relative band positions of these two materials (Figure 7.3c). From this scheme, it can be observed that the VB position of Si is slightly more positive than the CB position of WO_3 (less than 0.5 V). It has been reported that this negligible difference of these two band edge may result in limited OCV value when combining these two materials into a dual-absorber PEC. This might be the reason why in several reported WO_3 -Si based systems, usually no more than 1 mV can be generated upon illumination.^[5-7] In order to understand

the fundamental limiting factors for this system, WO_3 with other photocathodes materials have to be evaluated to reach a more solid conclusion.

Figure 7.1 (a) Mott-Schottky plot and (b) UV-vis absorption spectrum of p-type Si; and (c) schematic illustration of relative band positions of WO_3 photoanode and Si photocathode

It is hypothesized that another important factor for high OCV generation is the performance of both electrodes under low bias. Thus, the LSV photocurrent measurement of p-type Si photoelectrode has been carried out and shown in Figure 7.2. Results demonstrate that p-type Si is able to generate decent photocurrent under high voltage (more than -0.5 V vs NHE). However, under 0 V vs NHE condition, its photocurrent is as low as

$\sim 100 \mu\text{A cm}^{-2}$. This low current is caused by the poor charge separation efficiencies of the tested Si photocathode. As the thickness of Si photocathode is far too thick. Although it has been reported that Si has a fair long minority carrier diffusion length and long charge carrier life time. For a typical p-type 0.03 cm thick wafer, and a diffusion coefficient for electrons $D_n = 27 \text{ cm}^2 \text{ s}^{-1}$, the lifetime that can be expected for a non-passivated surface is $\tau_{\text{eff}} = 2.8 \text{ ns}$.^[8, 9] Thickness of 280 μm is too impenetrable to achieve an optimized efficiency. Here comes again the cost factor, as the cost increases dramatically when the thickness of the wafer reduces even slightly. Furthermore, another factor that hinders its performance is the native oxide layer (SiO_2) between Si and Au conductive layer which severely obstructs the charge collection processes. We attempted to remove this oxide layer with strong hydrofluoric acid but it seems it only has very limited effect. In conclusion, the LSV performance of as-prepared Si photocathode reveals that this material is not an ultimate choice for a self biasing dual-absorber PEC.

The OCV value has been measured within this system before and after photoelectrodes under illumination, as shown in Figure 7.2b. From which we can see the measured V_{oc} difference is $\sim 10 \text{ mV}$. Another thing worth noticing is it does not reach equilibrium even after 90 mins. Whereas, repeated test results show that the difference in OCV before and after illumination stays $\sim 10 \text{ mV}$ regardless of the equilibrium status. This low OCV value might be induced by the close band edges of these two materials like that mentioned in the literature.^[5-7] However, we believe that the poor charge separation efficiencies of the as-prepared Si photocathode especially under low voltage range is another important reason.

7.3.2. WO_3 -GaP

Similar with Si, GaP is another well-known traditional semiconductor. It is reported with an indirect band gap of 2.26 eV. Sulfur or tellurium are usually used as dopants to produce n-type GaP and Zinc is used for the p-type GaP.^[10] Here, we use commercially available p-type GaP as the photocathode (Semiconductor Wafer, Inc. 400 μm). Similar with the measurements done to Si photocathode, we first determine the CB edge and band gap of the purchased p-type GaP through Mott-Schottky and UV-vis absorption (Figure

Figure 7.2 (a) Photocurrent measurement of p-type Si photocathode and (b) OCV of WO₃-Si system before and after illumination. The measured V_{oc} is ~10 mV

7.3 a-b). The Mott-Schottky measurements locate its CB edge at 1.21 V vs NHE. From the reflection spectra we can calculate its band gap as ~2.1 eV. Based on these results, we draw the relative band positions of WO₃ photoanode and GaP photocathode (Figure 7.3c). From where we can calculate the difference between the VB of GaP and CB of WO₃ is ~850 mV. This difference here is much larger than the one of the WO₃-Si system. Thus, we expect

much higher OCV value generated by WO₃-GaP dual-absorber PEC compared with WO₃-Si PEC.

Another limiting factor for the WO₃-Si system is the inadequate charge separation efficiencies of as-prepared Si photocathode. Thus, LSV photocurrent measurement of p-type GaP photocathode has also been carried out, which is shown in Figure 7.4a. Although at high voltage range such as -1.0 V vs NHE, GaP's photocurrent ($\sim 1.2 \text{ mA cm}^{-2}$) is much smaller than that of Si photocathode ($\sim 2.0 \text{ mA cm}^{-2}$). GaP photocathode shows much better performance under low bias range ($< -0.5 \text{ V vs NHE}$). It is able to generate $\sim 0.3 \text{ mA cm}^{-2}$

Figure 7.3 (a) Mott-Schottky plot and (b) UV-vis absorption spectrum of p-type GaP; and (c) schematic illustration of relative band position of WO₃ photoanode and GaP photocathode.

at 0V vs RHE, which is almost three times higher than p-type Si at the same condition. This result indicates a much better charge separation rate of GaP. GaP is reported with an electron diffusion coefficient of $6.5 \text{ cm}^2 \text{ S}^{-1}$, which is smaller compared to that of Si.^[11] Thus, compared with Si photocathode, this higher photocurrent might be induced by the absence of defects (such as non-conductive oxide layer for Si) at the interface of GaP and Au charge collector layer.

Figure 7.4 (a) Photocurrent measurement of p-type GaP photocathode and (b) OCV of WO₃-GaP system before and after illumination. From the OCV we can calculate that the

$$V_{oc} \text{ is } \sim 150 \text{ mV}$$

At last, the OCV value between WO_3 -GaP before and after illumination has been measured, as shown in Figure 7.4b. The calculated V_{oc} difference under light and dark conditions is ~ 150 mV. This value is more than sevenfold higher than that of WO_3 -Si dual-absorber PEC. By comparing the system with GaP and the system with Si, we can conclude that better charge separation and better band alignment result in high OCV value of the WO_3 -GaP dual-absorber system.

7.3.3. WO_3 - Cu_2O

The last photocathode material being tested is the electrodeposited Cu_2O photocathode without further modification. Similar with Si and GaP, we measured the band gap and band position of the synthesized Cu_2O through Mott-Schottky and UV-vis

Figure 7.5 (a) Mott-Schottky plot and (b) UV-vis absorption spectrum of p-type Cu_2O ; and (c) schematic illustration of relative band position of WO_3 - Cu_2O system.

absorption (Figure 7.5 a-b). The relative band position in Figure 7.5c shows that the difference between the VB of Cu_2O and CB of WO_3 is ~ 420 mV. This value is higher than that between WO_3 and Si, but lower than that between WO_3 and GaP.

Figure 7.6 (a) Photocurrent measurement of p-type Cu_2O photocathode and (b) OCV of WO_3 - Cu_2O system before and after illumination. From the OCV we can calculate that the V_{oc} is ~ 180 mV

As mentioned above, the photoreponse of both photoelectrodes under low bias condition seem to be very important. Thus, LSV photocurrent measurement of Cu_2O photocathode is done and shown in Figure 7.6a. It reveals that Cu_2O photocathode is able

to generate $\sim 1.2 \text{ mA cm}^{-2}$ at 0V vs RHE, which is almost four times higher than as-prepared p-type GaP and more than 10 times higher than the photocurrent of as-prepared p-type Si at the same conditions. With this performance we expect a much higher OCV value considering Cu_2O photocathode's good charge separation efficiencies. In fact, the measured OCV value between WO_3 - Cu_2O system before and after illumination is as high as $\sim 180 \text{ mV}$ (shown in Figure 7.6b), which is even more than two times higher than the OCV of WO_3 -GaP.

Figure 7.7 Schematic illustration of band positions of tested photocatalysts

From the OCV results comparison of WO_3 -Si, WO_3 -GaP and WO_3 - Cu_2O systems, we can perceive that the photocatalytic properties of both photoelectrodes are important for a dual-absorber PEC, especially their performance under low bias. The summary of relative band positions of all the photocatalysts tested is shown in Figure 7.7. We can observe that the difference of the photoanode's CV and photocathode's VB vary greatly. The calculated V_{oc1} for WO_3 -Si system is the smallest, which corresponds to the minutest measured OCV value. Whereas, although the V_{oc2} (WO_3 - Cu_2O) is smaller than the V_{oc3} (WO_3 -GaP), the measured OCV shows the opposite trend. This can be explained by the big difference in their photocatalytic behavior under low bias range. As it is understandable that the self-generated OCV value is minute compared with the applied bias. This leads to extreme importance of the photoelectrode's charge separation and transportation performance under low bias towards a dual-absorber PEC overall efficiencies. The

photocurrent under low or zero bias is mainly determined by their charge separation efficiencies. Thus, it is expected that by improving their charge separation and injection rate, the OCV of a dual-absorber PEC can be greatly enhanced. In conclusion, considering both the photocatalytic properties and material properties (*e.g.* nontoxic, low cost and earth abundant), Cu₂O seems to be the most promising photocathode material for WO₃ based dual-absorber PEC water splitting.

7.4 Cu₂O-based system

After selecting the best photocathode material among the three candidates, the next step is to compare the commonly used photoanode materials' performances. Systems wherein Cu₂O coupling with WO₃, α -Fe₂O₃ or BiVO₄ were measured separately. BiVO₄ photoanode has been described in chapter 6, and α -Fe₂O₃ photoanode is prepared according to the literature.^[4] OCV measurement results are shown in Figure 7.8. It demonstrates that WO₃-Cu₂O and Fe₂O₃-Cu₂O systems show much smaller OCV value compared with BiVO₄-Cu₂O system. WO₃-Cu₂O generates ~180 mV upon illumination and Fe₂O₃-Cu₂O produces ~40 mV. Comparatively, Bare BiVO₄-Cu₂O systems generates 40 mV under dark condition and 294 mV under illumination. This leads to ~250 mV photovoltage generation (as shown in Figure 7.8c). The reasons can be the poor band position matching with Cu₂O in case of WO₃-Cu₂O system (as shown in Figure 7.9); and poor charge separation efficiencies in the case of Fe₂O₃-Cu₂O system. As it has been reported that plain Fe₂O₃ has very limited photocatalytic performance resulted from its poor electrical conductivity, short carrier lifetime and very short hole diffusion length (~4 nm).^[12-15] This comparison further confirms that the photoelectrodes' charge separation efficiency is an important factor affecting the OCV value when applied in a dual-absorber PEC. Thus, improving its performance under low bias range is the most efficient approach. From our previous results, of co-catalyst deposition on both Cu₂O photocathode and BiVO₄ photoanode, we can conclude that LDH co-catalyst can improve both the charge separation and charge injection towards the electrolyte. Thus, photoelectrodes of Cu₂O-BiVO₄ with the co-catalysts ought to enhance its OCV generation.

Results of the OCV generation of BiVO₄-Cu₂O system after co-catalyst depositions are shown in Figure 7.10. After 15 s deposition of NiCo-LDH on BiVO₄, the dark voltage

increases to 146 mV and light voltage increases to 500 mV. This results in a ~380 mV photovoltage generation (Figure 7.9b). Followed with 20 seconds NiFe-LDH deposition on Cu₂O photocathode, the dark voltage does not show big changes, it increases from 146 mV to 150 mV. But the light voltage increases further to 56 mV. This combination renders a remarkable ~410 mV photovoltage without external bias (Figure 7.9c). Through multiple testing we found that the dark voltage and light voltage varies slightly, but the difference in the dark and light voltage stays the same. The inconsistency of dark and light voltage might be resulted from the trivial difference in the testing conditions (*e.g.* temperature, humidity).

Figure 7.8 OCV measurement of (a) Fe₂O₃-Cu₂O dual-absorber PEC; (b) WO₃-Cu₂O dual-absorber PEC and (c) BiVO₄-Cu₂O dual-absorber PEC. The calculated V_{oc} value for Fe₂O₃-Cu₂O system is ~40 mV, for WO₃-Cu₂O system is ~180 mV and for BiVO₄-Cu₂O system is ~250 mV

Figure 7.9 A summary of band positions of common photocatalysts.^[10, 11]

Figure 7.10 OCV tests of integrated systems consists of (a) BiVO₄ photoanode with Cu₂O photocathode; (b) BiVO₄/NiCo-LDH (15 s) photoanode with Cu₂O photocathode and (c) BiVO₄/NiCo-LDH (15 s) photoanode with Cu₂O/NiFe-LDH (20 s) photocathode

7.5 Mechanism

There have been numerous studies in the self-biasing system in order to realize spontaneous PEC water splitting.^[1, 18] It has been proposed that the band position matching is the most important factor when combining an n-type semiconductor and p-type semiconductor.^[1-2, 19-21] Only in a way shown in Figure 7.11a, the photogenerated electrons in the photoanode can recombine with the holes generated in photocathode. Meanwhile, the holes in photoanode can be used for photo-oxidation and electrons in photocathode can be used for photo-reduction.

Figure 7.11 Energy-level diagram of the combination between Cu₂O photocathode and BiVO₄ photoanode for self-biasing water splitting (a) before and (b) after illumination on both photoelectrodes.

In this configuration, the OCV value measured in dark condition indicates the fermi level difference after both electrodes reach equilibrium with the electrolyte (as shown in Figure 7.11a). This is the reason for the measured OCV value ΔV_{dark} is relatively small (100 mV) although the fermi level difference of these two materials in vacuum is more than 1V.^[22] After illumination, both the photoanode and photocathode have fermi lever shift induced by the photogenerated charge carrier density change (as shown in Figure 7.11b). The difference in fermi level before and after illumination induces the increases in

OCV from ΔV_{dark} to ΔV_{light} . Overall, the OCV of the system under illumination can be premeditated based on:

$$\Delta V_{\text{light}} = \Delta V_{\text{dark}} + \Delta V_{\text{cathode}} + \Delta V_{\text{anode}} \quad (1)$$

Wherein, the ΔV_{dark} is predominantly determined by the appropriate band alignments; $\Delta V_{\text{cathode}}$ and ΔV_{anode} are indicators for the photocathode and photoanode efficiency. From equation 1 we can find the three key parameters in achieving high OCV for an integrated PEC under illumination. It is worth noticing that in water splitting reaction, it is expected that both ΔV_{light} value and the difference between ΔV_{light} and ΔV_{dark} (V_{oc} in the measurement) are important. Compared with WO_3 and Fe_2O_3 , BiVO_4 has a better band matching with Cu_2O , which gives a slightly higher ΔV_{dark} . Meanwhile, LDH co-catalysts improves the $\Delta V_{\text{cathode}}$ and ΔV_{anode} by improving the charge separation efficiency and charge carrier injection rate into the electrolyte. Thus, after LDH co-catalyst deposition, the system generates much higher OCV.

7.6 Summary

By combining different photocatalysts into dual-absorber PEC systems and investigating their performance, we can conclude that the major factors affecting the OCV value of a dual-absorber PEC system are the photocurrent of both photoelectrodes. Especially their photocurrent value under low voltage range. It is known that the efficiencies of charge separation and charge injection rate are the most important parameters for its photocurrent especially when it is under low external bias. Thus, improving these two features are the first priorities in achieving an efficient dual-absorber PEC. Moreover, as in water splitting reactions, the electrons generated by the photoanode are going to recombine with the leftover holes in the photoelectrode. The energy level of both charge carriers is another important factor. Additionally, the difference of the VB of photocathode and CV of photoanode affects the potential OCV value within a dual-absorber system. Result indicates the bigger the difference is, the higher the potential OCV value of a system. Whereas, compared with the photoelectrodes' band positions, the photoelectrodes' performances under low or zero bias play a more important role in achieving an efficient dual-absorber system for water splitting.

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Chapter 8

Reconnaissance studies – WO₃/TiO₂ tandem photoanode

In order to improve both the photocurrent and the stability of WO₃ photoanode, WO₃/TiO₂ tandem photoanode has been fabricated. Wherein, WO₃ was synthesized using magnetron sputtering method. Metallic W was initially sputtered on FTO conductive glasses. Followed by heat treatment under 500 °C in air for 4 hour. This simple process renders a monoclinic WO₃. The as-prepared pristine WO₃ achieves a 0.13 mA cm⁻² photocurrent under 1V vs Ag/AgCl in 1M HCl solution. Afterward, a thin layer of TiO₂ was applied as a protection layer. This serves two proposes. TiO₂ is a known stable photocatalyst, it can prevent WO₃ from reacting with the electrolyte, thus increasing its lifespan. In addition, TiO₂/WO₃ forms a tandem scheme which improves the light harvesting efficiency of the entire complex. The results indicate that WO₃ with 40 nm TiO₂ tandem photoanode achieves 0.2 mA cm⁻² photocurrent under 1V vs Ag/AgCl, which clearly shows enhancement of photoactivity. Meanwhile, stability test reveals that with 40 nm TiO₂ protection layer, WO₃ is stable for more than 12 hours in pH = 11 strong alkaline solution, a tenfold increase lifespan compared to bare WO₃.

8.1 Introduction

Due to its various oxidation states and good coloration efficiency, WO₃ is one of the most well-known working electrodes available for electrochromic devices.^[1] Additionally, WO₃ exhibits a good oxygen evolution catalyst properties, with a reported band gap 2.6 - 2.8 eV, which can be activated under the blue-UV region of the light spectrum. Moreover, compared with TiO₂ and Fe₂O₃, which are both popular oxygen evolution catalysts, WO₃ exhibits longer hole diffusion length of 150 nm.^[2] Moreover, the theoretical maximum conversion efficiency of WO₃ is about 6.3% for the photon absorption of energies higher than 2.6 eV ^[3]. All of these properties make it an excellent candidate for photoanode material. In order to improve its photostability, several methods have been studied, including doping ^[4], plasmonic particle loading ^[5], co-catalyst protection layer^[6]. Whereas, as mentioned in Chapter 4 WO₃ photoanode suffers greatly from chemical corrosion, resulting from its reaction with the electrolyte.

In order to improve the photocurrent and stability of WO₃ photoanode, WO₃/TiO₂ tandem scheme is attempted in this work, as TiO₂ have good stability against both chemical and photon corrosion. Thus, it is expected that the top TiO₂ layer can prevent the beneath WO₃ layer from reacting with the electrolyte. Meanwhile, as TiO₂ is the most well studied photocatalyst which can utilize the UV range of the light spectrum. The combination of WO₃/TiO₂ can, theoretically, improve the light absorption efficiencies. Ideally, TiO₂ top layer can absorb the short wavelength in the light spectrum and generate electrons and holes. Meanwhile WO₃ utilize the leftover solar energy. It is expected that compared with pristine WO₃, properly designed WO₃/TiO₂ tandem photoanode is able to generate a higher number of charge carriers. In order to study the performance of WO₃/TiO₂ tandem photoanode, different thickness TiO₂ has been applied, with a series of photoelectrochemical measurements and stability tests.

8.2 Sample preparation

W thin films were deposited at room temperature on FTO glasses by magnetron sputtering using a W target (99.99%). The FTO glasses were cleaned with methanol and DI water prior to sputtering and dried using an N₂ gas gun. After the sputter machine chamber pressure reaches 9×10^{-6} mTorr, the glasses were further cleaned by the argon

plasma for 10 minutes. The working pressure of argon gas was 18 mTorr throughout the deposition. The sputtering power was set to direct current (DC) 250 W, with varying deposition times. After sputter deposition, W films were oxidized to WO₃ by annealing in different temperatures in ambient condition.

TiO₂ thin films were deposited at room temperature by magnetron sputtering Ti target (with purity of 99.99%) on the top of WO₃ thin film at the same condition (with DC sputtering 250 W), followed by heat treatment 550°C for 4 h in air.

8.3 Results and Discussion

The crystalline structures of annealed WO₃ in different temperature and annealed TiO₂ with different thickness were characterized by X-ray diffraction (XRD) and are shown in Figure 8.1. The WO₃ after post annealing at 500 °C for 4 hours shows a monoclinic structure. Treatment temperature is crucial to achieve WO₃ crystal structure, when heated under below 500 °C, less photo-active orthorhombic phase WO₃ is predominant. Whereas, although there have been plenty of methods in improving the stability of WO₃, is has not been mentioned widely to use tandem scheme to realize both photostability and photoactivity simultaneously. TiO₂ is used here as the protection layer as well as a photocatalyst. After annealing at 550 °C for 4 hours, TiO₂ film shows anatase phase, as shown in Figure 8.1b, which is a well-known active photocatalyst that absorbs UV light.

In order to further study the stability of WO₃ and WO₃ with the TiO₂ protection layer, a series of stability tests were performed. Figure 8.2a illustrates the comparison of photocatalytic life span for bare WO₃ and WO₃ with 40 nm TiO₂ (test duration: 12 hours). The pH values of electrolytes were varied from 3 to 13, made by mixing certain amount of 0.1M HCl, 0.5M NaCl and 0.1M NaOH solution. Bare WO₃ catalyst loses its photoactivity after 9 hours at pH = 7 electrolyte, with TiO₂ it is stable after 12 hours of continuous illumination. Figure 8.2b shows the photocurrent of bare WO₃ and WO₃ with 40 nm TiO₂ thin layer in pH = 11 electrolyte with 0.347 V bias (1V vs. RHE). The photocurrent of bare WO₃ drops by 75% within the first 2 hours. This reduction in photocurrent continues until the photocurrent is totally diminished; while there is no sign of instability of WO₃ / TiO₂

within the test time, which indicates the presence of TiO₂ thin layer effectively limits the diffusion of OH⁻ species from the electrolyte and protects WO₃.

Figure 8.1 XRD patterns of: (a) WO₃ after different post annealing temperature, at 200 °C (amorphous), 300 °C (amorphous), 400 °C (amorphous) and 500 °C (monoclinic) (b) WO₃ and TiO₂ after post annealing temperature 500 °C.

Figure 8.2 Stability test: (a) WO_3 and WO_3/TiO_2 stability test in different electrolyte, pH = 3, 5, 7, 9, 11, 13 solutions; (b) WO_3 and WO_3/TiO_2 stability test in pH = 11 NaCl / NaOH electrolyte.

The band gap of WO₃ and TiO₂ were calculated from UV-vis absorption spectra. Figure 8.3 shows the spectra for of WO₃, TiO₂ and WO₃ / TiO₂ films. The initiate absorption of WO₃ is around 420 nm, and TiO₂ 380 nm. Based on the Tauc formula:

$$\alpha h\nu = A(h\nu - E_g)^n \quad (1)$$

where A is a constant, $h\nu$ is the incident photon energy, E_g represents the band gap energy, and the exponent n is equal to 2 for an allowed indirect transition, or 1/2 for an allowed direct transition [7], we obtained band gap energy (E_g) for WO₃ and TiO₂ to be 2.82 eV and 3.21 eV respectively, and both are indirect band gap semiconductors. Comparing the UV-vis spectra between bare WO₃ and TiO₂ protected WO₃, the latter has a boarder peak and no obvious shift for the wavelength range.

Figure 8.3 UV-vis absorption spectra of (a) WO₃ / TiO₂; (b) WO₃ and (c) TiO₂

The inset is the Tauc plots for determination of band gap accordingly.

For a WO₃ film in 1M HCl, a flat-band potential of $V_{fb} = 0.318$ vs RHE has been obtained through Mott Schottky plot, as shown in Figure 8.4a. The V_{fb} of TiO₂ was reported as -0.237 vs RHE.^[8] With the bottom of TiO₂ conductive band more negative than WO₃ conductive band, it is more favorable for electrons to flow from TiO₂ conductive band to WO₃ conductive band, suppressing the electron-hole recombination of WO₃ and

Figure 8.4 (a) Mott Schottky plots of WO₃ in 1 M HCl at AC amplitude of 10 Hz, 30 Hz and 50 Hz; and (b) diagram of WO₃ and TiO₂ heterojunction.

TiO₂, as illustrates in Figure 8.4b. This process improves the charge separation of WO₃ and TiO₂.

Figure 8.5a reveals that low bias is insufficient to drive the generated electron from WO₃ to FTO collector, thus, there is almost no photocurrent detected under 0.3 V bias. Whereas, 3 $\mu\text{A}\cdot\text{cm}^{-2}$, 14 $\mu\text{A}\cdot\text{cm}^{-2}$ and nearly 23 $\mu\text{A}\cdot\text{cm}^{-2}$ were detected for WO₃ with 40 nm, 70 nm and 150 nm TiO₂ separately. The result clearly shows that TiO₂ top layer efficiently drives away the hole generated by WO₃, thus improves the charge separation, resulting in certain photocurrent under low bias. That is why under 0.3 V bias, WO₃ with 150 nm TiO₂ shows more than 10-fold higher photocurrent than WO₃. Whereas, as illustrated in Figure 8.5b, 150 nm TiO₂ shows 17 $\mu\text{A}\cdot\text{cm}^{-2}$; which means under 0.3 V, a profitable part of photocurrent is contributed by TiO₂ layer, the rest contribution is provided by the TiO₂ and WO₃ heterojunction.

Whereas, WO₃ with 150 nm TiO₂ shows no increase in photocurrent since the bias increases to 0.5 V. The reason is the extra thickness of TiO₂ may have reduced the light absorbance of WO₃ layer in short wavelength; since the activation wavelength range for TiO₂ is less than 386 nm and for WO₃ is less than 440 nm. When TiO₂ is thicker than 100 nm, WO₃ does not have enough illumination to be fully activated, causing the low photocurrent for the WO₃ / TiO₂ photoanode (even lower than bare TiO₂, as shown in Figure 8.5b).

When the bias increase to 0.7 V, WO₃ with 70 nm shows the highest photocurrent ($93 \mu\text{A}\cdot\text{cm}^{-2}$), higher than WO₃ with 40 nm TiO₂. The reason is due to the contribution of TiO₂ layer as well as the improved charge separation due to the heterojunction. Whereas, surprisingly, WO₃ with 40 nm TiO₂ shows higher photocurrent than WO₃ with 70 nm TiO₂ when the bias further increases to 1.1 V. The possible reason is that, although 70 nm TiO₂ could utilize a certain proportional of UV light, it also limits the total number of electron generated from WO₃. When the bias further increase, most electrons collected from WO₃ with 40 nm TiO₂ are driven to the counter electrode, leading to the highest photocurrent.

Figure 8.6 illustrates that under 0.4 V bias, with the increase of TiO₂ thickness, the IPCE of tandem photoanode of WO₃ with 150 nm TiO₂ is 13 %, which is 3-fold higher than bare WO₃ under 340 nm illumination. Whereas, under 0.1 V bias, the efficiency decreases with the increase of TiO₂ thickness. WO₃ with 150 nm TiO₂ is not as good as bare WO₃. The efficiency of WO₃ with 40 nm TiO₂ achieves more than 30 % in 340 nm which shows a great enhancement than bare WO₃. These results are in good agreement with LSV photocurrent results. The thicknesses of TiO₂ should be chosen as such that it allows as much as possible visible light to reach WO₃ layer, while it absorbs as much as possible the light with shorter wavelength by itself.

Given the combined requirement of protection and absorption for UV light, the ideal thickness of TiO₂ layer should be 40 nm, and free of voids. As it shows above, this study demonstrated various ways that TiO₂ thin layer affects the photoactivity and photostability of WO₃ photoanode. The photostability is crucial for the application of WO₃ photoanode in artificial photosynthesis due to the water splitting neutral environment. TiO₂ thin layer effectively protects WO₃ from reacting with OH⁻ species in electrolyte, at the same time improves the photocatalytic ability as a tandem scheme.

Figure 8.5 LSV of (a) WO_3 , WO_3 with 40 nm TiO_2 , WO_3 with 70 nm TiO_2 and WO_3 with 150 nm TiO_2 ; (b) TiO_2 , WO_3 with TiO_2 .

Figure 8.6 IPCE action spectra of (a) WO_3 with different thickness TiO_2 under 0.4 V vs RHE; (b) WO_3 with different thickness TiO_2 under 1 V vs RHE.

8.4 Summary

The photoactivity and photostability of sputtered WO_3 and WO_3/TiO_2 tandem photoanode have been studied. The results further confirmed the reaction between WO_3

and the OH⁻ species in electrolyte results in a gradual loss of photoactivity of the bare WO₃. In order to explore the application of WO₃ in water splitting, at pH around 7. Stabilization of WO₃ in the neutral environment has been done through sputtering a thin layer of TiO₂ onto the bare WO₃. The resulted TiO₂ layer improves the photostability of WO₃ by isolating the WO₃ from contacting with electrolyte directly. Stability test exhibits that WO₃/TiO₂ has 3-fold longer lifespan than bare WO₃ (in pH 11 electrolyte). Meanwhile, TiO₂/WO₃ forms a tandem photoanode with an increased light harvesting efficiency and better charge separation.

The LSV characteristics demonstrate that WO₃/TiO₂ tandem photoanode has higher photoactivity. TiO₂ thin layer increases the photocurrent by improving the charge separation and this improvement is more significant with further increases in applied external bias. When the potential further increases, photoactivity of WO₃ with 150 nm TiO₂ turns out to be lower than both bare WO₃ and bare TiO₂, which is caused by a reduction of the amount of light transmitted through TiO₂ and utilized by WO₃. Thus, careful control of the TiO₂ thickness is essential for better photoanode activity.

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Chapter 9

Conclusions and recommendations for future work

This chapter summarizes the works that have been carried out in the thesis. It covers photoelectrode fabrication, performance evaluation and improvement, and the integrated dual-absorber PEC studies. Complications encountered during the course of work in this thesis are also summarized. At the end, a comprehensive recommendation for future work is described, including strategies for further performance enhancement and exploration of other dual-absorber PEC working mechanisms.

9.1 Conclusions

9.1.1. WO₃ photoanode

A triple layered WO₃ photoanode has been achieved through a one-step anodization method. By adjusting the anodization conditions, including the solvent type, solution temperature, anodization voltage, and anodization duration, a NRs/NPs/NFs triple layered WO₃ structure was fabricated. The triple layered structure offers superior properties such as low cost, good light harvesting capability and decent charge separation efficiency. The top nanoflake structure provides better light harvesting efficiency, attributed to its high surface area. The noble charge separation is contributed by the nanoparticles layer, and the continuity of the dense nanorods array ensures the charge carrier transportation towards the electron collector.

The triple layered WO₃ structure is grown from a bare W foil in a single step anodization process. To the best of our knowledge, this is the first reported instance of using a facile process to achieve three different nanostructures. Moreover, the resulting triple-layer WO₃ has an optimized thickness of approximately 3 μm , which solves the limited thickness problem when preparing WO₃ photoanodes.

It is widely known that WO₃ suffers from inferior stability, resulting in complete loss of photoactivity. In our case, the WO₃ photoanode loses 50% of its photocurrent within 2 hours. In order to address this problem, a thin layer of TiO₂ was deposited on top of the WO₃ triple-layer. With this protection layer, the stability of the WO₃ photoanode is improved 10 times folds compared to bare WO₃ photoanode.

With such optimized morphological and photoelectrochemical properties, the novel nanostructured WO₃ triple-layer can be very useful in other photoelectrochemical systems, especially in artificial photosynthesis.

9.1.2 Cu₂O photocathode

The fabrication and characterization of Cu₂O photocathodes modified with a NiFe layered double hydroxide co-catalyst are reported in view of enhancing the photoelectrochemical (PEC) performances under visible light illumination under low bias conditions. It is discovered that the NiFe-LDH considerably improves the PEC performance of Cu₂O. A fundamental understanding of the reasons behind the

improvement is also proposed in terms of band alignment at the NiFe-LDH/electrolyte interface.

First and most importantly, we have conducted investigations and in-depth comparative analysis of photocurrent generation with bare Cu₂O and Cu₂O/NiFe-LDH photocathodes. The operating mechanism of NiFe-LDH as an efficient co-catalyst in combination with Cu₂O is clearly understood. The NiFe-LDH improves the charge separation efficiency of Cu₂O photocathodes. Our experimental results unambiguously reveal a substantial photocurrent increase in the low negative voltage range from 0.0 to -0.3 V *vs* Ag/AgCl. When Cu₂O is coated by a NiFe-LDH overlayer corresponding to a 20 seconds deposition time, it exhibits a photocurrent density of 0.36 mA.cm⁻² under a -0.2 V *vs* Ag/AgCl bias, that is more than 7 times that of bare Cu₂O (-0.05 mA.cm⁻²). Importantly, we also observe a photocurrent current reversal taking place in the low voltage range going from +0.04 V to -0.04 V *vs* Ag/AgCl.

Second, we analyze the operating mode of these novel Cu₂O/NiFe-LDH photocathodes in terms of band alignment at the Cu₂O/electrolyte and Cu₂O/NiFe-LDH/electrolyte interfaces (see Figure 5.1). Based on a thorough literature survey, it appears that inefficient band alignment at the Cu₂O/electrolyte interface is the origin of the Cu₂O photocathodes inefficiency. Due to the unfavorable band bending direction at the Cu₂O/electrolyte interface, the photogenerated electrons accumulate at the interface and cannot be efficiently injected into the electrolyte. Consequently, this process greatly limits the photocurrent generation and induces Cu₂O instability when under illumination. By depositing the NiFe-LDH co-catalyst, we introduce a more favorable band alignment and band bending at both Cu₂O/NiFe-LDH and NiFe-LDH/electrolyte interfaces, which turns out to be highly beneficial for transport of the photogenerated electrons.

In conclusion, it is demonstrated for the first time that a NiFe-LDH co-catalyst can considerably improve the photocurrent intensity of Cu₂O photocathodes. The fundamental mechanisms of this phenomenon are revealed through a series of experimental comparison. It is believed that these findings are very important in designing new efficient and stable PEC systems for low bias or no bias photoelectrochemical water splitting.

9.1.3 Dual-absorber PEC integration

Self-biased PEC for artificial photosynthesis is ideal but difficult to realize. There are still a lot of unknown factors behind the performance of dual-absorber PEC. Our investigation reveals the key factors affecting the voltage generation by a dual-absorber PEC upon illumination. The OCV is important in achieving zero-biased or low bias PEC water splitting. We have measured the OCV values of several photoelectrode combinations. Results demonstrate that the photocurrent of both photoanode and photocathode are most important in achieving a high voltage value. Meanwhile, the band alignment of the photoelectrodes is also important. The difference between the CB of the photoanode and VB of the photocathode must be as large as possible. This difference plays a vital role in determining the OCV that can be generated in the PEC system. At a fixed difference between the photoanode CB and photocathode VB, the OCV generation relies on the photoelectrodes' performance under low bias conditions.

The comparison between systems of WO_3 with three different photocathodes (Si, GaP and Cu_2O) demonstrates that both photocathode's efficiencies at low bias and the band alignment are important factors. Whereas, the comparison amongst systems of Cu_2O with three different photoanodes (WO_3 , Fe_2O_3 and BiVO_4) shows that the photoelectrodes' performance under low bias seems more important than the band alignment. This has been proven by the BiVO_4 - Cu_2O dual-absorber system. With two types of co-catalyst deposition (NiFe-LDH on Cu_2O photocathode and NiCo-LDH on BiVO_4 photoanode), the OCV value increases dramatically (from 250 mV to 410 mV). This enhancement is corresponding to the photoelectrodes' charge separation and charge transportation efficiencies. A detailed discussion has been carried out in the mechanism behind the charge generation by a dual-absorber PEC (Figure 7.11).

In conclusion, in order to achieve an efficient dual-absorber PEC, improving the photoelectrode's performance is the first priority, especially their photoelectrochemical activities under low bias conditions.

9.2 Complications

There are several complications we have met along the way of developing the photoelectrodes and PEC, including

(1) Instability of WO_3 photoanode.

At the early stage of our study, we have encountered the dramatic loss of photocurrent during testing of photoanode performance. It was often noticed that the material loses its photocurrent within a few minutes (Figure 9.1). Through profound literature study, we realized that WO_3 reacts with the OH^- group in the electrolyte. Therefore, in the later stages, we applied a TiO_2 protection layer on top of the WO_3 , which has proven to be an efficient strategy in realizing high performance WO_3 photoanode.

Figure 9.1 LSV of WO_3 in pH=9 solution, the photocurrent reduces 80% in 1000 s.

(2) Instability of Cu_2O photocathode

Similar with WO_3 , Cu_2O is also plagued by its instability under aqueous conditions. Different from WO_3 , Cu_2O loses its performance through self-oxidation to CuO or self-reduction to Cu under a certain voltage (Figure 9.2). Thus, the voltage applied on this photocathode material must be controlled carefully. Various attempts to solve this problem have met with limited success as this material can be either reduced or oxidized. In the end, we have decided to improve the photocatalytic performance of this material under low voltage range instead of stabilizing it under high potential condition. Results show that Cu_2O is very stable under low bias ($-0.2 \text{ V vs Ag/AgCl}$).

Figure 9.2 FESEM image of Cu_2O after one LSV scan (light illumination). Small substances (white particles) were observed on the flake surface. Scale bar is 100 nm.

(3) PEC integration

Compared with the photoanode and photocathode material performance testing, PEC integration testing protocols are far less developed. Thus, we have to come up with our own testing cells and testing strategy. During these developments, we also realized that when testing the cell performance in dark condition, the environment must be completely dark, as slight light may interfere with the testing signal and results in noise. Also, it often takes a very long waiting time for the cell to stabilize before and after illumination.

9.3 Recommendation for future work

There are several aspects to be further developed in the future, including but not limited to the following points:

(1) Photoelectrode performance

As illustrated by the OCV mechanism of a dual-absorber PEC, the performance of both photoelectrodes are of upmost importance. Thus, further improvement in the charge separation and charge injection rate are needed. For example, the performance of triple layered WO_3 may be further improved by depositing a very thin co-catalyst layer on the top. Popular co-catalyst materials such as Ag, Co-Pi and LDHs can be considered.

(2) LDH co-catalyst

As shown in the results of Cu_2O photocathode and BiVO_4 photoanode, LDH shows superior electrochemical performance as a co-catalyst. It efficiently attracts photogenerated electrons (or holes) from the main photocatalyst, thus increases the charge separation efficiencies. At the same time, it also provides preferable band alignment, improving the charge carriers' injection rate towards the electrolyte. In the current work, only NiCo-LDH and NiFe-LDH are explored. There are many other LDHs that can potentially be used as co-catalyst in PEC applications. Moreover, a guideline of how to choose the suitable LDH should be generated to aid the development.

(3) Integration mechanism

Mechanisms other than OCV generation for dual-absorber PEC need to be developed and analyzed. More material pairs can be tested in order to find the most efficient system that can be used for artificial photosynthesis. Integrated PEC for actual water splitting reactions and its efficiencies study can also be carried out.